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Deposition and Application of Nanocrystalline Diamond Films on Silicon Carbide Substrates

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Abstract: Nanocrystalline diamond (NCD) films were gaining increasing interest as candidate materials in mechanical and tribological applications. The NCD films showed smooth granular surfaces where no facetted crystallites can be noticed. The pronounced Raman scattering intensity in the region of 1400∼1600 cm^{-1} made a further explanation that the grain size of the films has decreased to nanometer scale. The friction tests suggested that the fabricated NCD films exhibited much lower friction coefficients. Finally, NCD diamond films deposited on silicon carbide drawing dies were applied in the actual work environment and presented that the working lifetime was largely elongated more than ten times as that of conventional cobalt cemented tungsten carbide drawing dies and in the course of processing, copper tubes with high surface quality and uniform sectional area could be obtained.

Keywords: NCD films; characterization; friction tests; drawing die; application tests

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Introduction

Diamond films were promising for extensive applications in petrochemical and mechanical industries. However, traditional chemical vapor deposition (CVD) diamond films usually had coarse surfaces with micro-sized crystalline grains, which would lead to higher friction and wear coefficient, deteriorating the tribological performance of diamond films. So it was of great realistic significance to smooth the surface and further enhance the wear resistance property of diamond films.

In the past years, several methods for smoothing the surface of diamond films had been developed [1]. Particularly, an increasing interest had been focused on the synthesis of nanocrystalline diamond films due to their nanometer-scale grain size which ensured a very low surface roughness, as well as outstanding properties similar to micro-sized diamond films and natural diamond [2,3]. Moreover, the relatively low hardness of NCD films meant that further processing such as polishing was convenient.

Cobalt cemented tungsten carbide (WC-Co) materials had been widely used as substrates of diamond coated drawing dies. Nevertheless, the production of WC-Co materials required large quantities of strategic resources such as tungsten and cobalt. In addition, the relatively large thermal expansion coefficient difference between the WC-Co and the diamond might cause larger residual stresses in the films and the substrates near the interface, having detrimental influence upon the diamond coating adhesion. In contrast, ceramic materials such as silicon carbide were with rich and extensive resources in nature, proving to be the most promising alternative materials of WC-Co. Moreover, it was convenient to fabricate diamond films with strong adhesion on such substrates because the thermal expansion coefficient difference between the SiC (4.6×10^{-6} ∼6.3×10-6/℃ for 20∼800℃) and the diamond (0.8×10-6∼4.5×10-6/℃ for 20∼800℃) was small [4].

In present study, scratching pretreatment was adopted for SiC substrates to roughen the surfaces in order to increase the nucleation, and then NCD films were fabricated on both the surfaces of SiC plates and the inner surfaces of SiC drawing dies in an HFCVD apparatus, using argon gas as an important reactant gas. Thereafter, the microstructure and tribological performance of the NCD films were investigated by means of various characterization techniques. Furthermore, the polished drawing dies were applied under actual production conditions in order to evaluate the lifetime and the processing quality.

Experimental Details

The SiC plates (10×10 mm) and SiC drawing dies with size specification of 24×40 (aperture Φ18 mm) were used as the substrates. Prior to the deposition, the apertures of the dies should be amended to keep them in the required margin tolerances, and then scratching pretreatment was adopted to roughen both the depostion surfaces so as to ensure the nucleation density, which was beneficial to the diamond coating quality and the adhesion.

The NCD films were deposited in a home-made bias-enhanced HFCVD apparatus, adopting two kinds of typical hot filaments arrangements for the deposition on plate surfaces and inner holes, which had been reported in the open literature [5,6]. The deposition process was carried out in a vacuum reactor with the mixture of acetone, excessive hydrogen and especially argon gas as the precursor of the coating. A DC bias was applied to enhance the nucleation density. The detailed deposition parameters are listed in Table 1.

Table 1 Deposition parameters for SiC plate substrates and drawing dies

Reaction stage	Nucleation	Deposition
Acetone/H2/Argon Flow [sccm]	80/200/0	85/200/250
Pressure [Torr]	12	9.75
Deposition temperature [°C]	750-900	750-900
Filament temperature [°C]	1500-2200	1500-2200
Bias current [A]	4.0	3.0
Deposition time [h]	0.5	4

The working surfaces of several NCD coated drawing dies for application tests were polished repeatedly with diamond grits in different particle sizes (1 μm∼12 μm) in order to make the surface roughness meet the requirements of drawing production. Similar polished NCD films on the plate substrates were also obtained for tribological tests. The NCD coated drawing dies for characterization were cut into two equal portions along the axis direction by the wire-electrode cutting. The scanning electron microscopy (SEM) and atomic force microscopy (AFM) observations were respectively adopted to investigate the surface and cross-sectional morphology, as well as the surface roughness. The typical features of NCD films were analyzed by Raman spectroscopy.

