Chapter 9

Photochemical Machining: A Less Explored Non-Conventional Machining Process

Sandeep Sitaram Wangikar
Shri Vithal Education and Research Institute, India

Promod Kumar Patowari
National Institute of Technology Silchar, India

Rahul Dev Misra
National Institute of Technology Silchar, India

Nitin Dnyaneshwar Misal
Shri Vithal Education and Research Institute, India

ABSTRACT

The chapter focuses on the history and the development of photochemical machining in brief. The relevant studies related to photochemical machining and parametric effect are also discussed followed by gaps identified along with scope for the work and then the PCM process is explained in detail. The significant control parameters and their effect on the response measures are demonstrated with a fishbone diagram is explored. Further the detailed parametric effect on the response measures along with the scientific explanation of the effect is presented. The chapter is concluded with the two case studies (i.e., PCM of brass and Inconel 718).

INTRODUCTION

The stringent dimensional requirements with high surface finish and complex shapes are cannot be accomplished by the conventional machining processes. The hard materials are also constraints for the conventional machining methods. Furthermore, the augment in temperature and residual stresses generated in the work piece because of the conventional machining processes may possibly not be tolerable for various applications. Therefore, Now a day's, non-conventional machining processes are frequently

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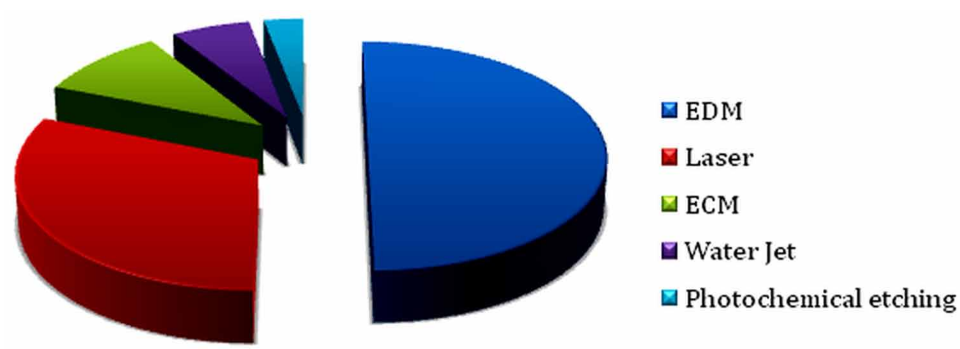
used for the manufacturing of a wide variety of parts. The non-conventional machining processes include Electrical Discharge Machining (EDM), Laser machining, Electrochemical Machining (ECM), Abrasive jet machining, Photochemical Machining (PCM), etc. The comparatively less studied non-conventional machining process is Photochemical etching (Figure 1) (Gamage and DeSiva, 2015). The PCM process is based on the amalgamation of photoresist imaging and chemical etching (Allen, 2004). Photochemical machining process is a precision contouring of metal into any shape, size or form without using of physical force, by a controlled chemical reaction. Material is etched by microscopic electrochemical cell action, as occurs in chemical dissolution or corrosion of a metal.

In photochemical machining, the difficult thin 2D flat metal components are produced which are free from stress and burr with low cost and less delivery time apart from other advantages. As this process is sovereign of intricacy of the machining, this process becomes an efficient, fast, cost competitive technique of producing components of metal with intricate designs unrivaled by any another conventional metal forming process. An additional benefit of the process is the possibility for etching a broad range of materials i.e. metals, alloys, glasses, ceramics, etc. However, the metals and alloys like copper, magnesium, zinc, aluminium, steels, nickel, monel, kovar, etc. are easily etched using PCM. Because of the assortment of materials used in the PCM process, the PCM is playing a dominant role in the precision parts manufacturing in different areas such as automotive, electronics, aerospace, optics, medical, jewelry, etc. Typical applications are the productions of integrated circuit lead frames, television shadow masks, mobile telephone gaskets, decoration on watch parts, suspension head assemblies, and jewellery (Yadev and Teli, 2014).

This chapter presents the parametric effect issues of the less explored photochemical machining process. The background focusing on the brief history and the selective literature review is discussed after this section. Further, the PCM process details along with the parameters for experimentation are presented in the succeeding section. Then, the influence of the process parameters on performance measures of the PCM is discussed. The surface topography of the photochemically machined sample specimens is also conferred using scanning electron microscopy (SEM) to reveal the process parameters influence. The scope for future work in this perspective for PCM is briefed following the summary of the chapter.

