Journal of the Ceramic Society of Japan 117 [5] 650-653 2009 Paper

Adhesion of nanodiamond seeded CVD diamond on ceramic substrate

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Conventional structural ceramic substrates were coated with 1 μm thick polycrystalline CVD diamond layer by using the hot filament CVD system and subsequently tested. The substrates chosen were silicate, alumina, silicon nitride, and silicon carbide ceramics. To achieve a high nucleation density and to improve the adhesion between the diamond and the ceramic substrate, the newly developed Electrostatic Self-Assembly of Nano Diamond (ESAND) seeding method was used. This seeding method initiates the growth of crystalline diamond. For this seeding procedure, each negatively charged substrate surface was covered with a cationic polymer monolayer. Next, anionic polymer coated cationic nanodiamond particles were attached to the substrate by the electrostatic self-assembly process. The degree of adhesion between the diamond film and each substrate was investigated by micro-scratch testing. These tests involved the use of a Rockwell C indenter (r = 0.2 mm), which scratched the samples at a speed of 10 mm/min under a progressive normal load (from 0 to 21N). The morphology of the poly-crystalline diamond films on the various substrates was analyzed using Raman spectroscopy.

Key-words : CVD diamond, Wear resistant coating, Ceramic wear

[Received November 14, 2008; Accepted February 19, 2009]

1. Introduction

Due to its hardness, strong chemical inertness, and low friction coefficient, CVD diamond has been regarded as an ideal coating material for wear resistant applications.[1),2)] However, the use of CVD diamond coatings on ceramic materials is difficult for a few reasons. For example, it is hard to achieve a high nucleation density (> 10^8/cm^2) of diamond nuclei on oxides, nitrides, or borides without them being pre-treated first. To enhance the density of nucleation on these hard and inert ceramic substrates, it is necessary to perform a mechanical damage-based seeding process. For instance, the ceramic may be subjected to ultrasonification whilst being immersed in a slurry of dispersed diamond particles. Alternatively, it may be polished using diamond powders. However, pretreatments based on mechanical damage cannot be used for MEMS pattern coatings or finely finished ceramic substrates. This is because such processes have been found to frequently result in nano-to micron-sized scratches and diamond particle residues on the ceramic surface.[3),4)]

We recently reported a newly developed pretreatment process called the Electrostatic Self-Assembly of Nano Diamond (ESAND) seeding method.[5)] In this method, cationic nanodiamond particles were encapsulated with anionic polymer chains and then spontaneously dispersed in aqueous solution. The anionic substrates were covered with cationic polymer monolayer.[6),7)] By simply dipping these substrates into the anionic-polymer-encapsulated nanodiamond solution, damage-free pre-treatment that guaranteed a superb nucleation density (> 10^{12}/cm^2) was achieved. This method can be used for any ceramic substrates that have charged surface. Since most ceramic surfaces show anionic properties in ambient air, the ESAND seeding method can be successfully used for various ceramic substrates.

The adhesion between the diamond film and the substrate is the one of the major issue. Many studies have shown that the adhesion is strongly depended on the substrate and introduction of interlayer. Pretreatment of substrate have been tried for improvement of the adhesion.[4),8),9)] The study of an adhesion of diamond growth on nanodiamond layer has been previously reported.[5)]

In this study, we chose ceramic materials as substrates for the ESAND-seeded diamond coatings. Even though high nucleation densities were attainable, it was still considered important to investigate adhesion behavior between the ceramic materials and the ESAND-seeding-induced diamond layers. Therefore, micro-scratch tests and scanning electron microscope (SEM) were used to elucidate the properties and overall potential of the ESAND-seeded CVD diamond protective coatings.

2. Experimental procedure

Sintered α-Si_3N_4, α-SiC, α-Al_2O_3 and α-SiO_2 (quartz) were used in this experiment. All of the specimens were prepared as 2.5 mm thick polished disks.

