Effects of high-temperature hydrogenation treatment on sliding friction and wear behavior of carbide-derived carbon films

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Abstract

In this study, we investigated the effects of a high-temperature hydrogenation treatment on the sliding friction and wear behavior of nanostructured carbide-derived carbon (CDC) films in dry nitrogen and humid air environments. These films are produced on the surfaces of silicon carbide substrates by reacting the carbide phase with chlorine or chloride–hydrogen gas mixtures at 1000 to 1100 °C in a sealed tube furnace. The typical friction coefficients of CDC films in open air are in the range of 0.2 to 0.25, but in dry nitrogen, the friction coefficients are 0.15. In an effort to achieve lower friction on CDC films, we developed and used a special hydrogenation process that was proven to be very effective in lowering friction of CDC films produced on SiC substrates. Specifically, the films that were post-hydrogen-treated exhibited friction coefficients as low as 0.03 in dry nitrogen, while the friction coefficients in humid air were ~0.2. The wear of Si\textsubscript{3}N\textsubscript{4} counterface balls was hard to measure after the tests, while shallow wear tracks had formed on CDC films on SiC disks. Detailed mechanical and structural characterizations of the CDC films and sliding contact surfaces were done using a series of analytical techniques and these findings were correlated with the friction and wear behaviors of as-produced and hydrogen-treated CDC films.

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1. Introduction

Carbon-based materials and coatings have enjoyed an overwhelming interest in recent years, mainly because of their unique microstructures and very attractive tribological properties. In particular, the magnitude of research activities in synthetic diamond and diamondlike carbon (DLC) films has been rather high and has led to several unique applications for these films [1,2]. Diamond films are mostly produced by plasma-based chemical vapor deposition (CVD) methods at high temperatures, and they may consist of grains ranging from nano- to micrometer sizes [3]. DLC films can be produced by all kinds of physical vapor deposition (PVD) and CVD methods even at room temperatures, and structurally they are amorphous. Quite recently, a new method has been developed for the production of a different kind of carbon films: nanostructured carbide-derived carbon (CDC) [4,5]. Unlike the plasma-based CVD and PVD methods that are necessary for the synthesis of diamond and DLC films, this new method does not require high vacuum or gas discharge plasmas. It is done at atmospheric pressures in a tube furnace by simply passing chlorine or a mixture of chlorine+hydrogen gases over carbide-base substrates (such as SiC or WC) at temperatures of 600 to 1100 °C. Chlorine in the gas mixture reacts preferentially with metal atoms and etches them away. In the case of SiC, the reaction product is SiCl\textsubscript{4}, which is volatile and thus removed easily. The carbon atoms left behind on the surface of the SiC rearrange themselves to form a truly nanostructured carbon film composed of nanocrystalline diamond and graphite phases, carbon nano-onions, and

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amorphous carbon. Recent systematic studies on CDC films have suggested that they are mechanically tough, electrically conductive, and tribologically quite lubricious [6]. By controlling process parameters, the structure and properties of CDC films can easily be manipulated or fine-tuned to meet the specific application needs of a given system.

In a series of papers, we presented the general tribological properties of CDC films and evaluated the effects of various tribological test parameters on friction and wear [6–8]. In this study, we investigate the effects of post-hydrogen treatment on the sliding friction and wear behavior of the CDC films. Earlier studies demonstrated that hydrogen plays a critical role in the friction and wear behavior of DLC films [9–11]. Specifically, it was shown that those films derived from highly hydrogenated discharge plasmas can provide friction coefficients as low as 0.01 or below. In the present study, we investigated if hydrogen can also play a similar role in the frictional behavior of the CDC films. We used Raman spectroscopy and scanning electron microscopy (SEM) to determine the microstructure and chemistry of these films and correlated these findings with the friction and wear data obtained under a wide range of test conditions.

2. Experimental details

2.1. Synthesis of CDC Films

The CDC films were produced on the surfaces of sintered SiC substrates (Hexoloy™) according to a procedure described in Refs. [4–6]. The SiC substrates were in a disk shape with a nominal diameter of 30 mm, and one of their faces was highly polished to a RMS surface finish of better than 0.01 μm. Conversion of SiC to CDC was performed in gas mixtures containing various amounts of Cl₂:H₂ and Ar at 1000 to 1100 °C for 3 to 6 h. The gases used in the tube furnace were supplied from cylinders of pure Cl₂, pure Ar, and H₂. They were passed through anhydrous CaSO₄ and concentrated H₂SO₄ to remove any traces of water vapor. Typical gas mixtures used in this study included pure Cl₂ and a 9% Cl₂–4.5% H₂–A gas mixture. The typical coating thickness was 20–100 μm, depending on the process parameters and duration. Post-treatment polishing of some samples to a mirror finish was done manually on a polishing wheel using an alumina suspension. Some of the polished samples were hydrogenated by annealing at 800 °C for 8 h in 5% H₂/Ar. The treated specimens were analyzed by micro-Raman spectroscopy using an Ar ion laser (514.5 nm line) at 500× magnification with a spot size of 2 μm.