The tribological tests conducted on the plate samples before and after polishing were accomplished with ball-on-plate type reciprocating friction tester in ambient atmosphere to evaluate their tribological performance. Steel balls 4 mm in diameter were used as counterpart balls. The normal load applied on the contacts was fixed to 4.0 N and the reciprocating frequency was constantly 5 Hz, which could provide an average sliding velocity of 0.06 m/s for a friction stroke of 6 mm. Before sliding process, the samples were rinsed with acetone in an ultrasonic vessel to eliminate impurities. The friction coefficients for the contacts were recorded automatically by the friction tester. Finally the polished NCD coated drawing dies were applied under working conditions.

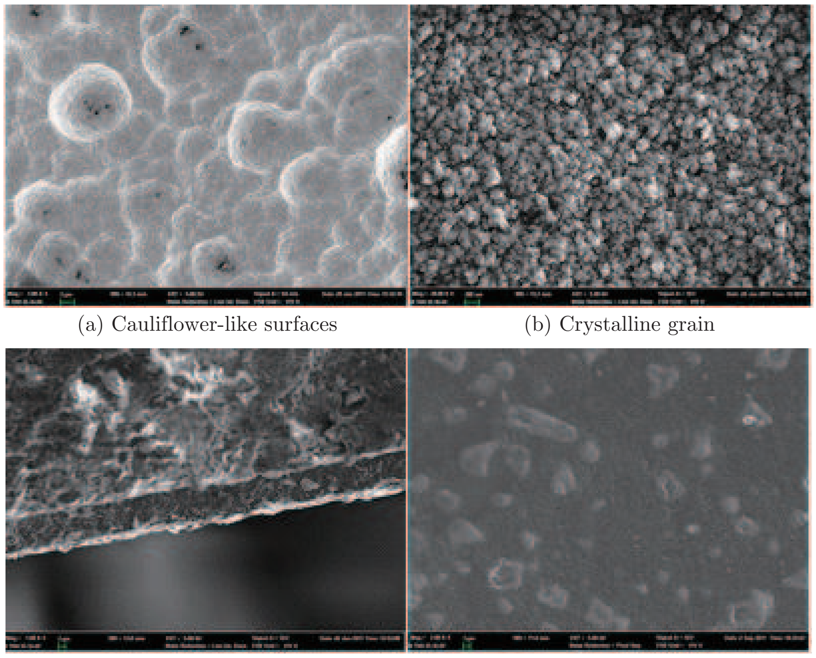
Results and Discussion

Characterization of NCD films. On the basis of SEM micrograph as presented in Fig. 1, it was noted that unpolished NCD films exhibited smooth and uniform cauliflower-like surfaces composed of nodular features ∼100-150 nm in diameter, where no facetted crystallites could be noticed. No apparent voids or cracks were found in the film and the film thickness was uniform over the entire substrate, which was gauged to be ∼10 μm. Moreover, the polished NCD films were with lower surface roughness outside the defect areas, according to Fig. 2 for detail.

The surface morphology of unpolished and polished NCD films imaged by AFM was presented in Fig. 2. The surface roughness values were respectively measured as Ra∼8.592 nm (RMS∼10.85 nm) and Ra∼4.03 (RMS∼5.001 nm) over a 10×10 μm^2 scanning region.

As illustrated in Fig. 3, the Raman spectra was achieved to analyze the chemical quality of NCD films, using an Ar+ laser with an excitation wavelength of 632.8 nm. The peaks near ∼1332 cm^{-1} were significantly broad, which indicated the existence of micro or nano-sized diamond grains. The pronounced Raman scattering intensity in the region of 1400∼1600 cm^{-1} suggested that the grain size of diamond films had decreased to nanometer scale. Besides, graphitic G band (1580 cm^{-1}) represented the contribution from the sp^2 component and peaks at 1480 cm^{-1} were assigned to the transpolyacetylene [7].

