EVALUATION OF CHANGES IN THE UTILITY PROPERTIES OF A BASE MATERIAL AFTER THE APPLICATION OF THIN COATINGS OF WC/C, TIC/C AND A CARBON-BASED COATING: Ta-C

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Abstract

Tribological coatings are mainly used to reduce adhesive wear, which often leads to the seizure or the formation of cold welds. The low coefficient of friction and good sliding properties make it ideal for applications with low lubrication or even dry running. The result is an ideal way to reduce surface fatigue and tribo-oxidation. Tribological coatings have good sliding properties, a low coefficient of friction and low adhesive wear. Thin layers of WC/C and TiC/C of the MeC/a-C: H coating group were deposited onto the surface of ISO 683/11-70 steel. The third tribological coating deposited on the same substrate was a ta-C coating - a tetrahedral amorphous layer (stoichiometry: sp^3 bonds > 50%). Tribological measurements were performed at a load of 10 N, a rotational speed of 60 rpm, and with a counterpart of ceramic material Al_2O_3.

Keywords: Nanocomposite coatings, surface morphology, mechanical properties, tribology and wear

1. INTRODUCTION

Thin coatings are used to protect the substrate and improve the useful properties of components. Insufficient lubrication and dry friction can occur during the working process. Therefore, thin layers can be applied (deposited on a certain substrate), which can perform the function of a lubricant [1]. The addition of metal to the carbon layers can in some cases improves the mechanical and tribological properties [2], for example a thin layer of WC/C that provides, chemical inertness and low coefficient of friction (0.12 to 0.15) [3]. WC/C coatings offer good adhesion to the base substrate, which is an integral part of industrial use [1] and a large modulus of elasticity [4]. WC/C layers contain a nanocrystalline WC layer with and an amorphous C phase [4]. Tungsten carbide with amorphous carbon is used in technical applications such as bearings, pumps, compressors, gear wheels, tools, [5] for anti-corrosion components, and to protect aircraft engine components etc. [6]. DLC layers are used in hard drives, shavers, damage-resistant glass, electronics, medicine and the automotive industry [7,8]. There are different types of DLC layers, which differ in composition, method of preparation and properties. One type of DLC layer is a ta-C coating, which has a low coefficient of friction and is wear resistant [9]. Diamond-like tetrahedral amorphous carbon (ta-C) films, which contain no hydrogen and high content of sp^3 bonds, have a very high hardness and elastic modulus (up to 600 GPa) [10]. TiC/C coatings have good sliding properties and is wear resistant. This type of coating is used as a protective coating with high hardness and toughness [11]. Mechanical and tribological properties are influenced by deposition conditions [12,13]. The modulus of elasticity of TiC/C thin films ranges from 160 to 430 GPa, nanohardness from 13 to 44 GPa and the coefficient of friction is around 0.14. TiC/C coatings are suitable for application on tools or machine parts [1].

The aim of this research is to improve the utility properties of surfaces after modification of basic materials with thin layers labeled ta-C, WC/C and TiC/C. Surfaces after modification are intended to provide better friction properties in contact with the counter-body during dry friction. The surface modification with the desired frictional properties was subsequently selected as suitable for a given industrial application.

2. MATERIALS AND METHODS

2.1. Used thin layers

For the experiment, thin carbon-based coatings: ta-C, WC/C and TiC/C (SHM s.r.o. and PLATIT a.s.) were applied on two steel substrates W.Nr. 1.7131 (with a hardness of 650 HV1) and W.Nr. 1.2379 (with a hardness of 730 HV1). The surface roughness and morphology, nanohardness, adhesion to the base material, wettability, homogeneity, thickness of coatings, tribological behavior and amount of wear were evaluated on the prepared coatings. **Table 1** shows the deposition conditions of the investigated thin coatings. PVD technologies used by SHM s.r.o. are based on two basic coating principles: low-voltage arc vapor deposition and magnetron sputtering. All thin films used in the research were applied by magnetron sputtering.