2.2. Friction and wear tests

The friction and wear of treated and control (untreated) SiC samples were tested in a ball-on-disk apparatus under 2- and 10-N loads and at speeds of 10 to 15 cm/s in dry nitrogen (with less than 1% relative humidity) and open air (with 17–32% relative humidity). The total sliding distance varied between 120 and 180 m, depending on the wear track diameters. A few samples were tested for up to 3 km to assess the long-duration tribological behavior and endurance limits of certain CDC films. The test balls (9.55 mm in diameter) were made of sintered Si₃N₄ and had a surface finish of better than 0.01-μm centerline average (CLA). The test method employed in tribological testing can be found in ASTM G99, Section 3 (i.e., Metals Test Methods and Analytical Procedures, Volume 3.02, Wear and Erosion; Metal Corrosion).

3. Results

3.1. Microstructure and mechanical properties

Fig. 1 shows the morphology of a typical CDC film formed on a SiC substrate. This film was produced in an Ar-35% Cl₂ gas mixture at 1000 °C over a period of 1 h. It is about 10–20 micrometers thick and appears to be strongly bonded to the SiC substrate. At such a magnification, there does not appear to be any columnar film morphology which is typical of most PVD films. Detailed electron microscopy studies revealed a 10-μm-thick transition layer between the SiC substrate and the CDC film [4,5]. The Raman spectroscopy of CDC reveals distinct D and G bands of graphite typically positioned at 1344 and 1590 cm⁻¹. However, detailed microstructural analyses by high-resolution transmission electron microscopy revealed that the structure is truly nanocrystalline and mainly composed of amorphous carbon, turbostratic graphite, carbon nano-onions and nanocrystalline diamond phases. Diamond nanocrystals were mostly detected near the interface and within the transition zone between SiC and CDC, while graphite was observed mostly near the top. Diamond nanocrystals were mostly detected near the interface and within the transition zone between SiC and CDC, while graphite was observed mostly near the top. Fig. 2 schematically illustrates the location of different phases observed in the CDC films.

Detailed nanohardness and mechanical characterization studies have revealed that the CDC films are rather soft in

![CDC Film](image-url)
their bulk. The typical nanohardness values as obtained by an MTS Nano Indenter equipped with a Berkovich tip ranged from 1 to 1.5 GPa (using 25-mN load) for carbon produced in pure Cl₂. The elastic modulus was in the range of 8 to 12 GPa. The hardness values measured within the transition zone were much higher, typically from 20 to 35 GPa. Films produced in pure Cl₂ gases were slightly harder and more resilient than the films produced in a mixture of Cl₂ and H₂ gases.

3.2. Tribological properties

For the tribological tests, two groups of CDC films were prepared and evaluated in a pin-on-disk machine. One group was produced in pure Cl₂, while the next group was prepared in a gas mixture that consisted of both Cl₂ (9.0%) and H₂ (4.5%) gases in an argon carrier gas. Fig. 3 compares the frictional behavior of CDC films produced in pure Cl₂. When similar friction tests were run with the base SiC substrates against the Si₃N₄ balls under the same test conditions, the friction coefficients were in the range of 0.7 (in air) to 0.9 (in dry nitrogen). As is clear from this figure, the friction coefficient of CDC against Si₃N₄ ball in air is around 0.21, but it decreases to around 0.15 in dry nitrogen. Post-hydrogen treatment seems to have a beneficial effect on the frictional behavior of the CDC films. With such treatment, the friction coefficient of CDC is reduced by about 10% in air, but more than 60% in dry nitrogen.

Fig. 4 summarizes the frictional behavior of CDC films produced in Cl₂+H₂. The friction coefficients in air before and after hydrogen treatment show a rather contrasting behavior. Specifically, while the friction coefficient of as-received CDC shows a tendency to become lower and lower as sliding goes on, the hydrogen-treated CDC shows the opposite behavior; its friction coefficient is initially low (0.13) but increases substantially with sliding time and reaches a value of 0.22 which is typical of non-hydrogenated CDC. The friction coefficient of the base CDC in dry nitrogen is around 0.15, but after hydrogen treatment it drops to 0.07.