Figure 1. PCM - Less explored Non conventional machining process (Gamage and DeSiva, 2015)



**For a more accurate representation see the electronic version.*

BACKGROUND

Photochemical Machining (PCM) process has originated from the knowledge of the acid attack on metals. The traces of this technology has been noted in the Greek and Egyptians ancient history as long ago as 2500 BC. The earliest reference to PCM process portrays an etchant made from the common salt, vinegar and charcoal acting through a hand scribed mask of linseed oil paint. The attractive patterns were also etched on the swords using a scribed wax as resist. The first photo etching was mentioned in 1826 but the first patent was assigned to William Fox Talbot in 1852, describing a photoetching process for etching copper with ferric chloride (Allen, 2004). But this process is explored very little by researchers in the latest past. Some of the recent trends of study are discussed as follows.

The simulation study related to etching has been reported by few researchers. The two dimensional simulation model for etching has been developed and the experimental analysis of the process parameters on micro geometry has been investigated by Bruzzone and Reverberi (2010). Furthermore, a single crystal silicon has been tested for three dimensional anisotropic wet etching employing a simulation model. A 3 dimensional simulation model has been developed by Lee and Won (2007) for the anisotropic wet etching of single-crystal silicon and reported that the developed simulation model promises for the thorough analysis of multifaceted three dimensional MEMS structures.

The micro-textures on carbon steel surfaces were fabricated using PCM and parametric study has been carried out by Zhang and Meng (2012). The surface textures have been produced on sheets of Monel 400 using PCM by Patil and Sadaiah (2015) and the effect of spinning speed on film of photoresist, and the effect of temperature and time of etching on the etched pattern have been studied.

The chemical machining of copper has been performed by Cakir (2005) using two different etchant as ferric chloride and cupric chloride and reported that the higher etching rate has been observed for ferric chloride etchant and the better surface quality has been produced with cupric chloride etchant. Further, Cakir et al. (2008) studied the chemical machining of aluminium for analyzing the influence of etching time and etchant temperature on the surface finish and rate of etching. The regeneration process for cupric chloride was also investigated by Cakir et al. (2006). The photochemical machining of inconel 600 using ferric chloride etchant has been carried out by Wagh et al. (2014) and discussed the parametric effect on the response measures. The influence sodium hydroxide concentration at constant temperature on the morphology of alumina nanotubes and nanowires has been investigated by Sadeghpour-Motlagh (2014). The PCM on OFHC copper has been carried out by Chaudhari et al. (2016) with ferric chloride etchant to observe parametric effect on undercut, surface roughness, and etch factor followed by optimization using Gray rational analysis. The optimization of process parameters for undercut and material removal rate was performed by using artificial neural network and Grey rational analysis (Saraf and Sadaiah 2013,Misal and Sadaiah 2013). Saraf and Sadaiah (2017) studied influence of magnetic field on an etch rate of SS316L. Further, they developed a novel 3D photochemical method for stent manufacturing. The effect of rolling direction on the PCM of Monel 400 has been studied by Patil and sadaiah (2016,2017). The PCM study for inconel 718 alloy has been performed by Misal and Sadaiah (2017) and reported the influence of grain size and selected parameters on the surface roughness through a surface topography study. The process parameter's optimization for PCM of inconel 600, brass, german silver, SS316, and SS316L steel have been carried out for the prophecy of material removal rate (MRR), surface roughness and undercut using response surface method and gray rational method. The control parameters have been considered as concentration, temperature, and time (Wagh and Dolas 2016, Wangikar et al.2017, 2018). The different manufacturing alternatives for fabrication of microchannel heat recovery unit has been discussed by Gao et al. (2016) and reported that photochemical machining has been employed as a patterning process for producing channels. The microchannels also have been fabricated using photochemical machining by Wangikar et al. (2017, 2018) and Das et al. (2017).

From the above literature, it can be noted that the photochemical machining study for different materials have been reported by different researchers. However, the overall effect of various parameters on the performance of PCM for different materials has not been summarized. Also, the scientific explanation of the parametric effect and mechanism of material removal has not been outlined. In this chapter, a brief introduction about the photochemical machining along with the process parameters are discussed. The detailed parametric effect and the scientific explanation for the same for two different materials as brass and inconel 718 is discussed which reveals the causes for the material removal rate and the surface roughness. The study is supported with the surface topography study for the brass and inconel 718.

