Monitoring Changes in the Tribological Behaviour of CrCN Thin Layers with Different CH_4/N_2 Gas Ratios at Room and Elevated Temperatures

Totka Bakalova[1], Nikolay Petkov[2], Hristo Bahchedzhiev[2], Pavel Kejzlar[1], Lukáš Voleský[1]
[1]Faculty of Mechanical Engineering, Department of Material Science, Technical University of Liberec, Studentska 2, 461 17 Liberec, Czech Republic. E-mail: totka.bakalova@tul.cz, pavel.kejzlar@tul.cz, lukas.volesky@tul.cz
[2]Central Laboratory of Applied Physics, Bulgarian Academy of Sciences, 61, St. Peterburg Blvd. 4000 Plovdiv, Bulgaria. E-mail: petkovnik@gmail.com, hristo_bah@abv.bg

This research is engaged in monitoring changes in the tribological behaviour of CrCN thin films at room and elevated (300°C) temperatures. The monitored thin films are deposited by cathodic arc deposition of a pure Cr (99.99 %) cathode under an atmosphere of a mixture of CH_4 and N_2 gasses. Tribological measurements were performed at a load of 10N, a rotational speed of 60 rpm, and a counterpart of ceramic material (Al_2O_3). The article also describes the evaluation of wear on the studied thin films due to tribological measurement and temperature.

Keywords: Cathodic Arc Deposition, CrCN coatings, Surface Morphology, Tribology, Wear

1 Introduction

CrN coatings are a very good choice in areas of application where abrasion resistance, corrosion resistance and oxidation resistance are required. High hardness and low brittleness make it possible to create a larger coating thickness with very good adhesion to the base material. The addition of carbon to the CrN matrix creates a thin layer of chromium carbonitride (CrCN) that has better frictional properties. However, the tribological behaviour of the CrN layers may vary considerably depending on the choice of the substrate material, the coating thickness, the wear type, and the experimental conditions.

CrCN coatings are not so widely studied. Literary sources claim that CrCN coatings improve tribological behaviour compared to CrN. Chromium nitride coatings show higher oxidation resistance compared to other nitride coatings. The coatings have a very good wear resistance under different tribological conditions (e.g. high temperature, speed and pressure). [1, 2] The states that wear tests on particular examples of CrCN coatings show better results than on CrN coatings. [3] However, the friction and wear characteristics of the CrCN coating are not well known, especially at elevated temperatures. In order to supplement the findings in this field of research, this study presents the friction and wear characteristics of CrCN coatings.

The presented work offers a comparison of the tribological properties of CrCN thin films at room temperature and at 300° C. The monitored coatings are deposited at different gas ratios CH_4/N_2 in the working chamber. The article evaluates the amount of wear on the layers after tribological experiments using a ceramic counterpart (Al_2O_3).

2 Experimental procedure

CrCN coatings were deposited by a cathodic arc evaporation method using a 99.99% Cr cathode in a reactor gas atmosphere of N_2 and CH_4 at a deposition temperature of 300 °C. During the thin film deposition process, the following parameters were used: arc current 85 A, bias voltage -100 V and deposition time 120 min. The interlayers of Cr and CrN were applied on the surface of the substrates prior to deposition of the thin films. These interlayers were intended to improve the adhesion between the layer and the base material (tool steel EN ISO HS 6-5-2).

The deposited CrCN thin films had different compositions and were labelled CrCN 20, CrCN 35, CrCN 50 and CrCN 65. The gas ratios used for deposition of the thin films and the thicknesses of the films are described in Table 1.

The thickness of the investigated coatings was evaluated using the Calotest method. The thickness of the coatings was measured with a 30-mm diameter steel ball and a diamond paste with 0.1 mm monocrystalline diamond grains. The thickness of the coatings was assessed at three different locations on the surface, and the mean values and standard deviations are shown in Table 1.

Tab. 1 *Gas ratios of N_2 and CH_4 used during coating deposition and film thicknesses*

Sample	CH_4 / N_2 [%]	CH_4 / N_2 [-]	d [μm]
CrCN 20	20	0.3	2.68 ± 0.02
CrCN 35	35	0.5	2.35 ± 0.02
CrCN 50	50	1.0	2.76 ± 0.01
CrCN 65	65	1.9	1.92 ± 0.02

The substrate material is a tool steel with the following chemical composition in [wt. %]: 0.9 C; 0.31Mn; 0.34 Si; 0.026 P; 0.0005 S; 4.43 Cr; 4.78 Mo; 5.93 W; 1.79 V and 0.65 Co. The prepared samples of the substrates were in the form of discs with dimensions of ø20 mm x 5 mm. The substrates were polished to a surface roughness (*Sa*) of 0.01 μm, and the measured hardness of the samples was 64-65 HRC.

