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# Comparative Study of the PVD Coatings on the Plasma Nitrided Steel

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In the current study, the cracking, impact and sliding wear resistance of the PVD single layer TiN (I generation), multilayer (Ti,Al)N-ML (II generation), gradient (Al,Ti)N-G and multilayer nanocomposite FiVIc® (both – III generation) coatings on the nitrided low alloy steel 42CrMo4 are analysed. The cyclic indentation test (normal load 50 N, 10 000 cycles) was carried out to determine the cracking resistance of the coatings. Impact wear test was performed at the normal load 16 N, strokes' frequency 25 Hz, $10^4 – 10^7$ strokes. Sliding wear test was applied, using the block-on-plate scheme, Ø 10 mm $Al_2O_3$ ball as the counterbody, at the normal load of 10 N, the frequency 5 Hz, the amplitude 10 mm and the test duration 10 min. Best resistance to cracks' formation is demonstrated by the gradient (Al,Ti)N-G coating, showing medium radial cracks' formation, whereas delamination of the coating can be observed in other cases. 1.6 – 1.7 times higher impact wear resistance is shown by the TiN coating in comparison with the other coatings. The FiVIc® coating demonstrates lightly better resistance to sliding wear in comparison with the TiN and (Ti,Al)N-ML coatings due to a lower coefficient of friction. The worst sliding wear resistance is observed in the case of the (Al,Ti)N-G coating due to a high affinity of the coating's and counterbody's materials.
*Keywords*: duplex treatment, PVD coating, I – III generation, cracking resistance, impact wear, sliding wear.

## 1. INTRODUCTION

Nitriding prior to deposition of a PVD coating allows improving the loading capacity of the substrate, what prevents the plastic deformation of the substrate and delamination of thin and brittle coating, as well as provides proper stress and hardness gradients between the coating and the substrate [1]. PVD coatings of different generations [2], deposited onto plasma nitrided steel substrates, demonstrate improved mechanical properties in the case of as I generation single component [3 – 7] and multicomponent [3, 8 – 11], as II generation multilayer [12, 13], as III generation nanocomposite [14] hard coatings in comparison with the same coatings, deposited onto non-nitrided steel. However, due to differences in steel substrates, nitridng processes, testing conditions, etc., no comparable data about the different generations of PVD coatings on a nitrided substrate is available. In this paper, the comparative analysis of the I – III generations of PVD coatings, deposited onto plasma nitrided low-alloy steel, is carried out, the resistance of the coatings to cyclic impact loading, impact wear and sliding wear are studied.

## 2. EXPERIMENTAL

### 2.1. Substrate preparation

Low-alloy steel 42CrMo4 was chosen as the substrate. Chemical composition and microhardness of steel are presented in Table 1. Specimens were milled to the dimensions of 50 mm × 25 mm × 10 mm and subjected to hardening (850 °C, oil) and tempering (500 °C, 2 h). Prior to nitriding the specimens were grinded to the surface finish of $R_a$ = 0.8 μm.

**Table 1.** Chemical composition of steel 42CrMo4

| Steel grade | Chemical composition, wt% | Hardness, HV0.05 |
|---|---|---|
| 42CrMo4 | 0.38 – 0.45 C; 0.60 – 0.90 Mn; ≤ 0.40 Si; 0.035 P; 0.035 S; 0.90 – 1.20 Cr; 0.15 – 0.30 Mo | 315 – 345 |

### 2.2. Plasma nitriding

Plasma nitriding process Plasnit® [15] was carried out at Bodycote OY (Finland). The temperature of the process was 500 °C – 520 °C and the internal pressure inside the chamber – 5 mbar. The applied gas atmosphere consisted of 80 % $N_2$ + 10 % $H_2$ + 10 % $CO_2$. The duration of nitriding was 10 h.

### 2.3. PVD coating process

The I generation single layer TiN coating, the II generation multilayer (Ti,Al)N-ML coating and the III generation gradient (Al,Ti)N-G and nanocomposite FiVIc® coatings were chosen as the objectives of the study. Before the coatings' deposition, a layer of thickness 0.02 mm was grinded down from the nitrided surface in order to remove the 'white layer' [15]. The coatings were deposited using the Platit π80 hardcoating unit. The parameters of coatings' deposition are presented in Table 2 and their thickness and mechanical properties – in Table 3.

