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Role of transfer layer on tribological properties of nanocrystalline diamond nanowire film sliding against alumina allotropes

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ABSTRACT

The tribological properties of nanocrystalline diamond nanowire (DNW) film treated in CH_4 atmosphere at 400 °C were studied in ambient atmosphere at room temperature using various allotropes of alumina ball as sliding counterbodies. Super low value of friction coefficient (~0.003) and extremely high wear resistance (~2.8×10^{-21} mm^3/Nm) were observed when the Al_2O_3 ball slides against the film. In contrast, high friction coefficients with the values ~0.06 and ~0.07 were observed while using sapphire and ruby balls, respectively. Wear loss was also high ~4×10^{-19} mm^3/Nm and 2.8×10^{-15} mm^3/Nm in DNW/sapphire and DNW/ruby sliding pairs, respectively. Such a behavior is fundamentally explained in terms of the chemical nature of the sliding interfaces and surface energy of ball counterbodies. As a consequence, the chemical affinity of Al_2O_3 ball towards the carbon atoms is less, which resulted in the absence of carbonaceous transfer layer formation on the Al_2O_3 ball scar. However, in the case of sapphire and ruby balls, the wear track was found to be highly deformed and significant development of carbonaceous transfer layer was observed on respective ball scars. This phenomenon involving transfer layer formation is related to high surface energy and strong chemical affinities of sapphire and ruby balls towards carbon atoms. In such a condition, sliding occurs between film and the carbonaceous transfer layer formed on the ball exhibiting high energy due to covalent carbon bonds that chemically interact and enhance sliding resistance.

1. Introduction

Tribological efficiency needs advanced materials for specific engineering applications where sliding occurs between alternate materials [1,2]. In this regard, it is technically important to investigate ceramic counterbodies sliding against carbon based films like nanocrystalline diamond (NCD) and DNW [3,4]. In NCD films, the typical size of the diamond crystallites falls in the range of 15–30 nm. However, in DNW films, ultrananocrystalline diamond grains with sizes 3–5 nm are embodied in the wires. These wires have typical dimensions of 100–130 nm in length and 10–15 nm in diameter. Such films are an advanced class of materials which have normally low/ultra-low friction coefficients with high wear resistance in a wide range of operating conditions [5–8]. It is revealed from several investigations that mainly, formation of carbonaceous transfer layer on sliding ceramic counterbodies often influences tribological properties of diamond-like carbon and NCD films [2,3]. Interestingly, high friction coefficient and high wear rate were measured when NCD slides against SiC and Si_3N_4 balls [3]. Such a characteristic was explained by the formation of carbonaceous transfer layer on these balls that causes the development of covalent chemical bonding between the sliding interfaces, resulting in high friction. In contrast, ultra-low friction coefficient and high wear resistance were obtained while sliding against Al_2O_3, ruby and Zr_2O_3 balls [2,3]. Furthermore, super-low friction coefficient and high wear resistance were measured on H_2/O_2 plasma treated nanocrystalline DNW film while using Al_2O_3 balls [9,10]. This happens due to weak chemical interaction between sliding interfaces which restricts formation of covalently bonded transfer layer. In the early work, it is shown that the value of friction coefficient consistently decreases with increasing the humidity levels during the tribo-test performed on ultra-nanocrystalline diamond (UNCD) films [7]. This value is ~0.13 in low humidity which is significantly decreased to ~0.004 at highly humid conditions. Such a reduction in friction coefficient was ascribed to passivation of dangling covalent bonds of carbon atoms occurring due to the formation of chemical species such as C – COO, CH_3COH and CH_2 – O. In another work, friction coefficient of as-deposited DNW film showed a high value of ~0.2 while sliding against Al_2O_3 ball [9]. However, this value was decreased to a super low value ~0.0001 in H_2 plasma treated DNW film. Such super low valued friction coefficient is described by the passivation of uncompensated carbon dangling bonds by

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hydrogen ingress and adsorption of H_2O molecules. However, in the same H_2 treated DNW film, the friction coefficient is found to increase at low humid atmospheres. This was explained by insufficient chemical passivation of carbon dangling bonds. In the light of abovementioned facts, it was observed that there are very few reports on tribological properties of NCD and DNW films sliding against ceramic balls [3,11]. The specific mechanism responsible for glaring variation in friction behavior remains a matter of study in DNW films [9–11].

In this regard, the present study aims to investigate tribological behavior of nanocrystalline DNW film sliding against three similar classes of ceramic balls such as Al_2O_3, sapphire and ruby. Frictional behavior was analyzed with regard to microstructure and chemical composition of the sliding counterbodies. In addition, surface topography and surface energy of the sliding counterbodies were investigated to bring out correlation with friction and wear mechanism. Wear tracks of the film were chemically characterized by micro-Raman spectroscopy and micro-XPS to determine the chemical changes and their effect on tribological properties.

