

Enhanced Diamond Nucleation on Cemented Carbide Cutting Tools by Employing Electrostatic Self-Assembly Seeding

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Abstract. Nanodiamond seeding is a well-established approach to enhance the nucleation density in chemical vapor deposition (CVD) diamond growth. However, nanodiamond seeding is highly dependent on the properties of nanodiamond particles, the solvent and the substrate. In this work we present a simple electrostatic self-assembly method to enhance the nucleation of diamond film on cemented carbide (WC-Co) substrates. The nanodiamond particles were adsorbed to WC-Co substrate surfaces governed by electrostatic interactions, which can be controlled by the surface groups of the particles and the pH of a solvent. By varying the pH of the media, the nanodiamond particles were rendered either positively or negatively charged. The positive charged nanodiamond particles (pH < 2.5) enhanced the nucleation of diamond on oxidized WC-Co substrates. The highest nucleation density of diamond on WC-Co substrates was achieved to be $1.0 \pm 0.1 \times 10^{10} \text{ cm}^{-2}$, which is comparable to the highest record achieved by applying bias voltage to generate plasma. The nanodiamond particles also shortened the incubation time of diamond nucleation to less than 10 min on TiB₂ interlayer. This electrostatic induced adsorption of diamond nanoparticles is crucial for the development of ultra-high nucleation densities for the growth of high performance nanocrystalline diamond films, especially for micro sized tools with sharp cutting edges applying for Micro and Nano Electro-Mechanical Systems.

Introduction

Diamond, a famous gemstone, is the hardest material ever known. Its hardness in combination with other outstanding properties such as high stiffness, high wear resistance, high thermal conductivity, semi-conductivity, and chemical inertness, makes diamond an excellent material for a variety of applications, such as protective coatings, heat spreader, optical windows and biological platforms, and so forth. [1-4] Research activities on nanocrystalline diamond thin films have increased rapidly. [5, 6] For the application in high performance Micro and Nano Electro-Mechanical System, carbide tools in micro size with sharp cutting edge are highly needed. Diamond can be coated on cemented carbide tools to improve the machining performance. However, it has been proven difficult to deposit continuous and adherent diamond films on a WC-Co substrate due to a strong catalytic effect cobalt, which promote the formation of graphite at the substrate interface. [2] As the nucleation process is crucial for dense, continuous and thin films, a number of methods have been devoted to enhance the nucleation of diamond films [7-9]. Different strategies involving substrate surface pretreatments and coating of different interlayers have been applied. [7, 10-12] However, the incubation time of diamond nucleation is still too long and growth rate of diamond film is low. Till now, the highest diamond nucleation density has been achieved by applying bias voltage to generate plasma over the substrate. [13-16] However, bias is not suitable for Micro-tools and tools with sharp cutting edge due to the discharge on the tip. Recent research has shown that electrostatic adsorption and self-assembly on modified substrate surface results in very

high nanocrystalline particle densities by taking advantage of the electrostatic interactions between the nanocrystalline particle and silicon surface. [17, 18] In this study, the diamond nucleation on WC-Co was enhanced by considering the charge of the nanocrystalline diamond particles at varying pH-values.

