Diamond & Related Materials 18 (2009) 877–880

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Pulsed laser processing of nano-polycrystalline diamond: A comparative study with single crystal diamond

Shoko Odake [a,*], Hiroaki Ohfuji [b], Takuo Okuchi [c], Hiroyuki Kagi [a], Hitoshi Sumiya [d], Tetsuo Irifune [b]

[a] Geochemical Laboratory, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
[b] Geodynamics Research Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan
[c] Institute for Study of the Earth's Interior, Okayama University, 827 Yamada, Misasa, Tottori 682-0193, Japan
[d] Electronics & Materials R&D, Sumitomo Electric Industries, LTD. 1-1-1, Koya-kita, Itami, Hyogo 664-0016, Japan

A R T I C L E   I N F O

Available online 12 November 2008

Keywords:
Microstructure
Nanocrystalline
Superhard materials
Synthetic diamond

A B S T R A C T

We have conducted laser processing of ultrahard nano-polycrystalline and single crystalline diamonds (NPD, SCD, respectively) using nano-pulsed near-ultraviolet laser, and the machining properties were compared through microstructural examinations by SEM, TEM and Raman spectroscopy. The cut depth of the laser-cut grooves was observed to be deeper for the NPD than for the SCD. This is probably due to the lower thermal conductivity feature of NPD, which provides higher absorption efficiency of the laser energy and decreases the laser ablation threshold. TEM cross-section observation showed that the processed grooves in the both types of diamonds are covered with identical laser-modified layers (~1 µm thick) composed of roughly oriented nanocrystalline graphite. A marked difference was observed between the laser-processed surfaces of NPD and SCD: in the former the diamond–graphite interface is almost linear and undamaged, whereas in the latter the boundary is slightly folded and significantly distorted. These textural features suggest that different laser-machining processes are involved between NPD and SCD in the microscopic scale. Our results demonstrate that pulsed laser can be used even more effectively for the fabrication of nano-polycrystalline diamond than the case for single crystal diamond.

1. Introduction

Nano-polycrystalline diamond (NPD) is a binderless, ultrahard diamond aggregate, synthesized by direct conversion of graphite under static high pressure and high temperature conditions without using any catalysts and binder materials [1]. NPD consists of granular diamond crystals ranging from several tens to a few hundreds nanometers in size, which are oriented in random directions and tightly bounded each other [2]. Because of such unique features, NPD has no cleavage feature and possesses extremely high Knoop hardness of 120–140 GPa, which is equivalent to or even higher than that of high-purity synthetic type IIa single crystal diamond, which ranges from 116 to 130 GPa [3]. It was also demonstrated that NPD maintains the hardness at higher temperature (~1000 °C) in comparison to single crystal diamond (SCD), which is also attributed to the nanocrystalline texture that prevents the development of dislocation movements (plastic deformation) and microcrackings [4]. These outstanding properties of NPD have attracted considerable interest for industrial applications such as cutting and drilling tools and for scientific applications such as diamond anvils for high-pressure generation [5].

In order to put NPD to practical use, a precise machining technique is required to fabricate such ultrahard diamond into desired shapes. Mechanical polishing using diamond abrasives is commonly used in grinding and polishing natural and synthetic diamonds. However, because of the extreme hardness and durability, mechanically polishing NPD is a fundamentally difficult task. Thus we are newly developing a scheme of precise micromachining of NPD using pulsed laser beam [6], and a part of this effort is given here as a preliminary report. Over the past decades, pulsed laser irradiation has been widely recognized to be effective for machining and polishing diamonds including chemical vapor deposited diamond films [7–19]. The laser ablation of diamond takes place via surface graphitization due to a combined thermal/photochemical effect, followed by sublimation and oxidation of the preformed graphite [7]. The laser etching proceeds by a pulse-by-pulse penetration of the graphitic "piston" into diamond; while the previously graphitized layer is partially removed, a deeper part of diamond is activated to form a new graphite layer [9]. The laser ablation also produces a laser-modified layer of a few hundreds nm to 1 µm thick at the irradiated surface of diamond, which consists mainly of nanocrystalline graphite and amorphous carbon [8,12]. The modified carbon layer can be readily removed by post-processing such as heat treatment and/or chemical etching [12]. These previous studies on laser-machining of SCD and CVD diamonds would also be beneficial for the laser-machining of NPD, for which the detail of the machining processes are not yet fully

* Corresponding author.
E-mail address: odk@eqchem.s.u-tokyo.ac.jp (S. Odake).