2. Experimental techniques

DNW films were deposited on silicon (100) substrates in N_2 (94%)/CH_4 (6%) plasma by an MPECVD (6 in. IPLAS-CYRANNUS) system, operating with microwave power and frequency of 1200 W and 2.45 GHz, respectively. During the deposition, the chamber pressure was kept at 70 mbar and total flow rate of gases was maintained at 100 sccm. An external heater was used to heat the substrate to a temperature of 700 °C. After the deposition of nanocrystalline DNW, the film was annealed in CH_4 atmosphere at 400 °C for 30 min. Surface morphology of the film was characterized by field emission scanning electron microscope (FESEM, JEOL, JSM-6500F). Atomic force microscope (AFM, Park XE-100) was used to investigate the topography of the film and corresponding local deformations in wear tracks. This was also used to investigate the topography and surface roughness (R_a) of the ball counterbodies. Chemical characteristics of the film and wear tracks were investigated by micro-Raman spectroscopy and micro-XPS. Raman spectra were recorded in back scattering geometry with a Renishaw micro-Raman spectrometer (Model INVIA), equipped with an Ar-ion laser operating at a wavelength of 514.5 nm. In these measurements, 100% laser power was used for 60 min of exposure time. More importantly, micro-XPS (ESCALAB 250) was carried out in wear tracks of nanocrystalline DNW film formed against Al_2O_3, sapphire and ruby balls to investigate C1s and O1s core levels and corresponding chemical compounds. Friction and wear behavior of films were measured by ball-on-disk tribometer (CSM, Switzerland) operating in a linear reciprocating mode. Al_2O_3, sapphire and ruby balls with 6 mm diameter were used as sliding counterbodies against nanocrystalline DNW film. The normal load and sliding speeds were kept constant at 5 N and 3 cm/s, respectively. A stroke length of 3 mm was used in each experiment. The tests were carried out in ambient (dry and unlubricated) atmospheric conditions with a relative humidity level of $66 \pm 3\%$. Each tribological experiment was performed three times and the data were found to be approximately similar. Wear profile after the test was measured by a Dektak 6M stylus profiler using 5 mg load with a scanning speed of 30 μm/s. In this method, tip of diamond stylus with a radius of curvature 12.5 μm was scanned across the wear track. Nanoindentation measurements were performed with a diamond Berkovich indenter at a loading–unloading rate of 2 mN/min. This was performed up to a maximum load of 2 mN. Oliver and Phar method was used to calculate the elastic modulus and hardness of the specimen [12]. Maximum penetration depth was kept less than 1/10 of the DNW film thickness to avoid the substrate effect during measurements. Similar parameters were used to measure the E and H of the ball used for tribology measurements. Measurements were repeated 5 times on each sample and no significant deviation was observed among experimental data.

3. Results and discussion

3.1. Film surface morphology

The top-view FESEM micrograph and cross section of CH_4 treated DNW film is shown in Fig. 1. It is observed that DNW film possesses dense and uniformly distributed wire-like granular morphology. These wires are composed of several NCD grains. The boundary of a wire consists of chemical impurities like a-C and $sp^2C{=}C$ bonded phases [13–15]. Thickness of the amorphous carbon and graphitic shield present around a nanowire varies from a few atomic layers to 5 nm [9]. The contact angle of such film is high (172°) and belongs to the hydrophobic class of nanostructured materials. Low surface energy can be attributed to the formation of microscopic cavities where air can be trapped and create the high pressure that repels the water droplet. In addition, surface energy of this film is lowered by chemical passivation of the surface by hydrogen atoms/molecules present during the nucleation/growth and CH_4 treatment.

3.2. Tribology test

Friction behavior of the nanocrystalline DNW film sliding against Al_2O_3, sapphire and ruby balls along with their wear profiles is shown in Fig. 2. Friction coefficient of DNW/Al_2O_3 sliding system is extremely low and its saturated value after a 300 m shows ~0.003. However, this value in DNW/sapphire and DNW/ruby is ~0.06 and ~0.07, respectively. These are more than one order of magnitude higher compared to DNW/Al_2O_3 sliding system. However, the trend in friction behavior measured in the sliding systems of DNW/Al_2O_3 and DNW/sapphire is similar. Conversely, such trend is not observed in the sliding system of DNW/ruby. The wear profile follows the trend of friction coefficient as shown in the inset of Fig. 2. Extremely low wear depth ~20 nm was observed in the sliding system of DNW/Al_2O_3 after 500 m sliding distance at 5 N normal load. This increases to ~45 nm and ~200 nm in the sliding systems DNW/sapphire and DNW/ruby, respectively. In all the cases, wear depth is much less than the film thickness which clearly indicates that sliding occurs well within the DNW film. Therefore, it is confirmed that there is no effect of substrate in friction and wear measurements. On the basis of wear track dimension, wear rate was calculated which is extremely low $\sim 2.8 \times 10^{-21}$ mm^3/Nm in DNW/Al_2O_3 sliding system. On the basis of data reported so far, this is the highest wear resistance of

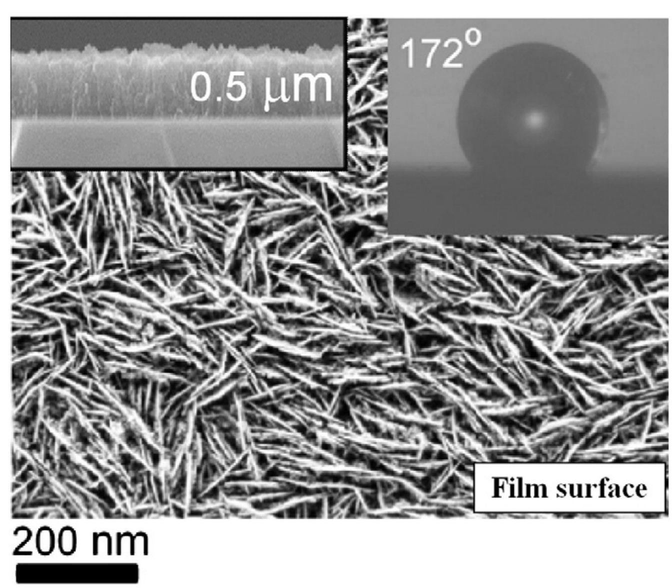

Fig. 1. Surface morphology and contact angle of nanocrystalline DNW film.