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Nano-Structured Carbide-Derived Carbon Films and Their Tribology

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Abstract: Carbide-derived carbon (CDC) is a form of carbon produced by reacting metal carbides, such as SiC or TiC, with halogens at temperatures high enough to produce fast kinetics, but too low to permit the re-arrangement of the carbon atoms into an equilibrium graphitic structure. The structure of CDC is derivative of the original carbide structure and contains nanoscale porosity and both sp^2 and sp^3 bonded carbon in a variety of nanoscale structures. CDC can be produced as a thin film on hard carbides to improve their tri-bological performance. CDC coatings are distinguished by their low friction coefficients and high wear resis-tance in many important industrial environments and by their resistance to spallation and delamination. The tribology of CDC coatings on SiC surfaces is described in detail.

Key words: carbon; coatings; tribology; friction; chlorination

Introduction

Carbide-derived carbon (CDC) refers to a unique structure of carbon produced when metal carbides, such as SiC, are exposed to halogens at moderately elevated temperatures. The halogens react with the metal component of the carbide to form volatile species, such as $SiCl_4$, but because CCl_4 is not thermodynamically stable at high temperatures, the carbon is left behind[1-3]. When the process is performed at temperatures that are low in comparison to the graphitization temperature of carbon, the structure of the CDC will be a metastable combination of nanoporous amorphous carbon, nanocrystalline diamond, and nested fullerene structures[4-7].

CDC materials have many potential applications

deriving from their unique physical and chemical properties. The applications that may be most easily exploited are in tribology, where CDC functions as a solid lubricant film. CDC layers in the thickness range from 1 to 100 μm can be grown quickly on hard car-bides, such as SiC or WC, by exposure to flowing chlorine gas at temperatures in the range of 800℃ to 1000℃. These carbides are widely used in wear-sensitive applications, such as bearings or pump seal rings, because of their high hardness and wear resis-tance. CDC coatings can be applied to the surfaces of SiC components with minimal dimensional change, and produce a substantial reduction in the friction coef-ficient during sliding[8-10]. The CDC coating is much more wear resistant than graphitic carbon. The me-chanical hardness of CDC is affected by structural variations, and changes gradually from a high value near the CDC/SiC interface to a lower value at the external surface. This graded hardness matches the

hardness of the underlying SiC and reduces the susceptibility of CDC to spallation and delamination in comparison to vapor-deposited diamond or diamond-like carbon.

The tribological properties of CDC can be related to the properties of the carbide substrate and the processing conditions under which the CDC conversion layer was produced. CDC layers have been formed on commercial SiC materials widely used in applications such as pump seal rings by exposure to flowing Ar-3.5% (vol) Cl_2 gas mixtures in fused silica furnace tubes at temperatures on the order of 1000℃. The resulting CDC coatings have been characterized by optical and electron microscopy, Raman and X-ray emission spectroscopy, mechanical testing by nano-indentation, and in a pin-on-disk tribology tester. The results provide some insights into the performance of these coatings and the mechanism by which they reduce tribological losses.

1   Experimental Details

The apparatus in which the CDC layers were grown has been described elsewhere[1,2]. It consists of a fused silica reaction tube in a resistance heated electric furnace, fitted to a gas flow and purification system set up for handling mixtures of argon, chlorine, and hydrogen. In a typical experiment, a SiC specimen is placed within the furnace, and the furnace is purged with the chlorine-containing gas mixtures before heating to the intended reaction temperature. The furnace is held at the test temperature for a fixed period of time (often on the order of one hour), and then the furnace is cooled to near room temperature in the flowing gas mixture so that the test specimen can be removed for characterization. The gas flow system is designed such that the chlorine flows only through glass or polytetrafluoroethylene (PTFE) tubing between leaving the supply cylinder and being exhausted to a fume hood to avoid corrosion losses of the gas. Halide deposits must be removed periodically from the reaction tube to avoid flow interruptions due to plugging.

CDC coatings on SiC and other carbides have been produced in varying thickness and have been characterized by optical and electron microscopy and by X-ray and Raman spectroscopy. The tribological performance of the layers has been evaluated in pin-on-disk tribology tests as well as more specialized seal tests.

