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Wear-Resistant, Self-Lubricating Surfaces of Diamond Coatings

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WEAR-RESISTANT, SELF-LUBRICATING SURFACES OF DIAMOND COATINGS

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Abstract

In humid air and dry nitrogen, as-deposited, fine-grain diamond films and polished, coarse-grain diamond films have low steady-state coefficients of friction (<0.1) and low wear rates ($\leq 10^{-6}$ $mm^3/N \cdot m$). In an ultrahigh vacuum (10^{-7} Pa), however, they have high steady-state coefficients of friction (>0.6) and high wear rates ($\geq 10^{-4}$ $mm^3/N \cdot m$). Therefore, the use of as-deposited, fine-grain and polished, coarse-grain diamond films as wear-resistant, self-lubricating coatings must be limited to normal air or gaseous environments such as dry nitrogen. On the other hand, carbon-ion-implanted, fine-grain diamond films and nitrogen-ion-implanted, coarse-grain diamond films have low steady-state coefficients of friction (<0.1) and low wear rates ($\leq 10^{-6}$ $mm^3/N \cdot m$) in all three environments. These films can be effectively used as wear-resistant, self-lubricating coatings in an ultrahigh vacuum as well as in normal air and dry nitrogen.

1. Introduction

Diamond's excellent tribological properties make it an ideal material for many tribological applications. Its extreme hardness, high abrasion and wear resistance, low coefficient of friction, high seizure and galling resistance, good fatigue strength, high thermal conductivity, good radiation and temperature resistance, chemical and thermal inertness, high corrosion resistance, and environmental compatibility suit it to applications such as the bearings, valves, and engine parts in the harsh environment found in internal-combustion and jet engines [1,2].

However, the applications of natural and high-pressure synthetic diamonds are limited because of their small size and high cost. Also, these crystals have to be bonded to a substrate in a separate operation. This requirement, coupled with their high cost, limits the general use of diamonds in tribological applications. On the other hand, chemically vapor-deposited (CVD) diamond offers a broader potential because size is, and eventually cost will be, less of a limitation [1]. CVD diamond is available in planar films or sheets. It opens the door to design engineering and tribology technology that can take full advantage of diamond's intrinsic properties in such areas as wear, solid lubrication, erosion, and corrosion applications.

The major drawback of CVD diamond is that its very high surface roughness and high deposition temperature restrict its applications in tribological coatings [1]. These problems must be solved before practical, reliable, and cost-effective diamond coatings become available as wear-resistant, self-lubricating barriers for many types of moving mechanical assemblies. A process must be developed that keeps the deposition temperature below 400 °C for metallic substrates such as steel, smooths the CVD diamond surface to minimize abrasion, and provides satisfactory adhesion to metallic and nonmetallic substrates, including steel and Si_3N_4.

Another drawback to CVD diamond is that its desirable properties are altered during tribological processes. The contaminant surface film adsorbed on diamond film can be removed when it repeatedly slides over the same track of counter-facing material in a vacuum. Then, a fresh, clean diamond surface contacts a clean counterfacing material, and strong bonds form between the two materials [2]. As a result, the coefficients of friction and wear rates of diamond films are considerably higher in a vacuum than in air [3]. Thus, to achieve the best performance for CVD diamond as a wear-resistant, self-lubricating barrier for many moving mechanical assemblies, we must have a good understanding of diamond, of the counterfacing material, and of the type of environment and operation.

The objective of this paper is to provide machine designers, manufacturers, tribologists, lubrication engineers, and end-users with the friction and wear properties of as-deposited, fine-grain; polished, coarse-grain; carbon-ion-implanted, fine-grain; and nitrogen-ion-implanted, coarse-grain CVD diamond films in humid air, dry nitrogen, and ultrahigh vacuum (10^{-7} Pa) environments. These properties can be considered as guides to the tribological applications of CVD diamond films. Some earlier data and experimental details on this research are given in the references [3-8].

