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Mechanical and tribological properties of gradient a-C:H/Ti coatings

D. BATORY[1,2*], W. SZYMAŃSKI[1], M. CŁAPA[1]

[1]Technical University of Lodz, Institute of Materials Science and Engineering, 1/15 Stefanowskiego St., 90-924 Lodz, Poland

[2]Institute for Nanomaterials, Advanced Technology and Innovation, Technical University of Liberec, 2 Studentska St., 461 17 Liberec, Czech Republic

The unusual combination of high hardness and very low friction coefficient are the most attractive tribological parameters of DLC (diamond-like carbon) layers. However, their usability is strongly restricted by the limited thickness due to high residual stress. The main goal of the presented work was to obtain thick, wear resistant and well adherent DLC layers while keeping their perfect friction parameters. As a proposed solution a Ti–Ti_xC_y gradient layer was manufactured as the adhesion improving interlayer followed by a thick diamond-like carbon film. This kind of combination seems to be very promising for many applications, where dry friction conditions for highly loaded elements can be observed. Both layers were obtained in one process using a hybrid deposition system combining PVD and CVD techniques in one reaction chamber. The investigation was performed on nitrided samples made from X53CrMnNiN21-9 valve steel. Structural features, surface topography, tribological and mechanical properties of manufactured layers were evaluated. The results of the investigation confirmed that the presented deposition technique makes it possible to manufacture thick and well adherent carbon layers with high hardness and very good tribological parameters. Preliminary investigation results prove the possibility of application of presented technology in automotive industry.

Keywords: *carbon layers; friction; adhesion; wear resistance*

1. Introduction

Diamond-like carbon layers present a wide spectrum of very interesting mechanical as well as physicochemical properties, which can be varied in every respect by changing the deposition method and process parameters. The resulting layers have diversified amounts of diamond and graphitic phases. Therefore, they may combine the useful features offered by carbon and graphite layers. [1, 2]. Excellent combination of some parameters which is unusual for other materials, makes DLC layers highly attractive for application in many areas of life, as the protective coatings deposited on machine and engine parts exposed to dry friction as well as on medical tools and implants as a mean to improve their corrosion features and protect living tissues against methalosis [3–7]. Excellent tribological properties, especially high wear resistance ($<10^{-8}$ $mm^3N^{-1}m^{-1}$) and low friction coefficient (0.005 – 0.5) obtained under dry friction conditions are the most characteristic for carbon layers. This phenomenon is connected with the sliding effect occurring in the transient layer, which appears in the contact area between co-working elements, mainly as the result of DLC layer graphitization processes. Such friction induced phase transformation leads to appearance of a thin layer with low resistance against shear, which acts as a solid lubricant. It gives protection against excessive wear for the surface of the element co-working with the layer, and decreases the wear degree of the layer itself [3, 9, 10]. Another significant factor, characteristic for a-C:H layers is the hydrogen content, which also has a great influence on the mechanical and tribological properties of the carbon layers. By the stabilization of σsp^3 structure, hydrogen prevents its inordinate disin-

*E-mail: damian.batory@gmail.com

tegration into the graphitic phase. High chemical affinity of carbon and hydrogen causes the termination of free σ bonds on the layer surface, which prevents their adhesive interaction with the particles of oxygen, aqueous vapour and other gases present in the working atmosphere. Those interactions usually negatively influence the value of friction coefficient [8, 11, 12].

