TRIBOLOGICAL CHARACTERISTICS OF PLASMA NITRIDED AND PVD COATED CR-MO-V STEELS*

M. Kolaříková, J. Suchánek

Czech Technical University in Prague, Faculty of Mechanical Engineering, Department of Manufacturing Technology, Prague, Czech Republic

The paper summarizes the results of tribological testing of duplex coating tool steels. Steel samples (31CrMoV9) were nitrated and subsequently treated by PVD process. There were deposited different types of coatings (TiN, CrN, TiAlN and multilayer 3 × (CrN-TiN)) with thickness 1 and 3 µm. Similar to these modified samples were tested and theirs characteristics were detected such as e.g. coating nanohardness (TiN – 35.5 GPa; CrN – 26.9 GPa; TiAlN – 32.9 GPa; 3 × (TiN-CrN) – 34.2 GPa), hardness of duplex coating, friction coefficient (Pin on Disc), coating thickness – Calotest (corresponds to information from the manufacturer), resistance against adhesive wear – Scratch test (TiN – 87 N; CrN – 52 N; TiAlN – 61 N; 3 × (TiN-CrN) – 61 N) and abrasion size – HEF (Hydromecanique Et Frottement) (TiN – 44.4 × 10^{-6} kg; CrN – 416.8 × 10^{-6} kg; TiAlN – 23.9 × 10^{-6} kg; 3 × (TiN-CrN) – 103.8 × 10^{-6} kg for distance 10 000 m).

friction coefficient; wear; duplex coating; pin on disc; HEF

INTRODUCTION

The requirements for materials used in the machine parts production, especially their functional characteristics and service life are currently increasing. The need of strength, ductility and toughness on one hand and low weight, corrosion and wear resistance on the other hand, are often contradictory and with standard materials hardly realizable (Liscano et al., 2006). One suitable solution of this formidable situation appears to be surface treatment, which can create a coating with special properties mentioned above. The example is a die, which keeps the basic material's characteristics and, thanks to the coating, the functional properties of its surface are improved. Thin ceramic coatings deposited on the surface of tools and machine parts by PVD (Physical Vapour Deposition) methods improve considerably their tribological properties. These hard brittle PVD coatings can be damaged rapidly if a plastic deformation initiates in the substrate near the coating-substrate interface when subject to relatively high intensity loading. Therefore, the strengthening of substrate surface layers, e.g. by plasma nitriding, appears to be a suitable solution of the low strength of the substrate (Bell, 1997; Suchánek et al., 2009).

Duplex coating means generally combination of two different surface treatments. In this case it is nitrided surface layer and PVD coating. The duplex treatment proceeded in two phases. In the first phase the specimens were pulse plasma nitrided at the parameters: atmosphere N_2:H_2 = 1:3, nitriding temperature – 540°C and dwell time – 20 hours. Compound layer with thickness 2–4 µm was eliminated by polishing. In second phase of duplex treatment there were deposited (HAUSER coating equipment; low-voltage arc) PVD coatings – TiN (1 and 3 µm), CrN (1 and 3 µm), TiAlN (3 µm) a multilayer 3 × (TiN-CrN) (3 µm) – Figs. 1a, 1b and 2a, 2b, 2c. The average surface roughness of the specimens was R_a = 0.19 µm.

METHODS AND MATERIALS

The material 31CrMoV9 is usually used for forming tools or agricultural machines. Therefore, this material was chosen. On the nitrided surface of material 31CRMOV9 (Č S N 4 1 5 3 3 0) was deposited a suitable PVD coating with required properties (V á l o v á et al., 2009).

The specimens were austenitized at 865°C and inert gas quenched and tempered at 600°C for 2 hours in nitrogen atmosphere, fine ground and polished.

Is it very important to know the thickness of PVD coatings. The thickness was measured by two methods. The first method was Calotest. The second one was measuring on chamber and cross cut (scratch pattern) by light microscope.

