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High temperature tribological behavior of tetrahedral amorphous carbon (ta-C) and fluorinated ta-C coatings against aluminum alloys

S. Bhowmick [a], A. Banerji [a], M.Z.U. Khan [a], M.J. Lukitsch [b], A.T. Alpas [a,*]

[a] *Mechanical Automotive and Materials Engineering Department, University of Windsor, Windsor, ON N9B3P4, Canada*
[b] *Chemical Sciences and Materials Systems Laboratory, General Motors R&D Center, 30500 Mound Road, Warren, MI 48090-9055, USA*

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ABSTRACT

Friction and wear behavior of tetrahedral amorphous carbon (ta-C) and fluorinated ta-C (ta-C–F) coatings were studied in the temperature range between 25 °C and 500 °C. Pin-on-disk type tests conducted on ta-C against Al–6.5% Si (319 Al) showed that the steady-state coefficient of friction (μ_s) decreased from 0.36 at 25 °C to 0.11 at 400 °C. The reduction in friction was attributed to sliding-induced sp^3 to sp^2 transformation (graphitization) of the coating and formation of oxygen rich transfer layer as revealed by X-ray photoelectron and micro-Raman spectroscopy. The coefficient of friction of ta-C–F also decreased with an increase in the test temperature. A low μ_s of 0.13 was observed at 400 °C compared to 0.39 at 25 °C. The maximum value of running-in coefficient of friction (μ_R) for ta-C–F tested at 400 °C was 0.38, lower than the μ_R of ta-C (0.65). Both coatings maintained low wear at elevated temperatures but at 500 °C they showed high wear and high coefficient of friction and did not reach a steady state friction regime. The atomic % of F transferred to the Al surface increased with an increase in the test temperature up to 400 °C. It was suggested that a sp^2 carbonaceous transfer layer passivated by F atoms was responsible for the further decrease in μ_s and μ_R of ta-C–F at elevated temperatures (200 °C–400 °C) compared to ta-C.

1. Introduction

Diamond-like carbon (DLC) coatings provide low friction to aluminum alloys by minimizing the adhesive transfer of aluminum in sliding components such as gears, piston rings, dies and machining tools [1–6]. However, tribological properties of DLC coatings deteriorate at high temperatures. The pin-on-disk tests conducted at elevated temperatures determined that the low coefficient of friction (COF) values of hydrogenated (H-DLC) tested against aluminum were maintained up to a temperature of 200 °C and for non-hydrogenated (NH-DLC) only up to 100 °C [7–9]. The NH-DLC coating has a high volume fraction of sp^2 bonded C atoms. The low COF (0.10–0.15) of NH-DLC coatings tested in ambient air (25 °C) was attributed to passivation of the dangling carbon bonds at the contact surfaces by OH and H atoms. High COF (0.50–0.60) observed at elevated temperatures was suggested to occur as a result of an increase in the sp^2 bonded C atoms and structural transformations in the C network [8,10–16]. The sliding induced compositional changes led to coating failure at above 300 °C causing significant aluminum adhesion to the substrate. However, in many manufacturing applications including aluminum alloy machining and warm forming temperatures range between 300 and 400 °C. The prospective DLC tool coatings intended for these applications should maintain their adhesion mitigating properties while operating at elevated temperatures. Recent studies have shown that Si and W addition to the DLC improved thermal stability of both H- and NH-DLC [11,14,17–20].