Experimental Procedure

Cemented carbide (WC-6 wt. % Co) is chosen as substrate. Prior to diamond film deposition, two methods were used for pre-treat of the substrates: 1) The substrates were treated with Murakami solution (10 g $K_3[Fe(CN)_6]$ + 10 g KOH + 100 mL H_2O) followed by an acid solution (10 ml 98% H_2SO_4 + 100ml 33% H_2O_2) to remove cobalt from the surface. 2) PVD interlayer was utilized to hinder the diffusion of cobalt from the substrate. The TiB_2 film was deposited on as-received WC-Co substrates by Magnetron Sputtering with a thickness of ca. 200 nm. During the deposition, the working pressure was kept constant at 0.5 Pa with Ar as working gas, and the deposition temperature was set as 350 °C. The DC power of the single TiB_2 target (300 mm×100 mm×10 mm in size and 99.5% in purity) was set as 2.4 kW with power density about 8 W/cm². The bias voltage was set as -50 V. Subsequently, nanodiamond crystallites were ultrasonically seeded on these two different types of substrates for 30 min by employing a dispersion containing nanodiamond. The diamond nanoparticles used for seeding is a commercially available detonation nanodiamonds (NDs) aqueous suspension (Plasmachem GmbH, PL-NanoPure, grade G01). The aqueous suspension of the ND were dispersed in pure water. Afterwards, the colloidal solution was adjusted to pH values ranging from 2 to 12 by utilizing HCl and NaOH with concentrations ranging from 0.1 M to 0.001 M. The concentration of nanodiamonds in water was kept the same for all measurements and was 0.005 wt.%. Dynamic light scattering measurements were carried out to determine the particle size distribution of colloids (Malvern Zetasizer Nano ZS, 633 nm laser). After the seeding procedure, the substrates were rinsed in ethanol and dried with N_2 . All the films were deposited in a hot filament chemical vapor deposition (HFCVD) chamber for 10 min. The HFCVD apparatus possessed nine tantalum wires with a diameter of 0.6 mm as filaments. The temperature of the filaments was determined to be 2400 ± 100 °C by an optical pyrometer. The substrate temperature was kept at 850 ± 20 °C. Diamond film deposition was carried out at a constant gas pressure of 40 kPa. The flow rates of the reaction gases H_2 and CH_4 were maintained at 800 sccm and 16 sccm, respectively.

Results and Discussion

Fig. 1 (a) shows the change of zeta potential of nanodiamond (ND) particles in deionized water. With increasing the pH value, the zeta potential gradually decreased with increasing pH. The diamond nanoparticles have a negative zeta potential over the vast majority of the pH range, with only a miniscule positive region at pH lower than approx. 2.4. This means that the ND particles are negatively charged in the solution with pH value higher than 2.4, whereas positively charged in the solution with pH value lower than approx. 2.4 in acidic medium. The isoelectric point is located at 2.4, indicating neutral nanodiamond crystallites at this pH. This result can be related to the surface termination of the particles. According to the producer's data and our own measurement (not shown here), the C=O stretching vibration of carbonyl groups, O-H, N-H amino-groups, etc., was found in the FTIR spectrum of ND particles. The surface termination originates from the chemical treatment, which impart a charge to ND particles in aqueous solution. The potential value and the sign of the charge depend on the dissociation constant of the functional groups, the concentration and the pH value, and the background-electrolyte concentration.[19] In this work, H^+ and OH^- varied the zeta potential of the NDs, which can be explained by the protonation/deprotonation of amino- groups and carboxyl groups, respectively [20]. In addition, Figure 1b shows the hydrodynamic particle size distribution in deionized water as determined by dynamic light scattering (DLS). The weighted average hydrodynamic particle size is ≈ 35 nm. The hydrodynamic radius varies between 30 nm and 40 nm, and ca. 90% of the particles belong to this range. The measured size value is larger than 5 nm (producer's value), which we ascribe to agglomeration of ND in suspensions.[21, 22].