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**Table 2.** Parameters of deposition of the PVD coatings [16]

| Coating | Type | Bias voltage, V | Ti-Al/AlSi cathode arc current, A | Pressure, mbar $\times 10^{-3}$ | Tempera-ture, °C | Ar flow, sccm | $N_2$ flow, sccm | $C_2H_2$ flow, sccm |
|---|---|---|---|---|---|---|---|---|
| TiN | Monolayer | (–75) – (–120) | 100 – 125 / – | 8 | 450 | 6 | 200 | – |
| (Ti,Al)N-ML | Multilayer | (–60) – (–150) | 85 – 125 / / 65 – 115 | 8 – 15 | 475 | 6 | 200 | – |
| (Al,Ti)N-G | Gradient | (–60) – (–150) | 60 – 125 / / 52 – 130 | 4 – 12 | 430 – 450 | 6 | 150 – 200 | – |
| FiVIc® (NaCo® + DLC) | Multilayer + nanocomposite | (–75) – (–150) | 82 – 125 / / 65 – 100 | 9 – 12 | 435 – 475 | 6 | 150 – 200 | 7 – 39 |

**Table 3.** Thickness and mechanical properties of the deposited PVD coatings [16, 17]

| Coating | Thickness, μm | Nanohardness, GPa | Modulus of elasticity, GPa | H/E ratio | $H^3/E^2$ ratio | Coefficient of friction | Residual stress, GPa |
|---|---|---|---|---|---|---|---|
| TiN | 2.3 | 28.5 | 438 | 0.065 | 0.121 | 0.55 | – 3.16 |
| (Ti,Al)N-ML | 3.1 | 19.9 | 301 | 0.066 | 0.086 | 0.6 | – 6.50 |
| (Al,Ti)N-G | 3.0 | 23.8 | 336 | 0.071 | 0.119 | 0.7 | – 2.94 |
| FiVIc® | 2.0 | 29.0 | 323 | 0.090 | 0.233 | 0.15 | – 4.11 |

## 2.4. Microstructure studies

Cross-section of a specimen was polished, etched with the 3 % nital and studied under the optical microscope (OM) Axiovert 25. Distribution of chemical elements inside the nitrided zone was determined by the means of energy dispersive spectroscopy (EDS) in the scanning electron microscope EVA 25 (Carl Zeiss).

## 2.5. Microhardness measurements

Vickers microhardness at the load of 0.49 N was measured at the polished cross-section of a specimen, beginning from the coating surface towards the middle part in order to determine the case depth. Micromet 2001 (Buehler) microhardness tester was used in the measurements.

## 2.6. Cyclic indentation testing

To estimate the cracking resistance of the coatings, cyclic indentation at a single point technique was used. Instron 8800 servo hydraulic fatigue test system with the Vickers diamond indenter were applied for this purpose. The scheme of the testing device is presented in Fig. 1. All coatings were subjected to 10 000 indentation cycles at the load 50 N. After the testing, the imprints were studied under the optical microscope Axiovert 25. Cracking resistance was estimated by the qualitative evaluation criteria (from weak craking 0 to VI – delamination) [18].

## 2.7. Impact wear testing

To study the impact wear resistance of the coatings at the dynamic loads, impact wear tests were performed at the impact wear tester, designed at TUT [18]. The scheme of the experimental device is presented in Fig. 2. The load of 16 N was applied at the stroke frequency of 25 Hz. The linear speed of hammers equalled to 2.75 m/s. The number of strokes varied in the range of $10^4 – 10^6$ with the step of $10^1$ cycles. The impact wear scars were studied under the optical microscope Axiovert 25 with the help of the computer program Buehler Omnimet. The dependence of the indentation stress $\sigma$ vs. the indentation depth $\delta$ was calculated on the base of the measurements' results.

