Effect of bottom micro-crystalline diamond (MCD) layer and top nano-crystalline diamond (NCD) layer onto the tribological behavior of (MCD/NCD) bilayer film

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Effect of bottom micro-crystalline diamond (MCD) layer and top nano-crystalline diamond (NCD) layer onto the tribological behavior of (MCD/NCD) bilayer film

Yijie Luo, Li Ma, Liang Li, Yubo Chen, Kechao Zhou, Mingkun Yi, Biao Deng, Haohui Yang, Xin Xia, Tengyu Hua, Dengfeng Yin and Qiuping Wei

Abstract

In this study, a comparative study of a series of (MCD/NCD) bilayer films with different MCD grain sizes and NCD layer thickness deposited on cemented tungsten carbide (WC-Co) flat substrates was conducted by changing the deposition time. Tribological behaviors of these diamond films were evaluated by using a reciprocal tribometer without lubrication. In friction test against Si₃N₄ balls, the (3hMCD/6hNCD) bilayer film showed the lowest coefficient of friction (0.059) and wear rates of counterpart balls (1.75 × 10⁻⁶ mm³ N⁻¹ m⁻¹) because of its lowest surface roughness and higher sp² content. This work provides a guide to choose suitable (MCD/NCD) bilayer basic structure in multilayer diamond film for getting a fine diamond film with low roughness and great tribological performance for different applications.

1. Introduction

With the widespread use of carbon fiber, glass fiber, high-silicon aluminum alloy, ceramics and graphite, cemented carbide and high-speed steel cutting tools can’t meet the cutting requirements of high precision, great efficiency and excellent surface quality [1–4]. Diamond has many excellent properties to process these materials, such as high hardness, high thermal conductivity, low friction coefficient, splendid friction resistance and chemical inertia [5–9]. By using chemical vapor deposition (CVD) method, diamond film can be deposited on the surface of cemented carbide tool, which not only uses the favorable toughness of cemented carbide, but also uses the outstanding hardness of diamond. However, shape accuracy and surface integrity of the machined surface are greatly influenced by the tribological and mechanical properties of diamond coated tools, which are determined by diamond surface morphology, structure, crystalline quality, etc [10, 11].

As we all know, typical MCD film owns many advantages like high hardness, super modulus of elasticity, good adhesion strength and so forth. But they can’t satisfy high precision machining, since their coarse grain and columnar structure result in high surface roughness [12]. Therefore, in order to smooth the diamond surface, NCD film is prepared by diminishing the diamond grain from micro-sized to nano-sized level (grain size < 100 nm). Meanwhile, the mechanical interlocking effect is weakened by abundant non-diamond phases and nano-sized crystalline grain of NCD film, resulting in its lower adhesion strength compared with MCD film [13–15]. Hence, considering that MCD film and NCD film can complement each other, multilayer technique is designed with MCD film as bottom layer and NCD film as top layer [16–18]. Recent studies have shown that the multilayer structure has superior friction performance, critical load and adhesion strength compared to monolayer structure [19–23].

For single-layer MCD or NCD films, the morphology and structure of diamond have great impact on the friction performance, residual stress and adhesion strength of diamond film. Abreu et al [24] have studied the
tribological behaviors of the friction performance of all samples. The objective of present work is to compare the characteristics and conducive to selecting optimal MCD

NCD. The as-deposited diamond YG6X (Ta content less than 0.5%) cemented carbide block (size 8 mm × 6 mm × 2 mm³) was used as the substrate material for CVD diamond deposition. It was provided by Zhuzhou Cemented Carbide Company. Mirror polishing was performed before pretreatment, and the surface roughness (Ra) after polishing was about 0.2 μm. Before deposition, a two-step pretreatment was carried out to decrease the content of surface metallic cobalt. The substrates were treated with Murakami reagent (10g K₃[Fe(CN)₆] + 10g KOH + 100 ml H₂O) for 15 min to roughen the substrate surface, and then etched with Caro’s (10 ml 98% H₂SO₄ + 100 ml 30% H₂O₂) acid for 30 s to remove the cobalt. Last, the substrates were seeded by diamond nanoparticles dispersed in deionized water for 30 min and then shaken in anhydrous ethanol solution for 5 min before drying.

