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Chemical/mechanical polishing of diamond films assisted by molten mixture of $LiNO_3$ and KNO_3

C.Y. Wang *, F.L. Zhang, T.C. Kuang, C.L. Chen

Institute of Manufacturing Technology, Dept. of Mechanical Engineering, Guangdong University of Technology, Guangzhou 510090, P.R. China

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Abstract

Chemical/mechanical polishing can be used to polish the rough surface of diamond films prepared by chemical vapor deposition (CVD). In this paper, a mixture of oxidizing agents ($LiNO_3$+KNO_3) has been introduced to improve the material removal rate and the surface roughness in chemical/mechanical polishing because of its lower melting point. It had been shown that by using this mixture the surface roughness R_a (arithmetic average roughness) could be reduced from 8–17 to 0.4 μm in 3 h of polishing, and the material removal rate can reach 1.7–2.3 mg/cm^2/h at the temperature of 623 K. Pure aluminium is compared with cast iron as the contact disk material in the polishing. Although the material removal rate of aluminiumdisk is lower than that of cast iron, it can eliminate the carbon contamination from the contact disk to the surface of diamond films, and facilitate the analysis of the status of diamond in the chemical/mechanical polishing. The surface character and material removal rate of diamond films under different polishing pressure and rotating speed have also been studied. Graphite and amorphous carbon were detected on the surface of polished diamond films by Raman spectroscopy. It has been found that the oxidization and graphitization combined with mechanical cracking account for the high material removal rate in chemical/mechanical polishing of diamond films.

PACS: 81.05.Tp; 81.65.Ps
Keywords: Diamond film; Chemical/mechanical polishing; Oxidizing agents

1. Introduction

Most of diamond films are synthesized by CVD (chemical vapor deposition) and have very rough surface, for instance R_a(arithmetic average roughness) is from tens of micrometers to hundreds of micrometers. Polishing of CVD diamond film is essential to achieve a smooth and planar surface before its application in various industrial fields. But it is very difficult to polish the diamond film because of its extreme hardness and chemical inertness. In the past decades, much research work had been undertaken to solve this problem. The proposed methods include the lapping, grinding [1], coupled-abrading [2] and thermochemical polishing assisted by metal powder [3] such as rare-earth [4] and manganese powder [5]. The high energy beam such as laser [6], ion beam [7], abrasive water jet [8] and electrical discharge [9,10] were also used to polish diamond films. In recent years, chemical/mechanical polishing has been regarded as a promising method [11].

In chemical/mechanical polishing, the compound effect of mechanical abrading and oxidant etching plays the main role in the material removal process. In respect of oxidizing effect, atomic oxygen reacts with diamond to form CO or CO_2, and diamond can be transformed into carbon black or graphite as well. Although the etching will result in some defects such as pits, if it is well controlled, high surface quality can be achieved [12]. The chemical/mechanical polishing is first used on diamond film by Thornton and Wilks [13]. They used a concentrated solution of KNO_3 between the surface of diamond films and a rotating disk. This method was further developed by Kühnle and Weis [14] and had been utilized to obtain the super-polishing surface [15].

Most of polishing disks are made of cast iron. Some other materials such as polycrystalline alumina has also been used to fabricate polishing disks [16–19]. In addition, some abrasives, such as diamond, Cr_2O_3 and Fe_2O_3 powder can be used to assist the polishing and increase the removal rate [17–20]. As

* Corresponding author. Tel.: +86 20 36627606; fax: +86 20 37627005.
E-mail address: cywang@gdut.edu.cn (C.Y. Wang).

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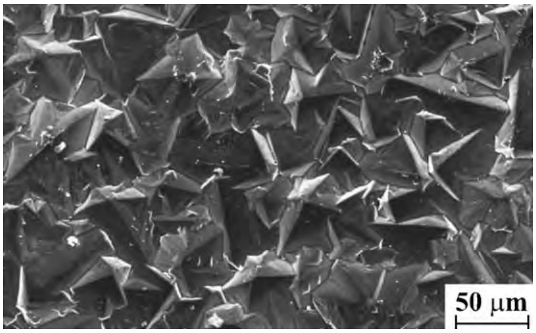

Fig. 1. SEM image of the surface morphology of the CVD diamond film.

for the oxidizing agents, besides KNO_3 and $NaNO_3$, there are also some other oxidizing agents, such as H_2O_2, HClO, HNO_3, H_2SO_4, AgO, Cr_2O_3, MnO_2, BaO_2, PdO_2 and so on.

