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RESEARCH

Vanadium Alloyed PVD CrAlN Coatings for Friction Reduction in Metal Forming Applications

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A B S T R A C T

Hard coatings deposited on forming tools are used to improve the forming process and to increase tool life. The decrease of tool wear and reduction of friction are the main motivations for the development of self-lubricating coatings for forming applications at elevated temperatures. In the present study (Cr,Al,V)N (Physical Vapour Deposition) coatings with 5, 11 and 20 at % vanadium were deposited via a combination of HPPMS (High Power Pulse Magnetron Sputtering) technology and direct current (DC) Magnetron Sputter Ion Plating (MSIP) PVD. The hardness and Young's Modulus of the coatings were investigated by nanoidentation. Furthermore, high temperature Pin-on-Disk (PoD) tribometer measurements against Ck15 (AISI 1015) were realized at different temperatures and compared with a (Cr,Al)N reference hard coating. The samples were analyzed by means of SEM (Scanning Electron Microscopy) and XRD (X-Ray Diffraction) measurements after Pin-on-Disk (PoD) tests. Moreover TEM (Transmission Electron Microscopy) analyses were carried out after 4 h annealing at 800 °C in ambient air to investigate the diffusion of vanadium to the coating surface. The tribological results at 800 °C show no improvement of the friction coefficient for the pure (Cr,Al)N coating and for the layer with 5 at % V. A time-dependent decrease of the friction coefficient was achieved for the coatings with 11 at % V (μ=0.4) and 20 at % V (μ=0.4) at 800 °C.

1. INTRODUCTION

Thermal shocks and high mechanical loads caused by contact of a tool with the work piece are characteristic features in forming operations of steel alloys. These demands cause thermal fatigue, plastic strain and a high wear of tool surface. Therefore, the material of such forming tools has to be resistant to wear, plastic deformation and must have high hardness, yield strength, creep resistance and toughness at elevated temperatures [1,2]. CrN-based hard coatings have widely been investigated for application on forming tools due to their excellent wear and oxidation resistance. However, the friction coefficient of most CrN-based hard coatings against steel counterpart is fairly high at RT as well as at elevated temperature [3]. In consideration of that, vanadium has been added in the hard coatings to improve the tribological performance under temperature influence and oxidizing environment. A variety of oxide phases called Magnéli-phases, which represent oxygen deficient homologous series with planar faults, show low shear modulus and have potential to be used as solid lubricants. High temperature wear tests of vanadium alloyed hard coatings against steel ball (100Cr6) and ceramic ball (Al_2O_3) showed a significant decrease of the friction coefficient at elevated temperature [4,5,6,7].

In order to investigate the influence of vanadium content on the tribological behaviour at elevated temperature, three (Cr,Al,V)N coatings were deposited on hot-forming steel Thyrotherm 2999 EFS Supra (1.2999, X45MoCrV5-3-1). The coatings were deposited via a combination of High Power Pulse Magnetron Sputtering (HPPMS) Physical Vapor Deposition (PVD) and direct current (DC) Magnetron Sputter Ion Plating (MSIP) PVD. The mechanical properties were investigated by means of nanoindentation. Afterwards, high temperature Pin-on-Disk (PoD) tribometer measurements were realized against Ck15 (AISI 1015) at different temperatures and compared with a (Cr,Al)N hard reference coating without vanadium. The wear tracks were analyzed by means of T2000 profilometer and SEM (Scanning Electron Microscopy) analyses. In addition, XRD (X-Ray Diffraction) measurements at room temperature and after the pin-on-disk tests at 800 °C were performed to observe the formation of Magnéli-phases. Consequently, the diffusion of vanadium to the top of the coating is necessary to offer a continuous self-lubricating effect during the application. TEM (Transmission Electron Microscopy) analyses were carried out to investigate the coating’s morphology and the diffusion of the vanadium to the surface after 4h annealing in an ambient air at 800 °C.

