The Influence of CH4/N2 Gas Ratio on the Structure and Chemical Composition of Cr(C, N) Coatings Deposited by CAD Technology

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This article presents the study of the influence of the bias voltage and CH4/N2 gas ratio on the structure and chemical composition of Cr(C,N) coatings. The coatings were deposited by cathodic arc evaporation of pure Cr (99.99 %) cathode under an atmosphere of a mixture of CH4 and N2 gasses at the low deposition temperature of 300 ˚C. The ratio of reactive gasses was changed from 0 to 100 %. Energy-dispersive spectroscopy showed a linear dependence of resulting C/N ratio on the process gas ratio. The roughness of layers prepared from a mixture of process gasses is higher compared to pure gasses.

Keywords: CAD technology, Cr(C,N) coatings, Surface morphology, Roughness

1 Introduction

In the last time, hard coatings are often applied on the surface of cutting tools to ensure a long service time and to achieve economically more effective construction parts machining. Thus, high demands are placed on the used hard coating. The layers must have a high chemical stability, high mechanical and fatigue strength, high impact resistance, high temperature and thermal shock resistance and high adhesion.

Cr(C,N) coatings are often chosen for application demanding abrasion, corrosion and oxidation resistance as well as the low coefficient of friction. These layers also excel in their high temperature and chemical resistance and exceptional adhesion strength. They also show good sliding properties at minimum lubrication and thus are a perfect choice for application as a coating for cutting and machining tools.

CrN coatings offer a combination of good wear performance [1, 2] oxidation resistance and ductility for a metal nitride system. These coatings can be grown relatively thick, which can be partly attributed to the favorable coating ductility. [3] The addition of carbon to chromium nitride has an important effect on the microstructure and properties of the coatings. A study performed by [3] found that a large amount of carbon in Cr(C,N) structure reduces the stress, hardness and critical load of the coatings. Studies by [4] and indicated that adhesion of Cr(C,N) coatings to the substrate is lower than CrN and CrC coatings and the oxidation resistance of Cr(C,N) coatings depends on the deposition process parameters.

Cr(C,N) coatings are predominantly used for drawing, punching, pressing and forming tools for the machining of non-ferrous metals. Especially for titanium and copper alloys. Additionally, these coating systems are typically used in aluminum and magnesium pressure die casting, e.g. for mold inserts and cores requiring increased levels of corrosion protection. One of the areas of application of Cr(C,N) coatings is the machining of copper and other non-ferrous materials. This coating protects milling tools, lathes, drilling and cutting tools when machining non-ferrous metals – especially those consisting of titanium and copper alloys.

The present work deals with the effect of variation of CH4/N2 gas ratio during PACVD/MS deposition of CrCN thin layers on the chemical composition surface morphology, occurrence, and size of droplets on the surface of the studied layers.

2 Experimental

Tool steel discs (EN ISO HS 6-5-2) with dimensions of $\varnothing$ 20 mm × 5 mm were used as a substrate. Their nominal composition is [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 discs were hardened to 64 – 65 HRC and polished to a roughness (Sa) of 0.01 μm. [5-7]

The thickness of coatings was measured by an image analysis of pictures taken in cross-sections. The thickness of the coatings was assessed at three different points; the mean value and the standard deviation are shown in Tab. 1.

CrN, CrC and Cr(C,N) coatings with different compositions were deposited by cathodic arc evaporation of pure Cr (99.99 % purity) in an atmosphere of reactive gasses N2 and CH4 at the deposition temperature of 300 ˚C. Arc current, bias voltage and deposition time were 85A, -100 V and 120 min. Table 1 shows the used gas flow of N2 and CH4. Contact layers of Cr and CrN were deposited before each main coating.

