# THE EVALUATION OF SELECTED PROPERTIES OF TI AND CR BASED COATINGS DEPOSITED ONTO HSS CO5

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This study investigates the properties of thin Ti and Cr based coatings applied by two PVD techniques. ARC and SARC PVD techniques were used for the deposition of thin coatings onto HSS Co 5 steel. Conventional types of coatings (monolayers TiN, TiAlN, CrAlN), and an advanced type of coating (Ti and Al based KTRN monolayer deposited by smaller drops on the surface) were analyzed by standard techniques for surface status and quality assessment – coating thickness, chemical composition by EDX analysis, hardness and coefficient of friction (COF) at room temperature. Measured nano-hardness of CrAlN, TiAlN, KTRN, and TiN coatings were 16.5 GPa, 34.7GPa, 34.9GPa and 14.3GPa, respectively. Measured COF values of CrAlN, TiAlN, KTRN, and TiN coatings were 0.58, 0.48, 0.57, and 0.82 respectively. The roughness $R_a$ of CrAlN, TiAlN, KTRN, and TiN coatings were 0.31μm, 0.31 μm, 0.58 μm and 0.76 μm, respectively. Lower deposition temperature and specimen distance to the target can be the reason of lower hardness of TiN and CrAlN coatings. High values of the roughness $R_a$ and higher contact surface size of the system coating-ball are the reasons for high COF of TiN coating.

K e y w o r d s: PVD coatings, properties, wear, COF, nan-ohardness

## 1 INTRODUCTION

Thin Ti and Cr based coatings are widely used as monolayers [1-8], multilayers [8-12] and gradient layers [7,12,13]. Thin coatings are used for extending the lifetime of machine parts. Thin Ti layers and in particular Ti based layers are frequently used for their good properties such as adherence, hardness, wear rate and COF as coatings on cutting tools [1,2].

In bioengineering applications like artificial heart valves, it is important to use materials with two major properties: good ductility combined with high hardness. It ensures long exploitation time of medical elements. Multilayer materials like gradient coatings on TiN, Ti(C,N) and a: C–N basis created in the processes of coating deposition fulfill both these demands [13,14].

Transition of metal nitrides were investigated widely due to their excellent intrinsic properties such as good conductivity, high hardness and wear resistance, being applied as diffusion barriers, hard or wear resistant coatings and anti-corrosion coatings [9,15–25]. Properties and the applications of TiN coatings have been studied extensively. The addition of other elements such as Al, Cr, etc., increases oxidation resistance above 450 °C. TiAlN coatings have been developed for engineering applications as an alternative to TiN coatings [1,4]. Accordingly, materials that can replace TiAlN are required. In the attempt of adding Cr, research shows that a slight addition of Cr to AlTiN results in excellent cutting performance in the cutting of hardened steels [26]. The unique advantage of advanced coatings of $(Al_1{-}xCrx)N$ types is in their exceptional properties [5-7], such as: very high oxidation resistance (above 900 °C) with a high hardness often above 30 GPa [7]. Other positive feature is the low coefficient of friction (COF) [5-7]. The mentioned layers can be deposited by both CVD [7,8,11] and PVD techniques. Among appropriate and frequently used methods belong ARC and LARC (lateral rotating arc-cathodes) [2,4,5,9,10], magnetron sputtering PVD techniques [6,25], with $N_2$ as a reaction gas, present during deposition. Special attention has to be paid to the number and distribution of sources during deposition of PVD coatings [27], because of possible influence on the microstructure and thus also on the properties of the deposited coatings.

The aim of this work was to determine selected properties, such as roughness, nano-hardness, and COF of thin coatings deposited by the PVD process on the high speed steel Co 5. The next aim of the article is to compare the measured values with the data from the producers and with results obtained by the above-mentioned authors.