2. Materials and experiments

YG6X (Ta content less than 0.5%) cemented carbide block (size 8 mm × 6 mm × 2 mm³) was used as the substrate material for CVD diamond deposition. It was provided by Zhuzhou Cemented Carbide Company. Mirror polishing was performed before pretreatment, and the surface roughness (Ra) after polishing was about 0.2 μm. Before deposition, a two-step pretreatment was carried out to decrease the content of surface metallic cobalt. The substrates were treated with Murakami reagent (10g K₃[Fe(CN)₆] + 10g KOH + 100 ml H₂O) for 15 min to roughen the substrate surface, and then etched with Caro’s (10 ml 98% H₂SO₄ + 100 ml 30% H₂O₂) acid for 30 s to remove the cobalt. Last, the substrates were seeded by diamond nanoparticles dispersed in deionized water for 30 min and then shaken in anhydrous ethanol solution for 5 min before drying.

Table 1. Deposition parameters for MCD and NCD layers.

<table>
<thead>
<tr>
<th></th>
<th>MCD</th>
<th>NCD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄/H₂/Ar flow (sccm)</td>
<td>1/49/0</td>
<td>2/18/30</td>
</tr>
<tr>
<td>Total pressure (kPa)</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>700–750</td>
<td>525–575</td>
</tr>
<tr>
<td>Current ΦA</td>
<td>36.5A</td>
<td>29.5A</td>
</tr>
<tr>
<td>Voltage ΦV</td>
<td>6.8–7.2V</td>
<td>5.5–6V</td>
</tr>
</tbody>
</table>

effect of different grain sizes on CVD diamond dry friction system and found that the larger grain sizes were, the thicker the coating was and the smaller the residual compressive stress was. However, there are relatively few studies devoted to the influence of each layer in multilayer system and much work so far has focused on adjusting the order of MCD and NCD layer or increasing the number of layers to improve performance [25–27]. Therefore, it remains challenging to choose a suitable structure of MCD and NCD layer in (MCD/NCD) multilayer film, getting the (MCD/NCD) multilayer films with matching friction coefficient, wear rates of counterpart product and wear resistance for satisfying the requirements of different applications. Based on this, the influence of morphology and structure of bottom MCD layer and top NCD layer on the morphology and friction performance of whole (MCD/NCD) bilayer film needs to be conducted firstly.

In this study, monolayer MCD with different deposition time, monolayer NCD and double-layer MCD/NCD films with different deposition time of each layer are deposited on cemented carbide substrates by HFCVD. The as-deposited diamond films are characterized by scanning electron microscopy (SEM) and Raman spectroscopy. The friction performance is evaluated in dry sliding condition by a reciprocating ball-on-plate tribometer. Finally, average friction coefficient and wear rates of counterpart pairs are used to further evaluate the friction performance of all samples. The objective of present work is to compare the characteristics and tribological behaviors of (MCD/NCD) bilayer films with different MCD or NCD deposition time. This is conducive to selecting optimal MCD/NCD structure in multilayer diamond film in different applications.

2.2. Characterization method

The surface morphology of the samples was characterized by scanning electron microscopy SEM (Quanta 250 FEG produced by FEI Company). LabRAM HR 800 produced by HORIBA Company of Japan was used to detect the composition of thin film samples. The light source was Ar⁺, and the wavelength was 532 nm. Furthermore, surface roughness was measured by surface profilometer (Dektak 6M).

2.1. CVD deposition processes

All diamond samples were deposited by a laboratory-developed hot filament chemical vapor deposition system. The filament wire was a single Φ 0.5 mm straight tungsten wire. The deposition process of bilayer diamond film was conducted by first depositing MCD and then in-situ depositing NCD. In the process, the transformation from MCD to NCD was realized by changing the gas pressure, current, atmosphere and gas flow ratio gradually. The deposition parameters are shown in table 1.