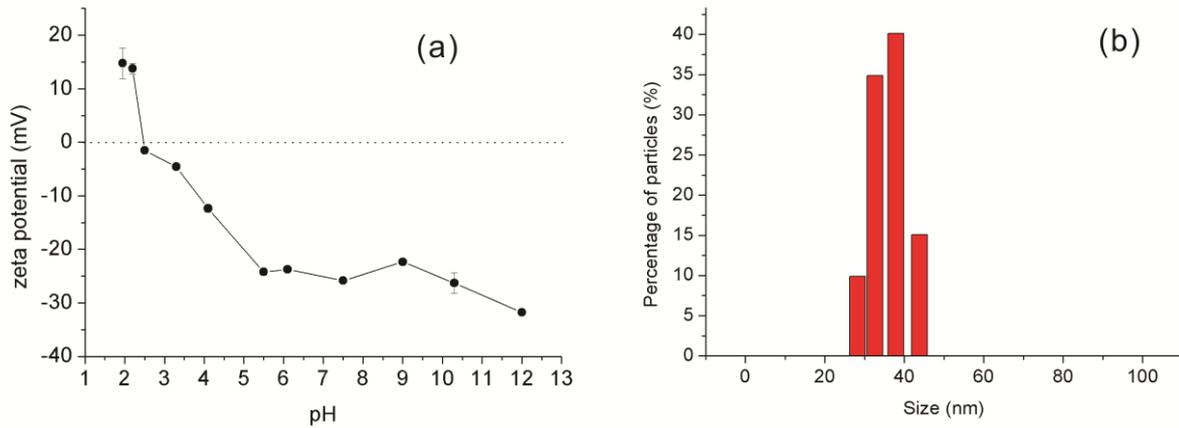


Fig. 1 (a) Zeta potential of as-received diamond nanoparticles as a function of pH and (b) hydrodynamic particle size distribution in deionized water as determined by dynamic light scattering

Due to the deteriorious effect of cobalt on diamond deposition, cemented carbide substrates has to be treated. The traditional method is to etch the cobalt away from the surface. Figure 2a shows the surface morphology of a WC-Co substrate after etching. The WC grains exhibit a high roughness Such a rough surface is helpful for enhancing the diamond film adhesion via an interlocking effect. The cobalt content is nearly 0 wt. % measured by energy-dispersive X-ray spectroscopy (EDS). Another method to treat the surface is the synthesis of TiB₂ barrier interlayer to hinder the diffusion of cobalt. A further consideration is that cobalt in the substrate could interact with boron in the interlayer to form stable components, i.e. cobalt boride (CoB, Co₂B). The TiB₂ barrier interlayer was deposited on as-received WC-Co substrate. Figure 2b shows the surface morphology of the interlayer. The WC grains were coated with nanocrystalline TiB₂ film. Furthermore, TiB₂ interlayers adhered stronger to the WC-Co surface than to the diamond film. This became evident, as film delamination mostly occurred at the interface between TiB₂ interlayers and diamond top layer.

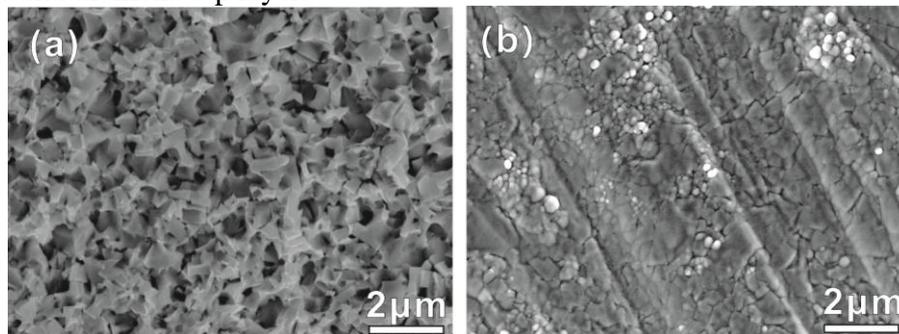


Fig. 2 SEM surface morphology image of (a) the WC-Co substrate after etching and (b) a WC-Co substrate coated with a TiB₂ interlayer

These two kinds of surfaces were seeded in diamond colloids with different pH value. Subsequently, diamond films were deposited on the seeded substrates for 10 min. Figure 3 shows the nucleation of diamond film on WC-Co substrate surfaces as a function of pH. Figure 3a and 3b represent ND particles at pH 2.2 and 9 at chemical etched WC-Co substrate, respectively. It is clear that the density of ND nuclei is higher at pH 2.2. As predicted from Figure 2, the positive charge of ND particles allowed the formation of two-dimensional assemblies by electrostatic adsorption on oxidized WC-Co substrate. The nucleation density was calculated by counting the total number of diamond nuclei divided by the occupied surface area. At pH 2.2, the nucleation density was calculated to be $1.0 \pm 0.1 \times 10^{10} \text{ cm}^{-2}$, which is two orders of magnitude higher than on bare WC-Co substrates [23], one order of magnitude higher than on W interlayer [24], and a little bit higher than applying plasma bias voltage [9]. At higher pH, the nucleation density is lower, but some larger particles were observed (see Figure 3b). The nucleation density in this

