



Tribological properties of undoped and boron-doped nanocrystalline diamond films

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ABSTRACT

Undoped and boron-doped nanocrystalline (NCD) diamond films were deposited on mirror polished Ti-6Al-4V substrates in a Microwave Plasma Assisted Chemical Vapor Deposition system. Sliding wear tests were conducted in ambient air with a nanotribometer. A systematic study of the tribological properties for both undoped and boron-doped NCD films were carried out. It was found for diamond/diamond sliding, coefficient of friction decreases with increasing normal loads. It was also found that the wear rate of boron-doped NCD films is about 10 times higher than that of undoped films. A wear rate of $\sim 5.2 \times 10^{-9} \text{ mm}^3/\text{Nm}$ was found for undoped NCD films. This value is comparable to the best known value of that of polished polycrystalline diamond films. Although no surface deformation, film delamination or micro-cracking were observed for undoped films, boron-doped NCD film undergoes a critical failure at a normal stress of 2.2 GPa, above which surface deformation is evident. Combined with high hardness and modulus, tunable conductivity and improved open air thermal stability, boron-doped nanocrystalline diamond film has tremendous potentials for applications such as Atomic Force Microscope probes, Micro-Electro-Mechanical System devices and biomedical sensors.

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1. Introduction

Superior properties, such as highest hardness and modulus of any materials, low friction and stiction make ultra-smooth nanocrystalline diamond film (NCD) an excellent candidate for many biomedical and Micro-Electro-Mechanical System (MEMS) applications [1–8]. Boron-doped diamond films have attracted interest because boron atoms can be readily incorporated into the diamond lattice and form a p-type semiconductor with tunable electrical conductivity [9]. Extensive studies regarding diamond and diamond sliding have shown that the Coefficient of Friction (COF) of such a friction pair lies between 0.05 and 0.15. The very smooth surface (root-mean-square [RMS] roughness around 20 nm) of NCD film makes it potentially useful as friction and wear-reducing coating on sliding mechanical components (e.g. seals, gears, and biomedical implants). It has been reported that fine grain Chemical Vapor Deposition (CVD) diamond film exhibited a low COF between 0.035 and 0.03 in dry nitrogen and humid air, respectively. Wear factor of $1.6 \times 10^{-7} \text{ mm}^3/\text{Nm}$ in dry nitrogen, and $1.8 \times 10^{-7} \text{ mm}^3/\text{Nm}$ in humid air for these smooth diamond films were also reported [3,4]. It was reported that NCD films made in Microwave Plasma assisted Chemical Vapor Deposition (MPCVD) system using $\text{H}_2/\text{CH}_4/\text{N}_2$ chemistry exhibit excellent wear resistance as compared to bare Ti-6Al-4V when tested in a dental temporomandibular joint (TMJ) simulator [10,11]. Significant improvement indicated the potential advantage of diamond/diamond sliding over the traditional metal condylar/ultrahigh molecular weight polyethylene sliding. However, it appears that the exact friction

and wear mechanism of such films is still not well understood and the effect of normal load and applied stress on their lifetime in sliding is not clear. On the other hand, recently there are tremendous interests in using conductive and non-conductive NCD or ultrananocrystalline diamond (UNCD) film for Atomic Force Microscope (AFM) probes and MEMS device [12,13]. Boron-doped NCD has also been considered as an outstanding candidate for these applications [2]. It is important to investigate and compare the tribological properties of undoped and boron-doped NCD films because sliding and wear performance studies for boron-doped NCD have been lacking in the published literature.

In this study, a general comparison between the undoped and boron-doped NCD is made under a variety of processing conditions. Systematic investigation of the relationship between applied normal load (stress), and COF for both undoped and boron-doped NCD was carried out to better understand the tribological behavior of undoped and boron-doped NCD films with respect to the boron content, film quality, grain size, and film morphology.