Before deposition of the thin films, several steps were taken to improve the adhesion of the coatings to the base material:

- the prepared tool steel substrates were cleaned in an alkaline solution in an ultrasonic bath for 5 minutes and then rinsed with deionized water and dried with boiling ethanol and hot air;

- after completion of the cleaning process, the prepared substrates were placed in a vacuum chamber and mounted on a sample holder;
- the tool steel substrates were cleaned with metal ions to remove traces of surface contamination and native oxide layers at a voltage of -1000 V and a pressure of 0.2 Ar. [4, 5]

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 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 analysed at an accelerating voltage of 10 kV.

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: *Sa* is the average arithmetic height (average surface roughness); *Sz* is the maximum height (height between the lowest recesses and the highest projection); *Sq* is the standard deviation of the distribution of heights (root mean square roughness); and *Sp* is the maximum height of the protrusion (height between the median plane and the highest projection).

Adhesion of the thin layers to the substrate was evaluated on a CETR UMI Multi-Specimen Test System - Scratch Tester. The scratch test is performed on the coatings using a scratch tester device with a progressive load from 2 to 100 N and speed of 10 mm/min, according to the ISO EN 1071-3:2005 standard. The normal load at which failure occurs is called the critical load, L_C. There are three normal load values characterizing the adhesion [6]: the minimum load at which a cohesive failure occurs is called the first critical load (L_{C1}); the load at which the first adhesion failure is verified is called the second critical load (L_{C2}); and the load at which more than 50 % of the coating from the scratch area is removed from the substrate is called the third critical load (L_{C3}). [7]

The tribometer for dry and liquid environments (company Anton Paar) in "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 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 46 ± 2 %.

3 Results

3.1 Chemical composition of the investigated thin films

The chemical composition of the thin coatings (CrCN 20, CrCN 35, CrCN 50 and CrCN 65) was evaluated using energy-dispersive analyses; the results are shown in Table 2.

Tab. 2 *Chemical composition obtained from EDS analysis [in at. %]*

Coating	C	N	Cr
CrCN 20	28.8	20.5	50.7
CrCN 35	36.3	12.6	51.1
CrCN 50	38.7	8.5	52.8
CrCN 65	44.2	7.2	48.6

3.2 Characteristics of the coating surface morphology

Three measurements were made using the material confocal microscope (according to the ISO 25178 standard) over different areas of 113.34 x 94.58 μm^2 for each thin layer. The average values of the measured surface parameters are given in Tables 3 and 4.

Tab. 3 *Parameters of surface morphology for the investigated CrCN coatings before heat treatment*

Coating	CrCN 20	CrCN 35	CrCN 50	CrCN 65
Sa [nm]	37.06 ± 1.82	27.54 ± 1.13	24.61 ± 1.21	37.28 ± 0.54
Sz [nm]	325.31 ± 9.29	417.08 ± 3.05	290.76 ± 4.62	605.94 ± 8.06
Sq [nm]	48.10 ± 1.85	41.22 ± 1.26	44.58 ± 4.68	54.10 ± 4.06
Sp [nm]	229.82 ± 6.45	313.48 ± 7.59	403.45 ± 30.15	495.93 ± 9.29

Tab. 4 *Parameters of surface morphology in the investigated CrCN coatings after heat treatment (T=300 °C)*

Coating	CrCN 20	CrCN 35	CrCN 50	CrCN 65
Sa [nm]	37.55 ± 4.29	33.00 ± 0.31	51.54 ± 2.37	35.23 ± 5.14
Sz [nm]	614.67 ± 20.99	490.33 ± 2.90	660.12 ± 20.32	427.48 ± 13.63
Sq [nm]	61.59 ± 7.41	51.10 ± 0.64	80.79 ± 7.65	50.13 ± 7.24
Sp [nm]	473.92 ± 13.43	378.40 ± 6.05	540.23 ± 17.28	327.49 ± 16.04

Increasing the amount of carbon in the coatings from 29% (CrCN 20) to 39% (CrCN 50) resulted in a decrease in the Sa parameter. A further increase in carbon (CrCN 65) did not have a beneficial effect on the surface roughness Sa (see Table 3). The highest roughness Sz was measured for sample CrCN 65 (Table 3).