Table 1 Thin coating deposition conditions

Thin coating	Deposition temperature [°C]	Overall magnetron performance [kW]	Magnetron power [W/cm²]	Pretension [V]	Pressure [Pa]
ta-C	110 - 150	10	500	100	0.3
WC/C	150 - 200	5	20	100	0.6
TiC/C	300 - 400	7	30	300	0.7

2.2. Used methods of thin film evaluation

The nanohardness and elastic modulus of the coatings were evaluated by a CSM Instruments indentation tester (Berkovich evaluation method). The maximum penetration depth during the measurement was no more than 10 % of the coating thickness.

A Zeiss Ultra Plus scanning electron microscope (SEM) equipped with an Oxford X-Max 20 energy dispersive spectrometer (EDS) was used for the local chemical analysis, homogeneity, and thickness of the thin layers. To minimize the influence of the substrate on the quant results due to the penetration of primary electrons through the deposited layers, the chemical composition of the layers was analyzed at an accelerating voltage of 10 kV. Before performing the SEM analysis, the samples were cleaned with a mixture of ethanol and water in an ultrasonic cleaner.

The coating surface morphology was evaluated using a Sensofar Metrology material confocal microscope according to the ISO 25178 standard. The used parameters were as follows: S_a is the average arithmetic height (average surface roughness); S_z is the maximum height (height between the lowest recesses and the highest projection). The size of the evaluated area was 1700.16 x 1418.64 µm.

The coating adhesion was evaluated using a CETR UMI Multi-Specimen Test System. A scratch test was performed using a progressive load from 2 to 80 N at a speed of 10 mm/min (according to the EN1071-3:2005 standard). The scratch test was performed at room temperature and a relative humidity of 36 ± 2 %.

The wettability of the nanostructured coatings was investigated on a Surface Energy Evaluation system, which is designed primarily for contact angle measurement and determination of surface energy. It features a robust aluminum housing, a 1.3 Mpx USB 2.0 color camera that moves vertically, and a 2D horizontal sample table. Distilled water was used for the evaluation and the tested oil with the trade name Paramo CLP 320 was used to approach the real conditions. The wettability evaluation apparatus was prepared according to the planned methodology and the samples were handled using gloves. The room temperature during the measurement was 22 °C, the air humidity was 36 ± 2% and the drop volume used was 5 µL. Ten drops were dripped onto each of the investigated surfaces to ensure repeatability.

A tribometer for dry and liquid environments (Anton Paar Czech Republic s.r.o.) in the *"Ball-on-Disc"* mode was used to estimate the tribology properties of the thin coatings (ASTM G99-95). An essential part of the test measurement was a friction sensor. The coefficient of friction (CoF) between the unit and the disc was determined during the test measurement. Tribological testing was conducted using a ball made of Al_2O_3 with a diameter of 6.00 mm, at a load of 10 N and at room temperature and a humidity of 34 ± 2 %. The rotation speed during the experiment was 60 rpm and the travelled distance was 500 m.

3. RESULTS

3.1. Morphology a surface roughness

Figure 1 shows the surface morphology of the investigated coatings labeled amorphous carbon (ta-C), WC/C and TiC/C by SEM analysis.

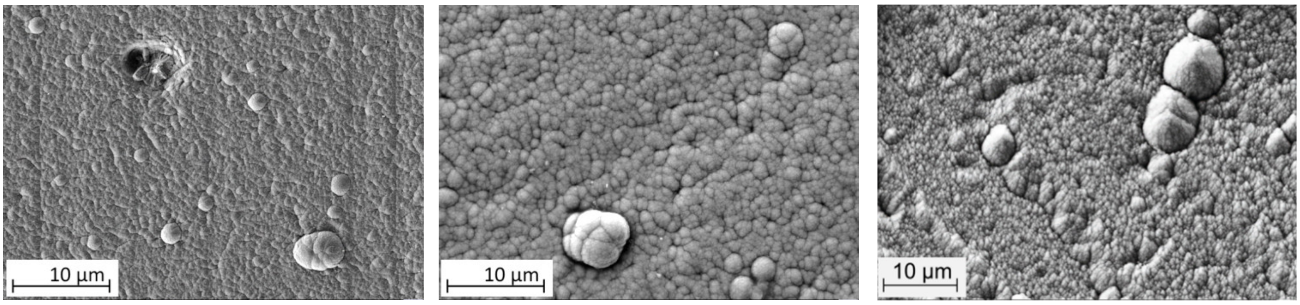

Figure 1 Surface morphology after deposition of a) thin coating of ta-C (left);
b) thin coating of WC/C (centered) and c) thin coating of TiC/C (right), evaluated by SEM