2. Experimental details

Titanium alloy (Ti-6Al-4V) spheres with 2.5 mm diameter and $0.125 \mu\text{m}$ surface RMS roughness were coated with diamond films and selected to serve as counterparts in sliding ball-on-disc wear tests. These spheres were cleaned and seeded by ultrasonic agitation in a diamond/water solution for 40 min prior to the film deposition. Three deposition runs were performed, and flow rates of processing gases are listed in Table 1. For these three samples, the operating pressure was 4.67 KPa, the forward microwave power was $850 \pm 15 \text{ W}$, the average substrate temperature was $780^\circ\text{C} \pm 20^\circ\text{C}$, and the deposition time was $\sim 2.5 \text{ h}$. The

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Table 1
Characteristics for diamond-coated spheres used as sliding counterparts for tribological studies

Sample names	H ₂ flow rate	CH ₄ flow rate	N ₂ flow rate	B ₂ H ₆ flow rate	Boron concentration (cm ⁻³)	Average grain size (nm)	Surface RMS roughness (nm)	Hardness (GPa)
NCD	500	88	8.8	0	0	18	20±5	75±10 GPa
B-NCD-1	500	88	8.8	0.2	4.5×10 ²⁰	36	35±5	68±10 GPa
B-NCD-2	500	88	0	0.2	8.2×10 ²⁰	Microcrystalline	76±4	40–80 GPa ^a

All samples were synthesized at a chamber pressure of 4.67 KPa and substrate temperature at 780 °C–810 °C.

^a As measured hardness is 80±11 GPa when nanoindenter hits diamond grain, and 50±7 GPa when it hits the boundary.

thickness of each film was measured from *in situ* optical interferometry and was ~3 μm.

For sliding partner, mirror polished 7 mm diameter and 2 mm thick titanium alloy (Ti–6Al–4V) discs with RMS roughness ~15 nm were used as substrates for NCD diamond film deposition. Hydrogen, methane and nitrogen flow rates were 500, 88, and 8.8 sccm respectively. The growth temperature was about 780 °C±30 °C, the forward power was 800±15 W, and the deposition time was about 2.5 h. Film thickness measured from *in situ* optical interferometry was about 2.5±0.18 μm.

With a Phillips X'Pert X-ray diffractometer system using Copper Kα₁ radiation of wavelength λ=1.54056 Å, glancing angle X-ray diffraction (XRD) with 5° incident beam was used to investigate the diamond lattice spacing variations of the film. Based on the model provided by Brunet [9], the change of the lattice constant of the boron-doped diamond can be presented as:

$$\Delta a/a = \beta[B] \quad (1)$$

where $\Delta a = a - a_0$, $a_0 = 3.5619$ Å for undoped diamond, and $[B]$ is the concentration per unit volume of the incorporated boron atom. β is given as:

$$\beta(\text{cm}^3) = 3.87 \times 10^{-25} + 3.73 \times 10^{-45}[B]. \quad (2)$$

The Scherrer Formula [14] was used to calculate the grain size based on the FWHM of the diamond (111) reflection for samples NCD and boron-doped NCD films. Micro-Raman spectra were obtained using an argon-ion laser with 514.5 nm excitation focused onto the film with a 1 μm spot size. Film hardness values were measured by using an MTS nanoindenter, and film RMS roughness values were obtained from optical profilometry. Tribological tests were performed by using a nanotribometer from CSM Instruments Inc. All wear tests on specimens were performed using the linear motion mode.

Three series of experiments were performed to investigate the tribological properties of undoped and boron-doped NCD films. These

sliding tests were performed in ambient air (RH: 50%, temperature 23 °C). For every series, friction and wear tests were carried out under the normal force of 60 mN, 150 mN, 250 mN, 350 mN, 450 mN, 650 mN, and 850 mN. Each test was carried out in ambient air for 2000 cycles with half amplitude 0.25 mm, and maximum sliding velocity 1 mm/s. COF data were obtained by calculating the ratio of tangential force to normal force. Wear volumes of undoped and boron-doped NCD coated on the Ti–6Al–4V spheres were calculated from the change in titanium sphere geometry.