PCM Process

Photochemical machining is one of the chemical machining processes in which the photographic and chemical etching techniques are employed. It utilizes chemical etching through a photoresists' stencil as the method of removal of material over the selected areas of the specimen. The technology is fairly modern and got recognized as a manufacturing process about many years before. Figure 2 shows the flow diagram of the PCM process which presents the main steps of photochemical machining applied to a metal plate viz. Photoresist Coating, etchants and scribing templates which have been summarized below:

The first step comprises the production of the photo-tool which is nothing but producing a required shape on a photographic film. The photo tool is a negative film of the image to be produced. The accuracy of the photochemically machined specimen principally depends upon the accuracy of Photo tool. The photo tools are generated by direct printing of the image from CAD drawing. The accuracy of the

Figure 2. PCM flow diagram

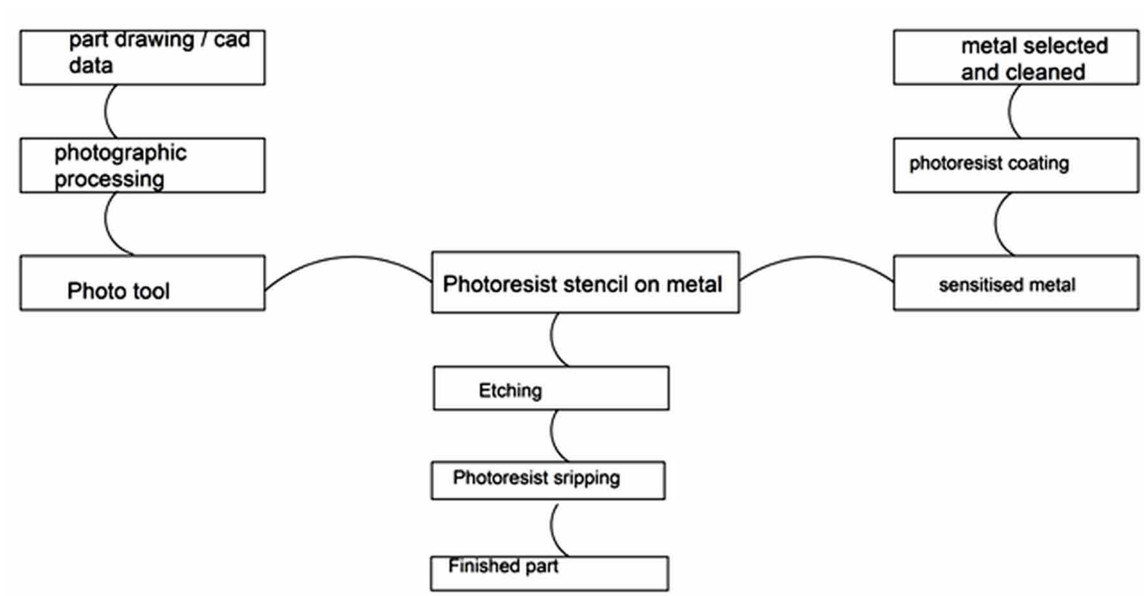


Photo tool is decided by the dpi (dots per inch) specification of the printer. The cartridge replacement and toner refilling also play a significant role in print quality. The photo tools are to be selected based on the edge deviation and overall quality. The sheet metals are cleaned chemically using solutions like acetone and coating of a photoresist film which is sensitive to light is applied. The photoresist will adhere to the surface of the specimen and acts as a stencil resist (protective layer) shielding the specimen surface throughout etching. Generally, the photoresist is available in liquid form and for application purpose, the specimen is required to be dipped in to the photoresist followed by drying. The photo-tools are employed in accurately registered pairs like one on the top, another at the bottom, and the material to be etched is sandwiched in between these two photo tools. This arrangement of photo-tool permits the both side etching of the material, which reduces the undercutting of photoresist and in turn produces straighter sidewalls on the specimen. The metal coated with the photoresist is afterward placed under the photo tool and exposed to an ultraviolet light source in an vacuum. This process transfers the image accurately onto the resist and becomes a replica of the desirable geometry after developing. Immersion or spraying then develop the exposed image. Each photoresist has its developing solution, like water, hydrocarbons, an alkaline solution, and other solvents. The exposed specimen is further washed to remove the unexposed photoresist on the areas of the specimen which is to be etched chemically. The imaged specimen passes through the solution (etchant) etch spray or dip where dissolution of the selected material of the specimen takes place. There are different etchants available for the various materials. The choice of the right etchant depends upon quality, cost, rate of material removal, and depth of etch.

