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Review of micromachining of ceramics by etching

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Abstract: In the last two decades, there has been an enormous surge in interest in ceramic materials and, as a result, there have been significant advances in their development and applications. Their inherent properties, such as capability of operating at temperatures far above metals, high level of hardness and toughness, low coefficient of thermal expansion and high thermal conductivity rendered ceramics to be one of the leading engineering materials. Many research works have been conducted in the past few years on machining of advanced ceramics using different processing methods in order to obtain a better surface roughness, higher material removal rate and improved tool life. Micromachining using chemical etching is one of those methods that do not involve the problem of tool life and direct tool−work piece contact. However, only a few research works have been done on micromachining of ceramics using chemical etching. Hence, study of chemical machining of advanced ceramics is still needed as the process has found wide application in the industry because of its relative low operating costs. In this work, we summarize the recent progresses in machining of different types of advanced ceramics, material processing methods such as wet etching and dry etching, and finally the prospects for control of material removal rate and surface quality in the process of ceramic micromachining.

Key words: micromachining; ceramics; etching

1 Introduction

The term "ceramic" covers inorganic non-metallic materials that are formed by the action of heat to produce hard and strong mechanical properties. Ceramics are divided into traditional ceramics and advanced ceramics (engineering ceramics). Nowadays, advanced ceramics can be classified into three distinct material categories: oxides (alumina, beryllium and zirconia), non-oxides (carbides, borides, nitrides and silicides) and composites (particulate reinforced combinations of oxides and non-oxides)[1].

The most common type of starting material for making ceramics is the chemically prepared powders. In making of ceramics, additional materials are added to the powder in order to form the ceramic particles into desired shapes. Some of the most common forming methods for ceramics include extrusion, slip casting, pressing and injection molding. After these processes, ceramics undergo heat treatment or sintering to produce strong products.

Advanced ceramics possess great mechanical properties, such as capability to operate under high temperature, high resistance to abrasion, high corrosion resistance, longer tool life and dimensional stability. Advanced ceramics have demonstrated their reliable applications in various industries with their excellent properties, great service life and cost effectiveness. Due to their excellent properties, advanced ceramics are widely used as aerospace materials, refractory materials, in electrical applications (magnet, capacitors and transducers), thermal applications (furnace roof hangers, thermocouple tubes and inspection tubes), structural applications (engine components, cutting tools, valves and fuel cells), and medical applications (bio-implant and internal bone growth stimulator)[2].

2 Ceramics micromachining

Machining that is employed for ceramic shaping can be categorized into two categories, conventional machining and non-conventional machining. Conventional machining includes grinding, drilling, turning, boring

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and milling, and non-conventional machining includes chemical machining, ultrasonic, abrasive water jet (AWJ), electrical discharge machining (EDM), laser beam machining (LBM) and laser-assisted machining (LAM), as listed in Table 1. The type of machining used for ceramic shaping is purely dependent on the industry and their requirements. Industries such as aerospace and automobile require products with high strength; while semiconductor industry requires high dimensional accuracy and high surface quality product. Machining operations should be chosen carefully in terms of time and cost efficiency considering environment concerns.

2.1 Conventional machining

Most engineering ceramic components have complex shapes and hence, require machining by diamond tools. They cannot be machined using conventional metal tools such as cemented carbides or high-speed steels[3]. Ceramics such as Al_2O_3/BN nano-composite exhibit relatively excellent machinability, which is very important. However, machining of Al_2O_3/BN nano-composite requires high cost of tooling and this will increase machining cost. Hence, this limits their application fields in the industry[4]. Advanced ceramics inherent brittleness always causes problems during machining, either facing wear conditions or high friction, which indirectly affects their machinability. Conventional machining of ceramics may result in poor surface quality. The increase in surface roughness is probably due to the formation of machining-induced surface pores during polishing or it may be generated by means of a grain fall-off mechanism. FREI and GRATHWOHL[5] showed ceramics strength could be correlated with the surface roughness rather than the compressive residual stresses. However, a negative influence on the strength was observed after conventional

Table 1 Comparison of different machining such as water jet, wire EDM, laser, plasma, milling, and chemical etching

Item	AWJ	EDM	Plasma	Laser	Milling	Chemical etching
Accuracy	Accuracy average of ±0.1 mm	Extremely precise parts at ±0.025 mm	In the range of ±0.762 to ±1.524 mm	Accuracy to ±0.025 mm	Very good, in the range of ±0.01 mm	Fair
Thickness	Mostly cut under 75 mm; Thicker parts can be cut with reduced accuracy and slower speed	Very thick parts can be cut with wire EDM. Over 30 cm reported	Plasma cutting usually cuts less than 31.75 mm	Usually cuts thin mild steel less than 6.35 mm	Able to work on 3D parts	Any thickness is applicable
Cutting speed	5 to 10 times faster than EDM when thickness is under 25.4 mm	Wire EDM cuts at very slow speed (5−10 times slower than AWJ)	Fast with thin sheets	Very fast cutting in thin, non-reflective materials	Fair	Fast
Quality of edge Water jet cutter yields	Good edge quality	Excellent	Fair	Excellent	Excellent	Not applicable
Heat affected zone (HAZ)	Water jet produces; No HAZ	Some HAZ	Some HAZ	Cuts by melting material, resulting HAZ	No HAZ	No HAZ
Material Distortion	Hazing near cut; No internal stress built up	Wire EDM cuts by melting, resulting material heat distortion	Cuts by melting, resulting material heat distortion	Cuts by melting, resulting material heat distortion	No distortion	No distortion
Other characteristics	Can pierce material directly without drill equipment; Fast setup and rapid programming	EDM is limited to cutting only conductive materials	Relatively low capital costs; Special gas need for laser cutting	Limited to nonreflective materials; May need different gas for cutting different materials	Needs special fixture and tools, also requires skilled operator and usually can not work on very large parts	Cost and time effectiveness

machining of Al_2O_3, ZrO_2-Al_2O_3 and Si_3N_4 ceramics. LIU et al[6] showed a relationship between surface roughness and material strength. Results showed the enhancement of strength with lower surface roughness. This might cause by the presence of compressive residual stress on surface layer.

Conventional machining is one of the most important material removal methods that use mechanical energy. It can be classified into turning, milling, drilling and grinding. Each of these processes requires a sharp cutting tool to mechanically cut the material to achieve the desired geometry. Most engineering ceramics components have complex shapes and hence, require machining by diamond tools. They cannot be machined using traditional metal tools[3]. Disadvantages of conventional machining include the use of lubricant, which is environmentally unfriendly; long processing time; high cost of tool, high energy consumption and relatively low product quality; and, in some cases conventional machining may not be feasible.

In conventional machining, surface roughness of substrate increases due to the formation of machining-induced surface pores during polishing or grain fall-off mechanism[5]. Yet, a few techniques have been introduced to improve surface roughness, such as fracture machining technique used to obtain compressive residual stress surface layer[7], laser assisted process[3] and stress enhanced process[6]. Thus, further improvement of oxidation resistance and wear toughness with less use of lubricants is still needed to meet the severe wearing conditions required by the coming automotive parts[8]. BOCCACCINI[9] once summarized that good machinability occurs when the brittleness index of the material is lower than 4.3 μm.