Despite very good physical and chemical parameters, poor adhesion of DLC layers to metal substrates, caused by high internal stress, limits their application possibilities. Stress, Young's modulus and hardness of carbon layers are dependent on each other in a way, that an increase in hardness or layer thickness always results in increased level of stress. On the other hand, a thick carbon layer (concerning its extended exploitation time) seems to be the most adequate for protective applications. Good adhesion of the layer seems to be a critical issue, however, exceeding the limit of the layer thickness usually results in self delamination of the coating, only as a result of generated stress, whose value can reach up to 10 GPa [1, 13, 14]. Therefore, the outcome properties of carbon layers should constitute the compromise between required parameters and expected thickness. Many efforts have been made during recent years in the field of adhesion improvement of carbon layers. Among many means and methods of adhesion improvement, doping and deposition of gradient or nanocomposite layers seem to be the most advanced and giving the best results. Application of materials with high chemical affinity to carbon can lead to formation of carbides in the form of nanocrystalline clusters embedded into amorphous carbon matrix, that influence the structure, topography and mechanical properties as well. The authors of works [15, 16] obtained very good adhesion and tribological properties of titanium doped carbon layers deposited using the magnetron sputtering technique. Noticeably improved surface topography was observed by the authors of work [17], where the doping process was realized using the ion implantation technique. Also application of silicon as a doping material has been considered by many authors as a very good solution, mostly because of high concentration of σsp^3 bonding, reduced stress and enhanced thermal stability [1, 18, 19]. Despite improved adhesion and useful properties of carbon layers deposited by variety of methods, which can be applied in a wide range of applications, only few reports have appeared on the industrial implementation of carbon coatings in the world literature [20, 21].

In our previous work we presented the positive influence of chemical composition gradient on the adhesion and tribological parameters of carbon coatings synthesized using hybrid PVD/CVD technique [22]. However, in spite of some improvement, the adhesion was far below our expectations. Further research in this field resulted in different approaches to this problem, namely we focused on the substrate material and its influence on the properties of gradient carbon coatings. In this paper we propose application of gradient carbon coatings deposited on pre-hardened austenitic steel substrates and present the preliminary investigation results connected with an attempt of application of the carbon layers in the automotive industry.

2. Experimental

The substrate material was a conventional plasma nitrided valve steel X53CrMnNiN21-9, commonly used in the automotive industry. Samples were Ø 25.4 mm × 6 mm flat discs and Ø 8 mm × 35 mm cylinders, with the same surface finish as the regular valves. They were ultrasonically cleaned in methanol and acetone bath directly before the deposition process.

Gradient a-C:H/Ti coatings were synthesized with use of a hybrid Radio Frequency Plasma Assisted Chemical Vapour Deposition/Magnetron Sputtering (RF PACVD/MS) technology. A detailed characteristics of the apparatus as well as structural and phase composition of the manufactured layers can be found in [23, 24]. The proposed synthesis technique employed the chemical composition gradient from pure Ti throughout intermediate Ti_xC_y layer up to pure DLC coating on the top. The overall thickness of the gradient interlayer did not exceed 200 nm and it appeared to be a nanocomposite structure of Ti_xC_y inclusions, randomly distributed in the amorphous carbon matrix. The thickness of the DLC top layer can be up to few micrometers while still maintaining the high level of adhesion.

The samples were mounted in sample holders and placed on the water cooled electrode in that way that the modified specimens were located several millimeters above the electrode to avoid too intense heat dissipation. Before the process, the reaction chamber was pumped out to a pressure of 2×10^{-3} Pa. The synthesis process was preceded by 10 min etching in argon atmosphere at negative self bias of 800 V. The gradient interlayer was synthesized using pulsed magnetron sputtering process of Ti cathode in Ar/CH_4 atmosphere, conducted in the plasma of the radio frequency electric field discharge. After the deposition of the adhesion promoting Ti–Ti_xC_y interlayer, the top DLC coating was synthesized by means of RF PACVD technique in methane atmosphere under a pressure of 20 Pa and negative self bias of 600 V. Basing on the results of our earlier investigation, the negative bias of 600 V allowing high deposition rate of carbon coating (30 nm/min) was considered as optimal.