2. EXPERIMENTAL SETUP

The coatings were deposited in an industrial CC800/9 HPPMS coating unit from CemeCon AG, equipped with two HPPMS power supplies and two DC sources. The used HPPMS power supplies generate a “Kouznetsov” pulse shape as described by Theiß et al. in [8]. Before deposition, the samples were ion etched in an argon atmosphere via two plasma cleaning methods at 500 °C as shown in Table 1. The (Cr,Al,V)N coatings were deposited via four cathodes while three cathodes (except vanadium cathode) were used for the deposition of (Cr,Al)N reference coating. A Cr target with 20 Al inserts (CrAl20) and a Cr target were connected to the HPPMS power supplies. Furthermore, an Al target with 20 Cr inserts (AlCr20) was connected to a DC power supply. The targets had a size of 88x500 mm² and had a purity of 99.95 % for the chromium and 99.9 % for the aluminium. Vanadium (purity: 99.5 %) was added in graded form using the second DC power supply after the deposition of a (Cr,Al)N interlayer. In order to obtain different vanadium contents in the (Cr,Al,V)N coating the power of vanadium cathode was varied from 1 kW to 2.5 kW and to 4 kW. The parameters of the plasma cleaning methods and deposition processes are listed in Table 1.

Table 1. Parameters of the plasma cleaning methods and deposition processes.

	Parameters	**Values**
MF-Etching	Bias-Voltage	- 650 V
	Frequency	240 kHz
	Revision time	1600 ns
	Argon pressure	350 mPa
Booster-Etching	Argon flow	200 sccm
	Bias-Voltage	- 200 V
	Anode current	20 A
Coating process	HPPMS cathode 1, 2 power	6.9 kW (average power)
	DC cathode 3 power	4 kW (ramp)
	DC cathode 4 power	1 kW, 2.5 kW, 4 kW
	Bias-Voltage	- 130 V
	Ar-Flow	200 sccm
	N2-Flow	pressure-controlled
	Pressure	520 mPa
	HPPMS pulse duration	200 µs
	HPPMS frequency	500 Hz

Table 2. Results of the coating thickness and mechanical properties.

	Coating thickness s (µm)	Hardness H (GPa)	Young's modulus E (GPa)
$(Cr_{0.69}Al_{0.31})N$	2.6	26 ± 3.6	476 ± 44
$(Cr_{0.72}Al_{0.23}V_{0.05})N$	2.7	24 ± 4.0	365 ± 40
$(Cr_{0.69}Al_{0.20}V_{0.11})N$	3.7	22 ± 3.5	374 ± 51
$(Cr_{0.63}Al_{0.17}V_{0.20})N$	3.1	25 ± 0.9	385 ± 14

2.1 Characterisation of coatings

The hardness and Young's modulus were determined using a Nanoindenter XP (MTS Nano Instruments). The indentation depth did not exceed 1/10 of coating thickness. The evaluation of the measured results was based on the equations according to Oliver and Pharr [9]. A Poisson's ratio of ν = 0.25 was assumed. Tribological tests were carried out using Pin-on-Disk (PoD) tribometer from CSM Instruments. The specimens were clamped into a rotating holding device. A pin (Ck15, AISI 1015) was pressed in off-centre position onto the specimen with a normal force of 5 N. A steel counterpart was used to consider the aforementioned metal forming application. The distance covered by the pin on the specimen was 500 m. The sliding speed was kept at 10 cm/s and the radius was maintained constant at 2.5 mm. All measurements were performed in ambient air at RT and 800 °C. EDS was used to determine chemical composition of the coatings and to analyse the wear tracks. Phase analysis was carried out by X-ray diffractrometry on specimens after the tribological tests. The possible diffusion processes of vanadium were determined by means of TEM (Transmission Electron Microscopy) after annealing in an ambient air at 800 °C.