3. Results and discussion

3.1. Film structure study by Micro-Raman spectroscopy

The NCD films are known to have polycrystalline structure, which contains diamond grains in nanometer scale and abundant amorphous carbon at the grain boundary [22]. Raman spectroscopy has been widely used for characterizing the structure and quality of such films [15–17]. Fig. 1 shows the Raman spectra of sample NCD, B-NCD-1 and B-NCD-2. NCD spectrum shows the typical features of nanocrystalline diamond including a weak diamond peak at 1337 cm⁻¹ attributed to crystalline cubic diamond under a compressive stress of 2.8 GPa [16,17]. A small peak center at 1140 cm⁻¹, and broad bands centered at 1340, 1490, 1550 cm⁻¹ are also present. All broad bands are typically associated with disordered carbon containing predominantly sp² bonding in hydrogenated amorphous carbon or graphite clusters [15–17]. While boron content increases, it is clear from Fig. 1 that the diamond center phonon line (1332 cm⁻¹) downshifts to lower wavenumber accompanying with the increase of a broad band at 1220 cm⁻¹, which are considered to be the result of the breakdown of the *k*=0 selection rule due to boron doping. A detailed analysis of the Raman spectrum can be found in a previous publication [17].

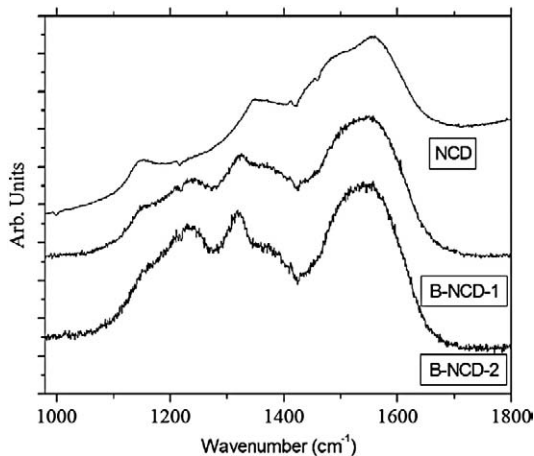


Fig. 1. Micro-Raman spectra for sample NCD, B-NCD-1, and B-NCD-2. An argon-ion laser with 514.5 nm excitation focused onto the film with a 1 μm spot size was used in this study.

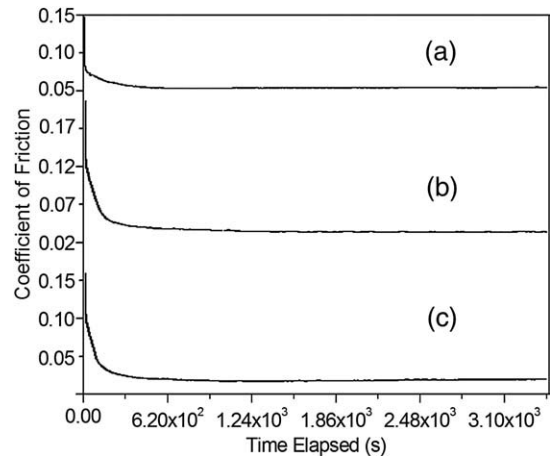


Fig. 2. The coefficient of friction of NCD coated Ti–6Al–4V sphere sliding against NCD coated Ti–6Al–4V tested under the normal loads (from above) of (a) 150 mN, (b) 650 mN and (c) 850 mN respectively.

Table 2

Calculated maximum normal stress, maximum shear stress, and maximum shear stress depth at various normal loads

Normal load (mN)	60	150	250	350	450	650	850
Max normal stress (MPa)	1126	1527	1809	2024	2200	2486	2718
Max shear stress (MPa)	237	320	379	423	460	519	568
Max shear depth (μm)	1.68	2.28	2.70	3.02	3.28	3.71	4.06

3.2. Tribological performance of undoped NCD film

Fig. 2 shows dynamic friction spectra as a function of time elapsed (in seconds) for three separate undoped NCD/NCD pair sliding tests. The COF starts with a high value and quickly drops to a low value because of initial acceleration, and it then gradually decreases to a steady state value. This run-in mechanism has been observed by many researchers and recognized as a polishing mechanism between two contact surfaces that have different surface roughness [18–22]. It is believed that, after the wear has progressed and the track has become more polished, the COF data will become stabilized. No oscillations could be found for all spectra after COF is stabilized. This indicates that no instrumental failure occurred and no film cracking or spalling was present during the measurement.

