Estonian Journal of Engineering, 2012, **18**, 3, 193–201 doi: 10.3176/eng.2012.3.04

# Tribological properties of PVD coatings with lubricating films

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Received 8 June 2012, in revised form 30 July 2012

**Abstract.** This work reports on the tribological performance of three different commercial hard PVD coatings (TiN, TiCN and nACo) with lubricating extra films of $Al_2O_3$, Ni-$WS_2$ and diamond-like carbon (DLC). WC-Co hardmetal has been used as substrate material. Wear tests, employing two counter bodies of $Al_2O_3$ and hardmetal WC-Co, were performed for the PVD coatings with and without the extra films. The results showed that the presence of DLC extra film reduces the coefficient of friction of the PVD hard coatings TiN and nACo. Furthermore, the wear of TiN coatings was reduced in the presence of an extra Ni-$WS_2$ lubricant film.

**Key words:** PVD coating, thin film, tribology, self-lubrication, coefficient of friction.

## 1. INTRODUCTION

Physical vapour deposited (PVD) coatings have established a strong position in the tooling industry. Thin hard coatings are widely used to protect the tools from wear, to use substrate steels with higher toughness in cutting elements and altogether to extend tool life time. However, there are some limits related to the application of PVD coatings. For example, it has been demonstrated that multilayer and gradient coatings on hardmetal and cold work tool steel substrates under the conditions of dry sliding wear tests have a tendency to increase the coefficient of friction (CoF) and to decrease the elasticity modulus ($E$) and hardness ($H$) ratio [1].

Different types of hard coatings like TiN [2], $Al_2O_3$ (Alumina) [3], diamond-like carbon [4–6] and sulphide-containing films [6,7] can be applied for wear protection to lower the CoF or suppress the adhesive wear in poorly lubricated and high stress contacts. Previous studies have reported that hybrid PVD + atomic layer deposited (ALD) hard coatings have a positive effect on corrosion protection [8]. However, the effect of the ALD film on the wear resistance has not been studied to our knowledge.

The present study is part of an assignment to create thin hard coating systems for tooling industry in order to improve the commercial coatings known today. In this work, thin lubricating extra films were deposited on top of PVD coated surfaces. The influence of the extra films on the CoF and wear was studied.

## 2. EXPERIMENTAL

WC-Co hardmetal (10 wt% of Co) specimens with hardness of 1640 HV were used as substrate materials for the base coatings. Three base coatings, all containing elements of Ti and N, were used in the study – monolayer of TiN, gradient coating TiCN and gradient nanocomposite nACo (nc-$Ti_{1-x}Al_xN$)/(a-$Si_3N_4$). Substrate specimens were polished to Ra 0.003 µm and cleaned in an ultrasonic bath with isopropanol. Immediately after the cleaning procedure, samples were placed into the vacuum chamber and sputter-cleaned in argon plasma. Thin metallic Ti layer was deposited onto substrates prior to the main coating. Deposition of TiN, TiCN and nACo coatings were carried out in the arc plating PVD unit PLATIT-π80 using Lateral Rotating ARC-Cathodes (LARC) technology. The deposition temperature was 450 ºC for each coating. Thickness of the coatings was measured using the kalotest method with the kaloMAX tester. Surface roughness was measured with Perthometer Concept M by Mahr and nanohardness was received from Platit [9]. Properties of base coatings are given in Table 1. Adhesion of the coatings was evaluated by Rockwell indentation test (A scale), according to technical specification CEN/TS 1071-8.

Extra films used in the experiment were atomic film of $Al_2O_3$, sub-micron diamond-like carbon film and a micrometer thick nickel and tungsten disulphide composite film (Ni-$WS_2$).

$Al_2O_3$ film was deposited in a flow-type low-pressure ALD reactor [10] in a flow of nitrogen (99.999%, AS AGA). Prior to deposition, the samples were pretreated with acetone (99.5%, Carl Roth GmbH&CO) and isopropyl alcohol

**Table 1.** Properties of PVD base coatings

| | Nanohardness, up to, GPa [9] | Average roughness Ra, µm | Average max height of the profile Rz, µm | Coating thickness, µm |
|---|---|---|---|---|
| TiN | 24 | 0.04 | 0.91 | 2.5 |
| TiCN | 32 | 0.04 | 0.95 | 3.1 |
| nACo | 40 | 0.08 | 1.26 | 2.3 |

(99.7%, Carl Roth GmbH&CO). For preparation of reference samples, $Al_2O_3$ films were deposited also on Si substrates. The Si(100) substrates were cleaned by etching in HF to remove the native oxide, and then rinsed in de-ionized water. The $Al_2O_3$ film was deposited using 400 cycles $Al(CH_3)_3$ (98%, Strem Chemicals) and $H_2O$ at 300 °C with the ALD cycle times 3/2/2/5 s. Mass thickness of $Al_2O_3$ films, grown by the ALD method on Si(100) substrates, was determined using EPMA data and STRATA and FLA programs [11].