Figure 1 is an optical micrograph of a CDC coating produced on sintered alpha SiC after one hour in flowing Ar-3.5% Cl_2 at 1000℃. The thickness of the layer ranges from 10 to 20 μm. The convolutions in the SiC/CDC interface result from local variations in the rate of conversion of SiC to CDC due to the differences in orientation of the SiC grains. These convolutions interlock the CDC coating with the SiC substrate and prevent delamination during tribological testing.
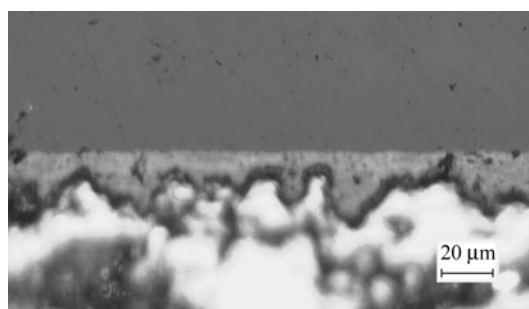
Fig. 1   Cross-sectional optical micrograph of CDC produced on sintered alpha SiC after one-hour treatment in flowing Ar-3.5% Cl_2 at 1000℃. The upper dark-grey layer is epoxy, CDC coating is in the middle, and the bottom part of the micrograph shows SiC.

The interface between the SiC and the CDC is further strengthened by a gradient in the mechanical properties of the CDC as it approaches the SiC/CDC interface.   Figure 2 shows the results of nano-
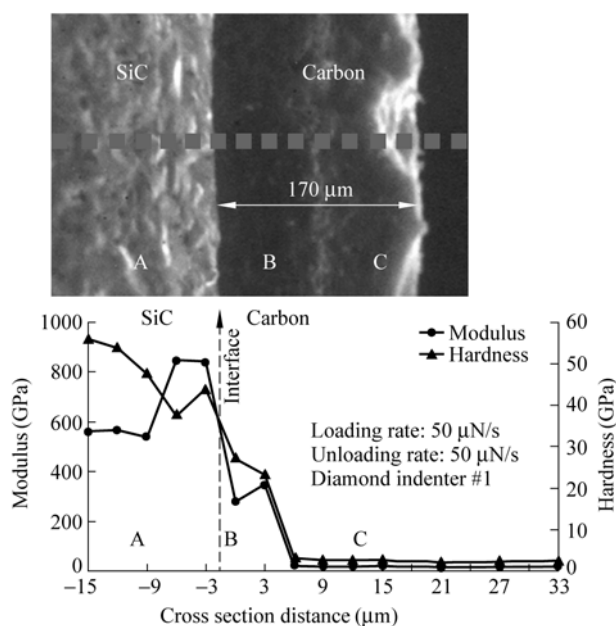

Fig. 2   Cross-sectional micrograph and results of nano-indentation tests on CDC near SiC/CDC interface on CDC produced in flowing Ar-3.5% Cl_2 at 1000℃.

indentation tests performed as a function of position every 3 μm across the CDC/SiC interface. In this experiment, a thick CDC layer was grown by exposing sintered alpha SiC to flowing Ar-3.5% Cl_2 at 1000℃ for 68 h. Throughout most of the CDC layer, the material is relatively soft, with a hardness of 1 to 2 GPa. However, within a few micrometers of the SiC/CDC interface, the hardness increases to the range of 20-30 GPa. The hardness of the CDC near the interface matches well with that of the SiC, so that there is no sharp change in mechanical properties at the interface that could concentrate stresses there, leading to delamination and spallation of the layer. No spallation failures of CDC have been observed in any of the tribological tests performed on CDC-coated SiC.

