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Tribological Characteristics and Applications of Superhard Coatings: CVD Diamond, DLC, and c-BN

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TRIBOLOGICAL CHARACTERISTICS AND APPLICATIONS OF SUPERHARD COATINGS: CVD DIAMOND, DLC, AND c-BN

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ABSTRACT

Results of fundamental research on the tribological properties of chemical-vapor-deposited (CVD) diamond, diamondlike carbon, and cubic boron nitride films in sliding contact with CVD diamond in ultrahigh vacuum, dry nitrogen, humid air, and water are discussed. Furthermore, the actual and potential applications of the three different superhard coatings in the field of tribology technology, particularly for wear parts and tools, are reviewed.

1.0 INTRODUCTION

Interest in commercializing diamond technology and related materials technologies for tribological applications continues to grow (ref. 1). The success of many tribological products or tribological systems depends on adequate control of the adhesion between two or more materials in relative motion. Studies on the surface design, surface engineering, and tribology of coatings of superhard diamond and related materials have shown that the adhesion, friction, and wear of these materials significantly depend on the various combinations of materials and environmental conditions (ref. 2).

This paper is divided into two sections: (1) properties and (2) applications of chemical-vapor-deposited (CVD) diamond, ion-beam-deposited diamondlike carbon (DLC), and reactive-ion-plated cubic boron nitride (c-BN) coatings. The first section is concerned with environmental effects on adhesion, which has contributed greatly, and should continue to contribute, to tribological problems—such as high friction, solid-state welding, scuffing or scoring, high wear, and a short coating life in tribological systems. Surface and tribological characteristics of the coatings with favorable coefficients of friction (≤ 0.1) and wear rates ($\leq 10^{-6}$ $mm^3/N{\cdot}m$) in specific environments are discussed. The investigation described herein examined the solid-lubrication, friction, and wear properties of fine-grain CVD diamond films, surface-modified CVD diamond films, ion-beam-deposited DLC films, and ion-plated c-BN films in different environments: humid air, dry nitrogen, ultrahigh vacuum, and water (refs. 3 and 4).

The second section is devoted to applications (ref. 1). Examples of the actual and potential applications of coatings, such as CVD diamond, DLC, and c-BN are described.

2.0 MATERIALS

The investigation encompassed three types of relatively smooth surfaces (6- to 37-nm rms) of as-deposited and surface-modified CVD diamond films: (1) as-deposited, fine-grain diamond; (2) polished, coarse-grain diamond; and (3) polished and then nitrogen-ion-implanted, coarse-grain diamond. In addition, smooth surfaces (22-nm rms) of DLC films ion-beam deposited at an ion energy of 700 eV and smooth surfaces (20- to 40-nm rms) of ion-plated c-BN films were investigated.

Wu et al. (refs. 5 to 8), Murakawa and Takeuchi (ref. 9), and Murakawa and Watanabe (refs. 10 and 11) give the details of CVD diamond, DLC, and c-BN deposition along with the modification techniques. Briefly, the as-deposited, fine-grain diamond films were produced on the flat surfaces of silicon, silicon nitride, and silicon carbide substrates by microwave-plasma-assisted chemical vapor deposition (ref. 5). The polished, coarse-grain diamond films were produced on the flat surfaces of silicon nitride substrates by hot-filament chemical vapor deposition using a 1:100 mixture of methane (CH_4) and hydrogen (H_2) (ref. 9). The nitrogen-ion-implanted, coarse-grain diamond films were produced by impacting nitrogen ions into polished CVD diamond film at an accelerating energy of 35 keV, resulting in a dose of 5×10^{16} ions/cm^2 in a calculated mean depth of 47 nm (ref. 6). The DLC films were deposited on silicon by the direct impact of an ion beam composed of a 3:17 mixture of argon (Ar) and CH_4 at a radiofrequency power of 99 W and ion energies of 1500 or 700 eV. DLC films thicknesses ranged from 520 to 660 nm (ref. 7). The c-BN films (approximately 500-nm thick) were deposited on silicon substrates by a magnetically enhanced plasma ion plating technique (refs. 10 and 11).

