

## Analyse of Tribological Properties of Layers Created by Plasma Nitriding + DLC

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Plasma technology of deposition of thin layers is currently the commonly used technology serving to influence the surface properties of various materials (metals, polymers, ceramics, etc.). The great advantage of applied thin layers is that although they can significantly change the surface properties of coated materials, their advantageous volumetric properties are preserved. The experimental part of work describes the evaluation of the properties of duplex system of the plasma nitrided layer with DLC coating and confronts them with the properties of plasma nitrided layers and polished surfaces. 42CrMo4 and 17Ni4CrMo steels were chosen for experiment. Experimental part deals with the practical analysis of the determination of tribological properties of thin film-substrate (specifically nitrided layer-DLC coating). The tribological properties of selected steels were evaluated using the "Pin on Disc" method. Modified layer formed by duplex system PN+DLC showed up to 8x lower coefficient of friction than nitrided or only polished surface.

**Keywords:** Plasma Nitriding, Layer, DLC, Pin-On-Disc, Friction

### 1 Introduction

Diamond-like carbon (DLC) thin films, prepared by plasma enhanced chemical vapor deposition (PECVD), are still one of the most attractive coatings for a wide range of applications like: tribological coatings, optical devices, microelectromechanical devices, biocompatible coatings, mainly because of its cost effectiveness and possibility to deposit on large substrates with good uniformity as mentioned by Catherine et al. (1986) [1], Robertson (2002) [2] and Sedlak(2015) [3]. Many optical devices use DLC thin films for antireflection coatings, gratings and recently plasmonics as stated Zajickova et al. (2007) [4]. However, the major use of DLC films is for mechanical components, which constitutes an attractive solution to several demanding engineering problems. DLC films are able to combine high hardness, low wear and low friction coefficient for large size components. The potential reductions of the friction coefficient on mechanical components make it very attractive for applications in automotive industry. The films can improve engine efficiency, lower fuel consumption and thus lowering pollution as mentioned by Schneider et al. (1998) [5].

Friction is the dissipation of energy as two surfaces move over each other as indicated Hutchings (1992) [6] and Rabinowicz (1965) [7]. Friction occurs by contact between the two surfaces at a few high points or asperities. The real area of contact is much less than the apparent area of contact, so that the real contact pressure is much greater than the average load pressure. The friction force arises either from adhesion, deformation or abrasion at the contact. According to Rabinowicz (1965) [7], if the true area of contact is  $A$ , and the shear strength of the contact is  $Y$ , then the lateral friction force is:

$$F = A \cdot Y \quad (1)$$

The true area of contact is given from the load  $W$  and real contact pressure, which equals the hardness of the softer material,  $H$ :

$$W = A \cdot H \quad (2)$$

where  $H$  is related to the shear strength by  $H = c \cdot Y$ , where  $c = 3-5$ , so the coefficient of friction  $\mu$  is given by:

$$\mu = \frac{F}{W} = \frac{Y}{H} \approx 0.2 \quad (3)$$

Deutchman et al. (2006) [8] and Kimock et al. (1993) [9] stated that DLCs are notable for their low friction coefficients. The friction properties of DLC have been reviewed recently by Grill (1997) [10], Donnet (1998) [11] and Gangopadhyay (1998) [12]. Gangopadhyay et al. (1997) [13] found that the unlubricated friction coefficient of DLC on steel is similar to the lubricated friction coefficient on steel.

The article is focused on the analysing of properties of duplex system, plasma nitrided layer with DLC coating and confronts them with the properties of plasma nitrided layers and polished surfaces of selected steels. To evaluate the tribological properties of selected steels were chosen method "pin on disc", which is one of most frequently applied methods. Method "pin on disc" is used to describe not only the tribological properties of the system, but also to determine the level of surface resistance at the contact stress.