The maximum normal stress and maximum shear stress under different normal loads can be calculated from the changes of the geometrical size of the sphere and the disc, and these values are listed in Table 2. Fig. 3 shows the COF values as a function of the normal load for sample NCD. A relationship close to a first order exponential decay is apparent. The relationship between the friction coefficient of diamond and normal load has been exploited repeatedly, and contradictory results have been reported. Grillo and Field [23] reported that friction decreases with decreasing normal load for polished natural diamond pin sliding on CVD diamond coatings. Fu et al. [24] supported Grillo and Field's argument by measuring the COF of (111) (100) textured coatings and NCD coatings. There are also published different trends that are similar to the results of our experiments [22]. For NCD, the abundant amount of sp^2 hybridised carbon at grain boundary has lubricating effect [23] and can significantly affect the COF. The higher the normal load, the larger contact area will be brought up between sliding surface, and therefore more lubricant will get involved, which will consequently decrease the COF. NCD by MPCVD has even lower COF, when compared with reported values of COF for diamond on diamond sliding (between 0.05 and 0.15). This can be attributed to two factors: initially very smooth film surface with resulting low COF [21], and the lubricating effect of amorphous carbon [23].

Inserted pictures in Fig. 3 show the volume loss of the NCD coated Ti alloy sphere and the wear tracks after sliding tests for applied normal load 60 mN, 250 mN, and 350 mN. Although all these pictures

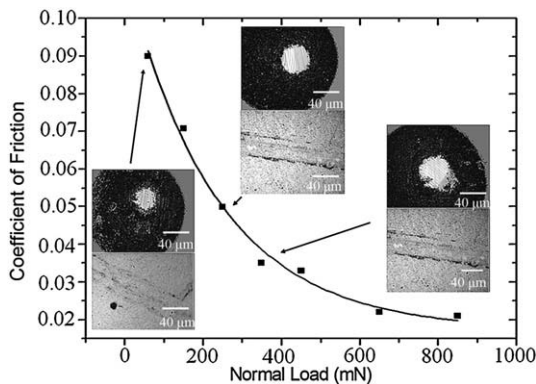


Fig. 3. Coefficient of friction as a function of normal load for a NCD coated sphere sliding against NCD coated disc. Inserted pictures show the wear surface of the NCD coated Ti-6Al-4V sphere and the corresponding NCD coated Ti-6Al-4V disc after the wear test.

show polished patterns on both sphere and disc, there is no evidence of film delamination and spalling, that is consistent with our observations from dynamic friction spectra. The worn surfaces have lower surface roughness than the untested surface as a result of surface polishing, and debris which mainly came out from NCD coated sphere was observed to pile up along the worn valleys. Micro-Raman spectroscopy taken at the very center of the polished area on the ball (where the thinnest film is presumably located) and within the wear track confirmed that the Ti-6Al-4V substrate had not been exposed and that no structural change of the NCD film had occurred. The Raman spectra features remained unchanged before and after the wear tests. The relationship between the wear volume and normal load is very obvious: the higher the normal load, the larger the wear volumes of diamond film. As a consequence of the increase of contact pressure, it is believed more asperities will be brought to contact and more asperity collisions will take place [5,21,25]. The wear volume of the sphere is represented by the shaded part shown in Fig. 4 and can be calculated using the relation:

$$V = \frac{\pi t^2 (3R - t)}{3} \quad (3)$$

where R is the radius of the ball plus the thickness of the diamond film ($3 \mu\text{m}$), and d is the diameter of the wear scar. It is possible to calculate the value of t (the highest wear, smaller than film thickness in all measurements) from the trigonometric relations:

$$t = R - \sqrt{R^2 - (d/2)^2} \quad (4)$$

and we can determine the wear volume by the following expression:

$$V = \frac{\pi \left(R - \sqrt{R^2 - (d/2)^2} \right)^2 \left(2R + \sqrt{R^2 - (d/2)^2} \right)}{3} \quad (5)$$

