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Mechanochemical Polishing of Single Crystal Diamond with Mixture of Oxidizing Agents

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Abstract. In order to achieve the smooth surface of diamond, several kinds of mixture oxidizing agents have been used to polish the single crystal diamond by a designed polishing apparatus. The existing of graphite and amorphous carbon has been found in the surface of diamond after polishing. The mechanochemical actions of oxidizing agents and the polishing iron plate have been proved. The mixture of oxidizing agents can decrease the polishing temperature so that the super-smooth surface of single crystal diamond can be achieved at lower temperature. The method provided is benefit not only to simplify polishing device and control the polishing process, but also to improve the removal rate and surface roughness.

Introduction

As a kind of widely used material with the highest hardness, high brittleness, it is difficult for diamond to achieve a smooth and planar surface. In the past years many studies of the polishing of diamond have been done. Traditional mechanical lapping or polishing using hard abrasive such as silicon carbide, corundum and diamond are common used. Residual grinding lines and cracks which make the surface quality worse are easily to be caused. In general the removal mechanism by means of diamond abrasive has been pointed out as the brittle breakage of diamond surface crashed by abrasives [1-3]. The microscopic characteristics were shown as nanoscale microchipping and grooves [4,5]. The lower density carbon caused in the process of polishing soft surface of diamond showed that the phase change of diamond surface is also a kind of removal mechanism [6-9].

It is a basic property for diamond that it can be etched by potassium nitrate at 327^{o} C or potassium chlorate at an elevated temperature. At temperature 625^{o}C the oxygen atoms can react with diamond and form CO or CO_2 causing the diamond black. In general the etching will result in rough diamond surface characters with defects such as pits [1]. But if the etching was controlled, the high surface quality could also be achieved. In terms of diamond etching the mechanochemical polishing experiments were carried out firstly by Thornton and Wilks [10]. They used the concentrated solution of KNO_3 to form a thin crystalline layer of potassium nitrate on the surface of a rotating disk. They found the polished surface quality was improved because of the using of potassium nitrate. This method was developed by Kühnle and Weis [11] and had been utilized to obtain super-polishing surface by Münzinger [12]. Diamonds moved on the surface of a rotating cast-iron disk. A special diamond holder was developed to force the crystal face of diamond to remain it always parallel to the disk surface during operation. The nitrate salt at 250-300 °C molten on the disk formed a thick salt coating. Using a suitable load the stationary superpolishing conditions had been obtained. By mechanochemical polishing with sodium or potassium nitrate, a residual roughness of about 0.2 nm and polishing rate 0.5 μm/h were achieved. It was considerably lower than the surface roughness obtained by conventional polishing methods.

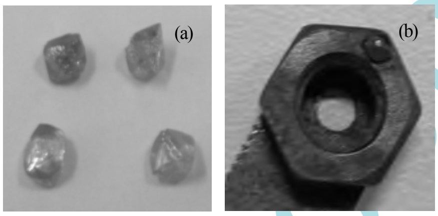
In this paper, a device was designed to polish single crystal diamond with mechanochemical method by molten oxidizing agents. Some of oxidizing agents and their novel mixture were investigated to decrease the operation temperature and improve the polishing removal rate and the polished surface roughness. The removal mechanism was also discussed.

Experimental

The oxidizing agents and the mixtures are listed in Table 1. The samples in the experiments are nature single crystal diamond as shown in Fig.1. In order to find out the oxidizing effect of oxidants on diamond, the static oxidizing experiments of single crystal diamonds were carried out firstly in a resistance furnace (SX-5-12). Four kinds of oxidizing agents shown in Table 1 were used to oxidize four single crystal diamonds at temperature 400° C, 500° C, 600° C, 700° C separately.

Table 1 Properties of oxidizing agents

Composition	Mol ratio	Melting point [° C]
KNO_3		334
$NaNO_3$		310
$LiNO_3$		220
KNO_3+$LiNO_3$	0.6:0.4	134
$NaNO_3$+KNO_3+ $LiNO_3$	1:2.5:2.1	120



(a) original (b) Brazed in a holder
Fig.1 Nature single crystal diamond

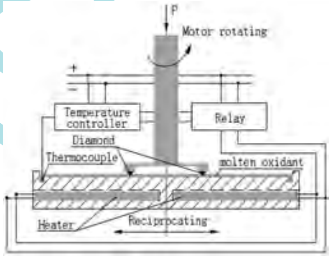


Fig.2 Sketch of device

The diamond polishing experiments were carried out on the device shown as in Fig.2. Two diamonds was brazed to a holder which was driven to rotate at a speed in the range of 10-100 RPM by a motor controlled by a transducer. The polishing press can be adjusted from 3N to 100N by the force added to the holder.

