Wear 352-353 (2016) 72–78

Contents lists available at ScienceDirect

Wear

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

Tribological performance of TiN, TiAlN and CrN hard coatings lubricated by MoS_2 nanotubes in Polyalphaolefin oil

S. Paskvale [a,*], M. Remškar [a,b], M. Čekada [a]

[a] Jožef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia
[b] Nanotul, Ltd., Teslova 30, 1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:
Received 20 September 2015
Received in revised form
20 January 2016
Accepted 24 January 2016
Available online 4 February 2016

Keywords:
PVD coatings
Nanoparticles
MoS_2 nanotubes
Oil
Lubricant additives
Friction modifiers

ABSTRACT

Hard coatings deposited by PVD (physical vapor deposition) tend to have a relatively high coefficient of friction, which means that in applications they are lubricated with conventional lubricants. Molybdenum disulfide (MoS_2) is a lubricant additive and a friction modifier, and when using the recently developed MoS_2 multi-wall nanotubes it is possible to decrease this coefficient of friction even further. For this reason the tribological behavior of MoS_2 nanotubes added to polyalphaolefin (PAO) synthetic oil was investigated for the lubrication of cold-work tool steel AISI D2 coated with TiN, TiAlN and CrN hard coatings. The experiments were performed with a ball-on-flat reciprocating machine under a contact pressure of 1.0–2.0 GPa (Hertz, max) and a sliding velocity of 0.5–1.0 cm/s, with a 100Cr6 steel counterpart body. The results were compared to pure PAO oil and to a mixture of commercially available MoS_2 platelets with PAO. It was found that the addition of the MoS_2 nanotubes leads to a significant reduction in the friction and an improvement in the wear behavior.

1. Introduction

Physical vapor deposition (PVD) hard coatings such as TiN, TiAlN and CrN have been used for decades as wear-protection coatings on various substrates. PVD hard coatings are either lubricated with conventional oils or used without any lubricant. A steel surface coated with a PVD hard coating has a higher roughness and is chemically more inert compared to uncoated steel. Conventional lubrication systems are not optimized for lubricating PVD coatings.

Some efforts have already been made in order to find a better lubrication system for PVD-coated surfaces, where the use of ZDDP (Zinc Dialkyl Dithiophosphate) should be omitted. For example, Gonzales et al. [1] tested TiN and CrN hard coatings lubricated with a special ionic liquid as a 1 wt% additive in polyalphaolefin oil (PAO). Here, the reduction of the coefficient of friction (CoF) was relatively small (less than 10%). Blanco et al. [2] tested a different ionic liquid as a 1 wt% additive in PAO on a CrN hard coating as replacement for ZDDP. According to their measurements the CoF reduction is about 15% using the ionic liquid; however, when using ZDDP the reduction is 24–37%.

To the best of our knowledge the tribological properties of solid lubricants as lubricant additives for PVD hard coatings have not yet been examined. Using recently developed MoS_2 multi-wall nanotubes (hereafter referred to as NTs), as an oil additive an additional decrease in the CoF and an increase in the lifetime of the PVD hard coatings are expected.

In 1992 it was realized that layered metal dichalcogenides (for example, MoS_2, WS_2) are capable of forming inorganic fullerene-like (IF) and nano-tubular (NT) structures [3]. The studies of these novel nanostructures have led to the observation of a number of interesting properties and some potential applications in sensors, nanoelectronics, high-energy-density batteries and in tribology. At that time, it was already known that lamellar solids such as MoS_2 offer a superior lubrication performance. Researchers later demonstrated that the tribological performance of IF-MoS_2 nanoparticles surpasses that of the corresponding lamellar structures [4,5].

Solid lubricants can also be added to lubricating oils in order to improve their friction and wear properties. MoS_2 in its standard plate-like form is the most commonly used solid-lubricant additive for a variety of oils. It is lubricious due to the weak Van der Waals bonds between the S–Mo–S molecular layers [6]. The IF-MoS_2 nanoparticles exfoliate under load and form an adherent film of thin flakes on the surfaces in contact. At high pressure, when greases or oils are squeezed out, this film can still act as a lubricant [5].

Finely ground IF-MoS_2 nanoparticles were added to oils in concentrations of a few wt% to form a colloidal dispersion. The IF-MoS_2 nanoparticles produced a very beneficial effect, particularly under boundary-lubrication conditions. Unfortunately, the tribological performances of these particles are often controversial due to the influence of the morphology, size and structure of the IF-MoS_2, along with the large influence of the test conditions [4,7–10].

---

[*] Corresponding author.
E-mail address: srecko.paskvale@ijs.si (S. Paskvale).

http://dx.doi.org/10.1016/j.wear.2016.01.020
0043-1648/© 2016 Elsevier B.V. All rights reserved.

The use of MoS_2 nanomaterials as an additive in oil is not straightforward. In general, the most acute problem is their tendency to agglomerate, which can be avoided to some extent by the addition of dispersants. However, the dispersants in oil, such as calcium sulfate, inhibit the lubricating action of MoS_2. MoS_2 also provides a limited reduction in the friction and wear when added to conventional oils that contain sulfur-based additives or ZDDP [11]. A recent report stated that 2 wt.% of MoS_2 NTs added to PAO reduced the friction in a steel contact by 40–65% [12] and in a diamond-like carbon (DLC) contact by up to 50% [13]. To the best of our knowledge, there is no report on hard coatings other than DLC that could be lubricated with MoS_2 NTs.