2 Tribological Performance

Figure 3 shows the friction coefficient during a pin-on-disk tribology test performed on sintered alpha SiC and CDC produced by treatment in flowing Ar-2.77% Cl_2 - 1% H_2 at 1000℃. In these tests, the pin was a 0.9525-cm-diameter silicon nitride ball sliding against a flat surface of SiC at a velocity of 1.25 cm/s with a load of 5 N. Untreated SiC shows a friction coefficient on the order of 0.6-0.7, typical of values for this ceramic. After treatment to produce a CDC layer, the friction coefficient drops to the range of 0.1 to 0.2, more typical of friction coefficients for graphitic lubricants. This lubrication effect was maintained throughout a long-term test continuing for over 6 h without showing any sign of lubrication failure or significant wear of the coating.
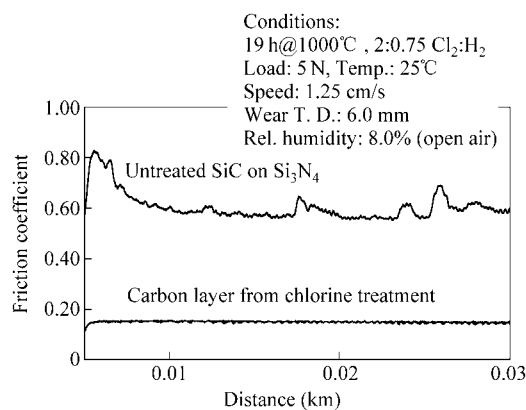
Fig. 3 Friction coefficient versus sliding distance from pin-on-disk tribology test performed on untreated SiC and CDC-coated SiC produced in Ar-2% Cl_2-0.75% H_2 at 1000℃.

Testing performed under conditions similar to that in Fig. 3 showed that the performance of CDC was insensitive to changes in the test conditions, including variations in applied load from 1 to 16 N, sliding velocity from 50 to 550 r/min, and changes in humidity level from dry nitrogen with 0% relative humidity to surfaces wet with liquid water. Friction coefficients were consistently in the range of 0.1 to 0.3 for all of these tests. The results of pin-on-disk tests performed in dry nitrogen are most illustrative of the advantages of CDC over graphitic carbon solid lubricants. Figure 4 shows the results of pin-on-disk tests performed in dry nitrogen on CDC and other forms of low friction carbon.
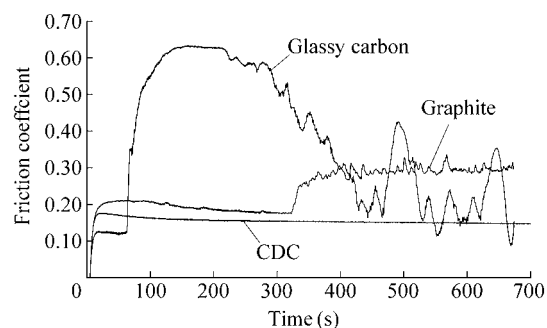
Fig. 4 Friction coefficient versus time for pin-on-disk tribology tests performed in dry nitrogen on graphite, glassy carbon, and CDC grown on SiC (Relative humidity is 0%).

Graphite and other sp^2 bonded forms of carbon have low friction coefficients in sliding wear because of the weak chemical bonding between the 2-D graphene layers in the structure. Water molecules terminate active bonding sites along graphene sheet edges, permitting them to slide past each other easily. In vacuum or in a dry, inert environment, this lubricant water is absent, and the friction coefficient is much higher.

As shown in Fig. 4, when a graphite sample is tested in dry nitrogen, its initial friction coefficient is comparable to that of CDC, but after approximately 5 min of testing, when the layer of graphite that had been hydrated during exposure to laboratory air before the test had worn through, the friction coefficient rose by about 50%. This rise is accompanied by drastically accelerated wear of the graphite, leading to rapid failure. Similar behavior is observed for glassy carbon in the same environment, with the accelerated friction and wear beginning after only about one minute of testing. CDC, in contrast, maintains a low friction coefficient throughout the test. Wear rates were determined by

profilometry at the conclusion of the tests. They were approximately 1.1×10^{-5} mm^3/Nm for graphite, approximately 1.9×10^{-6} mm^3/Nm for glassy carbon, and was below the detection limit for the instrument, estimated as 3×10^{-8} mm^3/Nm, for CDC. Both the friction and wear performance of CDC are far superior to those of other sp^2 bonded carbon under dry conditions.