Prior to the coating deposition, several steps were taken to improve the coating adhesion: (1) the tool steel substrates were cleaned in an alkaline solution in an ultrasonic bath for 5 min, and then rinsed in deionized water and dried with boiling ethanol and hot air; (2) immediately after the cleaning process, the substrates were placed into a vacuum chamber and mounted on a substrate holder; (3) the tool steel substrates were cleaned with metal ions to remove any traces of surface contamination and the native oxide layer at bias voltage of -1000 V and Ar pressure of 0.2 Pa. [5-7] Samples after the coating process are shown in Fig. 1.

Tab. 1 *Used gas flow of N_2 and CH_4 during coatings deposition*

Sample	N_2 flow [sccm*]	CH_4 flow [sccm*]	CH_4/N_2 [%]	CH_4/N_2 [-]	d [µm]
CrN	420	-	-	-	2.54±0.03
CrCN-20	336	84	20	0.25	2.50±0.02
CrCN-35	275	147	35	0.53	2.21±0.02
CrCN-50	210	210	50	1	2.51±0.01
CrCN-65	168	312	65	1.86	1.76±0.02
CrC	-	335	-	-	2.71±0.01

*sccm = standard cubic centimetre per minute
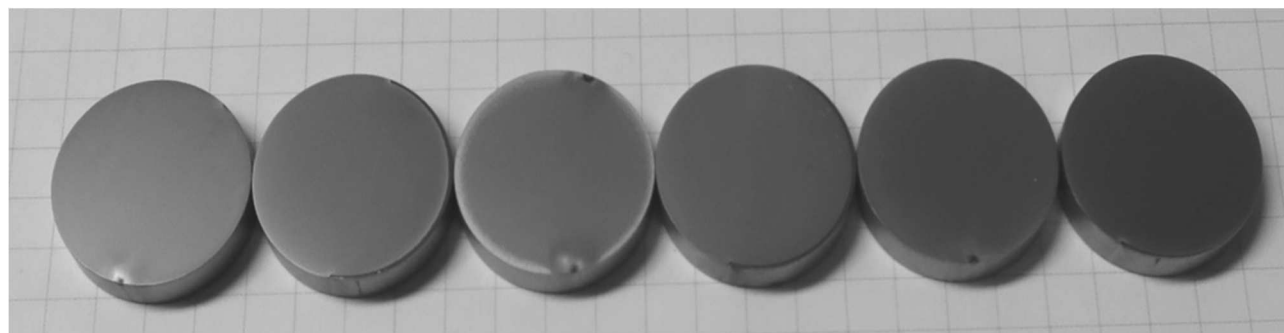
Fig. 1 *Investigated CrCN layers deposited on HHS steel cylinders $\varnothing$ 20 mm*

The chemical composition of the layers was evaluated using energy-dispersive spectroscopy (EDS) Oxford X-Max20 mounted on field emission scanning electron microscope (SEM) Zeiss Ultra Plus. Spectra were acquired at accelerating voltage of 10 kV and quantified in SW Aztec 3.3.

The structure was observed using the SEM Zeiss Ultra Plus in topographical contrast (InLens secondary electron detector) and also using an atomic force microscope (AFM) JPK Nanowizard 3 in a contact mode. The AFM data were processed in Gwyddion SW. AFM data was used also for evaluation of surface roughness.
Samples for metallographic observation od Cr(C,N) coatings in cross-section were hot fixed into a conductive resin and subsequently were grinded and polished. Colloidal silica (OP-S) was used as a final step of mechanical-chemical polishing.

3   Results and discussion

The chemical composition of the layers was evaluated using energy-dispersive analysis, results are summarized in Tab. 2. It's worth to notice, that carbon and nitrogen are very light elements and for this reason, the results of the quantification are burdened by an error. On the other hand, it should be noted that EDS was the only available method for the C/N ratio quantification. The obtained C/N ratio was plotted depending on the ratio of the reactive gas flow rate (see Fig. 2). The graph can be easily used for extrapolation of necessary gas flow ration to get desired layer composition. It is obvious that even a small addition of methane to nitrogen leads to a steep increase in the concentration of carbon in the layer. Considering that a total reactive gas flow was constant (420 sccm), the decrease of Cr concentration in the layers shows that methane reacts (forms the surface layer) with chromium more easily than nitrogen. This is probably related to

