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Enhancement on the tribological performance of diamond films by utilizing graphene coating as a solid lubricant

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ABSTRACT

The present study reports the significantly enhanced tribological performance of the microcrystalline diamond (MCD) film by utilizing the graphene coating on its surface as a solid lubricant. The graphene coating is fabricated by the electrophoretic deposition (EPD) method. A typical EPD processed graphene coating with compact and continuous surface morphology could be obtained with the applied voltage of 15 V or higher, and it is constructed by horizontally stacked micron-sized graphene single-sheets with randomly-orientated nano-sized multi-layered graphene (MLG) sheets embedded between them. The friction tests show that the EPD graphene coating could remarkably reduce the coefficient of friction (COF) of MCD film from ~0.08 to ~0.04–0.05 under the normal load of 1 N (0.48 GPa), decreased by more than 40%. Its wear rate is measured as 4.67×10^{-6} $mm^3/N \cdot m$. Furthermore, in a durability friction test adopting a higher normal load of 4 N (0.8 GPa) and a much longer duration of 36,000 sliding cycles, the stable COF of such graphene/MCD film are measured as ~0.06 and 1.32×10^{-6} $mm^3/N \cdot m$, respectively. This dramatically friction reducing effect is attributed to the realization of three-body abrasion regime by the residual graphene sheets wrapping around the Si_3N_4 particles in the sliding interface and acting as wear particles. Although a large portion of graphene coating is worn out as the sliding proceeds, the friction reducing effect maintains well and no sign of structural degradation in the residual graphene flakes is detected. The present study provides an economic and effective approach of utilizing graphene as a solid lubricant, combining with CVD diamond film, for a wide range of applications.

1. Introduction

Graphene, a two-dimension material, could be regarded as a single layer of a high ordered graphite. Since discovered in 2004, it has attracted continuously intensive attentions due to its wide range of exceptional properties, including very high electron mobility at room temperature, high Young's modulus (~1 TPa), remarkable thermal conductivity (~3000–5000 W/mk), excellent electrical conductivity and optical transparency [1,2]. Moreover, recent studies reveal that graphene has great potential to be utilized as a solid lubricant at engineering scale. Berman's exploring works in 2013 revealed that few layer graphene (generally 3–4 layers) fabricated from solution-processed graphene (SPG) could dramatically reduce both friction and wear of tribopairs in a wide range of sliding environments. For instance, in ambient humid air (RH 30%), 3–4 layer of graphene in-between the sliding interface of self-mated stainless steel (440 C grade) resulted in dramatically reductions in both COF (from 0.91 to 0.15) and wear of counterpart ball (from 179×10^{-7} $mm^3/N\ m^{-1}$ to 0.03×10^{-7} $mm^3/N\ m^{-1}$) [3]. In dry nitrogen, the COF reduced from ~1.0 for bare steel self-mated contact to 0.15 for steel covered by a low concentration of graphene flakes [4]. More amazingly, utilizing such few layer graphene fabricated from SPG, in combination with nanodiamond particles and diamond-like carbon (DLC), the macroscale superlubricity (COF ~ 0.004) was able to be realized in dry nitrogen atmosphere over a wide range of test conditions, i.e., normal load (0.5–3 N), velocity (0.5–25 cm/s), temperature (20–50 °C) and substrate (SiO_2, nickel, and bare silicon) [5]. In both humid air and dry nitrogen environment, SPG graphene could be utilized as solid lubricant for Au/TiN electrical contact, which not only suppressed the friction (by factors of 2–3) and wear (by 2 orders), but also resulted in stable low contact resistance [6]. In hydrogen atmosphere, even a single layer of graphene in-between two sliding stainless steel interface could produce a rather long (6500 cycles) and stable low-friction (COF = 0.22) sliding process. Further, with multilayered graphene, the durability of such low-friction regime could be further extended up to 47,000 cycles [7].

Moreover, graphene deposited by CVD method also demonstrated promising friction reducing effect. Won et al. [8] found that depositing 3–7 layers of graphene on copper surface resulted in a reduction in COF from 0.7 to less than 0.2 while sliding against stainless steel in low temperature ambient air (RH 45–55%, −24 °C) under the normal load of 20 mN. However, such tribopair failed to produce a long lasting

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low friction sliding process. In another study, Bhowmick et al. reported that CVD grown multilayer graphene on nickel foil could produce rather low COFs ranging from 0.11 to 0.17 when sliding against Ti-6Al-4V balls in humid air (relative humidity 10–45%) but its COF showed heavy dependence on humidity [9].

Electrophoretic deposition (EPD) is an economic and versatile processing technique that has been applied in deposition of thin films from suspensions. Compared with the CVD and SPG methods, the two most popular deposition methods of graphene adopted in above mentioned literatures, EPD method has many advantages in the fabrication of graphene coating, such as high deposition rate and controllable layer thickness, good uniformity, less limitation on the material or geometry of substrate, low-cost and simplicity of scaling up [10,11]. Recently, it has been reported extensively that the single-layer graphene films prepared by EPD display good field emission properties [11]. The graphene oxide (GO) film on silicon substrate via EPD is also proved to have good mechanical and tribological properties [12]. However, the study on the application of EPD prepared graphene coating as solid lubricant has not yet been reported.