The tetrahedral amorphous carbon (ta-C) coatings differ from the sp^2 rich NH-DLC and H-DLC coatings as they possess a high volume fraction (80%) of sp^3 bonded C atoms—close to the diamond and may be suitable for high temperature tribological applications [21–27]. Alam et al. [22] used nuclear magnetic resonance (NMR) spectroscopy to determine the sp^3 content of ta-C upon heating. A 2% decrease in the sp^3 content was observed after heating to 650 °C. Ferrari et al. [21] using electron energy loss spectroscopy (EELS) and ultraviolet Raman spectroscopy, observed that the initial high sp^3 fraction (87%) of the ta-C remained constant up to an annealing temperature of 700 °C and decreased slightly between 700 °C and 1100 °C, which was followed by an abrupt decrease to 20% at 1200 °C. Similar results were found by Orwa et al. [23] using transmission electron microscopy (TEM) combined with EELS and Raman spectroscopy that determined a small increase in sp^2 content of ta-C when the ta-C films were annealed up to 800 °C, whereas annealing above 1000 °C led to a large increase in the amount of sp^2 bonding. Chen et al. [24] used TEM/EELS studies and found no increase in the sp^2 fraction of ta-C content after annealing at 600 °C, but a significant structural change was noted at 1000 °C. Grierson et al. [25] investigated the thermally induced sp^3 to sp^2 conversion of carbon-carbon bonds in ta-C films using near-edge X-ray absorption fine structure (NEXAFS) and Raman spectroscopy. Again, no

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[*] Corresponding author.
E-mail address: aalpas@uwindsor.ca (A.T. Alpas).

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notable change in bonding structure occurred at temperatures as high as 600 °C, but at 1000 °C the sp^3 structure of ta-C converted to sp^2. Deng et al. [28] studied the elevated temperature tribological behavior of ta-C coatings between 100 and 500 °C against a Si_3N_4 counterface. The ta-C maintained a low COF of 0.06 up to 400 °C, while a high COF of 0.41 was observed at 500 °C. The low COF of ta-C was attributed to the formation of graphite like transfer layer on the counterface. In summary, laboratory studies indicated that the ta-C remained thermally stable up to 600–700 °C upon annealing and up to 400 °C during sliding contact. A micro-Raman and XPS based study [17] that investigated the annealing behavior of H-DLC showed that on annealing at 300 °C, H desorption of the coating occurred and coating became oxidized at 400–500 °C. On the other hand an addition of Si to the H-DLC coatings led to Si-C sp^3 bond formation that stabilized the C network at temperatures up to 600 °C [17]. A recent study [20] on the tribological behavior of Si-O-H-DLC coatings against an Al–6.5% Si (319 Al) alloy showed a low COF of 0.11 at 400 °C, which was attributed to Si–OH passivation and the delayed graphitization of the coating due to Si incorporation in the C network. W doped NH-DLC coatings tested against 319 Al and Ti–6Al–4 V alloys [14,15] also showed low friction at 420–500 °C range, but this time the formation of WO_3 at these temperatures was found responsible for the low COF.

Further studies aimed at understanding mechanisms of sliding friction of ta-C at high temperatures are necessary. It is pertinent to note that an addition of F (3–5 at.%) to H-DLC coatings can contribute to friction reduction [29–32]. When tested against Al 1100 [29] and AZ91 alloy [32] counterfaces F-H-DLC coatings formed a graphitized transfer layer containing F. First principles calculations [29] showed that the F in the transfer layer and on the coating surface exhibited large interatomic repulsions possibly reducing the friction. Using these notions, this study focuses on the tribological behavior of both ta-C and ta-C–F coatings sliding against a cast 319 Al at elevated temperatures. The chemical and microstructural changes that occurred at the contact surfaces were determined using X-ray photoelectron spectroscopy (XPS), micro-Raman and cross-sectional focus ion beam (FIB) microscopy, using the same methodology adopted by the authors for examination of other DLC coatings at elevated temperatures [15,20].