The measured surface roughness values (see **Table 2**) show that the modification of the surface leads to an increase in its roughness (according to the parameters S_a and S_z). The greatest influence on the increase of surface roughness compared to the roughness of the base material was measured on the surface of the coating labeled TiC/C (W.Nr. 1.7131), then on the surface of the coatings labeled ta-C (W.Nr. 1.2379) and TiC/C (W.Nr. 1.2379).

Table 2 The measured surface roughness values S_a and S_z and their standard deviations in [µm]

Steel substrate	W.Nr. 1.7131				W.Nr. 1.2379			
Thin coating	*W.Nr. 1.7131*	ta-C	WC/C	TiC/C	*W.Nr. 1.2379*	ta-C	WC/C	TiC/C
S_a [µm]	0.17 *± 0.02*	0.23 *± 0.02*	0.20 *± 0.01*	0.30 *± 0.03*	0.21 *± 0.01*	0.29 *± 0.05*	0.21 *± 0.01*	0.25 *± 0.03*
S_z [µm]	1.39 *± 0.09*	1.82 *± 0.11*	2.30 *± 0.14*	2.61 *± 0.16*	2.08 *± 0.07*	3.18 *± 0.16*	2.16 *± 0.14*	2.66 *± 0.12*

3.2. Hardness and modulus of elasticity

The parameters of the process of evaluation of nanohardness were as follows: approach distance 2 µm; linear loading with approach speed 1 µm/min; max depth 0.30 µm; retract speed 2 µm/min; loading rate 1.00 µm/min;

unloading rate 1.00 μm/min; stiffness threshold 500 μN/μm. **Table 3** shows averaged values from five measurements of the hardness, modulus of elasticity and the plasticity index (H/E).

Table 3 The values of nanohardness and elastic modulus of the coatings in [GPa]

Steel substrate		**W.Nr. 1.7131**			**W.Nr. 1.2379**	
Thin coating	*ta-C*	*WC/C*	*TiC/C*	*ta-C*	*WC/C*	*TiC/C*
H [GPa]	24 ± 2	12 ± 2	28 ± 2	33 ± 2	9 ± 1	26 ± 2
E [GPa]	270 ± 22	127 ± 31	340 ± 22	391 ± 46	99 ± 11	333 ± 22
H/E	0.089	0.094	0.082	0.084	0.091	0.078

The applied thin coatings significantly increased the base surface hardness; the highest nanohardness values were measured for the thin coatings labeled ta-C (24 - 33 GPa) and TiC/C (26 - 28 GPa), see **Table 3**.

3.3. Scratch test results

Three measurements were taken at different points for each sample, and the average values of the measured critical loads (L_C) are given in **Table 4**. Based on the scratch tests, the critical load corresponding to a load leading to the appearance of the first crack L_{C1} (cohesive failure) lied within the range of 16 - 22 N, and the next critical load L_{C3} (adhesion failure) lied within the range of 45 - 59 N.

Table 4 The adhesion properties of the investigated coatings in [N]

Steel substrate		W.Nr. 1.7131			W.Nr. 1.2379	
Thin coating	*ta-C*	*WC/C*	*TiC/C*	*ta-C*	*WC/C*	*TiC/C*
L_{C1} *[N]*	21.8 ± 1.3	16.5 ± 1.4	18.1 ± 1.9	20.7 ± 1.2	16.5 ± 2.4	16.3 ± 2.4
L_{C3} *[N]*	56.5 ± 4.2	48.4 ± 4.8	44.7 ± 2.4	58.8 ± 3.6	50.3 ± 5.3	47.7 ± 3.5

The measured adhesion values show that all of the types of surface modification have very good adhesion to the base material (W.Nr. 1.7131 and W.Nr. 1.2379). The best adhesion properties were measured with the thin coating of amorphous carbon (ta-C) on both types of substrate.