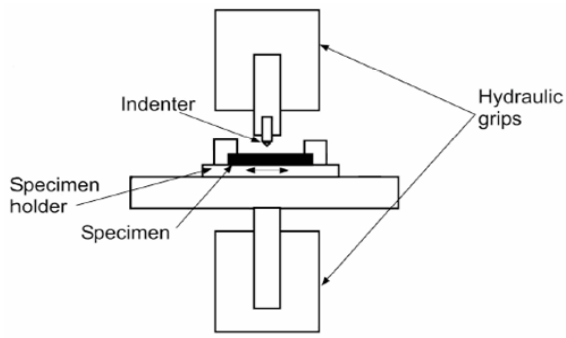


**Fig. 1.** Schematic representation of the cyclic indentation tester [18]

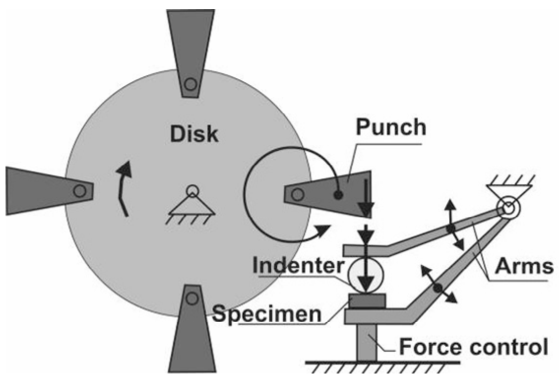


**Fig. 2.** Scheme of the impact wear tester [18]

## 2.8. Sliding wear testing

Sliding wear resistance of the coatings was tested, applying the ball-on-plate scheme on the Wasau tribometer. The $Al_2O_3$ ball of the diameter 10 mm was used as the counterbody, the normal load was 10 N, the frequency – 5 Hz, the amplitude of movement – 10 mm, the duration of the test – 10 min. Each coating was tested 3 times at the same specimen. After the sliding wear test, the depth of the wear scars was determined applying the Mahr profilometer. The average of the measurements' results and the standard deviation were calculated.

## 3. RESULTS AND DISCUSSION

## 3.1. Microstructure studies

Microstructure of a plasma nitrided specimen is shown in Fig. 3.

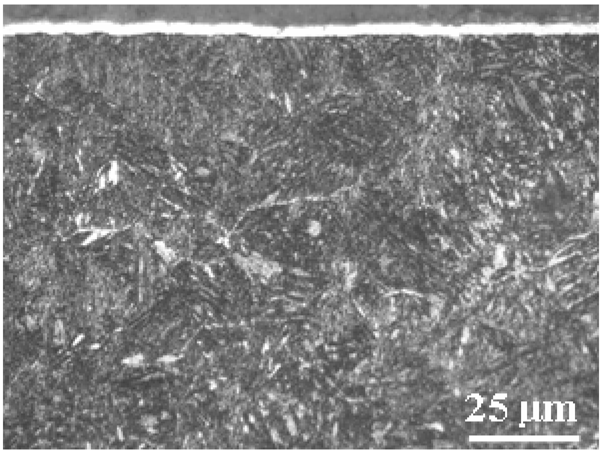


**Fig. 3.** Microstructure of the plasma nitrided PVD coated specimen (TiN coating)

As follows from Fig. 3, no white layer [15] can be observed, thus it can be concluded it has been completely removed during grinding. The observed diffusion layer has an eutectic microstructure. The structure contains the α phase (Fe(N)) and γ' ($Fe_4N$) phase, as well as nitrides and carbonitrides [19].

## 3.2. Microhardness measurements

Microhardness distribution in the nitrided layer is shown in Fig. 4.

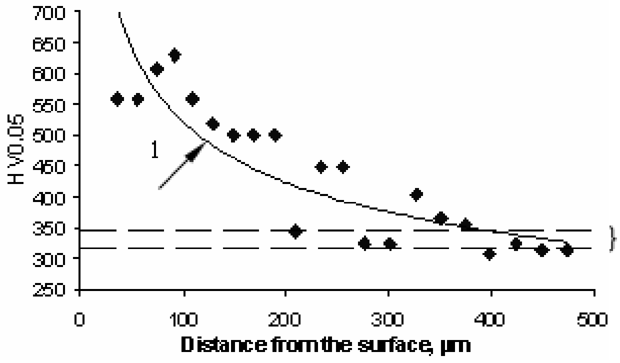


**Fig. 4.** Microhardness distribution inside the nitrided zone (1) of the PVD coated steel (TiN coating) and initial microhardness (2)

Microhardness measurements (Fig. 4) show that the depth of the nitrided zone equals to at least 250 µm, which is in correspondence with the nitrogen's diffusion depth, reported by the manufacturer [15]. The decrease in the microhardness values is caused by the reduction of the nitrogen's content in the nitrided layer.