Herein, we report the fabrication and tribological properties of EPD graphene coatings which are deposited on the microcrystalline diamond film (MCD) surface as solid lubricant. In available study, the MCD film is extensively studied as protective coatings for a variety of cutting tools [13,14], drawing dies [15,16], and mechanical seals [17–19]. The present study reveals that applying a continuous layer of graphene coating prepared by EPD method on the surface of MCD film could result in a dramatically enhanced friction reducing effect and anti-wear performance. The surface morphology, microstructure and composition of as-received multi-layered graphene (MLG) sheets and as-deposited graphene coating are examined by transmission electron microscope (TEM), atomic force microscope (AFM), scanning electron microscope (SEM), surface profilometer, Raman and X-ray photoelectron spectroscopy (XPS) spectrum. The friction and wear tests are carried out on a reciprocating ball-on-plate friction tester adopting silicon nitride balls as counterpart material, and the sliding regime behind the friction and wear behaviors of EPD prepared graphene coatings are discussed based on the results of investigations on the worn surfaces of both graphene coating and counterpart balls.

2. Experimental details

2.1. Deposition and characterization of EPD graphene coatings

In present study, we adopt the electrophoretic deposition (EPD) method to deposit graphene coating on the surface of microcrystalline diamond (MCD) film, which is deposited on a tungsten carbide flat (15 × 15 × 3 mm) by hot filament chemical vapor deposition (HFCVD) method. The graphene used in present study is in forms of ethanol solution processed graphene (SPG, 1 mg/ml), which is provided by Simbatt Energy Technology Company. Graphene flakes are synthesized via Hummers method using highly oriented pyrolytic graphite (HOPG) as raw materials and then chemically reduced.

The EPD process is carried out on a home-made electrolytic cell system, in which a cemented carbide plate was mounted on the positive platinum electrode, and the MCD coated tungsten carbide flat is mounted on the negative platinum electrode. These two electrodes are fixed a quartz holder that holds them in parallel manner and the distance between them is fixed by 10 mm. when a DC voltage is applied between the two electrodes, the positively charged graphene sheets would move toward the negative electrode driven by the generated electric field and finally arrive and adhere on the surface of target substrate. Before the EPD process, the graphene solute in colloid is required to be charged. In general, the inherent surface charges of graphene sheets are insufficient to generate driving force that is strong enough to drive them move toward the target electrode. Therefore, the magnesium nitrate ($Mg(NO_3)_2 \cdot 6H_2O$) is used to modify these MLG sheets by dispersing 10 ml of SPG and 10 mg of $Mg(NO_3)_2$ into 200 ml of anhydrous isopropyl alcohol with the aid of ultrasonic cleaner at 0 °C for 30 min. Then the prepared graphene-Mg^{2+} solution (0.05 mg/ml) is used as the electrolyte [20]. Its Zeta potential and PH value are measured as ~11.2 mV and 6.4 respectively.

To understand the role that the applied voltage plays on the EPD process, we fabricated four samples adopting applied voltages of 5 V, 10 V, 15 V and 30 V, which are respectively referred as Gr5V, Gr10V Gr15V and Gr30V, and conducted further characterizations on the Gr5V and Gr15V to reveal the effect of the applied voltage on the surface morphology, microstructure and composition of EPD prepared graphene coating. The duration for each EPD process is set to 20 min. After the EPD process, field-emission scanning electron microscope (FESEM, Zeiss ULTRA 55), AFM (Dimension FastScan, BRUKER), 3D surface profilometer (SENSOFAR S neox), Raman spectrum (SENTERRA R200, the excitation wavelength of 532 nm, 5 mW), as well as XPS (AXIS ULTRA DLD, Kratos) are adopted to investigate the microstructure and composition of deposited graphene coatings.

2.2. Friction tests

To examine the friction and wear performance of the graphene coatings deposited on the MCD film, we carry out a series of ball-on-plate reciprocating friction tests on a Universal Micro-Tribotester (UMT-2, CETR). In these friction tests, the fabricated graphene coatings are fixed onto a reciprocating worktable and slid against a silicon nitride ball (Φ 4 mm). Firstly, a standard friction test is conducted for Gr5V and Gr15V, in which the sliding processes are carried out under ambient atmosphere (60% RH) with a normal load of 1 N (the correspond average Hertz contact pressure is 0.48 GPa) applied on the sliding interface, the sliding stroke and frequency were 6 mm and 5 Hz respectively and each sliding test is carried out for 9000 sliding cycles. Then, a durability test is further conducted for the Gr15V sample, in which an increased normal load of 4 N (the correspond average Hertz contact pressure is 0.8 GPa) is applied on the sliding interface and the sliding duration is elongated to 36,000 cycles. The sliding condition and other sliding parameters are identical with that adopted in the standard friction tests. After each sliding test, the worn surfaces of examined sample and its counterpart surface are investigated by high resolution optical microscope (OM, Leica DM4000), FESEM, EDX, 3D surface profilometer and Raman spectrum.

3. Results and discussion

3.1. Characterizations

Firstly, we adopt TEM and AFM to characterize the dimension of graphene sheets dispersed in the solution, as shown in Fig. 1. It is seen from Fig. 1(a) that folds appear on the edge of graphene flakes, indicating the thickness of graphene sheet is ultra-thin. Fig. 1(b) presents a 2-D AFM image of several dispersed graphene sheets as well as five 2-D surface profiles obtained from different locations, which are indicated with black lines in the 2-D AFM image. As seen, the thickness of these graphene sheets is measured as around 3–4 nm indicating that their layer numbers are around 10. Furthermore, the lateral dimension of these graphene sheets is up to several microns.

After EPD process, SEM is adopted to examine the surface morphology of graphene coatings deposited on MCD surface, as presented in Fig. 2. The MCD film used as the substrate for graphene coating shows a rugged surface, on which well-faceted diamond grains with grain size of ~1–2 μm distribute compactly and homogeneously (Fig. 2(a)). After the EPD process with an applied voltage of 5 V, the MLG sheets scatter as separate spots on the surface of MCD film, failing to coalesce into a continuous coating, as shown in Fig. 2(b). It is also noted that most of these separate MLG sheets are nano-sized in lateral dimension and only very few of them are close to 1 μm. Thus, they even fail to fully