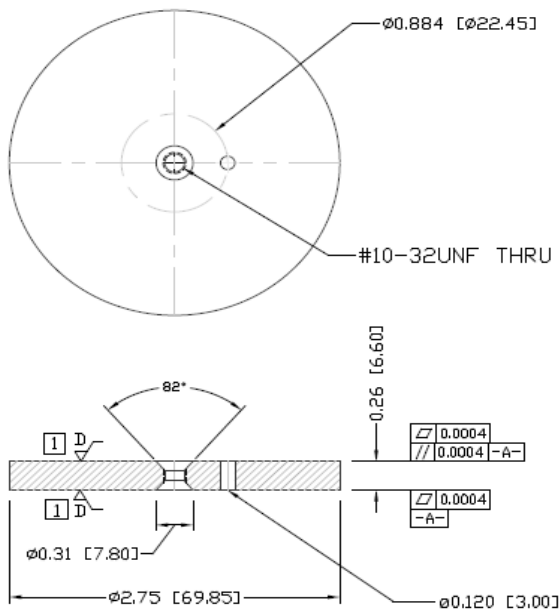
### 2 Experimental Part

Experimental samples for the evaluation of the tribological properties of the duplex system: nitrided layer-DLC coating (hereinafter PN-DLC), were made from steel 42CrMo4 and 17Ni4CrMo. Dimensions of the samples of selected steels were chosen in accordance with requirements for the experimental samples used for tribological tests on a Bruker device. These dimensions are shown, together with the produced experimental sample, in Figure 1. Experimental samples were heat treated according to the parameters specified in Table 1. After heat treatment, 42CrMo4 steel achieved a hardness of 47-54

HRC and 17Ni4CrMo steel achieved a hardness of 45-48 HRC.

**Tab. 1** Heat treatment of experimental samples

Steel	Process	Me- dium	Temperature [°C]
42CrMo4	Quen- ching	Water	840
	Tempe- ring	Water	600
17Ni4CrMo	Quen- ching	Oil	850
	Tempe- ring	Air	600



**Fig. 1** Drawing of the experimental sample with said manufacturing dimensions (left) and the appearance of the sample after the measurement of the coefficient of friction using the "Pin on disc" (right)

A total of nine pieces of samples of each material were divided into three series according to surface finishing (tempered-ground surface, tempered + PN, tempered + PN+DLC).

The first series of heat treated experimental samples, without surface treatment, was left as a reference (ground surface). The second series of heat treated experimental samples were plasma nitrided (PN) in the PN 60/60 device from RÜBIG, using a single-stage nitriding process according to the parameters specified in the Table 2.

**Tab. 2** An overview of input parameters of plasma nitriding process

Process	Input parameters								
	Temp. [°C]	Time [h]	Pressure [Pa]	Pulse length [μs]	Length of delay [μs]	Voltage [V]	Gas proportion [l/h]		
Sputtering	480	0.5	80	100	100	800	H <sub>2</sub> 20	N <sub>2</sub> 2	Ar 4
Nitriding	500	6	280	100	100	530	H <sub>2</sub> 8	N <sub>2</sub> 24	Ar 0

The third series of heat treated experimental samples were processed by plasma nitriding and coating in one process - so called DUPLEX coating in RÜBIG device. By duplex coating was achieved during one process both creating a nitrided layer and the DLC coating (DLC + PN). The parameters of duplex coating are shown in Table 3.

Three experimental samples of each series were cut after the application of PN and PN+DLC on the metallographic circular saw MICRON 150 MTH. One part of the samples was used for evaluation the chemical composition and the second part for metallographic analysis and microhardness measurements.

**Tab. 3** An overview of input parameters of plasma nitriding process

Process	Input parameters								
	Temp. [°C]	Time [h]	Pressure [Pa]	Pulse length [μs]	Length of delay [μs]	Voltage [V]	Gas proportion [l/h]		
Nitriding	500	6	80	100	100	800	H <sub>2</sub> 20	N <sub>2</sub> 2	Ar 4
Coating (DLC)	450	9.5	-	-	-	-	-	-	-

### 3 Results and Discussion

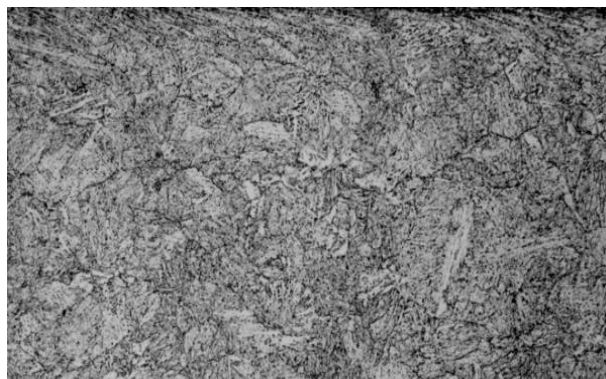
After preparation of the samples the chemical composition of steels was verified and subsequently assessed microstructure of the steels after heat treatment. The chemical composition was verified by GDOES / BULK on the device SA 2000 LECO and analysis results were compared with standardized values (see Table 4 and Table 5).