Deposition of diamond-like carbon films was carried out in the PVD unit PLATIT-π80 using LARC technology at the temperature of 400 ºC. Recipe parameters were set according to recommendations from Platit in order to achieve film thickness of approximately 300 nm.

For the deposition of Ni-$WS_2$ composite coatings, an eutectic mixture of choline chloride and ethylene glycol, containing $NiCl_2$ and $WS_2$ powder, was employed. Electrodeposition experiments were carried out in open air conditions, using a three-electrode cell setup. During deposition process, the bath was stirred by a magnetic stirrer (10 rpm) in order to keep the particles dispersed and prevent sedimentation. Composite coatings were deposited at potential –0.9 V and temperature 70 ºC. After deposition, samples were rinsed with iso-propanol to ensure removal of the ionic liquid, and subsequently dried under vacuum at room temperature for 2 hours. The gravimetric method (weight gain) was used to calculate the coating thickness.

Reciprocating wear experiments were conducted using CETR-UMT-2 tribometer. Tests were carried out with two different counter bodies (supplied by Redhill): corundum ($Al_2O_3$) and tungsten carbide-cobalt (WC-Co) with 6 wt% of cobalt. Hardness and modulus of elasticity of $Al_2O_3$ was 1700 HV and 350 MPa, respectively; and for WC-Co 1500 HV and 640 MPa, respectively. Diameter of the ball was 3 mm, reciprocating distance 1 mm, contact force 2 N, frequency 5 Hz and time 10 min. All of the experiments were repeated at least twice and additional experiments were conducted for those samples where differences in the first two results were observed. Average CoF was determined over the period of 1500–3000 cycles, i.e. after stabilization depths of wear scars were determined using Bruker ContourGT-K0X White Light Interferometric Optical Profiler.

## 3. RESULTS AND DISCUSSION

### 3.1. Adhesion of PVD coatings and thickness of additional films

Adhesion between base coatings and the substrates was determined with Rockwell indentation test. Adhesion was very good – Class 0 (no cracks or adhesive delamination within the indent region) for nACo, or good – Class 1 (cracking without adhesive delamination of the coating) for TiN and TiCN coatings. Table 1 shows the thickness of PVD coatings of TiN, TiCN and nACo. The thickness of extra films was the following: $Al_2O_3$ – 0.04 μm, DLC – 0.3 μm and Ni-$WS_2$ – 1.0 μm.

### 3.2. Reciprocating sliding wear of different coating systems

Among the base coatings, TiCN demonstrated the best wear resistance in the specific conditions. TiN and nACo coatings were most susceptible to wear. Repeating the experiments with both counter bodies revealed some differences derived from the material of the counter body.

#### *3.2.1. Effect of the counter body material on the CoF of base coatings*

Wear behaviour of base coatings was studied using $Al_2O_3$ and WC-Co counter bodies. CoF dependence on the sliding ball material is shown in Fig. 1. Both of the nACo and TiN coatings showed more stable behaviour and lower CoF with WC-Co counter body. With nACo base coating $Al_2O_3$ counter body demonstrated remarkably higher CoF and wear depth, probably due to higher hardness of $Al_2O_3$. SEM secondary electron images of worn surfaces of nACo coating are presented in Fig. 2 and those with nACo + DLC coating in Fig. 3. With $Al_2O_3$ counter body (Fig. 2a), the wear is greater but the wear track is smoother. Larger contact pressure takes place with WC-Co (Fig. 2b) and the counter body is transferring and tearing the coating leaving a smaller wear track.