3. RESULTS

After deposition the chemical composition of the coatings was characterized by means of EDS. In addition, the specimens were analysed regarding the mechanical properties. The results of the hardness and Young's modulus are shown in Table 2. The results of the mechanical properties show that the vanadium alloyed coatings displayed high hardness ($(Cr_{0.72}Al_{0.23}V_{0.05})N$: 24 GPa; $(Cr_{0.69}Al_{0.20}V_{0.11})N$: 22 GPa; $(Cr_{0.63}Al_{0.17}V_{0.20})N$: 25 GPa) as well as the reference coating ($(Cr_{0.69}Al_{0.31})N$: 26 GPa). A significant influence of vanadium can be observed in the Young's modulus. With 5 at % V shows the coating lower Young's modulus (365 GPa) than the one with 11 at % V (374 GPa) and the one with 20 at % V (385 GPa). The highest Young's modulus was achieved for the $(Cr_{0.69}Al_{0.31})N$ (476 GPa) coating.

Considering the elevated temperature of the aforementioned forming application tribological tests were performed against steel counterpart (Ck15) at RT and 800 °C (see Fig. 1).

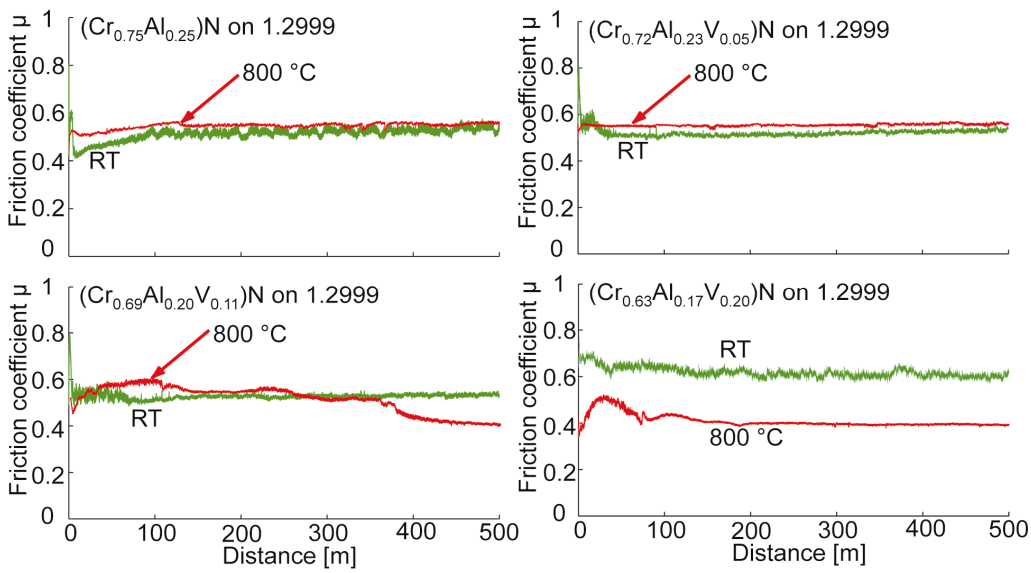

Fig. 1. Friction coefficient µ of the $(Cr_{0.75}Al_{0.25})N$ reference coating, $(Cr_{0.72}Al_{0.23}V_{0.05})N$, $(Cr_{0.69}Al_{0.20}V_{0.11})N$ and $(Cr_{0.63}Al_{0.17}V_{0.20})N$ at RT and 800 °C.

Table 1. Results of the wear analyses after pin-on-disk tests at RT and 800 °C.

	RT	**800 °C**
$(Cr_{0.75}Al_{0.25})N$		
Pin wear rate [mm^3/Nm]	$3.80 \cdot 10^{-05}$	$3.40 \cdot 10^{-05}$
Coating wear rate [mm^3/Nm]	-	-
$(Cr_{0.72}Al_{0.23}V_{0.05})N$		
Pin wear rate [mm^3/Nm]	$3.30 \cdot 10^{-05}$	$1.10 \cdot 10^{-05}$
Coating wear rate [mm^3/Nm]	-	-
$(Cr_{0.69}Al_{0.20}V_{0.11})N$		
Pin wear rate [mm^3/Nm]	$4.60 \cdot 10^{-05}$	$1.00 \cdot 10^{-05}$
Coating wear rate [mm^3/Nm]	-	-
$(Cr_{0.63}Al_{0.17}V_{0.20})N$		
Pin wear rate [mm^3/Nm]	$5.02 \cdot 10^{-05}$	$0.96 \cdot 10^{-05}$
Coating wear rate [mm^3/Nm]		