PROCESS PARAMETERS

The process parameters include control parameters (Input parameters) which will have effect on the process and the response parameters (output parameters). Some parameters kept constant during experimentation which are called as Fixed parameters.

Control Parameters: The performance of PCM has been influenced by many parameters and setting of these parameters strappingly depend on operator's experience and the parameters. So the primary task is to choose the input parameters. On the basis of review of literature, operators experience and from some pilot experiments, input parameter are generally selected. These input parameters are also called as control parameters. During experimentations, the control parameters are varied in a range in order to study their influence on performance measures. The control parameters have been given below:

- Temperature of etchant
- Concentration of etchant
- Etching time

In addition to these main control parameters, the photoresist thickness, ultraviolet light intensity, photo tool characteristics, etc. may also have the effect on the performance of PCM. Also, the different types of etchants and the addition of acids in etchant also have effect on the performance measures of PCM.

- **Response Parameters:** The parameters which have effect of selected control parameters are the responses or output parameters of the experimentation. The response parameters will be selected on the basis of their significance related to work or application. The performance of any photochemical machining process is stated by the following factors:
- **Material Removal Rate (Etch Rate):** The etching rate or rate of material removal depends on the chemical and metallurgical uniformity of the specimen and the homogeny of the solution temperature. Normally, the castings have the largest grain sizes which show the roughest surface along with the lowest rate of machining. The rate of machining rate together with the best surface quality is generally given by rolled metal sheets. The etching rates are lower for hard metals and higher for the softer metals.
- **Surface Finish:** In PCM, the machining phase is observed for both the cases i.e. at the individual surface of the grains as well as at the grain boundaries. The fine grain size and a homogenous metallurgical structure are thus, necessary for fine surface quality of homogeneous appearance. The photochemically machined surfaces do not have a regular lay pattern. Based on the grain size and orientation, heat treatment, and previously induced stresses, each material has a fundamental surface finish which results from PCM for a certain period of time. While surface imperfections will not be eradicated by PCM, any prior surface indiscretion, dents, waviness, or scratches will be somewhat altered and reproduced in machined surface. Generally, slow etching will produce a surface finish similar to the original one.
- **Undercut:** During the etching process, the removal of material takes place depth wise in the unexposed portion as well as in the inward direction under the photoresist. The distance etched under the photoresist is called as undercut and the distance etched in the exposed portion is termed as depth of cut. After etching a bigger slot than that of requirement is produced due to the undercut. There is a requirement of consideration of undercut before etching for getting accurate dimension.
- **Etch Factor:** The etch factor is the ratio of undercut to the depth of etch. This ratio should be considered when scribing the mask using templates in chemical etching.
- **Edge Deviation:** The nonconformity of the edge of the machined component is referred as Edge Deviation (ED). It refers to the straightness of the edge produced while machining. The edge deviation plays a vital role in fabrication of micro parts like microchannels, heat sinks, etc. where the accuracy of the fabricated geometry is having significant effect on the performance of the part/device.
- **Etchants:** The different etchants are used in PCM for different materials. These etchants includes ferric chloride, cupric chloride, sodium hydroxide, and addition of acids for better performance like hydrochloric acid, nitric acid, hydrofluoric acid, etc. Ferric chloride ($FeCl_3$) is a universal etchant and generally used for materials like steels, aluminum and its alloys, copper and its alloys, nickel, etc. It is cheap, providing a high etch rate and is reliable.

Mechanism of Etching

The removal of material takes place by chemical etching in which the three main stages can be identified as follows:

1. Molecules or Ions from an solution of etchant diffused towards the exposed area on the specimen surface through boundary layer.

2. Soluble and gaseous by-products formed during the chemical reaction between etchant and the exposed specimen surface
3. A by-product from the surface of the work piece gets diffused through the boundary layer into the etchant solution.