2. CVD Diamond

2.1. As-Deposited, Fine-Grain Diamond Films

As-deposited, fine-grain diamond films were produced by microwave-plasma-enhanced CVD (Table I) and were primarily polycrystalline (Table II). Rutherford backscattering spectroscopy revealed that the diamond films consisted of carbon

Table I. Deposition Conditions for Diamond Films

	As-deposited, fine-grain diamond films	Polished, coarse-grain diamond films
Deposition technique	Microwave plasma CVD	Hot-filament CVD
Substrate	Si (100), α-SiC, Si_3N_4	Si_3N_4
Flow rate, cm^3/min		$CH_4:H_2$ = 1:99
CH_4	4	
H_2	395	
O_2	1	
Pressure, Pa	665	—
Microwave power, kW	0.5	—
Deposition temperature, °C	860 ± 20	900
Deposition time, h	10.5 and 21	—
Thickness, nm	1000 and 800	—

Table II. Comparison of As-Deposited, Fine-Grain Diamond Films and Polished, Coarse-Grain Diamond Films Deposited on Silicon, α-SiC, and Si_3N_4

	As-deposited, fine-grain diamond films	Polished, coarse-grain diamond films
Composition	Essentially carbon, <2.5 at.% hydrogen	Essentially carbon
Microstructure	Polycrystalline	Polycrystalline
Crystal orientation	<110>	<111>
Grain size, nm	20 to 100 nm	10 000
Raman spectrum	Sharp peak centered near 1330 cm^{-1} and broad humps centered near 1320 cm^{-1} and in the 1500 to 1530 cm^{-1} range	Sharp peak centered near 1330 cm^{-1} and broad humps centered near 1320 cm^{-1} and in the 1500 to 1530 cm^{-1} range
Atom-bonding state	sp^3 and sp^2 (variable ratio, very roughly 1:1)	sp^3 and sp^2 (variable ratio)
Surface morphology	Granulated or spherulitic: spherical asperities of different sizes	Flat, polished
Surface roughness, rms, nm	6 to 37	6
X-ray photoelectron spectroscopy (XPS) spectrum	Carbon and oxygen peaks	Carbon and oxygen
C/O ratios in XPS spectrum	8 to 12	————

and some elements from the substrate material, such as silicon. From the proton recoil detection data, the hydrogen concentration was estimated to be 2.5 at.% in the fine-grain diamond films.

X-ray diffraction data revealed that the crystallites were oriented along the <110> direction. In the smooth, fine-grain diamond films, grain sizes—which were determined from the dark-field images of transmission electron microscopy— ranged from 20 to 100 nm. The lattice constants calculated from the transmission electron diffraction pattern matched well with diamond's known lattice constants [4].

When the Raman spectrum of the as-deposited, fine-grain diamond film was deconvolved, three bands characteristic of CVD diamond films were revealed: (1) a sharp band centered near 1330 cm^{-1}, (2) a broad band centered in the 1500 to 1530 cm^{-1} range, and (3) an even broader band centered near 1320 cm^{-1}. The sharp band centered near 1330 cm^{-1} is characteristic of diamond's sp^3 bonding. The two broad Raman shift bands near 1320 cm^{-1} and in the 1500 to 1530 cm^{-1} range are characteristic of the nondiamond form of carbon. They are referred to as the D band and G band, respectively. The G-band Raman shifts are attributed to the sp^2-bonded carbon, whereas the D-band Raman shifts are attributed to the disorder of the nondiamond carbon present in the diamond films [1]. The as-deposited, fine-grain diamond films contained a considerable amount of nondiamond carbon.

Scanning electron microscopy and surface profilometry revealed that in the as-deposited, smooth, fine-grain diamond films, crystallites had a granulated or spherulitic morphology. The surfaces contained spherical asperities ranging from 6 to 37 nm root mean square (rms) (Table II). X-ray photoelectron spectroscopy (XPS) spectra of the surfaces of the as-deposited, fine-grain diamond films contained oxygen, with C/O ratios ranging between 8 and 12.