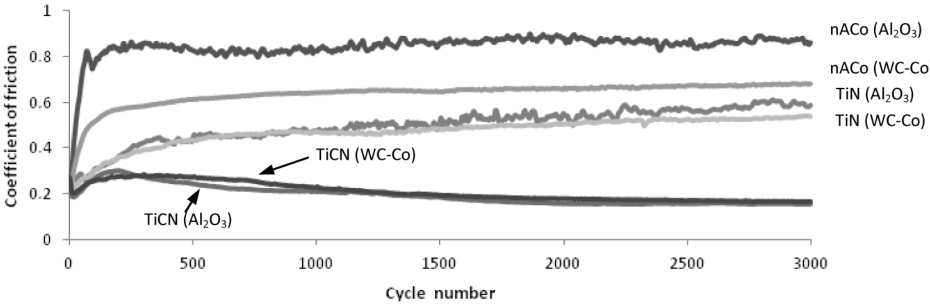

**Fig. 1.** Effect of the counter body material on the CoF of the base coatings.

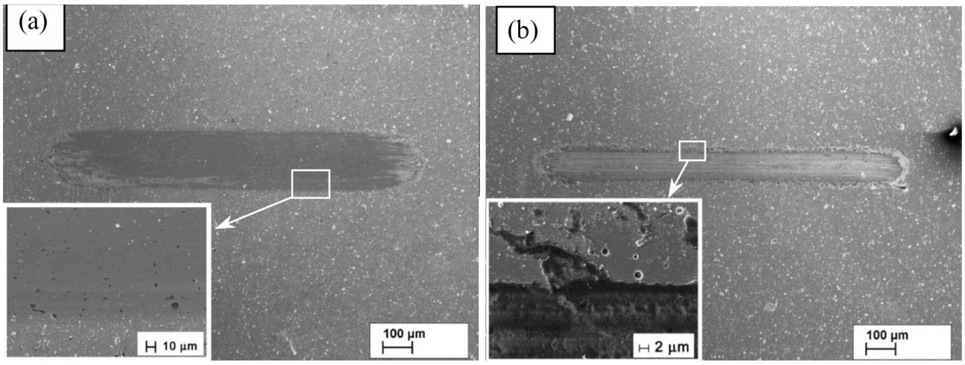

**Fig. 2.** SEM images of the nACo base coating, sliding against $Al_2O_3$ (a) and WC-Co (b) ball counterface.

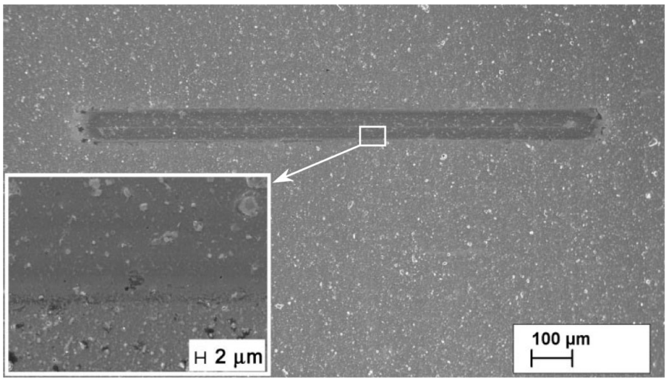

**Fig. 3.** SEM image of reciprocating wear experiment with nACo+DLC coating.

### *3.2.2. Effect of different extra films on CoF*

It was observed that the presence of $Al_2O_3$ extra films on PVD coatings did not add tribological advantage to the PVD coatings (Fig. 4a). Some changes in the CoF during the “run-in” period are visible though for robust applications such influence will probably not be detectable. The effect of an ultra-thin extra film of $Al_2O_3$ disappears after the first 100 cycles and the CoF for the samples with the extra film levels off to the coefficient of PVD base coatings. Probably the extra film thickness is insufficient in order to provide protection to the base coating.

The presence of thin sub-micron DLC extra films on PVD coatings decreases the CoF and improves wear performance of the base coatings (Fig. 4b). On the basis of our experiment, it was noticed that the DLC film was able to provide remarkable protection to the substrate regardless of the base coating. Wearing out of the DLC coating was not noticed for any of the coating systems. SEM-secondary electron image of nACo+DLC is presented in Fig. 3. Wear track is remarkably smaller than for nACo coating without the extra film (Fig. 2).

Figure 4c represents the results for PVD coatings with Ni-$WS_2$ extra film (corundum counter body). For nACo+Ni-$WS_2$, CoF was lower up to 1000 cycles, however, afterwards the extra film failed and CoF reached the level of nACo base coating. The Ni-$WS_2$ extra film on TiN and TiCN was able to keep a reasonably stable low CoF up to 3000 cycles.

Sulphide-containing film of Ni+$WS_2$ was reliant on the base coating as it behaved differently for all three PVD coatings. The effect of Ni-$WS_2$ film on top of base coatings is presented in Fig. 5 where the wear behaviours of base coatings with and without the extra lubricant films are compared. The effect of the Ni-$WS_2$ film is remarkable for the TiN coating, while in case of the nACo coating, the effect depends on the counter body.