Parametric Effect

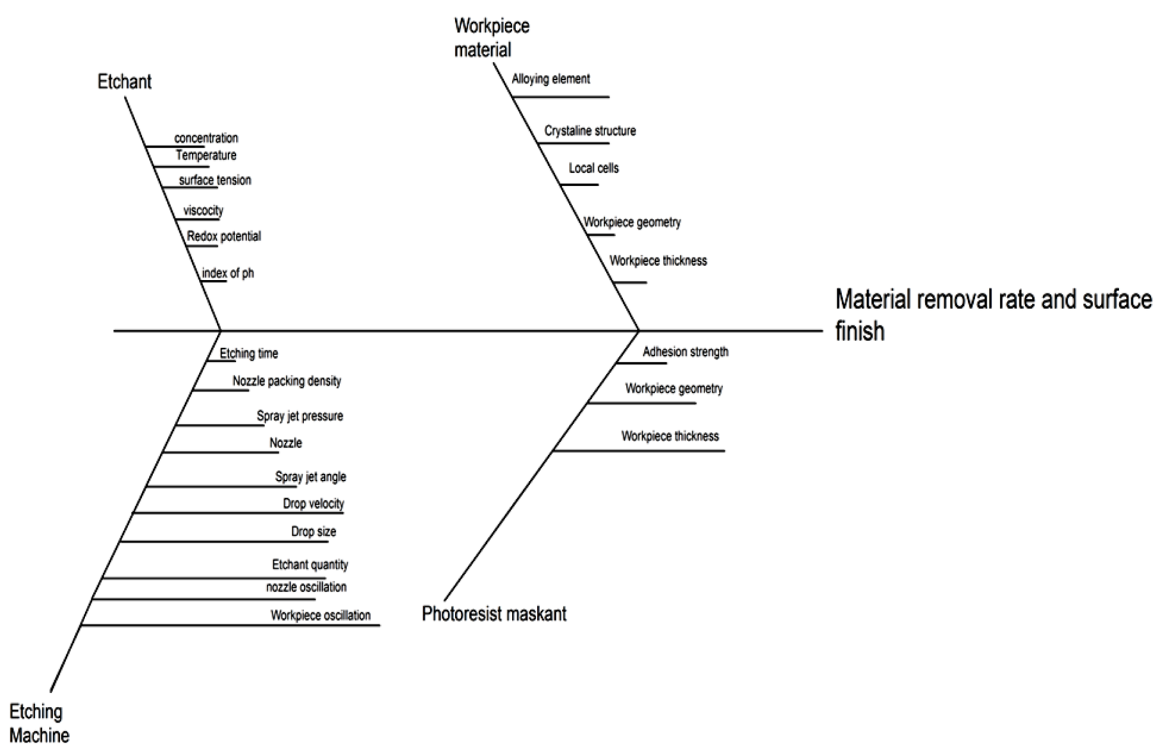
There are various control parameters having the effect on the performance of photochemical machining. The different response parameters for PCM are discussed above. But, the performance of PCM is principally governed by the two parameters viz. material removal rate and surface roughness. These two parameters have also been reported by various researchers.

It is observed from Figure 3 that there are four main elements that have prominent effect on the material removal rate and surface roughness in PCM.

Workpiece Material

The workpiece material may be a metal, an alloy, ceramics or glasses. The composition of the elements present in the material, their nature (crystalline or amorphous) have a significant effect on material removal rate and surface roughness. The geometry of the part to be produced is also an important consideration. There is also influence of the specimen thickness and shape.

Figure 3. Fishbone diagram for material removal rate and surface roughness



Photoresist Maskant

There are different (four types) photoresists like positive and negative and further wet and dry. The wet photoresist can be applied by dipping or by spin coating. The application method of photoresist decides the resist thickness in micron on the specimen and its uniformity. In this case also the workpiece shape, thickness and the geometry to be machined have influence on the performance. The different types of photoresists are available having different adhesion strength. Therefore photoresist application is primarily govern the PCM performance.

Etching Machine

The etching may be carried out in etching machine for or in a beaker depending upon the quantity of specimens to be produced. The etching machine generally gives the spray etching facility which enhances the performance of the PCM process. The some important parameters in etching machine are etching time, nozzle packing density, spray jet pressure, nozzle type, spray jet angle, drop velocity, drop size, etchant quantity, nozzle oscillation, workpiece oscillation, etc.