The observed parameter Sz was lower for all of the coatings at room temperature than the coatings affected by heat treatment at 300 °C, except for the CrCN 65 coating. There was a reduction in the surface roughness Sz after heat treatment (Table 4). This can be caused by reducing the number of droplets on the surface of the coating. The occurrence of droplets on the surface of the coating is one of the drawbacks of this coating method.

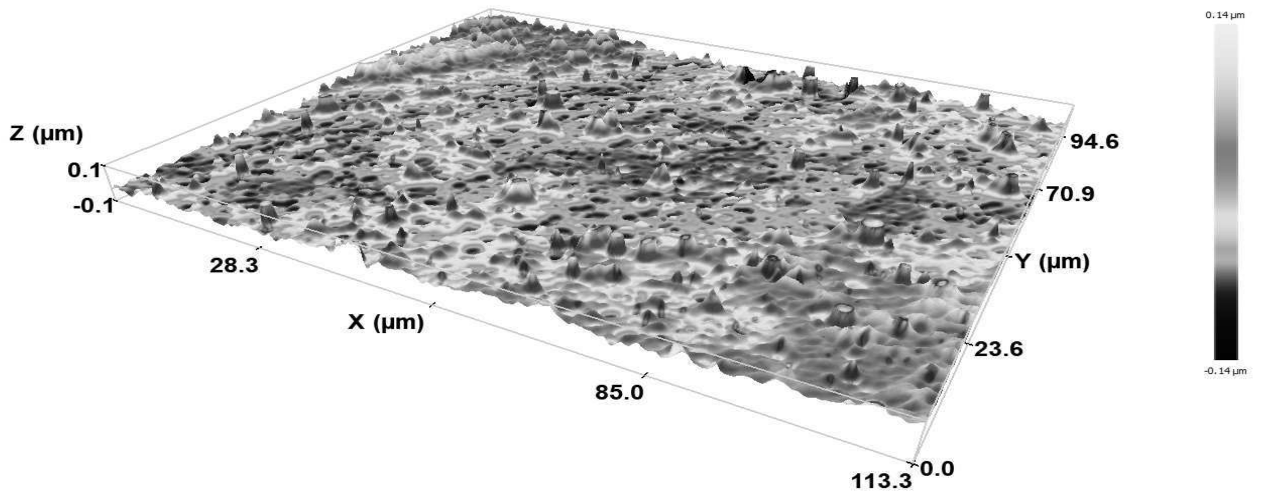

Fig. 1 Surface morphology for the CrCN 20 coating before heat treatment

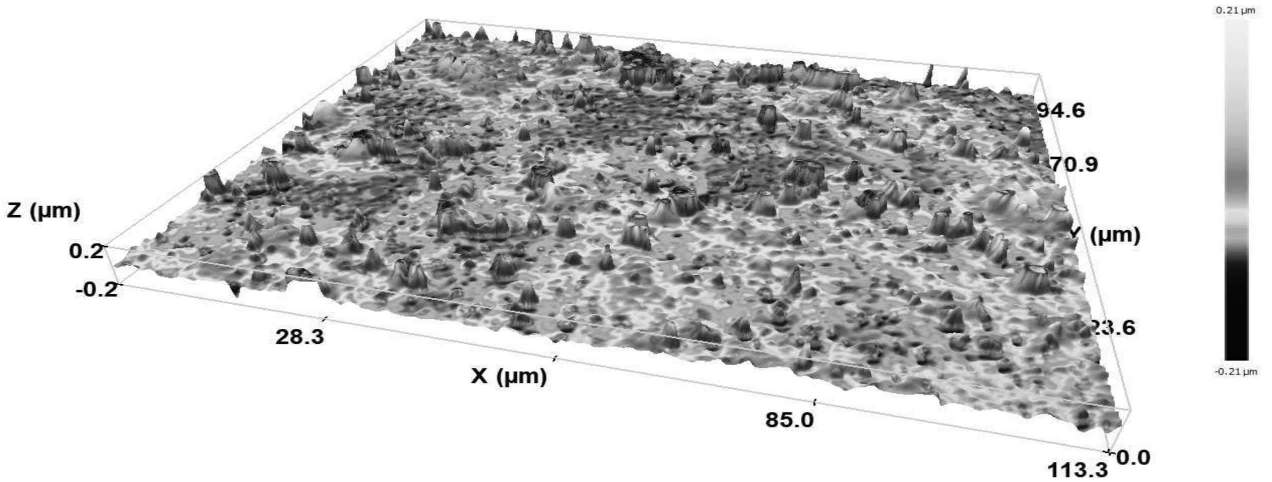

Fig. 2 Surface morphology for the CrCN 20 coating after heat treatment (T=300 °C)

3.3 Evaluation of adhesion of coatings to the substrate, scratch test

The scratch test of the coatings was performed at room temperature and a relative humidity of 52 ± 2%. Three measurements were made at different places for each sample, and the average values of the measured critical loads (L_{C1} and L_{C3}) are given in Table 5.

Tab. 5 Critical loads of the thin layers [in N]

Coating	L_{C1}	L_{C3}
CrCN 20	31.3 ± 5.5	61.2 ± 9.3
CrCN 35	28.2 ± 2.5	57.4 ± 6.9
CrCN 50	23.7 ± 4.4	52.5 ± 4.1
CrCN 65	30.2 ± 2.9	56.3 ± 4.1

The layers showed very good adhesion to the base material (Table 5). Similar results were obtained for the CrCN coating (Cr - 40%; C - 18%; N - 42% in [at. %]), where the following critical loads L_{C1} - 22 N and L_{C3} - 52 N were measured [4]. The best adhesion to the base material was measured for the CrCN 20 coating (Cr - 51%; C - 28%; N - 21% in [at. %]) with a thickness of 2.7 µm. An increase in the gas ratio of 0.3 to 1.0 (CrCN 20, CrCN 35 and CrCN 50) resulted in a reduction in the adhesion of the studied coatings of the substrate (see Table 5). A further increase in the gas ratio to 1.9 resulted in improved adhesion to the CrCN 65 coating.