Table 2 shows an overview of the reciprocating wear experiment results and grouping of the wear behaviours. From the data, a relation between CoF and

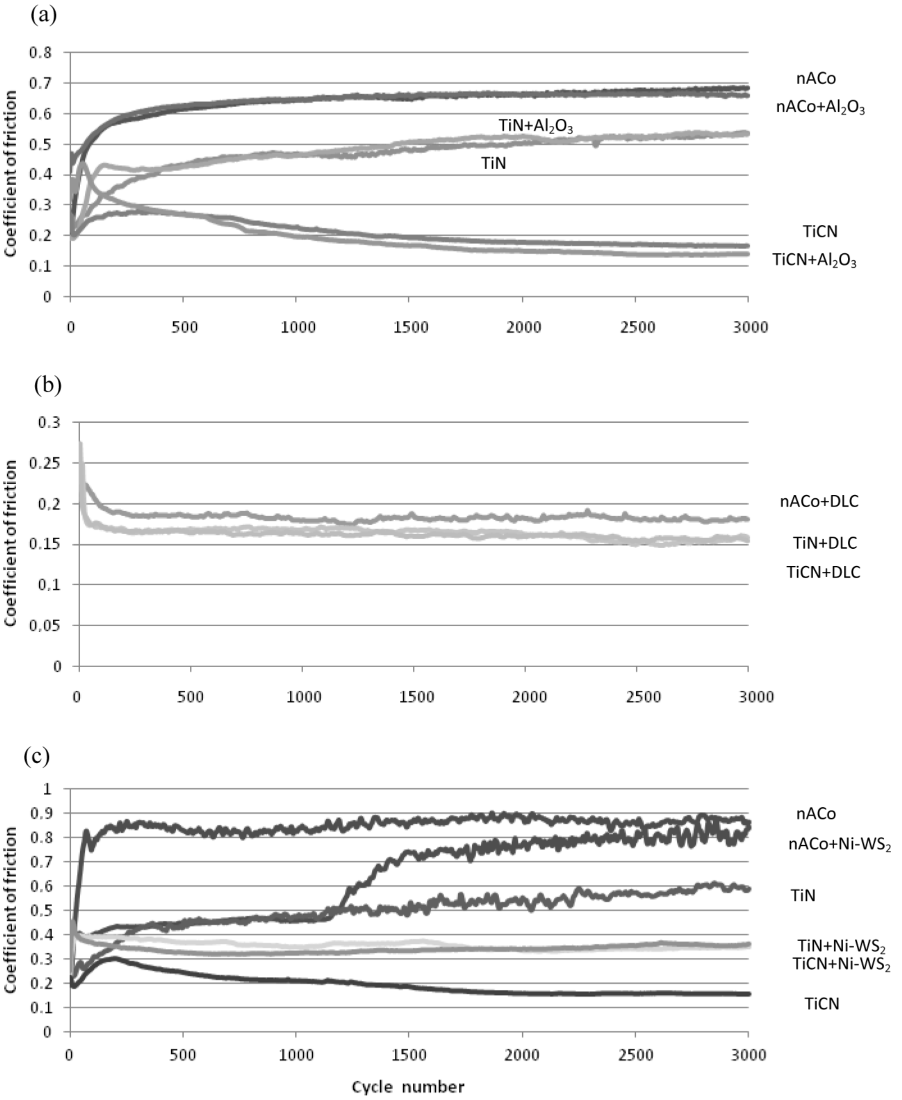

**Fig. 4.** Effect of extra films: (a) $Al_2O_3$ atomic film (sliding against WC-Co ball counterface); (b) DLC film (sliding against WC-Co ball counterface); (c) Ni-$WS_2$ film (sliding against $Al_2O_3$ ball counterface).

depth of the wear scar was noticed. Larger wear scars indicate a greater frictional coefficient. However, there were some exceptions. For the nACo coating systems (Table 2, group 4), depth of the wear scar was relatively deep, while the CoF remained low (0.4) with the hardmetal counter body. Ni-$WS_2$ in “group 2” coatings was able to suppress wear until the failure of the extra layer.