**Tab. 4** Chemical composition of 42CrMo4 steel

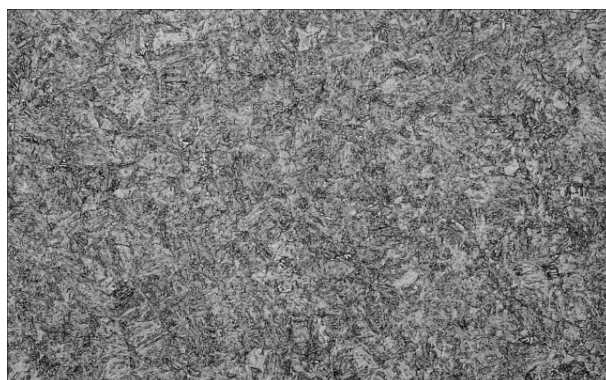
C	Mn	Si	Cr	Mo	Ni	P	S
GDOES/Bulk							
0.40	0.64	0.28	1.14	0.16	0.32	0.012	0.012
DIN standard							
0.38	0.50	<	0.90	0.15	<	<	<
0.40	0.80	0.37	1.20	1.30	0.50	0.030	0.030

**Tab. 5** Chemical composition of 17Ni4CrMo steel

C	Mn	Si	Cr	W	Ni	P	S
GDOES/Bulk							
0.17	0.48	0.22	1.63	1.11	4.09	0.015	0.012
DIN standard							
0.14	0.25	0.17	1.35	0.80	4.00	<	<
0.21	0.55	0.37	1.65	1.20	4.50	0.035	0.035



1000x



1000x

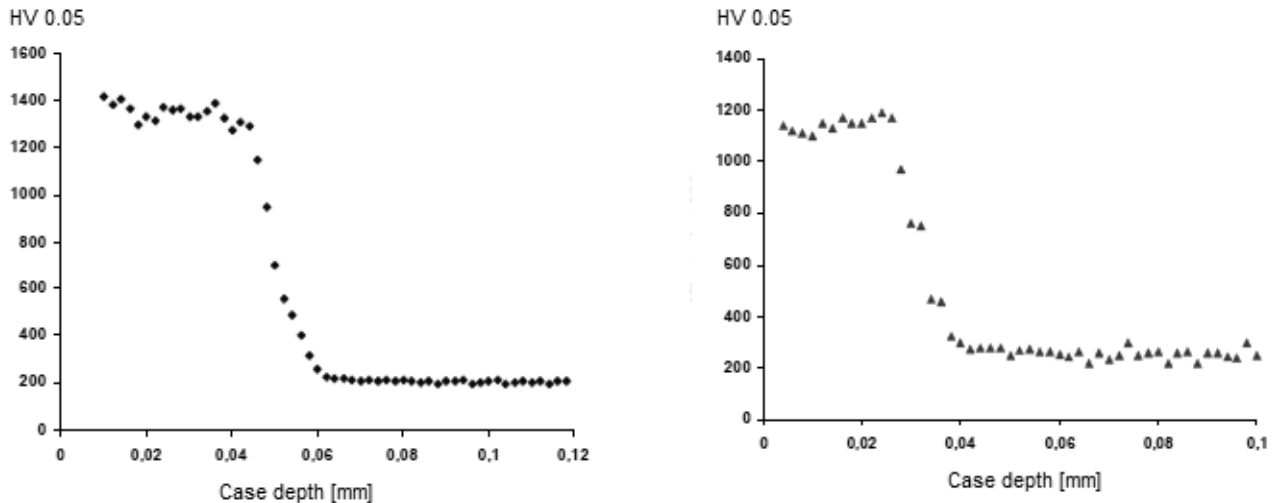
**Fig. 2** Microstructures of steels from optical microscope, 42CrMo4 – left, 17Ni4CrMo – right. NITAL 5 %

The next step was the measurement of microhardness of a diffusion layer and DLC coating of each sample by the method according to the Vickers with using the microhardness automated LECO LM 247 AT. Microhardness

After etching by Nital the characteristic initial structures of steels are documented with using the light optical microscope OLYMPUS GX 51 (Figure 2). Baseline structures of steels were assessed as relatively heterogeneous with values of microhardness about HV0.05 200 in case of 42CrMo4 and HV0.05 300 in case of 17Ni4CrMo, which approximately equates to a lower bainite with numerous free zones of excluded ferrite.