## 2 PREEPARATION OF SPECIMENS AND EXPERIMENTAL PROCEDURES

Experiments aimed at the evaluation of coatings were made using ***specimens*** from the high speed steel HSS Co5 (STN 19852, AISI M35) which are used on drills fabrication. The HSS Co 5 is containing C = 0.92% , W = 6.40%, Mo = 5.0% , V = 1.90%, Co = 4.80% and Cr = 4.10%. The specimens were heat-treated in the salt bath furnace. Austenitization took place at the temperature of 1180 °C and triple tempering at the temperature of 540 °C. After its heat treatment, the steel obtains hardness of 63 HRc (STN 19852, AISI M35). Before depositing the coatings the specimens were grinded to roughness $R_a$ = 0.4 – 0.6 μm. The selection of materials, the preparation of specimens and deposition of coatings were carried out by the producer, Staton company, which also provided nominal values of the mentioned technological parameters.

Testing samples were prepared according to requirements of particular tests. The samples for tribological characterization were prepared for the Pin-on-disc test – discs with 30 mm diameter and 5 mm thickness. The samples for coating thickness measurements had dimensions 6x5x35mm. Adhesion and roughness were measured on the Pin-on-disc test samples.

TiN (Fig. 3), TiAlN (Fig. 2) and CrAlN (Fig. 4) coatings were ***deposited*** using arc PVD method and KTRN (TiAl) coating (Fig. 1) was prepared by Sarc PVD method (it denotes the arc method by Staton – deposited with smaller microdrops) according to parameters shown in the table 1. For all coatings the deposition time was 30min, the samples rotated and only one surface was coated – the samples were lying horizontally on one side, rotation rate 4 - 5 rpm, cathode – sample distance was 20 cm.

Before coating deposition on substrates were ultrasonically cleaned in acetone and subjected to Ar plasma etching – P = 0.2 Pa, U = 1.2 kV, t = 20 min. and heating – P = 5 Pa, U = 1.24 kV, t = 60 sec.

*Table 1* Main process parameters for the CrAlN, TiAlN, KTRN and TiN coatings depositon.

| | Technique | Pressure [Pa] | Temperature [°C] | $I_{catode}$ [A] | U [V] | Flow $N_2$ [$cm^3min^{-1}$] |
|---|---|---|---|---|---|---|
| CrAlN | ARC PVD | 0,2 | 400 | 80 | -150 | 120 |
| TiN | | | | | | |
| TiAlN | | | | | | |
| KTRN | SARC PVD | 0,1 | 500 | 100 | -200 | - |

***The thickness and chemical compound*** of investigated coatings were determined by scanning electron microscope Tesla 340BS and EDX analysis. Thickness was measured on a brittle fracture surface of broken samples. All specimens were ultrasonically cleaned in an organic solvent for 5 min and subsequently dried by hot air blowing for 2 mints.

***The nano-hardness tests*** of coatings were made on the CSM ultra-microhardness tester. Test conditions were selected so that the penetration depth was maximum 0.1 of the thickness of evaluated coatings, thus eliminating influence of the substrate on the measurement results. Measurements were made at loads up 0.07 N, using sinus mode in order to obtain the depth profile of nano-hardness and Young´s modulus. Measurements were done using Berkovich indenter. The presented values of the nano-hardness of evaluated coatings are the maximum measured values from 10 performed measurements.

***The surface roughness*** investigations of samples and deposited coatings were made on a stylus profiler Surftest SJ-310 by MITUTOYO.

***Tribological*** tests were carried out on the CSM Instruments "Pin-on-disk" tester in the following conditions: counter-specimen was a ball made from the 100Cr6 steel with the 6mm diameter and hardness 850 HV (65 HRc), normal load − 0,5N, friction radius − 6mm, linear velocity − 0,15 m/s, respectively, distance – 50m, ambient temperature − 20 °C, humidity – 40%. Pin-on-disc test was performed without lubrication.

## 3 RESULTS AND DISCUSSION

### 3.1 Thickness, nano-hardness

The studied CrAlN, TiN, TiAlN and KTRN (Fig. 1-4) coatings had ***thickness*** presented in the table 2. Presented values of the coating thickness were determined using micrographs obtained by scanning electron microscopy. Individual samples with the measured coatings together with respective EDX spectra are depicted in Figs. 1-4.

Nano-hardness testing found that the uncoated HSS Co5 has nano-hardness 7.48 - 7.75 GPa (STN 19852, AISI M35). Deposition of evaluated PVD coatings onto the HSS Co5 steel caused the increase of surface nano-hardness up to values from 14.3 GPa to 34.9 GPa, which is 100% more in comparison with the nano-hardness of the substrate. The highest nano-hardness 34.9 GPa was observed in the case of the KTRN coating. It was found out, that it is in good agreement with value 35 GPa given by the producer (Staton, Slovakia). Shown values of nano-hardness are the maximum measured values.