Structure, morphology and qualitative chemical composition of the manufactured coatings were examined using Hitachi S-300 N scanning electron microscope equipped with Thermo Noran EDS analyzer. The phase composition of nitrided layer was measured with an X-ray diffractometer working with Co Kα radiation (0.178 nm). Hardness and the Young's modulus were determined using a standard Berkovitch diamond tip. The investigations were performed with a nanoindenter G-200 (MTS NANO INSTRUMENTS) using the Continuous Stiffness Measurement (CSM) mode. The adhesion of a-C:H/Ti coatings was measured with the scratch tester equipped with 200 μm round diamond tip. Surface topography and roughness parameters before and after the deposition were investigated with the use of AFM multimode microscope equipped with a Nanoscope V controller (Bruker Corporation, USA) working in tapping mode. Tribological parameters (friction coefficient and resistance against wear) were determined using two methods. T-01 ball on disc method was applied to measure the friction coefficient. The investigations were performed under a load of 10 N and 20 N with the sliding speed of 0.1 m/s on a distance of 1000 m. As the counter-sample ¼ inch 100Cr6 bearing steel and ZrO_2 balls were used. After the investigation, the resulting wear track and its profile were analyzed with a profilometer and Olympus GX-71 optical microscope. Wear resistance was measured with a T-04 three-cylinder-cone tester under a load of 300 MPa. The tests were performed during 100 minutes with the use of heat treated C45 steel cone with the hardness of 30 HRC. Both investigations on T-01 and T-04 testers were carried out under dry friction conditions at room temperature and normal humidity.

3. Results and discussion

3.1. Structure, phase and chemical composition

Fig. 1 presents the microscope image and X-ray diffraction pattern of a nitrided layer on the surface of X53CrMnNiN21-9 steel. For the comparison, the diffraction pattern of an untreated substrate is added. The thickness of the nitrided layer is about 30 μm. It has a two-phase structure consisting of diffusion Feγ(N) layer with CrN inclusions. There is lack of "white layer" in the very top part of the nitrided layer. According to the authors of work [25] this thin layer, consisting of ε and γ' iron nitrides may negatively affect the adhesion of gradient carbon coatings, especially due to the fact that titanium is used as the adhesion promoting interlayer.

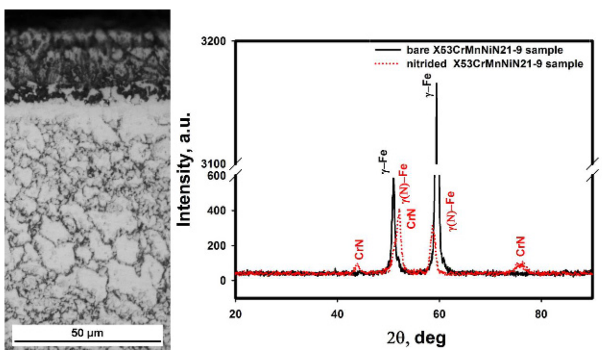

Fig. 1. Optical microscope image and X-ray diffraction pattern of nitrided X53CrMnNiN21-9 steel; for comparison, the spectrum of bare X53CrMnNiN21-9 steel is added.

The SEM view of the cross section of the sample covered with a-C:H/Ti layer is presented in Fig. 2a, whereas the chemical composition analysis results are shown in Fig. 2b. The coatings are rather uniform and homogeneous and despite the thickness of about 1 – 1.2 μm there are no microcracks or other signs of discontinuities that may affect their overall quality. Small defects, virtually unnoticeable may be a reason of poor corrosion behavior when the coating is subjected to aggressive working environment, as reported in [26]. Moreover, the occurence of microcracks resulting from high residual stress may significantly decrease the resistance against corrosion. Our earlier examination results proved very high resistance against corrosion of gradient a-C:H/Ti coatings up to the thickness of 1.7 μm [27]. The EDS analysis results, besides the elements typical for the substrate material, revealed the presence of carbon coating and Ti interlayer.