So far the main conclusion has been that IF-MoS_2 can be beneficially used as a trial additive in lubricating oil for special applications. The MoS_2 NTs contain more defects than the platelets and are therefore easily exfoliated. The ability of the particle to exfoliate and the third-body transfer of molecular sheets onto asperities is the prevailing mechanism for the improved tribological behavior of MoS_2 NTs. In the contact, i.e., in the boundary regime, the larger particles (MoS_2 platelets) have a lower availability since they can be easily pushed out of the contact and/or cannot penetrate into the contact. In addition, the smaller MoS_2 NTs suspended in the oil are less prone to sedimentation than the larger MoS_2 platelets. In view of this, it can be suggested that MoS_2 NTs have a clear advantage over the platelets of MoS_2 for use in a real tribological application. Conversely, it was recently reported that MoS_2 NTs used in a 5 wt% concentration in PAO oil using a ball-on-disk configuration under unidirectional sliding in a 100Cr6 – 100Cr6 contact do not have an advantage [14] over conventional MoS_2 platelets.

In this work we present the performance of PAO oil with added MoS_2 NTs developed for the lubrication of TiN, TiAlN and CrN PVD hard coatings. The main goal was to demonstrate that the tribological properties of PVD coatings are enhanced with MoS_2 NTs compared to conventional MoS_2. The tribological tests were performed in reciprocal mode and the results were compared with those obtained using commercial MoS_2 platelets. There is clear evidence of better lubrication performance with the MoS_2 NTs than with the MoS_2 platelets.

2. Experimental

2.1. Deposition and properties

The test disks made of cold-work tool steel AISI D2 were used as substrates for the deposition of hard coatings (Fig. 1). The disks, 22 mm in diameter and 3 mm in thick, were ground and polished with diamond paste to a mean surface roughness of $R_a \sim 0.02$ μm. Prior to mounting in the deposition chamber, they were cleaned in detergents in an ultrasound bath, rinsed in deionized water and dried in a dry box at 100 °C. In the chamber, they were first heated to about 450 °C and then in-situ cleaned by ion etching in order to obtain good adhesion of the deposited coating. Three types of PVD hard coatings were deposited. The CrN and TiN coatings were prepared using thermoionic arc evaporation in an industrial deposition system BAI730 (Balzers), while the TiAlN coatings were prepared in an industrial magnetron-sputtering system CC800/7 (CemeCon).

The Vickers hardness was measured with a Fischerscope H100C indenter using a 50-mN maximum load. The data for the hardness was determined with the median value from at least 10 measurements. The standard deviation was around 5%. The surface morphology was examined with a 3D stylus profilometer (Bruker Dektak XT). The measuring area was 1×1 mm^2 with an applied resolution of 1 μm along the *x*-axis, 2 μm along the *y*-axis and a few tens of nm along the *z*-axis. The topography was evaluated by counting the number of peaks higher than 0.5 μm and the number of pits deeper than 0.5 μm, as described in [15]. The density of the pits was low, normally less than 5 per mm^2, but the density of the peaks was an order of magnitude higher. S_a is the average roughness, which represents the arithmetic mean height above the entire 3D surface.

The MoS_2 multiwall nanotubes were synthesized by sulfurizing the $Mo_6S_4I_6$ nanowires at 800 °C for 1 h in a reactive gas composed of 98 vol% Ar, 1 vol% H_2S and 1 vol% H_2 [16]. During sulfurization the iodine was completely removed from the starting material and substituted by sulfur. The nanotubes have a typical diameter below 0.1 μm and are up to 3 μm long (Fig. 2a). The walls of the nanotubes are less than 10 nm thick (Fig. 2b). A relatively high

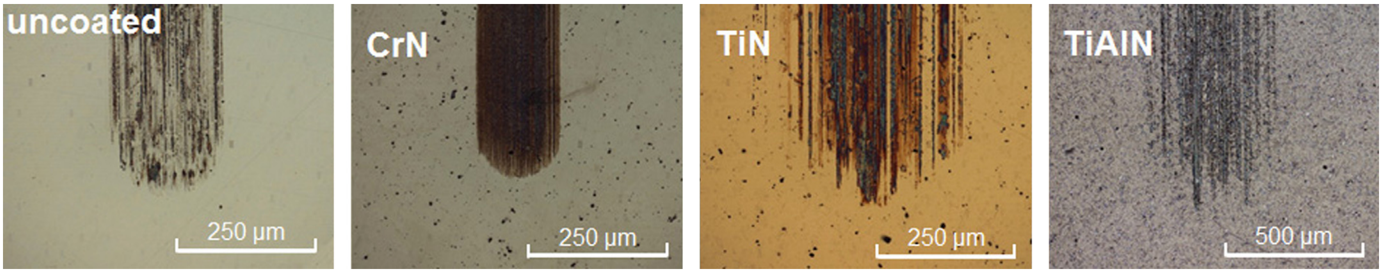

Fig. 1. Optical micrographs of the substrates used for tribo testing with a visible wear scar.

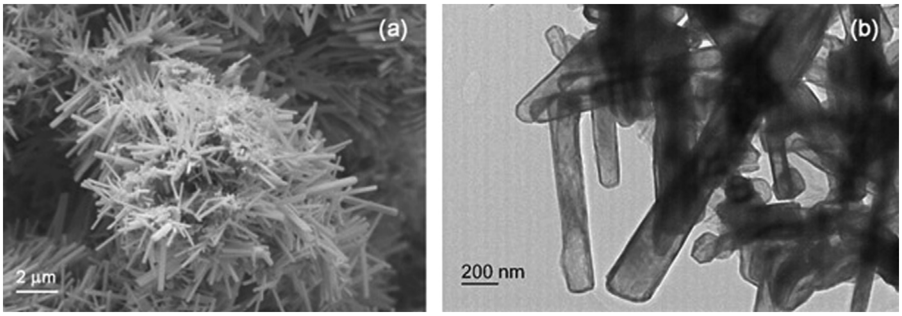

Fig. 2. The MoS_2 nanotubes: a) scanning electron micrograph; b) transmission electron micrograph.

concentration of structural defects is present in the form of sub-cylinders or parts of separated lamellas inside the nanotubes. These defects may influence the mechanical properties of the nanotubes, which can, as a consequence, be more easily exfoliated under a shear stress.