2.2. Carbon-Ion-Implanted, Fine-Grain Diamond Films

Carbon ions were implanted into the as-deposited, fine-grain diamond films with an ion implanter operating at an accelerating energy of 60 keV and a current density of 50 $\mu A/cm^2$ for approximately 6 min, resulting in a dose of 1.2×10^{17} carbon ions/cm^2 (Table III). The carbon ions penetrated to a calculated mean depth of 88 nm.

XPS spectra of the surfaces of the carbon-ion-implanted, fine-grain diamond films contained oxygen—with C/O ratios ranging between 8 and 12—like those of the as-deposited diamond films. Furthermore, during XPS analysis, the carbon-ion-implanted, fine-grain diamond films were more conductive than the as-deposited diamond films. This increased conductivity indicates that carbon ion implantation

Table III. Carbon-Ion-Implanted, Fine-Grain Diamond Films and Nitrogen-Ion-Implanted, Coarse-Grain Diamond Film

	Carbon-ion-implanted, fine-grain diamond films	Nitrogen-ion-implanted, coarse-grain diamond films
Ion implantation	Carbon ions implanted at 60 keV and 50 $\mu A/cm^2$ for 6 min; a dose of 1.2×10^{17} carbon ions/cm^2	Nitrogen ions implanted at 35 keV; a dose of 5×10^{16} nitrogen ions/cm^2
Composition	Essentially carbon	Essentially carbon and nitrogen
Microstructure	Layered structure—amorphous layer on crystalline diamond	Layered structure—amorphous layer on crystalline diamond
Raman spectrum	Broad humps centered near 1320 and in the 1500 to 1530 cm^{-1} range	Broad humps centered near 1320 and in the 1500 to 1530 cm^{-1} range
Surface morphology and roughness	No significant change resulted from carbon ion implantation	No significant change resulted from nitrogen ion implantation

alters the normally insulating diamond surface to an electrically conductive carbon surface and eventually to a graphitic surface.

In the Raman spectra of the carbon-ion-implanted, fine-grain diamond films, a very broad band with a peak centered in the 1500 to 1530 cm^{-1} range and a shoulder near 1320 cm^{-1}, indicative of the amorphous, nondiamond form of carbon, was the prominent feature. The characteristic diamond peak was absent from the Raman spectra of the carbon-ion-implanted diamond films. Furthermore, transmission electron microscopy observation of cross sections of diamond films implanted by carbon ions at 160 keV revealed a layered structure containing an amorphous layer formed on the crystalline diamond layer [6]. No significant changes in surface morphology and roughness resulted from the carbon ion implantation (Table III). The surface features of the carbon-ion-implanted, fine-grain diamond films were almost the same as those of the as-deposited, fine-grain diamond films. The only morphological effect of carbon ion implantation was the rounding of edges. Carbon ion implantation on the fine-grain diamond films with a granulated or spherulitic morphology produced surfaces with somewhat blunt, rounded grains.

2.3. Polished, Coarse-Grain Diamond Films

Polished, coarse-grain diamond films were produced by hot-filament CVD (Table I). They were primarily polycrystalline (Table II), and X-ray diffraction data revealed that the crystallites were primarily oriented along the <111> direction. The grain size was approximately 10 000 nm (10 μm).

When the Raman spectrum of the polished diamond film (surface roughness, 6 nm rms) was deconvolved, three bands were revealed: (1) a sharp band centered near 1330 cm^{-1} (the sp^3 bonding of diamond), (2) a broad band centered in the 1500 to 1530 cm^{-1} range (the sp^2-bonded carbon), and (3) an even broader band centered near 1320 cm^{-1} (the disorder of the nondiamond carbon).