For ESAND seeding method, commercial nanodiamond powder (JinGangYuan New Material Development Co., Ltd.) was used as diamond seeds. To encapsulate the cationic nanodiamond particles with anionic polymer chains, a mixture of PSS (poly sodium 4-styrene sulfonate, 50 ml), ND (0.4 g), and DI water (200 ml) were vigorously agitated using an attrition mill (Nanoin Tech Co., Ltd.).

The ceramic substrates were dipped into a 10% PDDA (poly diallyldimethyl ammonium chloride) aqueous solution. The substrates were then rinsed with DI water. These steps resulted in each substrate having a PDDA cationic monolayer directly attached to its surface.[6),7)]

Some specimens were pretreated by ultrasonic nucleation

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method. The samples were treated with DI water solution containing suspension of diamond paste and nanodiamond powder for 1 h.

Diamond films, each 1 μm thick, were grown using a conventional hot-filament CVD system. 11 tungsten wires (d = 0.5 mm) were hung on graphite electrodes for filament and the distance from the substrate was 8 mm.

The filaments were carbonized with a gas mixture of H_2 (97 vol%) and CH_4 (3 vol%) before deposition. To deposit the diamond films, a gas mixture of H_2 (99 vol%) and CH_4 (1 vol%) was fed at a flow rate of 100 sccm and a pressure of 60 torr. The substrates were kept at a temperature of 700°C.[5)]

The surface and cross-sectional structures of the films were analyzed by SEM (Hitachi, Ltd., S–4300). In addition, all of the specimens were studied using Raman spectroscopy (LabRam HR model, Jobin-Yvon, France, 514.5 nm Ar-ion laser) in order to determine their crystallinity and residual stress.

Scratch adhesion tests were performed on the diamond coated samples using a Rockwell indenter. In each case, the diamond tip (r = 0.2 mm) was drawn across the sample under a progressive load (3 N/min, 0–21 N). The speed at which the tip was moved was 10 mm/min.[10),11)]

From these tests, we obtained the tangential force and the images of scratches in order to determine the critical load for delamination.

3. Results and discussion

3.1. Diamond film characterization

Every specimen shows a characteristic sp^3 Raman peak at around 1332 cm^{-1} (see **Fig. 1**(a)). Figure 1(b) shows that the position of this peak is slightly shifted for the different substrates. These shifts strongly depend on the difference between the linear thermal expansion coefficient of the diamond and ceramic substrate. The residual stress was calculated based on the diamond peak shift and shown on **Table 1**.[12),13)] Negatively-shifted peaks (SiO_2, SiC, Si_3N_4) mean that tensile stress is present in the diamond thin film, while positively-shifted peaks (Al_2O_3) means that there is compressive stress in the diamond film. Such compressive stress is caused by a difference between the thermal expansion coefficients of the film and substrate.[13),14)] These shifts also suggest that there is a large adhesive force that is strong enough to bend the atomic bonding status. The residual stress shown in Table 1 would contribute to the cracking during the scratch test. **Figure 2** shows SEM micrographs of the surface of the diamond films on the various ceramic substrates. Looking at the cross-sectional images in **Fig. 3**, it is clear that there are no observable pores or pin holes in diamond films. However, as shown in the SEM images of **Fig. 4**, there are some micro cracks in the diamond film deposited on SiO_2 substrate. These are caused by a large residual tensile stress in the diamond film. Using the extent of the negative shift in the Raman peak, the residual tensile stress at the SiO_2/diamond interface is calculated to be 3.48 GPa.[13),14)]

Table 1. Comparison of Coating Thickness, Residual Stress and Critical Load for Various Substrates

Substrate	Seeding method	Coating thickness (nm)	Raman peak shift (cm^{-1})	Residual stress (GPa)	Critical load (N)	Aver. Crack width (μm)
SiO_2	ESAND	808	– 6.61	3.48	13.0	104.62
SiC	ESAND	841	–1.93	1.01	5.8	94.84
Si_3N_4	ESAND	979	–1.48	0.78	7.9	92.40
Al_2O_3	ESAND	1012	6.22	–3.27	6.1	224.97