In general, it is important to setup an oxidizing environment for diamond films in the process of polishing. However different oxidizing agents have different melting temperatures. Normally the oxidation happens at temperature above melting point. So if we can find oxidizing agents with lower melting points, it will benefit the oxidation reaction in the high temperature, and also lower the working temperature and simplify the process and apparatus. In this paper, $LiNO_3$ and KNO_3 and their mixtures are introduced in the polishing process to decrease the operating temperature and increase the material removal rate. The aluminium disk is also used in comparing with cast iron in the polishing process, with the purpose of eliminating carbon contamination from cast iron disk to the diamond films. The effect of rotating speed and polishing pressure on surface roughness and material removal rate are also investigated.

2. Experimental details

2.1. Materials

The initial CVD diamond films produced by hot filament method own the surface roughness of 8~17 μm and the surface morphology of the film are shown in Fig. 1. In the Raman spectrum of the diamond films, there are no characteristic peak of graphite at 1580 cm^{-1}. All the samples are prepared in the shape of square with an area of 1.1 cm^2 and the thickness of 0.4–0.6 mm. The properties of CVD diamond films are listed in Table 1. The oxidizing agents and the mixtures are listed in Table 2, and the melting point of mixtures is tested in one resistance furnace (SX-5-12).

2.2. Apparatus and procedures

The experiment is carried out on a designed polishing machine with the schematic structure shown in Fig. 2. The sample of diamond film is pressed onto the surface of the disk heated by a semiconductor heater placed underneath. This heating system can control the disk temperature at about 623 K, which is higher than all the melting point of oxidizing agents and the mixture in Table 2. Cast iron and aluminiumare selected as the material of polishing disks, and the surfaces of the disks are machined with shallow crossing slots in order to contain the molten oxidizing agents.

The disk is driven to rotate at the speed range of 1.7 to 1350 revolutions per minute (RPM) by a motor and the sample holder reciprocated in the radial direction. The load added on the holder can help to adjust the polishing pressure. Three rotating speeds (67.5, 81 and 94.5 RPM) and three pressures (0.06, 0.1 and 0.13 MPa) are tested in this experiment.

Prior to the polishing process, the CVD diamond films are cleaned by acetone and dried in an oven. The surface roughness is tested by a surface roughness tester (TR100), which owns the resolution of 0.05 μm. The atomic force microscopy (AFM, CSPM 2003, contact mode, tip radius 10 nm, resolution 0.1 nm, scanning range 100 × 100 μm) is used to examine the micro-arithmetic average roughness (Micro-Ra) of the polished surface of diamond films. The carbon status on surface of diamond film after chemical/mechanical polishing is analyzed by means of Raman spectroscopy (Renishow Micro-Raman RM-1000, laser wavelength 514.5 nm), and the surface morphology observation is carried on the scanning electron microscopy (SEM, PHILIPS XL 30 FEG, 18 KV).

Table 1
Properties of CVD diamond film

Hardness (HV)	Young's modulus (GPa)	Bending strength (GPa)	Heat conductivity (W/m K)
8300–12000	1000	2.0	1100

Table 2
Properties of oxidizing agents

Composition	Mol ratio	Melting point (K)
NaOH		591
KNO_3		607
NaOH + KNO_3	1 : 1	573
KNO_3 + $LiNO_3$	(0.57–0.60) : 1	403

3. Results and discussion

3.1. Effect of oxidizing agents

In this experiment, the aluminium disk is first used to carry out the chemical/mechanical polishing with different oxidizing agents. By 3 h polishing at 81 RPM, it seems that all the