The results of the reference (Cr0.69Al0.31)N and of the coating with 5 at % V exhibit no considerable friction reduction at elevated temperature. The coating with 11 at % V shows a decrease of friction coefficient at 800 °C after 380 m. Compared to the other coatings, the lowest value of 0.4 was reached for the coating with 20 at % V at 800 °C after 80 m due to the formation of lubricant oxides, as reported by Bobzin et al. in [6]. The results of the present study show that the lubricant effect of vanadium containing coatings depends on the vanadium content as well as on the time.

In Table 1 pin and coating wear rate are presented. The adhesion of counterpart material on the sample surface was not considered in the wear measurement. All examined coatings exhibit no measurable abrasive wear on their surface at all examined temperatures due to the high wear resistance provided through the (Cr,Al)N hard matrix. At RT the lowest pin wear rate ($3.3\ 10^{-05}$ mm^3/Nm) was observed for $(Cr_{0.72}Al_{0.23}V_{0.05})N$. In consideration of the friction reduction of $(Cr_{0.63}Al_{0.17}V_{0.20})N$ at 800 °C demonstrated in Error! Reference source not found. a slight lower pin wear rate was found out for this coating in comparison to the pure hard $(Cr_{0.75}Al_{0.25})N$ matrix ($3.4\ 10^{-05}$ mm^3/Nm), to the coating with 5 at % V ($1.1\ 10^{-05}$ mm^3/Nm) and to the coating with 11 at % V ($1.0\ 10^{-05}$ mm^3/Nm).

For detailed investigation of the coating surface after pin-on-disk test at 800 °C SEM micrographs of the wear track were taken (see Error! Reference source not found.). According to Table 1, all considered coatings show no abrasive wear on their surface. At 800 °C a widening of the wear track can be observed for the $(Cr_{0.75}Al_{0.25})N$ (a).

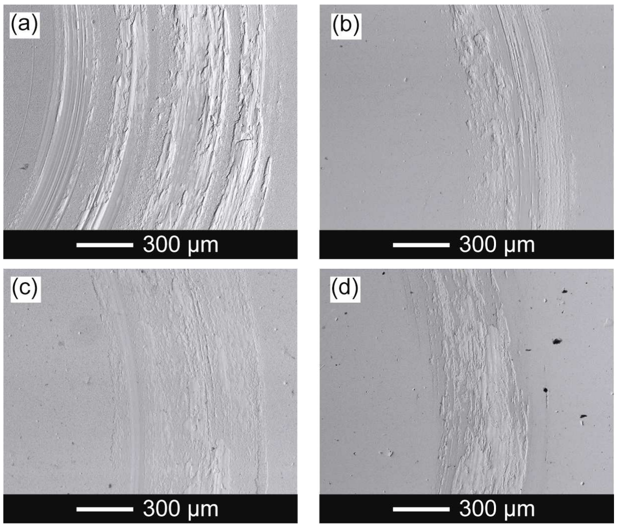

Fig. 2. (a) SEM micrographs of the wear track of $(Cr_{0.75}Al_{0.25})N$; (b) $(Cr_{0.73}Al_{0.23}V_{0.05})N$; (c) $(Cr_{0.69}Al_{0.20}V_{0.11})N$ and (d) $(Cr_{0.63}Al_{0.17}V_{0.20})N$, after pin-on-disk tests against Ck15 at 800 °C.

It indicates a rise of the pin wear at 800 °C as listed in Table 1. In contrast to that, a reduction of material transfer from the counterpart to the coating surface can be observed for the vanadium alloyed layers (b,c,d).