In order to study the influence of morphology and structure of bottom MCD layer and top NCD layer on the morphology and friction performance of (MCD/NCD) bilayer film, the deposition time of bottom MCD and top NCD layer were changed. Nine kinds of composite coatings were deposited by combining different MCD deposition time: (i) 3 h (ii) 6 h (iii) 12 h, and NCD deposition time: (i) 0 h and (ii) 3 h (iii) 6 h. And monolayer 3hNCD film was also deposited. Samples are listed in table 2. For convenience, (AhM/BhN) bilayer film means that bilayer film with bottom MCD layer with deposition time of A h and top NCD layer of B h.
The initial surface morphology of the diamond films observed by SEM is shown in figure 1. The samples from the top of figure 1 to the bottom correspond to the increase of the MCD deposition time: 3 h → 6 h → 12 h, and from the left to right corresponds to the increase of the NCD deposition time: 0 h → 3 h → 6 h. The last one corresponds to the monolayer 3hNCD film. The layout of the subsequent Fig is the same as it. As can be seen in figures 1(1#), (4#), (7#), the surface of three MCD films presents a typical morphology that is rough and covered with many well-faced sharp diamond crystals. With prolongation of deposition time, the diamond grain sizes increased from 1.0 ± 0.4 um to 5.2 ± 1.7 um, and the gap areas among grains increase. As for bilayer MCD/NCD films in figures 1(2#), (3#), (5#), (6#), (8#), (9#), they have unique nano-characteristics with the appearance of typical cauliflower-like grains like the monolayer NCD film in figure 1(10#). By contrasting figures 1(1#), (4#), (7#) and (2#), (5#), (8#), the size of NCD clusters increases with growth of the underlying MCD grains. This phenomenon should be explained by the effect of surface replication effect [29]. And by observing the thumbnails in figure 1, it can be found that the grain sizes of NCD basically remains the same.

Figure 2 shows the cross-sectional morphology of diamond films. Figures 2(1#), (4#), (7#) shows the cross-section of the MCD layer with their distinct columnar grain growth. Figure 2(10#) shows the grainy structure of NCD film. As for bilayer MCD/NCD films in figures 2(2#), (3#), (5#), (6#), (8#), (9#), the interfaces between MCD and NCD layer are slightly unclear because of in-situ depositing NCD. By comparing the thickness of MCD layer and NCD layer, 8# (12M + 3N) has the thinnest NCD layer than MCD layer, which results in that the NCD layer cannot completely cover the MCD layer and the shape of the NCD cluster is close to the original MCD grain as the example in figure 1(8#) shows. When the thickness of NCD layer and MCD layer is close, the shape of NCD cluster is nearly circular and has a smoother surface as the example in figure 1(3#) shows. Therefore, the morphology of MCD layer and the thickness of NCD layer have great influence on the morphology of (MCD/NCD) bilayer film. Moreover, the influence of film morphology on roughness would be further explored below.

<table>
<thead>
<tr>
<th>Table 2. Sample number and Deposition time of each diamond layer during deposition.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond film</td>
</tr>
<tr>
<td>1#(3M + 0N)</td>
</tr>
<tr>
<td>2#(3M + 3N)</td>
</tr>
<tr>
<td>3#(3M + 6N)</td>
</tr>
<tr>
<td>4#(6M + 0N)</td>
</tr>
<tr>
<td>5#(6M + 3N)</td>
</tr>
<tr>
<td>6#(6M + 6N)</td>
</tr>
<tr>
<td>7#(12M + 0N)</td>
</tr>
<tr>
<td>8#(12M + 3N)</td>
</tr>
<tr>
<td>9#(12M + 6N)</td>
</tr>
<tr>
<td>10#(0M + 3N)</td>
</tr>
</tbody>
</table>

2.3. Friction and wear experiments
Friction experiments of nine samples were carried out with MFT-4000 multifunctional surface tester produced by Lanzhou Huahui Instrument Technology Co., Ltd. The friction pair was a Si3N4 ball with a diameter of 6 mm. The friction environment was 50% (+5%) humidity at room temperature (28 ± 3°C). The friction condition included reciprocating speed of 240 mm min⁻¹, friction length of 5 mm, and loading force of 100 N under constant load. Before each friction experiment, absolute ethanol was used to clean the sample and Si3N4 sphere for 5 min to remove surface impurities. The wear situation of friction pairs was observed with SMZ-171 stereoscopic microscopy made by Motic.

After the friction experiment, the wear rate of counterpart ball (K) was calculated by the following formula: $K = (\pi \times d^2) / (64 \times r \times F \times S)$ [28].

Among them, d is the diameter of the wear scar near the circular shape on the surface of the friction pair ball, r is the radius of the friction pair ball (3 mm), F is the loading force (100 N), and S is the total sliding distance of the friction pair.