lower ionization energy of carbon than nitrogen (11.26 vs. 14.35 eV) [8].
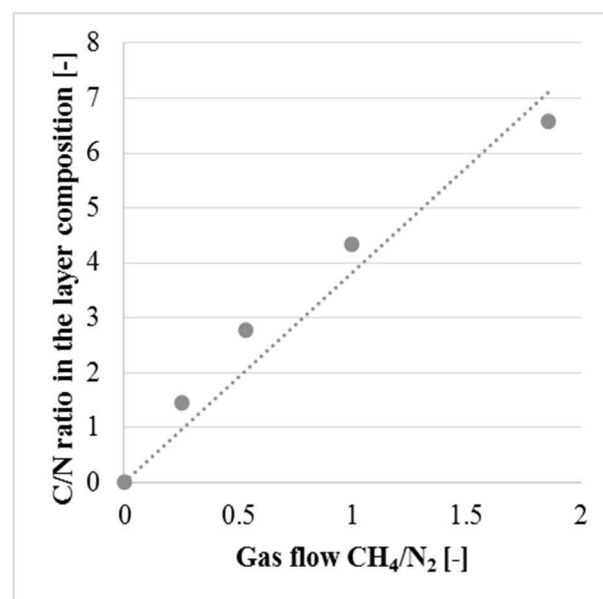
Fig. 2 *Graph showing the dependence of resulting C/N ratio in the layer composition on CH_4/N_2 gas flow ratio*

The surface structures of Cr(C,N) layers are shown in Figures 3-8. First two pictures (from left to right) contain images taken by AFM in contact mode (scans 25 x 25 µm, 5 x 5 µm respectively); the third column shows images taken by SEM (magnification of 5kx). The surface of all samples is quite smooth, we can observe small defects - globules with diameters of hundreds of nanometres. The appearance of these globules is probably caused by uneven sputtering of the Cr target. The occurrence of these particles emitted from a cathode material was previously described in [9-11].