2.4. Nitrogen-Ion-Implanted, Coarse-Grain Diamond Film

Nitrogen ions were implanted into a polished, coarse-grain diamond film with an ion implanter operating at an accelerating energy of 35 keV, resulting in a dose of 5×10^{16} nitrogen ions/cm^2 (Table III). The nitrogen ions penetrated to a calculated mean depth of 47 nm.

The Raman spectrum of the nitrogen-ion-implanted diamond film revealed a very broad band with a peak centered in the 1500 to 1530 cm^{-1} range and a shoulder near 1320 cm^{-1}, indicative of the amorphous, nondiamond form of carbon. The characteristic diamond peak was absent from the Raman spectrum of the nitrogen-ion-implanted diamond film.

No significant changes in surface morphology and roughness resulted from nitrogen ion implantation (Table III). The surface features of the nitrogen-ion-implanted diamond film were almost the same as those of the polished diamond film.

3. Friction and Wear Properties of CVD Diamond

Figure 1 presents steady-state (equilibrium) coefficients of friction and wear rates in humid air (40 percent relative humidity), in dry nitrogen, or in an ultrahigh vacuum (10^{-7} Pa) for the as-deposited, polished, carbon-ion-implanted, and nitrogen-ion-implanted diamond films. Conditions that reduce friction, such as a particular combination of environment and material, usually reduce wear rate as well.

To be an effective wear resistant, self-lubricating material, a material must have a coefficient of friction less than 0.1 and a wear rate of 10^{-6} $mm^3/N \cdot m$ or less.

In humid air and in dry nitrogen, both the steady-state coefficients of friction and wear rates of as-deposited, fine-grain; polished, coarse-grain; and nitrogen-ion-implanted, coarse-grain diamond films were generally low.

In an ultrahigh vacuum, however, both the steady-state coefficients of friction and the wear rates of the as-deposited, fine-grain diamond films and of the polished, coarse-grain diamond film were high. On the other hand, the carbon-ion-implanted, fine-grain diamond films and the nitrogen-ion-implanted, coarse-grain diamond