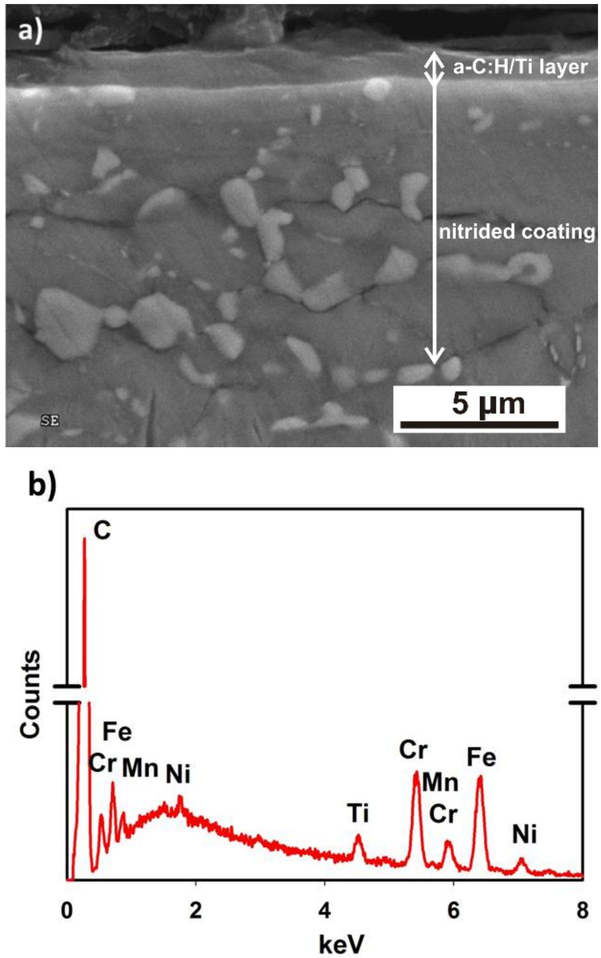

Fig. 2. Scanning electron microscopy results: a) cross section view, b) surface EDS analysis.

3.2. Mechanical properties

Thickness and mechanical properties of the carbon coatings and nitrided layers are presented in the Table 1, whereas in Fig. 3, the distribution of hardness vs. cross profile distance of nitrided layer is presented.

Table 1. Mechanical properties of nitrided layers and a-C:H/Ti gradient coatings.

Layer	Thickness (μm)	Hardness (GPa)	Young's modulus (GPa)
Nitrided	30	17 ± 0.7	204 ± 7
a-C:H/Ti	1.2	21.7 ± 2	191 ± 6.6

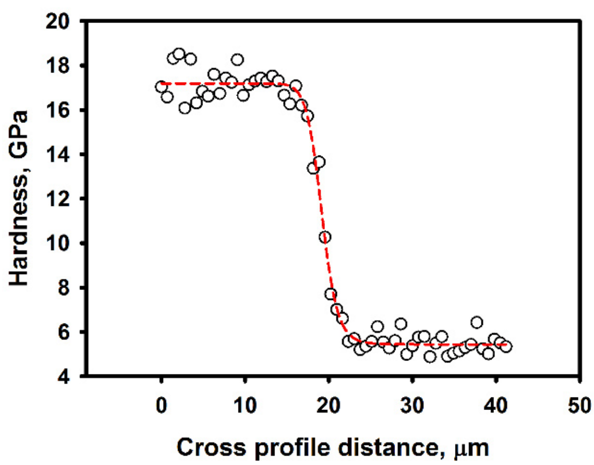

Fig. 3. Distribution of hardness vs. depth perpendicular to the surface of nitrided layer.

The thickness of nitrided layer is about 30 μm whereas the hardness distribution on the cross section shows effective increase in hardness to a depth of about 20 μm. Nevertheless, it is enough to ensure the good hardness of the substrate in the area of Hertz stress concentration. In case of hard coatings deposited onto soft substrates this parameter is critical. Too soft substrate materials yield to applied loads, which results in cracking and delamination of the layer [28].

The hardness measured for carbon layers is typical for this type of coatings [1]. It means that there is high concentration of sp^3 bonds in the chemical structure, however this amount seems to be optimal if very good lubricating properties, assured by the graphitic phase, are taken into consideration [3, 10].

