Thin Solid Films 518 (2010) 4336–4344

Contents lists available at ScienceDirect

Thin Solid Films

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

Metal-doped (Ti, WC) diamond-like-carbon coatings: Reactions with extreme-pressure oil additives under tribological and static conditions

M. Kalin [a],*, E. Roman [b], L. Ožbolt [a], J. Vižintin [a]

[a] Centre for Tribology and Technical Diagnostics, University of Ljubljana, Bogišičeva 8, 1000 Ljubljana, Slovenia
[b] Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, Cantoblanco, E-28049, Madrid, Spain

ARTICLE INFO

Article history:
Received 19 August 2009
Received in revised form 18 February 2010
Accepted 26 February 2010
Available online 6 March 2010

Keywords:
Diamond-like carbon (DLC)
Additives
Lubrication oil
Wear
Friction
X-ray photoelectron spectroscopy (XPS)
Fourier transform infrared spectroscopy (FTIR)
Raman spectroscopy

ABSTRACT

In contrast to non-doped diamond-like-carbon (DLC) coatings, reliable chemical evidence of the reactions between metal-doped DLC coatings and oil additives under tribological conditions using state-of-the-art surface-sensitive chemical analyses is still scarce. In this study we have investigated the reactivity of metal-doped (Ti, WC) DLC coatings with the extreme-pressure (EP) dialkyl dithiophosphate additive — without the presence of a steel counter body in the contact that befogs the actual coating reactions. Static "reactivity" experiments without any tribological or mechanical effects were also performed to provide a further insight into the lubrication mechanisms. The results confirmed the chemical reactions between the EP additive and all the DLC coatings, as well as their oxidation during the tribological contacts. We measured an about 10-times higher chemical activity (a 25-fold P/S ratio increase) for the Ti-doped DLC compared to the WC-doped or non-doped DLC, which also agrees with it having the lowest amount of wear in this study. We suggest that the Ti-DLC boundary lubrication is achieved via binding sites at the O vacancies present in the Ti-doped DLC coating. The data also clearly show, in contrast to most of literature reports, that even though small, some direct chemical activity between the W-DLC and the dialkyl dithiophosphate EP additive is also possible without any iron catalytic effect. However, the chemical changes were significantly smaller, also allowing coating graphitization, which might be one of the reasons for the 50% higher wear of the WC-doped compared to the Ti-doped DLC.

1. Introduction

The improvements in our understanding of the appropriate deposition parameters, operating conditions, tribological mechanisms, as well as the coating-property variation and the resulting better diamond-like-carbon (DLC) coatings have been impressive developments over the past decade, and this has been comprehensively presented in several earlier [1–5] and recent reviews [6–9]. As a result the range of possible applications has expanded significantly; DLC coatings are nowadays frequently used in applications under high stress and/or under boundary or mixed oil lubrication [10–14] and the range of uses for DLC coatings continues to grow rapidly.

Nevertheless, information about the mechanisms of oil lubrication and the function of the additives is still scarce. Individual studies have suggested explanations for the observed specific tribological behaviour, including chemical evidence for the interactions [15–19]. However, generalized mechanisms as known for the boundary lubrication of steels have not been proposed yet, as reviewed in [8,9]. One of the reported suggestions was that doping DLC coatings with metal or non-metal elements can lead to DLC coatings with a higher surface energy, thus promoting the interactions between the coatings and the additives and oils via mechanisms known for metals. This phenomenon and the clear effect of additives on the tribological performance of metal-doped DLC coatings was indeed found empirically in previous studies of steel/DLC contacts [16,20–24], and an almost identical phenomenological parametric dependence to that with reference steel, i.e., "metal-like", was reported for self-mated metal-doped DLC/DLC contacts [20,25]. In contrast, a distinctively different tribological behaviour and mechanisms were found in self-mated DLC/DLC contacts of pure, non-doped DLC coatings under the same conditions [20,25], where no metal or doping element can affect the additive's interactions. In spite of these results, convincing chemical evidence of the reactions with additives using relevant surface-sensitive techniques was typically not obtained for metal-doped DLC coatings under "chemically" well-controlled self-mated metal-doped DLC/DLC contacts. For example, in an earlier report also using X-ray photoelectron spectroscopy (XPS), no reactions between the W-DLC/W-DLC coatings and the extreme-pressure (EP) additive were found (in contrast to results with the steel in the contact) [21], implying W-DLC coating non-reactivity or inertness with these additives.