case is $4.4 \pm 0.7 \times 10^9 \text{ cm}^{-2}$. According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the total interaction energy consists of the long-range van der Waals and the short range electrostatic forces. The low nucleation density is due to the repulsive potential between negative charged ND particles and oxidized WC-Co surface. In the case of TiB_2 interlayer, a continuous diamond film was observed in Figure 3b. After the seeding procedure, a diamond film was deposited on the TiB_2 interlayer, which was shown in Figure 2b. The diamond crystals are much larger than that on etched WC-Co substrates. This indicates that diamond nucleation on TiB_2 interlayer needs a shorter incubation time than on etched WC-Co substrates. A diamond mono-layer thin film with a grain size of ca. 200 nm was obtained on WC-Co substrates. In a range from pH 2.5 to 9, the diamond nucleation on TiB_2 interlayer is similar. No cobalt droplets were found along diamond crystals, and EDS results showed also no cobalt on the backside of the diamond films. These results indicate that the TiB_2 interlayer can be a good candidate as barrier interlayer to hinder the diffusion of cobalt from the bulk material. Compared to bare WC-Co substrate, the barrier layer function is assumed to be the reason for the rapid growth of a continuous diamond films.

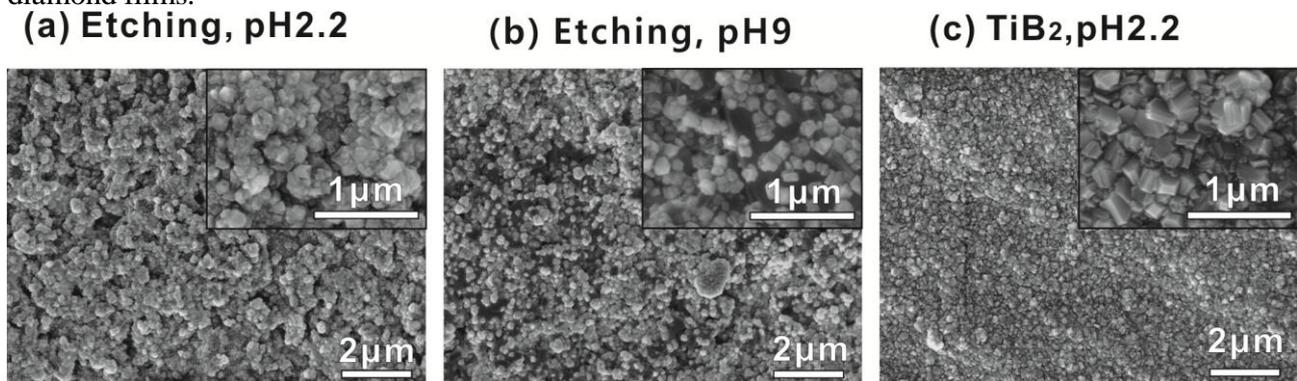


Fig. 3 SEM images of diamond films deposited for 10 min on (a) chemical etched WC-Co surfaces seeded with colloids at pH 2.2 (positive charged particles), (b) chemical etched WC-Co surface seeded with colloids at pH 9 (negative charged particles), and (c) TiB_2 interlayer seeded with colloids at pH 2.2

Summary

In this study, we demonstrated that the adsorption of nanodiamond particles to the WC-Co substrate surface is governed by a simple electrostatic process, which can be controlled by the surface groups of the particles and the pH of the solution. The positive charged nanodiamond particles enhanced the nucleation of diamond on oxidized WC-Co substrates. The highest nucleation density of diamond on WC-Co substrates was achieved at pH (2.2) ($1.0 \pm 0.1 \times 10^{10} \text{ cm}^{-2}$), which is comparable to the highest record achieved by applying bias voltage to generate plasma. Furthermore, a continuous diamond mono-layer was deposited on a TiB_2 interlayer. This electrostatic induced adsorption of diamond nanoparticles is crucial for the development of ultra-high nucleation densities for the growth of high performance nanocrystalline diamond films, especially for micro-sized cutting tools with sharp cutting edges in the Micro and Nano Electro-Mechanical Systems.

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