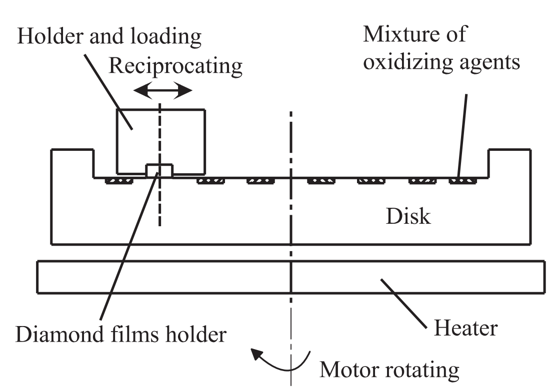

Fig. 2. Schematic structure of chemical/mechanical polishing apparatus.

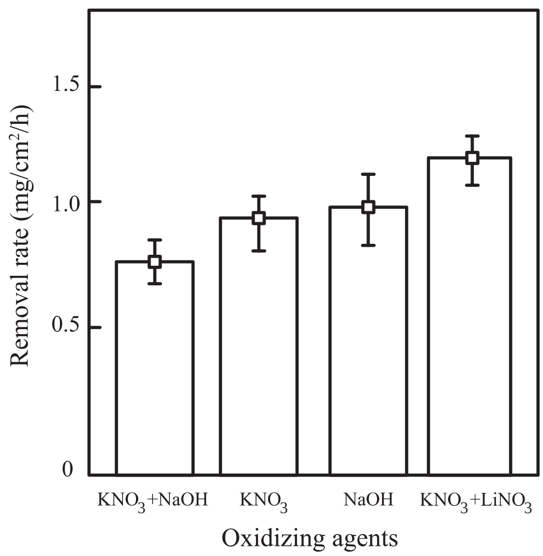

Fig. 3. Dependence of the removal rate of diamond film polished by Al disk on different oxidizing agents at the pressure of 0.1 MPa and rotating speed of 81 RPM.

oxidizing agents have an obvious effect on the polishing of diamond films, and the mixture of $LiNO_3$ and KNO_3 developed the highest material removal rate of 1.2 mg/cm^2/h, as shown in Fig. 3. From Table 2 it is found that the mixture of $LiNO_3$ and KNO_3 own the lowest melting point among the four oxidizing agents. At 623 K the ionized oxidizing ions' fraction in the mixture of $LiNO_3$ and KNO_3 is higher than that of other agents with higher melting point. There were more reaction between the diamond film and the oxidizing ions, such as OH^-, NO_3^-. From the SEM images in Fig. 4, the surface morphology of polished diamond films is shown. There is no much difference among the four oxidizing agents. But a general characteristic of the chemical/mechanical polishing on diamond film can be found. For instance, in Fig. 4(a, d) one diamond pyramid is etched away severely and some small pits are formed on the fresh surface of the etched diamond, which resulted from the severe reaction between diamond and oxidizing ions. However, only few pits remained on the unpolished smooth surface. This may be because the oxidation happened firstly in the places with high surface energy. In the surface of solids, the vertex and edges usually have higher surface energy than plane. The peaks of pyramid are etched by oxidation and then cracked by the mechanical etching. The fresh surfaces generated by the etching and cracking are fairly rougher than the original surface of the diamond facets, so that oxidizing and mechanical etching can continuously take place until the surface is flattened with fine finish.

3.2. Effect of disk materials

In this experiment, aluminium disk and cast iron are used. Although the hardness of aluminium is very low, it can eliminate the contamination of carbon between the disk and diamond films. It will benefit the following analysis of carbon status on the surface of diamond films. In Fig. 5 the material removal rate of cast iron is higher than that of aluminium. In Fig. 6(a), the SEM image showed that the surface polished by aluminium disk had some facets, which meant that there are still some places that have not been etched. While in the surface polished by the cast iron disk, the diamond pyramid had been flattened and only some small pits could be observed as illustrated in Fig. 6(b). There are twofold reasons. Firstly Al is very soft and has little mechanical polishing effect on diamond film. Secondly Al can easily be deformed and scratched by the diamond pyramid, and the oxidizing agent cannot be homogeneously distributed on the surface of diamond film, then chemical etching of diamond film only happens at some peaks and edges of the diamond grains, which can also be seen in Fig. 4.