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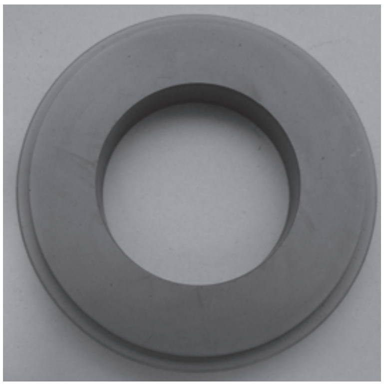

Fig 1a. Specimen with PVD coating TiN

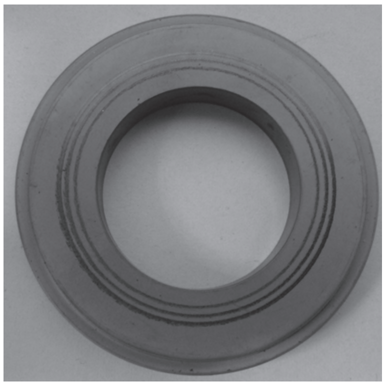

Fig 1b. Specimen with PVD coating TiAlN

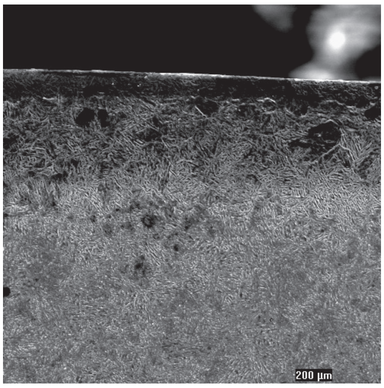

Fig 2a. TiN coating on nitrided surface SEM

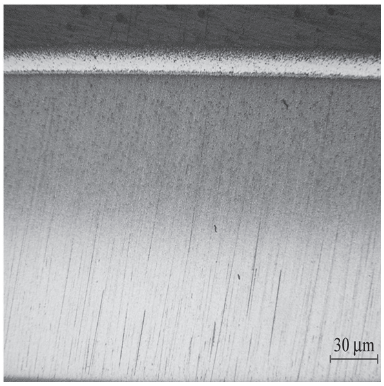

Fig 2b. TiN coating on nitrided surface light microscope (angled section)

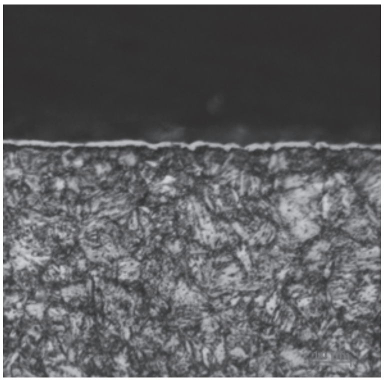

Fig 2c. TiN coating on nitrided surface light microscope (magnification 500 × – cross-section)

The coating adhesion to parent nitrided steel was tested by the Scratch test. There was evaluated critical load L_C parameter.

Both microhardness (load 200 g) and nanohardness (indentation hardness (EN ISO 14577-1)) were measured. Microharness is not suitable for harness measuring of entire cross section of duplex coating, because the thickness of PVD coating is only about 1 μm. For this thickness nanohardness is used.

Nanoindentation was made on Nanoindentor XP with CSM modulus. This additional device allows reading the contact stiffness during the whole process of indentation. The principle of this measurement consists in oscillation along primary load with frequency of 0.05–200 Hz and amplitude of 60 nN–300 mN.

Instrument analyses dynamic response of tested material and it is possible to estimate material parameters like hardness and modulus, by this way.

The contact depth h_c was determined:

$$h_c = h - \varepsilon \frac{P_{max}}{S} \quad [\mu m] \qquad (1)$$

where:

h – the total indenter displacement corresponding to the load P; ε – a correction factor for non-circular shape of the indenter ($\varepsilon = 0.75$ for Berkovich indenter); and S – the contact stiffness.

The formulas quoted above allowed determining a reduced elastic modulus of, E_r, from the dependence:

$$E_r = \frac{\sqrt{\pi} \times S}{2 \times \beta \times \sqrt{A_p(h_c)}} \quad [GPa] \qquad (2)$$

where:

S – contact stiffness; A_p – contact area, where permanent deformation is taken into account, β – correction constant for the indenter tip shape (for Berkovich indenter, $\beta \approx 1.034$).