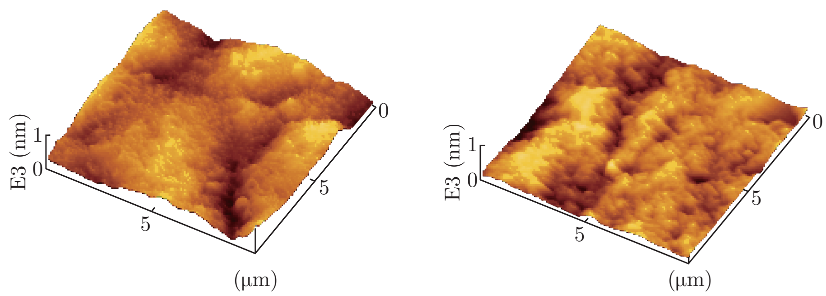
Tribological performance of NCD films. Fig. 4 plotted the friction coefficient curves as a function of sliding time for unpolished and polished NCD films sliding against copper balls. For the sliding contact of unpolished film and copper counterface, the interlocking effect among sharp-shaped asperities distributed on the sliding interface produced high friction coefficients



(a) Cauliflower-like surfaces (b) Crystalline grain

(c) Thickness (d) Polished surface

Fig. 1 SEM images of surface and cross-sectional morphology.



(a) Unpolished (b) Polished

Fig. 2 The surface morphology of NCD films imaged by AFM.

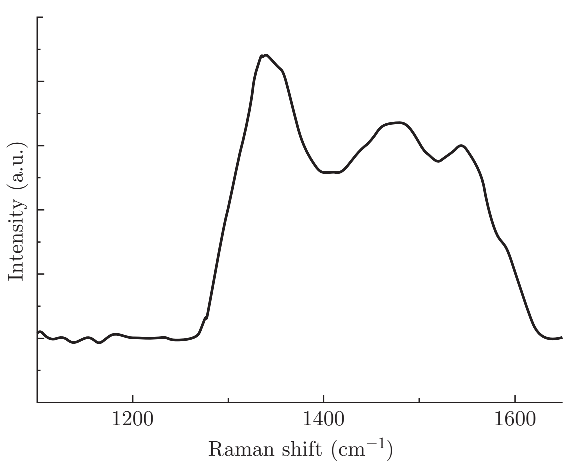


Fig. 3 Raman spectrum of NCD film.

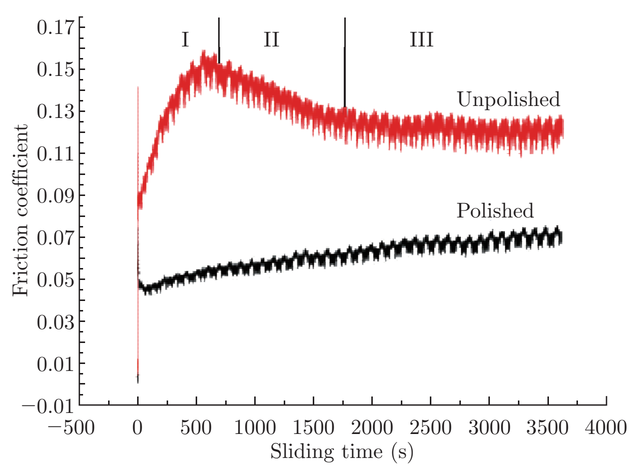


Fig. 4 The friction coefficient curves as a function of sliding time.

at the beginning of the sliding pass (regime I). After this initial phase, a range with rapidly decreasing friction coefficient values took place (regime II). This corresponded to a running-in phase of accommodation between opposing surfaces. Afterwards a relatively equilibrium of very low frictional response set in for the rest of the test when leveled diamond plateaus were in mating contact (regime III). For that of polished films and copper counterface, the interlocking effect and running-in phase were unconspicuous. The average friction coefficients during the relatively stable period were 0.12 and 0.06 for unpolished and polished NCD films in dry sliding against copper counterfaces respectively, which were low enough to meet the practical demands.

Results of application tests. The NCD coated drawing dies after polishing were applied to processing copper tubes. The results presented that the working lifetime of the NCD coated drawing dies could be prolonged by a factor of above 10 compared with the conventional ones. Besides, the material wastage during the processing was reduced slightly and the copper tubes with high surface quality and uniform sectional area could be obtained.

Conclusion

NCD films were fabricated on both the surfaces of SiC plates and the inner surfaces of SiC drawing dies in a vacuum reactor with the mixture of acetone, excessive hydrogen and especially argon gas as the precursor of the coating. The SEM, AFM and Raman were adopted to exhibit that NCD films with typical surface morphology and features were obtained and the surface roughness reduced obviously from Ra$\sim$8.592 nm and RMS$\sim$10.85 nm to Ra$\sim$4.03 and RMS$\sim$5.001 nm after polishing. Very low friction coefficients of 0.12 and 0.06 were obtained for unpolished and polished NCD films in dry sliding against copper counterfaces. The application test results also presented that the NCD films with outstanding hardness and frictional characteristics could observably prolong the working lifetime of drawing dies and improve the processing quality.

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