3.0 EXPERIMENT

A variety of analytical techniques were used to characterize CVD diamond, DLC, and c-BN films: scanning and transmission electron microscopy (SEM and TEM) to determine surface morphology and grain size and to study wear surfaces and wear debris; Rutherford backscattering spectroscopy (RBS) and hydrogen forward scattering to identify impurities (if any) in the films and to determine carbon and impurity concentrations; Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) to characterize carbon bonding and structure; x-ray photoelectron spectroscopy (XPS) to characterize surface chemistry; x-ray diffraction to determine the crystal orientation; and surface profilometry and scanning probe microscopy to determine film surface morphology, roughness, and wear.

Unidirectional, rotating sliding friction experiments were performed at room temperature in humid air (40-percent relative humidity), in dry nitrogen (<1-percent relative humidity), in ultrahigh vacuum (10^{-7} Pa), and in distilled water (ref. 3). The friction apparatus used in the investigation was mounted in a chamber. This apparatus can measure friction in a variety of environments, including humid air, dry nitrogen, ultrahigh vacuum, and water. All experiments were conducted with CVD diamond, surface-modified CVD diamond, DLC films, and c-BN films in contact with CVD diamond pins (radius, 1.6 mm) at a load of 0.49 N (a mean herzian contact pressure of approximately 2 GPa) and at a constant rotating speed of 120 rpm (sliding velocity, 31 to 107 mm/s, depending on the range of wear track radii involved in the experiments). The wear rate, known as the dimensional wear coefficient, is defined as the volume of material removed at a unit applied load and in a unit sliding distance expressed as cubic millimeters per newton-meter.

4.0 TRIBOLOGICAL CHARACTERISTICS

Figures 1 to 5 present the steady-state (equilibrium) coefficients of friction and wear rates at room temperature in humid air (40-percent relative humidity), in dry nitrogen (<1-percent relative humidity), in an ultrahigh vacuum (10^{-7}Pa), and in water (refs. 3 and 4). For a direct comparison, the coefficients of friction and the wear rates were plotted from 0.01 to 1 and from 10^{-10} to 10^{-3} mm^3/N·m, respectively. An effective wear-resistant, self-lubricating material must generally have a coefficient of friction less than 0.1 and a wear rate less than 10^{-6} mm^3/N·m. The results presented in Figs. 1 to 5 indicate that both the steady-state coefficients of friction and the wear rates of the CVD diamond, DLC, and c-BN films depended on the environment.

The as-deposited, fine-grain CVD diamond films (Fig. 1) and the polished, coarse-grain CVD diamond films (Fig. 2) had low coefficients of friction (<0.1) and low wear rates (order of 10^{-6} mm^3/N·m) in three environments: humid air, dry nitrogen, and water. However, in ultrahigh vacuum these films had high coefficients of friction (>0.1) and high wear rates (order of 10^{-4} mm^3/N·m), which are not acceptable for solid-film lubricating applications. Interestingly, the polished, coarse-grain CVD diamond films (Fig. 2) revealed an extremely low wear rate in water, far less than 10^{-10} mm^3/N·m. The nitrogen-ion-implanted CVD diamond films (Fig. 3), the DLC films (Fig. 4), and the c-BN films (Fig. 5) had low coefficients of friction (<0.1) and low wear rates (order of 10^{-6} mm^3/N·m), regardless of the environment investigated.

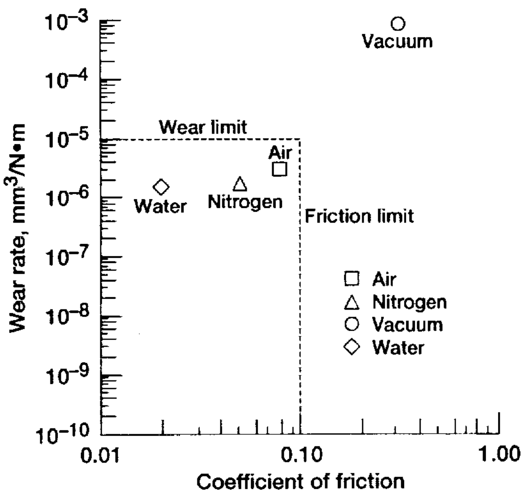

Fig. 1. Coefficients of friction and wear rates of fine-grain CVD diamond film in sliding contact with CVD diamond pins in humid air, dry nitrogen, ultrahigh vacuum, and water.

