In situ tribochemical formation of self-lubricating diamond-like carbon films

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A B S T R A C T

Diamond-like carbon (DLC) films were tribochemically formed from ambient hydrocarbons on the surface of a highly stable nanocrystalline Pt-Au alloy. A sliding contact between an alumina sphere and Pt-Au coated steel exhibited friction coefficients as low as $\mu = 0.01$ after dry sliding in environments containing trace (ppb) organics. Ex situ analysis indicated that the change in friction coefficient was due to the formation of amorphous carbon films, and Raman spectroscopy and elastic recoil analysis showed that these films consist of sp^2/sp^3 amorphous carbon with as much as 20% hydrogen. Transmission electron microscopy indicated these films had thicknesses exceeding 100 nm, and were enhanced by the incorporation of worn Pt-Au nanoparticles. The result was highly wear-resistant, low-friction DLC/Pt-Au nanocomposites. Atomistic simulations of hydrocarbons under shear between rigid Pt slabs using a reactive force field showed stress-induced changes in bonding through chain scission, a likely route towards the formation of these coatings. This novel demonstration of in situ tribochemical formation of self-lubricating films has significant impact potential in a wide range of engineering applications.

1. Introduction

Surface catalysis routes are often employed in industrial and commercial applications to process organic species [1–4]. Examples include the use of precious metals like Pt, Rh and Pd in catalytic converters to convert toxic constituents found in combustion engine exhaust gas (e.g. complex hydrocarbons such as unburned alkanes) into simpler and less toxic compounds like carbon dioxide and water [1]. In many cases, surface reaction rates are enhanced by increasing the temperature of the catalyst, or applying a shear stress [5–11].

While the promise of Pt-Au alloys has been previously discussed in the catalysis literature [12,13], we show that a unique subclass of Pt-Au alloys showing highly stable nanocrystallinity [14] and extraordinary wear resistance [15] enabled the formation of diamond-like carbon (DLC) films — one of the most wear resistant and lubricious materials known — either from ambient organics or intentionally supplied hydrocarbons (alcohols or hexanes). Unlike conventional synthesis routes for DLC coatings, we show it is possible to generate highly lubricious and wear-resistant hydrogenated amorphous carbon films in situ through shear of a Pt-Au alloy surface in the presence of organic adsorbates at room temperature in the absence of free oxygen.

DLC films can exhibit extraordinarily high hardness and wear resistance, and, when sufficiently hydrogenated, some of the lowest friction coefficients of any solid [16–18]. Hydrogenated DLC, or more generally hydrogenated amorphous carbon (a-C:H), is used in a wide range of commercial applications (e.g. bearings, gears and mechanical linkages in satellites, wind turbines and automobiles), primarily as thin films, to impart low friction and high wear resistance [16,17,19]. When a-C:H exhibits extremely low friction in inert or vacuum environments ($\mu \cong 0.001 - 0.05$; 10 N load) [20], it is generally attributed to hydrogen passivation of unterminated carbon surface bonds [21]. Unlike other low friction carbonaceous coatings that require humid environments (e.g. a-C, graphite), a-C:H typically exhibits increasing friction coefficients with exposure to humidity ($\mu \cong 0.2 - 0.3$; 10 N load) [20,22]. DLC coatings are routinely manufactured via plasma enhanced-chemical vapor deposition (PECVD) from hydrocarbon feed gases [17]. A recent publication demonstrated how transition metal-nitride coatings can act as a catalyst for the formation of low-friction solid carbon films from fluid lubricants [6], but these films were observed

outside of the region of contact and did not confer enhanced lubricity. Here we show in situ tribochemical formation of thick, persistent, low friction a-C:H films from adventitious carbon and ambient organics, including simple alcohols and alkanes, at room temperature.

2. Methods

2.1. Material synthesis

Thin films of Pt with 10 at. % Au (hereafter Pt-Au) were deposited by direct current (DC) magnetron sputtering using a cryo-pumped vacuum system with a base pressure of 2×10^{-7} torr. Films were prepared from a single, high purity Pt-Au deposition target (Refining Systems) that was pre-sputtered for approximately 5 min prior to the start of each deposition to avoid incorporation of adventitious carbon or other impurities in the deposited films. Ultra-high purity Ar (99.999%) was used for all sputter processes, and substrates did not exceed 50 °C during deposition. A quartz crystal monitor was used to determine film thickness with Angstrom-level precision. Film composition was verified by Electron Microprobe Analysis (EMPA). A JEOL model JXA-8530F Microprobe operating at 7.0 keV incident energy (20 nA, 2 μm beam diameter) was used to determine the composition of a 1 μm thick Pt-Au witness film. The average of 50 spaced measurements was used to demonstrate a film composition of $Pt_{.90}Au_{.10}$, with an experimental accuracy of 1.89% relative to measured standards. Reference materials of known compositions for Pt and Au were used from Taylor Metal Standards (Charles Taylor Multi Element Standard No. 202, Sept 1976), utilizing Pt M_{α} line and Au M_{β} line for composition calculations. Friction experiments were performed on 2 μm thick Pt-Au films deposited on polished 440C stainless steel coupons.