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

| Sample	C [at. %]	N [at. %]	Cr [t. %]	C/N [-]	Gas flow CH_4/N_2 [-]
CrN	-	40±1	60±1	0	-
CrCN-20	29±1	20±1	51±1	1.5	0.25
CrCN-35	36±1	13±1	51±1	2.8	0.53
CrCN-50	39±1	9±1	53±1	4.3	1
CrCN-65	46±1	7±1	48±1	6.6	1.86
CrC	52±1	-	48±1	-	-
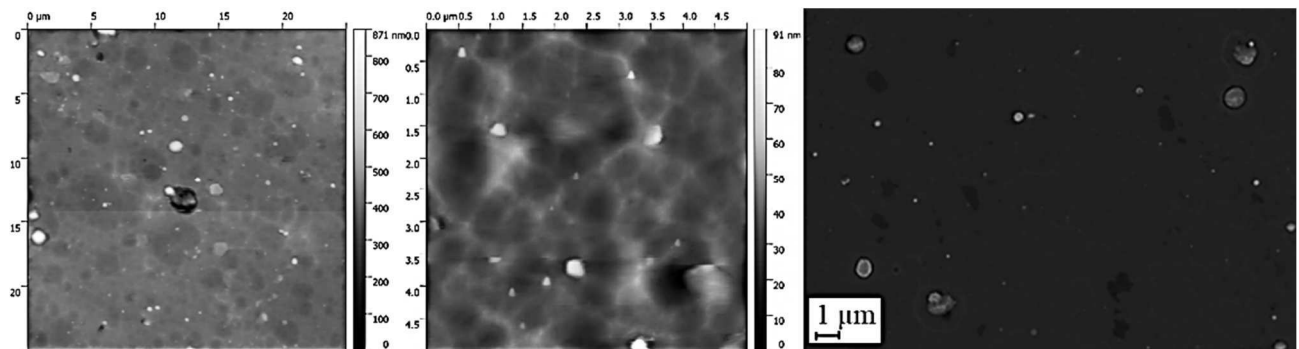
Fig. 3 *The structure of samples CrN surface taken by AFM and SEM, from left to right AFM 25x25 µm, AFM 5x5 µm and SEM, mag. 5000x*
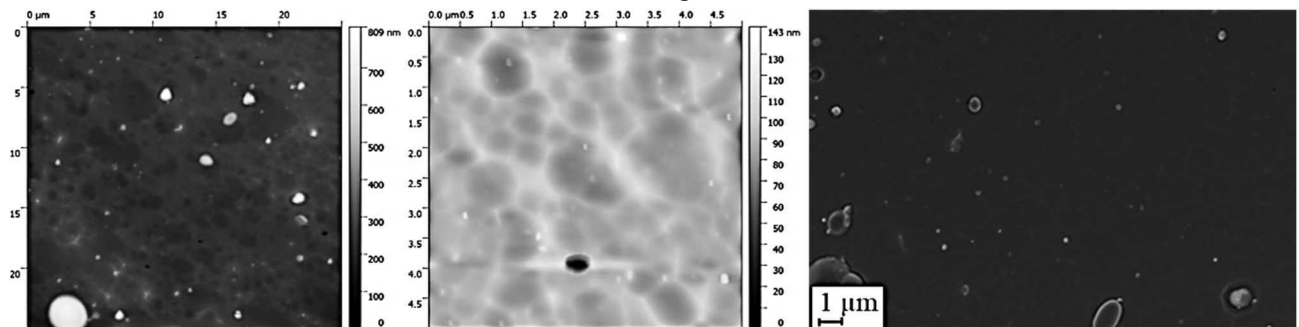
Fig. 4 *The structure of samples CrCN-20 surface taken by AFM and SEM, from left to right AFM 25x25 µm, AFM 5x5 µm and SEM, mag. 5000x*
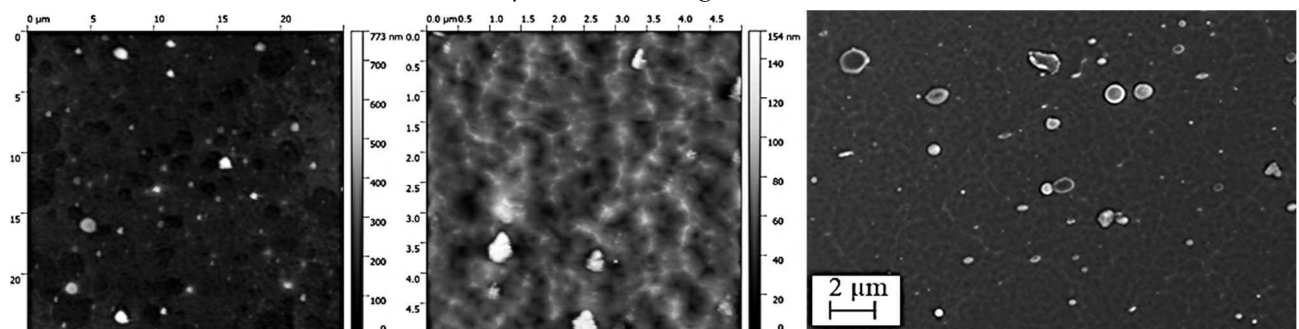
Fig. 5 *The structure of samples CrCN-35 surface taken by AFM and SEM, from left to right AFM 25x25 µm, AFM 5x5 µm and SEM, mag. 5000x*