**Table 2.** Results of reciprocating wear tests with different PVD base coatings and extra films

| Classification based on wear behaviour | Coating | Counterbody1) | Depth of wear scar, μm | CoF |
|---|---|---|---|---|
| **Group 1:** TiCN coating and DLC extra film on PVD base coatings. Low CoF and depth of wear scar. | TiN+DLC | WC-Co/$Al_2O_3$ | 0.10 | 0.16 |
| | TiCN+DLC | WC-Co/$Al_2O_3$ | 0.13 | 0.16 |
| | TiCN / TiCN+$Al_2O_3$ | WC-Co/$Al_2O_3$ | 0.15 | 0.16 |
| | nACo+DLC | WC-Co/$Al_2O_3$ | 0.14 | 0.18 |
| **Group 2:** Ni-$WS_2$ extra film on base coatings. Increased CoF for TiCN and TiN but low wear. For nACo lower CoF for a short period is achieved, however, extra film wears out during the experiment.2) | TiCN+Ni-$WS_2$ | WC-Co/$Al_2O_3$ | 0.05 | 0.35 |
| | TiN+Ni-$WS_2$ | WC-Co/$Al_2O_3$ | 0.11 | 0.35 |
| | nACo+Ni-$WS_2$ | $Al_2O_3$ | 0.952) | 0.45/0.782) |
| **Group 3:** TiN coating. CoF is lower than for nACo, wear is high. | TiN / TiN+$Al_2O_3$ | WC-Co/$Al_2O_3$ | 0.77 | 0.54 |
| **Group 4:** nACo, nACo+Ni-$WS_2$ and nACo+$Al_2O_3$ coatings with hardmetal counter body. Although nACo has higher CoF compared to TiN coating, wear is lower. | nACo+Ni-$WS_2$ | WC-Co | 0.45 | 0.64 |
| | nACo / nACo+$Al_2O_3$ | WC-Co | 0.40 | 0.66 |
| **Group 5:** nACo / nACo+$Al_2O_3$ with $Al_2O_3$. Highest CoF and wear. | nACo / nACo+$Al_2O_3$ | $Al_2O_3$ | 1.65 | 0.84 |

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1) WC-Co/$Al_2O_3$ – no difference in results with different counter bodies.

2) The Ni-$WS_2$ coating wears out after about1200 cycles and therefore two values of CoF are given: CoF over a period of 100–1100 cycles / CoF over a period of 1500–3000 cycles. Wear scar depth is given only after the end of experimental 3000 cycles.

## 4. CONCLUSIONS

The paper considers tribological properties (wear and coefficient of friction) of commercial PVD coatings with lubricating extra films of $Al_2O_3$, DLC and Ni-$WS_2$. From the study the following conclusions can be made.

1. TiCN coatings showed the lowest coefficient of friction (0.15–0.20) and wear independence of the counter body material or of the extra lubricant films.
2. Atomic layer deposited $Al_2O_3$ extra films on PVD coatings did not add tribological advantage to the base coatings, probably due to insufficient thickness of the film. Wear and CoF remained on the same level as for PVD

commercial coatings, only minor changes in the “run-in” period were noticed.

3. Addition of DLC extra film on top of the base coatings resulted in a reduced CoF (to the level of 0.16–0.18) and wear of commercial PVD coatings TiN and nACo.
4. Extra film of Ni-$WS_2$ was able to provide good protection against wear of TiN and TiCN coatings in our experimental conditions; behaviour on nACo base coating was dependent on the counter body material. Extra film Ni-$WS_2$ needs further studies before it is possible to make more profound conclusions. For example, it remains unclear whether the protective effect of Ni-$WS_2$ will be preserved under higher loads or different setups and what is the reason for different behaviour with varied counter bodies.

## ACKNOWLEDGEMENT

The work was supported by the Ministry of Education and Research (target financed project SF 01400091S08) and Graduate School „Functional materials and technologies”, financed by Archimedes in Estonia. The authors are thankful to F. Endres from Clausthal University of Technology for support and to V. Mikli from Materials Research Centre of Tallinn Universtity of Technology for SEM studies of worn surfaces.

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# Määrivate katetega füüsikaliste aurustussadestuspinnete triboloogilised omadused

Liina Lind, Eron Adoberg, Lauri Aarik, Priit Kulu, Renno Veinthal ja Alsayed Abdel Aal

Artikkel käsitleb isemäärivate katetega ($Al_2O_3$, DLC ja Ni-$WS_2$) kaetud tuntud õhukeste kõvapinnete (TiN, TiCN ning nACo) triboloogilisi omadusi. Alusmaterjalina on kasutatud WC-Co kõvasulamit. Kulumiskatsete alusel võrreldi isemäärivate katetega kaetud katsekehasid puhaste kõvapinnetega. Katsetused viidi läbi erinevast materjalist kuulidega (kõvasulam WC-Co ja alumiiniumoksiid $Al_2O_3$). Teemandilaadne (DLC) kate vähendas hõõrdetegurit TiN-i ja nACo kõvapinnete puhul ning Ni-$WS_2$ lisakate vähendas TiN-pinde kulumist.