The ***nano-hardness*** of the TiN coating was 14.3 GPa. This is significantly lower that 22.12 GPa [11,28] found for coating deposited by PVD on Si3N4 substrate and it is comparable to the lowest nano-hardness (16.3 – 29.8 GPa [12]) found for coatings PVD deposited on sintered high speed steel ASP 30 by magnetron sputtering. Deposition parameters were: temperature – 400V, 500V and 540V, specimens distance to the disc: 70mm, 90mm and 125mm [12].

The nano-hardness of TiAlN coating was 34.7 GPa, which is 10% higher than that given by the producer (STATON) and 15% higher than reported in [7].

The nano-hardness of CrAlN coating was 16.5 GPa, which is 10 to 20 GPa lower than found in [6]. It is also significantly lower than reported in [25], which evaluated nano-hardness (15 GPa to 36 GPa – deposited from two targets), Young´s modulus (331 GPa to 520 GPa), coating thickness (2 μm to 3 μm) and COF (0.6 to 0.7) depending on content of Al in CrAlN coating and Al and Cr bias voltage. Our result is in good agreement with CrAlN coating deposited using Cr bias voltage -700 V. Differences of our measured values of nano-hardness and Young´s modulus can be caused by different methods of coating deposition and technological parameters.

Values of ***Young´s modulus*** for CrAlN, TiN, KTRN, and TiAlN coatings were 418.12 GPa, 326.45 GPa, 620.23 GPa, and 463.19 GPa, respectively. Our measured values were determined from diagram (Fig.6) after depth of penetration approximately 80 nm due to high values of roughness $R_a$.

The ***roughness*** of CrAlN, TiN, KTRN, and TiAlN coatings were 0.31 μm, 0.76 μm, 0.31 μm and 0.58 μm, respectively.

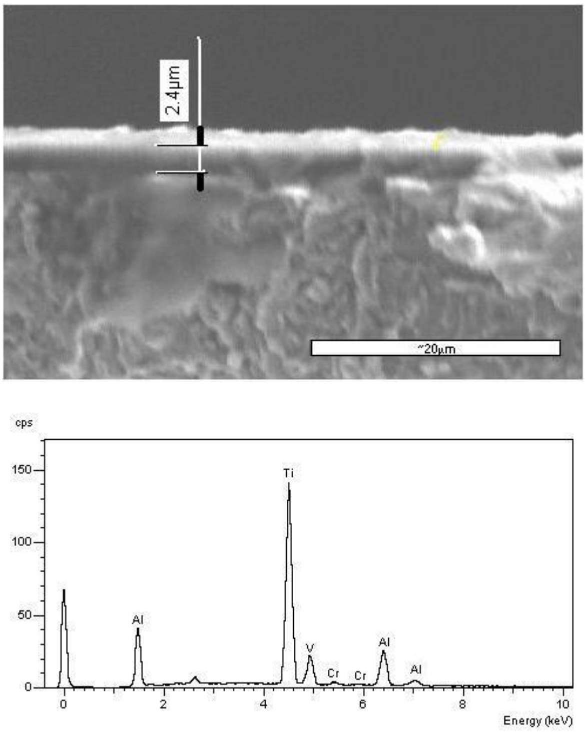


*Figure 1* Brittle fracture (micrograph) and EDX spectrum of KTRN coating on HSS Co 5 steel, thickness 2,4 µm.