2.2. Tribological tests

The tribological experiments were performed at room temperature (24–27 °C) in the ball-on-flat configuration (CSM instruments Tribometer) with commercially available 100Cr6 balls ($d=6.00$ mm) as counterparts. Four samples were used in the testing: uncoated steel, the CrN coating, the TiN coating and the TiAlN coating. All the tests were made using three types of lubricants: a) PAO 8 oil with a kinematic viscosity of 48 cSt at 40 °C (referred to as PAO) from ExxonMobil (USA); b) PAO 8 with 2 wt% of MoS_2 NTs (referred to as PAO+NT); and c) PAO 8 with 2 wt% of MoS_2 platelets (2 μm in size) purchased at Aldrich (referred to as PAO+PT). The suspension of the oil and the MoS_2 was thoroughly mixed using ultrasound for two hours. Just before being used in each batch experiment, the oil was additionally mixed in ultrasound for an hour. The MoS_2 NTs were structurally unaffected by this procedure. A well-dispersed suspension, stable for several hours, was obtained in this way.

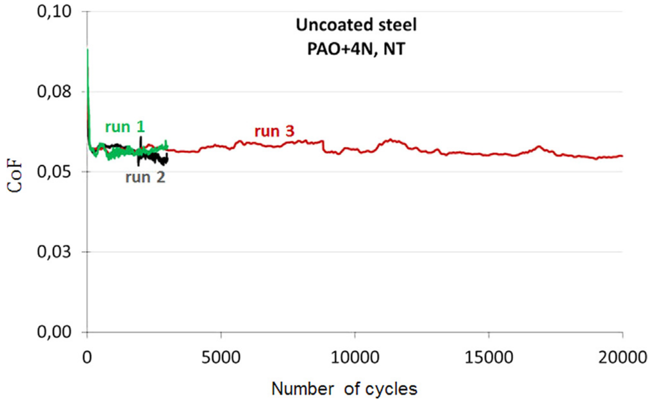

Fig. 3. Three tribological tests with identical settings, except the number of cycles.

The measurements were performed using a linear mode (reciprocating with 4 N and 20 N of load) and a 100Cr6 steel ball as a counterpart. The loads correspond to maximum Hertzian contact pressures of approximately 1.0 GPa and 2.0 GPa, respectively. The stroke length was set to 5 mm. The MoS_2 NTs work best with slow movements [14], so a low testing velocity was chosen. For the test with the 4-N load the average velocity was 5 mm/s and the sliding distance was 30 m. In order to be able to measure the wear on the specimens the sliding distance was set to 50 m in the tests with the higher load, and the average velocity was 10 mm/s to decrease the necessary time with the longer sliding distance.

Each experiment was made 2–4 times in order to obtain reliable results. In about 90% of cases the results from the second tests were equal to within 5%, which demonstrates that our results are repeatable. In other cases additional tests were carried out. Our tests of 20,000 cycles showed that the coefficient of friction is relatively steady over the longer term after reaching the so-called steady state after a few hundred cycles (Fig. 3). However, it may happen that the tribological properties change because of the MoS_2 additive's segregation and by pushing the additive out of the tribo-contact. Thus, 3000–5000 cycles is an optimal number.

Additionally, the wear scars on the balls were measured with a confocal optical microscope (Axio Vision, Zeiss) in order to calculate the wear rate of the steel balls (samples in Fig. 4). Whenever the wear of the steel balls was not clearly visible, additional measurements were made with a profilometer.

3. Results

3.1. Surface hardness and morphology

The hardness, the number of surface defects on the specimen surfaces and the average roughness measured before the tribological tests are presented in Table 1.

3.2. Friction results

The evolution of the friction in the lubricated tests as a function of the number of cycles is shown in Fig. 5. The figure presents the CoF for the 100Cr6 balls sliding on uncoated steel, CrN, TiN and

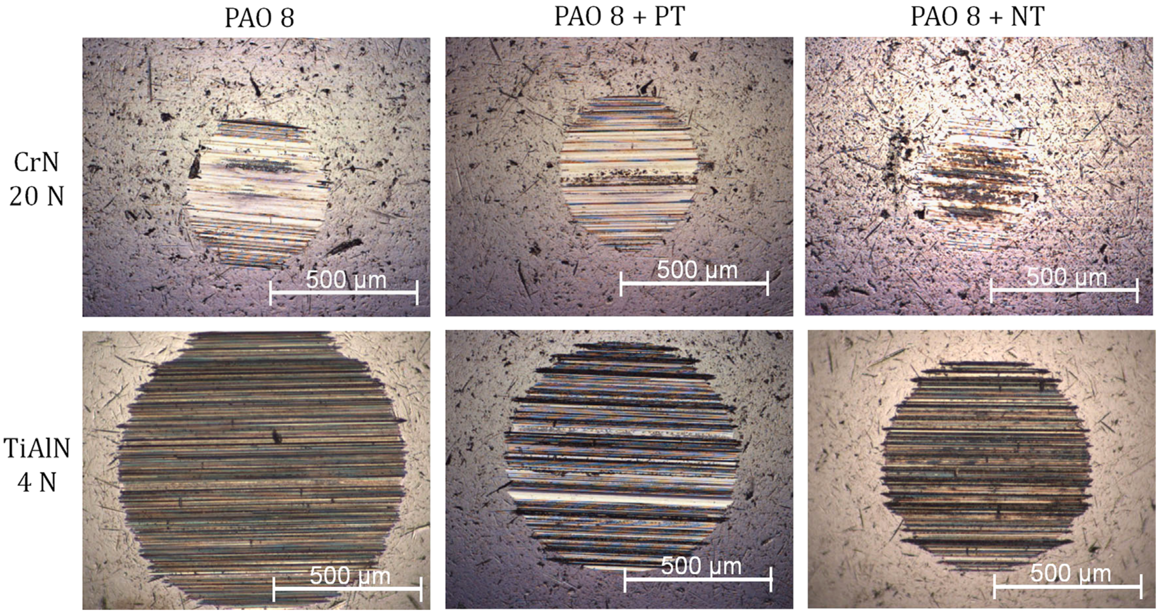

Fig. 4. Wear on selected steel balls for testing the CrN coatings at 20 N and the TiAlN coatings at 4 N with all three lubricants.

