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Additive effects on the tribological performance of WC/a-C:H and TiC/a-C:H coatings in boundary lubrication

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ABSTRACT

Although diamondlike carbon coatings like WC/a-C:H have a proven history of tribological performance in many mechanical applications, studies have reported that these coatings can sometimes experience high wear rates when operating in lubricants with large concentrations of phosphorous- and sulfur-based additives. In this study, WC/a-C:H and TiC/a-C:H coatings have been tribologically tested against AISI 52100 steel and Si_3N_4 counter faces under boundary lubrication in ISO 320 mineral oil, mineral oil with 1% aryl zinc dithiophosphate and 1% molybdenum dithiocarbamate, and a fully formulated wind turbine gear box oil. Results revealed that the wear coefficients of TiC/a-C:H were much smaller than those of WC/a-C:H in testing performed in lubricants with additives. A thionization wear mechanism was proposed to explain these results.

1. Introduction

Tungsten carbide amorphous hydrocarbon (WC/a-C:H) and titanium carbide amorphous hydrocarbon (TiC/a-C:H) coatings have desirable combinations of mechanical and tribological properties that make them well suited for many automotive, aerospace, power generation, and other industrial applications [1]. Although sometimes referred to as metal-doped diamondlike carbons, these coatings are actually nanocomposites consisting of nanocrystalline metal carbide precipitates in amorphous hydrocarbon matrices [2]. TiC/a-C:H and WC/a-C:H have elastic moduli (approximately 110 and 125 GPa, respectively), and hardness values (approximately 11 and 14 GPa, respectively) that enable these coatings to both elevate the surface hardness and accommodate the magnitude of elastic and plastic deformation that steel alloys experience in mechanical applications [3].

In rolling or mixed mode (i.e., rolling/sliding) contact, these coatings often wear by fracture of the columnar (~150–250 μm sizes) microstructures unless processing steps are employed to eliminate the columnar morphologies [4,5]. On the other hand, hydrogenated diamondlike carbon coatings are believed to wear through graphitization in dry sliding contact [6]. Since metal carbide/amorphous hydrocarbons are routinely utilized as tribological coatings in lubricated applications, it is important to ascertain how these materials interact with the base oils and additives in the lubricants. In applications where the contact is either rolling (i.e., bearings) or rolling/sliding (i.e., gears), some of these coatings have been operating extremely effectively for more many years in highly additized lubricants [7]. However, in laboratory tests conducted in unidirectional and/or reciprocating sliding contact with additized lubricants, diamondlike carbon coatings can sometimes exhibit exceptionally high or exceptionally low wear rates [8–18].

The ability to determine from the literature if mineral or synthetic base oils, or sulfur- and phosphorous-based additives are beneficial, detrimental, or neutral to the tribological performance of diamondlike carbon coatings is complicated by the fact that coating properties, especially composition and microstructures, are highly sensitive to deposition process conditions. In this study, the effects of mineral oil, mineral oil with two sulfur-containing additives, and a fully formulated mineral oil on the friction and wear of laboratory generated WC/a-C:H and TiC/a-C:H films similar to those known to operate well in commercial applications were studied in reciprocating sliding contact.

2. Materials and methods

2.1. Tribological testing

Testing was performed with a reciprocating pin-on-plate tribometer (PCS Instruments High Frequency Reciprocation Rig HFRR). Prior to testing, each specimen was rinsed in heptane followed by

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isopropyl alcohol. Tests were conducted with a static fill (3 mL) of lubricant at 120 °C, a load of 7 N ($p_{max} = 1.27$ GPa for the steel ball and 1.42 for the Si_3N_4 ball), and 2 mm stroke amplitude at 20 Hz ($v_{max} = 0.08$ m/s). The initial film thickness ratio was calculated using common equations for elastohydrodynamic lubrication (EHL) [19]

$$\lambda = \frac{h_{min}}{\sqrt{R_{ab}^2 + R_{ad}^2}}$$

$$h_{min} = 1.79 \times R' \times U_\Sigma^{0.68} \times G_\Sigma^{0.49} \times W_\Sigma^{-0.073}$$

$$U_\Sigma = \left(\frac{U\eta_0}{2E'R'}\right); \quad G_\Sigma = (2\gamma E'); \quad W_\Sigma = \left(\frac{P}{2E'R^2}\right) \tag{1}$$

where λ is the film thickness ratio, h_{min} is film thickness, R_{ab} is average rms roughness for ball, R_{ad} is average rms roughness for disc, U is the sliding velocity, η_0 is the dynamic viscosity, E' is the equivalent modulus of elasticity, R' is the reduced radius of curvature, γ is the pressure–viscosity constant, P is the applied force. Using the parameters for the surface roughness, lubricant, and tribological testing conditions, λ was calculated to be 0.12, well within the boundary lubrication regime.

Since the TiC/a-C:H and WC/a-C:H coatings were of different thickness, friction and wear data used in the analyses were collected entirely within the coatings. That is, tests that wore through the coating were excluded from the wear volume analysis.