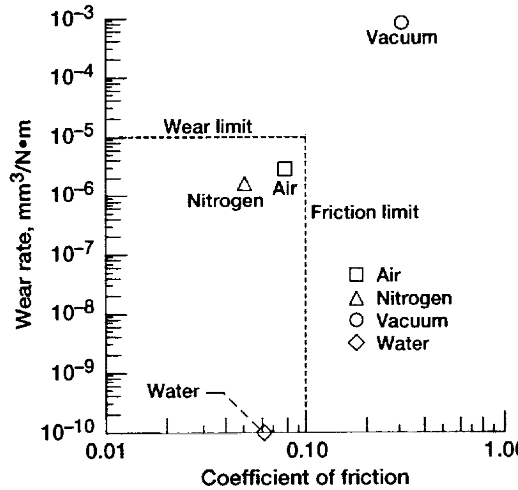

Fig. 2. Coefficients of friction and wear rates of polished coarse-grain CVD diamond film in sliding contact with CVD diamond pins in humid air, dry nitrogen, ultrahigh vacuum, and water.

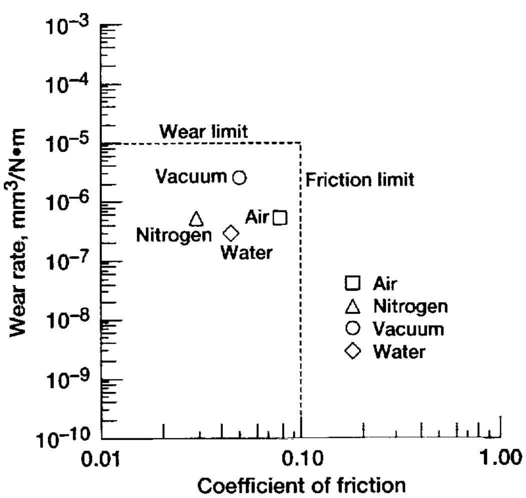

Fig. 3. Coefficients of friction and wear rates of nitrogen-ion-implanted CVD diamond film in sliding contact with CVD diamond pins in humid air, dry nitrogen, ultrahigh vacuum, and water.

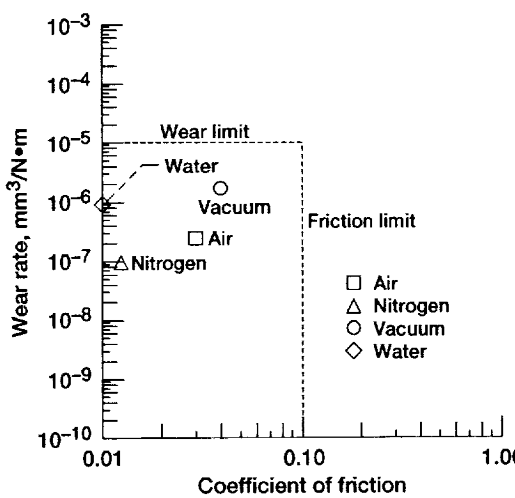

Fig. 4. Coefficients of friction and wear rates of ion-beam-deposited DLC film in sliding contact with CVD diamond pins in humid air, dry nitrogen, ultrahigh vacuum, and water.