The polishing plate contacting tightly with the diamonds reciprocates in the horizontal direction while the diamonds holder was rotating. To get a continuous polishing the oxidizing agents was added in the convex surface of cast-iron plate with cross grooves. The polishing plate was heated by four resistance heaters placed in the holes drilled in the plate. The temperature of the molten oxidizing agent on the plate or the plate surface can be measured by thermocouples placed in the slot of the plate. The temperature controller switched on or off the relay according to the set value and the temperature measured by the thermocouple, thus the temperature of oxidizing agent can be kept around the set value with a tolerance of ±3ºC. After starting the motor, the mechanical polishing will be caused when the diamonds contacts the plate and the chemical reaction will be caused as the diamonds moves over the surface of trough of the polishing plate.

The diamonds were cleaned and dried to remove the extra before and after the testing. Optical microscope (PHILIPS XL 30 FEG SEM) and atomic force microscope (AFM SPA-300HV and AFM CSPM-2003) were utilized to observe the morphology. The surface structure of diamond was analyzed by means of Renishow Micro-Raman RM-1000, laser wavelength 514.5 nm.

Results and Discussion

Oxidizing Effects of Oxidants on Diamond. The oxidizing agents play an important role in achieving ideal polishing results. As shown in Fig.3, it can be inferred that the oxidization of diamonds could not be obvious until the temperature exceeded 500° C as they were placed in the oven covered by molten oxidizing agents statically. Considering the increase of fresh surface contact between diamond and oxidants, the oxidizing temperature would be lower than 500° C. The performance of oxidizing agents rose quickly when temperature went up. It showed that the loss of weight of single crystal diamond caused by one pure nitrate was larger than those by their mixture at higher temperature.

Diamond Surface by Mechanochemical Polishing. Fig.4 showed the optical photos of diamond polished with press 0.2 N, rotating speed 65 RPM and reciprocating speed 30 mm/min with oxidizing agents NaNO3+KNO3+LiNO3. With the increasing of polishing time the diamonds tips was worn and surface quality was improved and the inner defects appeared (Fig.4c). As the polishing time reached to 24 hours, the surface of diamond showed super smoothness with higher magnification by optical microscope (Fig.4d). The AFM image of the smaller zone of diamond surface was presented in Fig.5 by AFM SPA-300HV. The surface defect of nature diamond and small polishing grooves caused by polishing plate could also be observed (Fig.5a 5b). The surface roughness was less than 5 nm. The irregular and uneven profile of nanoscale caused by the chemical action of oxidants, see Fig.5c). It was measured that the roughness Ra of polished diamond surface reached 1.14 nm in an area of 6246.15 nm×6246.15 nm with AFM CSPM-2003.

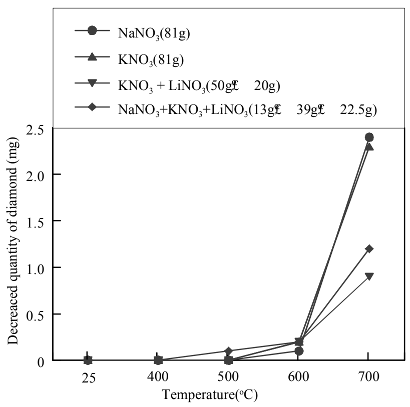
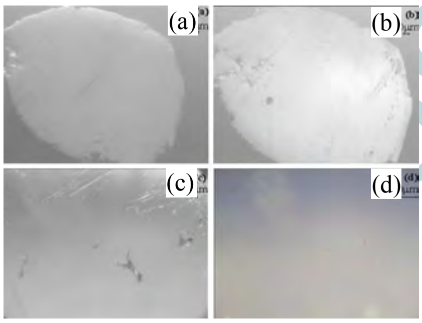


Fig.3 Static oxidation of diamond in different oxidizing agents and temperature



(a)after 6 hrs (T=400 ºC)
(b)after 12 hrs (T=290 ºC)
(c)after 18 hrs (T=290 ºC)
(d)after 24 hrs (T=400 ºC)