![Fig. 2. A schematic illustration of the location of various phases in CDC films.](image1)

![Fig. 3. Friction behavior of as-received and hydrogen-treated CDC films in open air and dry nitrogen environments. This film was prepared in pure Cl₂.](image2)

![Fig. 4. Friction behavior of as-received and hydrogen-treated CDC films in open air and dry nitrogen environments. This film was prepared in Cl₂+H₂.](image3)

![Fig. 5. Effect of test load on friction performance of a CDC film in dry nitrogen. This film was produced in Cl₂+H₂ and then hydrogen-treated.](image4)
Fig. 5 shows the effect of contact load on the frictional behavior of the same sample as in the previous case. Specifically, it shows that under higher loads, the friction coefficient becomes even lower, i.e., 0.03, but the lifetime of the film declines. Also note that the initial friction coefficient is lower and the time required to reach the steady-state friction value is shorter under the heavier load.

In another test, we explored the long-duration frictional behavior of a hydrogen-treated CDC film in dry nitrogen. As shown in Fig. 6, the friction coefficient remains fairly low (i.e., 0.05) after an initial run-in period and shows a tendency to decrease even further as sliding continues. The friction value toward the end of the test is about 0.04.

The primary goal of this study was to elucidate the effect of a hydrogenation treatment on the frictional behavior of two kinds of CDC films in two different test environments, open air and dry nitrogen. However, attempts were also made to measure the wear of sliding ball and disk surfaces. In all cases, a wear track was formed on the disk side, and its size was found to be strongly dependent on the test environment. The tracks formed in open air were much wider than those formed in dry nitrogen. The wear of Si$_3$N$_4$ balls was, in most cases, minimal (perhaps due to the short duration nature of the tests) and hard to quantify. A typical 3D image of one of the wear scars is shown in Fig. 7a. A dark contrasting transfer layer was often observed on some of the sliding ball surfaces, especially after tests in dry nitrogen (see Fig. 7b).

4. Discussion

The results presented above demonstrate that the CDC films tested in this study exhibit low friction to sliding surfaces in both open air and dry nitrogen. However, the most striking finding is that if such films are subjected to a high-temperature hydrogenation, their friction coefficients become even lower, especially in dry nitrogen (see Figs. 3 and 4), under heavier loads (see Fig. 5), and at longer sliding distances (see Fig. 6).

Studies to date have confirmed the existence of a very strong relationship between the frictional behavior of other carbon films (diamond, diamondlike or graphitelike carbon films) and the gaseous species that may be present within their structures as well as within the test environments [1,12–17]. Some of these studies [1,10–12,14,17,18] have shown that if a film is intrinsically hydrogen-free or-poor (i.e., having little or no hydrogen within its bulk or on its sliding surface or undergoing testing in a hydrogen-free environment), then very high friction coefficients may result (especially in inert or vacuum environments). It is now generally believed that the surface termination states of these films are key to their frictional behavior. If their sliding surfaces are fully terminated by some gaseous species like hydrogen and oxygen, then these films may provide fairly low friction coefficients. Conversely, if their surfaces are chemically active and some or most of the covalent $\sigma$-bonds are unoccupied (this situation may occur if tests are performed in ultrahigh vacuum and at high temperatures), then the friction coefficients of diamond and hydrogen-free or -poor DLC films may become very high, mainly due to very strong covalent bond interactions.
across the sliding interfaces. In addition to covalent bonding, other types of short- and long-range chemical and/or physical interactions (van der Waals forces, electrostatic and $\pi-\pi^*$ attractions, capillary forces, etc.) may be present at sliding carbon film surfaces and contribute to overall friction.

We believe that most of the frictional interactions mentioned above are relevant to the behavior of the CDC films tested in this study. After all, these films are largely made of the same element as diamond, graphite and amorphous carbon, and the hybridization states of carbon atoms ($sp^2$, $sp^3$) on their surface are essentially the same. In dry and inert test environments, strong covalent and relatively weak $\pi-\pi^*$ interactions, as well as van der Waals forces, may be present at the sliding interfaces and may control the frictional behavior of CDC films. The $\pi-\pi^*$ interactions are more relevant to the sliding interfaces of graphite or graphitic carbons, such as $sp^2$-bonded DLC films and perhaps CDC (Raman spectroscopy and electron microscopy analyses have confirmed large graphitic domains within these films). Also, the frictional behavior of the CDC films tested in open air could be largely controlled by the graphitic phase, and these friction coefficients (i.e., 0.2) measured in air are typical of graphite. However, when these films are tested in dry nitrogen, their friction coefficients become even lower; this behavior is not the case for pure graphite, which generally provides low friction in moist air. For such an observation, we provide the following explanation.

