Surface & Coatings Technology 260 (2014) 290–302

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Tribological behavior and machining performance of non-hydrogenated diamond-like carbon coating tested against Ti–6Al–4V: Effect of surface passivation by ethanol

S. Bhowmick, A. Banerji, A.T. Alpas *

Mechanical Automotive and Materials Engineering Department, University of Windsor, Windsor, ON N9B3P4, Canada

ARTICLE INFO

Available online 15 July 2014

Keywords:
Diamond-like carbon
Running-in friction
Surface passivation mechanism
Ethanol blended lubricant
Machining performance
Ti alloys

ABSTRACT

The role of an ethanol environment on the tribological behavior of non-hydrogenated DLC (NH-DLC) coatings sliding against Ti–6Al–4V was investigated. Pin-on-disk tests were performed under different test atmospheres consisting of dry argon (0% RH) and ambient air (40% RH) and also while the samples were submerged in water (H_2O) and ethanol (C_2H_5OH). The running-in friction of the NH-DLC coatings under each condition was studied and the results were used to rationalize the drilling behavior of Ti–6Al–4V by NH-DLC coated tools. The highest running-in coefficient of friction ($\mu_R = 0.55$) was observed under a dry argon atmosphere. In ambient air, the μ_R was 0.42, while a reduction in μ_R to 0.21 was recorded when the tests were carried out in H_2O. The observed reductions in μ_R were attributed to OH passivation of the NH-DLC surfaces. Ethanol was effective in providing OH passivation, as evident from the lowest μ_R of 0.15. Consistent with the friction measurements, a 45% reduction in drilling torque was obtained when 10% ethanol was blended with the metal removal fluid (MRF) consisting of water–oil (1:3) mixture compared to an ethanol free MRF.

1. Introduction

Diamond-like carbon (DLC) coatings have consistently displayed low coefficient of friction, COF or μ, values when tested against technologically significant lightweight aluminum, magnesium and titanium alloys. Several studies that used counterfaces coated with DLC have shown that DLC coatings minimized the adhesion and restricted material transfer from the surfaces of these alloys. The DLC coatings provide significant opportunities for expanding the applications of lightweight materials by improving their performance in components operating under sliding contact conditions (e.g. powertrain elements in combustion engines). The use of DLC coated tools and dies was reported to improve the surface quality of aluminum and magnesium sheets or castings during machining and shaping operations [1–8]. A shortcoming of DLC coatings is the fact that their tribological properties are highly sensitive to the environmental conditions as their friction, wear, adhesion behavior may change drastically with small changes in the composition of the gas or liquid atmospheres present in the tribosystem. The friction behavior of the hydrogenated (a-C:H or H-DLC) and non-hydrogenated DLC (a-C or NH-DLC) coatings was found to exhibit almost opposite trends under vacuum and inert (i.e. N_2 or Ar) atmospheres. Among the studies conducted on ferrous materials, Erdemir [9] showed that H-DLC coatings tested in dry N_2 atmosphere against H-DLC coated H13 grade steel disks generated a coefficient of friction (COF), μ of 0.005, while the NH-DLC produced a μ of 0.75. The very low μ value in the case of H-DLC was attributed to the passivation of σ-carbon bonds at the contact surface by the hydrogen atoms. For aluminum alloys, Konca et al. [10] reported a high μ of 0.52 for NH-DLC against an Al-6.5% Si alloy, under vacuum (6.65×10^{-4} Pa). The same NH-DLC when tested in an ambient atmosphere (47% RH) produced a low μ of 0.16. The μ of NH-DLC tested against Al alloys was shown to decrease with increasing the moisture in the surrounding environment [5, 13]. The decrease in μ of the NH-DLC coating in moist air was attributed to the passivation of the dangling carbon bonds by the OH groups dissociated from the water vapor in the atmosphere during the tribological contact as described in [10]. First principle atomistic study [11] provided quantitative support for this mechanism, by showing that the dissociation of water to OH molecules at the interface is possible and the static work of separation between the OH−C (111)/OH−C(111) atoms is considerably lower than Al/non-passivated coating surface thus resulting in lower magnitudes of μ in the case of OH passivated surfaces. An ab initio study [12] based on density-functional theory (DFT) and

* Corresponding author. Tel.: +1 519 253 3000x2602; fax: +1 519 973 7085.
E-mail address: aalpas@uwindsor.ca (A.T. Alpas).

http://dx.doi.org/10.1016/j.surfcoat.2014.06.066
0257-8972/© 2014 Published by Elsevier B.V.

generalized gradient approximations (GGA) of two (2 × 1)-C(001) surfaces terminated by hydroxyl groups showed that repulsive interactions between them were greater than termination due to H groups and thus could account for the low friction experimentally observed in [10].