To investigate the formation of lubricant oxides on the coatings with different vanadium content XRD analyses were carried out after pin-on-disk tests at 800 °C and compared with measurements of the coatings as deposited (see Fig. 3). To get a clear diagram all peaks are not indexed. Before the pin-on-disk tests the phase analyses of all vanadium containing coatings show a formation of cubic crystal consisting of c-CrN, c-AlN and c-VN (see Fig. 3). At 800 °C $(Cr_{0.72}Al_{0.23}V_{0.05})N$ shows a thermal stability because no formation of oxides can be identified in the XRD results. In contrast to that

$(Cr_{0.69}Al_{0.20}V_{0.11})N$ exhibits a slight formation of new peaks. That indicates the possible formation of the first Cr and V oxides. The significant formation of oxides can be shown for $(Cr_{0.63}Al_{0.17}V_{0.20})N$. Its exhibits formation of Magnéli-phase V_3O_7 as well as $CrVO_4$. Further peaks of Cr_2O_3 phase can be detected. The results of the coating with 20 at % V are in accordance to the XRD investigation of Bobzin et al. demonstrated in [6] after 4 h annealing tests in ambient air.

For further investigation of oxidation and diffusion processes of $(Cr_{0.63}Al_{0.17}V_{0.20})N$, the samples were analyzed using TEM. Figs. 4 and 5 shows TEM cross-sectional micrographs (left) and EDS Line scan across the coating thickness (right) as deposited (RT) and after 4 h annealing in ambient air at 800 °C. Before annealing the coating exhibits a fine and dense crystalline morphology. After annealing at 800 °C $(Cr_{0.63}Al_{0.17}V_{0.20})N$ shows a change of morphology on the top of the coating. This change is the result of oxidation and diffusion processes during the annealing test. By means of EDS the content of Cr, V, Al and O were investigated. Here, an increase of the vanadium content and an oxidation zone on the top of the coating were identified. Furthermore, a layer with oxidized metal was formed in the middle region. The vanadium content in this layer is low due to the outwards diffusion. The diffusion of vanadium into the near-surface region can be confirmed by these results as reported in [6].

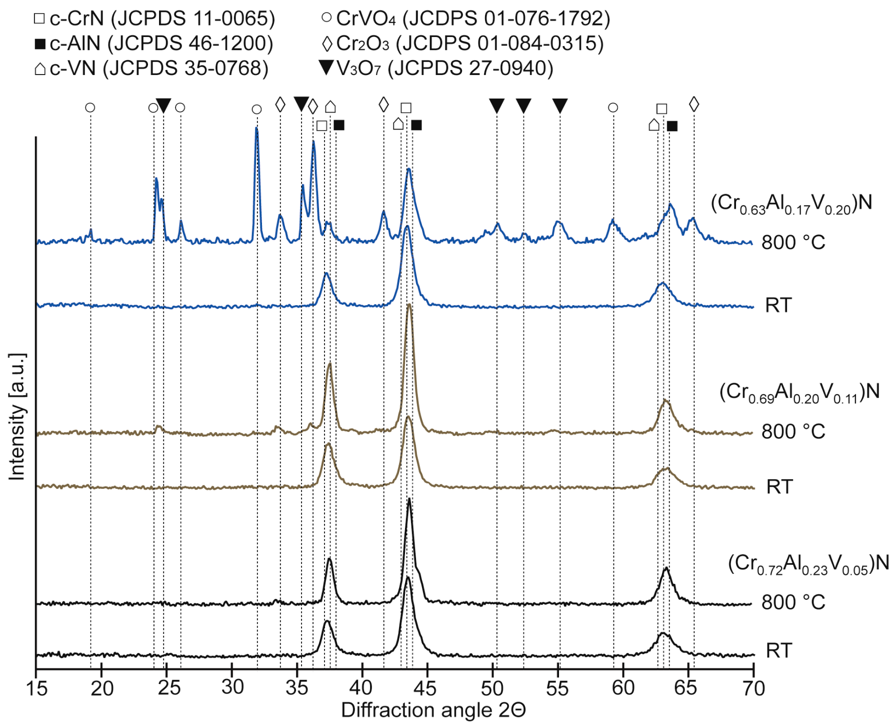

Fig. 3. XRD phase analyses of $(Cr_{0.73}Al_{0.23}V_{0.05})N$, $(Cr_{0.69}Al_{0.20}V_{0.11})N$ and $(Cr_{0.63}Al_{0.17}V_{0.20})N$ as deposited and after pin-on-disk tests at 800 °C.