3.4 Coefficient of friction (CoF)

Tribological testing was conducted using a ceramic ball (Al_2O_3) with a hardness according to Vickers: < 1500 (HV10) and density of 3.860 g/cm³. The counterpart moves through a path length of 150 m. Testing of tribological properties at room temperature was performed using rotary tribology. The rotation speed during the tribological measurement was 60 RPM. Tribological properties at 300 °C were evaluated using linear tribology. The linear velocity of the sample relative to the ball at a rotational tribology was 3.8 cm/s and at a linear tribology - 3.1 cm/sec. Table 6 shows the measured coefficient of friction values and standard deviations for the investigated CrCN layers at room temperature and at 300 °C.

It can be seen from Table 6 and Figure 3 that at room temperature the coefficient of friction values decrease with increasing amounts of carbon in the coating (sample CrCN 20 – 29% C and sample CrCN 65 – 44% C). At a temperature of 300 ° C, the tendency to reduce the coefficient of friction is less pronounced (Figure 3). The lowest coefficient of friction at room temperature was measured for the CrCN 65 coating.

***Tab. 6** Average coefficient of friction values*

Thin coating	CrCN 20	CrCN 35	CrCN 50	CrCN 65
CoF [-], T=21 °C	0.55 ± 0.06	0.42 ± 0.06	0.43±0.04	0.26±0.02
CoF [-], T=300 °C	0.73 ± 0.06	0.69 ± 0.03	0.63 ± 0.02	0.63 ± 0.03

