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Graphene nano scrolls responding to superlow friction of amorphous carbon

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ABSTRACT

Amorphous carbon films are widely used as solid lubricant coating. However, the mechanism response for its superlow friction has not been well explored. The previous results indicated that graphitic tribofilms are formed at rubbing interfaces, which leading to decreasing of friction coefficient. But in some cases, the friction coefficients of graphite (0.1–0.6) are much high than the amorphous carbon films (0.05–0.01), where the graphitic theory is quite limited and the interpretation is poor. Using high resolution transmission electron microscopy and Raman spectra, we monitor the structure evolution of tribofilms and friction coefficient drop during running-in. We demonstrate that a kind of graphene nano scroll particle was developed in the tribofilms consisting of outer graphene shell and inner amorphous core. And the relationship between friction drop and graphene nano scroll evolution suggests that, incommensurate contact of such nano scrolls, may be the dominant dissipation modes for amorphous carbon.

1. Introduction

Amorphous carbon (a-C) film is one of the most promising solid lubricant coating in various tribological applications, for it can considerably reduce friction and wear, and extend lifetime of moving parts [1–3]. Common wisdom holds that low friction of a-C film is attributed to shear induced tribofilm formation at rubbing interfaces [4], whereas the soft graphitic tribofilms with low shear resistance, which ensure the easy slippage and lead to the friction decreasing to low value [5,6]. Generally, the a-C is metastable amorphous material composed of sp^3 and sp^2 bonds, and the sp^3 bonds embedded in the amorphous evolutes to sp^2 bonds during friction and form a graphitic tribofilm [7,8]. Molecular dynamics simulations also confirmed the above sp^3-to-sp [2] graphitic transformation [9]. Thus, the formation of such graphitic layers was considered to be an important reason for superlow friction of a-C [7–9]. Since, under incommensurate contact, the friction coefficient of carefully prepared C-plane of HOPG is as low as 7×10^{-5}, which is known as "superlubricity" [10–12]. However, similar to friction induced graphitic structures [7], general graphite materials are multi-crystal and the coefficient of friction varies from 0.1 to 0.6 [13]. According to these results, it will be self-supported that the coefficient of a-C can be as low as that of graphite. Howbeit, in some cases, a-C had been proved to be with superlow frictional behavior, and the friction coefficient can be below 0.05,[14] which is much lower than graphite ($\mu > 0.1$) [13]. This phenomenon hints that the superlow friction is related to graphitic transformation but not limited to this, since the sp^2 carbon has many allotropes with diverse structures and friction properties.

For many a-C surfaces with superlow friction, the superlow friction was proved not to present immediately at sliding start but after two common stages [1–6]. First, a high friction coefficient (>0.1) emerges, then it decreases to low or superlow friction (<0.05) and tends to be stable [14]. These two stages of friction coefficient evolution processes are called running-in. Time of flight secondary ion mass spectrometry (TOF-SIMS) studies demonstrated that the initial a-C surfaces are covered by oxygen rich layers when exposed to air [15]. At the start of friction, the contaminant surfaces are removed by shear force, and the contact surface of a-C detaches, reacts, and transfers to the counterface [16]. During this stage, the surface presents a higher friction because of the above interfacial actions. Then the amorphous structure begins to evolve to the graphite structure, and a thick graphitic tribofilm formed on the counter surface [4,5], accompanied with friction coefficient decrease. Hence, the running-in has a very important significance for understanding the origin of the low friction of a-C,

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and here we design an experiment to investigate structure evolution in running-in to reveal the underlying physical mechanism.

In this paper, we studied the nanostructure evolution of tribofilm to probe the running-in of a-C film. High resolution transmission electron microscopy (HRTEM), Raman spectrum and friction experiments demonstrate that unique graphene nano scrolls (GNSs) with outer graphene shell and inner amorphous core formed in the tribofilm. The growth of such nanoscrolls in tribofilm accompanied with the decrease of friction coefficient, which suggests that the evolution from a-C to GNSs is responding to the friction drop during running-in. Consequently, the evolution of GNSs indicates that incommensurate and rolling contact within the friction interface may be the dominant dissipation modes for amorphous carbon. The evolution path of GNSs was divided into two stages: 1) amorphous to graphene, 2) graphene to nanoscroll, which probably responds to the physical origin of superlow friction of a-C films.

2. Experimental

2.1. Sample preparation

The hydrogenated a-C films used in this study were synthesized by plasma enhanced chemical vapor deposition technique (PECVD) using a negative voltage of −800 V to a substrate and a chamber pressure of ~20 Pa. The source gases used for deposition were CH_4 and H_2 with a flow rate of 1:2. And the thickness of a-C films were controlled about 1000 nm. For nanostructure analysis, the HRTEM samples were grown on freshly cleaved NaCl wafers with a thickness about 20 nm. Then the NaCl wafers were placed into the deionized water, using micro grid picked up the floating a-C fragment. The HRTEM samples of tribofilms were prepared using micro grid polishing the fragments of tribofilms surfaces from the sliding balls after friction tests.

