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Friction-induced rapid restructuring of graphene nanocrystallite cap layer at sliding surfaces: Short run-in period

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A B S T R A C T

Amorphous carbon film is vastly applied for low-friction protective coatings at contact sliding surfaces. However before reaching steady low friction status, the film always endures a high friction period known as the "run-in" period, sometimes taking thousands of sliding cycles, causing remarkable energy dissipation. Here, we report that the run-in period of amorphous carbon film could be drastically shortened to 22 ± 5 cycles by fabricating a 5-nm graphene nanocrystallite cap layer. The cap layer gave rise to rapid formation of graphene nanocrystallized transfer film, which responds to the short run-in period. We found two key factors for the rapid formation of transfer film. Firstly, the cap layer had lower wear resistance than the amorphous carbon, severing as a quick-wearing sacrificial layer. Secondly, the nanocrystallization of transfer film was mainly due to friction-induced restructuring of graphene nanocrystallite but not friction-induced heat. In addition, the friction test of amorphous carbon film covered with multilayer graphene micro-flakes also verified that friction-induced rapid restructuring of graphene sheets at sliding surfaces resulted in short run-in period.

1. Introduction

Amorphous carbon (a-C) film is an important class of tribological materials for its excellent properties such as low friction coefficient, high wear resistance and hardness [1–3]. It has been used worldwide as surface protective coatings in everyday devices ranging from magnetic disks to razor blades as well as manufacturing and automobile industries [3]. The low friction of a-C film can ensure long operation life of devices with minimal interruptions and negligible energy dissipation by friction. However, before reaching low friction steady stage, a-C film always has a high friction period ($\mu > 0.1$), so-called "run-in" period. The duration of run-in period is uncertain to some extent and sometimes it would take thousands of sliding cycles [4–6]. So in order to make the low-friction application more effective, the run-in period is necessary to be shortened or even eliminated.

The run-in period is a transient stage during which some sort of interfacial conditioning necessary for low friction occurs. At the beginning of friction, high friction force arises from the initial interaction between a-C surface and the counter surface. As sliding continues, the contact surface of a-C detaches, reacts, and transfers to the counterface [6]. Meanwhile, the a-C structure is transformed to the graphite-like nanocrystallite structure by the heat generated by friction and/or the stress provided by the mechanical/friction force [7–12]. Then, a graphite-like nanocrystallite transfer film forms on the counter surface, which always coincides with the decreasing of friction coefficient [13]. The formation of graphite-like nanocrystallite transfer film lowers the interaction force between the sliding surfaces from strong covalent bonds to mainly weak van der Waal forces. Hence, in order to shorten the run-in period, one feasible way is to accelerate the formation of graphite-like nanocrystallite transfer film. Many studies have shown that the formation of the transfer film was affected by sliding conditions [14–17]. At elevated temperatures, transfer films tended to form faster and shorten the run-in period [14]. High load or high sliding speed led to faster formation of transfer film and had a crucial effect on the nanostructure transformation [15,16]. Counterface material also play an important role on the formation of transfer film. Transfer film build-up faster on clean surfaces of steel pins than those that are covered by an oxide layer, as carbon film surface reacts preferentially with metallic iron [17]. However, the above sliding conditions are often uncontrollable in the low-friction application. Some researchers also pointed out that the

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surface contaminant layer [18,19], surface roughness [20] and sp^2/sp^3 ratio [21] of carbon film had effects on the length of run-in period. But few methods have been proposed for effective shortening or eliminating the run-in period.

As mentioned above, the formation of transfer film depends on the migration of carbon from a-C film to counter surface, and the nanostructural transformation from amorphous to graphite. Therefore, the main obstacles for the rapid formation of transfer film are the high wear resistance of a-C film and the pure amorphous structure without any graphene sheets for directly serving as raw material. In this study, we propose a method for facilitating the formation of transfer film and shortening the run-in period by depositing a thin graphene nanocrystallite (G-N) cap layer on the a-C film. The effects of cap layer thickness and G-N size on the run-in period were studied. Investigations of the formation of transfer films and nanoscratch tests of the carbon films were carried out to reveal the role of G-N cap layer on rapid formation of nanocrystallized transfer film. The nanostructure transformation mechanism of transfer film was discussed by comparing the annealing effects on the nanostructures of 5 nm-thick a-C film and 5 nm-thick G-N film. Multilayer graphene micro-flakes were employed to further verify the short run-in period mechanism.

2. Experimental

The a-C film and G-N cap layer were fabricated by using an electron cyclotron resonance (ECR) plasma sputtering system. The detailed description of the sputtering system was reported in our previous works [22,23]. The a-C film was deposited on silicon substrate (p-type <100>) with ion irradiation in divergent electron cyclotron resonance (DECR) plasma sputtering type [22]. The background pressure of the vacuum chamber was pumped down to 8×10^{-5} Pa and argon was inflated keeping the working pressure at 1×10^{-1} Pa. During the film deposition, ion irradiation was realized with a substrate bias voltage of -10 V. The deposition time was 30 min and the film thickness was 90 nm. The G-N cap layer was deposited on the a-C film with electron irradiation in mirror-confinement electron cyclotron resonance (MCECR) plasma sputtering type [23]. The argon working pressure was 4×10^{-2} Pa. Electron irradiation energies varied from 10 eV to 50 eV with different positive substrate biases to change the size of graphene nanocrystallite in the cap layer. The deposition time was used to control the cap layer thickness. The deposition rate was about 1 nm/min, and cap layers with thicknesses of 1 nm, 2 nm, 5 nm and 10 nm were obtained.