Scratch test results point out very good adhesion of the carbon coatings onto the nitrided X53CrMnNiN21-9 steel. During the investigation, a complete separation of the layer from the substrate was observed under a load of 45 N. The obtained adhesion value seems to be at a reasonable level in comparison to the results presented in other works (which were in the range between 25 and 70 N) [16, 29, 30]. Moreover, the highest adhesion value was reported for the nanostructured coating composed of three interlayers (Ti/TiN/TiCN/DLC) not one, as in our case.

Scratches obtained in the adhesion tests were analyzed to determine the character of the damage to the surface. In Fig. 4, a view of the scratch is presented.

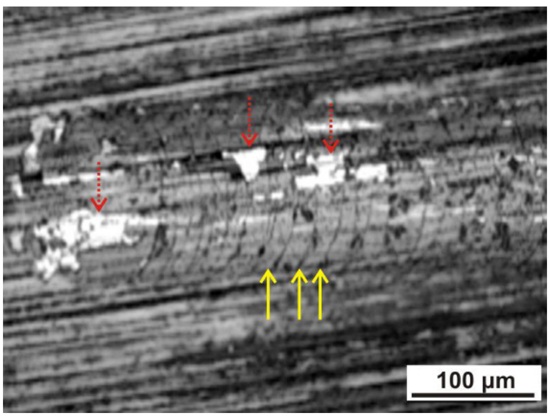

Fig. 4. View of the scratch of a-C:H/Ti gradient carbon layer after the adhesion measurement; the solid line arrows indicate tensile cracks, the dotted line arrows indicate layer delamination.

As it is visible there is a lack of complete delamination of the coating. On the distance of very last 300 µm of the scratch, characteristic tensile cracks can be observed (solid line arrows) [31]. They directly correspond to the character of the damage, which is related to the occurrence of microcracks that result in crumbling of the layer material (dotted line arrows).

3.3. Surface topography

In Fig. 5, AFM topography scans of examined samples are presented while their roughness parameters are gathered in Fig. 6. As it is visible, the surface geometrical structure of the nitrided layer and the a-C:H/Ti coating do not significantly differ from each other. Nevertheless, it can be stated that carbon layer slightly decreased the surface parameters of the samples, possibly by filling up the defects which occurred during the surface machining process.

Noteworthy is the more negative value of Rsk parameter of the gradient carbon coating compared to that of the nitrided layer (Fig. 6). This indicates the better tribological parameters of the a-C:H/Ti coatings. According to the authors of the work [32], more negative skewness is always associated with lower friction and shorter run-in period, which ensures the lower distance to obtain the steady state condition.

3.4. Friction coefficient and wear resistance

The investigation of tribological parameters confirmed the very low friction coefficients which were expected for the gradient carbon layers. In Fig. 7, the coefficients of friction for DLC layers sliding against the steel (~ 0.1) and ceramic (~ 0.02) balls are presented. Because of the lack of a wear profile after the test with use of the ceramic ball under load of 10 N, the test was rerun under a load of 20 N. Thus in Fig. 7 the run of the friction coefficient for this load is presented.

The lower value of the coefficient of friction, registered for the ceramic ball results from more intensive graphitization processes connected with higher ball hardness and temperature, caused by increased load of the friction couple [33, 34]. In case of the tests performed with use of the steel ball, the removed ball material that was wiped off and the oxidation processes were the reason of a third body effect, taking part in the tribological process. An optical microscope and a profilometer were used to