Another requirement for the attainment of low μ observed in the case of NH-DLC is the formation of a carbonaceous transfer layer on the counterface [13]. Surface analysis studies [7,14] suggested that the carbonaceous transfer layers were possibly hydrated, and hence contributed to low friction. These transfer layers form early in the sliding process during the running in period where the peak running-in coefficient of friction (μ_R) is high followed by a low steady state coefficient of friction (μ_S). Notable reductions in COF have been observed in case of NH-DLC (0.14–0.18) sliding against Mg and Ti alloys, in addition to Al alloys, for tests conducted in air with 29–85% RH [5,15–17] again with a high μ_S and a low and stable μ_R.

Parallel to the tribological studies summarized above, Bhowmick and Alpas [18] examined cutting performances of NH-DLC coated HSS drills using an aqueous minimum quantity of lubrication method (H_2O-MQL). During H_2O-MQL drilling of Al-6.5% Si with NH-DLC coated drills, using water sprayed at a rate of 30 ml/h, an average drilling torque of 1.65 N-m was measured, which represented a significant reduction compared to dry drilling that generated a torque of 4.11 N-m. Machining of magnesium alloy AZ91 using NH-DLC coated drills under similar (H_2O-MQL) conditions was also examined [19]. The application of H_2O-MQL reduced the drilling torque to 1.46 N-m compared to the dry drilling using NH-DLC (12.73 N-m). The OH passivation of NH-DLC was cited as the possible reason for the reduced torque values. It was found that the range of average drilling torque values generated during H_2O-MQL drilling using NH-DLC coated tools (0.98–1.05 N-m) was lower than that observed in the case of flooded drilling (1.93–2.42 N-m) of Mg using conventional tools.

In summary, the above review indicates that surface passivation of NH-DLC by OH has a positive effect on the friction performance of these coatings. There is also some evidence that OH enrichment of the lubricants used in tribological tests may lead to the friction reduction. Kano et al. [20] reported very low μ of 0.03 for NH-DLC sliding against itself for tests lubricated with ester based lubricant glycerol monooleate (GMO). Using time-of-flight secondary ion mass spectroscopy (ToF-SIMS) formation of an OH-terminated carbon surface was detected. The low μ was discussed in terms of Van der Waals interactions between the two carbon surfaces passivated by OH groups originating from the GMO lubricant. Matta et al. [21] performed similar sliding experiments in which NH-DLC sliding against itself was lubricated with glycerol in the presence of hydrogen peroxide resulting in a μ value of 0.03. X-ray photoelectron spectroscopy (XPS) and ToF-SIMS observations supported the earlier view that carbon surfaces terminated by OH would lead to low values of friction.

The objective of this paper is to investigate the effect of surface passivation mechanism on the tribological behavior of NH-DLC coatings. Sliding experiments are designed to measure friction and wear under controlled atmospheres that provided potential different degrees of passivation. Ti–6Al–4V pins were used as counterfaces against NH-DLC coated M2 steel disks in such a way that the Ti–6Al–4V/NH-DLC contact interface was submerged either in water or in ethanol Tests were also performed in dry argon (0% RH) and ambient air (40% RH) atmospheres, i.e., under the conditions that are known to create high μ values. Surface characterization methods were used to investigate the compositions of the contact surfaces and transfer layers with particular attention to the detection of OH passivation effect. The surface tribochemistry was studied using Fourier transform infrared spectroscopy (FTIR) and micro-Raman spectroscopy. Low friction results obtained from tribological tests during NH-DLC sliding against Ti–6Al–4V alloy in ethanol suggested that the use of the NH-DLC in combination with metal removal fluid (MRF) blended with ethanol would facilitate machining of this alloy.