3.4. Evaluation of the wettability of nanocomposite surfaces

The wettability evaluation was performed according to the described methodology and the measurement results together with the standard deviation are shown in **Table 5**.

Table 5 Measured values of contact angle on the surface of the investigated coatings in [°]

Steel substrate		W.Nr. 1.7131			W.Nr. 1.2379	
Thin coating	ta-C	WC/C	TiC/C	ta-C	WC/C	TiC/C
with distilled water [°]	79 ± 5	89 ± 4	82 ± 4	76 ± 5	83 ± 3	86 ± 5
with oil PAR.CLP 320 [°]	52 ± 4	54 ± 3	50 ± 2	52 ± 2	57 ± 4	53 ± 4

The measured values indicate surfaces with hydrophilic properties, contact angles using distilled water and oil with the trade name Paramo CLP 320 were less than 90°.

3.5. Homogeneity and thickness of the thin coatings

The thickness and homogeneity of the coatings was evaluated from their cuts (**Figure 2**). The evaluation was performed by linear and area analysis of chemical composition and using an SE detector.

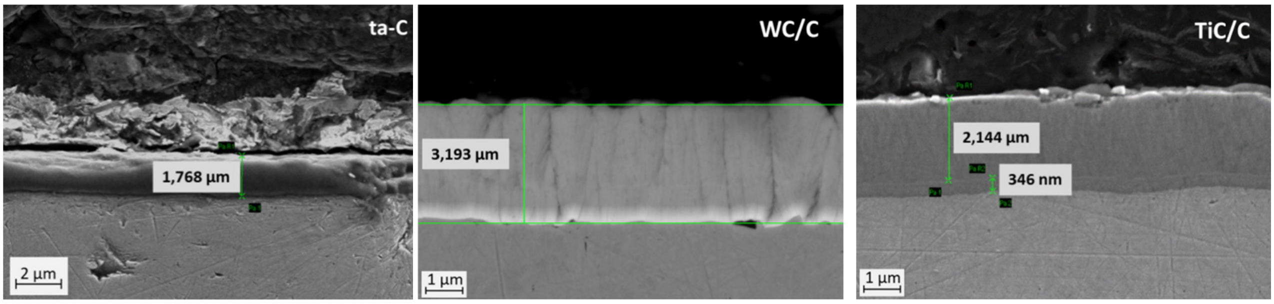

Figure 2 Thickness of the evaluated coatings of ta-C, WC/C and TiC/C displayed by means of cuts, by SEM

The ta-C, WC/C, TiC/C coatings were cast into the resin and polished with diamond paste, and the ta-C layers had to be silver plated. The thin layers deposited on the steel substrates (W.Nr. 1.7131 and W.Nr. 1.2379) are highly homogeneous. No major defects or cracks were observed on the coatings or on the boundaries of the coatings - substrate.

3.6. Tribological behavior and surface wear rate

A comparison of the changes in friction coefficients is made firstly by contacting the observed coatings with an Al_2O_3 ceramic ball. Furthermore, the nanostructured surfaces were evaluated using a lubricating medium (Paramo CLP 320), while the counterpart remained of the same material (Al_2O_3). The working temperature of the oil during the tribological experiment was 45 °C. The last part of the experiment was conducted with the addition of the Paramo CLP 320 oil with nanoparticles (SiO_2 NPs and SiO_2 + Al_2O_3 NPs at a concentration of 0.5 g/L) under the same conditions.