Tester was equipped with software AMH 43. The microhardness was determined by the thickness of the nitrided layer. Nitrided layer with DLC was measured at five locations (five vectors), wherein the measuring step was set at 0.01 mm. The load was selected 0.05 kg for 10 seconds. To evaluate the indentation punctures was elected lens with magnification  $\times 1000$ . In the interval 0 - 1.1 mm was carried out 30 measurements. The final value of microhardness then was calculated as the arithmetical mean of all hardnesses at a given distance from the edge of the sample (Figure 3). Thickness of DLC coating reached the value of approximately 30  $\mu\text{m}$  for both steels.

The coefficient of friction on the amount of wear has unequivocal link and roughness of contact surfaces. Prior to evaluating the tribological properties, i.e. the coefficient of friction, were measured roughness parameters of the surface of experimental samples to determine the influence of roughness on the value and the course of the friction coefficient and wear tribological tracks. Roughness parameters were measured by universal system for measuring surface texture TALYSURF CLI 1000. Measurements were performed inductive touch method to a given surface of 10x10 mm, of which were selected 3 profiles cut (2D) which were evaluated by program Talymap Platinum. The results of surface roughness parameters of grinded surfaces experimental samples after heat treatment, the nitrided samples (PN) and the duplex coated samples (PN + DLC) of both steels are shown in Table 6 and Table 7. From the measured values it is evident that after the application of PN + DLC decreased of all monitored parameters of roughness approximately about 50% in case of 42CrMo4. However, in case of steel 17Ni4CrMo occurred after process of PN + DLC to worsening of the parameters of roughness, amplitude parameters have risen by about 20%. Similar results were achieved also in work Klanica et al. (2015) [14].



**Fig. 3** Microhardness of PN+DLC. 42CrMo4 – left, 17Ni4CrMo – right

**Tab. 6** Surface roughness parameters of 42CrMo4

Parameter	Ra [ $\mu\text{m}$ ]	Rq [ $\mu\text{m}$ ]	Rz [ $\mu\text{m}$ ]	Rt [ $\mu\text{m}$ ]	RSm [mm]	Rdq [ $^\circ$ ]	Rda [ $^\circ$ ]	R3z [ $\mu\text{m}$ ]
Grinded	0.45	0.59	3.20	3.47	0.0273	13.60	8.38	2.86
PN	0.65	0.82	3.87	4.30	0.0400	13.00	8.10	3.52
PN+DLC	0.21	0.27	2.20	3.11	0.0218	11.53	6.69	1.64

**Tab. 7** Surface roughness parameters of 17Ni4CrMo

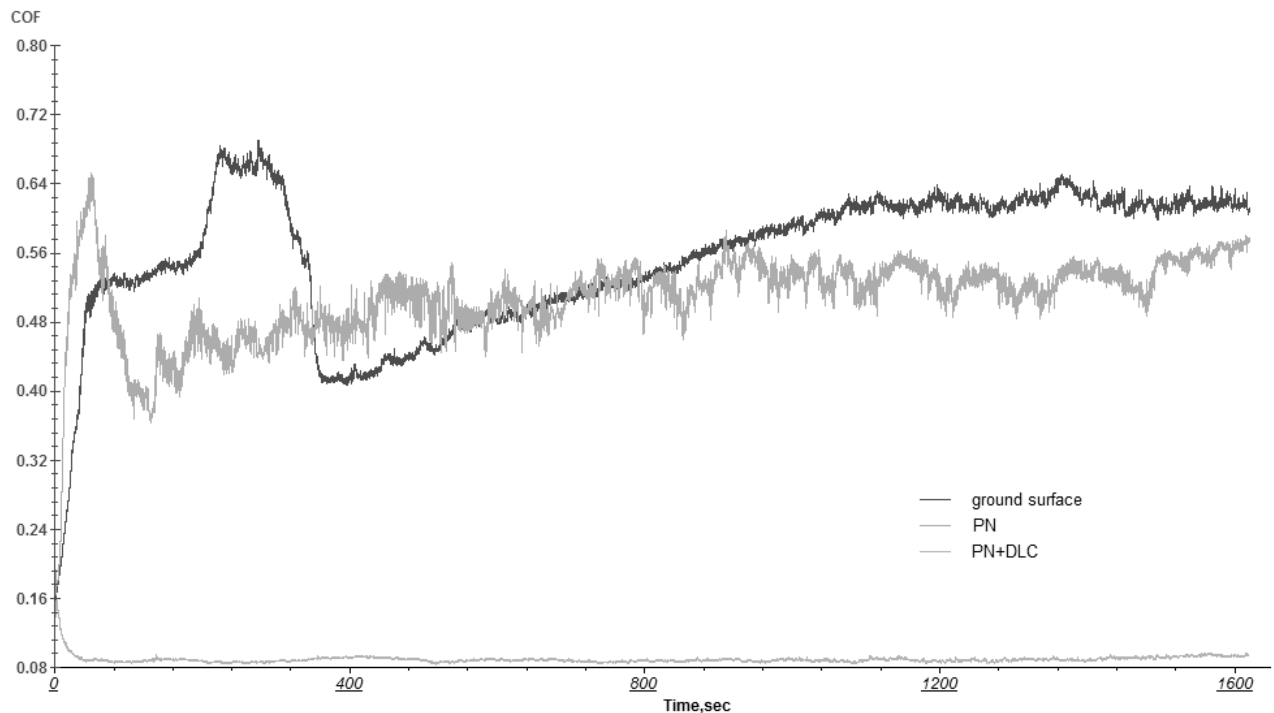
Parameter	Ra [ $\mu\text{m}$ ]	Rq [ $\mu\text{m}$ ]	Rz [ $\mu\text{m}$ ]	Rt [ $\mu\text{m}$ ]	RSm [mm]	Rdq [ $^\circ$ ]	Rda [ $^\circ$ ]	R3z [ $\mu\text{m}$ ]
Grinded	0.62	0.79	4.06	5.08	0.0569	12.77	7.12	3.47
PN	0.66	0.86	4.17	5.68	0.0695	12.90	6.89	3.73
PN+DLC	0.81	1.00	4.95	5.90	0.0551	13.47	8.03	4.43