Turning operations can be used to produce cylindrical products from ceramics. A few studies have been conducted on turning operation of advanced ceramics. The major issues found are tool wear and surface damage. Tool wears that take place in machining of advanced ceramics are mainly affected by the tool materials and cooling condition[10]. The extremely high tool wear rate and surface damage of ceramics produced during machining are mainly due to the high cutting temperature and the extreme hardness of work materials. WANG et al[11] introduced liquid nitrogen (LN) cooling to control the temperature in the cutting zone. Results showed that LB cooling was able to decrease the temperature in the cutting zone and better surface roughness was produced. DABNUM et al[12] presented turning process in glass-ceramics using RSM method and showed that conventional machining was able to machine ceramics with some additives or supportive methods. It was shown that the feed rate was the main influencing factor on the roughness, followed by the cutting speed and depth of cut. YAN et al[13] indicated that the sintering temperature of ceramic materials plays a significant role in turning process. It was found that polycrystalline diamond (PCD) tool is superior to the other tools, whilst the carbide inserts and the ceramics tool are unsuitable for machining ceramics. It was also found that turning ceramics with a sucker in cool and highly humid whether moistens the tool face and promotes tool wear. Few researches have been carried to enhance the turning performance in ceramics material, such as VERMAEULEN et al[14] who designed an optical diamond turning machine. This machine was designed to create deterministic behavior required for submicrometer shape accuracy and mirror surface quality thereby minimizing tolerances in the manufacturing, reducing requirements on conditioning of ambient temperature as well as the effort on software error compensation.

Grinding process introduces strength-inhibiting defects into ceramics. A few methods are required to prevent this damage, such as ‘ductile-regime’ grinding, lapping, polishing or ion beam implantation and this will end up increasing their machining cost[15]. Pre-machining processes, such as surface polishing, weaken the flexural strength. There are doubts, however, as to the effectiveness or economics of such treatments, and alternative measures should be undertaken. HUANG and LIU[16] investigated advanced ceramics machining characteristics and removal mechanisms. They observed that fractured and smeared areas generated on Al_2O_3-TiO_3 surface after grinding process. These defects increased with smaller depths of cut. Chipping and cracking were clearly observed under SEM. The damage layer right underneath the machined surface seemed to be generated via ‘chipping’, as shown in Figs.1−3[16]. The work at University of Tokyo[17] used a modified Norton Co.-controlled milling centre and cast-iron-bonded diamond grinding tools for creep-feed grinding, and reported stock removal rates in complicated 3D shapes from Si_3N_4 and SiC. TSUTSUMI et al[18] found that the application of electric-discharge machining in grinding showed an increase in wheel cutting ability. The surface roughness of silicon nitride ground with the in-process dressing decreases with decreasing the grit diameter.

2.2 Non-conventional machining

Non-conventional machining has been well known in ceramics processing due to their high productivity and cost effectiveness. In the past, many researchers have studied machining of advanced ceramics conducted by chemical machining (CM), electrical discharge machining (EDM), laser beam machining (LBM) and ultrasonic machining (USM). Non-conventional machining

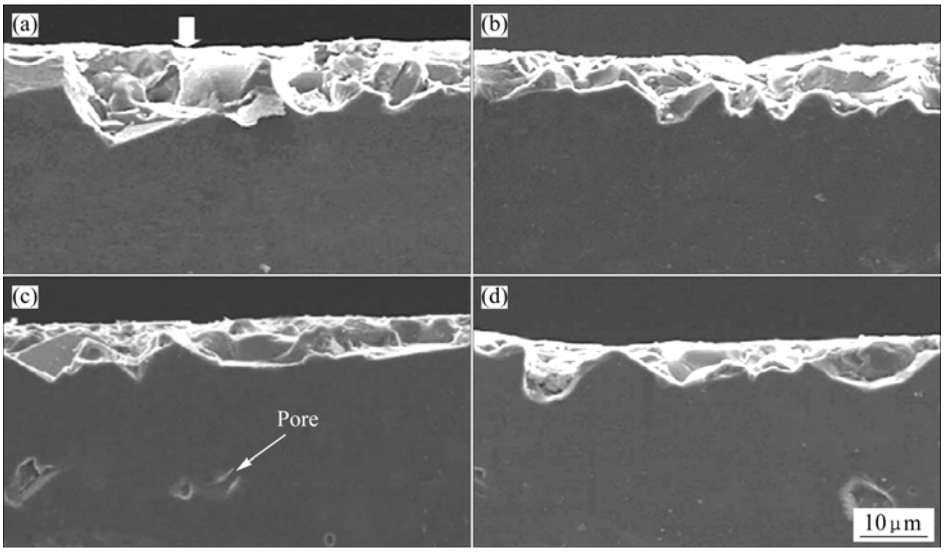


Fig.1 Subsurface damage layer of Al_2O_3 for various wheel depths of cut (Larger arrow indicates machined surface) [16]: (a) 0.1 mm; (b) 0.5 mm; (c) 1.2 mm; (d) 1.5 mm

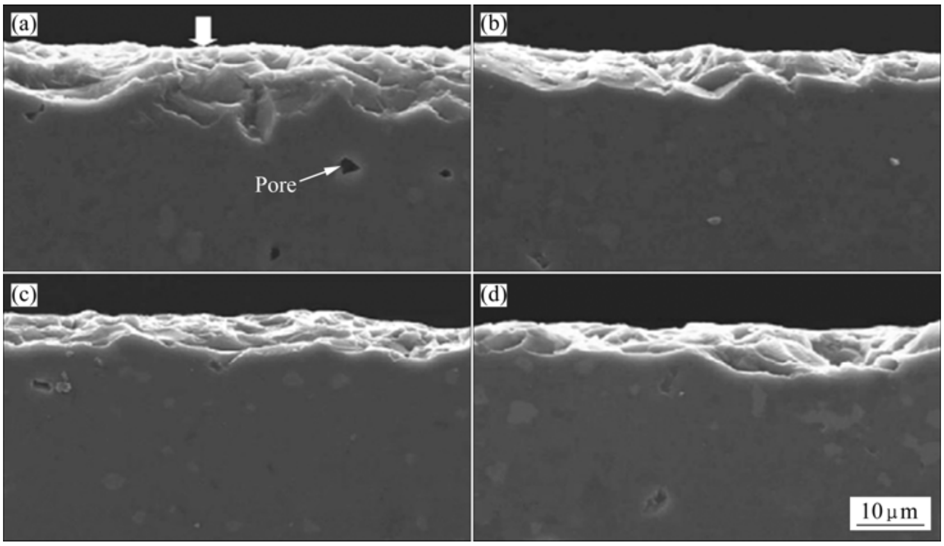


Fig.2 Subsurface damage layer of Al_2O_3-TiO_2 for various wheel depths of cut (Larger arrow indicates machined surface) [16]: (a) 0.1 mm; (b) 0.5 mm; (c) 1.2 mm; (d) 1.5 mm

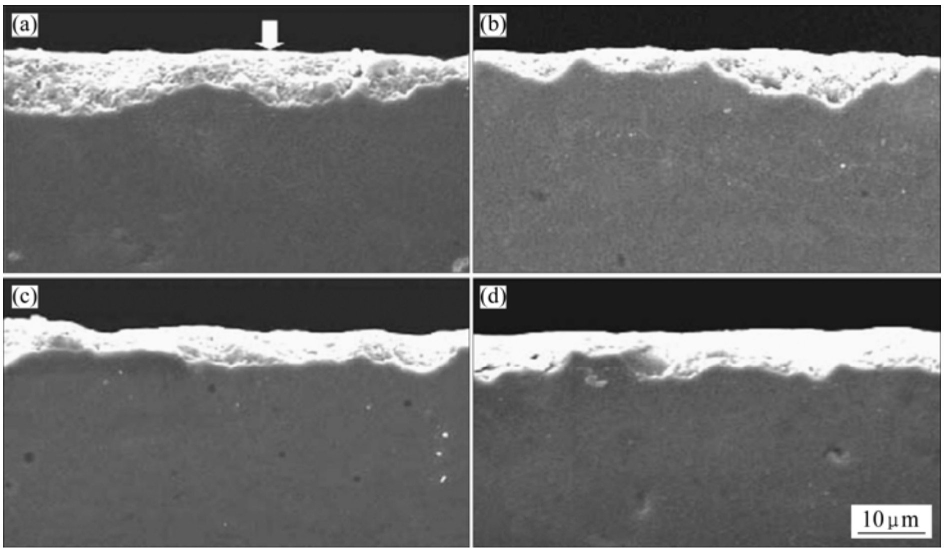


Fig.3 Subsurface damage layer of Y-TZP for various wheel depths of cut (Arrow indicates machined surface) [16]: (a) 0.1 mm; (b) 0.5 mm; (c) 1.2 mm; (d) 1.5 mm

utilizes other forms of energy different from mechanical energy. The energies used in non-conventional machining are thermal energy, chemical energy and electrical energy.