0925-9635/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.diamond.2008.10.066

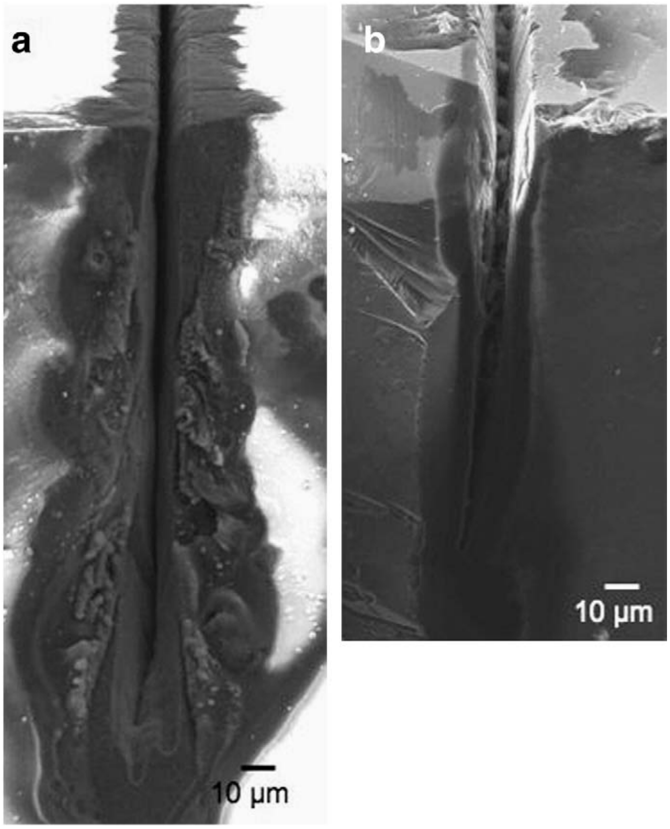

Fig. 1. SEM images of laser-cut grooves in (a) NPD and (b) SCD, which were excavated respectively by 10 and 12 laser-scans (5 and 6 round-trip). The images were taken at an angle of 60° relative to the sample surface.

understood. In this study, therefore, we carried out laser-cutting experiments of both NPD and SCD, and compared the macroscopic and microscopic features of the cutting grooves. The cutting depth, as well as the damage and microstructures of the laser-cut surfaces, are clearly different between these two types of diamonds.

2. Method

NPD samples used for the laser-processing experiments were synthesized by direct conversion of high-purity graphite at a pressure of 15 GPa and a temperature of about 2600 K. The samples were as-sintered cylindrical pellets with dimensions of about 4 mm in diameter and thicknesses ranging from 0.5 to 2.8 mm. A synthetic type Ib single crystal diamond (SCD) containing nitrogen impurity of about 100 ppm (Sumicrystal®; Sumitomo Electric Industries, Ltd.) was also subjected to the experiments for comparison.

Laser processing was conducted using a RAPYULAS micro-processing system developed by Laser Solutions Co. Ltd. (Kyoto, Japan). The system is equipped with a diode-pumped solid state Nd:YAG laser with a wavelength of 355 nm. The laser was operated at an averaged power of 1 W, the pulse width of 100 ns and its repetition rate of 60 kHz. The beam was vertically irradiated on the surface of the samples and focused to 2 μm diameter at 10 μm below the surface. The sample was scanned at a rate of 2 mm/s by moving a motorized stage.