2.2. Tribological testing

The wear, friction, fatigue, and other mechanical properties of these films are described in detail in separate manuscripts [15,23]. Briefly, we found that these films exhibited extraordinary wear resistance (specific wear rates of about $3 \times 10^{-9} \pm 1 \times 10^{-9}$ mm^3/N-m), low friction coefficients ($\mu \cong 0.25 - 0.30$ over 100k sliding cycles in laboratory air), and high nanoindentation hardness (7.1 ± 0.4 GPa) [15]. In the following, we show that the ability of these films to withstand high applied stresses favorably coupled with the well-known catalytic properties of pure Pt and Pt-Au alloys to enable the formation of DLC films.

Friction coefficients were measured for 3.2 mm diameter sapphire spheres sliding against Pt-Au thin films deposited on 303 stainless steel using a 1 N normal force, corresponding to a 41 μm contact diameter and a 1.1 GPa maximum Hertz stress. A sliding speed of 1 mm/s and wear track length of 2 mm were used in bidirectional sliding motion, exposing any given location on the wear track to the ambient environment in the test chamber for approximately 2 s per contact pass. Tribological testing was performed on a modified Anton Paar Nano Tribometer housed in an acrylic glove box; modifications include a stepper motor (PI Instruments PLS 85), National Instruments data acquisition hardware (PXIe 1073 and 6361) and custom LabVIEW software. Position encoded normal and friction forces were acquired at 50 Hz. Experiments performed in lab air were performed with the gloves removed from the chamber, exposing the tribometer to ambient air that was temperature regulated to 20—22 °C at a relative humidity of 12—17%. To create an oxygen-free environment, the box was purged using 34 L/min flow of ultra-high purity (UHP) nitrogen until < 10 ppm of O_2 and H_2O were present, as measured using an

Alpha Omega 3000 series oxygen analyzer and Michell Instruments S8000 precision chilled mirror hygrometer. Samples were also exposed to mixed flows of N_2 and isopropyl alcohol (IPA), or N_2 and anhydrous hexanes, in a nitrogen purged glove box. In both instances, a 34 L/min ultra-high-purity nitrogen stream was used to continuously purge the chamber, while a second 1.4 L/min stream of ultra-high-purity nitrogen was routed through a vessel filled with approximately 3L of either water and liquid IPA or anhydrous hexanes. A diffuser stone was used to maximize exposure of the nitrogen gas to the liquid medium. In referencing data from these experiments below, the term "high concentration" is used to describe situations in which the hydrocarbon stream was directed at the sliding contact, while "low concentration" is used when the hydrocarbon stream was directed away from the contact, resulting in dilution from mixing with the continuously flowing UHP nitrogen purge stream.

2.3. Microscopy

Raman Spectroscopy was performed on tribofilms using a Horiba LabRam HR Spectrometer equipped with a 600 grooves/mm grating, a Synapse CCD detector, and a 50x microscope objective with a spectral resolution of 0.3 cm^{-1} at 680 nm and 1800 gr/mm. A 532 nm laser line set at an output of 10 mW was used as the excitation source, resulting in an incident 1.5 mW on the sample surface as measured by a Pocket Laser Power meter 840011 with a 1.55 signal correction factor. Sampling was performed using a DuoScan method over a spot size of approximately 80 μm × 60 μm. Using a pinhole setting of 100 μm, typical collection times ranged from 5 to 20 s with 20 scans collected to increase the signal to noise ratio. An FEI Helios G3 dual beam focused ion beam (FIB) with electron imaging and Ga-ion milling capabilities was used to image the wear track surfaces and to prepare electron transparent cross-sectional specimens for imaging via transmission electron microscope (TEM). An FEI Titan™ G2 80—200 scanning transmission electron microscope (STEM) with a Cs probe corrector operated at 200 keV was used in this study. An electron probe smaller than 0.13 nm with a convergence angle of 18.1 mrad, and a current of ~75 pA was used for data acquisition. A Bruker Contour GT-I optical interferometer was used to determine wear volumes. The entire length of each wear scar was imaged using the stitching feature on the Vision64 software, using a 10x objective and 2x magnified, providing a pixel resolution of 500 nm in the lateral and <1 nm in the vertical (height) directions. Wear rates were determined using topographical data from each track, excluding the ends of the wear tracks where sliding speeds vary and wear debris pile-up occurs from the reciprocating motion of the slider. The specific wear rate (K) of the Pt-Au track was calculated using the expression $K = \frac{A}{F_n \cdot N} \cdot 1000 \frac{mm}{m}$, a ratio of average wear track cross-sectional area (A), contact force (F_n), and number of cycles (N). A more detailed explanation of volumetric wear rate calculations based on mean cross-sectional wear track area and the uncertainty in this calculation is provided elsewhere [24,25].

2.4. Gas composition analysis

Analysis was performed to identify the concentrations of organic species present in the dry nitrogen purged glove box that housed the friction testing apparatus. Samples were tested using a Perkin Elmer (Groton, CT) Turbo Matrix ATD thermal desorption unit. Gas samples were pumped through a pre-conditioned thermal desorption tube (Perkin Elmer Tenax TA Thermal Desorption Tubes, ¼" (6.35 mm) O.D. x 3.5" (89 mm) long), and desorbed at 300 °C for 10 min. The outgassed species were trapped on a M041-3628 Air