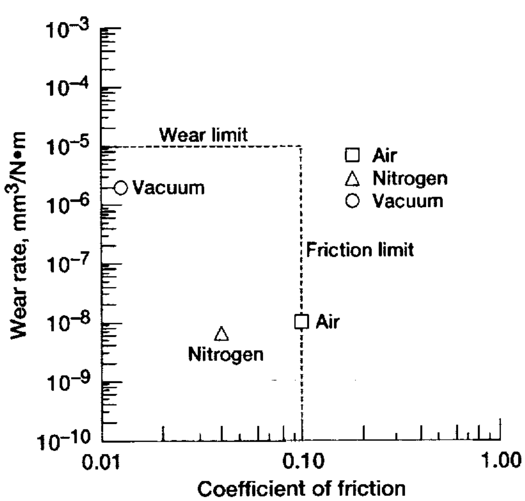

Fig. 5. Coefficients of friction and wear rates of reactive-ion-plated c-BN film in sliding contact with CVD diamond pins in humid air, dry nitrogen, ultrahigh vacuum, and water.

Thus, as-deposited, fine-grain CVD diamond films and polished, coarse-grain CVD diamond films can be used as effective, wear-resistant, self-lubricating coatings in humid air, dry nitrogen, and water, even though they have a high coefficient of friction and a high wear rate in ultrahigh vacuum. The nitrogen-ion-implanted CVD diamond films, ion-beam-deposited DLC films, and reactive-ion-plated c-BN films can be used as effective wear-resistant, self-lubricating coatings regardless of the environment investigated in the present study.

5.0 TRIBOLOGICAL APPLICATIONS

5.1 CVD Diamond Films

Diamond film technology looks promising and has the potential to revolutionize products and industrial and consumer applications across industries, particularly in the field of tribology technology and in the wear parts industry (refs. 1 and 12 to 15). Diamond coatings offer a broader tribological potential (use for more applications) than do natural and high-pressure synthetic diamonds because size, geometry, and cost will not be as limiting. In most cases, however, the advantages and utility of diamond coatings as industrial ceramics will only be realized if the price is right. According to Windischmann (ref. 16), that concern may no longer be valid because of two advances made by leading CVD diamond suppliers in the past few years: (1) vastly improved deposition speed and efficiency have reduced the cost of CVD diamond deposition, and (2) industries have now reached production capacity. Suppliers use efficient methods, such as a focused laser or a direct-current arc jet as a plasma source for chemical vapor deposition. Now that they are cost effective, diamond coatings—with their extreme properties—can be used in tribological applications. Diamond coatings can improve many of the surface properties of engineering substrate materials, including wear resistance, hardness, lubrication, and erosion and corrosion resistance.

Actual applications of CVD diamond in the field of tribology technology, particularly on cutting and forming tools, wear parts, rotors, and seals, are an industrial reality (ref. 1). Unlike other diamond cutting tools, such as fabricated polycrystalline diamond, diamond coatings can be applied to cutting inserts with multiple cutting surfaces, chip breakers, and widely different configurations not possible with polycrystalline diamond. In addition to the cutting inserts, diamond-coated end mills, drills, knives, abrasive discs and wheels, and other tools have been used for machining nonmetallic work materials. Such work materials include aluminum alloy, high silicon-content aluminum alloy, silicon-carbide-incorporated aluminum alloy, copper alloy, semisintered green ceramic (SiC, Al_2O_3, Si_3N_4, WC, ZrO_2, etc.), polymer composites (carbon-fibre-reinforced polymer (CFRP), glass-fibre-reinforced polymer (GFRP), etc.), metal matrix composites (e.g., 25SiC–75Al composite), epoxy resins, carbon, and graphite. The advantages of diamond-coated tools are versatile tool geometry, higher cutting speed, long endurance (wear) life, and lower cutting force. For example, Fig. 6 shows that when a CVD-diamond-coated square end mill was used for machining 17Si–83Al alloy (ref. 17) it was over 10 times more durable than an uncoated WC-Co square end mill.

In microelectronics assembly technology, diamond coatings have been applied to the contact surfaces of tools—such as tab tools, bonding tools, tubes, and push pins—to provide wear-resistant chemical barriers. In the wear parts and seal industries, diamond coatings have been applied to bearing surfaces (plates, tubes, slide rails, and sliders), extrusion and drawing dies, transport guides (tapes, papers, sheets, fibers, threads, and wires), pins (rods and followers), tips (styluses, scratch tips, and conductive atomic force microscope (AFM) tips), indenters (pyramidal, cone, or spher-ical), abrasion-resistant scratch-free watch parts, engine parts (valves and rotors), nozzles, and seals for providing a self-lubricating, wear-resistant chemical barrier for moving mechanical assemblies.