TiAlN coatings using all three types of lubricant at two different loads. Although there is some noise in the signal, the difference in the CoF remains significant.

Fig. 5a shows a large difference between the CoF curves for the sliding 100Cr6 ball on the uncoated steel using all three types of lubricants at two different loads. For all the tests the initial CoF was around 0.10. When lubricated with PAO only, the CoF roughly stabilized at around 0.12 for 4 N and 20 N. When the MoS_2 NTs were added, the CoF dropped below 0.06 at low and high loads where it remained relatively steady. At the 20-N load the maximum Hertzian contact pressure was doubled with respect to the 4-N load, but the contribution of the MoS_2 NTs to the reduction in friction was even more pronounced, i.e., the CoF was around 0.05. The lubricant with platelets also reduced the CoF, but not so significantly. The reduction of the CoF with MoS_2 platelets is most visible for sliding at 4 N, where it was on average half of the reduction obtained with the NTs. The CoF using PAO+PT was also rather unstable with time, especially for the lower load.

The CoF for the CrN coating (Fig. 5b) decreased from around 0.11 when lubricated with pure PAO, to ~0.06 (at 4 N and 20 N) when the MoS_2 NTs were added to the PAO. The decrease of the CoF was also evident, but not so intense in the case of the 4-N load with the addition of MoS_2 platelets. The platelets used at 4 N caused some instabilities in the CoF curve, but on average they do not reduce the CoF.

Table 1
Hardness, defect density and average roughness of the specimen surfaces.

Coating	Hardness [HV]	Defect density [mm^{-2}]	S_a [nm]
Uncoated	700	N.A.	20
CrN	1800	30	35
TiN	2500	60	50
TiAlN	3500	90	70

In the case of the TiN coating lubricated with MoS_2 NTs and platelets a similar friction reduction was observed. At the lower load the CoF dropped by nearly three times (from ~0.14 to ~0.05) when the MoS_2 was added, either NTs or platelets. The drop time (running-in period) was lower for PAO+NT. For the 20-N load the contribution of the MoS_2 NTs was relatively less effective, although they still reduced the CoF by 20%, i.e., from ~0.12 to ~0.10. For the same load the MoS_2 platelets had no effect on the CoF.

The addition of the MoS_2 NTs to the PAO oil for the lubrication of the TiAlN coating still reduced the CoF, although to a much lesser extent than in the previous cases. The friction curves were qualitatively different. The starting CoF was more than three times larger, above 0.3, then very quickly dropped to lower values (0.12–0.13) depending on the lubrication type and remained relatively steady throughout the rest of the measurements. A substantial improvement to the friction behavior when using the MoS_2 NTs is visible only for the 4-N load, where the MoS_2 platelets are less affective.

The results of the CoF for all four samples are summarized in Table 2.

It should be stressed that even at the start of the measurement the MoS_2 NTs effectively reduced the CoF (Fig. 6). The lowest initial CoF obtained under a 4-N load on the uncoated 100Cr6 surface was obtained with PAO+NTs (Fig. 6a), on CrN after 50 cycles and on TiN after 10 cycles (Fig. 6b and c). The initial CoF tested under the 20-N load was also the lowest for lubrication with PAO+NT in