Once the wear volume is determined, the wear rate can be calculated by using the relation: wear rate (k) = $V/(W \times S)$, where V is the volume loss in mm^3 , W is the normal applied load in Newtons, and S is the sliding distance in meters. Fig. 4 shows the wear rate of

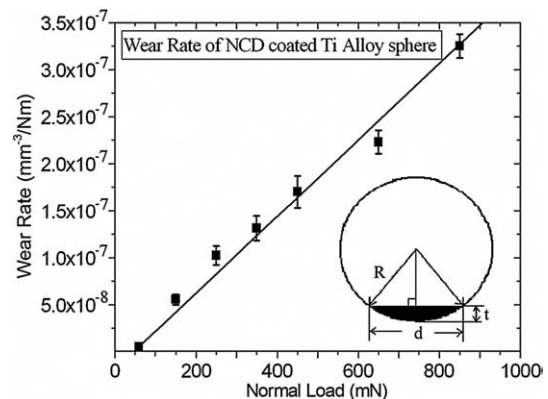


Fig. 4. NCD coated Ti alloy sphere wear rate as a function of applied normal load. Inserted picture shows the geometry of the diamond-coated Ti-6Al-4V sphere after friction test for the purpose of the calculation of the wear volume.

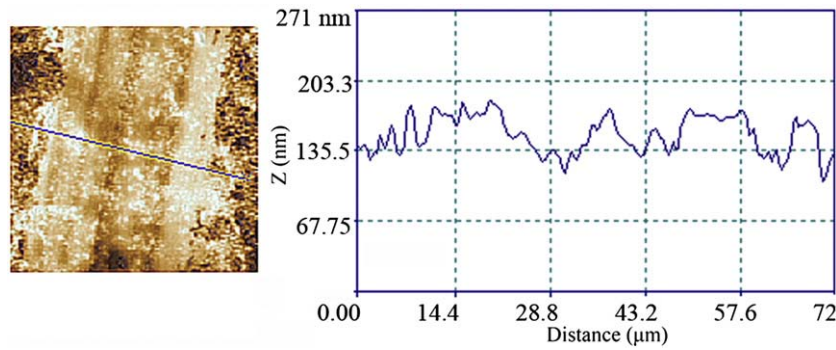


Fig. 5. Atomic Force Microscope (AFM) images taken from a wear track. Linear surface profile (to the right) was measured from the straight line on the image to the left.

diamond-coated sphere as a function of normal load which can be fitted with a linear expression. The minimum load (60 mN, 1.13 GPa max normal stress) and the maximum wear rate (850 mN, 2.72 GPa max normal stress) gave wear values of 5.2×10^{-9} and 3.25×10^{-7} mm³/Nm, respectively. Extensive studies have been carried out to investigate wear rate of different types of diamond on diamond contacts [20–26]. For polycrystalline diamond film, it is reported that as-grown CVD polycrystalline diamond has a high wear rate value of approximately $4\text{--}5 \times 10^{-7}$ mm³/Nm with the normal stress of 1.1 GPa [25,26], and it can be decreased to 2×10^{-9} mm³/Nm by means of mechanical polishing of

diamond films [26]. Because diamond polishing is considered to be a very hard and time consuming process, NCD coating process offers a simple way to achieve low friction between two diamond-coated surfaces.

Wear in the groove were measured by using an AFM in contact mode. Fig. 5 shows a typical image of a wear scar. A surface polishing/asperity removal process is obvious. However, although the AFM can image the wear track, there is no distinct measurable boundary between the edge of track and the un-scathed film since the peak/valley heights are similar in both regions. Therefore, compared to the wear on diamond-coated sphere, groove wear can be ignored.