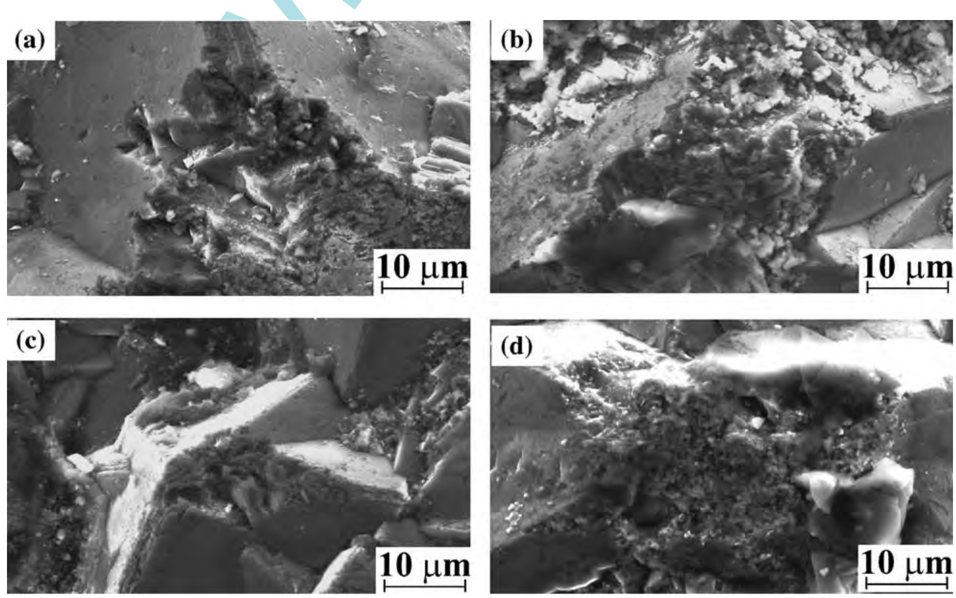

Fig. 4. SEM images of diamond films polished by Al disk in molten NaOH (a); KNO_3 (b) ; NaOH+KNO_3 (c) and $LiNO_3$+KNO_3 (d) at the pressure of 0.1 MPa and the rotating speed of 81 RPM.

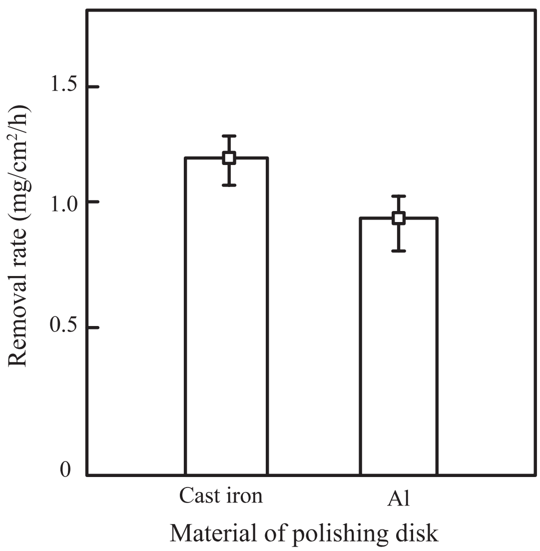

Fig. 5. Dependence of the removal rate of diamond films on different disk materials in the molten KNO_3+LiNO_3 at the pressure of 0.1 MPa and rotating speed of 81 RPM.