## 3.3. Cyclic indentation testing

Results of indentation tests are brought in Fig. 5.

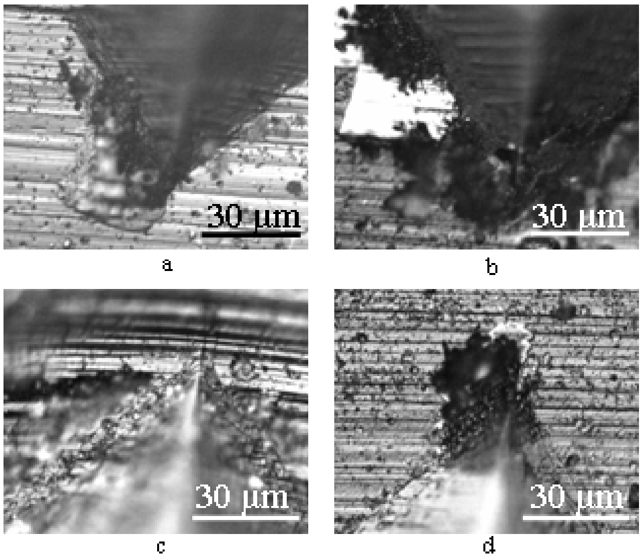


**Fig. 5.** Impressions' corners at the PVD coated plasma nitrided steel after 10 000 indentation cycles: a – TiN, VI class; b – (Ti,Al)N-ML, VI class, c – (Al,Ti)N-G, III class, d – FiVIc®, VI class

As seen in Fig. 5, the PVD deformed according to the upfit model (delamination around the corners of the imprint with formation of cone cracks without or with minor radial cracks' formation) [16]. According to the crack evaluation criteria, the crack resistance of these coatings can be estimated as the VI criteria. The best cracking resistance was demonstrated by the PVD III generation (Al,Ti)N-G coating, what can be related as the III criteria (medium cone cracking). The reason for such behaviour of coatings can be related to the gradient structure of this coating. This provides the lowest residual stress in the coating and leads to a better adhesion of the coating to the substrate due to a lower mismatch between the stress values in the coating and the substrate [17].

## 3.4. Impact wear testing

The II – III generation PVD coatings demonstrate similar impact wear resistance. The best impact wear resistance is demonstrated by the PVD I generation TiN coating (1.6 – 1.7 times higher than the remaining ones). Such response to impact loads can be explained by the higher value of modulus of elasticity of the TiN coating, what allows it to avoid brittle failure during impact better, and similar values of the modulus of elasticity of other coatings (see Table 3). No clear correlation between H/E and $H^3/E^2$ values [18] and impact wear resistance of the coatings was revealed.

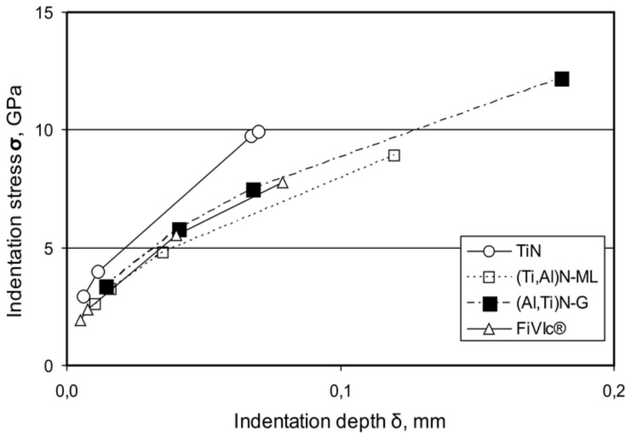


**Fig. 6.** Comparison of the indentation depth of the PVD coatings on the plasma nitrided steel

### 3.5. Sliding wear resistance

The average depths of wear scars are presented in Fig. 7.