Chemical machining is one of the oldest micromachining technologies. This process applies reactive etchants to remove unwanted part from the workpiece surface. It is a corrosive-controlled process. Many studies have been done on CM to investigate its etching rate, surface roughness and dimensional accuracy. CM includes photochemical machining (PCM). PCM is a method of fabricating component using reactive etchants to corrosively oxidize selected areas of the component. This process can produce highly complex products with very fine details, at high accuracy and low cost. They present a number of advantages, such as simple set up, quick preparation and no tool required; hence problems such as tool wear, machine tool deflections, vibrations and cutting forces are eliminated. In addition, chemical machining minimizes the effect of ceramics brittleness and low fracture. Disadvantages of chemical machining include chemical disposal, the presence of uncontrollable parameters, especially material structure and their rate of chemical reaction with solutions. In addition, high attention is required during processing. ZUBEL[19] studied the silicon anisotropic etching process in water solution of KOH and TMAH with and without both organic and inorganic addition. This study shows that the etching rate is affected by the attendance of organic and inorganic agents. KIM et al[20] employed the etching process with a lower O_2 gas flow ratio and found that this action reduces etching damage to the low-*k* materials.

Abrasive water jet (AWJ) is a technique that involves forceful impingement of abrasive particles to achieve the removal of surface material. AWJ depends on the water jet pressure, stand-off distance, abrasive type's size and flow rate. However, these choices are significantly affected by external factors such as the machined material structure and geometry of the jet nozzle[15]. The most common advantage of AWJ is that it yields little heat during machining process therefore no heat affected zone (HAZ) happens, hence the process does not require heat treatment and no damage is reported. Compared with traditional machining technologies, AWJ offers the following advantages: fast speed, able to cut thick material, good accuracy, finishing surface and it cuts virtually anything with no HAZ. Unfortunately, some burr will occur near the cutting area. AWJ is widely used in metal, glass, ceramic, marble and granite cutting machines. GI and GI[21] made a conclusion in their research that AWJ had a great potential as a machining method for brittle and hard materials. Unfortunately, they found a large-scale fracture that easily developed on the backside of the workpiece and affected surface finish. Although AWJ has been recognized as the most efficient method to machine ceramics, result showed that the damage in surface always happens in the lower zone of the surface, where a lot of pits were found and lower the surface quality[22]. To overcome this problem, a new cutting head oscillation technique has been introduced. This technique applied to the cutting process produces superior results and shows that the smooth zone depths increase by more than 30% with oscillation as compared with that without oscillation. However, a further study is required to reduce the pits effect that occurs at the lower surface layer[23−24].

Electrical discharge machining uses spark erosion to remove small particles from electrically conductive material. The acceleration of EDM material removal rate increases with the discharge current and working voltage, but decreases with increasing pulse duration. EDM is especially well-suited for cutting intricate contour that would be difficult to produce with traditional machining. Advantages of EDM include high dimensional accuracy, good surface finish, lack of burr and little HAZ. Ti_3SiC_2 with excellent electrical conductivity and thermal conductivity is easily machined by EDM but high power is needed[25]. In order to obtain a high material removal rate and better surface roughness, LIU et al[26] suggested using a suitable chemical additive, dielectric strength, washing capability and viscosity of the machining fluid. They also suggested using a water-based emulsion as the machining fluid as harmful gas is not generated during machining, and the equipment is not corroded. Another suggestion by MUTTAMARA et al[27] to improve the material removal rate is by employing positive polarity in the case where the conductive layer is sufficient. Study on the EDM of conductive ceramics shows EDM performance is purely dependent on the level of intensity. It has been observed that increasing intensity will tend to increase surface roughness and electrode wear[28]. HU et al[29] investigated EDM on Ti_3SiC_2 using water as dielectic and found typical thermal shock cracks and loose grains in subsurface, which result in about 25% of strength degradation. Results of EDM reveal a wide variation in removal rates and surface finishes, as shown in Figs.4 and 5[30] shows the material removal and tool wear for EDM under roughing condition; and Fig.6 indicates the TiB surface after EDM[30].

Electrochemical discharge machining (ECDM) is a modification of EDM. Materials are removed or deposited with the transferring of ions based on the anodic dissolution mechanism, so that high precision is achievable and it has the feasibility of micromachining. In order to obtain better machining accuracy and smaller machining size, many research works have been done on electrolyte, electrode's insulation and systematic control

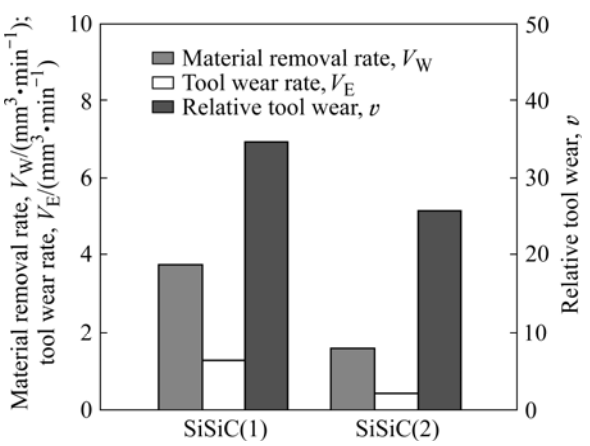


Fig.4 Material removal and tool wear under roughing condition (SiSiC) [30] (Test-conditions: tool, Cu(+); i_e, 24 A; t_e, 25 μs; t_0, 100 μs)

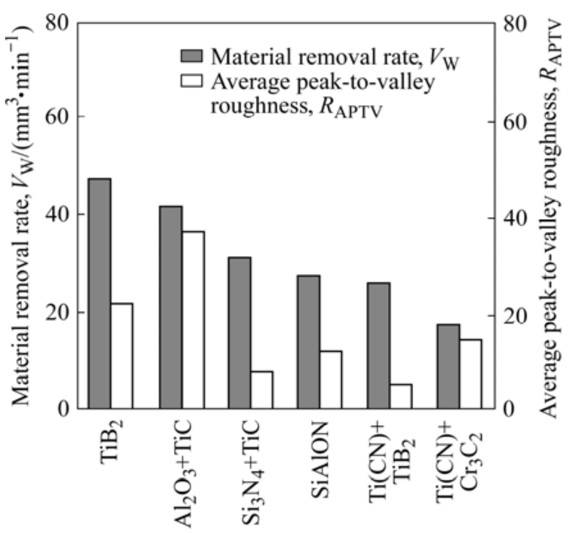


Fig.5 Material removal and tool wear under roughing condition (TiB) [30] (Test-conditions: tool, Cu(+))