3.3. Effect of rotating speed of disk

As we all know that with the increase of rotating speed, the contact points on surfaces of the polishing disk would increase at the same time, so does the material removal rate. In the diamond polishing, the amounts of cracks and the fresh surfaces exposed in the oxidizing agents would increase with the rising of rotating speed. As a result, the removal rate increased as well, which is illustrated in Fig. 7. But it must be noticed that higher disk rotating speed may cause the molten oxidizing agents to be distributed unevenly on the disk and the surface of diamond film. By the centrifugal force, the molten

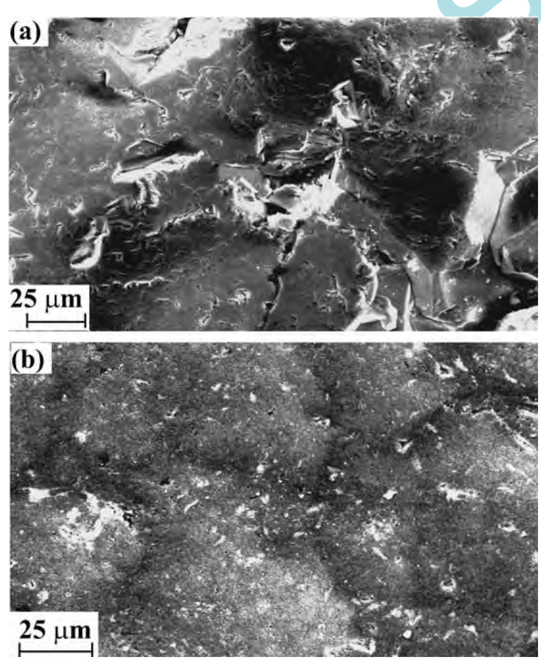

Fig. 6. SEM images of surface morphology of diamond films polished by Al disk (a) and cast iron disk (b) in molten KNO_3+LiNO_3 at pressure of 0.1 MPa and rotating speed of 81 RPM.

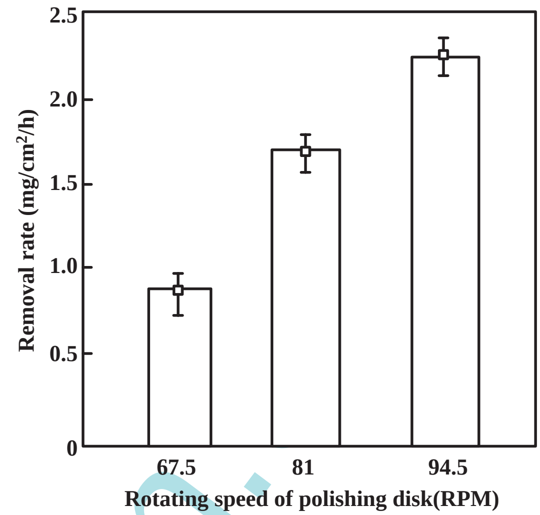

Fig. 7. Dependence of the removal rate of diamond films polished by cast iron disk on different rotating speed in molten KNO_3+LiNO_3 at the pressure of 0.1 MPa.

may also flow to the outer range of the disk, or spilled out. In this study, we selected the acceptable rotating speed of 81 RPM to carry out the following polishing.

3.4. Effect of polishing pressure

The relationship between polishing pressure and material removal rate is illustrated in Fig. 8, in which the material removal rate increased with the rising of pressure. This happens in all the grinding and polishing processes on almost all materials. In respect to diamond polishing, increasing of polishing pressure cause the increase of friction force and the shear stress on the surface of diamond film. As a result, there are more cracks generating at the contact areas of diamond peaks. More diamond oxidation will take place because of the increase of contact area between diamond film and oxidizing agents.

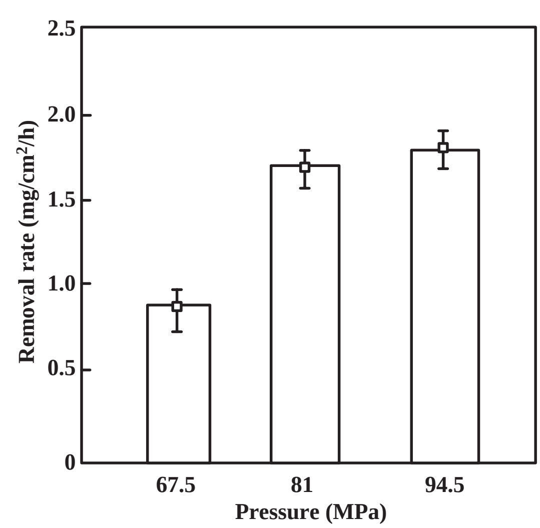

Fig. 8. Dependence of the removal rate of diamond films polished by cast iron disk in molten KNO_3+LiNO_3 on different pressure at the rotating speed of 81 RPM.