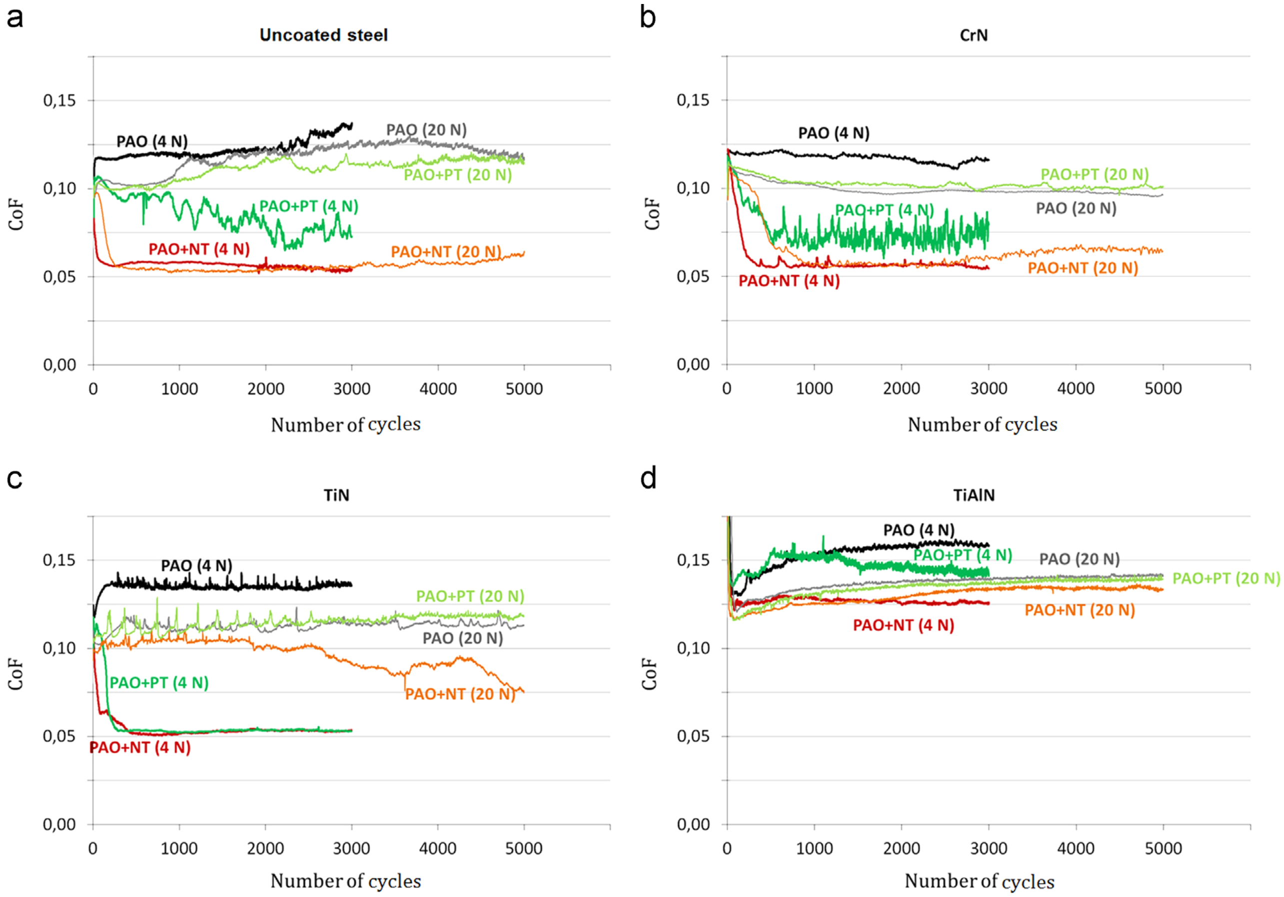

Fig. 5. Coefficient-of-friction curves for the 100Cr6 balls sliding with 4-N and 20-N loads on: a) uncoated steel; b) CrN coating; c) TiN coating, and d) TiAlN coating.

the case of the uncoated 100Cr6 and CrN, whereas in the case of TiN it became the lowest after 25 cycles.

The running-in peak for sliding on TiAlN (Fig. 6d) was lower in the case of lubrication with PAO+PT for both loads. As an additive the MoS_2 NTs provided a lower CoF on the TiAlN compared to the MoS_2 platelets, except for very few cycles, where the platelets were found to be better. The CoF for lubricating with PAO+NT had a high peak, but reached the minimum value after just 30 cycles. After 60 cycles, the CoF curves reached similar values for all four cases around 0.12.

3.3. *Wear results*

The size of the wear disc on the steel ball was used to determine the anti-wear properties of the additive. The sliding traces on the samples were clearly seen with an optical microscope; however, the topographic changes are comparable to the roughness, and difficult to extract from the waviness. Nevertheless, the upper limit of the wear coefficient on the most worn sample (i.e., uncoated steel) was estimated to be around 20 $\mu m^3/Nm$. For other samples no such estimate was possible.

The diameter d of the worn discs was measured using an optical microscope. Table 3 indicates the wear coefficient, calculated for each case according to the equation:

$$w_b = \frac{\pi d^3}{4}\frac{d}{R}(lF)^{-1} \qquad (1)$$

where R is the ball radius, l is the sliding distance and F is the normal load.

The comparison in Table 3 shows the better the anti-wear properties of the MoS_2 NTs with respect to the MoS_2 platelets. The MoS_2 NTs strongly decrease the wear of the steel balls in all four cases. The wear coefficient of the ball tested on the uncoated steel using 4 N is reduced about four times, and using 20 N the reduction is as much as ten times. The MoS_2 platelets were far less

Table 2
Coefficients of friction (CoF) for the 100Cr6 balls sliding on uncoated steel, CrN, TiN, and TiAlN coatings after 3000 cycles with a 4-N load or 5000 cycles for a 20-N load.

CoF	Lubricant	Uncoated	CrN	TiN	TiAlN
4 N	PAO	0.12	0.11	0.14	0.16
	PAO+MoS_2 NT	0.06	0.06	0.05	0.12
	PAO+MoS_2 PT	0.08	0.07	0.05	0.14
20 N	PAO	0.12	0.1	0.11	0.14
	PAO+MoS_2 NT	0.05	0.07	0.08	0.13
	PAO+MoS_2 PT	0.12	0.1	0.12	0.13

Table 3
Wear coefficients of steel balls [μm^3/Nm].

Load	Lubricant	Uncoated	CrN	TiN	TiAlN
4 N	PAO	14	180	850	8000
	PAO +MoS_2 NT	4	80	220	2300
	PAO +MoS_2 PT	52	130	270	3200
20 N	PAO	32	55	220	1200
	PAO+MoS_2 NT	3	25	220	1100
	PAO+MoS_2 PT	21	55	500	1300