Researchers are using free-standing CVD diamond films to develop potential applications, such as diamond shafts and gears for microtransmission mechanisms of microelectromechanical systems (MEMS), microengines, and micromachines, and diamond shafts and bearings for blood or heart pumps. Other potential applications are diamond-coated ball and roller ceramic bearings, and hard disks.

5.2 DLC Films

Tribological applications of DLC coatings are already well established in a number of fast-growing markets such as magnetic recording media, high-density magnetic recording disks and sliders (heads), process equipment, abrasion-resistant optical products, medical devices, implant components including hip joints and knee implants, process equipment (e.g., copy machines and digital video camcorders), packaging materials, electronic devices, plastic molds, gear pumps, stamping devices, forming dies, blades (e.g., razor blades and scalpel knives), engine parts (e.g., gudgeon pins), washers (e.g., ceramic faucet valve seats), seals, valves, gears, bearings, bushings, tools, and wear parts. The cost is generally similar to that of carbide or nitride films deposited by CVD or physical vapor deposition (PVD) techniques. The surface smoothness, high hardness, low coefficient of friction, low wear rate, and chemical inertness of DLC coatings, along with little restriction of geometry and size, make them well-suited for applications involving wear and friction. For example, Fig. 7 shows a cross-sectional SEM of DLC-coated, metal-evaporated magnetic videotape, a

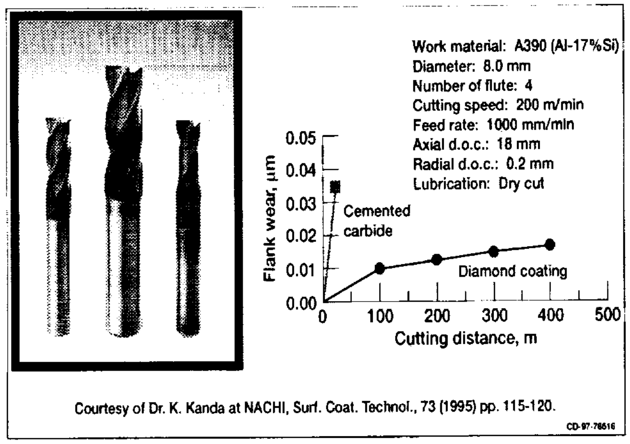

Fig. 6. CVD diamond-coated end mills and flank wear behavior in cutting.

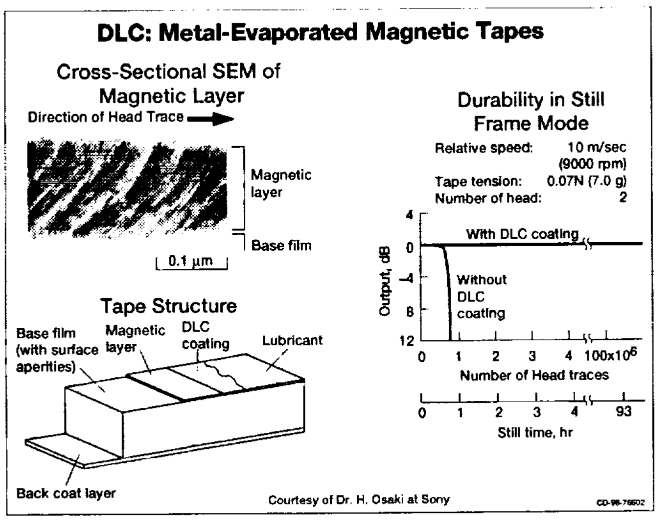

Fig. 7. DLC film deposited on a metal-evaporated magnetic tape and its durability.