2. Experimental details

2.1. Material properties

NH-DLC coatings were deposited on AISI M2 grade tool steel disks and WC–Co drill using an unbalanced magnetron sputtering system equipped with one chromium and two graphite targets. A 0.10 μm Cr interlayer was deposited on 25.10 mm diameter M2 disks to promote coating adhesion followed by the deposition of 1.50 μm thick NH-DLC coating on top. The hydrogen content of the NH-DLC coating measured using elastic recoil detection (ERD) was <2.00 at.%. The hardness and the elastic modulus of the coatings were calculated from the loading–unloading curves obtained by a Berkovich type nano-indenter that penetrated to a maximum depth of 200 nm below the surface. Average hardness and elastic modulus values were 13.00 ± 1.10 GPa and 158.55 ± 6.82 GPa. The NH-DLC coated coupons were tested against Ti–6Al–4V pins with a rounded tip of 4.01 mm in diameter. Ti–6Al–4V had the following composition (in wt.%): 5.50–6.75% Al, ≤0.08% C, ≤0.4% Fe, ≤0.03% N, ≤0.2% O, ≤0.02% H, 3.50–4.50% V and the balance Ti. The microhardness of the Ti–6Al–4V was 380.00 ± 3.01 HV.

2.2. Pin-on-disk tests

Pin-on-disk type wear tests were performed on NH-DLC coated coupons using a CSM tribometer. Tests were done in four different environments consisting of (i) dry Ar atmosphere with 0% RH, (ii) ambient air with 40% RH (iii) distilled water and (iv) anhydrous (99.9%) ethanol. During the last two tests the NH-DLC coated M2 steel disks were submerged in reservoirs filled with fluid. Sliding tests were performed at a linear sliding speed of 0.12 m/s and under the application of 5.00 N normal load (Hertzian contact pressure = 1095.5 MPa) for 3.00 × 10^3 cycles where the peak running in coefficient of friction (μ_R), number of revolutions of the running-in (t_R) and the steady state coefficient of friction (μ_S) were recorded. Each test was repeated at least 3 times.

Following the sliding tests, the Ti–6Al–4V pin contact surfaces were examined by a scanning electron microscope (SEM) and their compositions were analyzed using energy dispersive spectroscopy (EDS), Fourier transform infrared spectroscopy (FTIR) and micro-Raman analyzer. The energy dispersive X-ray spectroscopy (EDS) spectra were recorded using an FEI Quanta 200 FEG SEM equipped with an EDAX SiLi detector spectrometer. FTIR analyses were conducted using a Thermoelectron Nicolet 760 spectroscope in reflectance mode at two different spots using a 100 μm × 100 μm aperture. The Raman spectra of the transfer layers were obtained using a 50 mW Nd-YAG solid state laser (532.00 nm excitation line) through the 50× objective lens of a Horiba Raman micro-spectrometer.

2.3. Drilling tests

Drilling tests were conducted on the Ti–6Al–4V alloy using NH-DLC coated and uncoated WC–Co drills with 6.35 ± 0.01 mm diameter. The drilling tests were performed at a cutting speed of 2500 rpm (50 m/min) using a feed rate of 0.25 mm/rev. The time interval between consecutive holes was 5 s. The flow rate used for supplying MRF was 30,000 ml/h and the temperature of the MRF at the inlet was 18 °C. A total of 100 holes were drilled with a horizontal center to center spacing of 10 mm between them. Each hole was 19 mm deep. The temperature measurements presented in the paper are taken from the last hole. The tests were conducted under the following conditions: (i) dry: drilling without using MRF; (ii) flooded: drilling using a water based MRF, consisting of a mixture of water and oil blended at a ratio of 1 to 3 and (iii) flooded with 10 vol.% ethanol: drilling using the same water/oil (1:3) based MRF as in (ii) but with an addition of 10 vol.% ethanol. Exploratory experiments that used different volume percentages of ethanol mixtures showed that MRF blended with 10% or greater percentage of ethanol by volume showed no difference in the torque