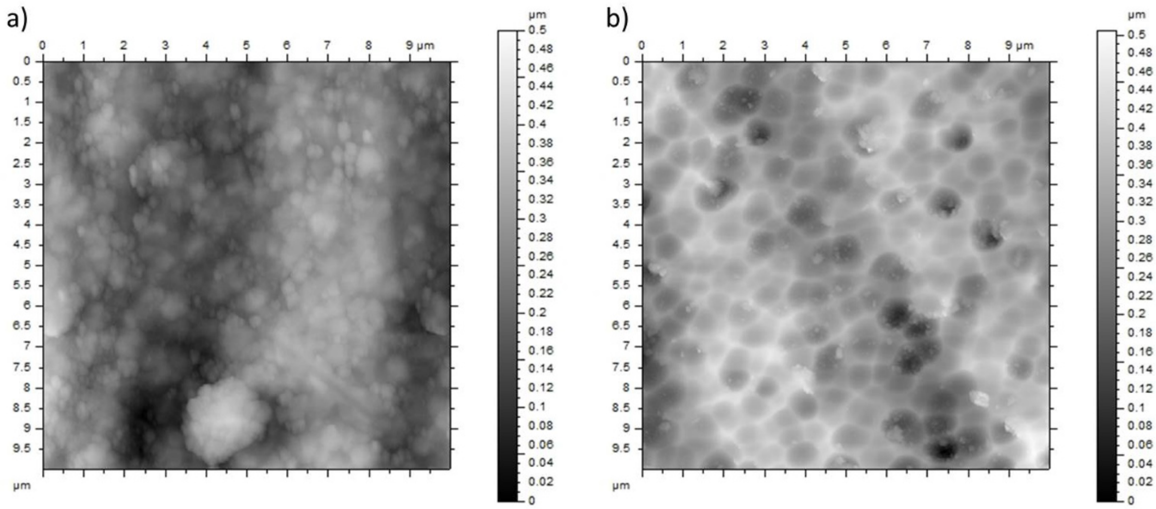

Fig. 5. Atomic force microscopy results: a) 2D AFM view of nitrided layer; b) 2D AFM view of a-C:H/Ti layer deposited onto nitrided sample surface.

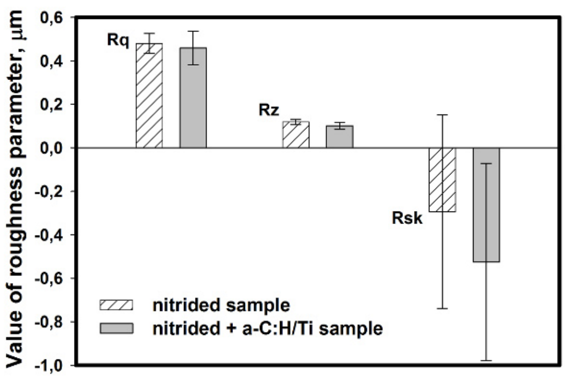

Fig. 6. Roughness parameters of nitrided layer and a-C:H/Ti coating deposited onto nitrided sample surface.

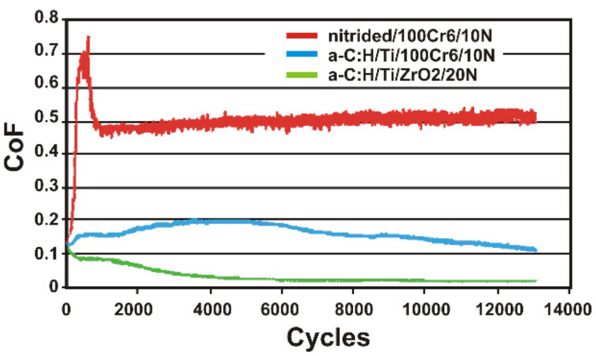

Fig. 7. Friction coefficients of the samples examined by the ball-on-disc method.

investigate the shape and dimensions of the wear profiles. In Figs. 8, 9 and 10, the results of the optical microscopy examination are shown whereas in Table 2, the results of wear profiles measurement are presented.

In case of the investigation of the sliding track obtained on the surface of nitrided layer, a structure typical for seizing processes was observed (Fig. 8). Many temporary sticking areas of friction faces are visible. The third body effect was the dominant process causing the sample and ball abrasion (noticeably more intensive than the one for carbon layers). For the samples covered with gradient layers, the hydrogen effect and graphitization phenomena which occurred during the sliding process resulted in the lack of the wear profile and much lower abrasion of the steel ball (Fig. 9). The lack of the depth profile on the surface of the a-C:H/Ti layers proves their high wear resistance. In the investigations performed using the ceramic balls, the wear profile was obtained only after the test with increased load (Fig. 10). As the result, 189 µm wide and 185 nm deep abrasion was observed. But it is worth to notice that the abrasion was rather a result of the layer roughness flattening.