Evaluation of tribological properties was performed on a Bruker UMT tribometer which allows measurement of the coefficient of friction in combination with various materials of counterpart. For friction measuring of the frictional contacts was elected test "Pin on Disc" under controlled conditions of load, speed and temperature. For evaluation of tribological properties, respectively friction coefficient of experimental samples from 42CrMo4 and 17Ni4CrMo steel were selected following measurement parameters:

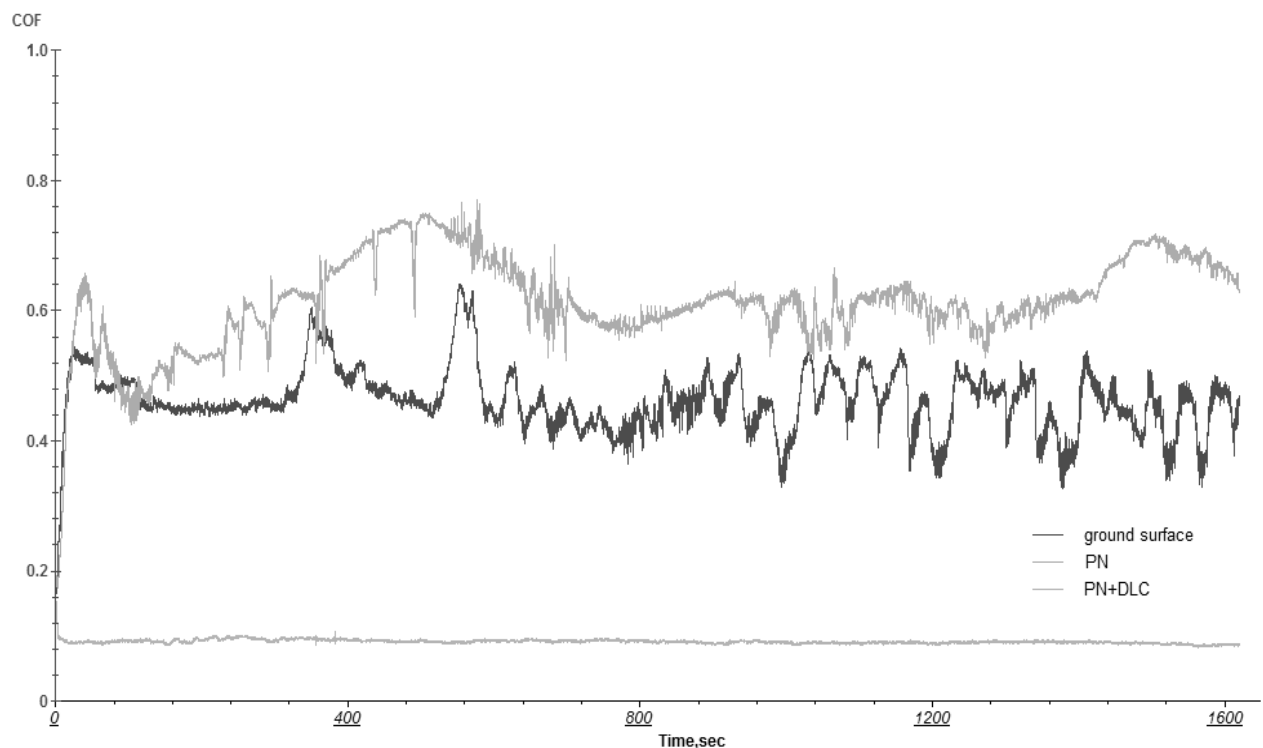
- indenter: WC ball (diameter 6.3 mm),
- relative humidity: 20%, test temperature = 23 °C,
- rotation speed:  $n = 500$  rev/min,
- time measurement:  $t = 27$  min,
- radius of wear mark:  $r = 24$  mm,
- normal force:  $F_z = 20$  N.