On the other hand, similar "metal-like" behaviour was always observed in the contacts between steel and DLC, regardless of whether

---

* Corresponding author. Tel.: +386 1 4771 462; fax: +386 1 4771 469.
E-mail address: mitjan.kalin@ctd.uni-lj.si (M. Kalin).

0040-6090/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2010.02.066

non-doped or metal-doped DLC coatings were used. It is understandable, therefore, that the predominant effect of the steel counter body was actually observed in the interactions of these contacts [16,20–24,26]. The effects of steel on the mechanisms and behaviour in steel/DLC contacts were extensively presented and discussed in [24] and in particular in a recent review [7]. Therefore, it is interesting to note that reliable evidence for direct chemical reactions between DLC and additives, without the interference of a steel counter body, which affects the reaction products and befogs the actual reactivity of the coating, were confirmed with pure DLC coatings in self-mated contacts [15–18,27], but such evidence are still greatly missing for reactions between the metal-doped DLC coatings and additives.

Accordingly, it was the aim of our study to investigate the reactivity of metal-doped (Ti, WC) DLC coatings with an EP additive and compare it with non-doped DLC and steel as references under “well-defined” and clear tribological conditions, without the influence of steel in the contact. Namely, under boundary lubrication steel reacts extensively with (tailored) additives and the reaction products may modify the additive reaction pathways and shield the actual coating reactions. In addition to conventional tribological experiments under severe boundary-lubrication conditions, specially designed static experiments were performed to evaluate the reactivity between the selected coatings and additives, also without tribological or mechanical effects. The approach of static “reactivity” tests [28] was found in the past to be very useful for complementing the tribological results and explaining the tribochemical mechanisms in other applications. XPS, attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and Raman analyses were employed to study the interactions with a high surface sensitivity.

2. Experimental details

2.1. Samples

Two types of doped DLC coatings — a single-layer Ti-doped DLC (Ti-DLC) and a multilayer WC-doped DLC (W-DLC) — deposited on DIN 100Cr6 steel were investigated. For comparison, a pure, non-doped hydrogenated DLC (H-DLC) coating was used. Samples in the shape of a ball and a flat disc were used. The steel balls were commercially available, standard balls with a diameter of 10 mm, a hardness of 850 HV (corresponding to 8.3×10^9 Pa) and a surface roughness (R_a) better than 0.03 µm. The steel flat samples were 24 mm in diameter and had a thickness of 7.9 mm. They were heat treated to the same hardness as the balls. The steel discs were ground and polished in several steps to a final roughness R_a of 0.05 (+/− 0.01) µm, which was measured using a stylus-tip profilometer (T8000, Hommelwerke GmbH, Schwenningen, Germany). Some of the flat samples were used as reference steel specimens in the tribological and static reactivity tests, while the rest of the discs were further coated as described below. After the deposition, the roughness was measured again, but the average value did not change significantly, i.e., it was less than 0.01 µm.

