Diamond & Related Materials 76 (2017) 50–57

Contents lists available at ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

The influence of normal load on the tribological performance of electrophoretic deposition prepared graphene coating on micro-crystalline diamond surface

Sulin Chen, Bin Shen*, Fanghong Sun

School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.

ARTICLE INFO

Keywords:
Load capacity
Graphene
Tribology
EPD

ABSTRACT

In the present study, the friction and wear behaviors of a graphene/diamond coating are examined under a variety of normal loads ranging from 4 N to 10 N, which correspond to contact pressures of 0.77–1.04 GPa on the sliding interface. The graphene coating is deposited on the surface of a microcrystalline diamond (MCD) film by electrophoretic deposition (EPD) method. Friction tests are carried out on a ball-on-plate reciprocating Universal Micro-Tribotester (UMT-3, CETR) in ambient air condition (60% RH). Silicon nitride balls (Φ 4 mm) are used as the counterpart materials. The results show that a steady-state coefficient of friction is maintained in the range of 0.07–0.09, showing no discernable dependence on the applied normal load. The highly similar equilibrium sliding interfaces formed under varying normal loads are supposed to attribute to this effect largely. Mixtures of graphene flakes and wear particles (Si_3N_4 or SiO_2) produced during the sliding promote the transition from two-body abrasion to three-body abrasion. Meanwhile, the exposed diamond crystallites on the sliding interface are protected from being polished and smoothened thanks to the existence of residual graphene flakes, even though only a portion of the wear track is covered. After the sliding tests, the remaining graphene flakes within the wear track on the Gr/MCD film present no structural damage or degradation, but become thicker sheets by overlapping with each other under the relatively high pressure.

1. Introduction

Due to its lamellar structure and low shear strength, graphene has drawn a lot of attention as a potential solid lubricant [1,2]. A number of studies have been conducted on the tribological behaviors of CVD grown graphene and few-layered graphene flakes and the graphene examined in these studies presented remarkable friction reducing effect in a variety of sliding conditions. Kim et al. [3] reported that the transferred Cu-grown graphene and Ni-grown graphene reduced the coefficient of friction (COF) for SiO_2 substrate from 0.68 to 0.22 and 0.12, respectively. It was found by Won et al. [4] that depositing 3–7 layers of CVD grown graphene on Cu surface resulted in a drastic reduction in COF under the normal load of 20 mN, and thicker graphene showed higher durability. Bhowmick et al. [5] also 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-4 V balls in humid air (relative humidity 10–45%). Besides the continuous CVD grown graphene coating, Berman et al. [6–11] reported 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. 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 $179 \times 10^{-7}\,mm^3\,N^{-1}\,m^{-1}$ to $0.03 \times 10^{-7}\,mm^3\,N^{-1}\,m^{-1}$) [6]. 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 [7]. For Au/TiN electrical contact, SPG graphene could suppress the friction (by factors of 2–3) and wear (by 2 orders) in both the humid air and dry nitrogen environment [8]. In hydrogen atmosphere, even a single layer of graphene in-between two sliding stainless steel interfaces 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 [11]. Graphene layers are supposed to act as a two-dimensional nanomaterial and form a conformal protective coating on the sliding contact interfaces. These factors facilitate shear and slow down the tribo-corrosion, and thus drastically reducing the wear.

Electrophoretic deposition (EPD) is an attractive technique for the

* Corresponding author.
E-mail address: binshen@sjtu.edu.cn (B. Shen).

http://dx.doi.org/10.1016/j.diamond.2017.04.008
Received 10 December 2016; Received in revised form 10 April 2017; Accepted 10 April 2017
Available online 17 April 2017
0925-9635/

deposition of graphene-related materials [12,13]. The process parameters can be easily manipulated to form graphene deposits with controlled thickness [12] and dense packing [14], which is promising for its utilization as solid lubricant at engineering scale. Many researches have been conducted to investigate the application of EPD-processed graphene in fields of field emission devices [15,16], energy storage [17], anti-corrosion resistant coatings [18] and so on. However, few studies have been conducted to explore the lubricating performance of EPD graphene film. In our previous study, significantly reduced friction and wear have been observed for the MCD film surface when a top-layered graphene coating is deposited on its surface (by EPD or spraying) [19,20]. It is noted that as the normal load applied on the sliding interface increases from 1 to 4 N, which corresponds to the contact pressures between two contacted surfaces rising from 484 to 768 MPa, such excellent friction reducing effect and anti-wear performance disappeared for the graphene coating prepared by the spraying method; while that for the EPD prepared graphene coating retain. A similar phenomenon has also been observed in an available literature, in which the spraying graphene protection is more pronounced at lower loads (1 N), while for higher loads (3 N, 470 MPa; 5 N, 560 MPa), the graphene layer would be worn out or quickly removed out of the wear track and hence its beneficial effect disappears [7]. In addition, we also find that such enhanced friction reducing and wear resistance effect brought by the graphene coating for the nanocrystalline diamond (NCD) film is not as significant as it is for the MCD film. The unique surface morphology of the underneath MCD film is supposed to play a crucial role on the exceptional friction performance of Gr/MCD film [21]. For the engineering applications, the load capacity is a vital criterion to evaluate the performance of a tribological coating [22,23]. Nevertheless, the critical load for the EPD prepared graphene film as a tribological coating has not yet been revealed in available literatures.