3. Results and discussion
3.1. Surface morphology and structural characterization

The initial surface morphology of the diamond films observed by SEM is shown in figure 1. The samples from the top of figure 1 to the bottom correspond to the increase of the MCD deposition time: 3 h → 6 h → 12 h, and from the left to right corresponds to the increase of the NCD deposition time: 0 h → 3 h → 6 h. The last one corresponds to the monolayer 3hNCD film. The layout of the subsequent Fig is the same as it. As can be seen in figures 1(1#), (4#), (7#), the surface of three MCD films presents a typical morphology that is rough and covered with many well-faced sharp diamond crystals. With prolongation of deposition time, the diamond grain sizes increased from 1.0 ± 0.4 um to 5.2 ± 1.7 um, and the gap areas among grains increase. As for bilayer MCD/NCD films in figures 1(2#), (3#), (5#), (6#), (8#), (9#), they have unique nano-characteristics with the appearance of typical cauliflower-like grains like the monolayer NCD film in figure 1(10#). By contrasting figures 1(1#), (4#), (7#) and (2#), (5#), (8#), the size of NCD clusters increases with growth of the underlying MCD grains. This phenomenon should be explained by the effect of surface replication effect [29]. And by observing the thumbnails in figure 1, it can be found that the grain sizes of NCD basically remains the same.

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The average surface roughness (Ra) measured by a surface profiler with 1 mm scanning length is shown in figure 3(a). The roughness of single-layer MCD film increases with prolongation of deposition time. The MCD (12M + 0N) film has the roughest surface (Ra 404 nm) while the NCD (0M + 3N) film shows the smoothest surface (Ra 96 nm). By depositing an NCD layer on MCD layer, the roughness can be further reduced. This result can be explained by the changes in the surface grain sizes. However, it is worth noting that even if the NCD deposition time remains the same, the roughness of the (MCD/NCD) bilayer film with different MCD grain sizes is still different. And the roughness of bilayer films with longer NCD deposition would still reduce taking into account the same grain sizes of NCD. This can be explained by the deposition model of the (MCD/NCD) bilayer film shown in figure 3(b): (i) At the beginning, the NCD layer is very thin, which results that the NCD cluster shapes like the original MCD grain; (ii) With prolongation of NCD deposition time, gaps formed between MCD grain boundaries are covered by NCD and the shape of the cluster begins to change to a hemispherical shape; (iii) And adjacent NCD clusters would combine to form a larger cluster. In the progress, the degree of surface undulation would continue to decrease, causing the roughness to decrease. In this process, since the NCD cluster is formed by covering the bottom MCD grain, its original cluster size and undulation would be affected by the bottom MCD layer, so the larger the bottom MCD roughness, the larger the (MCD/
Figure 2. Cross-sectional micrographs of diamond coated WC-Co substrates.

Figure 3. Average surface roughness of diamond films (a) and the deposition model of the (MCD/NCD) bilayer film (b).
NCD) bilayer film roughness. After exploring the influence of the bottom MCD and top NCD layer on the overall morphology, the structural change would be investigated below.

Figure 4 shows the Raman spectra of the prepared diamond films before and after tribo-tests. The black line represents the Raman spectra of the sample before friction experiment, and the red line represents the Raman spectra taken from the center point of wear mark after friction experiment. For three MCD samples in figure 4, there is a sharp peak (diamond peak) near 1332 cm\(^{-1}\), revealing their good crystallinity. In addition, some small peaks are observed elsewhere: sp\(^2\) carbon at G band (around 1580 cm\(^{-1}\)) and trans-polyacetylene (TPA) (around 1140 cm\(^{-1}\) and 1480 cm\(^{-1}\)) [30–32]. As for monolayer NCD, the peak at 1200 cm\(^{-1}\) begins to appear, which originates from NCD [33]. Furthermore, the diamond peak becomes broader because of the appearance of the peak around 1350 cm\(^{-1}\) as well as the overlap effect of the two peaks. The appearance of peak around 1350 cm\(^{-1}\) (D peak) results from the breathing modes of sp\(^2\) atoms in rings [34]. For bilayer MCD/NCD diamond films, it could be observed that non-diamond carbon peaks become more obvious and diamond peak is getting blunt with the decrease of MCD deposition time and the increase of NCD deposition time. The monolayer NCD (0M + 3N) loses Raman signal after tribo-test, indicating the diamond film in the center point of wear mark has been completely worn out.