Multilayer (1–5 layers) graphene micro-flakes were purchased from Tanfeng Tech. Inc. Firstly, the graphene micro-flakes were suspended in ethanol. The weight concentration of graphene flakes was 10 mg/L. Then, 1 mL graphene-flake-containing ethanol solution was spread on the a-C film surface, and evaporated in the atmosphere.

The nanostructures of the carbon films were analyzed with Raman spectroscopy (HORIBA, HR-Resolution; wavelength of 532 nm) and transmission electron microscopy (TEM, JEOL, JEM-3200FS). The cross-sectional TEM specimens were cut from the films and progressively thinned to about 100 nm thick by using a focused ion beam (FIB, FEI, Scios). A Pt protective layer was deposited on the top of the specimen and the final polishing was done with a beam current of only 27 pA to avoid possible damages (including ion doping) or thermal recrystallization caused by ion bombardments.

Frictional tests of the films sliding against a Si_3N_4 ball (radius of 3.17 mm) were performed with a Pin-on-Disk tribometer. The normal load was 2 N. The sliding velocity was 26.4 mm/s, corresponding to a constant disk rotational speed of 180 rpm with a frictional radius of 1.4 mm. The tests were operated in a clean room with a temperature of 24 °C and a relative humidity of 45–50%. The tests were repeated more than five times for each film. The structures of the transfer films on the Si_3N_4 ball surfaces were analyzed with optical microscope and Raman spectroscopy. The cross-sectional nanostructure of the transfer films were observed with a Cs-corrected TEM (FEI, Titan3 Themis G2). The TEM specimens were cut out from the ball surface and were thinned to about 100 nm by using the FIB. Au and Pt layers were subsequently deposited on the specimens to make them conductive and protect from possible damage.

The nanoscratch tests of the carbon films were carried out with an atomic force microscope (AFM, Bruker, Dimension edge). A stainless steel cantilever with an 80 nm-radius diamond tip was attached to the cantilever holder of the AFM. The scratch normal load was 200 μN. The nanoindentation tests of the carbon films were performed with a nanoindenter (Hysitron, TI-950). A Berkovich diamond indenter with a tip radius of 100 nm was used and the maximum load for indentation was 500 μN. A pre-test on quartz standard sample was done to calibrate the equipment. The value of hardness was given by averaging five different measurement results. The annealing experiments of 5 nm-thick a-C film and 5 nm-thick G-N film were performed with a tube heating furnace under 1 L/min flowing argon gas. The films were heated from room temperature to 500 °C, 750 °C, 1000 °C in 20 min, then kept for 30 min. The films were naturally cooled to RT after annealing.

3. Results and discussion

3.1. Effect of G-N cap layer on run-in period of friction

The cross-sectional TEM images of a-C film and a-C film with G-N cap layer (electron irradiation energy, 40 eV; deposition time, 5 min) are shown in Fig. 1(a). It can be seen that the thicknesses of the a-C film and G-N cap layer were 90 nm and the 5 nm, respectively. The enlargement TEM images of region I and region II show that a-C film was pure amorphous structure and the cap layer was consisted of sheets stacks. The interplanar spacing of the sheet was approximately 0.36 nm, matches the interplanar spacing of graphene sheets. The orientation of graphene sheets was perpendicular to the substrate. Comparing Raman spectra of the two films, as shown in Fig. 1(b), a sharp D peak appeared with the existence of G-N cap layer, which further indicates that the nanostructure of the G-N cap layer was nanocrystallite. Fig. 1(c) shows the typical friction curves of the a-C film and a-C film with G-N cap layer. The friction coefficient of the a-C film was about 0.20 at the beginning, then slowly decreased to a stable lower value of 0.06 after about 470 sliding cycles. The run-in period of the a-C film is about 470 cycles. For the a-C film with G-N cap layer, friction coefficient rapidly reduced to stable value of 0.06 with only 17 cycles. These results indicate that the run-in period of amorphous carbon film could be significantly shortened with G-N cap layer.

G-N cap layers with different G-N sizes and layer thicknesses were fabricated by varying irradiation energy and deposition time to systematically investigate the effect of G-N cap layer on the reduction of run-in period. The ratio of D band to G band (I_D/I_G) was obtained by fitting the D band and G band of Raman spectrum with a Lorentzian line and a Breit-Fano-Wagner (BFW) line, respectively. According to the three-stage amorphization proposed by Ferrari and Robertson [24], the a-C film and a-C films with different G-N cap layers were in stage 2 ranging from amorphous carbon type to nanocrystalline type. The nanocrystallite size was proportional to the I_D/I_G. Fig. 2(a) shows run-in cycles and I_D/I_G of a-C film and a-C films with 5 nm-thick G-N cap layers prepared by different electron irradiation energies. The I_D/I_G increased with the increasing of