CIRP Annals - Manufacturing Technology 59 (2010) 255–258

Contents lists available at ScienceDirect

CIRP Annals - Manufacturing Technology

journal homepage: http://ees.elsevier.com/cirp/default.asp

An Experimental Evaluation of an Etching Simulation Model for Photochemical Machining

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ARTICLE INFO

Keywords:
Etching
Surface
Simulation

ABSTRACT

Photochemical machining can satisfy the large demand coming from the microproducts market. The metal etching technologies lack however a precise control over the micro-geometry of surfaces. Metal etching results from diffusive and kinetic phenomena whose relative importance depends on process parameters. The effects of the chemical kinetics on the etching regime and, consequently, on the surface generated by wet-chemical etching need a thorough investigation. This paper reports an experimental assessment of a 2D simulation model of etching, where also the role of reaction products dynamics is considered. Furthermore an experimental analysis of the process parameters on micro-geometry is reported.

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1. Introduction

Among the production processes available to manufacture innovative products, etching technologies are very attractive for the high volume production they can provide. Dry and wet etching technologies are widely used in many emerging applications which require metal removal to produce micro-components and micro-systems [1–3]. The development of environmentally safe processes contributes furthermore to the industrial diffusion of chemical etching [4]. Photochemical machining (PCM), in particular, seems a good etching technology to satisfy the large request coming from the microproducts market [5]; furthermore this technology could play an important role for the development of functional surfaces [6]. PCM lacks however a precise control over the surface micro-geometry.

Metal etching is basically a result of diffusive and kinetic phenomena: their relative importance depends on the process's parameters, such as temperature and dilution of the etchant solution. Analytic models and simulation techniques provide valuable tools for the theoretical study of the etching process. The effects of the chemical kinetics on the etching regime and, consequently, on the surface generated by wet-chemical etching have been theoretically investigated by many authors [7]. Recent studies have considered both the diffusive resistance and the chemical kinetics, proposing models of diffusion and reaction controlled etching, including convection phenomena [8,9].

At micro-scale the experimental study of chemical etching poses several problems; the in-process evaluation of fundamental parameters, such as the local concentration and velocity of the etchant and reaction products, is currently impossible. These limits suggest the use of simulation techniques. An experimental assessment of a new 2D simulation model that considers the effects of the chemical kinetics on the etching regime and the role of reaction products dynamics is discussed.

2. Theoretical aspects

Chemical etching is a complex disaggregation process resulting from two subsequent phenomena, diffusion and reaction, which evolve through the following phases:

1. diffusion of the etchant reagent towards the substrate subject to disaggregation;
2. chemical reaction as a consequence of an activated hit between the etchant molecule and the single surface atom or molecule;
3. diffusion of the reaction products towards the bulk of the eroding bath.

The timescales of steps 1 and 3 are usually of the same order of magnitude, and are very different from those typical of the chemical reaction. Therefore, the global process can be diffusion-limited or reaction-limited according to whether the slower step is represented by pure diffusion or chemical reaction, respectively [7].

The modelling of the aforementioned phenomena can be based on two different schemes. The first relies upon a deterministic approach based on the numerical or analytic solution of moving boundary problems [10]; the second is based on statistical and simulation models [9].

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0007-8506/$ – see front matter © 2010 CIRP.
doi:10.1016/j.cirp.2010.03.070

For 2D geometries, Kuiken [11] proposed a perturbative method to solve the Fick second law of diffusion:

$$\frac{\partial c}{\partial t} = D \cdot \nabla^2 c \tag{1}$$

where c is the etchant concentration, t is the time, D is the diffusion coefficient.

The moving boundary condition is related to the chemical kinetics according to:

$$\nabla c \cdot \boldsymbol{n} = -\frac{R(T,c)}{D} \tag{2}$$

where **n** is the unit vector normal to the eroded surface and $R(T,c)$ contains the expression of the intrinsic chemical kinetics function of temperature T and concentration c.

An alternative analytic approach is based on a level set formulation to solve the problem of surface motion in a topography simulation of deposition, etching and lithography processes [12]. This method requires the solution of a Hamilton–Jacobi system of equations using techniques borrowed from hyperbolic conservation laws.

The most critical drawback limiting the use of continuum models is the intrinsic difficulty in describing surface details with undercuts, where the local surface height is not a single-valued dependent variable. Furthermore, an analytic approach is possible only in its approximate form when the expression of the kinetics, $R(T,c)$, is linearly dependent on the concentration c.

For these reasons a statistical approach based on a Monte Carlo technique is useful in modelling beam-etching and ballistic selective disaggregation processes in 2D and 3D cases.

In Monte Carlo simulation of reaction-limited decay processes, the fractal properties of the relevant interfaces are reported in the pioneering work of Blonder [13]. Some authors proposed several atomistic rules to take into account a multi-cluster decay, a bond strength with a site-dependent detachment probability and the presence of a quenched disorder or "poisoning" in the bulk structure under deconstruction [14].