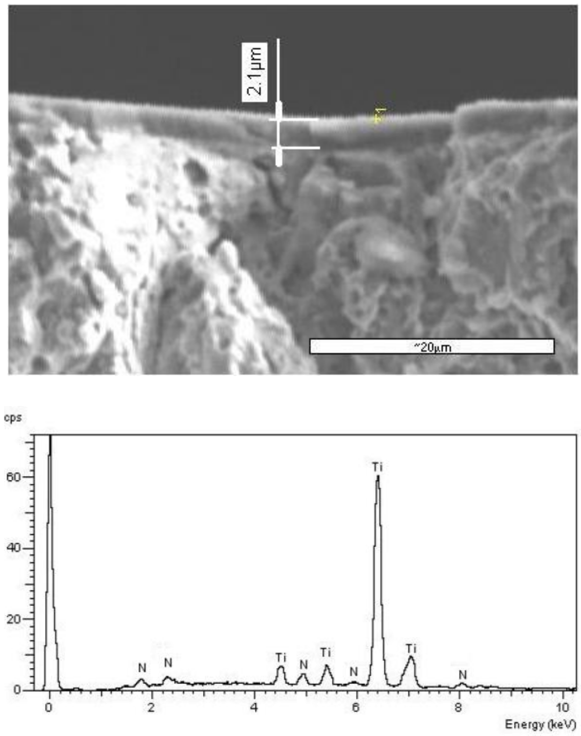


*Figure 3* Brittle fracture (micrograph) and EDX spectrum of TiN coating on HSS Co 5 steel, thickness 2,1 µm.

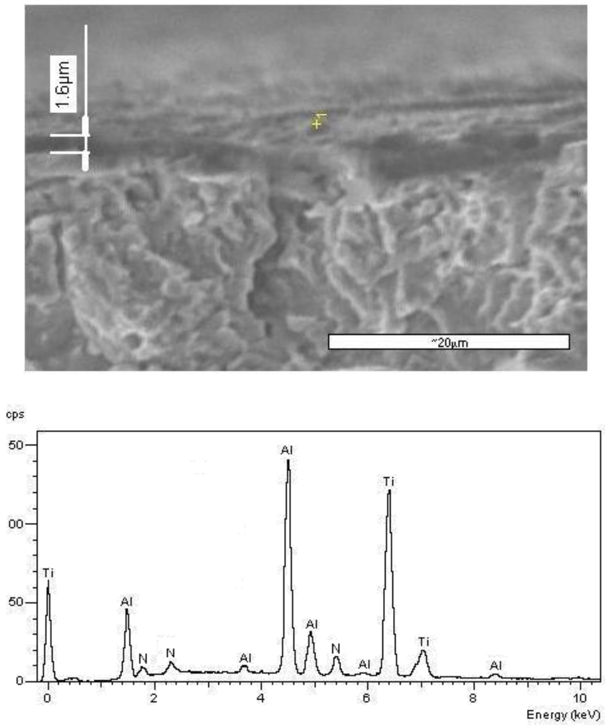


*Figure 2* Brittle fracture (micrograph) and EDX spectrum of TiAlN coating on HSS Co 5 steel, thickness 1,6 µm.

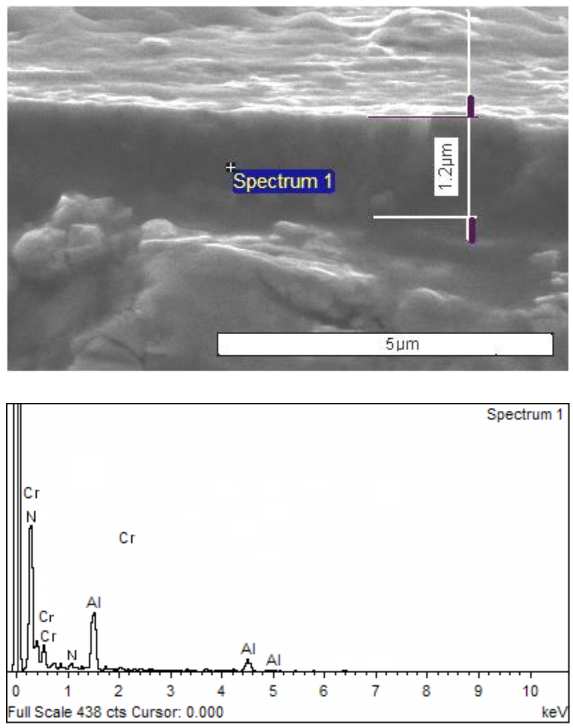


*Figure 4* Brittle fracture (micrograph) and EDX spectrum of CrAlN coating on HSS Co 5 steel, thickness 1,2 µm.