The excellent performance of CDC in dry environments indicates that the mechanism for low friction in this material may be different from that in other sp^2 bonded carbons. This finding suggests that CDC may have applications in vacuum systems and other environments where conventional lubrication is difficult. A possible explanation for this behavior is the presence of nested fullerenic structures, described as carbon onions, in the CDC coating[4,7]. Figure 5 is a transmission electron micrograph of these structures at the surface of the CDC. The physical transformations of the carbon leading to the formation of such structures have been discussed elsewhere[6,7]. Because of their unique morphology, the friction-reducing characteristics of these structures may be less dependent on the presence of adsorbed water molecules than for other sp^2 bonded carbons.
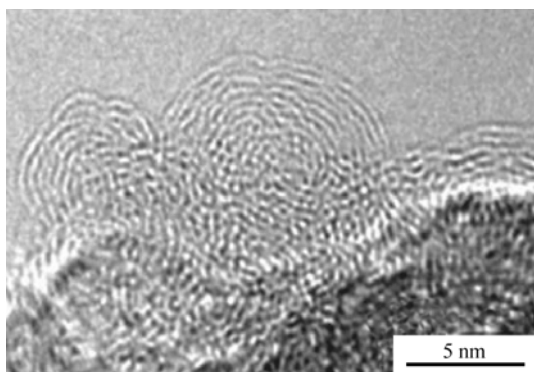

Fig. 5   Transmission electron micrograph showing nested fullerenic structures or carbon onions on the CDC surface.

3   Hydrogen Treatment of CDC

The friction coefficients of CDC sliding against silicon nitride are substantially reduced when the CDC is treated in hydrogen gas at 800℃ for several hours after synthesis, as shown in Fig. 6. The friction coefficient is reduced by approximately a factor of two after the hydrogen treatment, and the friction coefficients in this test fall well below 0.1, demonstrating an improvement
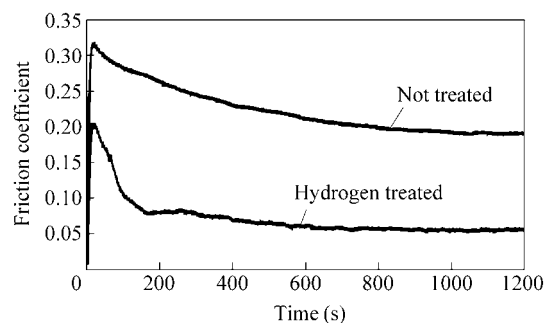
over graphite, even in humid conditions.

Fig. 6   Friction coefficients versus time for pin-on-disk tests performed at 60 r/min under 2 N load in dry nitrogen using CDC as-synthesized and after an 8-h treatment in Ar-5%H$_2$ at 800℃.

The effect of the hydrogen treatment may be to change the adsorbed gas species on the carbon surfaces. Because of their nano-porous nature, CDCs have a substantial capacity for adsorption of gases, such as hydrogen[11,12]. The presence of adsorbed gases can have a substantial effect on tribological performance of carbon films[13]. In the as-synthesized state, CDC contains a substantial amount of residual chlorine. This chlorine may contribute to the low friction performance of the CDC, but it may not be the optimum adsorbed gas species for producing low friction coefficients. Although this chlorine is not removed by high temperature treatments in vacuum or inert gas, hydrogen treatment at 800℃ substantially reduces the chlorine content of the CDC. Hydrogen can react with adsorbed Cl to produce HCl (g), which is a more stable gas molecule than Cl$_2$ (g), the form in which it must vaporize when hydrogen is not present. Excess hydrogen in the environment is likely to replace chlorine on the available adsorption sites on the carbon surfaces. With hydrogen termination of the chemical bonds on the carbon surfaces, the interactions between the contact surfaces are minimized, and the friction coefficient for the CDC is reduced compared to that in the as-synthesized material.

4   Summary

Carbide-derived carbon can be synthesized as coatings on SiC and other hard carbide ceramics by exposure to flowing chlorine at temperatures on the order of 1000℃. CDC-coated SiC shows reduced friction coefficients in sliding compared with untreated SiC.

The CDC coatings are resistant to wear and to spallation and delamination in comparison to other low-friction carbon coatings. The tribological performance of CDC may be related to the nanoscale structure of the carbon produced by the halogenation reaction, which contains nanoscale diamond, carbon onions, and nanoporous amorphous carbon. Further treatment of CDC in hydrogen at high temperature reduces the content of residual chlorine in the structure and further reduces the friction coefficient during sliding.

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