Etchant

The dissolution of material takes place in the solution which is called as etchant. There are different etchants used for etching of different materials. Therefore etchant selection is also important in order to achieve better etching rate. The etchant concentration, temperature and etching time play a vital role in PCM process and governs the material removal rate and surface roughness in a significant manner. In addition to that the redox potential, index of Ph, surface tension and viscosity are also effective parameters in for etchant.

From the above study of parameters and their effect on PCM performance, it can be noted that the workpiece material, photoresist and its application method and the way of etching (in beaker-for study purpose or using etching machine) once decided using the literature and some pilot experiments (if required) can further be considered as fixed parameters for the PCM experimentation. In case of etchant, the etchant selected based on the material can also be treated as the fixed parameter. Thus, the concentration of etchant, etchant temperature and the etching time may be considered as the variables for the PCM process. Further, the ranges for these can be decided based on the past study and pilot experimentations. The influence of concentration, temperature and etching time on material removal rate and surface roughness along with the detailed mechanism is explained below.

Effect of Concentration

Concentration of etchant is one of the prominent factor having effect on the performance of the PCM. The number of molecules present in the etchant solution is decided by the concentration of the solution. The chemical reaction occurs when the molecules collides on the surface of the specimen. For lesser etchant concentration, less number of molecules will collide on the surface of surface of the specimen, which leads to less diffusion at the surface and in turn less etching means less material removal and good surface finish. With increase in concentration, the molecules in the etchant will increases. Hence, higher the number of molecules of reactant (reagents) present per unit volume in the etchant, there are greater chances for reactive collisions to occur. As more molecules present in the etchant, more reactive collisions will occur at the specimen surface. This will results in enhanced diffusion and thus better etching means higher material removal rate but produces an uneven surface and hence poor surface finish. This is justified by the Fick's first law of diffusivity. The concentration gradient is directly proportional to the diffusion flux. The equation on the basis of which relation between diffusive flux and etchant concentration is given as:

$$J = -D\frac{dC}{dx} \quad (1)$$

where C: gradient of concentration, D: coefficient of diffusion, and J: diffusion flux.

From Eq. 1, it is clear that the concentration of etchant acts as a driving force.

The increase in concentration up to certain limit has significant effect on the material removal rate and surface roughness. The material removal rate and surface roughness will decrease with increase in concentration. The main reason behind this is the effect of viscosity. The etchant solution becomes more viscous which reduces flow ability and the movement of the formed product and fresh etchant goes on decreasing.

Effect of Temperature

The chemical reactions occurs when the molecules (reagents) will collide with one another in a energetic way. The movement of molecules is governed by temperature as the temperature is a means of the kinetic energy present in molecules. The molecules will react only when they have a sufficient quantity of energy for a reaction. The molecular energy intensity will increase with the rise in the temperature of etchant which causes enhanced collisions between particles results in a better reaction rate. Normally, with an increase in temperature, etching rate increases. As the temperature increases, there is increase in the molecular energy level which leads to reactive collisions of the molecules on the specimen surface which results in better diffusion. Thus, a higher quantity of material will be removed from the surface leads to a rough surface. This results in better MRR and higher Ra with increase in temperature. The surface roughness as well as the etch rate is directly proportional to the diffusion coefficient (D). Stokes-Einstein's equation for the diffusion coefficient is as given:

$$D = \frac{kT}{6r\pi\mu} \quad (1)$$

where μ is the viscosity of etchant, r is the radius of etchants particle; T is a temperature of etchant and k is Boltzman constant. Also the viscosity of the etchant changes with temperature