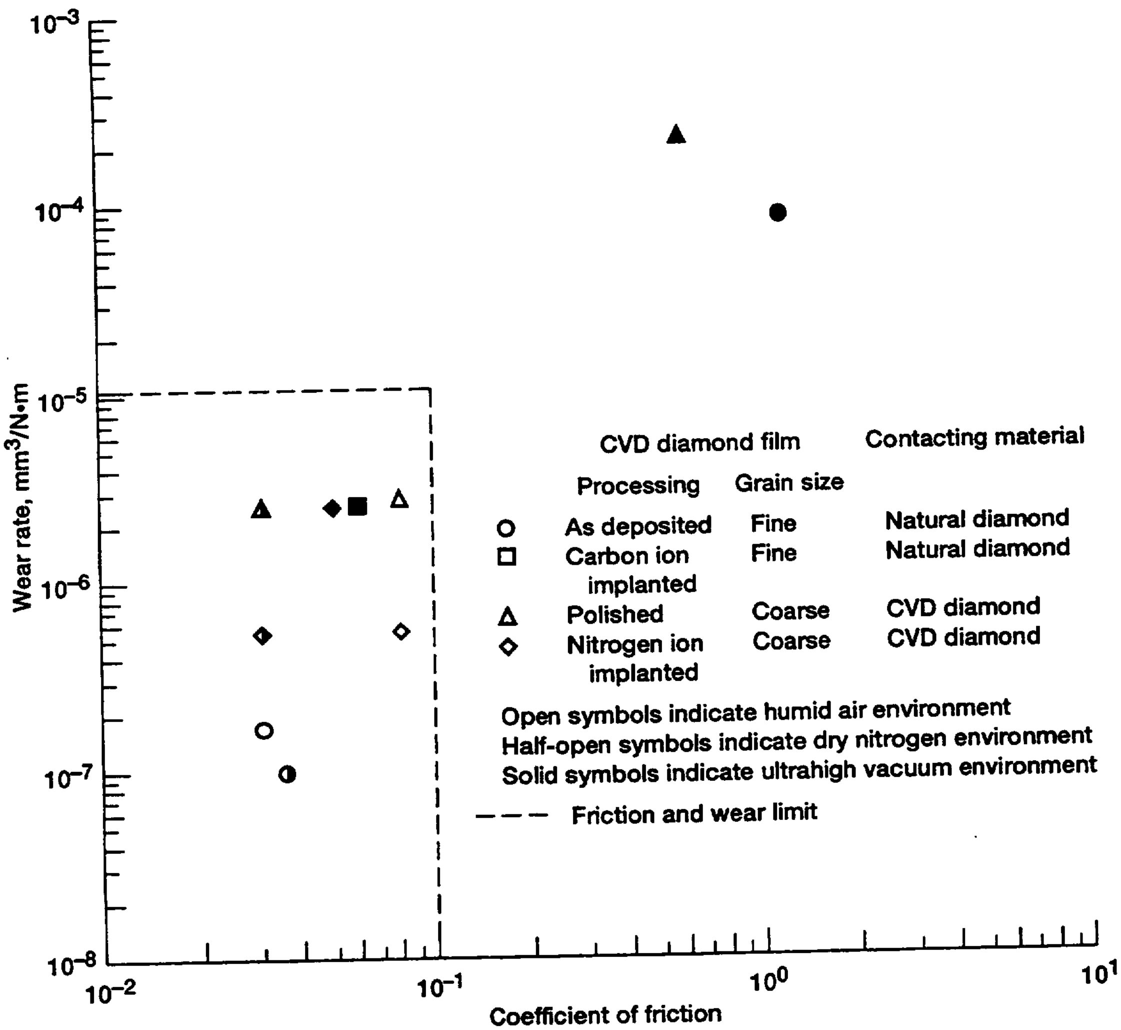

Figure 1.—Relationship between wear rate and coefficient of friction for chemically vapor-deposited (CVD) diamond films.

film had a low steady-state coefficient of friction (<0.1) and a low wear rate ($\leq 10^{-6}$ $mm^3/N{\cdot}m$). Thus, the ion-implanted diamond films are effective wear-resistant, self-lubricating films.

4. Concluding Remarks

Both as-deposited, fine-grain diamond films and polished, coarse-grain diamond films can be effective wear-resistant, self-lubricating coatings in humid air and in dry nitrogen, but they are not effective in an ultrahigh vacuum.

Both carbon-ion-implanted, fine-grain diamond films and nitrogen-ion-implanted, coarse-grain diamond films can be effective wear-resistant, self-lubricating coatings in all three environments (i.e., humid air, dry nitrogen, and ultrahigh vacuum).

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13. ABSTRACT *(Maximum 200 words)*

In humid air and dry nitrogen, as-deposited, fine-grain diamond films and polished, coarse-grain diamond films have low steady-state coefficients of friction (<0.1) and low wear rates ($\leq 10^{-6}$ mm^3/N·m). In an ultrahigh vacuum (10^{-7} Pa), however, they have high steady-state coefficients of friction (>0.6) and high wear rates ($\geq 10^{-4}$ mm^3/N·m). Therefore, the use of as-deposited, fine-grain and polished, coarse-grain diamond films as wear-resistant, self-lubricating coatings must be limited to normal air or gaseous environments such as dry nitrogen. On the other hand, carbon-ion-implanted, fine-grain diamond films and nitrogen-ion-implanted, coarse-grain diamond films have low steady-state coefficients of friction (<0.1) and low wear rates ($\leq 10^{-6}$ mm^3/N·m) in all three environments. These films can be effectively used as wear-resistant, self-lubricating coatings in an ultrahigh vacuum as well as in normal air and dry nitrogen.

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