For carbon-based film, its mechanical properties would be affected by the sp\(^3\) phase content [35]. For diamond film, its residual stress can be calculated by the formula: \(\sigma(\text{GPa}) = \alpha \Delta \nu = -0.567 (\nu - \nu_0) \text{ (cm}^{-1}\)\)), where \(\Delta \nu\) is the difference between the measured and natural stress-free diamond peak shifts \(\nu_0\) that is taken to be the Raman peak position of the natural diamond when no pressure is applied [36]. And the sp\(^2\) phase content can be roughly compared by the \(I_D/I_G\) and the lower value of \(I_D/I_G\) signifies the presence of higher sp\(^2\) bonding [37]. To gain a better understanding of the chemical structure changes in diamond films before and after tribo-tests, the Raman spectra is analyzed by Gauss–Lorentz (G–L) deconvolution integrated peaks. Table 3 displays...

![Figure 4. Raman spectra of all diamond films before (the black line) and after (the red line) tribo-tests.](image)
the summary of peak location, the full width at half maximum (FWHM), stress and the integrated intensity ratio of D and G peaks ($I_D/I_G$) of diamond films.

The table shows an increase of stress after tribo-tests as well as FWHM broadening resulting from improved compressive state and anisotropic stress distribution. This result is consistent with Abreu et al [24]. In general, the lower $I_D/I_G$ value represents the higher sp² C–C bond in films, which has a low friction coefficient because of its easy in-plane shearing [38]. Moreover, with the decrease of MCD deposition time and the increase of NCD deposition time, the $I_D/I_G$ would decrease overall. This may result in the decrease of the hardness and wear-resistance of diamond film. It is clearly the value of $I_D/I_G$ ratio decreases after tribo-tests, which mainly comes from the more regularly arranged sp² carbon atoms in diamond films introduced by the linear scratching of the counterpart balls. Because all diamond films are mechanically scratched in a straight line by counterpart balls repeatedly during the tribo-tests, which would result in the regular arrangement of sp² carbon atoms combined with the heat generated by frictional actions. It is known that the moving directions of carbon atoms are in a line in the $E_{2g}$ symmetry mode (G mode), but the moving directions of carbon atoms are different in $A_{1g}$ symmetry mode (D mode) [39, 40].

### 3.2. Tribological behaviors

The coefficient of friction (COF) curves for nine diamond films against Si$_3$N$_4$ balls in dry sliding environments are illustrated in figure 5(a). It could be seen that all the tribo-tests have similar COF evolution except monolayer NCD film: an initial sharp-peak with a rapid rise and decline, and then gradually reaching a steady-state. It can be divided into three stages: (I). A first sharp-peak stage: The stage results from an intense mechanical interlocking among sharp-shaped asperities between the contacting surfaces. (II). The running-in stage: The sharp asperities are worn down or removed from the contact. (III). A steady-state stage with dynamic equilibrium [27]. However, for monolayer NCD film, it has a rising friction curve which the final COF exceeds 0.2, indicating the NCD would be quickly worn off in the high load (100 N). So the average-COF and K of sample 10# (0M + 3N) were not calculated below. This is also in accord with the loss of Raman signals after tribo-tests in figure 4 (0M + 3N). Because the adhesion of NCD film is lower than MCD film, it has a relatively low critical load before delamination [26]. So the monolayer NCD film is easily worn off under high load. This proves the importance of