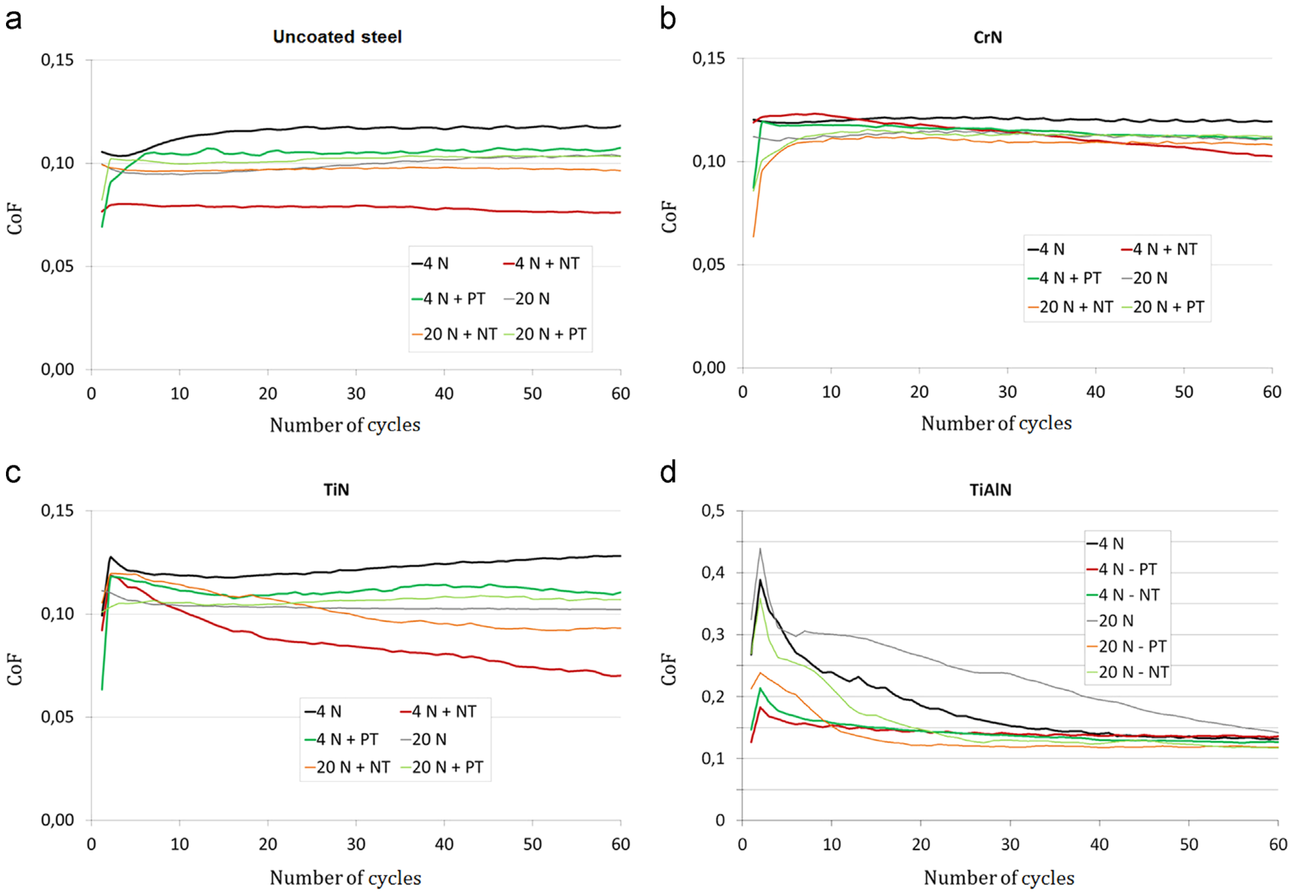

Fig. 6. Initial part of the coefficient-of-friction curve for the 100Cr6 ball sliding on all four types of surfaces: a) uncoated, and coated with b) CrN, c) TiN and d) TiAlN.