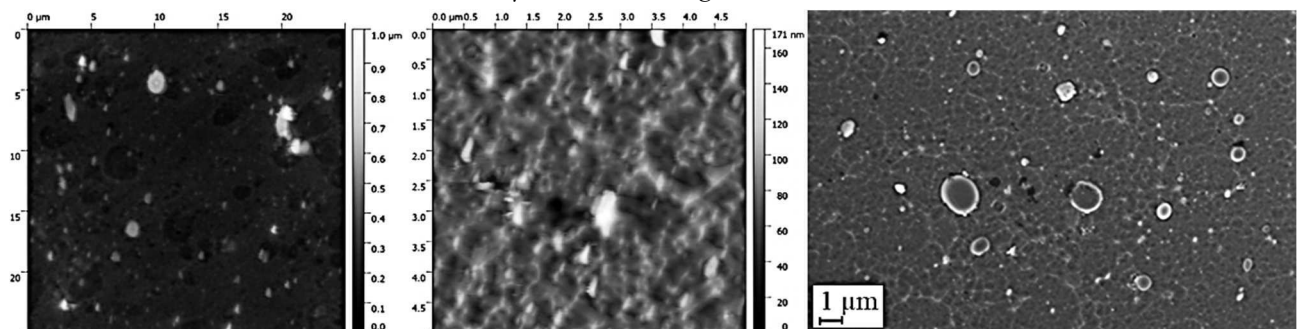
Fig. 6 *The structure of samples CrCN-50 surface taken by AFM and SEM, from left to right AFM 25x25 µm, AFM 5x5 µm and SEM, mag. 5000x*
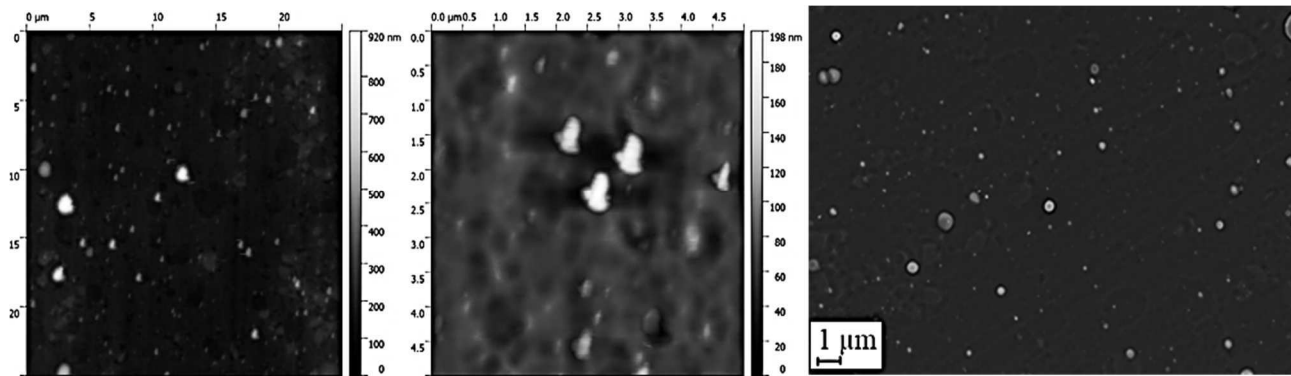
Fig. 7 *The structure of samples CrCN-65 surface taken by AFM and SEM, from left to right AFM 25x25 µm, AFM 5x5 µm and SEM, mag. 5000x*
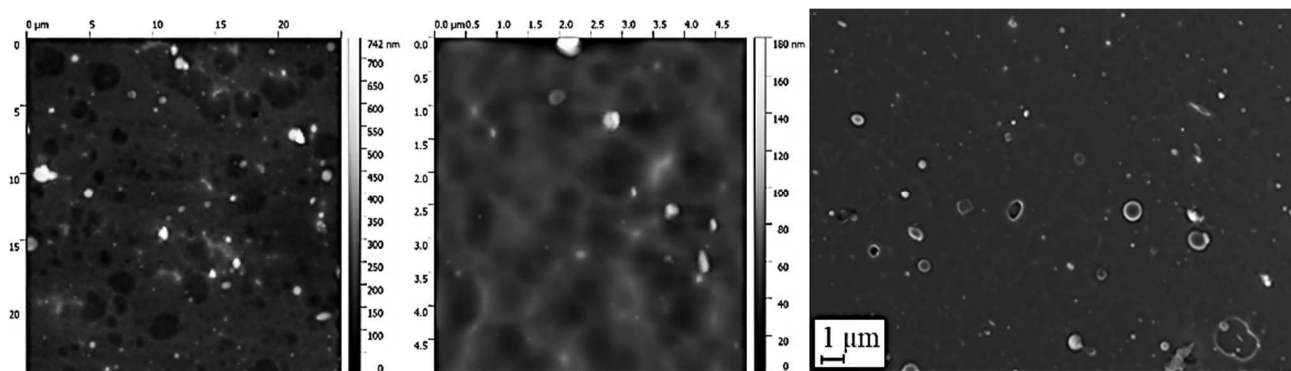
Fig. 8 *The structure of samples CrC surface taken by AFM and SEM, from left to right AFM 25x25 µm, AFM 5x5 µm and SEM, mag. 5000x*
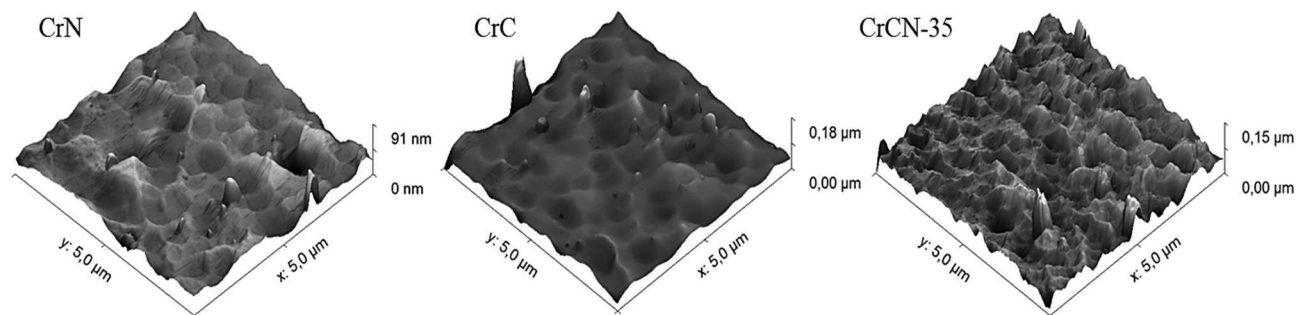
Fig. 9 *3D reconstruction of layer's surfaces obtained from pure gasses (CrC and CrN) and from a mixture of CH_4+N_2 (CrCN-35)*