The reduced modulus, E_r, is used to account for the fact that elastic displacements occur in both the indenter and the sample. The elastic modulus of the test material, E, is calculated from E_r, using:

$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i} \quad [GPa^{-1}] \qquad (3)$$

Table 1. Parameters of measurement with pin on disc tribometer

Diameter of pin (mm)	Material of pin	Diameter of distance (mm)	Speed (cm.s^{-1})	Distance (m)
7.94	HSS	15.00	10	100
7.94	HSS	16.00	10	100
7.94	HSS	17.00	10	100

Table 2. Coating's thickness measured with Calotest

Coating	t (μm) (Calotest)	t (μm) (light Microscope)
TiN	1.1	1.6
CrN	1.6	2.1
TiAlN	1.9	2.4
3 × (TiN-CrN)	1.6	2.2

Table 3. Values of critical loads Lc2 and Lc3 measured with Scratch test

Coating	Lc2 (N)	Lc3 (N)
TiN	78	87
CrN	34	52
TiAlN	52	61
3 × (TiN-CrN)	52	61

where:

E, v – elastic modulus and Poisson's ratio for the investigated material, E_i, v_i – elastic modulus and Poisson's ratio for the material of the indenter (for diamond E = 1141 GPa, v = 0.07).

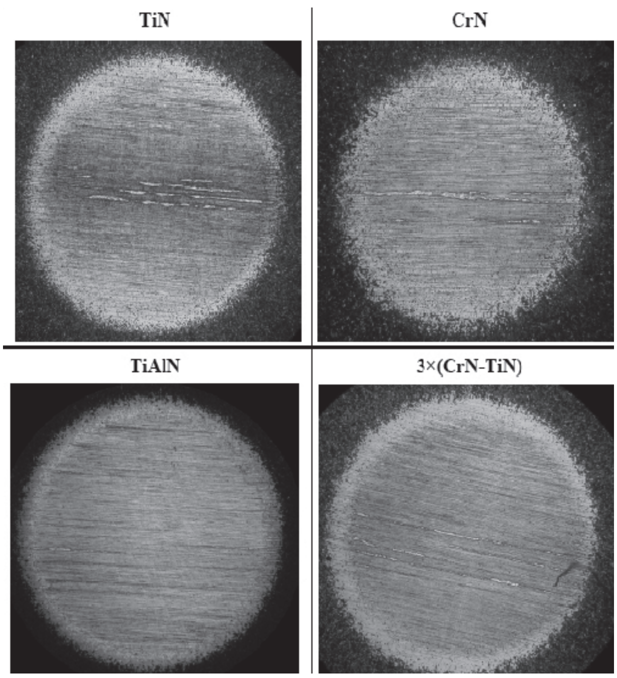

Fig 3. Photos of samples Calotest testing

The hardness was determined as a ratio of the maximum load P_{max} imposed on the indenter and the projection contact area, A_p, the latter being a function of the indenter shape at the contact depth, h_c:

$$H = \frac{P_{\max}}{A_p} \text{ [GPa]} \quad (4)$$

Nanohardness was evaluated by CSM method with maximum load $P_{\max}$ = 670 mN (according to specification EN ISO 14577-1).

The duplex treated samples were subsequently tested on a 'pin-on-disc' tribometer. The experiments were carried out at the temperature 22°C and 350°C. The loading of the specimens was 1, 2 and 5 N. Other parameters of measurement are in Table 1.

The samples were tested in dry conditions. The recorded friction coefficient values were processed using the program OriginLab®.

The duplex treated specimens were also tested on a tribometer HEF type 'ring-on-block'. This tribometer simulated friction and wear conditions in linear contact. The specimens were tested at two loads (50 and 150 N) in the conditions of dry friction. The morphological changes on the surfaces of tested specimens were evaluated with light microscopy.

In addition to visible wear marks in the form of tiny grooves there were detected transfer of material from counterpart. The transferred material was studied with surface and point EDX (Energy Disperse X-Ray) method with equipment JEOL – JSM – 5410. Changes of chemical composition of nitrided and duplex treated specimens were studied with GDOES (Glow Discharge Optical Emission Spectroscop).

RESULTS

The reading of values from Calotest marks (Fig. 3) was difficult. Measured values are only approximate and they are different from the values measured by microscope. All values measured by Calotest are about lower by 0.5 μm (Table 2). The thickness of nitrided layer is 400 μm (the microscope method).