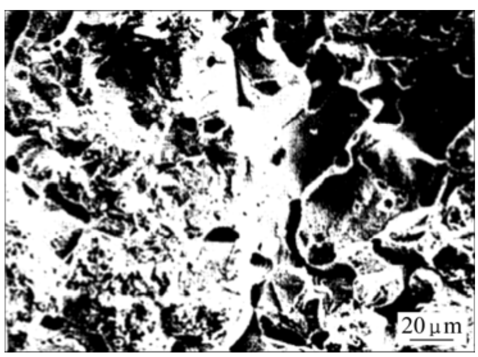
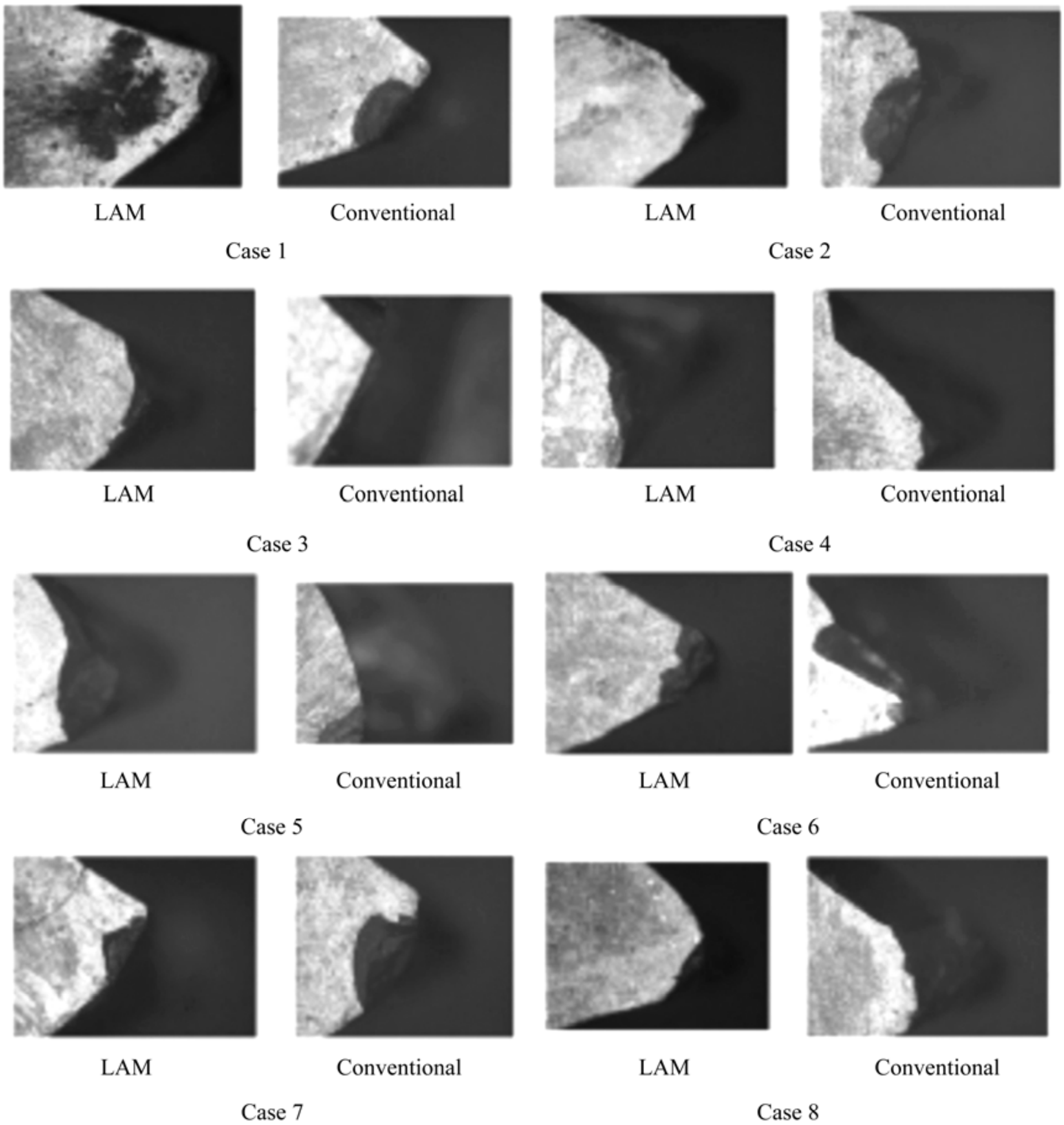


Fig.6 TiB surface morphology after EDM [30]

of machining process[31−34]. BHATTACHARYYA et al[35] found that the machining rate and accuracy could be enhanced through effective and precise control of the spark generation. Taper side wall and flat front tool tip are the most effective parameters for controlled machining. The advantages of ECDM include higher material removal rate, use of nontoxic electrolyte components with very little changes in their composition during operation, minimal waste disposal, monitoring and control of electrolyte[36].

Laser assisted machining (LAM) is a thermal process. The laser is used as a heat source with the beam focused on the un-machined section of the workpiece. The addition of heat softens the surface layer of the material, so ductile deformation happens rather than brittle deformation during cutting. LAM power requirements depend largely on the material and the nature of the machining process[3]. In LAM, cutting force is obviously significantly reduced and the ease of cutting is increased accordingly, resulting in evident improvement in surface roughness[3]. The possibility of vaporizing material during LAM may cause surface problems due to its severity in much the same way as in discharge machining[15]. The advantages of laser are that it provides high speed and precise cut when cutting thin material; laser yields no burr and a little HAZ. LAM has demonstrated its ability to reduce cutting force and lower dynamic forces, less sharp segmented chip and smooth surface finish is produced[37]. It is suitable to cut non-reflection mild steel. LAM disadvantages include it requires high energy, high cost and must be conducted in a specify condition. The power of laser must be controlled properly to obtain a satisfactory result and a lot of power is needed to conduct this machining. CHANG and KUO[38] showed that LBM clearly appropriate for predicting the temperature distribution of difficult-to-machine materials during the LAM process. Tool wear is a major factor affecting the surface roughness of the workpiece. Fig.7 shows the comparison of tool wear in LAM with conventional machining[3]. They found that cutting resistance of processing aluminum oxide ceramics is extremely large, thus increasing the tool wear and affecting surface quality. TSAI and CHEN[39] found that generation of tensile stress was concentrated at the edge of groove-crack and induced the extension of the groove-cracks during LBM. BLACK et al[40] showed that surface glaze usually possesses a different linear expansion rate to the underlying substrate. The large thermal gradient due to laser beam causes the lower substrate to expand at a different rate, resulting in cracking of the glaze.

Ultrasonic machining (USM) is a process where material is removed primarily by repeated impact of the abrasive particles. The main parameters, which are static force, vibration amplitude, and grit size, have significant effects on the material removal rate[41−43]. Material removal occurs when the abrasive particles, suspended in the slurry between the tool and work piece, impact the work piece due to the down stroke of the vibrating tool.



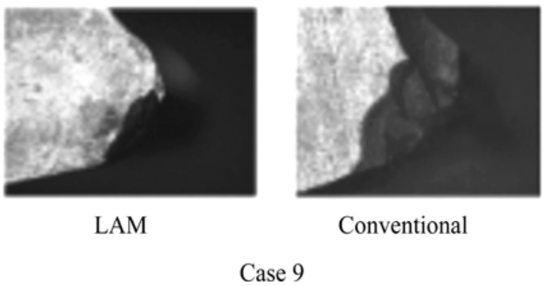


Fig.7 Comparison of tool wear in LAM with that in conventional machining [3]

It is mentioned in many reports that, for deeper cut, a vacuum-assist to ensure adequate flow of the suspension is strongly recommended. Another type of USM is rotary ultrasonic machining (RUM). RUM combines material removal mechanism of diamond grinding and USM. The difference between USM and RUM is the tool used. USM uses a soft tool and slurry loaded with hard abrasive particles, while in RUM the hard abrasive particles are bonded on the tools. The major advantage of USM is that it is a non-thermal, non-chemical, and non-electrical process. Therefore, metallurgical, chemical or physical properties of work piece remain unchanged. However, in USM, the material removal rate is considerably slow and even stops as penetration depth increases; the slurry may wear away the wall of the machined hole as it passes back towards the surface, which limits the accuracy; and considerable tool wear happens, which in turn makes the process very difficult to hold close tolerances. Efforts have also been made to develop models to predict the material removal rate in

RUM from control variables[44−45]. ZENG et al[46] concluded that RUM tools could be designed in a way so that the lateral face is shorter. Tools with shorter latter face use less diamond grains and hence lower manufacturing cost. The relationship between the cutting force and tool wear stage could be used in indirect monitoring of tool wear during machining processes. THOE et al[42] summarized that tool materials should have high wear resistance, good elastic and fatigue strength properties, and have optimum values of toughness and hardness for application.

2.3 Chemical etching of ceramics

Chemical etching is categorized into etching in aqueous etchants and defect-selective etching in molten salt. There are two major classes of etching processes, wet etching and dry etching. The major difference is that wet etching is an isotropic process, which have selectivity that depends on crystallographic direction, masking and underlying layers.