In this work, the dependence of the tribological behavior of Gr/MCD film on the normal load is studied in a set of ball-on-plate reciprocating friction tests, in which the examined Gr/MCD films are brought to slide against Si_3N_4 balls under normal loads of 4 N to 10 N (768–1040 MPa). Before and after the friction tests, scanning electron microscopy (SEM), atomic force microscopy (AFM) and micro-Raman spectroscopy are adopted to characterize the surface morphology, microstructure and quality of graphene sheets.

2. Experimental details

In present study, we adopt the electrophoretic deposition (EPD) method to deposit the graphene coating on the surface of microcrystalline diamond (MCD) film. Firstly, we deposit a layer of 3-μm thick MCD film on the surface of a 15 mm × 15 mm × 3 mm cobalt cemented tungsten carbide plate (WC-6%Co, Ra ~ 20 nm) using hot filament chemical vapor deposition (HFCVD) method. The detailed deposition process has been reported in previous papers [24,25]. Subsequently, we carried out the EPD process in a tailor-made electrolytic cell system, in which a WC-Co plate is mounted on the positive platinum electrode, and the MCD coated tungsten carbide flat is mounted on the negative platinum electrode acting as the substrate for the deposition of graphene coating. These two electrodes are fixed a quartz holder that holds them in parallel manner and the distance between the surfaces of WC-Co and MCD coated WC-Co plates is 10 mm. During the EPD process, a DC voltage of 15 V is applied between them and the duration of each EPD process is set to 20 min.

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 crystalline graphite powder (~ 13 μm) as raw materials and then chemically reduced. Most of them are 3–8 layers. Prior to the EPD process, these GNs are required to be charged as the inherent surface charges of GNs themselves are generally insufficient to generate a driving force that is strong enough to drive them move toward the target electrode under an electric field, even if a high voltage is applied between the two electrodes. In present study, we disperse 10 mg SPG and 10 mg $Mg(NO_3)_2$ into 200 mL anhydrous isopropyl alcohol in an ultrasonic vessel and carry out a 30-min ultrasonic process at 0 °C to make Mg^{2+} ions attach to the edge or surface of GNs. Then, the prepared graphene-Mg^{2+} solution (0.05 g/L) is used as the electrolyte in the EPD process [26].

The frictional performance of the EPD prepared graphene coating are examined in a set of ball-on-plate reciprocating friction tests, which are carried out on a Universal Micro-Tribotester (UMT-3, CETR). In the friction tests, the graphene coated MCD films (Gr/MCD) are fixed on a reciprocating worktable and slide against a mounted silicon nitride ball (Φ 4 mm) in ambient air condition (60% RH). The stroke and frequency of the reciprocating motion are 10 mm and 2 Hz, respectively. To investigate the influence of the normal load on the frictional behaviors of Gr/MCD films, we adopt four normal loads ranging from 4 N to 10 N, which correspond to Hertz contact pressures of 0.77–1.04 GPa, in the friction tests.

For the characterizations of as-prepared MCD and Gr/MCD film, field-emission scanning electron microscopy (FESEM, Zeiss ULTRA 55) and atomic force microscopy (AFM, Dimension FastScan, BRUKER) are adopted to investigate their surface and cross-section morphology and Raman spectroscopy (SENTERRA R200, the excitation wavelength of 532 nm, 2 mW) is used to analyze their composition. After the friction tests, for each tribopair, the worn surface of the Gr/MCD film and its counterpart ball are examined using high resolution optical microscopy (OM, Leica DM4000), SEM, energy-dispersive spectrometry (EDS) and Raman spectroscopy.

3. Results and discussion

3.1. Characterizations of as-deposited MCD and Gr/MCD films

The SEM images of the surface and cross-section morphology of as-deposited MCD and Gr/MCD films are presented in Fig. 1. As seen in Fig. 1(a), the MCD film shows a rugged surface on which well-faceted diamond crystallites with grain size of ~ 1 μm distribute compactly and homogeneously. Its cross-sectional image exhibits a typical columnar grain structure, as presented in Fig. 1(c), in which the thickness of MCD film could be measured as ~ 3 μm. After the EPD process, a layer of continuous and compact graphene coating is formed on the surface of MCD film, and a large amount of folds and winkles could be observed on its surface, as seen in Fig. 1(b). From the cross-section of Gr/MCD film, as exhibited in Fig. 1(d), it could be observed that the interface between the graphene coating and the MCD film highly conforms to the surface contour of MCD film, without discernable defect forming. It is also worthy to note that the thickness of the top-layered graphene coating is not uniform, but varies within the range of ~ 200–400 nm due to the rugged surface contour of the underneath MCD film. Furthermore, the microstructure of as-deposited graphene coating could also be observed from the cross-section morphology of Gr/MCD film. As seen in Fig. 1(d), it is clear that the graphene coating is constructed by randomly orientated graphene flakes stacking layer by layer. The random orientations of graphene flakes are supposed to be the result of the random attachment of Mg^{2+} ions on the edges or surface of graphene sheets in the decoration process. During the EPD process, those locations where the Mg^{2+} ions attach on will preferentially move toward the negative electrode under the applied electric field and thus result in the random orientation of graphene sheets in the deposited graphene coating [26].

Fig. 2 presents the 3-D AFM images obtained from the surfaces of both MCD and Gr/MCD films, with a scanning area of 10 × 10 μm^2. Moreover, for each film, a 2-D surface profile is obtained from the position indicated by the red dash line in its 3-D AFM image. In Fig. 2(a), the rugged surface morphology of MCD film is obvious and the grain size of the diamond crystallites could be estimated as ~ 1 μm