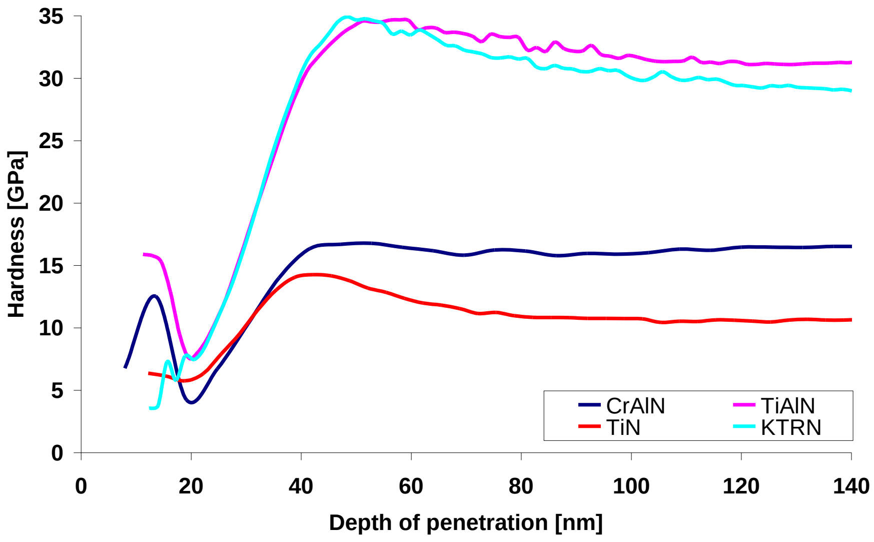


*Figure 5* The nano-hardness of CrAlN, TiAlN, KTRN and TiN coatings

### 3.2 Coefficient of friction

Using the mentioned test conditions for the CrAlN, TiAlN, KTRN I, and TiN coatings COF values of 0.58, 0.82, 0.48, and 0.57, respectively, were found.

As shown in plots COF vs. sliding distance (Fig.6), COF of KTRN coating in the first part (approximately up to 20 m) increased intensively to the values close to the maximum. Then it is almost constant. In the case of CrAlN coating it was similar. The COF of TiAlN coating grew gradually from value 0.26 to the maximum. The COF of the TiN coating in the first part (approximately up to 25 m) increased to about 0.8 and than increased slowly up to the maximum 0.82. The profile curve of the COF of the TiN coating was affected by high value of the roughness $R_a$.

Based on the performed experiments it can be stated that the COF for CrAlN coating (0.58) is higher than that in [25] and comparable with [7]. This can be caused by significantly lower roughness ($R_a$=0.15μm) than was that in our case $R_a$=0.31μm. Another reason can be different testing parameters such as loading, sliding speed, and material of the counter-body, which the producer did not specify. Also the size of contact area can affect COF. This was observed in the case of TiN coating (Fig. 7)

COF value of the tested TiAlN coating is higher than that in [7], where a value approximately 0.2 is reported. COF value of KTRN is higher than COF given by the producer (STATON, Slovakia) which is 0.35. COF of the TiN coating is also significantly higher than 0.4 given by the producer (Staton, Slovakia) and it is comparable with the values in [11], where the COF approximately 0.8 was found. This can be caused by the high roughness value Ra=0.76 μm.

In the cases where values of the COF markedly increased after 10 to 15 meters and then remained constant or increased only slightly in linear way, one can state that the great increase of COF was caused by transfer the coating material to the borders of the track (Fig. 7d). An example is COF of TiN coating where the friction if the highest of all coatings (Fig. 6).

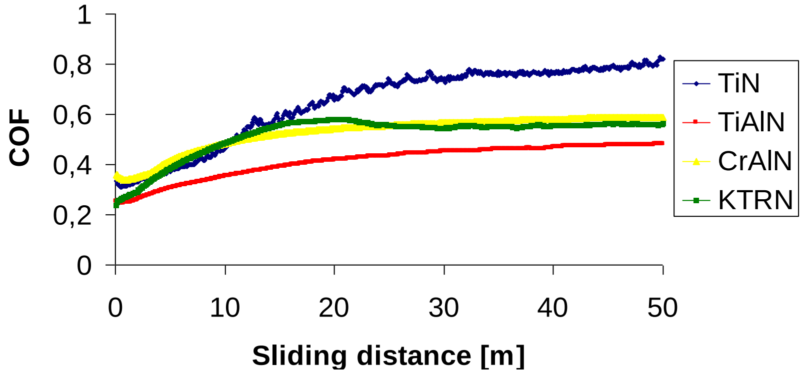


*Figure 6* Coefficient of friction of CrAlN, TiN, TiAlN and KTRN coatings.