Wet chemical etching involves removal of unwanted material by the exposure of the workpiece to a corrosive solution. The exposed material is oxidized by the reactivity of the etchant to produce reaction products [47]. The etch rate depends strongly on the ion/electron impact mechanism. There are two types of wet etching, which are isotropic etching that will etch the material in all direction; and anisotropic etching that will only etch at selective direction. The most popular anisotropic etchant is potassium hydroxide (KOH) and it is the safest to use. In MEMs industry, complicated design is always desirable. Thus, patterning and shaping is carried out in conjunction with photoresist masks. The masks properties must be compatible with the selected solution and must be etched at slower rates than the substrate[48]. Master art work production, surface preparation, choice of proper photoresist and imaging are the main concerns in producing successful patterning.

Isotropic etchants having dissolution rates independent of orientation are also used. These chemical mixtures tend to uniformly remove material, and are limited by the mass transport of chemical species to the crystal surface. The actual surface reaction rates are so great that variations to atomic structure do not alter the reaction speed relative to chemical transport[49].

In order to obtain better results in terms of productivity and surface quality of machined ceramics, researchers have created many types of etchants. These include molten salt and Secco etch, which commonly used in the industry; Dash etch, Jenkins Wright etch and Sponheimer etch.

The simplest example of a molten salt would be to take sodium chloride (table salt) and heat it to a red heat (801 ℃) where it would melt into a liquid. This liquid is stable, has a heat capacity similar to water and flows much like water does[49]. Molten salt functions are not limited to solvent, and its characteristic includes good heat transfer characteristics. It is able to attain very high temperatures. Molten salt technology has been used commonly in industries, such as diverse technologies, electrochemistry, heat transfer, chemical oxidation, and nuclear reactors.

Secco etch mainly consists of hydrofluoric and chromium oxide. There are few type of Secco etch being used today, and their differences are controlled by their acid composition. As an example, JACQUES[50] used Secco etch of 2 mL HF and 1 mL Cr_2O_3 to etch Si_3Ni_4 and RAVI[51] used 2 mL HF:1 mL $K_2Cr_2O_7$:1 mL CH_3COOH in etching advanced ceramics. Secco etch is used to delineate crystalline defects on silicon substrate of water. It is a useful chemical etching method for characterization of defects on surface of bare silicon wafer[52]. However, HUA[53] concluded that Secco etch alone does not fully deprocess the die to substrate where crystalline defects may be covered by the oxide. 152 Secco etchant consists of hydrofluoric acid and potassium dichromate, and its compositions are 67% HF: 33% 0.15 mol/L $K_2Cr_2O_7$ in H_2O. This mixture is the innovation of Secco etch, which was created by CHU and KEIM[54] for etching of silicon wafer. 152 Secco etch has advantages of delineating crystalline defects through two main processes, where it is in well-defined etching pits with elliptical shape; it preparation is simply and fast and it is a reliable method. The disadvantage of 152 Secco etch is that it cannot identify the orientation of wafer plan compared with the other Secco etch[53].

Thermal etch involves heating of polished ceramic specimens to around 200 ℃ of the sintering temperature. It is performed under argon in vertical tube furnace with silicon carbide hearth. The specimens are then annealed in vacuum or inert atmosphere and used primarily at high temperature[47]. Thermal etch is not normally applied to non-oxide ceramics owing to problems with oxidation. In principle it could be carried out under vacuum or inert atmosphere. From previous works, pressure-less-sintered β-SiC produced by sintering SiC powders was successfully etched[55]. COOK et al[55] successfully built a useful guideline in fabricating engineering ceramics. They found only SiC was able to successfully thermally etch and gave a low value of surface roughness. JARDIEL et al[56] tested $Bi_4Ti_3O_{12}$ with HF solution under temperatures ranging from 25 to 50 ℃. They found that etching effect at 50 ℃ for 180 s showed the best etching effect. SEM micrograph showed thermal etching modified the morphology of the microstructure, where the shape of $Bi_4Ti_3O_{12}$ changed from rounding plate-like grain to platelets under the action of the chemical agent, as shown in Figs.8 and 9[56].

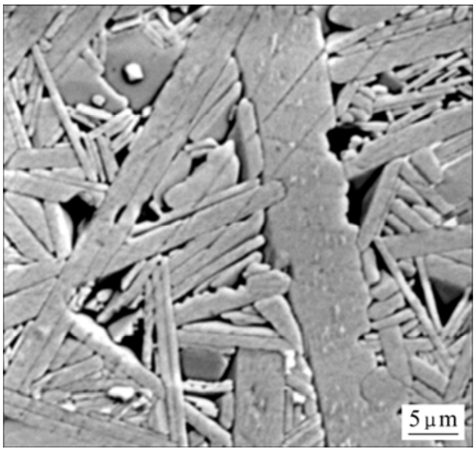


Fig.8 SEM micrograph of $Bi_4Ti_3O_{12}$ before thermally etch[55]

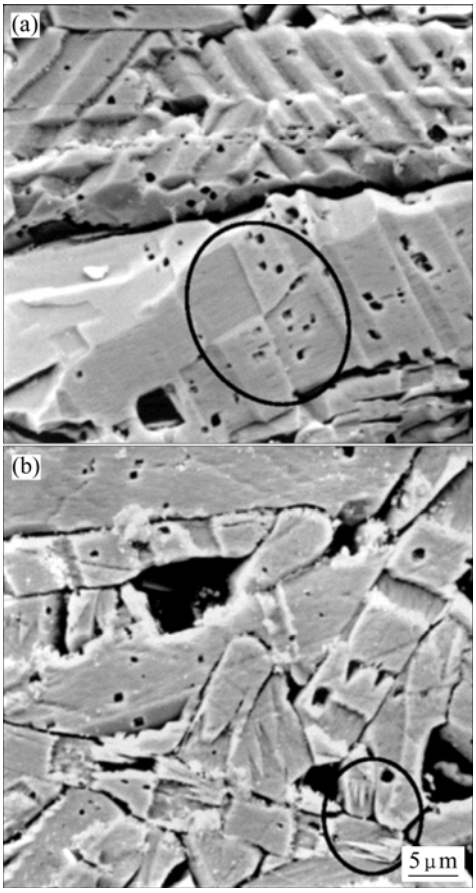


Fig.9 SEM micrographs of $Bi_4Ti_3O_{12}$ after thermal etch at 50 ℃ for different etching time[56]: (a) 3 min; (b) 6 min

Other etchants are Sirtl solution, which contains 1 mL HF:1 mL C_2O_3[47]; Silver etch with 2 mL HF:1 mL HNO_3:2 mL $AgNO_3$[51]; Dash etchant with 1 mL HF:3 mL HNO_3:1 mL CH_3COOH; Jenkins Wright, which contains 60 mL HF:30 mL HNO_3:60 mL H_2O:60 mL CH_3COOH:30 mL (1 g CrO_3 to 2 mL H_2O)[57]; Sponheimer Mills, contains 5 gm H_3IO_6:5 mg KI in 50 mL H_2O:2 mL HF[58]; Copper etch, contains 600 mL HF:300 mL HNO_3:28 g $Cu(NO_3)_2$:3 mL H_2O[59]; Copper Displacement, contains 55 g $CuSO_4$:SH20:950 mL H_2O:50 mL HF; CP-4, contains 3 mL HF:5 mL HNO_3:3 mL CH_3COOH[50]; and Sailer etchant, contains 300 mL HNO_3:600 mL HF:2 mL Bs:24 g $Cu(NO_3)_2$: dilute 10:1 with H_2O[54].