Comparison of the values of the coefficient of friction  $\mu$  of the grinded surface of experimental sample after heat treatment with nitrided sample (PN) and with the sample coated with a duplex system (PN + DLC) illustrates for the steel 42CrMo4 Figure 4. From the waveform of dependence of the coefficient of friction  $\mu$  is evident decrease of the value  $\mu = \sim 0.6$ , in case of grinded surface,  $\mu =$

$\sim 0.5$  after plasma nitridation (PN) and  $\mu = \sim 0.08$  when using PN + DLC, which can be considered very significant reducing the coefficient of friction  $\mu$ . Increase values of the coefficient of friction  $\mu$  at the initial stage of the measurement (particularly in the case of the ground surface and the surface after PN), which is shown in Figure 4 is caused by the emergence of so-called "stagnant layer". According to Kříž (2004) [15], "stagnant layer" is associated with the presence of large quantities of soft macroparticles resulting adaptation of the contact surfaces (separating the projections of surface roughness) which forms a continuous layer in tribological track, which causes an increase of the coefficient of friction  $\mu$ . After removal this layer, due to continuing test, will again decrease the coefficient of friction  $\mu$ . Steel 17Ni4CrMo reached lower values of the friction coefficient  $\mu$  in the case of the grinded surface, in comparison with steel 42CrMo4, which is evident from the dependence of the coefficient of friction  $\mu$  on the duration test (Figure 5). The measured value approached  $\mu = \sim 0.45$ . Conversely, after the application of PN + DLC was again a substantial decrease of friction coefficient  $\mu$ , and to a value of  $\mu = \sim 0.14$ , which is almost twice the value in comparison with 42CrMo4 with PN + DLC. Plasma Nitrided surfaces (PN) of experimental samples reached the coefficient of friction  $\mu = \sim 0.63$ , which in the case of this steel was higher value than in the case of grinded surface.



**Fig. 4** Comparing of dependencies of the coefficient of friction  $\mu$  (COF) versus time for a grinded surface and a surface coated by PN + DLC of steel 42CrMo4



**Fig. 5** Comparing of dependencies of the coefficient of friction  $\mu$  (COF) versus time for a grinded surface and a surface coated by PN + DLC of steel 17Ni4CrMo

The large dispersion values of friction coefficient  $\mu$  during measuring steel 17Ni4CrMo which is noticeable from Figure 5 resulted in a smaller amount of macroparticles, which caused uneven movement of the "PIN" indenter (balls) on the surface of the experimental sample