2. Experimental details

2.1. Material properties

The ta-C coatings were deposited on WC–Co disks by a pulsed vacuum-arc plasma technique using a pure graphite electrode. The

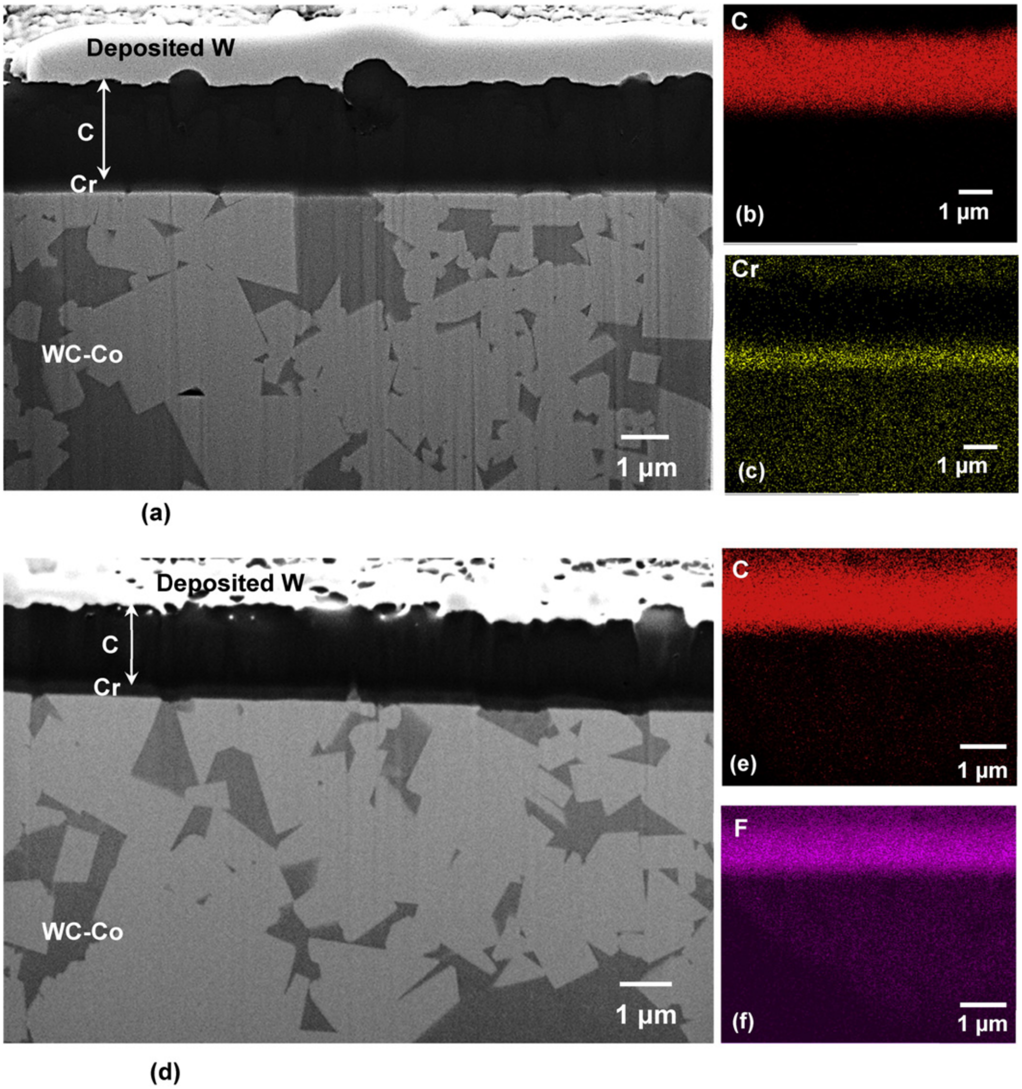

Fig. 1. (a) Focussed ion beam (FIB) secondary electron image of the cross-section of ta-C; EDS maps showing the distribution of (b) C and (c) Cr through the cross-section of ta-C; (d) FIB secondary electron image of the cross-section of ta-C–F; EDS maps of the distribution of (e) C, and (f) F through the cross-section of ta-C–F. Protective W layer deposited on the top of the coatings prior to FIB milling is indicated in (a) and (d).