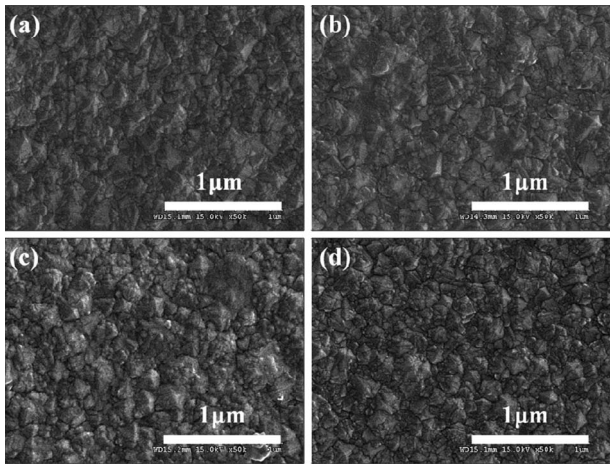

Fig. 2. SEM images of the as-grown diamond surfaces on (a) SiO_2, (b) SiC, (c) Si_3N_4 and (d) Al_2O_3.

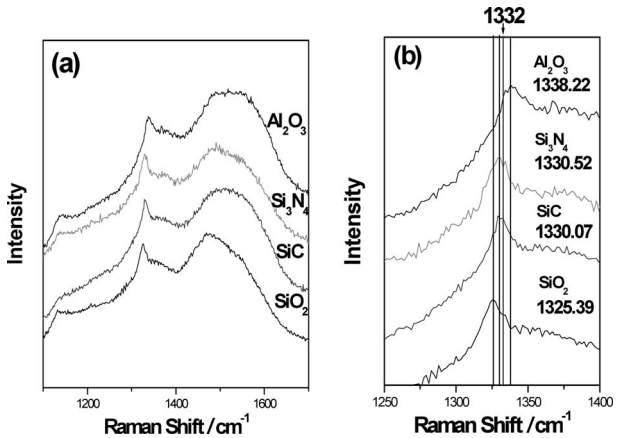

Fig. 1. Raman spectra of the CVD diamond surfaces grown on various ceramic substrates (a). And negatively-shifted peaks (SiO_2, SiC, Si_3N_4) mean that tensile stress and positivelyshifted peaks (Al_2O_3) means that there is compressive stress in the diamond film (b).

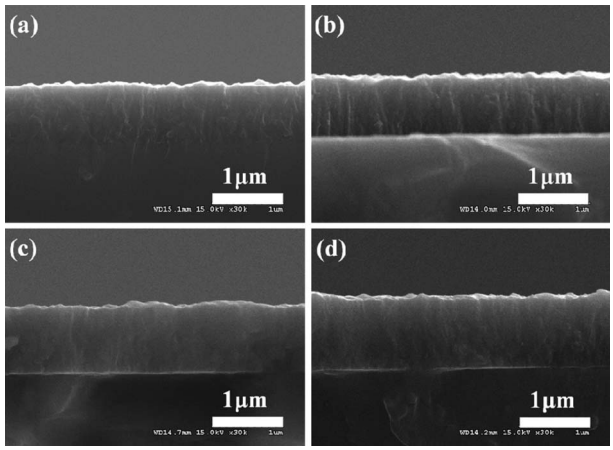

Fig. 3. Cross-sectional SEM images of as - grown diamond films on (a) SiO_2, (b) SiC, (c) Si_3N_4 and (d) Al_2O_3.

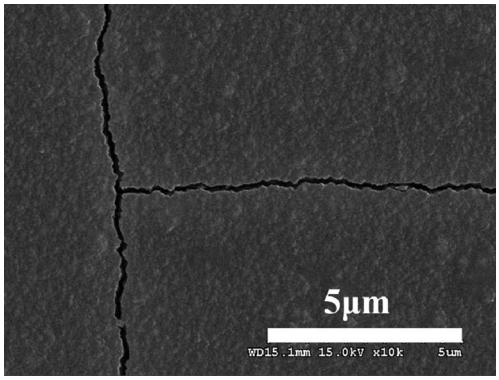

Fig. 4. Micro-cracks of diamond film caused by tensile stress on the SiO_2 substrate.

