Evolution of transfer layers on steel balls sliding against hydrogenated amorphous carbon coatings in ambient air

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ABSTRACT

The evolution of transfer layers derived from a-C:H coating/steel ball tribopairs sliding in ambient air is tracked by performing one set of overlapping tribotests on a ball-on-plate device with acceptable repeatability of friction coefficients. After sliding tests, counterparts were separated and probed by optical microscopy, SEM/EDX and XPS. Carbon-based transfer layers were built up in the first cycle of sliding. Except for the typical graphitization of transferred carbon materials, a chemisorbed layer rich in C/O groups was also found on the top surface of transfer layers, and considerably affected the friction behavior of a-C:H coating/steel tribopairs in ambient air.

1. Introduction

Since the first deposition of diamond-like carbon (DLC) coating by Aisenberg and Chabot [1], hydrogenated amorphous carbon (a-C: H) coating has attracted great interesting for their outstanding performance such as high hardness and wear resistance, low friction in various conditions, chemical inertness and environmental friendship as solid lubricants [2,3]. While the mechanical property of a-C: H coating is critically affected by the deposition methods, carbon sources, working pressure, substrate temperature, post-treatments of coating, etc., its tribological performance is additionally affected by other factors such as friction atmosphere, relative humidity, loading conditions, sliding velocity, type of sliding motion, counterpart materials, etc., and the contribution from each factor to the overall friction varies from one type of a-C:H coating to another [3–8]. Generally, the friction coefficient (CoF) of a-C:H coating ranges between 0.05 and 0.3 in ambient atmosphere [3–6], and falls down to 0.01 in inert atmospheres (e.g. ultra-high vacuum (UHV) [9–13], dry N_2 [5,14–16]) and dry H_2 [10–13].

The presence of H_2O and O_2 molecules in sliding atmosphere affects CoF strongly, and generally causes additional friction force of a-C:H coating. Typically, Erdemir [5] reported a great increase of CoF from 0.001 in dry nitrogen to 0.04 in humid N_2 with additional presence of O_2 and to 0.06 in humid air. The reason put forward in Ref. [5] is that lots of free σ-bonds are created on sliding surfaces,

which chemically bond to active species in surrounding atmosphere and form strong adhesion forces between counterfaces. Similar degradation of friction caused by increasing adhesion force has also been discussed by others [11,13,17]. Kim [8] observed a different dependence of humidity on the CoFs of a-C:H coating sliding in Ar atmosphere and ambient air. In his experiment, when the relative humidity of Ar atmosphere increased from 0% to 50% and 100%, the steady CoF grew up from 0.06 to 0.19 and 0.99, whereas in the air of same humidity the CoF only fluctuated from 0.16 to 0.08 and 0.19, respectively. Yuichi [18] found that when the plasma-deposited a-C:H coating was exposed in ambient air with relative humidity of 50% for hours, an oxidation layer as thick as ~1 nm with high content of C=O and C–O–C groups was formed on the top surface and led to a rise of CoF from 0.2 to 0.4 in humid air. However, different phenomena were also reported by Donnet et al. [19] by controlling the partial pressure of H_2O and O_2 in UHV. When the partial pressure of O_2 in UHV increased from 0 to 60 hPa, the ultra-low friction behavior of a-C:H coating did not change markedly. In contrast, when the partial pressure of water vapor in UHV only increased from 0 to 0.5 hPa (relative humidity 2%), the CoF jumped from 0.01 to 0.1. They attributed this jump of friction to the reduced thickness of transfer layer [19]. Similarly, a weaker tribochemical role of O_2 than H_2O in high CoF behavior was described in Ref. [20].

In the study of steady low friction in various atmospheres, the formation of a durable transfer layer has been considered as a dominant factor which keeps rubbing counterparts apart and makes shear strength mainly occur between transfer layer and underneath coating. The shearing ability of transfer layer strongly

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depends on the nature of atmosphere and the tribochemical interactions between counterfaces [21]. In order to investigate the chemical characteristic of transfer layer, various detection methods have been applied and generally observed a disordered graphitic structure which was different from parent amorphous coating [14,15,22,23]. Raman spectroscopy is particularly popular in the structural analysis of wear marks because of its simplicity, time efficiency and high sensitivity to C/C bonds. Typically, a Raman spectroscopy designed for in situ detection of transfer layer was applied by Scharf and Singer et al. [24–29] to track the shift of G and D peaks with increasing sliding distance without counterpart separation. However, in order to make a compromise of data acquisition and spectra resolution, all the tribotests in their study were performed at a low sliding velocity as 1 mm/s, and the obtained Raman spectra represented comprehensive information on transfer layer and underneath coating. Besides, the carbon oxides [8,18] and metal oxides [29] mixed in transfer layer can hardly be analyzed unambiguously by Raman.

The major objective of this study is to track the friction and wear of a-C:H coating/steel ball tribopairs sliding in ambient air and identify the effect of tribochemical oxidation of transfer layer on CoFs. Instead of using in situ techniques, the tracking of friction at moderate sliding speed was achieved by performing one set of overlapping tribotests which contains various sliding distances under the same conditions. Based on a reasonable repeatability of CoF curves, the structural evolution of transfer layers in long-duration friction was investigated quantitatively by ex situ X-ray photoelectron spectroscopy (XPS).