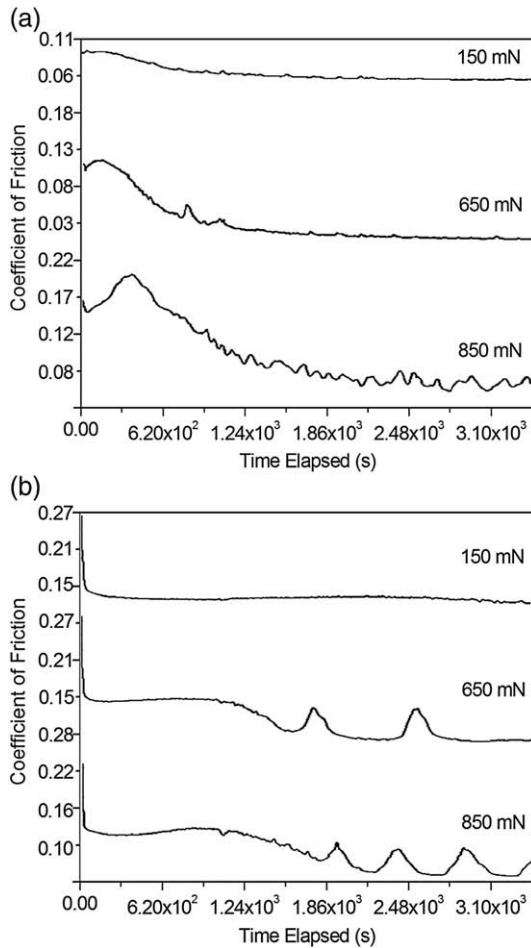


Fig. 6. Dynamic friction spectra of boron-doped NCD coated Ti-6Al-4V spheres with different film structure and surface morphology (B-NCD-1 to the left, B-NCD-2 to the right) sliding against NCD coated Ti-6Al-4V discs tested under the normal loads (from above) of (a) 150 mN, (b) 650 mN, and (c) 850 mN.

3.3. Tribological study of boron-doped NCD films

Deposition parameters and characteristics of two boron-doped NCD films are listed in Table 1. The boron content in sample B-NCD-2 is almost twice than that of sample B-NCD-1. The measured values of hardness for sample B-NCD-2 show some scatter because of the composite nature of the coating as it contains hard grain of diamond in micron scale embedded in an amorphous carbon matrix (confirmed by Raman spectra in Fig. 1). In general, we believe the average hardness of B-NCD-1 is higher than sample B-NCD-2.

Fig. 6 shows the dynamic friction spectra of B-NCD-1 and B-NCD-2 for the tests under normal loads of 150, 650 and 850 mN normal loads. Comparing Fig. 6 with Fig. 1, it is seen that a longer sliding distance is necessary to obtain a stabilized COF for the boron-doped films. These spectra are characteristically different from spectra measured from NCD/NCD sliding. We averaged the COF data for every spectrum and plotted the COF as a function of normal load for sample B-NCD-1 and B-NCD-2 in Fig. 7. It is to be noted that the COF for B-NCD-2 is about 2

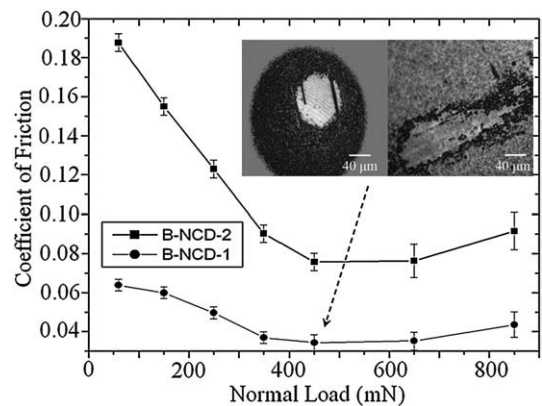


Fig. 7. Coefficient of friction as a function of normal load for boron-doped NCD coated Ti-6Al-4V spheres (B-NCD-1, B-NCD-2) slide against NCD coated Ti-6Al-4V, respectively. Inserted picture shows the polished sphere and wear track after sliding test of B-NCD-1 coated Ti alloy against NCD at a normal load of 450 mN.