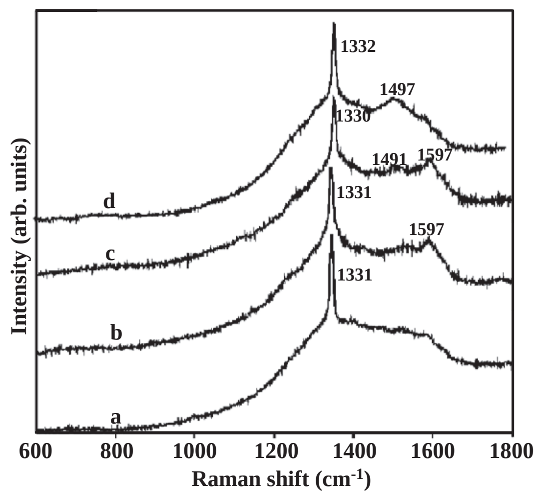

Fig. 9. Raman spectrums of the diamond films before (a) and after chemical/mechanical polishing by Al disk in molten $LiNO_3+KNO_3$ (b), NaOH (c) and $LiNO_3+KNO_3$ (d) at the pressure of 0.1 MPa and rotating speed of 81 RPM for 3 h.

3.5. Surface analysis of diamond films

When polishing the mixture of $LiNO_3$ and KNO_3 with cast iron disk, the surface roughness of diamond film can be reduced from R_a 8–17 to 0.4 μm in 3 h. The micro-R_a is also tested by AFM in the range of 40×45 μm with the value of 26.7 nm. In order to analyze the possible phase transformation of carbon on diamond film in chemical/mechanical polishing, several samples are examined by Raman spectroscope. These samples are polished with aluminium disk carefully to prevent possible carbon contamination from contact disk or environment. It is obvious that the surface of diamond films presents new Raman peaks at 1497, 1491 and 1597 cm^{-1} that do not characterize the diamond as shown in Fig. 9. Raman peak at 1597 cm^{-1} depicts the characteristics of graphite and the peaks at 1497 and 1491 cm^{-1} amorphous carbon. That means that there is transformation from diamond to graphite or amorphous carbon in the polishing. The mechanism of transformation may result from three aspects: First, the oxidizing ions react with diamond by the Eq. (1):

$$\text{Diamond} + \text{O} \rightarrow \text{C} + \text{CO}. \quad (1)$$

The carbon from Eq. (1) can be in the form of graphite or amorphous carbon [21]. Secondly, the diamond can transform to graphite in the elevated temperature. In this experiment, the disk temperature is about 623 K. But the temperature of the contact area may be higher because of the friction heat from the polishing. Thirdly, the stress on the diamond films may also reinforce the transformation from the diamond to graphite or amorphous carbon. The mechanically induced transformation of diamond and diamond films were also found in Ref. [22]. So there are different forms of carbon on the surface of polished diamond films. In general, it can be concluded that material removal of diamond films in the chemical/mechanical polishing came from the compound results of oxidization graphitization and the cracking by the mechanical friction.

4. Conclusions

An oxidant mixture of $LiNO_3$ and KNO_3 can be used in the chemical/mechanical polishing to decrease the melting temperature and increase the material removal rate. When polishing with this mixture, the surface roughness of diamond film can be reduced from R_a 8–17 to 0.4 μm and the material removal rate can reach 1.7–2.3 mg/cm^2 /h at the temperature of 623 K. Aluminium can be used as the material of contact disk to eliminate the carbon contamination from the disk material to the contact surface of diamond films. The material removals of diamond films in the chemical/mechanical polishing come from the compound effect of oxidization, graphitization and the cracking by the mechanical friction.

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