The results of the Scratch test are in Table 3. Values of critical loads *Lc* were measured according to specification EN 1071-3. The highest adhesion to the basic material was detected in the TiN coating and the lowest adhesion in the CrN coating (Fig. 4). The adhesion of all tested PVD coatings was sufficient.

Hardness was measured on chamfer cut and crosscut. Measured data (Fig. 5) clearly show that the nitrided layers increased the hardness of the substrate subsurface layer. The hardness gradually drops from the values near 850 HV to the values common for a heat-treated steel (575 HV) (Fig. 5).

The dependence of the microhardness on distance from surface (Fig. 6) shows that the nitride hardening process could be much more favourable with regard

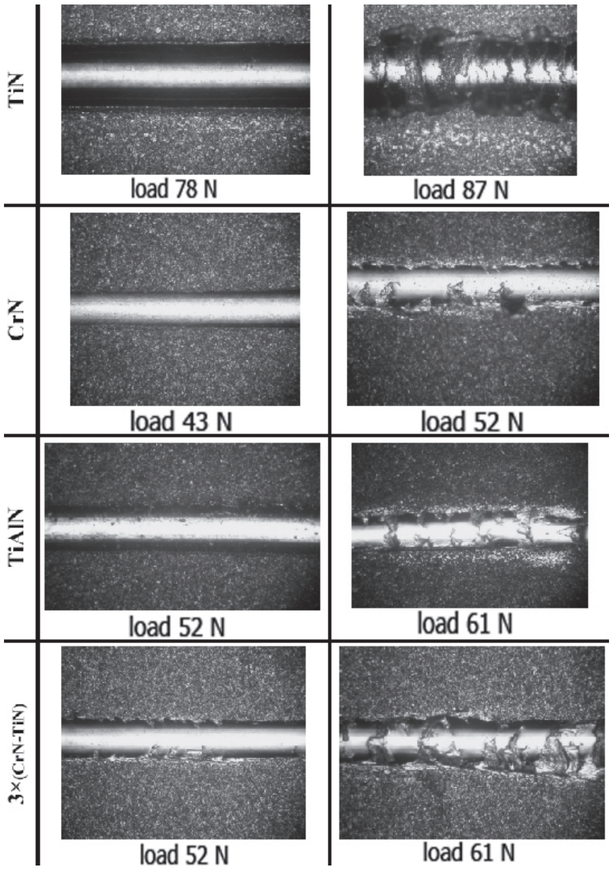

Fig 4. Results of the coating adhesion by a scratch test (indicated forces are maximum loads in given locations, magnifications is 50 x)

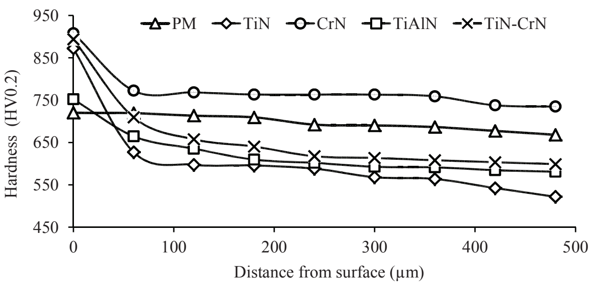

Fig 5. The hardness of nitride layer on measured samples. (Hardness of coatings was not measured)

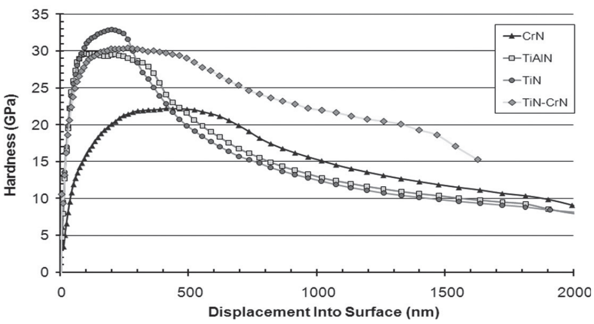

Fig 6. Nanohardness of coatings

Table 4. Modulus and hardness of coatings

Coating	H (GPa)	E (GPa)
TiN	35.8 ± 4.6	504 ± 80
CrN	26.9 ± 3.4	327 ± 43
TiAlN	32.9 ± 5.8	497 ± 98
TiN-CrN	34.2 ± 8.1	566 ± 83