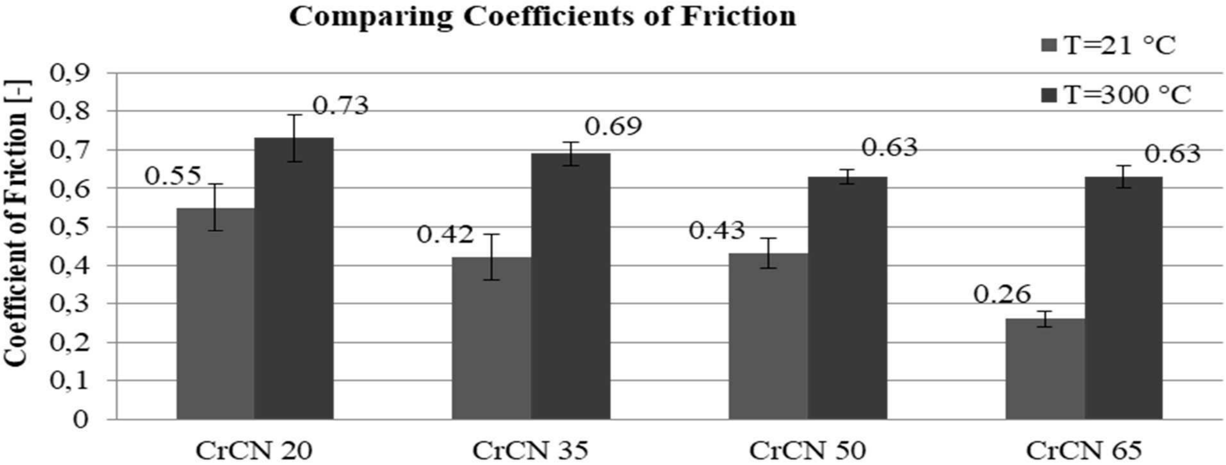

***Fig. 3** Average coefficient of friction values*

3.5 Evaluation of wear rate after tribology

A Leica DVM6 digital microscope and a SENSOFAR Metrology material confocal microscope were used to evaluate the wear of the friction pairs. The digital microscope was used to evaluate the spot size on the Al_2O_3 ball, and the confocal microscope was used to evaluate the width and depth of the ploughed profile.

The wear of the Al_2O_3 ball against the CrCN coatings was evaluated according to the EN 1071-13:2010 standard and the results are shown in Table 6. The amount of wear on the balls was calculated by equation (1).

$$V_{pin} = \frac{\pi A^3 B}{32D} \qquad (1)$$

Where: V_{pin} is the amount of wear on the balls [mm^3]; A is the smallest diameter of the machining track [mm]; B is the diameter in the direction perpendicular to the smallest diameter [mm]; and D is the diameter of the ball [mm].

Figures 4 and 5 show the wear of the friction pair after tribology at room temperature and at 300 ° C.

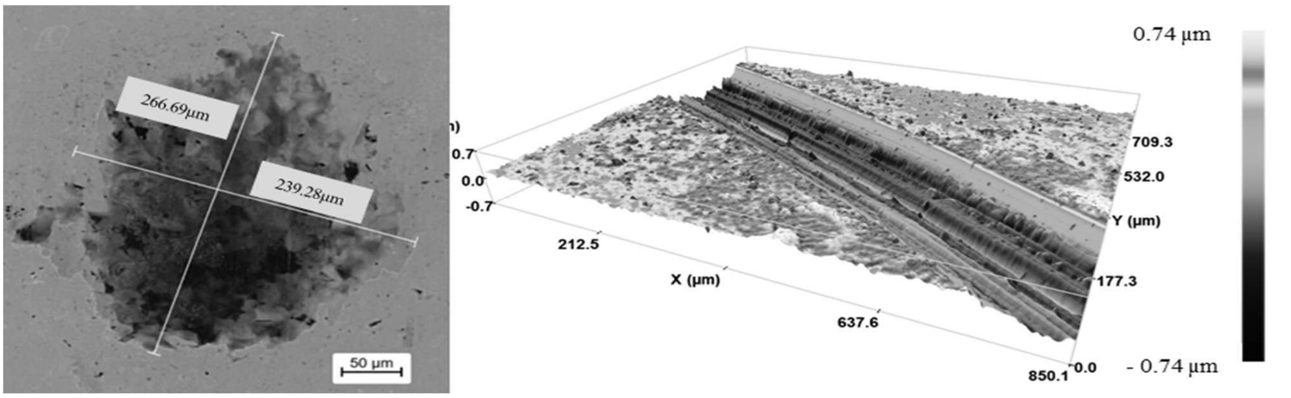

***Fig. 4** Wear of the Al_2O_3 balls (left) and wear of the CrCN 20 coating (right) after tribology at room temperature*