The results of three-cylinder-cone investigation showed noticeable improvement of the wear

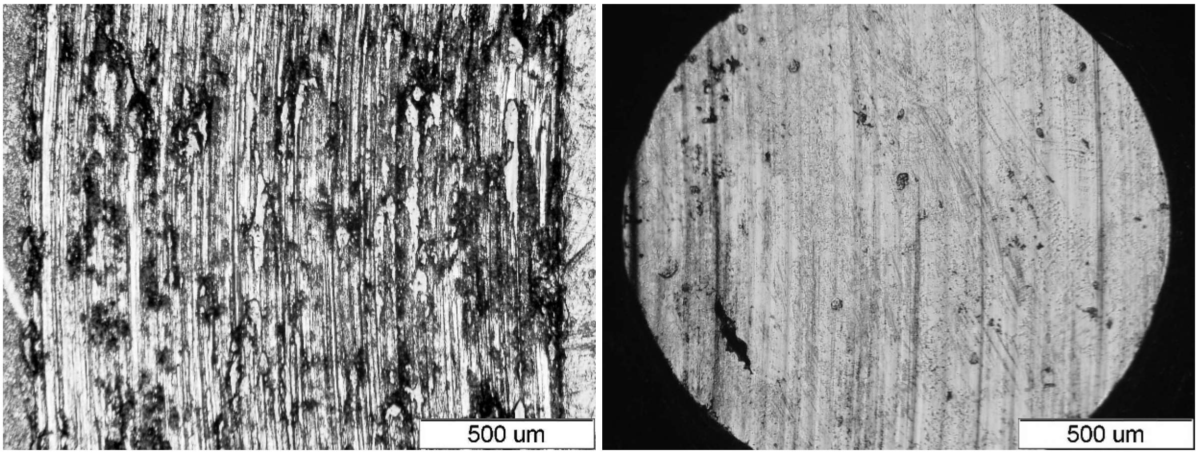

Fig. 8. Optical microscope view of the wear profiles for nitrided layer/100Cr6 friction couple.

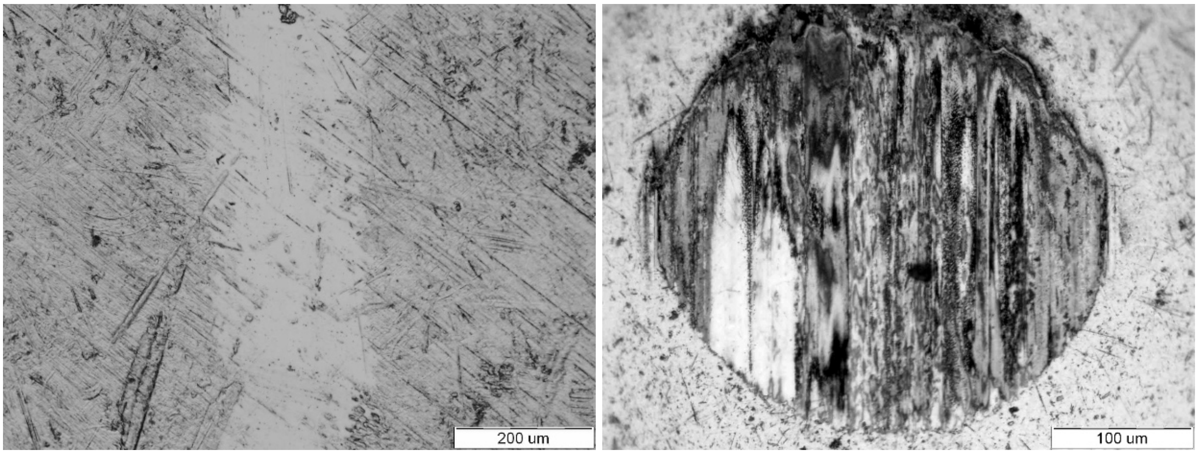

Fig. 9. Optical microscope view of the wear profiles for DLC layer/100Cr6 friction couple.

resistance for the samples modified by the process of deposition of the gradient layer. The results of the experiment are presented in Fig. 11.