Table 5. Friction coefficient for all coatings at the load of 1, 2 and 5 N and temperature of 22°C and 250°C after 100 m of wearing

	22°C	250°C
1 N		
TiN	0.38	0.74
CrN	0.48	0.79
TiAlN	0.46	0.76
TiN-CrN	0.41	0.8
2 N		
TiN	0.52	0.8
CrN	0.64	0.7
TiAlN	0.62	0.8
TiN-CrN	0.57	0.72
5 N		
TiN	0.74	0.81
CrN	0.74	0.8
TiAlN	0.76	0.82
TiN-CrN	0.71	0.81

to coating break than with common treatment without plasma nitriding. The curves substantiate that the coating's microhardness gradually goes down, despite our expectation of steep change.

The most favourable nanohardness curve was measured on TiN coating. The hardness curve of multilayer 3 × (TiN-CrN) shows good valuable as well. As measurement indicate the other two coatings (TiN and TiAlN) exibit a markedly steeper hardness drop. However, they show the highest hardness (almost 35 GPa) as well (Table 4).

The most suitable wear resistant coating for dies in term of service life at the temperature of 22°C was the TiN coating. This coating had the lowest values of friction coefficient and the smallest wear. The most unfavourable results were obtained for TiAlN coating at the temperature of 22°C. The same results were achieved at all loads (Table 5).

During tests at the temperature of 250°C, the coating 3 × (CrN-TiN) peel off even under low load. TiN coating became the optimal for lower loads. TiAlN showed the poorest performance of all tested coatings (Table 5). Experimental results showed that during testing of the duplex treated steel with different PVD coatings the friction coefficients increased.

The mechanism of deterioration of the duplex coated steel is a combination of adhesive and abrasive wear.

Table 6. The average mass wear after HEF testing

Duplex coating	Average mass wear (10^{-6} kg)			
	1 000 m	2 500 m	5 000 m	10 000 m
PN + TiN (3 µm)	0.45	3.35	13.1	44.4
PN + CrN (3 µm)	29.6	111.15	216.1	416.8
PN + TiAlN (3 µm)	+ 1.75	+ 0.3	4.1	23.9
PN + 3 × (TiN-CrN) (3 µm)	8.1	20.33	39.2	103.27