Theoretical models to determine the surface micro-topography in both diffusion- and reaction-limited etching rely on the Family-Vicšek criterion [7]; it establishes the dependence between the standard deviation of profile height and the length of the examined profile and time, introducing static (spatial) and temporal (dynamic) scaling parameters. This approach permits consideration of local surface rearrangements and annealing in surface growth, site selection criteria in etching, local anisotropies and sticking phenomena [7].

3. Simulation model

In order to describe the etching process, a Monte Carlo simulation 2D model that examines the section perpendicular to the eroded surface, has been developed (Fig. 1).

The dimension of the section is measured in lattice units. Specifically the elements, or sites, $N(i,j)$ considered during the simulation, are located at the lattice units $1 \leq i \leq L$ and $1 \leq i \leq H$, where L and H are respectively the length and the height of the area; S is the length of the mask's slit. Each site $N(i,j)$ can assume different status:

- liquid (0), representing the etchant solution;
- active (1), if the site is subject to extraction, their set constitutes the hull;
- inert (2), corresponding to the mask; and
- reacted (3), denoting products of reaction.

The algorithm uses three tuning parameters γ, β, $\mu \in [0,1]$ to consider a matching between surface chemical kinetics and diffusion phenomena (γ), the effects of a drift on the etchant motion (β) and the mobility of the reaction products (μ).

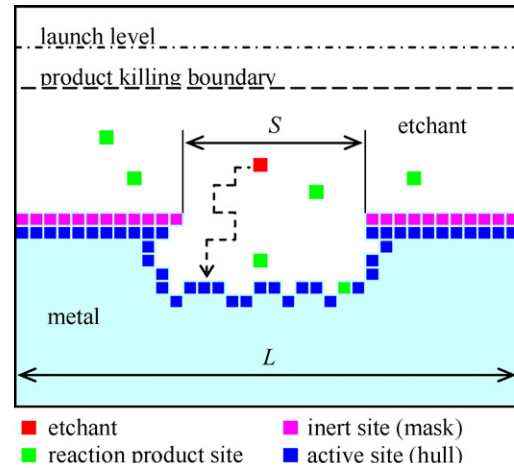

Fig. 1. 2D etching simulation model.

The simulation is carried out by iterating the following six steps:

1. A pseudo-random number $x \in [0,1]$ is generated with uniform distribution.
2. If $x < \gamma$ a particle is launched from a random position at the launch level height; the particle performs a biased random walk according to a parameter β describing the probability s for an eroding particle to move vertically:

   $s = 1 - 3 \cdot \beta/4$ with $0 \leq \beta \leq 1$.

   When $\beta = 0$, the motion is pure ballistic, while $\beta = 1$ corresponds to a Brownian (nonbiased) motion [9]. The etchant can only travel on sites with a liquid status ($N(i,j) = 0$).

   When the etchant strikes on a surface active site ($N(i,j) = 1$), a reaction product is instantaneously formed and the element's status changes to reacted ($N(i,j) = 3$); no reaction occurs if the etchant strikes on an inert, nonetchable site ($N(i,j) = 2$).
3. Otherwise, if $x \geq \gamma$, an active site ($N(i,j) = 1$) belonging to the hull surface is randomly chosen according to a uniform distribution, and after etching becomes a reaction's product ($N(i,j) = 3$) as in the previous case.
4. To decide whether all reaction sites ($N(i,j) = 3$) leave the surface by diffusion, a pseudo-random number $y \in [0,1]$ is generated with uniform distribution.
5. If $y < \mu$, the reaction sites undergo a single-step of Brownian motion. If some product sites reach a prefixed product killing boundary line above the mask, they are removed.
6. Otherwise, if $y \geq \mu$ the reaction sites remain motionless.

The profiles obtained by each simulation run are eventually averaged in order to reduce the statistical deviation of the profile.

This model is able to capture the fundamental physical–chemical aspects of the mask-etching process; specifically it describes the reaction-limited case when $\gamma = 0$, and the diffusion-limited disaggregation when $\gamma = 1$.

Besides, the parameter μ determines the concentration of reaction products in the zone surrounding the eroded surface. In particular, $\mu \cong 0$ corresponds to an hindered diffusion of reaction products that stay a long time close to the surface, thus preventing active sites from further erosion, whereas $\mu \cong 1$ implies a fast diffusion of reaction products whose low concentration has little influence on the etchant motion.

Fig. 2 shows the effect of the parameter μ on the eroded profile keeping $\gamma = \beta = 1$. As μ decreases, the depth of the eroded profile near the mask boundaries decreases due to the larger number of motionless product sites which remain on the surface and impede further erosions.

The proposed simulation model considers indirectly the effect of temperature on the etching process. Indeed low temperature or

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