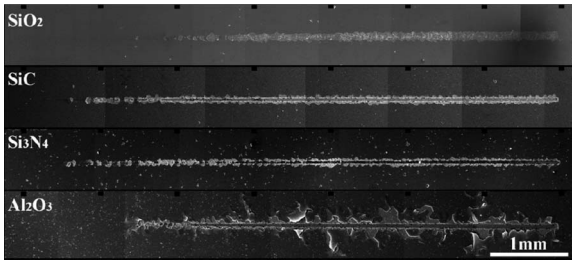

Fig. 5. Scratch track images of the diamond films deposited with ESAND seeding method on various ceramic substrates.

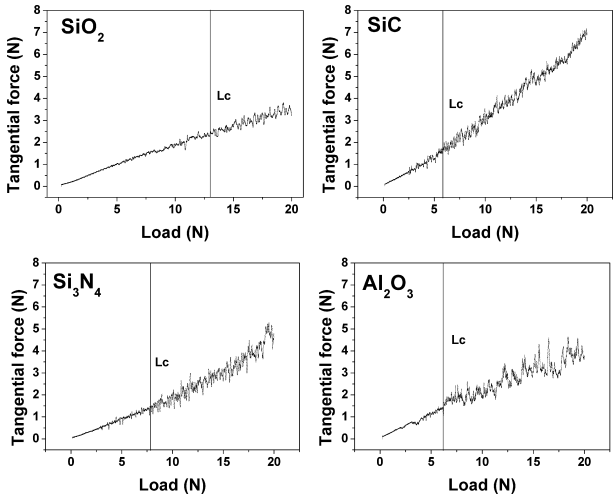

Fig. 6. Tangential force-load graphs obtained from scratch measurements of the diamond films on various substrates.

3.2. Adhesion properties

Figures 5, **6** and **7** show the results of the scratch tests of the diamond thin films on the different substrates. Figure 5 is SEM micrographs of the scratched tracks. In each samples, diamond films under the tip was not delaminated by any of the loads used during the test. As the indentation load increases, there is severe crack propagation and film delaminating is observed on diamond layer coated on the Al_2O_3. However, in the case of the film deposited on the SiO_2, Si_3N_4, and SiC, there were minimal crack growths, which can be emerged by the plastic deformation of substrate ceramics adjacent to scratch groove, is observed even at the highest load. On the Al_2O_3 substrate, the width of film

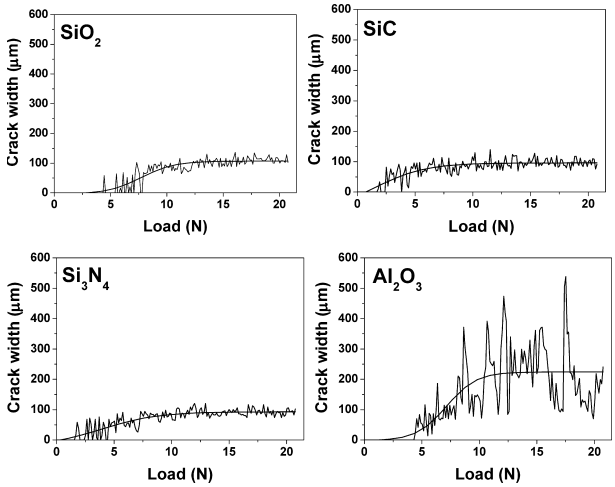

Fig. 7. Variation in the crack width as a function of applied load on the different substrates.