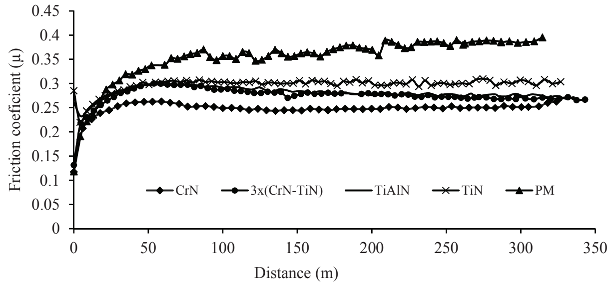

Fig 7. Friction coefficient dependent on distance at 22°C and load 5 N

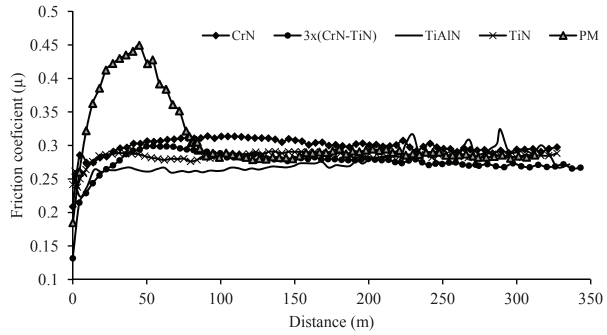

Fig 8. Friction coefficient dependent on distance at 350°C and load 5 N

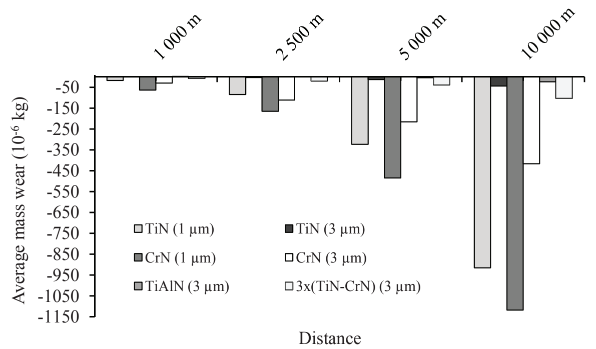

Fig 9. Average mass wear dependent on distance under load 150 N

The adhesive wear took place on the disk during experiment while the ball was worn down in an abrasive manner. The evidence of abrasive wear can be seen on the grooves formed on the ball during experiment.

Measured results of friction coefficient at temperatures 22°C and 350°C (Figs. 7 and 8). The duplex treatment of low alloyed steel 31CrMoV9 improved its wear resistance in comparison to steel without duplex treatment. The highest wear resistance was recorded in the plasma nitride specimens with the PVD coating 3 × (TiN-CrN).

Generally speaking, at the room temperature friction coefficients achieve approximately the same values as at increased temperature, though are a little lower. In case of only nitrided steel both run in period and process itself are different. At the room temperature the curve considerably increases, but at higher temperature after a marked increase in run in phase and subsequent drop the friction coefficient value is stable (0.28).

Results of tribological testing on tribometer HEF are shown in Table 6 and Fig. 9.

CONCLUSION

As far as the coating microhardnes-depth profile is concerned, the most favourable is the coating CrN and the multilayer coating 3 × (TiN – CrN). In respect to results of measurement of the friction coefficient and wear, it can be seen that hardness profile on nitrided surface is slow enough and it should not reach a coating cracking also when coatings TiN and TiAlN are used. The friction coefficient is low and the coating exhibits better service live.

The conclusions drawn from the experiment indicate that duplex treatment is a useful way to increase the die service life and that the most suitable coating is the PVD coating TiN. This coating in combination with a nitrided base material had a low friction coefficient and a small wear.

Current thin abrasion-resistant surface layers and coatings bring remarkable extension of service life and reliability to machine parts and dies. Most technologies have not managed to reach the limits of their possibilities so far.

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KOLAŘÍKOVÁ, M. – SUCHÁNEK, J. (České vysoké učení technické v Praze, Fakulta strojní, Praha, Česká republika)

Tribologické vlastnosti plazmově nitridované Cr-Mo-V oceli s PVD povlakem

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Článek shrnuje výsledky tribologického zkoumání duplexně povlakovaných nástrojových ocelí. Ocelové vzorky (31CrMoV9) byly nitridovány a následně povlakovány PVD procesem. Byly naneseny různé typy povlaků (TiN, CrN, TiAlN a multivrstva 3 × (CrN-TiN)) s tloušťkou 1 a 3 µm. Takto upravené vzorky byly testovány a jejich vlastnosti byly zjišťovány různými metodami jako např. nanotvrdost povlaku (TiN – 35,5 GPa; CrN – 26,9 GPa; TiAlN – 32,9 GPa; 3 × (TiN-CrN) – 34,2 GPa), tvrdost duplexního povlaku, koeficient tření (pin on disk), tloušťka povlaku – Calotest (odpovídá údajům od výrobce), odolnost proti adhezivnímu – Scratch test (TiN – 87 N; CrN – 52 N; TiAlN – 61 N; 3 × (TiN-CrN) – 61 N) a abrazivnímu opotřebení – HEF (Hydromecanique Et Frottement) (TiN – 44.4 × 10^{-6} kg; CrN – 416.8 × 10^{-6} kg; TiAlN – 23,9 × 10^{-6} kg; 3 × (TiN-CrN) – 103,8 × 10^{-6} kg for distance 10 000 m).

koeficient tření; opotřebení; duplexní povlakování; pin on disk; HEF

Contact Address:

Ing. Marie Kolaříková, IWE, České vysoké učení technické v Praze, Fakulta strojní, Ústav strojírenské technologie, Technická 4, 166 07 Praha 6, Česká republika, tel: +420 224 352 628, e-mail: marie.kolarikova@fs.cvut.cz