Factors that influence etching rate are solution, solution concentration, temperature, material properties, agitation and stirring[60−62]. A small change in each of these parameters will result in producing a big different product at the end of the process. Solutions and their concentration are the main concerns. In order to obtain good results, solution and substrate (ceramics) must be matched perfectly. Due to ceramics mechanical properties, the ceramic grades are stable even at high temperature conditions. Thus, ceramics are always etched at extremely high temperature for several hours. Agitation and stirring process are considered as an additional process to stimulate the reactions and to enhance its performance. WILLIAMS et al[60−61] summarized the relationship between etchants and substrates after carrying out chemical etching experiment at different temperatures and etching periods. In their works, they tested with some variables, such as temperature, solution types and solution concentrations. They highlighted that not all materials were able to be etched in all etchants, which happened because of material properties and contamination concern. Usually, only certain solutions and concentrations are suited for certain materials[63].

The difficulties in micromachining of advanced ceramics are mostly related to etching rate, surface roughness and dimensional accuracy. Etching rate is the main concern in term of cost and productivity. Other external parameters are stirring process and aided material. From previous research works, it has been proved that stirring action was able to increase the etching rate by removing the ion concentration during etching process[64] and aided material, such as trithanolamine, supersonic aided, are able to increase the etching rate[62, 65−66].

Surface conditions specify the quality level of the micromachining process. A good surface quality possesses a low value of roughness and surface damage. The substrate microstructures and solutions have been categorized as uncontrollable parameters in this process. Different types of advanced ceramics possess different microstructure, such as grain size, crystallization and dislocation density[60]. Pre-preparation is required for substrates with bad surface roughness. Solution concentration is changed when the experiment is carried out and the composition or the concentration of solution is changed with time and temperature[61−62]. Dimensional inaccuracy due to the undercut always occurs, especially in wet anisotropic etching process. This process etches substrates at all directions at same rate or speed. In order to reduce the undercut effect, a suitable photoresist should be used, which may provide higher protection to subtract[67].

3 Performance of chemical micromachining by etching

Wet chemical etching techniques provide high degree of uniformity and repeatability, and adjustable etch rate by changing the ratio of components in the etching solution. Performance of chemical micromachining by etching is determined by etching rate/material removal rate, surface roughness and dimensional accuracy.

3.1 Etch rate

Nowadays, manufacturing industries required high productivity. Thus, etching rate has become an important issue. Previous works summarized that the etch rate varies as a function of temperature, elapsed time from start of etch and etching period, solution type and concentration, agitation method and substrate to be etched[63].

Agitation material/processes have been proved to influence etching rate. Additive materials have shown their ability in affecting etching rate in wet etching process. It was found that ethylenediamine (EDTA), triethanolamine (IPA), pyrazine and hydrazine, have caused reduction in etching rates[62, 66]. These organic compounds probably have a little coordinating action. When they are adsorbed on the silicon surfaces, they could restrict access of the etching agent (OH^- or H^+ ion and water molecules). On the other hand, viscosity of the etching solutions is increased. This will lower the diffusion rate of the ions produced in the etching processes and decrease the etching rates. DATTA and HARRIS[36] added chrohydric acid (HCl), kalium chloride (KCl) and sodium chloride (NaCl) into etchant to investigate their influences on etching rates. Their experiments showed that addition of KCl increased etching rates; HCl had rare effects on etching rates and NaCl had negative effects on etching rates. PENG et al [65] studied etching process on Gallium Natrium and etching rate was proved to be increased significantly with photoassisted process. Fig.10 indicates both of the solute (KOH) and solvent (H_2O) play an important role in the PEC etching of GaN[65]. With an increase of the OH^- concentration, the hydration effect continuously reduces the H_2O concentration. These competing effects therefore produce a peak in the etch rate whose location is very sensitive to the mean hydration number of the solute. ZUBEL and BARYCKA[68−69] found that etching rate was decreased significantly in etching process without IPA. UV excitation can impart considerable energy to the photogenerated carriers at the GaN/electrolyte interface and enhance the oxidative dissolution process.

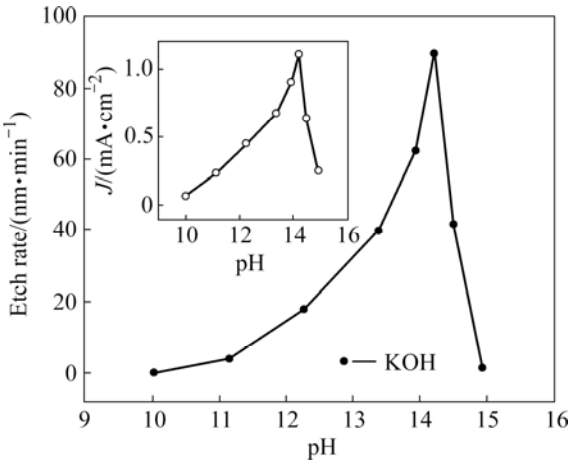


Fig.10 pH dependence of GaN etch rate in KOH solution[65]

Stirring process increases the inflow of the active agent to the surface of silicon during etching in diluted solutions. During etching, substrate will react with solution and release hydrogen ions. This reaction stops only when etch product blocks the chemical flow and causes an invisible wall between ions and substrate [69].

Substrate influences etch rate by its microstructure, film stress, impurities in or on the material itself. VARTULI[70] reported a decrease in etch rates with increasing crystal quality, as the reactions occurred favorably at grain boundaries and defect sides. Buffer layers grown on foreign substrates are suitable for wet chemical etching, the etching attack and thus the resulting etching features are limited to the layer thickness, because of heteroepitaxial growth. Such layers generally suffer from high defect density, surface features, and low crystalline quality, which detract defect identification[71]. One of the most significant reasons for etch-rate variation is the properties of the material, which are a result of the production method and subsequent processing/treatment. Etching process in the deposition method of pure materials tends to produce much greater differences in etch rate[60].

Solution affects etch rate by loss of reactive ions, loss of liquids to evaporation, etch product blocking the chemical flow and concentration of solution. WILLIAMS et al[60−61] showing the information of 620 etch rates of 53 materials in 35 etches that have been used/may be used in future fabrication of microelectromechanical systems (MEMS) and integrated circuit (ICs). Solution concentration is related to the content of ion hydrogen in solution. Higher concentration solution or higher ion hydrogen will be facilitated in etching the substrate. This concept is applied to all types of solutions, either acidic or alkaline solutions. ZUBEL and BARYCKA[68−69] concluded that etching rate of various plane in low concentration solutions are similar to one another due to the low anisotropy in KOH etchant. PENG et al[65] studied the role of solvent or H_2O in etching and its role in etching. LIU et al[72] indicated that the etch rate, to a large degree, was limited by the removal rate of non-volatile components. This was supported by the observation that etching rate was increased significantly by concentration of solution. YUAN et al[66] showed the differences between solution concentrations through the heights of the micro-protuberance. They found the heights of micro-protuberance increased with increasing concentration. PENG et al[65] concluded etch rate was not solely depended on etchant concentrations. For hydrofluoric-acid-based (HF) etching of various types of silicon dioxide, WILLIAM and GUPTA[60] found that for weaker concentrations of HF, the etch rate increases almost linearly with concentrations, but rises much faster going to concentrated HF.

Water content in the low concentration solution influences etching rate significantly. MAKINO et al[64] proved that etching rate had a close relationship with the water content in the solution. Etching rate decreased significantly in the open condition with high temperature compared with close condition. During open condition, water content in PA was vaporized during the process changing the composition of PA, which caused water content to increase and chemical ion or PA content to decrease. Period of etching affects etch rate significant by two ways: elapsed time from the start of etch and etch prolonged.

Temperature is one of the main issues affecting the efficiency of chemical etching. Many works clearly showed the temperature effect on etching rate relationship at range from room temperature (25 ℃) up to 800 ℃ for certain type of advanced ceramics[62−63, 65, 72−73]. Increasing temperature will increase etching rate and decrease surface quality. NIEBUHR[74] and FANG et al[75] showed the relationship of etching rate and temperature, and gave similar results. An increase in temperature will tend to stimulate corrosive attack by increasing the rate of electrochemical reaction and diffusion processes. GELDER and HAUSER[76] investigated etching of silicon nitride with silicon dioxide as a mask. They showed that etching rate was affected by water content and temperature. Etching rate of silicon nitride in refluxed boiling phosphoric acid was measured as a function of temperature and proved that all etch rates increased with temperature.