2. Experimental details

2.1. a-C:H coating deposition

Four a-C:H coatings grown by ion vapor deposition were studied in this paper. A base pressure less than 3×10^{-3} Pa was achieved in vacuum chamber before deposition. Carbon source toluene (C_7H_8) was ionized by a hot filament, and the components of resulting ionized species were detected by a quadruple mass spectroscopy. Results revealed that due to the low ionization efficiency of the hot-filament method, the fragmentation degree of C_7H_8 was low with larger content of $C_7H_7{}^+$ and other less species such as $C_8H_{10}{}^+$, $C_5H_9{}^+$, $C_3H_3{}^+$, $C_2H_4{}^+$, CH^+, C^+, H^+ in ion vapor. Ionized species were coated onto negatively pulse-biased Si (100) substrates (atomically smooth) at 200 °C for 3 h. The negative pulse voltage was applied in frequency of 1 KHz at duty of 25%. All the coatings were typically amorphous with sp^2 C/ sp^3 C ratio as 1.4–1.6 (measured by XPS), contact angle as 65–70° (measured by dripping distilled water droplets on coatings in ambient air) and average roughness Ra below 0.3 nm (measured by AFM scanning). More detailed deposition parameters and properties of studied coatings are listed in Table 1.

The microhardness and elastic modulus shown in Table 1 were measured by an Elionix ENT-2100 nanoindentation system. 1000 μN load was applied lineally on a well-profiled Berkovich pyramid diamond indenter (edge angle 115°, inclination angle 65.03°, tip defect ∼10 nm) in 500 steps at a loading speed of 0.1 mN/s. The maximum load was kept for 1000 ms and induced full plasticity on tested spots, and then unloaded at the same speed of 0.1 mN/s. The elastic modulus of studied coatings E_S was determined by the equation [30–32]:

$$\frac{1}{E^*} = \frac{1 - \nu_S{}^2}{E_S} + \frac{1 - \nu_I{}^2}{E_I}$$

in which

$$E^* = \frac{S\sqrt{\pi}}{2\sqrt{A}}$$

$$A(h_A) = 3\sqrt{3}\tan{}^2 65.03° \, h_A{}^2$$

$$h_A = h_{max} - 0.75F_{max}/S$$

where E^* is the reduced elastic modulus, E_I the elastic modulus of diamond indenter, ν_S and ν_I the Poisson's ratio of tested coating and diamond indenter respectively, S the experimentally measured stiffness of upper portion of unloading curve equals to $|dF/dh|_{Fmax}$, A the projected area of elastic contact, h_{max} the maximum deformation at peak load, h_A the calibrated elastic deformation considering tip defect [32], F_{max} the peak load. More than 30 points were tested on each coating for average evaluation. The indentation depth was generally 4–7% of coating thickness to eliminate the deformation effects of silicon substrate.

Additionally, the hydrogen content of studied coatings was measured by applying high-resolution elastic recoil detection analysis (ERDA) with a probe beam of 0.5 MeV nitrogen ions N$^+$ incident on the coating at an angle of 67.5° with respect to the surface normal. Detection of recoiled protons was performed at an angle of 45.6°. The coating thickness was measured by SEM cross-sectional observation.

2.2. Tribotests of a-C:H coatings

Sliding tests were performed in ambient air (relative humidity 25 ± 2%) at room temperature by applying a standard CSM ball-on-plate tribometer in overlapping pattern, namely all the sliding tests were started from the first cycle by using a new ball and new a-C:H coated plate and continued for various pre-selected number of cycles $N=\{1, 5, 45, 681, …, 2274, 4547, 11,368, 45,473, 68,209\}$, correspondingly $d=\{0.022 \text{ m}, 0.044 \text{ m}, 0.11 \text{ m}, 5 \text{ m}, …, 50 \text{ m}, 100 \text{ m}, 250 \text{ m}, 1000 \text{ m}, 1500 \text{ m}\}$ under the same sliding condition, where N was the number of sliding cycles, d the sliding distance. Well polished ISO 4957 100Cr2 (JIS SUJ-2, hardness 8 GPa, Young's modulus 210 GPa, $Ra=10$ nm) steel balls in diameter of 6 mm was used as stationary counterparts, and approximately made a Hertz contact pressure of 0.6 GPa (see detail in Table 2) under 5 N normal load. Detailed chemical composition of 100Cr2 steel is shown in Table 3. Circle tracks in radius of 3.5 mm were generated on studied coatings at a sliding velocity of 15 cm/s always in one direction. The CoF curve (as a function of sliding cycles expressed as $f(N)$) of the longest duration test, i.e. $f(N=68,209)$ was compared with $\{f(N=1), f(N=5),…, f(N<68,209)\}$ for the confirmation of data repeatability. At least 9 couples of coating/steel

Table 1
Deposition parameters and properties of a-C:H coatings.

Samples of coating	Working pressure (Pa)	Bias voltage (KV)	Thickness (nm)	Microhardness (GPa)	Elastic modulus (GPa)	Roughness Ra (nm)	Hydrogen (atomic %)	Avg. CoF in air
1#	0.1	−2	945	16.30	160.60	0.245	19.5	0.148
2#	0.1	−1.5	810	14.40	189.76	0.138	21.9	0.149
3#	0.4	−1.5	1760	18.06	180.54	0.247	20.5	0.134
4#	0.4	−2.5	2400	16.93	176.58	0.135	19.0	0.137