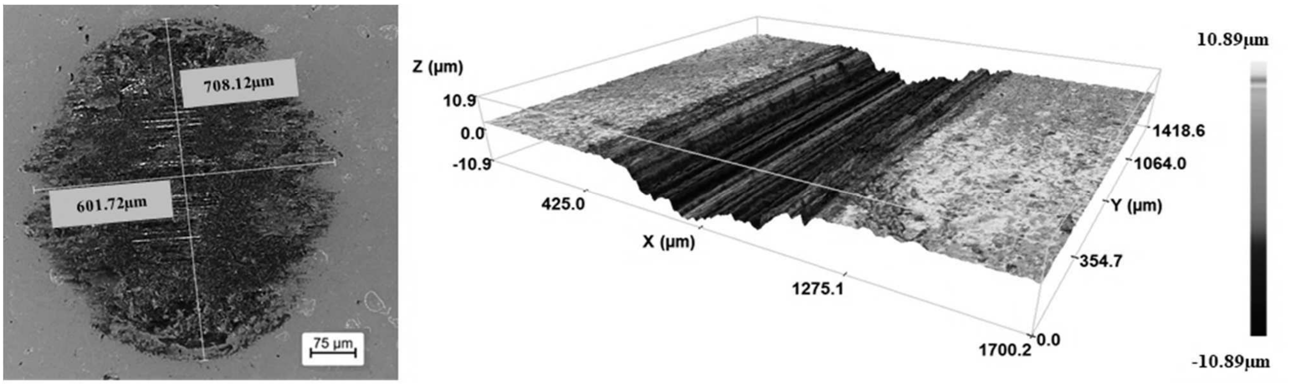

***Fig. 5** Wear of Al_2O_3 balls (left) and wear of the CrCN 20 coating (right) after tribology at 300 ° C*

The wear values of the Al_2O_3 ball after tribology at room temperature and at 300 ° C are shown in Table 6.

The depths of wear of the studied coatings were measured using the confocal microscope, according to the ISO 25178 standard. Three measurements were made over an area of 1700.16 x 1418.64 μm^2 for each thin coating. The average values and standard deviations are shown in Table 8.

***Tab.** 7 Wear of Al_2O_3 balls [mm]*

Coating	CrCN 20	CrCN 35	CrCN 50	CrCN 65
T=21 °C	$5.98x10^{-5}$	$10.25x10^{-5}$	$8.34x10^{-5}$	$5.26x10^{-5}$
T=300 °C	$895.55x10^{-5}$	$252.40x10^{-5}$	$223.00x10^{-5}$	$305.2\ x10^{-5}$

***Tab. 8** Depth of coating wear after tribology [μm]*

Coating	CrCN 20	CrCN 35	CrCN 50	CrCN 65
T=21 °C	1.12 ± 0.13	0.92 ± 0.02	2.15 ±0.13	0.99 ± 0.05
T=300 °C	9.94 ± 0.54	15.14 ± 1.58	19.25 ±0.25	18.44 ± 0.29

The CrCN 20 coating was more wear resistant (Table 8) both at room temperature and at 300 °C. Increasing the amount of carbon in the coating decreased the wear resistance, which was best shown at 300 °C.

After completion of the tribological process at room temperature coatings CrCN 20 and CrCN 65 were the least affected by contact with the counterpart (Table 7). The greatest wear at a temperature of 300 °C was measured by contact between the counterpart and the CrCN 20 coating (Table 7).

4 Conclusion

Monitoring of the changes in the tribological behaviour of CrCN thin coatings with different CH_4/N_2 gas ratios at room and elevated temperatures (300 °C) showed that increasing the amount of carbon significantly improves the sliding properties of the coating, where the CoF value for the CrCN 65 coating was 0.26±0.02. After raising the temperature to 300 °C, better sliding properties of the layer were not determined (CoF 0.63 ± 0.03). A higher value of surface roughness in contact with the Al_2O_3 ball was measured for the CrCN 65 coating, which showed 2x more wear than the CrCN 20 coating.

Evaluation of the wear rate (abrasion resistance against the Al_2O_3 ball) shown that the CrCN 20 coating with the smallest amount of carbon (29 %) had the best abrasion resistance. The CrCN 20 layer also showed the best adhesion to the base material (L_{C1} 31 N a L_{C3} 61 N).

Acknowledgement

This paper was supported by the project "Dynamic multi-axis electro-hydraulic recovery units", registration number CZ.01.1.02/0.0/0.0/15_019/0004853, through the financial support of the Ministry of Industry and Trade in the framework of the targeted support of "Application I", the Operational Programme Enterprise and Innovations for Competitiveness.

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