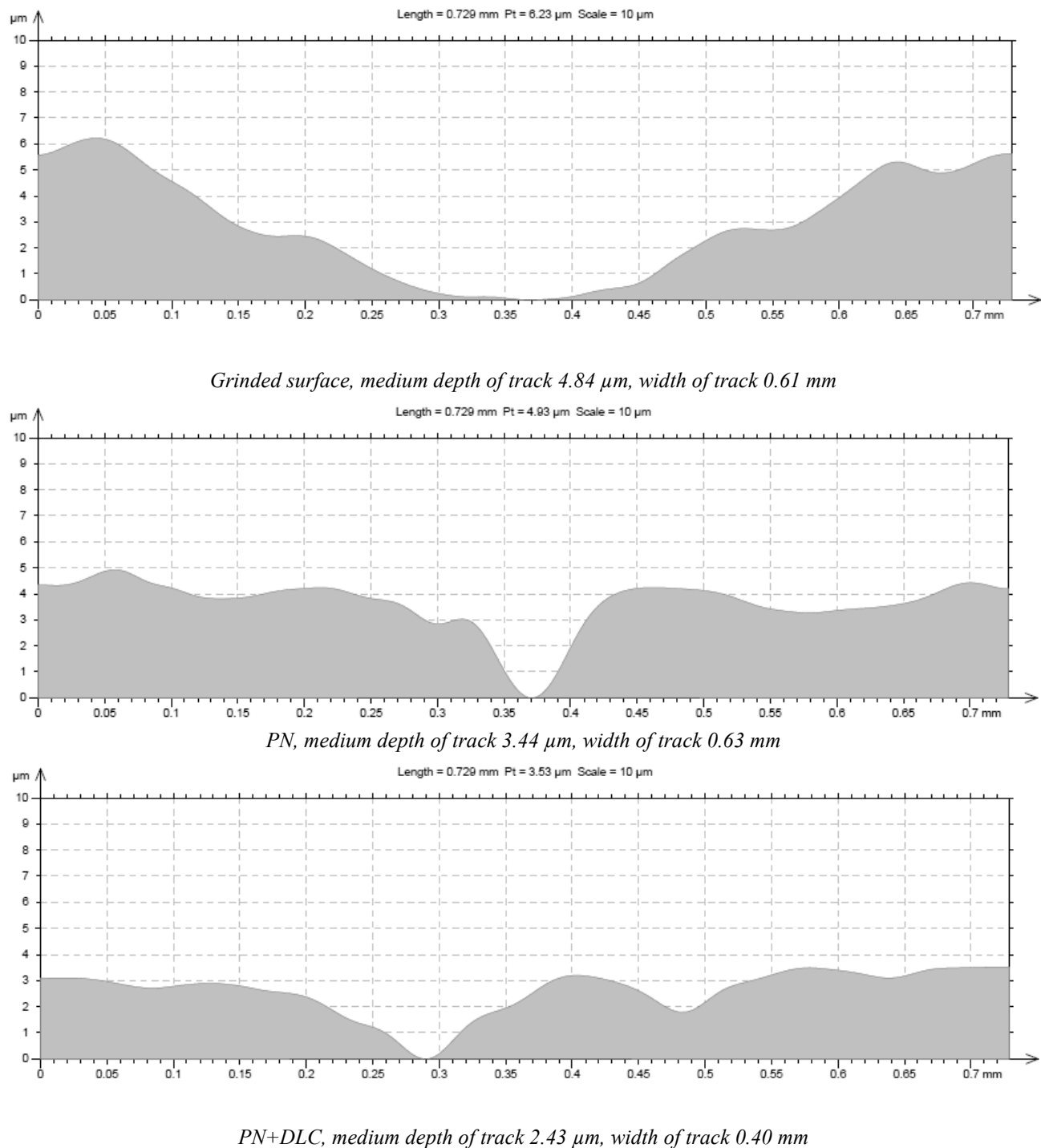
during measurement.

After measuring the friction coefficient  $\mu$  was carried out measuring of depth and width created tracks of wear. This measurement was again carried out universal system for measuring surface texture TALYSURF CLI 1000, and

inductive touch measurement method.

Track of wear was evaluated on a sample at the measurement length of 3 mm and the total evaluation length 0.729 mm, in cross section (2D) at four sites every 90 degrees. The results were evaluated in the program Talymap