### Table 3. Checklists of characterizations and experimental results for all samples.

<table>
<thead>
<tr>
<th></th>
<th>1#</th>
<th>2#</th>
<th>3#</th>
<th>4#</th>
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<th>7#</th>
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<tbody>
<tr>
<td>Peak location before tribo-tests (cm$^{-1}$)</td>
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<td>1336.2</td>
<td>1335.8</td>
<td>1335.8</td>
<td>1336.2</td>
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<td>1335.2</td>
<td>1336.3</td>
<td>1335.5</td>
<td>1334.5</td>
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<tr>
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<td>1336.8</td>
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<td>1336.1</td>
<td>1336.7</td>
<td>1336.9</td>
<td>1335.8</td>
<td>1335.4</td>
<td>1336.0</td>
<td>—</td>
</tr>
<tr>
<td>Stress before tribo-tests (GPa)</td>
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<td>−2.8</td>
<td>−2.5</td>
<td>−2.5</td>
<td>−2.8</td>
<td>−3.2</td>
<td>−2.1</td>
<td>−2.9</td>
<td>−2.3</td>
<td>−1.5</td>
</tr>
<tr>
<td>Stress after tribo-tests (GPa)</td>
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<td>−3.2</td>
<td>−2.7</td>
<td>−2.7</td>
<td>−3.1</td>
<td>−3.2</td>
<td>−2.5</td>
<td>−2.2</td>
<td>−2.6</td>
<td>—</td>
</tr>
<tr>
<td>FWHM before tribo-tests</td>
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<td>10.3</td>
<td>10.7</td>
<td>9.1</td>
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<td>9.9</td>
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<td>11.3</td>
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<td>10.0</td>
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<td>10.4</td>
<td>10.0</td>
<td>10.9</td>
<td>—</td>
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<tr>
<td>$I_D/I_G$ before tribo-tests (%)</td>
<td>17.3</td>
<td>0.9</td>
<td>0.5</td>
<td>17.0</td>
<td>1.4</td>
<td>0.6</td>
<td>26.3</td>
<td>2.9</td>
<td>1.7</td>
<td>0.5</td>
</tr>
<tr>
<td>$I_D/I_G$ after tribo-tests (%)</td>
<td>16.3</td>
<td>0.8</td>
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<td>0.5</td>
<td>23.8</td>
<td>2.7</td>
<td>1.5</td>
<td>—</td>
</tr>
</tbody>
</table>

**Figure 5.** The coefficient of friction curves as a function of sliding time for ten diamond films (a) and the average coefficient of friction of nine samples (b).
MCD layer as the bottom layer to improve the adhesion of multilayer diamond films, thus enabling NCD film to work effectively under heavy loads. To further understand the friction performance of samples, the average COF in the steady-state is obtained by calculating the mean values data collected between sliding time of 50 min and 240 min, as plotted in figure 5(b). It can be seen that the variation trend of the COF is good consistent with that of the roughness. Because for the same material, the roughness has the greatest influence on the COF. Nevertheless, it must be noted that the drop rate of COF is faster than that of roughness with the extension of NCD deposition time. This would be explained by the decrease of $I_D/I_G$ with the extension of NCD deposition time in table 3, indicating that $sp^2$ C-C bond acting as a lubrication phase increases.

The surface morphology of the center position of the wear mark after tribo-tests is shown in figure 6. After tribo-tests, it can be obviously seen that two distinguished zones can be observed except monolayer NCD film. One is unworn MCD grains or NCD clusters in a lower position. The other is the smooth morphology of the ablated clusters or diamond grains which have contact with friction pair. And there is only a bit wear debris chipped in the valley of diamond crystals. So the main wear mechanism of the diamond film during this experiment is the micro-fracture and flattening of the diamond film. The decrease in COF mainly comes from the continuous polishing of the diamond film. As for monolayer NCD film (10#), it can be found the substrate are exposed and only some residual film can be seen, which also proves that the single-layer NCD film could not
work effectively under large load. It is clearly that the sample 7# with the biggest diamond grains is harder to
find obvious polished surface, but other single-layer MCD film (1#, 4#) has obvious polished surface. This is
because with the increase of deposition time, diamond crystals become more and more complete and get more
and more wear-resisting [41]. And with the increase of NCD layer thickness (7# → 8# → 9#), the polished
areas are becoming obvious and getting larger because the hardness of NCD is lower than MCD. Only samples
2# and 3# have completely reached the steady-state stage in which the friction surface completely polished.
Apparently, with extension of MCD deposition time and decrease of NCD deposition time, the
(MCD/NCD) bilayer film requires a longer wear time to reach the uniform polishing stage, causing its Ra is harder to decrease
and COF increases. Therefore, the surface smoothness degree reflected by SEM is also consistent with the
previous average coefficient of friction in figure 5(b). However, the result also implies that the wear-resistance of
bilayer diamond film would fail with extension of MCD deposition time and decrease of NCD deposition time.