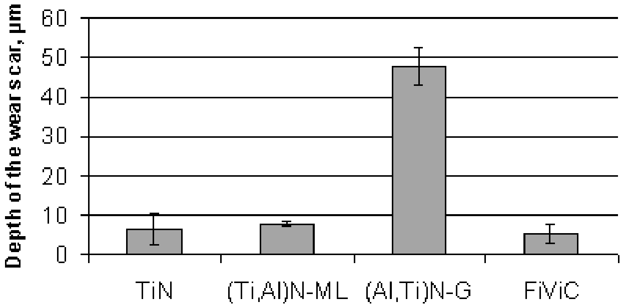


**Fig. 7.** Depths of the wear track on the PVD I – III generations coatings on the nitrided steel

As can be observed in Fig. 7, the PVD I generation TiN, II generation (Ti,Al)N-ML and III generation FiVIc® coatings demonstrated similar wear resistance, whereas the lowest average wear value was shown by the FiVIc® coating (1.2 times lower than the TiN and 1.4 times lower, than the (Ti,Al)N-ML coating (Fig. 7)). This fact can be explained by the lowest coefficient of friction among all studied coatings (see Table 3). The highest wear value, demonstrated by the PVD III generation (Al,Ti)N-G coating (8.9 times higher than FiVIc®) may be caused by different factors, such as E/H ratio, residual stress, etc. The one probable reason is the highest adhesive affinity of the coating's and the counterbody's material among the studied coatings [20], which is, in its turn, caused by the chemical similarity of these materials [21] (an alumina layer naturally forms at the top of the (Al,TI)N coating [22]). Further experiments are needed to confirm this hypothesis.

The obtained profiles of the wear scars are shown in Fig. 8. The smoothest wear scar's profile is obtained in the case of FiVIc® coating (Fig. 8, d), what evidences the smallest amount of abrasive particles, formed during the process. This fact can be explained by the low CoF of DLC layer at the surface of the coating, what prevents the formation of a large amount of wear debris. As it can be seen from Fig. 8, d, the width of the wear scar on the FiVIc® coating is also the smallest among the others, what is a prove of effective support of the underlying nanocomposite NaCo® layer.

The widest wear scar's profile, formed at the (Al,TI)N-G coating, and deeper grooves at the bottom of it indirectly witnesses about larger wear debris and about more brittle nature of the coating's failure (Fig. 8, c).

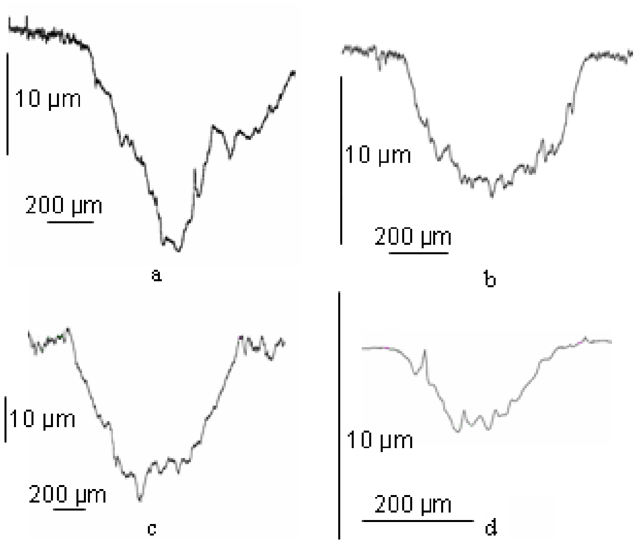


**Fig. 8.** Profiles of the wear scars: PVD a – TiN; b – (Ti,Al)N-ML; c – (Al,Ti)N-G; d – FiVIc® coating

## 4. CONCLUSIONS

1. The hard 250 μm deep nitrided zone, consisting of Fe(N), $Fe_4N$, other nitrides and carbonitrides, has formed during the nitriding process. The microhardness of the nitrided zone varied in the range of 450 – 630 HV0.05.
2. The PVD III generation (Al,Ti)N-G coating demonstrated the best cracking resistance (III class of the cracking evaluation criteria) in comparison with the other coatings (VI class of the cracking evaluation criteria) due to the gradient structure, having the lowest residual stress and thus the best adhesion to the substrate.
3. The 1.6 – 1.7 times higher impact wear resistance was demonstrated by the PVD I generation TiN coating in comparison with the other studied coatings due to the highest modulus of elasticity
4. The PVD III generation FiVIc® coating showed the 1.2 – 8.9 better wear resistance in comparison with the other studied coatings due to the lowest coefficient of friction


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