Nano-Groove Generation by Diamond Turn Machining and Chemical Processing

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Abstract

Nano features like texturing, channels, grooves, wells, pillars, etc., have very wide range of applications in many areas. Different techniques are developed by various researchers to generate these features on various engineering materials. An attempt is made in this study to generate nano grooves on an aluminium alloy, grade-6061 pre-machined by diamond turning process. In this study, the deterministic spiral lay pattern generated on the surface has been subjected to chemical processing. Of the two developed processes, one has resulted in smoothening of the surface and another has resulted in generating nano grooves along the spiral pattern on the flat surface of the substrate. The experimental results of this study are presented and discussed in this paper. The developed process has potential to fabricate various types of nano features like optics, gratings, micro-nanostructures, nano-fluidic chips, etc.

Keywords: Nano features, DTM, surface finish, chemical treatment, nano-channel

1 Introduction

Nano features like texturing, channels, groove, pillars, etc., play a major role in many of the functionalized surfaces in terms of improved functionality and new effects which were not possible otherwise. Many techniques are being developed by various researchers and are being employed to generate different types of nano features on engineering materials. Generation of nano features solely by mechanical machining process is highly ineffective as the control of the tool geometry to nano level of dimensions keeping the tool wear in consideration is very difficult. Since chemical processes are more versatile and fast, the possibility of employing them for generating nano features has tremendous research and development scope. A study has been carried out in which specific chemical processes are employed on diamond turned flat surface with an objective of generating nano grooves. Effects of the chemical process on the DTM surface for improving the surface finish and for generating nano grooves were explored.

Size and form control within few hundred of nanometers (nm) and surface finish within few tens of nm are simultaneously controlled in process like Diamond Turn Machining (DTM). DTM is a path controlled process carried out with single crystal diamond tool on ultra precision machine [1]. DTM generated surfaces contain irregularities due to errors on tool cutting edge. Diamond turned surfaces contain sharp peaks which are highly unstable due to higher potential of atoms. The presence of these peaks are also responsible for increasing the surface roughness typically, few nm to few tens of nm. Hebd et.al., [2] have studied the effect of various shape of superficial layer on their Gibb’s free energy. Among various types of surfaces, the surface with high level of discontinuity exhibits high potential energy on the particular atom which is part of such discontinuity. Fig.1 shows sharing of neighbouring atoms as indicated by arrow marks at different locations. Arrow marked atom in Fig.1(c) shares only 2 atoms against 8,5,5 atoms in Fig.1(a) and 5,3 atoms in Fig.1(b). Hence, the free energy available to the atom in Fig.1(c) is much higher than that of others. Similar study was carried out by William French, et al.[3]. Fig.2 shows the effect on potential per atom due to variation in sharing of atoms in a nanowires. It indicates that atoms having lesser neighbourhood atoms have high degree of unsaturation. Atoms of such surfaces shall have more affinity towards environmental chemicals and solid particles. Hence, sharp peaks on the surface are highly unsaturated, i.e. these peaks are having very high surface energy, try to attract environmental matter towards it and make it stable. Whenever they are subjected to chemical reaction, such surface atom tries to reduce their potential, tries to reach the level of saturation and
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thereby increase the efficiency of the chemical reaction.

**Fig. 1** Schematic representation of field of forces on surface of different shapes: a) plane surface; b) edge; c) corner. [2]

**Fig. 2** Effect on potential per atom due to variation of sharing atoms of nanowires. [3]

**Fig. 3** Types of pressure applying on the work surface due to turning operation [4]

**Fig. 4** Schematic of residual stress distribution on DTM surface

Even though DTM being a nano-regime deterministic process, the generated surface contains imperfection like sharp edges instead of perfect surface. As a results of any tool based machining including DTM, the machined surface is left with residual stresses. Even though the cutting edge sharpness of single crystal diamond tools used in DTM is few hundred nm, typically 200nm, some amount of tensile residual stresses is always left on the machined surface due to ploughing action. Fig.3 illustrates the presence of both normal and tangential pressure acting on the machined surface. The thrust force induces compressive residual stresses on the sub surface after machining. Fig.4 shows the schematic of the magnified view of the DTM surface with residual stress distribution on it. These variations in geometry and residual stress lead towards variation in surface energy [2].

2 Methodology

As the DTM provides highly controlled dimensions with typical spiral lay pattern on the surface, it was selected as the basic pre-process for generating the specimen necessary for generating nano grooves. Of many alternative materials like Cu & its alloys, aluminium alloy, silicon, etc., aluminium alloy Grade-6061 with T-6 condition was selected due it’s better surface integrity after machining. Fig.5 shows the schematic diagram of the experimental set-up. The chemical reactions have been carried out by submerging the DTM surface in the bath of the chemicals. The surface is held vertically downward to maintain good natural circulation in the chemical by perturbation of chemical products (precipitates and gas). The workpiece is enclosed in chamber of the chemical. The work piece was clamped with the cap. A vent is provided in the chamber to release the gasses produced during the chemical reaction.