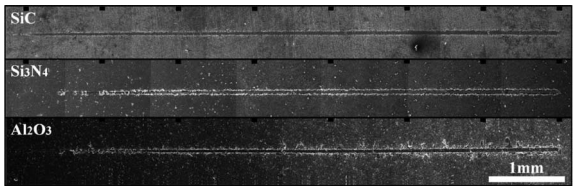

Fig. 8. Scratch track images of the diamond films deposited with conventional ultrasonic seeding method on various ceramic substrates.

delamination is dramatically increased after the critical load (L_c). According to the scratch test, silicon based ceramic substrates have stronger adhesion strength with diamond than aluminum oxide substrate which has strong ionic bonding characteristics. Si–C covalent bonding formation at the interface between Si based material and CVD diamond can induce the strong adhesive tendency. Figure 6 shows that the slopes of the averaged tangential force fluctuations changed after the critical load. A steeper slope means that more force is needed to move the scratching corn peeling out the film. There is large vibration of delaminating force on the Al_2O_3 specimen, which means irregular tangential stress file up and release. When the calculated residual stress is smaller than 1 GPa (for α-Si_3N_4 and α-SiC), more tangential force is consumed to overcome the adhesive force.[15)–18)]

Figure 7 shows the average crack width on different substrates. The first crack on Al_2O_3 substrate appeared lately because it is hardened by the compressive residual stress. But after the first crack, the diamond film on the Al_2O_3 substrate became extensively delaminated. This means that the large residual compressive stress does not have a positive effect on the film adhesion. On the other hand, the SiO_2, SiC and Si_3N_4 samples, which all experienced tensile stress, all showed a very narrow delaminated area.

In **Fig. 8**, SEM images of the scratch tracks of diamond films seeded with ultrasonification are shown. Less damage due to the crack and delamination compared to SEM images of scratch tracks of diamond films with ESAND seeding is observed (Fig. 5).

High magnification images of near the end of the scratch tracks on Al_2O_3 substrate show the delamination of the diamond film from the substrate (**Fig. 9**). Larger delamination area is

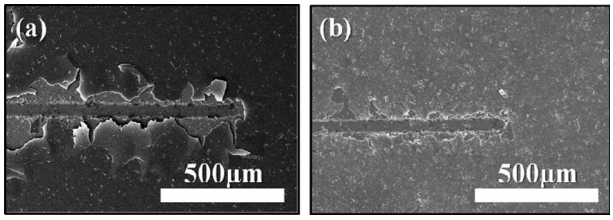

Fig. 9. High magnification images of delaminated area on Al_2O_3 substrate. (a) ESAND seeded sample and (b) a sample. treated by ultrasonication.

observed on ESAND seeded one. Difference in cracking and delamination between two types of seeding methods can be explained by the difference in adhesion strength between diamond film and substrate depended on seeding method. Buijnsters et al. reported that the most important factor influencing the adhesion is the interlayer formation during the diamond growth.[19),20)] Since adhesion is determined by the density of interfacial bond. Possibility of the formation of the interlayer is low for ESAND seeding since it involves direct diamond deposition on nanodiamond layer.

Better adhesion for ultrasonification seeding might be attributed to the interlayer formed during the nucleation and diamond deposition and rough surface created during the ultrasonification process. Higher possibility of formation of interlayer and rough surface during the ultrasonification and diamond deposition leads to the stronger adhesion.

4. Conclusions

Polycrystalline diamond thin film was successfully deposited on different substrates by HFCVD. The use of the ESAND seeding process made it possible to seed nano-sized particles on ceramic substrates. And these films had very good adhesion property enough to endure great residual stress. The diamond thin films on the SiO_2, SiC and Si_3N_4 substrates experienced tensile stress, while the film on the Al_2O_3 substrate experienced compressive stress. According to the results of scratch tests, silicon based ceramic substrates shows higher bonding strength than alumina substrate. Strong Si–C covalent bonding can contribute to this interface property. High residual tensile-stress-induced micro cracks were observed in CVD diamond films. In addition, it was found that the residual compressive stress did not have a re-enforcing effect on the brittle CVD diamond coating. Compared to adhesion of diamond films with ultrasonification seeding, inferior adhesion was observed for diamond films deposited on ESAND substrates. Even though high nucleation density and uniform diamond deposition without surface damage was achieved by ESAND seeding, adhesion strength should be improved further.

Acknowledgments This study was supported by the Korea University Grant.

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