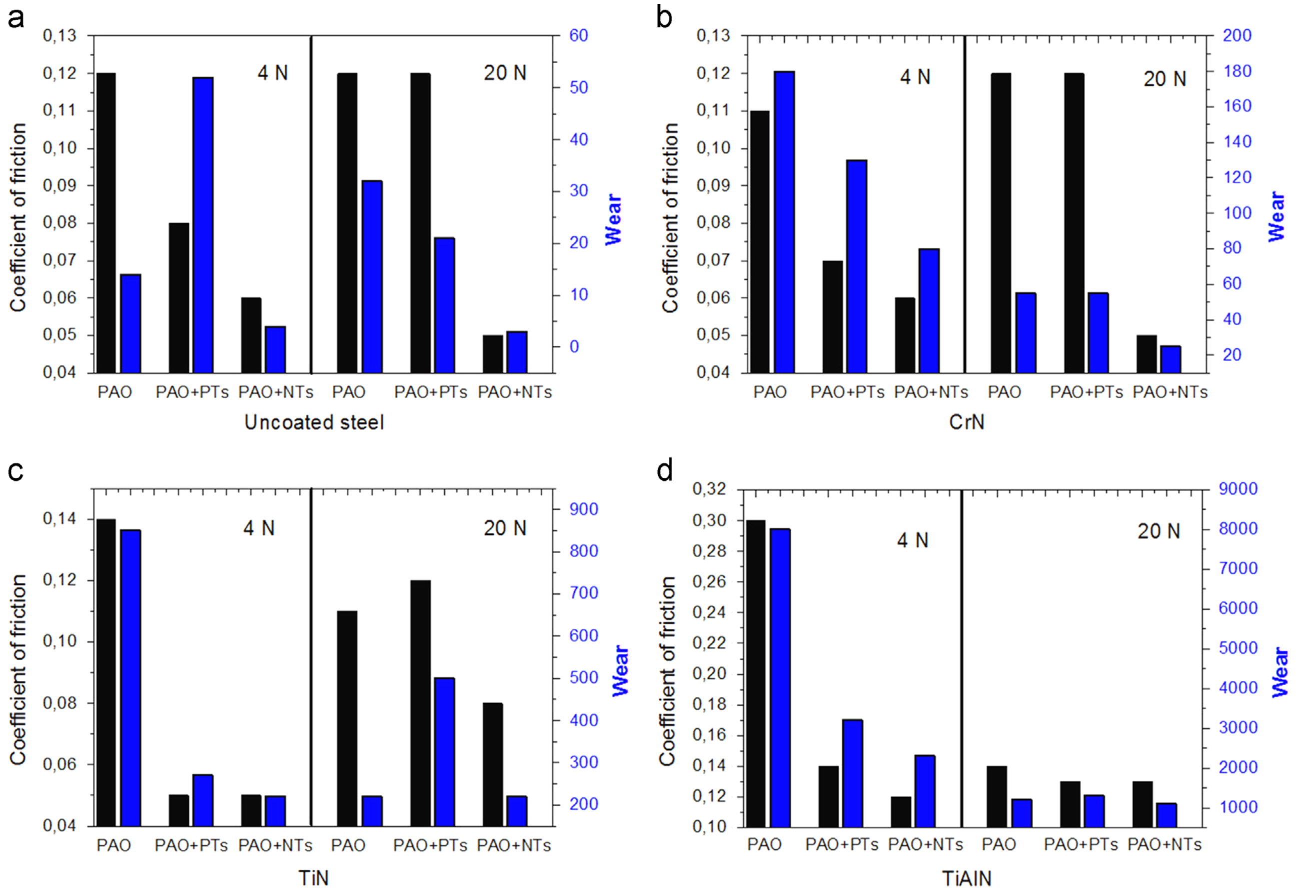

Fig. 7. Friction and wear coefficients [$\mu m^3/Nm$] under 4-N and 20-N loads of: a) uncoated steel; b) steel coated with CrN; c) steel coated with TiN; d) steel coated with TiAlN, all lubricated with pure PAO oil, PAO with MoS_2 platelets (PT), and PAO with MoS_2 nanotubes (NT).

effective. For the 4-N load the wear of the ball actually increased, while for the 20-N load the MoS_2 platelets reduced the wear by only 30%.

The wear and friction reductions for the different lubricant types are summarized in Fig. 7. There is a comparison of the average coefficient of friction and wear of steel balls for the two types of lubricant and the two loads.

Comparing the PAO and PAO+NT, the MoS_2 NTs decrease the wear rate by nearly four times at 4 N on the PVD coatings (Fig. 7c). The wear reduction is best observed on the TiN and TiAlN. On CrN the wear reduction is around 50%, with the lowest wear among the PVD-coated surfaces. The MoS_2 platelets also decreased the coefficient of wear in a similar manner as the MoS_2 NTs, but were much less effective (Fig. 7a).

The wear reduction using the MoS_2 NTs on PVD coatings at the higher load (20 N) is much less pronounced. Generally, MoS_2 as an additive, i.e., NTs and platelets, had no significant effect on the wear at the higher load on the PVD coatings. But there were two major exceptions. The first exception (Fig. 7b) was the wear escalation by two times for the combination of PAO+PT on TiN. The second exception (Fig. 7d) was the wear reduction by two times for the combination of PAO+NT on CrN.

4. Discussion

The effects of MoS_2 NTs as a lubricant additive on the tribological properties for “steel to PVD coatings” contacts were not studied so far. The better performance of the NTs with respect to the platelets observed in our study might be in contradiction with the recent report by Kogovsek et al. [12], where the size and shape of the MoS_2 were found not to influence the friction and wear behavior in the 100Cr6–100Cr6 contact. Although a similar testing configuration was used, there are some important differences between the two experiments, e.g., uni- or reciprocal sliding, different wt.% of added MoS_2, the viscosity of the PAO oil, and the surface roughness. The comparison of the results opens questions about the influence of the concentration of the MoS_2 NTs or platelets on the friction reduction through the viscosity of the PAO+MoS_2, and on the formation of the tribo film during uni-or reciprocal sliding. The confinement of the lubricant in the boundary area squeezes oil out of the contact and locally changes the presence of the additive, its concentration and its orientation with respect to both counterparts. The cylindrical geometry of the nanotubes enables a parallel orientation of the (001) basal planes relative to the surfaces in contact, but only under the assumption of a relatively low concentration. The agglomerates of pristine MoS_2 NTs were weakly bonded, but when the nanotubes became partially or completely exfoliated under the load, they form strongly connected patches, whose orientations with respect to the counterparts are random and therefore the lubrication is not optimized [17,18].

In all cases the NTs more or less reduced the friction, while the platelets may in some cases lead to worse tribological results, for example, they increase the CoF on TiN by nearly 10% or increase the wear on uncoated steel by more than three times in comparison with the pure PAO oil. This deterioration can be explained by the non-parallel orientation of the MoS_2 platelets in relation to the surfaces in the contact [19]. MoS_2 as a layered material can be easily exfoliated along the basal planes under parallel forces, while the perpendicular component of a force needs to break covalent bonds among interlayer atoms, which is energetically costly. The same reason is behind the increased instabilities of the friction curves when platelets are used as an additive. In the parallel orientation the friction is lower, while it increases again when the flakes are no longer in the parallel orientation. This change in orientation is more pronounced at lower loads (Fig. 3) and under reciprocal sliding.

Although MoS_2 NTs added to PAO were found to be very good friction modifiers and anti-wear additives, they are not equally effective on different hard coatings. The largest contribution of the MoS_2 NTs to the tribological properties is on the CrN using the 4-N load, and the lowest on the TiAlN coatings using the 20-N load. The wear of the ball sliding on the TiAlN, as the hardest and roughest sample, was decreased nearly four times with the 4-N load, while it was only 15% for the 20-N load. This indicates that MoS_2 NTs were squeezed from the local contact on top of the sample asperities and pushed into the surface pits. In contrast, CrN with the smoothest surface and the lowest hardness enabled the effective exfoliation of the MoS_2 with both shapes at 4 N, while the higher load of 20 N led to shape differentiation: the MoS_2 NTs were still effective friction and wear reducers, although the platelets were not.

MoS_2 is chemically a very inert compound on the basal plane, but it has reactive sites at the crystal edges. The exfoliation of MoS_2 NTs leads to very thin MoS_2 flakes with a thickness below the wall thickness of the pristine NTs, i.e., 10 nm. Due to the intrinsic partial exfoliation of the NTs, which is the result of the growth mechanism [13], the energy of the running-in process is smaller than in the case of the MoS_2 platelets. This results in a lower running-in peak and a lower initial friction.