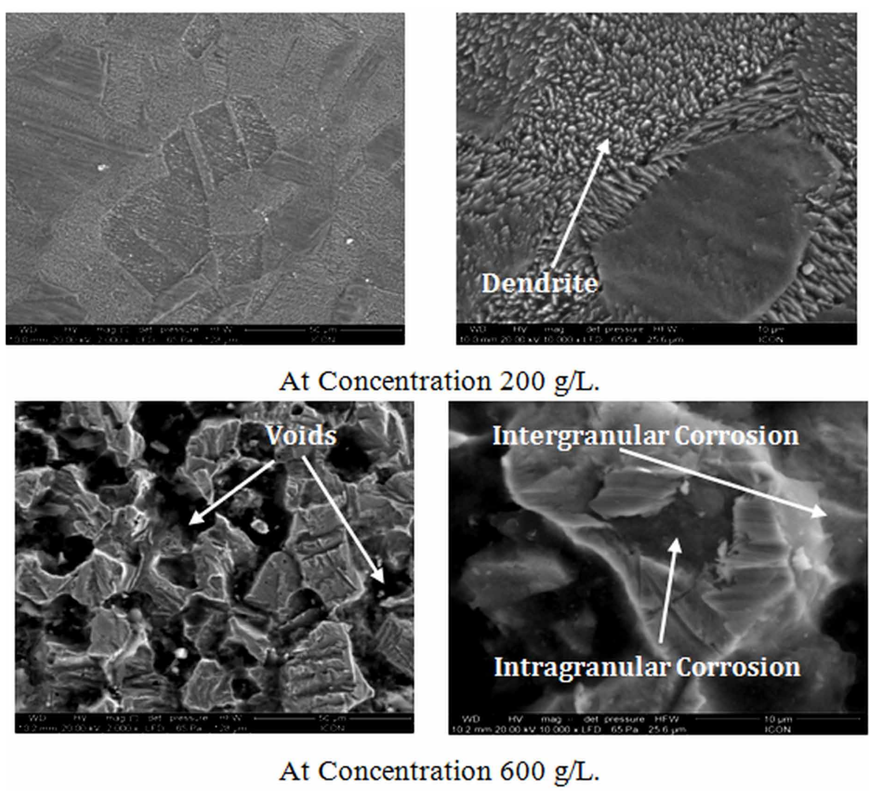
Effect of Etching Time

If the molecules in the etchant will collide on the specimen surface for lesser time, then lesser diffusion will occur. This results in lower material dissolution in the etchant solution which in turn gives lower MRR but good surface finish (i.e. lesser Ra). The collision of molecules on the surface of specimen for the longer time will improve the diffusion and material removal rate. But the surface obtained may be uneven due to collisions for a higher time leads to higher Ra. This gives an incessant increase in material removal rate and surface roughness with time.

Case Study 1: Photochemical Machining of Brass

The photochemical machining of brass has been reported by Wangikar et al. (2017). The effect of the process parameters on the material removal rate and surface roughness are discussed with the help of scanning electron microscopy (SEM) images. The effect of concentration on the material removal rate and surface roughness has been explained with the help of SEM. At lower concentration, due to less molecules attack on the surface of the specimen, lesser material removal rate with a better surface roughness has been reported. The diffusion starts at grain boundaries characterized by inter-granular corrosion and further diffusion grows within the grain i.e. trans-granular corrosion. The dendrite structure has been reported for brass. The more molecules will attack on the surface for an etchant with higher concentration results in enhanced material removal rate with a rougher surface. This is depicted in Figure 4 for photochemical machining of brass with 200 g/L and 600 g/L concentration. The void formation due to combined intergranular and transgranular corrosion at higher concentration is reported and demonstrated in Figure 4. The increase in material removal rate and surface roughness with increase in temperature and etching time have also been reported.

Figure 4. SEM images of Photochemically machined brass specimens at different concentrations (Wangikar et al. 2017)