Raman spectra were measured using a 30 cm single polychromator (250is; Chromex), equipped with an optical microscope (BX60; Olympus Optical Co. Ltd.) and a charge-coupled device (CCD) camera with 1024 × 128 pixels (DU-401-BR-DD; Andor Technology). Excitation was provided by an Ar^+ laser (514.5 nm, 5500A, Ion Laser Technology) operated at 5 mW and the spatial resolution was ~1 μm.

Surface of processed samples was observed with a field-emission SEM (JSM-7000F; JEOL) operated at 15 kV after coated with 15–20 nm thick gold or carbon. The samples were then transferred to a focused ion beam (FIB) system (JEM-9310FIB; JEOL) to prepare a cross-section (~10 × 5 × 0.1 μm) across each laser-cut groove for TEM observations. TEM observations were performed using a TEM microscope (JEM-2010; JEOL), operated at 200 kV.

3. Results and discussion

Fig. 1 shows the SEM images of laser-cut grooves in (a) NPD and (b) SCD blocks produced by 10 and 12 repetitive laser-scans, respectively. The opening widths and depths of the cut grooves were 10 and 195 μm (20 in the aspect ratio) for the NPD and 15 and 145 μm for the SCD (10 in the aspect ratio), respectively. The observed cut depth and aspect ratio of the processed grooves on the NPD were deeper and twice larger than those of the SCD, despite that the number of the laser scans performed is fewer for the former. This implies that NPD has a lower ablation threshold and absorb the laser energy more efficiently than SCD. A possible reason for this is the relatively low thermal conductivity of NPD, which is intrinsically associated with the grain boundary effect. It has been known that the bulk thermal conductivity of polycrystalline materials such as metals and ceramics decreases with decreasing grain size due to grain boundary scattering [20,21]. The thermal conductivity of NPD was measured to be, at least, five times lower than that of type Ib SCD [22]. Since materials with lower thermal conductivity are heated and vaporized more easily by laser irradiation, such a thermal property of NPD contributes to decrease the ablation threshold. The presence of lattice defects at the surface of the

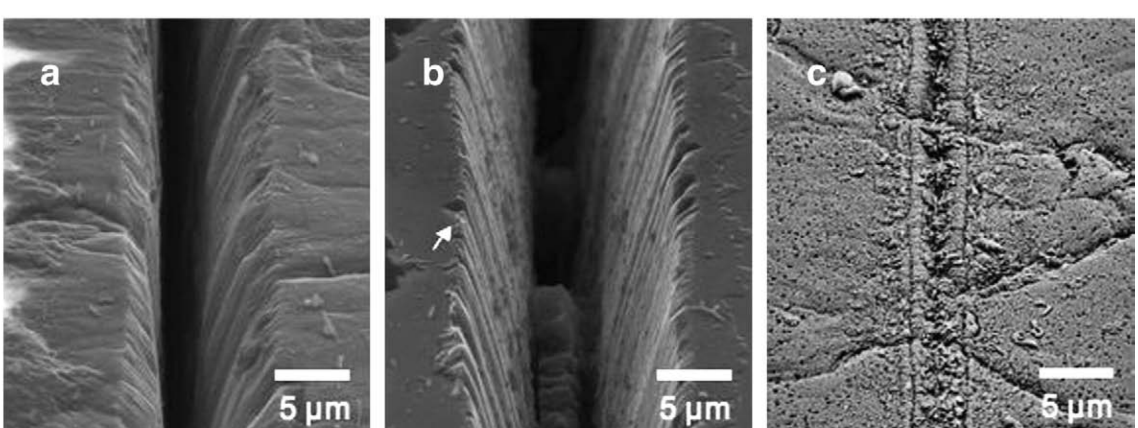

Fig. 2. Magnified images of laser-cut grooves: (a) NPD (10 laser-scanned), (b) SCD (12 scanned), and (c) NPD (single scanned).