5. Conclusions

The tribological behavior of MoS_2 multi-wall nanotubes (NTs) added to polyalphaolefin (PAO) synthetic oil for lubricating CrN, TiN and TiAlN hard coatings was investigated. The coatings were deposited on cold-work tool steel AISI D2 by physical vapor deposition (PVD). The following major conclusions can be drawn:

1. In general, the MoS_2 NTs and MoS_2 platelets are very effective friction modifiers and anti-wear additives. MoS_2 NTs greatly improved the tribological properties. The friction coefficient was reduced by a factor of three and the wear rate by a factor of ten.
2. In the case of PVD hard coatings, the addition of MoS_2 NTs to the PAO oil in a tribological contact strongly reduced both the CoF and the wear, even in the cases when this was not expected.
3. If MoS_2 platelets were used instead of NTs, the improvement was limited. In some cases the tribological results were inferior compared to pure PAO oil.
4. MoS_2 NTs effectively decreased the CoF on CrN coatings from 0.10–0.12 to 0.05 for both (4 N and 20 N) loads. The reduction of the CoF on the TiN coatings was from 0.14 to 0.05 at a low load and from 0.12 to 0.07 at a high load. The decrease of the CoF on the TiAlN coatings was from 0.16 to 0.12 at the lower load, whereas at the higher load the reduction was minimal.

Acknowledgments

This work was supported by the Slovenian Ministry of Education, Science and Sport within the project: “Researchers at the start of career”. We also wish to express our gratitude to Mr Janez Jelenc for the synthesis of the MoS_2 NTs.

References

[1] R. González, A. Hernández Battez, D. Blanco, J.L. Viesca, A. Fernández-González, Lubrication of TiN, CrN and DLC PVD Coatings with 1-Butyl − 1-Methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate, Tribol. Lett. 40 (2010) 269–277 2010/11/01.

[2] D. Blanco, A.H. Battez, J.L. Viesca, R. González, A. Fernández-González, Lubrication of CrN coating with Ethyl-Dimethyl-2-Methoxyethylammonium Tris (pentafluoroethyl)Trifluorophosphate ionic liquid as additive to PAO 6 2011/01/01, Tribol. Lett. 41 (2011) 295–302.

[3] R. Tenne, L. Margulis, M. Genut, G. Hodes, Polyhedral and cylindrical structures of tungsten disulphide, Nature 360 (1992) 444–446.

[4] L. Cizaire, B. Vacher, T. Le Mogne, J.M. Martin, L. Rapoport, A. Margolin, et al., Mechanisms of ultra-low friction by hollow inorganic fullerene-like MoS2 nanoparticles, Surf. Coat Technol. 160 (2002) 282–287.

[5] R. Rosentsveig, A. Gorodnev, N. Feuerstein, H. Friedman, A. Zak, N. Fleischer, et al., Fullerene-like MoS2 Nanoparticles and Their Tribological Behavior 2009/11/01, Tribol. Lett. vol. 36 (2009) 175–182.

[6] J.M. Martin, C. Donnet, T. Le Mogne, T. Epicier, Superlubricity of molybdenum disulphide, Phys. Rev. B 48 (1993) 10583–10586.

[7] L. Joly-Pottuz, F. Dassenoy, M. Belin, B. Vacher, J.M. Martin, N. Fleischer, Ultralow-friction and wear properties of IF-WS2 under boundary lubrication, Tribol. Lett. 18 (2005) 477–485.

[8] L. Rapoport, Y. Bilik, Y. Feldman, M. Homyonfer, S.R. Cohen, R. Tenne, Hollow nanoparticles of WS2 as potential solid-state lubricants, Nature 387 (1997) 791–793.

[9] J. Tannous, F. Dassenoy, A. Bruhács, W. Tremel, Synthesis and tribological performance of novel Mo x W $1-x$ S 2 $(0 \le x \le 1)$ inorganic fullerenes, Tribol. Lett. 37 (2010) 83–92.

[10] I. Lahouij, B. Vacher, J.-M. Martin, F. Dassenoy, IF-MoS2 based lubricants: Influence of size, shape and crystal structure, Wear 296 (8/30/2012) 558–567.

[11] G.W. Stachowiak, A.W. Batchelor, Engineering Tribology, Elsevier Butterworth-Heinemann, UK, 2005.

[12] M. Kalin, J. Kogovšek, M. Remškar, Nanoparticles as novel lubricating additives in a green, physically based lubrication technology for DLC coatings, Wear 303 (6/15/ 2013) 480–485.

[13] M. Kalin, Designing tribological interface for efficient and green DLC lubrication: the role of coatings and lubricants, Tribol. Online 7 (2012) 112–118.

[14] J. Kogovšek, M. Kalin, Various MoS2-, WS2- and C-based micro- and nanoparticles in boundary lubrication, Tribol. Lett. 53 (2014) 585–597 2014/03/01.

[15] P. Panjan, M. Čekada, M. Panjan, D. Kek-Merl, F. Zupanič, L. Čurković, et al., Surface density of growth defects in different PVD hard coatings prepared by sputtering, Vacuum 86 (2012) 794–798.

[16] M. Remskar, A. Mrzel, M. Virsek, M. Godec, M. Krause, A. Kolitsch, et al., The MoS2 nanotubes with defect-controlled electric properties, Nanoscale Res. Lett. 6 (2011) 26.

[17] M. Kalin, J. Kogovšek, M. Remškar, Mechanisms and improvements in the friction and wear behavior using MoS2 nanotubes as potential oil additives, Wear 280–281 (3/20/ 2012) 36–45.

[18] M. Kalin, J. Kogovšek, J. Kovač, M. Remškar, The formation of tribofilms of MoS2 nanotubes on steel and DLC-coated surfaces, Tribol. Lett. 55 (2014) 381–391 2014/09/01.

[19] A.R. Lansdown, Molybdenum Disulphide Lubrication, Elsevier Science, USA, 1999.