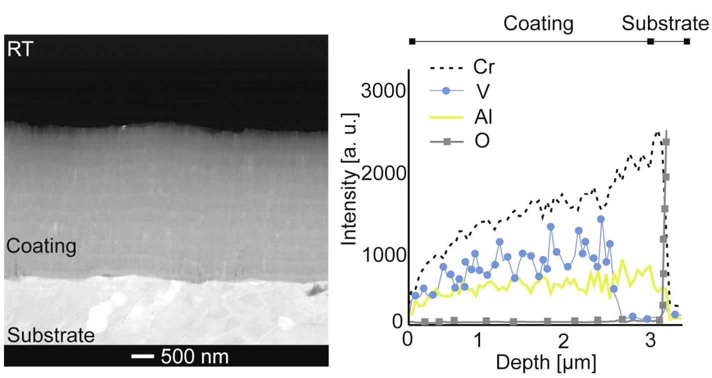

Fig. 4. TEM cross-sectional micrograph (left) and EDS line scan across the coating thickness (right) of the $(Cr_{0.63}Al_{0.17}V_{0.20})N$ as deposited (RT).

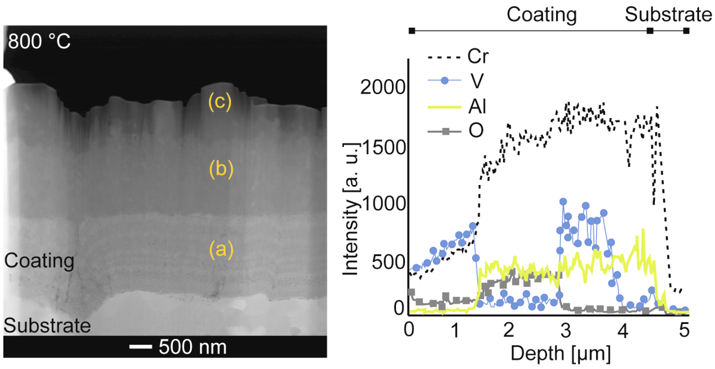

Fig. 5. TEM cross-sectional micrograph (left) and EDS line scan across the coating thickness (right) of the $(Cr_{0.63}Al_{0.17}V_{0.20})N$ after 4 hours annealing at 800 °C.

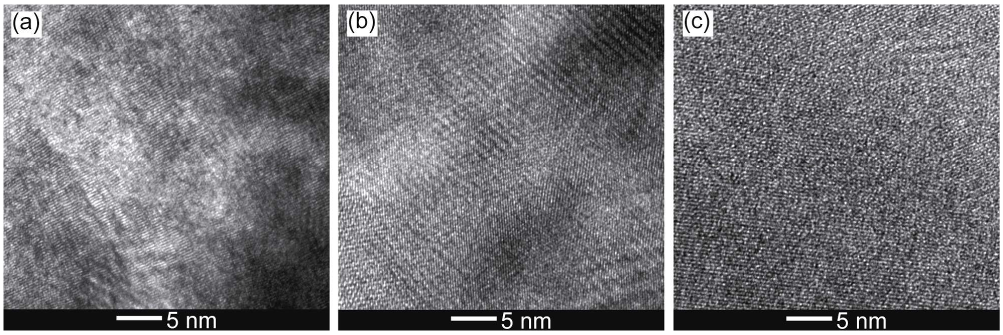

Fig. 6. HRTEM plan-view image of the bottom (a), middle (b) and top (c) area of $(Cr_{0.63}Al_{0.17}V_{0.20})N$ after 4 hours annealing at 800 °C.