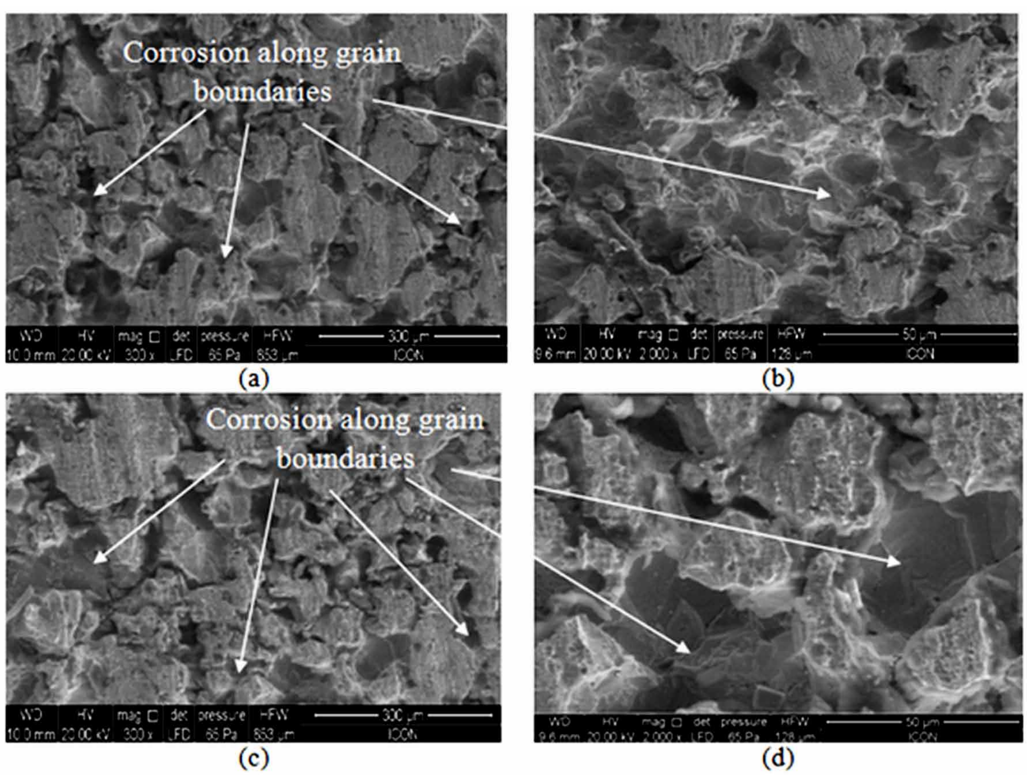
Case Study 2: Photochemical Machining of Inconel 718

The PCM study of Inconel 718 has been reported by Misal et. al. (**Misal et al. 2017**). The effect of process parameters and the grain size on material removal rate and surface roughness has been reported. The effect of grain sizes at different temperatures have been investigated and reported that the smaller grain size results in higher material rate and surface roughness as compared to larger grain sizes. The influence of temperature on the surface topography is be revealed using the SEM images as shown in figure 5. The etching progresses through intergranular corrosion as shown in figure 5 (a) and with higher magnification 5 (b). With an increase in temperature up to 65 °C, the etching rate increase as an effect of enhanced reaction rate. This is due to increased kinetic energy and improved collisions at the grain boundaries which results in enhanced corrosion at grain boundaries as shown in figure 5 (c), and also formation of voids have been reported (as presented in the magnified view- figure 5 (d)). Hence, increase in material removal rate and surface roughness with increase in temperature has been reported.

SCOPE FOR FUTURE WORK

The photochemical machining process is one of the least explored non-conventional machining process and it has applications in various areas and capability to produce parts with complex shapes and geom-

Figure 5. SEM images of photochemically machined Inconel 718 at different temperatures
(a, b)- at 45 °C and (c, d) - at 65 °C (Misal et al. 2017)



etries. In this regard, in view of the above mentioned discussion on various aspects of PCM, the scope for future work can be possible with respect to the following aspects.

- Parametric optimization for PCM of different materials and prediction of the optimum ranges of process parameters
- Comparative PCM study of different alloys (e.g. Copper alloys, Aluminium alloys, etc.)
- Effect of photoresist thickness on the PCM performance
- UV exposure effect on the PCM characteristics
- Regeneration of etchant
- Fabrication of nano particles from the dissolved metal in etchant and their characterization
- 3D PCM investigation and fabrication of micro parts using 3D PCM

CONCLUSION

In this chapter, the least explored non conventional machining process viz. photochemical machining is discussed along with a thorough discussion on the various related aspects of the process. The PCM process is introduced in the first part of the chapter along with the detail stages in it. The history of PCM, background for the PCM process and the recent trends in the PCM are discussed. The different control parameters and performance parameters are discussed and the material removal rate and surface roughness are focused as the most significant performance parameters. The various factors contributing to material removal rate and surface roughness are briefed. The influence of the most important parameters i.e. concentration of etchant, temperature and etching time on the material removal rate and surface roughness is elaborated in detail with the mechanism. To support this, two case studies on PCM of brass and Inconel 718 has been reported in which the parametric effect is explained using SEM. The guidelines for further work in PCM are given which are focusing on the demanding areas for work in PCM.

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