A hybrid plasma vapour deposition/chemical vapour deposition (PVD/CVD) process was also used for a single-layer Ti-DLC coating, combining reactive magnetron sputtering and plasma-assisted CVD. About 5 at.% of Ti was introduced into the Ti-DLC coating. The coating thickness was 2.38 +/− 0.29 µm, including a gradual Ti-interlayer. On the other hand, the W-DLC coating was prepared as a multilayer WC/C structure using reactive magnetron sputtering. The target material that was used was made of WC, with Ni as a binder. The coating consisted of two types of 50–100-nm-thin lamellas, rich in WC and C, respectively. The adhesion-promoting interlayer was about 0.13 µm thick, consisting of pure (>99%) Cr, while the total coating thickness was 2.61 +/− 0.05 µm. The non-doped H-DLC coating was a commercially available coating, also produced with a hybrid PVD/CVD process as a single-layer coating. The average H-content of this non-doped H-DLC was around 30 at.% and the $sp^3/(sp^3+sp^2)$ ratio was 35–40%, as reported by producer (NV Bekaert SA, Kortrijk, Belgium). This coating had a thick, TiN interlayer of about 1 µm, making a total coating thickness of 2.67 +/− 0.04 µm. The thickness of the coatings was determined by ball-cratering technique (TE 66, Phoenix Tribology Ltd, UK). The hardness and the Young's modulus of the coatings were measured using a depth-sensing indentation technique (NanoTest 600 instrument with Berkovich indenter, Micro Materials Limited, UK), and the data are presented in Table 1. It is clear that both the hardness and the Young's modulus were higher for the non-doped H-DLC coating than for the doped Ti-DLC and W-DLC coatings.

2.2. Oil and additive

For the tribological tests as well as for the experiments performed under static conditions, a high-purity paraffinic mineral base oil (M) of viscosity grade ISO VG 46 was used. A mixture (M + EP) of base oil with 1 wt.% of extreme-pressure (EP) additive was prepared for investigating the additive reactions with the DLC coatings. The EP additive was a typical, strong, extreme-pressure additive, i.e., dialkyl dithiophosphate, containing 9.3% of P and 19.8% of S in its structure.

2.3. Tribological experiments and surface analyses

The tribological tests were performed in a reciprocating sliding machine consisting of a stationary base, a holder (which is driven in a linear oscillating motion), a loading cell and a computer-based regulation system. The lower, flat samples were fixed in the base, while the upper specimens, i.e., the balls, were fixed in the oscillating holder. In all the experiments, 10 N of normal load was applied through the loading system, which resulted in an initial Hertzian contact stress of about 0.7×10^9 Pa (1×10^9 Pa max.). A stroke of 1 mm and an oscillating frequency of 50 Hz were used, resulting in a relative contact velocity of 0.1 m/s. In each test, the total sliding distance was 100 m, corresponding to 10,000 loading cycles. Since the contact temperatures under such slow-speed conditions are rather low, and would increase significantly only for very small values of the real contact area [29,30], the specimens were pre-heated to 80 °C to ensure conditions that would enhance the EP additive's interactions with the surfaces. Under the selected conditions, the calculated Lambda value (Tallian parameter) [31] was between 0.04 and 0.06, depending on the final roughness of a particular coating (0.05–0.06 µm). This suggests that the conditions used were relatively severe and always within the boundary-lubrication regime.

The frictional force was monitored throughout the test with a load transducer, and was digitally recorded. Before each experiment the specimens were ultrasonically cleaned in high-purity benzene and ethanol. A small amount of oil was spread on the surface of the flat specimen prior to each experiment. After the test, the specimens were carefully cleaned in ethanol to remove any residual oil, and then dried in a stream of air.

The wear volume of the balls was calculated using the wear-scar diameter measured with an optical microscope (Leitz Miniload 2, Ernst Leitz Wetzlar, GmbH, 6330 Wetzlar, Germany) and a geometrical equation for the volume of a spherical segment [32,33]. A total of six diameter measurements were made on each wear scar and the mean value of these measurements was used in the wear-volume

Table 1
Mechanical properties of selected coatings.

Coating	Hardness (10^9 Pa)	Young's modulus (10^9 Pa)
Ti-DLC	11.59 ± 0.43	120.21 ± 1.49
W-DLC	13.61 ± 0.66	150.34 ± 5.08
H-DLC	25.64 ± 3.16	187.97 ± 15.8