3.2 Surface quality

Surface quality is concerned with surface roughness, surface damage and surface mechanical properties. Surface conditions specify the quality level of micromachining. A good surface has low value of roughness without surface damage, such as pits. Surface quality is usually determined by scanning electron microscopy (SEM), atomic force microscopy (AFM) or transmission electron microscopy (TEM). Surface quality has a close relationship with etching rate. Researchers have found that surface quality uncertainly deteriorates with the temperature due to higher etching rate. Increasing etch rate will cause the unevenly etching process and eventually higher surface roughness[62, 66]. Different etch rate will significantly result in different types of surface quality. Surface quality is also affected by solution concentration, temperature, agitation material and type of photoresist. A small change of these parameters will result in unnecessary product[64].

Agitation material affects surface quality. With agitation materials' abilities to increase and decrease etch rate, they will change surface quality indirectly. TEHRANI and IMANIAN[62] observed an improvement in surface finish by adding triethanolamine (TEA) which was able to decrease etch rate. It happened because TEA was able to decrease the difference between corrosion rate of grain and grain boundaries, therefore surface finish was better and pitting defects were reduced. While IPA solution will lead to the conclusion that, better surface roughness is obtained in any type of etchants[66, 69]. Besides, prolonged etching period, also increase etch rate under same solution concentration and temperature. At the same time, irregular hillocks will appear and this will cause defects on material surface[66].

VLADUTA[77] summarized the relationship between material properties, contact angle and surface quality through surface energy. Surface energy is an important property influencing the wettability and surface energy depends on the chemical structure of the solid. The wettability also depends on the surface morphology and the contact liquid. The higher the surface energy is, the better the surface quality and finer grain size it is.

Preparation before etching is a necessary procedure to improve the results at the end of the process. A few types of preparation methods have been carried out by researches to improve substrate machinability by controlling the composition of ceramics, type of 'green material' used to produce ceramics, treatment and cleaning process. KUECH et al[78] found the buried interfaces prepared through wet chemical processes resulted in a high concentration of traps localized at the interface. LIU et al[72] applied treatment to glass-ceramics due to its insensitivity to cleaning process. Through treatment process, the microstructure of the glass-ceramic was changed, creating a better machinability material. A thin SiO_2 layer, as shown in Fig.11[72] was formed in glass-ceramic during exposure to NH_4OH/H_2O_2. In the buffered HF dip, SiO_2 layer was dissolved and re-deposition of dissolved elements would take place in these areas.

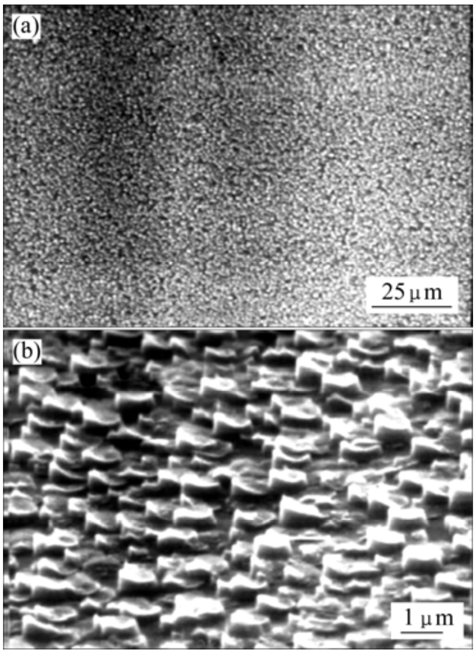


Fig.11 SEM images of etched _green_ GC6 glass sample cleaned by procedure[72]: (a) In low magnification; (b) In high magnification

Solution concentration is determined by its content. Higher hydrogen ion indicates high concentration and vice versa. In the other words, material will be removed faster in high concentration as explained previously. Fig.12(a) proved that quality of surfaces is strongly influenced by the etchant concentration[69]. As the concentration increased, surface quality became smoother. This condition will become worse once etchant concentration is over the peak limit. KINDER and TAUSLEY[63] found surface roughness of GaN reduces significantly while etching by KOH solution concentration from 0.02 to 0.04 mol/L. During etching, reaction process takes place between hydrogen ion and substrate to produce reaction material. Reaction material will increase if etchant concentration is too high, causing these unsoluble reaction products to start forming, which will erode material surface[79]. A very smooth

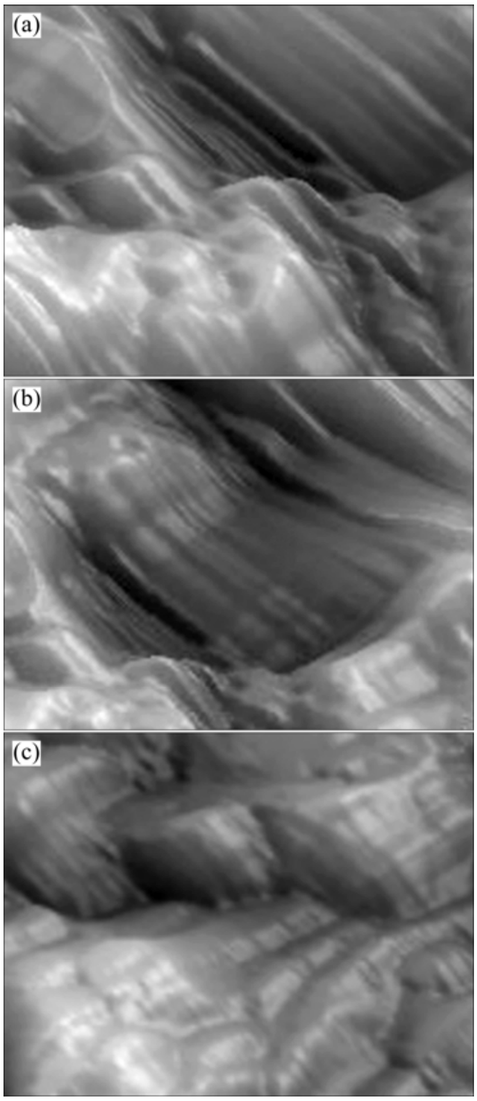


Fig.12 SEM images of molten salt etched SiC (a), Si_3N_4 (b) and sialon (c)[55]

surface may be obtained when light intensity is high and solution concentration is low, where the reaction rate becomes limited by the KOH concentration and the diffusion of reactants to the surface[55]. KINDER and TAUSLEY[63] showed the surface roughness of GaN/SiC (0.2 μm) etched surface with decreased KOH concentration. By reducing KOH concentration from 0.04 to 0.02 mol/L, the surface roughness was significantly reduced, as seen in Fig.12(a) (surface roughness=2.5 μm while etching in 0.04 mol/L KOH). COOK et al[55] studied the different ways of preparing four engineering ceramics to determine the most effective etching methods. All materials then underwent different types of etching methods. COOK et al[55] summarized that silicon carbide (SiC), silicon nitride (Si_3N_4) and sialon, which were polished using a Buehler Motopol polisher and underwent different stages of diamond paste on a Textmet cloth etched excellently in molten-salt etch. Fig.12 shows secondary electron images of thermally etched SiC, Si_3N_4 and sialon[54]. Microstructure in Fig.12(a) showed a fibrous nature, consisting of elongated, high aspect ration SiC grains with finer grains between them. The molten-salt etch (in Figs.12(b) and (c)) removed the grain boundary phase and the Cr-rich particles, leaving the matrix untouched.

Temperature plays crucial role in surface roughness through ion reaction. Temperature will change material morphology at the end of the process. Indirectly, changes of temperature will affect surface quality. Many researches have proved that temperature increasing allows one to obtain better surface quality in various concentrations of solution[64, 66, 68, 69−72, 80]. Increasing temperature will stimulate reaction and increase the surface quality. JARDIEL et al[56] observed the shape of grains changed from rounding plate-like grain to platelets after being etched thermally.