Table 6 Measured values of coefficient of friction and their standard deviations

Thin coating / *CoF [-]*	**W.Nr. 1.7131**	ta-C	WC/C	TiC/C	**W.Nr. 1.2379**	ta-C	WC/C	TiC/C
dry friction	0.67±0.07	0.11±0.01	0.19±0.01	0.25±0.03	0.68±0.18	0.10±0.01	0.20±0.02	0.24±0.02
CLP 320	0.12±0.01	0.11±0.01	0.12±0.02	0.13±0.02	0.13±0.01	0.09±0.01	0.11±0.02	0.12±0.02
SiO_2 NPs	-	0.10±0.01	0.12±0.01	-	-	0.10±0.01	0.13±0.02	-
SiO_2+Al_2O_3NPs	-	0.11±0.01	0.12±0.01	-	-	0.10±0.01	0.11±0.01	-

The evaluation of the coefficient of friction in the lubricating medium Paramo CLP 320 (**Figure 3** left) with the addition of SiO_2 NPs (**Figure 3** center) and SiO_2 + Al_2O_3 NPs (**Figure 3** right) was performed on thin layers of ta-C and WC/C, the layers showed the lowest values of CoF during dry friction. **Figure 3** shows the amount of wear of the thin coatings labeled ta-C upon contact with the Al_2O_3 ceramic ball and use of oil with and without nanoparticle additivation.

Lubricant friction had a beneficial effect on the CoF and wear of the friction pair. It was further determined that the nanoparticles had no effect on the size of the CoF (see **Table 6**). The addition of the SiO_2 NPs to the lubricant (Paramo CLP 320) had a positive impact on the wear process, resulting in a reduction in the size of the damaged area after tribology (**Figure 3** - right). Conversely, the combination of nanoparticles (SiO_2 + Al_2O_3 NPs) resulted in increased wear after the tribological process (**Figure 3** - center) compared to the oil without additivation.

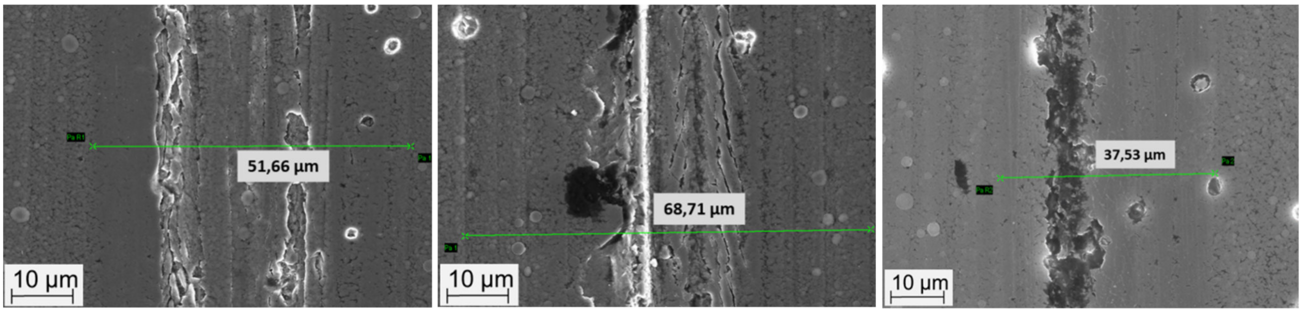

Figure 3 Wear of the amorphous carbon (ta-C) thin coating during friction with lubrication and after additivation of the oil by nanoparticles, evaluated by SEM

4. CONCLUSION

Three types of thin coatings (ta-C, WC/C and TiC/C) applied by low-voltage arc vapor deposition and magnetron sputtering were investigated. The study led to the following conclusions:

- Modification of the material surface with thin coatings leads to a slight increase in surface roughness.
- After the application of the thin coatings there was a significant increase in hardness on the surface of the test samples.
- The best adhesion to the base material was shown by the coating labeled ta-C for both types of base material.
- The applied thin layers did not affect the wettability of the base material surfaces; the PARAMO CLP 320 oil used has a good surface wettability.
- The deposited thin coatings of ta-C, WC/C and TiC/C on the substrates reduced the CoF by up to 85 %. The coatings labeled ta-C and WC/C in combination with the PARAMO lubricant with SiO_2 NP additivation resulted in the best results, i.e. lower CoF and reduced wear.

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