In this study, two types of chemical reactions have been explored for

- Smoothening the peaks of the surface profile
- Generating nano grooves

Before generating the nano grooves, it is important to smoothen the surface by rounding of the peaks of the surface profile. Subsequently, nano groves are generated on it. To achieve the above two objectives different chemical processes are identified and employed. In nano-groove generation case, chemical reaction is introduced with highly energetic radicals & ionic particles with high vibration and kinetic energy to fabricate nano-structured surface with the help of residual
Fig. 5 Schematic of the experimental set-up

![Fig. 5 Schematic of the experimental set-up](image)

**stresses on the surface. For further tuning on the nano-structures, slow and controlled chemical treatment is carried out to smooth the nano-features.**

2. Chemical treatment for smoothening the surface profile peaks

As mentioned earlier, surface generated by DTM is chemically unsaturated due to high potential \[2\]. For surface smoothening two types of chemical processes were used. In the first route hydrogen peroxide was used and in the second route ammonia & deionised water was used for the chemical reaction. The chemicals react with the Al-alloy as follows [6];

With hydrogen peroxide as the chemical agent, the reactions is as follows;

\[
2\text{Al} + 3\text{H}_2\text{O}_2 \rightarrow 2\text{Al(OH)}_3
\]

With ammonia as the chemical agent, the reactions is as follows;

\[
\text{HN}_4\text{OH} \rightarrow \text{NH}_3^{(+)} + \text{O}^{(-)}
\]

\[
\text{Al} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 + \text{e}^-
\]

After chemical reaction with hydrogen peroxide or with aqueous ammonia, precipitates of aluminium hydroxide are formed. This hydroxide is comparatively softer than aluminium as well as alumina and it also gets dissolved in the solution itself. Rate of chemical reaction depends on the degree of unsaturation i.e. the level of discontinuity on the surface and the precipitates get removed subsequently by diffusion action [7&8]. Fig.6 depicts this sequence.

Fig.6(a) is cross-sectional 2-D profile of DTM surface. This profile shows very sharp peaks and concave smooth valleys. After chemical reaction, the sharp portion (or highly unsaturated region) gets chemically reacted at higher rate as compared to the smooth zone at the valley of the profile. Removal of the chemically reactive zone produces smooth peaks as shown in Fig.6(c), which leads to smooth surface finish, better reflectivity and chemically stable surface as well.

Fig. 6 DTM surface smoothening

![Fig. 6 DTM surface smoothening](image)

3. Chemical treatment for generating nano grooves

Chemical agents are introduced to cause more reaction on mechanically stressed surface rather than the chemically unstable region. It has been experimentally observed that the chemical reaction rate is intensified on mechanically stressed surface by using highly energetic radicals or ions. These radicals and ions are produced by mixing aqueous ammonia with hydrogen peroxide. This phenomenon of causing chemical reaction on mechanically stressed portions is made use to generate nano grooves. In DTM, surface has been generated by using ultra precision lathe and a mono-crystalline diamond tool which imparts compressive stress with some pattern. The stress is dependent on the tool geometry and cutting parameters like feed and cutting speed and this...
stress sets residual stress on the surface [4, 5]. Due to the residual stress, crystals of stressed region get deformed and reaction rate is intensified due to unstable crystals (or deformed crystal). Finite Element Simulation was carried out to comprehend the stress distribution on the work surface using single point diamond tool and the resulting stress distribution is shown in Fig.7. After machining on DTM with multiple depth of cuts in DTM, the stress pattern on the surface would be similar to Fig.8.

The chemical reactions, involved in this phenomenon of nano groove generation are as follows [9];

Mixing of H₂O₂ and NH₄OH results exothermic reactions to intensify dissociation of hydrogen peroxide

\[ H_2O_2 + 2OH^- \rightarrow 2H_2O + O_2 + e^- \] (4)

\[ 2H_2O_2 \rightarrow 2H_2O + O_2; \Delta H = -196.5kJ \] (5)

\[ NH_3 + 3H_2O_2 \rightarrow HNO_2 + 4H_2O \] (6)

\[ 2HNO_2 \rightarrow 2NO \uparrow + H_2O + O' \] (7)

4. Experiments

Experiments have been carried out on DTM machined Al-alloy under different chemical reactions and reaction time. DTM was carried out with single crystalline diamond tool of 2.5mm tool nose radius, cutting edge sharpness of 200nm at a spindle speed of 1500rpm, feed of 25µm/rev and depth of cut of 10µm. The chemical treatments as shown in Table-1 has been carried out.