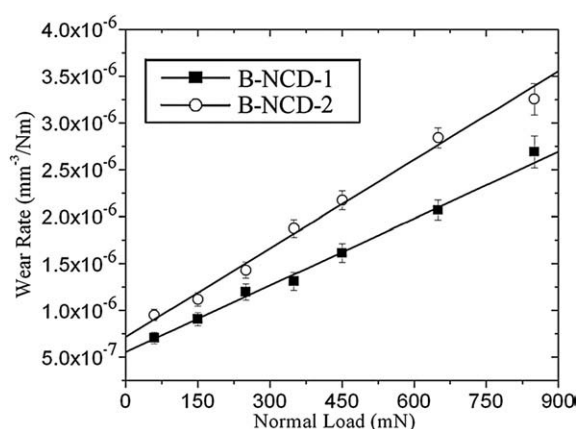


Fig. 8. Wear rate of boron-doped NCD coated Ti-6Al-4V spheres as a function of normal load.

to 3 times higher than that of B-NCD-1. It is widely believed [27,28] that film hardness and toughness play important roles in the COF. And it is usually accepted that when the film is harder and tougher, it will effectively support loading, exhibit less deformation, and eventually will result in smaller contact area. Our measurements are consistent with these published trends.

A trend showing a decreasing COF similar to that of undoped NCD films is observed under relatively low normal loads (up to 450 mN), and then the COF starts to spike as seen in the spectra shown in Fig. 7. Apparently, boron-doped NCD films undergo significant surface morphology transformation around 450 mN. Film failure occurs under higher normal load: part of the boron-doped diamond film delaminated by the abrasive polishing, which contained diamond grains were grinded between the sphere and the disc until they were gradually removed from the center of the wear track. Inserted pictures in Fig. 7 show the deep scratches resulted from such grinding process. From the correlation in Table 2, we can conclude that 2.2 GPa is the critical shear stress boron-doped NCD films can withstand. Boron-doped NCD film experiences significant surface transformation above that stress value, and film failure starts.

Interestingly, a comparison between COF dynamic spectra of undoped NCD films and boron-doped NCD film (Figs. 2 and 6) shows that under relatively low normal load (up to 150 mN) boron-doped diamond film has lower COF than undoped NCD films. This is completely contradictory to what we have described earlier because B-NCD-1 has larger grain size, rougher surface, and lower hardness. The absolute amount of sp² content in the film doesn't appear to explain it because from Fig. 1, B-NCD-1 has more crystalline structure than NCD (also reflected by difference in grain sizes listed in Table 1). This is why B-NCD-1 possesses less amorphous carbon at the grain boundary. One possible explanation is that the interaction mechanism between two contact surfaces was changed because of boron incorporation. The existence of boron carbide and boron hydride chemical bonds would help change the surface frictional energy dissipation and thus change the coefficient of friction.

Similar to the undoped NCD case, wear volumes on both sliding partners are very low and can be ignored. Wear rates for sample B-NCD-1 and B-NCD-2 were plotted on Fig. 8. Both these wear rates were fit to a linear function of the applied normal load, and the wear rate on B-NCD-2 is much higher than that of B-NCD-1. This can be explained as a consequence of different contact area sizes because of various surface roughness and hardness. A higher surface roughness results in more abrasive wear between contact areas, leading to more volume loss. With lower film hardness, the contact area is increased because the film cannot substantially support sliding counterpart and deformation occurs. Comparing Fig. 4 with Fig. 8, the wear rate of NCD over NCD sliding is about ten times lower than that of B-NCD over NCD sliding.

4. Conclusion

A systematic study of the relationship between applied normal load (stress) and COF for both undoped and boron-doped nanocrystalline diamond was carried out. A self-polishing mechanism was observed for diamond on diamond sliding which leads to a very low COF. Under the normal stress of 1.13 GPa, the wear rate of undoped nanocrystalline diamond film is about 5.2×10^{-9} mm³/Nm, which is similar to the best up-to-date value of polished polycrystalline diamond films under similar test conditions. No surface deformation was observed for undoped nanocrystalline diamond films. A critical failure normal stress of 2.2 GPa, above which the surface deformation occurs, was observed for boron-doped NCD films. Interestingly, despite its relatively higher surface roughness, boron-doped diamond films demonstrate lower COF under the relatively low normal load. This low coefficient of friction combined with the increased thermal stability under oxidizing environment [29] would enable applications of conductive, boron-doped NCD films to be used in many research areas, such as MEMS devices, AFM probes and biomedical sensors.

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