2.2. Structure characterizations

The nanostructures of a-C films and wear debris were analyzed on HRTEM JEM 3010(JEOL, JP) and Tecnai-G2 F20 (FEI, US). In addition to HRTEM, further information regarding the structural arrangement, chemical state and chemical bond were studied from micro Raman spectrometer (LABRAM HR 800 at a wavelength of 532 nm (2.3eV)) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI equipped with a monochromatic X-ray source), respectively.

2.3. Mechanical characterization

The mechanical properties of as prepared a-C films were measured by nanoindentation (Hysitron Ti-950) with a trigonal Berkowich diamond tip. The elastic recovery R is obtained by calculation ($R = d_{max} - d_{res}/d_{max} \times 100\%$), where d_{max} and d_{res} are the maximum and residual displacement.

2.4. Friction and wear characterization

A rotating ball-on-disk tribometer was used to measure friction coefficient by dual balls from Al_2O_3, Si_4N_3, ZrO_2 and steel with a diameter of 5 mm. The applied load spans from 2N to 20N, under the frequency of 500r/min with a rotating radius of 4 mm. The test condition is atmospheric with a humidity about 20% and the temperature is 20 °C. After friction test, the wear of the substrate and tribofilms on the balls were imaged by optical microscope using Olympus BX53 (Olympus, Tokyo, Japan) with a magnification ten.

3. Results and discussions

As mentioned in the instruction section that running-in might depend on the tribofilm structure, therefore, to characterize the structure of carbon film is the first step so as to probe the nanostructure evolution of tribofilm. The a-C films for the friction test are prepared by the PECVD method using the Si (100) as the substrate (Fig. 1a). HRTEM image (Fig. 1b) presents that the as-prepared carbon films show a typical amorphous structure without any ordered structure. The inset selected area electron diffraction (SEAD) image also illustrates that the amorphous nature of so-made a-C film, in which no diffusing ring can be observed. And the fine bonding structures in the amorphous network were analyzed from their Raman spectra, shown in Fig. 1c with two bands at 1332 cm^{-1} and 1532 cm^{-1}, corresponding to the D and G modes of a-C, respectively [17]. XPS is used to investigate the chemical nature of the amorphous carbon network (Fig. 1d). The C_{1s} spectrum indicates a max intensity located at 284.8eV, which presents the composite structure of sp^3 and sp^2 bonds [18].

The mechanical properties of carbon film have a decisive influence on their friction properties [1]. Table 1 summarized the mechanical property parameters of the a-C film from their nanoindentation test, which indicate a hardness of 11.4 GPa, elastic module of 90.2 GPa and elastic recovery about 77%.

Friction behaviors of specimens were evaluated by the ball-on-disk rotating method (Fig. 2a). A typical running-in process (Fig. 2b) can be observed from their friction curves, with an initially maximum friction of 0.16 decreased slowly to a finally stable value of 0.016 after about 2000 cycles. Induced by stress, the surfaces of the counterparts transformed, and tribofilms different from sliding balls and a-C films were formed. Fig. 2c shows the morphology of new surfaces of counterpart Al_2O_3 balls (top) and a-C surfaces (bottom) at different stages of running-in. Tribofilms were rapidly developed on the balls with the evolution of friction. The width of the wear track on a-C films and balls increased gradually along with the wear debris accumulated. While, accompanied with friction surface evolvement, the atoms of tribofilms rearrangement and form graphitic layers [5–8]. But the specific structure type, evolution process, and lubricity mechanism of such graphitic layers are not yet clear. These questions will be investigated in detail in the following aspects: 1) the nanostructure of the tribofilms, 2) the elemental composition of tribofilms, 3) and the physical original of superlow friction.

Fig. 3a shows a series of Raman spectra of the tribofilms at different sliding cycles, corresponding to those in Fig. 2c. Remarkably, with increased friction cycles, the D and G mode were separated gradually and shift to high wave number. In this conversion process, amorphous carbon transform into a graphitic structure [19–21]. For more details, these Raman spectra were decomposed by Gauss module. Generally, the D peak and G peak can be discussed separately. The D peak strength is proportional to the probability of finding a six-fold ring in the cluster [22]. And, the G peak relates only to bond stretching of sp^2 pairs [22]. Fig. 3b presents additional information of the peak shift and the I_D/I_G values. Both the D and G peak moved to high wave number, and the I_D/I_G value increased accordingly. In amorphous carbon, the increase of I_D/I_G value implies an improvement in the degree of order [23]. At the same time, the full width at half maximum (FWHM) can value the crystallinity of materials. The increase in the degree of order was also convinced by G peak's FWHM (Fig. 3c), which confirmed the structure evolution from amorphous to graphitic structure [23]. These results indicate that a large number of ordered graphitic structure are generated in the tribofilm during friction, where an interface self organizing process may occurred.

The friction behavior and lubricity mechanism of tribofilm