Since CDC results from selective etching of metal atoms in carbides by $Cl_2$, some portion of $Cl_2$ is likely retained within the growing CDC structure (either in the atomic or bonded form). Such a possibility may serve the same purpose as water molecules do in a graphitic structure by simply overcoming or reducing the extent of “so called” $\pi-\pi^*$ interactions. Another halogen gas, fluorine, is used in the making of fluorinated graphite, which provides very low friction and possesses friction properties that are relatively insensitive to large fluctuations in relative humidity. Fluorine in graphite is believed to reduce the detrimental effects of $\pi-\pi^*$ interactions [19]. Also, fluorine doping of DLC films has substantial beneficial effects on the wear behavior of such films [20]. We believe that a similar mechanism may have been responsible for the relatively lower friction coefficients of the CDC films in dry nitrogen. EDAX analysis of CDC has indeed suggested the presence of some $Cl$ in the structure, but we did not specifically quantify the exact amount.

As for the much lower friction coefficients (the lowest of all measured) of hydrogen-treated CDC films in dry nitrogen, we provide the following mechanistic explanation. Within the mostly amorphous and disordered graphitic microstructure of CDC films (especially near the top), there are many voids, defects, and active atomic and/or molecular sites, which may contain dangling or unsatisfied $\sigma$-bonds. The existence of such bonds at sliding contact interfaces is undesirable (especially in inert and vacuum environments) as they can easily cause adhesive interactions during sliding motion. During the high-temperature hydrogenation, we believe that most of these bonds are effectively eliminated by the thermally active and highly energetic hydrogen atoms. Such a situation will undoubtedly lead to a higher degree of chemical passivation of the carbon atoms at or near the CDC surface. When such surfaces are rubbed against other materials (Si$_3$N$_4$ in our case), they can cause much lower adhesion (hence, friction). Some of the hydrogen may diffuse or migrate well into the structure and remain there as interstitials, while others may eliminate active $\sigma$-bonds within the film as well. Remember that C–H bonding is very strong (i.e., stronger than single C–C bonds) and that thermal desorption of hydrogen from carbon does not occur below 700 °C [21]. In short, elimination of the possibility of strong covalent bond interactions at sliding CDC interfaces is a major reason for the very low friction behavior of CDC films in dry nitrogen. This explanation is consistent with the mechanistic model proposed for the superlubricity of highly hydrogenated DLC films [10,12].

As shown in Figs. 3 and 4, the friction coefficients of CDC films increase substantially when they are tested in open air. In fact, these coefficients are comparable to those of the as-received CDC films. Such an increase in friction in open air can be attributed to the physisorption and/or chemisorption of water and oxygen molecules on sliding surfaces in open air. In recent studies with superlow-friction DLC films, the presence of such adsorbed films was verified by neutron scattering [22], and such films were found to have a detrimental effect on the friction and wear behavior of these DLC films [10,23]. If the relative humidity of the test environment is high, the development of meniscus and, hence, capillary forces on such sliding interfaces is also feasible, and such a situation can also lead to higher friction. Overall, as with other carbon films (i.e., diamond and DLC), the tribological properties of CDC films are also strongly affected by the presence or absence of certain chemical species within their structures as well as within the test environments. In particular, our studies have demonstrated that the presence of hydrogen (and possibly chlorine) on the surface and/or within the structure has a strong beneficial effect on frictional behavior of CDC films (especially in dry nitrogen). The adsorption or accumulation of water molecules (and perhaps other species, such as oxygen) on sliding surfaces may also have significant effects on their frictional behavior.

5. Conclusions

The results of our study have further confirmed that CDC films are self-lubricating and capable of providing very low friction coefficients to sliding surfaces, especially in dry nitrogen. The presence of certain chemical species (such as hydrogen and possibly chlorine) in CDC appears to
significantly affect its friction and wear performance. In dry nitrogen, the lowest friction was observed on films that were subjected to a hydrogen treatment. The as-received CDC samples also provided relatively lower friction in dry nitrogen. In open air, the friction coefficients of both the as-received and hydrogen-treated samples were similar (i.e., around 0.2). Based on these experimental observations, we proposed that the frictional behavior of CDC films in dry nitrogen was largely controlled by the presence and/or absence of free $\alpha$-bonds at sliding interfaces. Hydrogen treatment may have effectively reduced or eliminated such bonds and, hence, provided the very low friction coefficients observed in dry nitrogen. In open air, we believe that the frictional behavior of these films was largely dominated by the adsorbed water and other chemical species on sliding surfaces. In particular, oxygen may have impaired the beneficial effect of hydrogen, and hence in open air even the hydrogenated CDC films exhibit relatively high friction.

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References