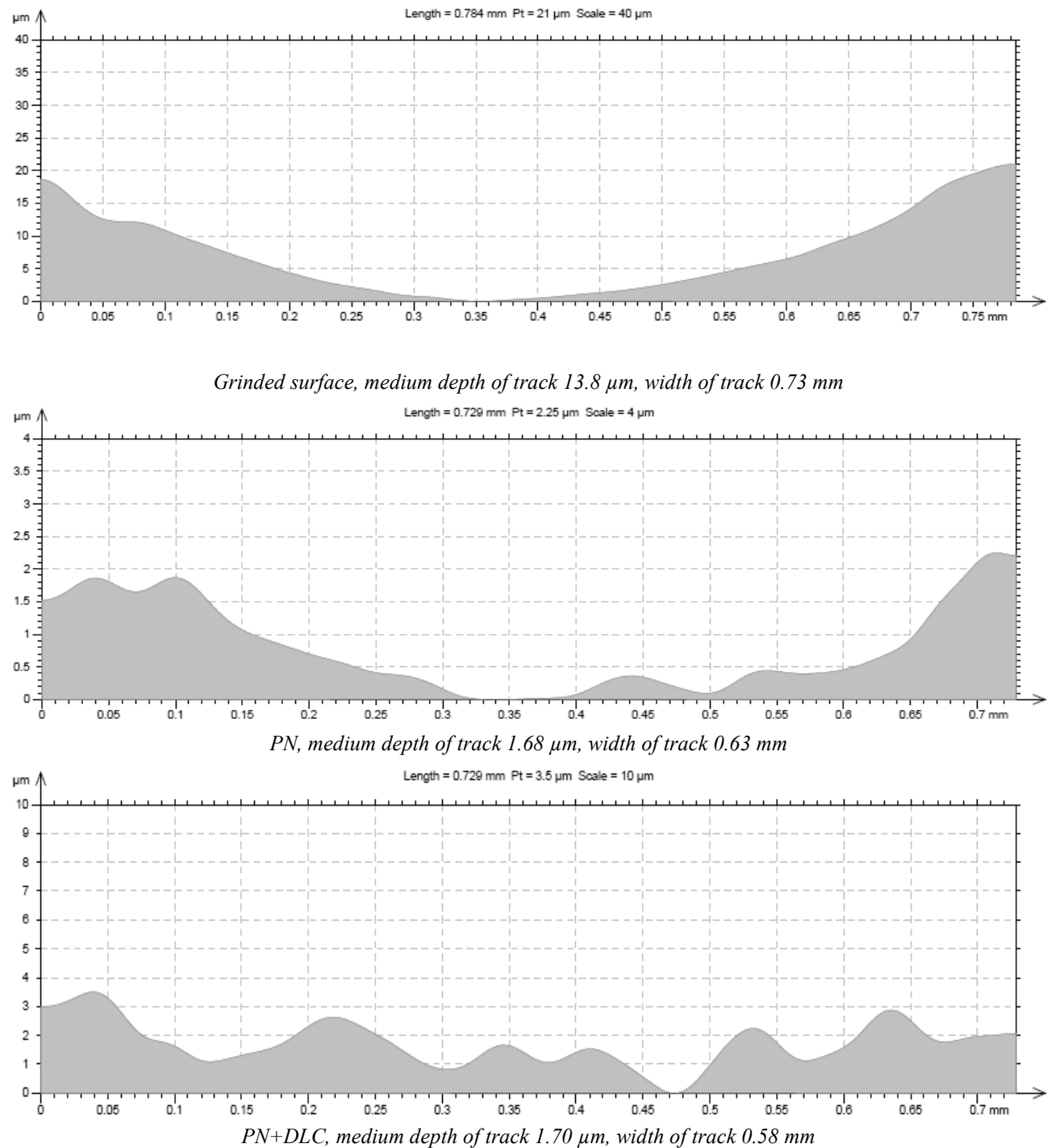
Platinum. Comparison of tracks of wear of the grinded surfaces of experimental samples, the nitrided samples (PN) and the samples with the PN + DLC are shown in Figure 6 and Figure 7.



**Fig. 6** Comparison of tracks of wear, 42CrMo4

From the measured dimensions of the wear tracks it is clear that for both steels occurred, after application of PN + DLC, to rapid decline depth of penetration of the indenter and the associated decline of width of track, which corresponds to the increase of surface hardness after application PN + DLC. Change of size tracks of wear after

the process of plasma nitriding (PN) has not reached such significant differences in comparison with grinded surface of experimental samples, particularly in case of 42CrMo4. In contrast, in case of 17Ni4CrMo the dimensional parameters of tracks of wear were after PN and PN + DLC almost identical.



**Fig. 7** Comparison of tracks of wear, 17Ni4CrMo

#### 4 Conclusions

The aim of the experimental part was to verify the properties of duplex system PN + DLC, created on specimens of steel 42CrMo4 and 17Ni4CrMo and compare these with the properties of layers formed by plasma nitriding and reference (grinded) surfaces. Modified layer formed by duplex system PN + DLC showed the best tribological properties. Compared with grinded surfaces and nitrided surfaces of the experimental samples there was a rapid decline in the coefficient of friction (steel 42CrMo4 - up to 8x, steel 17Ni4CrMo - up to 4.5x). With the increase in surface hardness of duplex system PN +

DLC was associated reduction of dimensional parameters of tracks of wear caused indenter (ball) on the surfaces of experimental samples when testing a "Pin on Disc". These results correspond with Doan (2015) [16].

It can be stated that in the experiment were confirmed the conclusions in the publications concerning the evaluation of the properties of DLC coatings. Selected duplex system PN + DLC has shown that it can be applied wherever it is necessary to delay or prevent surface degradation such as applications with wear or where it is necessary to reduce friction. Successful deployment the duplex system PN + DLC is only possible subject to certain

principles, especially suitable choice of the proper material (substrate), a suitable heat treatment and suitably prepared surface.

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