Fig.4 Surface of polished diamond by optical microscope observation

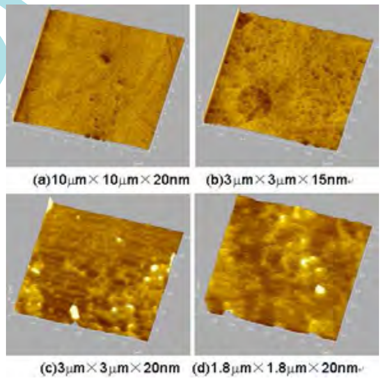


Fig.5 AFM images of polished diamond

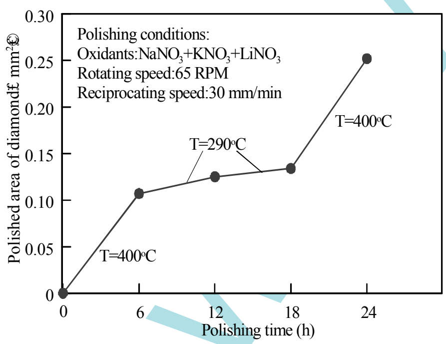


Fig.6 Polishing time versus polished area of diamond

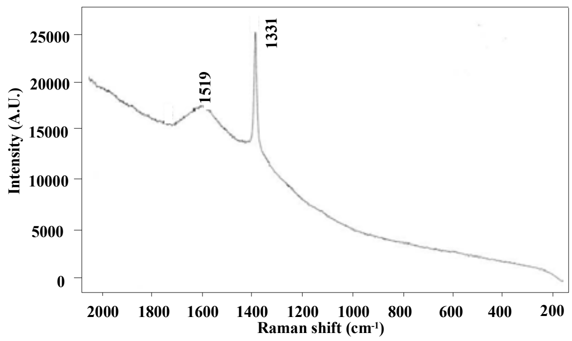


Fig.7 Raman spectrum of the diamond polished by mechanochemical method

The temperature of molten oxidizing agents in the polishing process was 290 to 400° C. At these temperatures the chemical action are more effective than in static oxidization test even if they are lower than 500 ° C. As the temperature rises to 400 ° C, the increment of polishing area of diamond is much rapidly than that of 290 ° C, as shown in Fig.6. The lower temperature and molten point of mixture of $NaNO_3$+KNO_3+$LiNO_3$ (120 ° C) means that the polishing could be carried out with a simpler device and the polishing process could be controlled easily. The polishing press also takes an important action in polishing process. Higher polishing press would not only carry away the oxidized diamond surface material, cause new fresh surface for oxidizing agents, but also wear off the diamond by mechanical chipping. Mechanical polishing will make more microcracks which are benefit to the increase of the oxidizing actions by supplying more contact area. In this test we don't consider the orientation of diamond facet, but the results show the mechanochemical will be effective for any surface of diamond.

Mechanism of Polishing Diamond by Mechanochemical Method. In order to analyze the possible structure transformation of diamonds during the mechanochemical polishing, several samples were detected by Raman spectroscope. These samples were obtained by polishing with cast iron plate carefully. As shown in Fig.7, Raman peak at 1519 cm^{-1} depicts the characteristics of amorphous carbon. The Raman peak of graphite was not shown in the Fig.7 as the cleaning of this sample, but found in others. These results indicate that there is transformation from diamond to graphite or amorphous carbon in mechanpchemical polishing of diamond. So the essential characteristics of mechanochemical polishing of diamonds is a process of graphitization, which lead lower density of graphite on the surface of diamond resulting from the escape of CO or CO_2. The continuous oxidization of the diamond immersed in the oxidizing agents occurs at the contact points with polishing plate and produce the continuous removal of diamond. The mechanically induced transformation of diamond exists also. These results are consistent to previous studies in Refs [1, 6, 11, etc.]. In the mechanochemical polishing by oxidizing agents and rotating polishing plate, the diamonds were immersed into the molten oxidizing agents. The surface of the diamond will not only be etched by the action of mechanical wear with polishing plate, but also be etched by the oxidation in the cracks caused by the press. Some of the diamonds would be transformed to graphite and amorphous carbon due to the oxidation of oxidizing agents. The polishing plate would help the transformation from amorphous carbon to graphite by increasing the temperature at contact points. The polishing plate could also remove the graphite generated in the process by mechanical friction.

Conclusions

One novel kind of mixed nitrate salt has been introduced as oxidizing agent to not only decrease melting point and the cost of experiments, but also improve the effects of mechanochemical polishing of diamonds. The polishing process can be described as the combination of the oxidization of diamond caused by chemical reaction, the abrasion caused by mechanical polishing and the structure transformation generated by the increasing of the temperature at contact points.

Acknowledgments

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