After 100 minutes of the test, the linear wear of the a-C:H/Ti layer was lower than 1 μm whereas for the nitrided sample it was about 12 μm. Since the three-cylinder-cone method is highly destructive and was conducted under very hard conditions it can be stated, that the obtained results prove the very high wear resistance of the DLC gradient coatings.

4. Conclusions

Carbon layers with the gradient of chemical composition (about 1.2 μm thick) have been manufactured on the surface of nitrided X53CrMnNiN21-9 steel. SEM investigation proved that the manufactured layers were uniform with repeatable thicknesses, the same on the whole coated area, without any cracks and defects. High adhesion level obtained in the scratch tests proved the possibility of application of these gradient layers in those fields of the industry where this parameter is critical. Very low friction coefficients were observed for the carbon layers in the ball on disc tests. Good lubricating properties of the a-C:H/Ti gradient carbon layers offer an excellent protection against excessive wear caused by friction for both the modified element as well as the second part of the friction couple. Moreover, the wear and friction behavior of the gradient carbon

Table 2. Investigation results of wear profiles.

Sample / ball / load	Sample		Ball
	width (μm)	depth (μm)	width (μm)
Nitrided / 100Cr6 / 10	1523	3	1600
DLC / 100Cr6 / 10	215	–	328
DLC / ZrO_2 / 10	180	–	–
DLC / ZrO_2 / 20	189	0.185	–

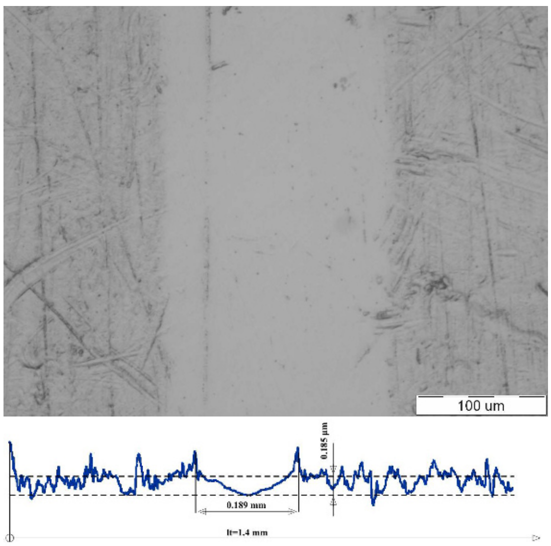

Fig. 10. Optical microscope view and the profile of the wear track for DLC layer/ZrO_2 friction couple tested under load of 20 N.

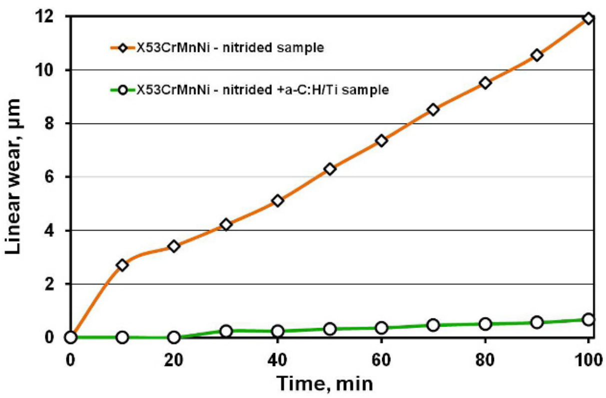

Fig. 11. Three-cylinder-cone test examination results.

layers may protect friction systems against the most destructive form of wear-scuffing. In wear resistance tests, the carbon coatings gave 1200 % wear resistance improvement in comparison to nitrided layers.

Acknowledgements

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