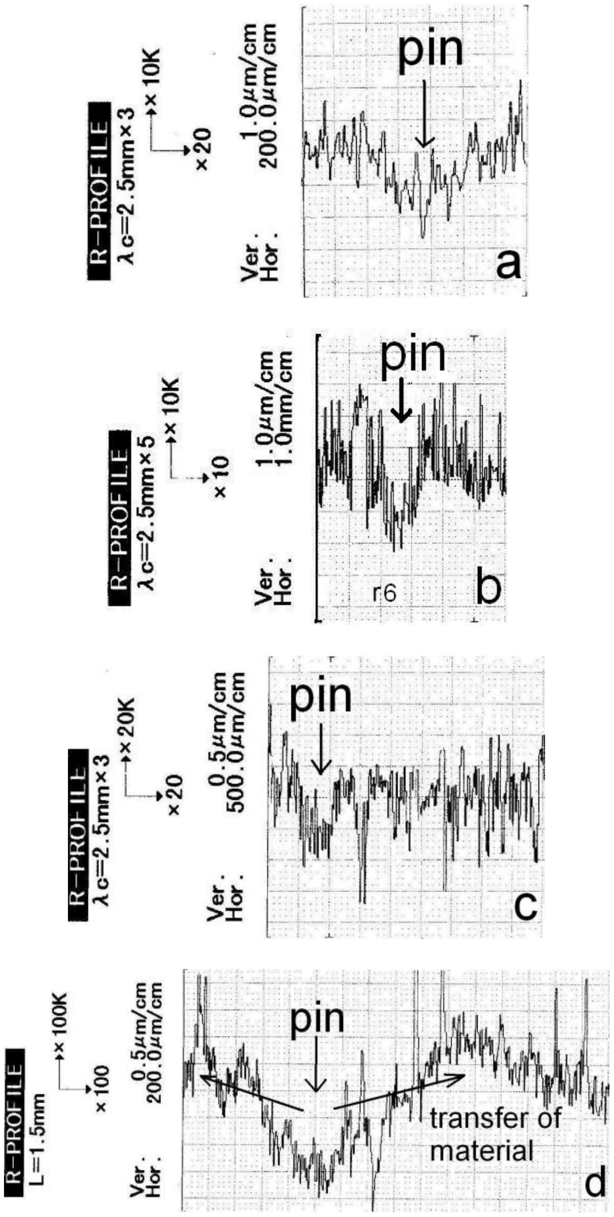


*Figure 7* Profiles of the pin-on-disc wear tracks in:
a- CrAlN coating, b- TiAlN, c- KTRN coating, d- TiN coating.

## 4 CONCLUSION

According to the measurements and following analyses, these following conclusions can be introduced:

- Nano-hardness of the KTRN and TiAlN coatings advertised by the producer was confirmed.
- Nano-hardness of the CrAlN and TiN coatings was 16.5 GPa and 14.3 GPa, respectively. In these cases exceeding the substrate annealing temperature and specimen distance to the target can be reason of lower values of the hardness of TiN and CrAlN coatings. By exceeding of the substrate annealing temperature the substrate hardness decreases and this affects the hardness of the coating, too. That is why it is important to keep the process parameters during the deposition. Apparently, in this case the deposition temperature indeed exceeded the substrate annealing temperature.
- The reason for the differences in COF with respect to those given by the producer or those found in literature could be different parameters of tribological tests, such as normal load, sliding speed and material of counter-body (its hardness). COF of CrAlN, TiAlN, KTRN, and TiN coatings were 0.58, 0.48, 0.57, and 0.82, respectively. The results also suggest that another cause could be higher roughness Ra, as it is in the case of TiN coating. Next cause of the high COF of the coating (TiN) is higher contact surface size of the system coating-ball which was caused by transfer of the coating material to the borders of the track. Lower values of COF were measured on surfaces with lower roughness $R_a$ (TiAlN and CrAlN coatings).

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