Friction coefficients were collected by the tribometer and averaged every second. Wear volumes of the coatings and of the AISI 52100 and Si_3N_4 6mm diameter balls ($R_a < 0.05$ μm) were measured by 3D optical interferometry (Zygo NewView 7300) as a function of test duration. Whereas the wear volumes of the coatings were obtained directly from the interferometer software, wear volumes of the balls were obtained from a subtraction of the 3D interferometer data from the spherical balls.

Wear volumes measured on the coatings and the balls were analyzed as a function of dissipated energy (E_d) following the method outlined by Fouvry et al. [20]. In this work, dissipated energy is defined as

$$E_d = \mu\, P\, d(\text{Joules}) \tag{2}$$

where μ is the average coefficient of friction, P is the applied load (7 N), and d is the total sliding distance in meters. Wear volume is a linear function of dissipated energy, so the energy wear coefficient or alpha parameter (α) was calculated from a linear least square fit to the data. That is,

$$V = \alpha\, E_d + V_0. \tag{3}$$

The onset or threshold energy for wear can be determined as

$$E_d^0 = -\frac{V_0}{\alpha} \tag{4}$$

At least three repetitions were conducted for each experimental condition listed in Table 1.

Compositional analysis of the wear tracks formed in the TiC/a-C:H and WC/a-C:H coatings as a result of testing with additive-containing lubricants was performed using a PHI VersaProbe II Scanning X-ray Photoelectron Spectrometer Microprobe.

Table 1
Experimental tests.

Experiment	Duration (min)	Distance (m)
1	5	24
2	10	48
3	15	72
4	30	144
5	45	216
6	60	288

2.2. Materials

WC/a-C:H and TiC/a-C:H thin film coatings were deposited by closed-field unbalanced magnetron sputtering onto M50 disc specimens (10 mm diameter, $R_a = 0.02$ μm). Both coatings incorporate ~0.1 μm metal adhesion layers (Cr for WC/a-C:H and Ti for TiC/a-C:H). The approximate metal to carbon atomic ratio in both coatings is between 18% and 20%, and the approximate hydrogen to carbon ratio is 30%. The majority of the metallic constituents in the coatings are in the form of carbides, but previous atom probe tomography experiments indicated that metal atoms also reside in the amorphous hydrocarbon matrices [4]. Prior to coating, the M50 discs were ultrasonically cleaned in a Crest 275 Ultrasonic cleaning system with an alkaline detergent and rinse at 65 °C and then dried at 110 °C. Chromium and tungsten-containing targets were used for WC/a-C:H deposition and titanium targets were used for TiC/a-C:H. Argon and acetylene were used as the sputtering and reactive gases, respectively. After evacuation of the chamber, the discs were argon sputter etched (-500VDC for 30 min) to thoroughly remove any residual contaminants. In the deposition chamber, the discs were manipulated in a 2-axis planetary type motion during the coating process, which created nano-laminate structures consisting of alternating metal-rich, and metal-poor layers [21]. The compressive stress in each coating was calculated from the Stoney Formula [22] to be about $\sigma_C = -1$ GPa. The thickness of WC/a-C:H is about 1.1 μm while the TiC/a-C:H thickness is about 2.7 μm. Physical properties of the coatings, substrates, and pins are displayed in Table 2, where hardness values were ascertained by nanoindentation, coating thickness by calotest, compositions by x-ray photoelectron spectroscopy (XPS), and surface roughness from 3D optical interferometry.

Mineral oil (MO) with a viscosity of 320 mm^2/s was formulated from Group III 410 mm^2/s and 220 mm^2/s oils. Samples were also formulated with 1% aryl-zinc-dithiophosphate (Aryl-ZDTP) and 1% molybdenum dithiocarbamate (MoDTC) and added to the MO base oil. A fully formulated (FF), commercially available 320 mm^2/s mineral oil was also tested.

3. Results

3.1. Friction

Fig. 1a-d and Fig. 2a-d display plots of friction versus distance for the pairings of AISI 52100 and Si_3N_4 with the TiC/a-C:H and WC/a-C:H coatings, respectively. Fig. 1a-d reveal that the pairings of the TiC/a-C:H and 52100 and Si_3N_4 yielded similar friction coefficients in all lubricants. However, Fig. 2a-d show a much larger difference in friction between the 52100 and Si_3N_4 pairings

Table 2
Properties of Coatings and Materials.

Properties	M50 Disc	52100 Ball	Si_3N_4 Ball	WC/a-C:H	TiC/a-C:H
Coating Thickness				1.1 μm	2.7 μm
Adhesion Layer				Cr (0.1 μm)	Ti (0.1 μm)
Hardness	8 GPa	6 GPa	14 GPa	14 GPa	11 GPa
M/C Ratio				18–20%	18–20%
H/C Ratio				~30%	~30%
Roughness R_a	0.02 μm	0.07 μm	0.004 μm	0.04 μm	0.04 μm