Photoresist also plays a part in surface quality. Type of photoresists, such as their adhesive has challenge researcher during their study in surface quality. LIU et al [72] who tried to prove the relation between mask and surface quality had compared their result covered by fused silica wafer and chromium mask. Result showed that ‘grass’ was found in chromium mask but not in fused silica wafer covered. Photoresists should be chosen carefully before etching because they sometimes react with the solution or material during etching process. Therefore, surface quality is affected at the same time. The removal of the native oxide by the latter solution again changes the surface morphology, while the surface etched by AZ400K has evidence of micromasking[70]. Lift-off is because of the etch solution attacking the interface between the two materials that is defective and is usually a mixture of stacking faults and dislocations in this region because of lattice mismatch.

3.3 Dimensional accuracy

Dimensional accuracy is another main concern during micromachining by chemical etching. Industries seek for a solution to overcome dimensional inaccuracy without affecting substrate mechanical properties. DATTA and HARRIS[59] showed that dimensional accuracy was controlled by several phenomena such as dissolution kinetics, surface films, mass transport and fluid mechanics. Many studies showed that higher temperature will be able to etch the surface in higher rate causing unwanted surface properties but lower rate will be caused under etching [63−65].

Isotropic wet chemical etching causes undercutting beneath the etch mask. Reasons causing undercut accounted for the choice of process, parameters and substrate surface properties. Undercut always happens, especially in wet anisotropic etching process. This process will etch substrate at all directions at same rate or speed. In order to reduce the undercut effect, a suitable photoresist should be used, which provides higher protection to subtract[67]. Parameters such as period of etching, temperature and solution concentration are sometimes used for controlling the dimensional accuracy during etching process. With higher temperature, etch rate will increase proportionally and result in lower dimensional inaccuracy and vice versa. HUA[53] showed that Secco etch was unsuccessful in delineating crystalline defects on silicon wafers because over-etching occurred on crystalline defects and the layers were not totally removed. The size of pits increased as the etching time in Secco etches solution increased as shown in Fig.13[53]. After ‘152’ Secco etch, no crystalline defect was found at the centre of the wafer.

As mentioned previously, photoresist is an issue during etching process to obtain higher dimensional accuracy. Photoresist should be matched chemically to the type of solution applied during the process to avoid dimensional inaccuracy due to their weak adhesive and peel-off. Sometimes, dimensional inaccuracy happens because photoresist is etched faster than substrate, causing the unwanted shape or pattern at the end of the process[60].

4 Conclusions

1) Ceramics have been widely used and applied in the modern industry. With the inherent brittleness and toughness, ceramics are attractive to researchers and industries to improve its performance in order to fulfill the requirement needed in certain field, such as turbine application. Advanced ceramics are created with different alloying metal and different mechanical and chemical properties.

2) Chemical machining is an advanced machining process, which only involved chemical solution. Aided and without aided chemical machining show different results of etching during etching process. A few parameters are taken into account when chemical machining is to be considered as the method of machining. This included temperature, solution type, concentration of solution, etching time and etching environment.

3) Photoresist is another matter of concern in etching process. Different content of photoresist is only adapted to certain kind of solution. In order to produce an accurate dimension of material, photoresist plays an important role.

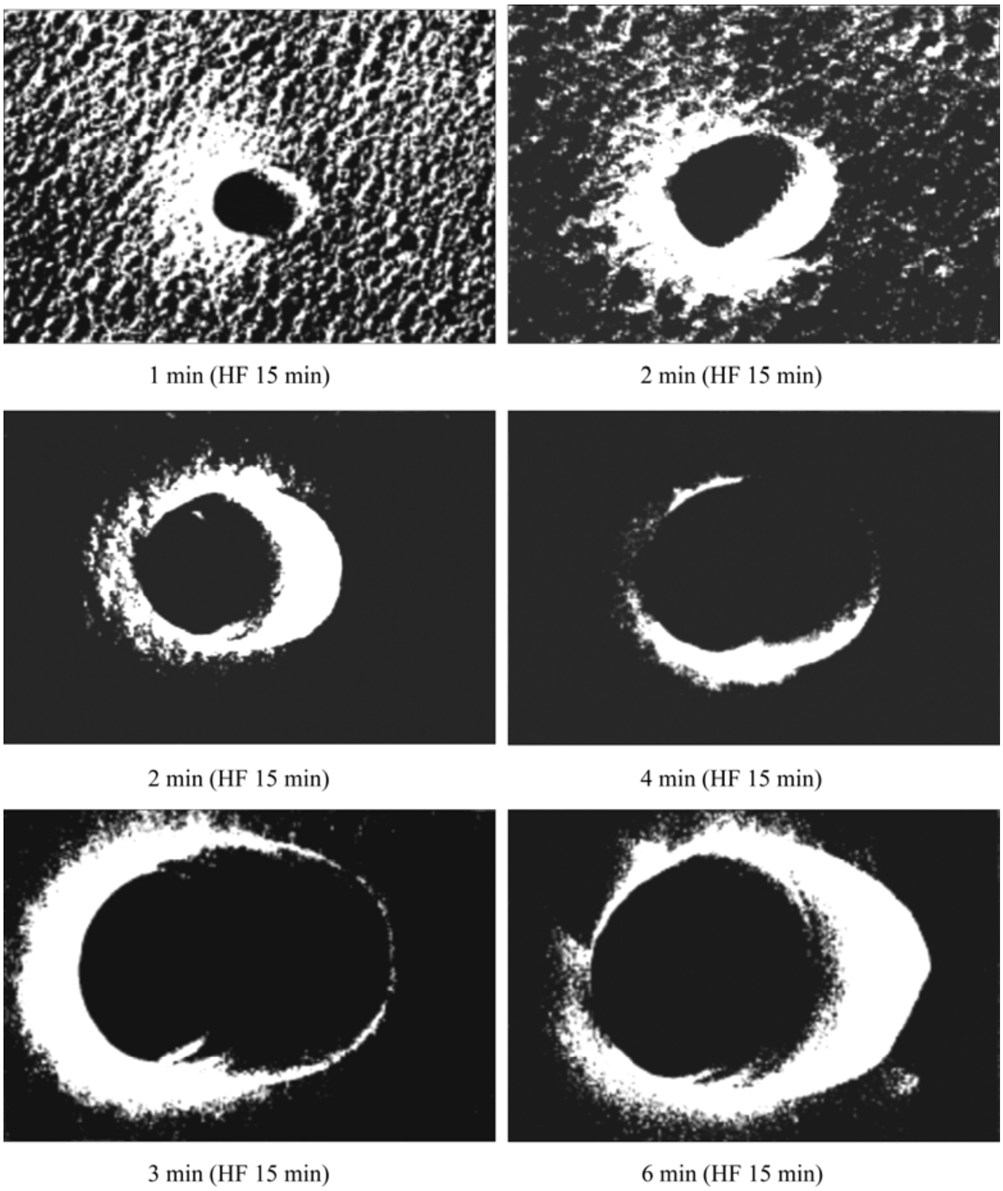


Fig.13 Close-up SEM micrographs showing that size of pits increase with increasing etching time in Secco etch[53]

4) Damage caused by chemical etching are less than conventional machining. Internal damage such as dislocation, pits, flexural strength, thermal shock, corrosion and erosion are one of the common defects happened in ceramics under chemical etching.

5) Production of etching, including surface roughness, rate of removal and dimensional accuracy is investigated. Surface roughness, which is the most important external characteristic always, attracts the attention during etching process. With controlled temperature, solution concentration and aided material, we are theoretically allowed to obtain a perfect surface roughness (or low value of surface roughness). Rate of removal in chemical etching is related to surface roughness. With increasing rate of removal, value of surface roughness also increases. This is a problem facing in the research of many works, whereby they wish to process in high rate of removal and fine surface roughness, which is hard to success.

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