![Peaks at pitch of 25µm](image)

![Fig.9 3-D and 2-D views of of DTM surface](image)

Initial DTM machined surface topography is measured using coherent correlation interferometer (CCI), which is presented in

<table>
<thead>
<tr>
<th>Table-1</th>
<th>Duration for chemical treatment in min.</th>
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<tbody>
<tr>
<td>Surface smoothing with</td>
<td></td>
</tr>
<tr>
<td>H₂O₂</td>
<td>15, 45, 90, 150, 270</td>
</tr>
<tr>
<td>NH₄OH</td>
<td>15, 30, 45, 90, 120</td>
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</tbody>
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Fig.9 with 3-D as well 2-D profile. This 2D profile exhibits major peaks with a pitch of 25µm which corresponds to tool feed employed for machining.

The chemical treatments were carried out on the DTM machined surface for different time span. The duration of chemical treatment for surface smoothing was decided as per the results obtained with preliminary experiments. In case of chemical treatment with hydrogen peroxide, the finishing improvement starts saturating after 120 minutes and it does not offer significant improvement. Hence, upper duration is limited upto 270 minutes for safer side to observe behaviour of the treatment. In case of chemical treatment with aqueous ammonia, the surface finish initially improves and after 30 minutes, the surface finish gets deteriorated. Hence, 120 minutes is selected as upper time or duration for chemical treatment to realise the behaviour of surface finish with time duration.

Second type of experimentation was carried out under a solution which is mixture of hydrogen peroxide and aqueous ammonia with 1:1 (v/v) composition. It was observed that the behaviour (fabrication of nanogrooves) of the treatment gets saturated after 190 minutes. Hence, 300 minutes is selected as extreme time for this experiment.

5. Results and Discussions

5.1 Improvement on surface finish
Fig. 10: Effect of time on surface smoothness due to hydrogen peroxide

Fig. 10 shows the improvement in smoothness of the surface measured in terms of surface roughness parameter $S_q$. It improves with increasing time when treated with hydrogen peroxide. Initial one hour has shown very fast improvement and further improvement was taking place very slowly. Initially, peaks of the surface were sharp and the chemical reaction rate became significantly higher resulting in faster improvement. In this chemical reaction, hydrogen peroxide dissociates in to OH radicals. This radical is highly energetic because the dissociation takes place due to exothermic reaction. OH radical generation occurs on the superficial layer of workpiece and the chemical products of the surface moves away from the surface.

Effect of aqueous ammonia for surface smoothening is shown in Fig. 11. The surface finish improves during initial 30 minutes followed by its degradation. In initial level of finishing improvement, the sharp peaks get smoothened by formation of chemically passivated layer followed by chemical diffusion.

After initial improvement, formation of passivation layer dominates over chemical diffusion and it keeps building on the parent layer of the workpiece. Formation of the passivating layer takes place in different fashions as it varies from grain to grain and also on grain boundary at different scale.

Therefore, this smoothening of the peaks by chemical process improves the surface finish value of the DTM surface. In this particular case, the $S_q$ value has been improved from 30 nm to 11 nm by hydrogen peroxide and 29 nm to 17 nm by aqueous ammonia. Hence, this process has potential to enhance the mechanically nano finished surfaces by chemical means without undergoing any other expensive super finishing process.

5.2 Generation of nano-grooves

Fig. 12 shows effect of chemical reaction time on depth of the nano-groove generated. It has been observed that the depth of the groove increases with time till 75 minutes and after this time, it started decreasing. During nano groove generation, two types of chemical reaction was taking place simultaneously. First one is the chemical reaction taking place on highly stressed region due to energetic radicals. Second is the chemical reaction on chemically unsaturated regions (sharp peaks) due to ions of the chemicals. Initially first reaction dominates over second chemical reaction till optimal value. At optimal value, both reaction rates become similar. After optimal value, first chemical reaction becomes much slower as compared to the second chemical reaction because of etching or dissolution of residual stressed regions. It means, initially groove depth increases with time and after optimum value, the depth starts decreasing. Hence, the nano-grooved depth is fully dependent on chemical-surface interaction, stress pattern and chemical reaction time. In this chemical reaction, all products or debris of chemical reactions do not make passivation on the workpiece surface. Fig. 13 shows actual nano-grooves which are generated on the diamond turned surface after 120 minutes of chemical treatment.
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6. Conclusions

In this paper, two different phenomena have been observed.

1. By using post chemical treatment, surface finish of the DTM machined components has been enhanced significantly. With the help of proper parameters like chemical composition and chemical treatment duration, the surface finish can be enhanced and tuned.
2. Another major observation of this paper is very significant in field of nano-engineering, where nano features like grooves, channels, etc., can be fabricated with control on depth and shape by the combination of mechanical and chemical processes.

References

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