The wear rates of the diamond films under such the experimental condition (low sliding speed) are too little
to be measured, but that of the counterpart ball is much easier to be detected. Full views of the spherical worn
crowns of the Si$_3$N$_4$ balls sliding against different diamond films, which are obtained by the stereoscopic
microscopy, are shown in figure 7. It can be noted that all the friction interface of the Si$_3$N$_4$ becomes fully
flattened after friction tests, and there are no residual impurities such as abrasive dust. Meanwhile, no evidence
of tribo-mechanically induced cracking can be seen for all contacts, indicating good adhesion. Generally
speaking, a new tribo-layer is easily generated at the interface of the friction-pair due to the accumulation of
abrasive debris, which has a significant impact on the friction coefficient [42]. But there is no obvious material
transfer observed in the Si$_3$N$_4$ balls and mainly the trace of obvious ploughing effect can be found. This is
because that Si$_3$N$_4$ is very hard among common friction-pairs such as copper, stainless steel, hard alloy, so it is
hard to generate a large number of tribo-layers [19]. It further shows that the main wear mechanism is mainly
the micro-fracture and flattening of the diamond film.

By viewing the diameter of wear scars, specific wear rates of counterpart balls (K) can be calculated and
plotted in figure 8. The (MCD/NCD) bilayer films have a minor K than MCD single-layer film as a result of

\[ \text{Figure 7. Optical micrograph taken from Si}_3\text{N}_4 \text{ interfaces after dry sliding against the diamond coated WC-Co substrates.} \]
higher hardness of MCD in comparison to NCD. Because the presence of amorphous carbon or graphite at grain boundaries and lower sp$^3$/sp$^2$ ratios would result in the decrease of hardness, elastic modulus of NCD films compared with MCD films [43]. And the variation trend of K for (MCD/NCD) bilayer film is also consistent with that of roughness in figure 3(a). This is related to the surface morphology of diamond film during the friction process. By seeing back to figure 6, it can be explained by that the bilayer film with longer MCD deposition time is harder to be polished and the surface is rougher. This would increase the ploughing effect between diamond film and friction pair, causing more volume loss of friction pair. Therefore, (3M + 6N) bilayer film with smoothest surface topography has the lowest K ($1.75 \times 10^{-6}$ mm$^3$ N$^{-1}$ m$^{-1}$), indicating the minimum material waste and highest machining accuracy.

The grain sizes of bottom MCD layer and thickness of NCD layer affect the surface morphology, sp$^2$ phase content, eventually affecting the roughness and friction behavior of (MCD/NCD) bilayer film. The roughness of MCD film would increase dramatically with the increase of MCD grain sizes, eventually increasing the COF and K. By depositing an NCD layer on MCD layer, the roughness, COF and K can be decreased by the nano-sized grains and higher sp$^2$ phase. But the NCD layer can’t completely eliminate the effect of the roughness of bottom MCD layer because of the surface replication effect. Considering all the diamond films, the sample 3# with lowest roughness, average-COF and K is most suitable as the top unit in the (MCD/NCD) multilayer film. But for improving the wear-resistance of multilayer film, the MCD layer closer to the substrate should increase the grain sizes appropriately.

4. Conclusion

MCD films, NCD film and (MCD/NCD) bilayer films with different deposition time of every layer were deposited on the WC-6% Co substrates by HFCVD method. The results show that the bottom MCD layer is useful to provide a good adhesion for the NCD layer to work under large load (100 N). And the bottom MCD layer and top NCD layer would have a combined effect on the morphology and structure of (MCD/NCD) bilayer film, affecting its roughness, COF, K and wear-resistance.

The roughness of MCD film would increase dramatically with the increase of MCD grain sizes, eventually increasing the COF and K. By depositing an NCD layer on MCD layer, the roughness, COF and K can be decreased by the nano-sized grains and higher sp$^2$ phase. But the NCD layer can’t completely eliminate the effect of the roughness of bottom MCD layer unless it’s thick enough, since the NCD cluster is formed by covering the bottom MCD grain. For the as-deposited (3hMCD/6hNCD) bilayer diamond film, it has the lowest average-COF (0.059) and K ($1.75 \times 10^{-6}$ mm$^3$ N$^{-1}$ m$^{-1}$) owing to its lowest roughness and higher I$_{D}$/I$_{G}$. So it is an ideal top structural unit among multilayer diamond film for different applications. Meanwhile, with the decrease of MCD deposition time, the wear-resistance of diamond film would decrease. It is also important to choose suitable grain sizes of the MCD layer close to the substrate to improve wear-resistance of the multilayer diamond film.
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