Figure 6 exhibits HRTEM plan-view image of $(Cr_{0.63}Al_{0.17}V_{0.20})N$ in three different regions after 4 hours annealing at 800 °C. The considered areas are indicated in Figs. 5 and 6 and represent the bottom (a), middle (b) and top (c) region. By means of the HRTEM investigations a possible formation of amorphous phases in the bottom (a) and in the middle (b) region of the coating can be considered due to the dark contrast. The micrograph of the top region of the coating shows a uniform crystalline structure with similar orientation. It indicates the formation of fairly large grain.

4. CONCLUSIONS

Vanadium alloyed (Cr,Al)N hard coatings have been deposited on hot-forming steel (1.2999) via a combination of DC-MSIP and HPPMS PVD technology. The coatings were analyzed regarding their mechanical and tribological properties at RT and 800 °C and compared with a reference coating $(Cr_{0.75}Al_{0.25})N$ without vanadium. Further XRD analyses of the vanadium containing coatings were carried out after the pin-on-disk tests. In addition, $(Cr_{0.63}Al_{0.17}V_{0.20})N$ was investigated by means of TEM after 4 h annealing. The vanadium alloyed coatings show high hardness ($(Cr_{0.72}Al_{0.23}V_{0.05})N$: 24 GPa; $(Cr_{0.69}Al_{0.20}V_{0.11})N$: 22 GPa; $(Cr_{0.63}Al_{0.17}V_{0.20})N$: 25 GPa) as well as the reference coating ($(Cr_{0.75}Al_{0.25})N$: 26 GPa). A significant influence of vanadium can be observed in the Young's modulus. The coating with 5 at % V show lower Young's modulus (365 GPa) than the one with 11 at % V (374 GPa) and the one with 20 at % V (385 GPa). $(Cr_{0.69}Al_{0.31})N$ displays a Young's modulus of 476 GPa. The results of the $(Cr_{0.75}Al_{0.25})N$ and $(Cr_{0.72}Al_{0.23}V_{0.05})N$ coating exhibit no considerable decrease of the friction values at elevated temperatures. $(Cr_{0.69}Al_{0.20}V_{0.11})N$ with 11 at % V shows a decrease of the friction coefficient at 800 °C after 380 m. Compared to the other layers, the lowest mean value of 0.4 was reached for $(Cr_{0.63}Al_{0.17}V_{0.20})N$ coating with 20 at % V at 800 °C. The wear analysis shows no measurable abrasive wear on the coating surfaces at all considered temperatures due to the wear resistance provided through the $(Cr_{0.75}Al_{0.25})N$ hard matrix. At RT the lowest pin wear rate ($3.3\ 10^{-05}$ mm^3/Nm) was observed for $(Cr_{0.72}Al_{0.23}V_{0.05})N$. At 800 °C $(Cr_{0.63}Al_{0.17}V_{0.20})N$ exhibits the lowest pin wear rate ($9.6\ 10^{-06}$ mm^3/Nm). With the help of the SEM micrographs a widening of the wear track can be found out for $(Cr_{0.75}Al_{0.25})N$ at 800 °C. In contrast to that, a reduction of material transfer from the counterpart to the coating surface can be observed for the vanadium alloyed coatings. The XRD results of the coatings after pin-on-disk tests show that the significant formation of oxides can be shown for $(Cr_{0.63}Al_{0.17}V_{0.20})N$. Its exhibits a formation of V_3O_7, $CrVO_4$ and Cr_2O_3. By means of EDS across the coating thickness the content of Cr, V, Al and O was investigated for $(Cr_{0.63}Al_{0.17}V_{0.20})N$. Here, an increase of the vanadium content and oxidation zone on the top of the coating at 800 °C was identified. Furthermore, a layer with oxidized metals was formed in the middle region. The HRTEM plan-view images of $(Cr_{0.63}Al_{0.17}V_{0.20})N$ indicate a possible formation of amorphous phases in the bottom (a) and in the middle (b) region of the coating. In the top region a uniform crystalline structure with similar orientation can be observed. Finally, it can be concluded that specially (Cr,Al)N alloyed with 20 at % V offers a high potential for the application as wear resistant and self-lubricating coating on tools for metal forming operations.

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