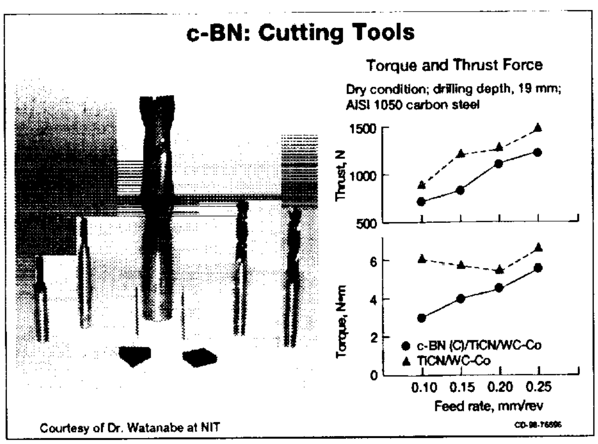

Fig. 8. c-BN-coated end-mills and torque and thrust force in dry cutting.

schematic of the videotape structure, and experimental results on the durability of the DLC-coated videotape and uncoated videotape (ref. 18). The still frame mode (pause picture mode) of a commercial digital videotape recorder was used to evaluate durability at the experimental conditions listed in Fig. 7. For this experiment, 80Co-20Ni alloy was deposited on a polyethylene terephthalate (PET) base film by an electron beam evaporation process to produce the approximately 0.2-µm-thick, metal-evaporated magnetic layer. The cross-sectional SEM reveals an oblique columnar structure. A sputtering or CVD process was used to deposit the DLC (several nanometers to more than 10 nanometers thick) on the metal-evaporated videotape, where a lubricating film was coated on the DLC. The presence of DLC coating markedly improved the durability in the still frame mode. The durability, judged by the readback signal (output in dB), of the DLC-coated magnetic tape was greater than that of the uncoated magnetic tape, as shown in Fig. 7. The performance of the magnetic tape with the sputtered DLC was almost same as that with the chemical-vapor-deposited DLC.

5.3 c-BN Films

Tribological applications of CVD diamond may be limited by its pronounced reactivity with iron and iron-based alloys. c-BN is an alternative that overcomes this problem. Because c-BN, which is chemically and thermally inert, is second only to diamond in hardness, interest in c-BN films is receiving attention. It can be used on tools to machine ferrous materials or on wear parts in sliding contact with ferrous materials. For example, the left portion of Fig. 8 shows c-BN-coated WC-Co alloy cutting tools, including end mills, cutting inserts, and twist drills (ref. 19). The right portion of this figure shows the cutting performance of two types of TiCN/WC-Co twist drills (6 mm in diameter): one coated with c-BN (c-BN/TiCN/WC-Co) and the other consisting of bare TiCN/WC-Co. Both the thrust force and torque of the c-BN-coated TiCN/WC-Co twist drills required during the machining of AISI 1050 steel carbon steel were lower than those for bare TiCN/WC-Co alloy twist drills (ref. 19). Note that the c-BN-coated TiCN/WC-Co alloy twist drills were implanted with nitrogen ions at an ion energy of 135 keV in a dose of 1×10^{16} ions/cm^2 and with carbon ions at an ion energy of 90 keV in a dose of 8×10^{15} ions/cm^2, respectively. Although c-BN coatings are promising as wear-resistant, self-lubricating coatings, they are not yet practical because of difficulties and inconsistency in their synthesis that results in high internal residual stresses in the films, which in turn limits the film thickness.

6.0 CONCLUDING REMARKS

On the basis of fundamental studies conducted with CVD diamond, DLC, and c-BN, the following remarks can be made. CVD diamond can be used as an effective, wear-resistant, self-lubricating coating material in terrestrial, nonvacuum environments. Ion-implanted CVD diamond, ion-beam-deposited DLC, and reactive ion-plated c-BN can be used as effective wear-resistant, self-lubricating coating materials both in a vacuum, spacelike environment and in nonvacuum environments.

Tribological applications of CVD diamond and DLC coatings are continually growing. The technology and commercial applications of c-BN coatings are being developed but at a slow pace.

7.0 ACKNOWLEDGMENTS

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