Tab. 3 *Surface roughness parameters (obtained from AFM scans 25x25 µm)*

Sample	Sa [nm]	Sq [nm]
CrN	20.0	31.6
CrCN-20	29.0	57.2
CrCN-35	27.9	45.5
CrCN-50	37.5	67.3
CrCN-65	27.7	48.6
CrC	27.1	46.9

The surface roughness was evaluated from AFM data (scan 25 x 25 µm) using Gwyddion SW and the results are summarised in Tab. 3. The surface roughness results are affected by the presence of globules on the surface and thus is dependent on the selected scanned area. The smoothest surfaces values were obtained for pure reactive gasses (pure CH_4 or pure N_2), the mixture of gasses results in rougher layer surface. The same tendency can be observed in detailed AFM scans (see the comparison of 3D reconstructions of surfaces CrN, CrC and CrCN-35 in Fig. 9). The increase of roughness after carbon addition was previously described e.g. in [9, 12]

The structures of individual layers taken by the SEM at magnification of 15kx are visible in Fig. 10. Columnar grains are observable in the case of CrN, CrCN-35, and CrCN-50. Thin strips parallel to the sample surface are visible at higher concentration of carbon (samples CrCN-65 and CrC). Further analysis (XRD) are necessary to describe the phase composition and crystal structure of the layers.
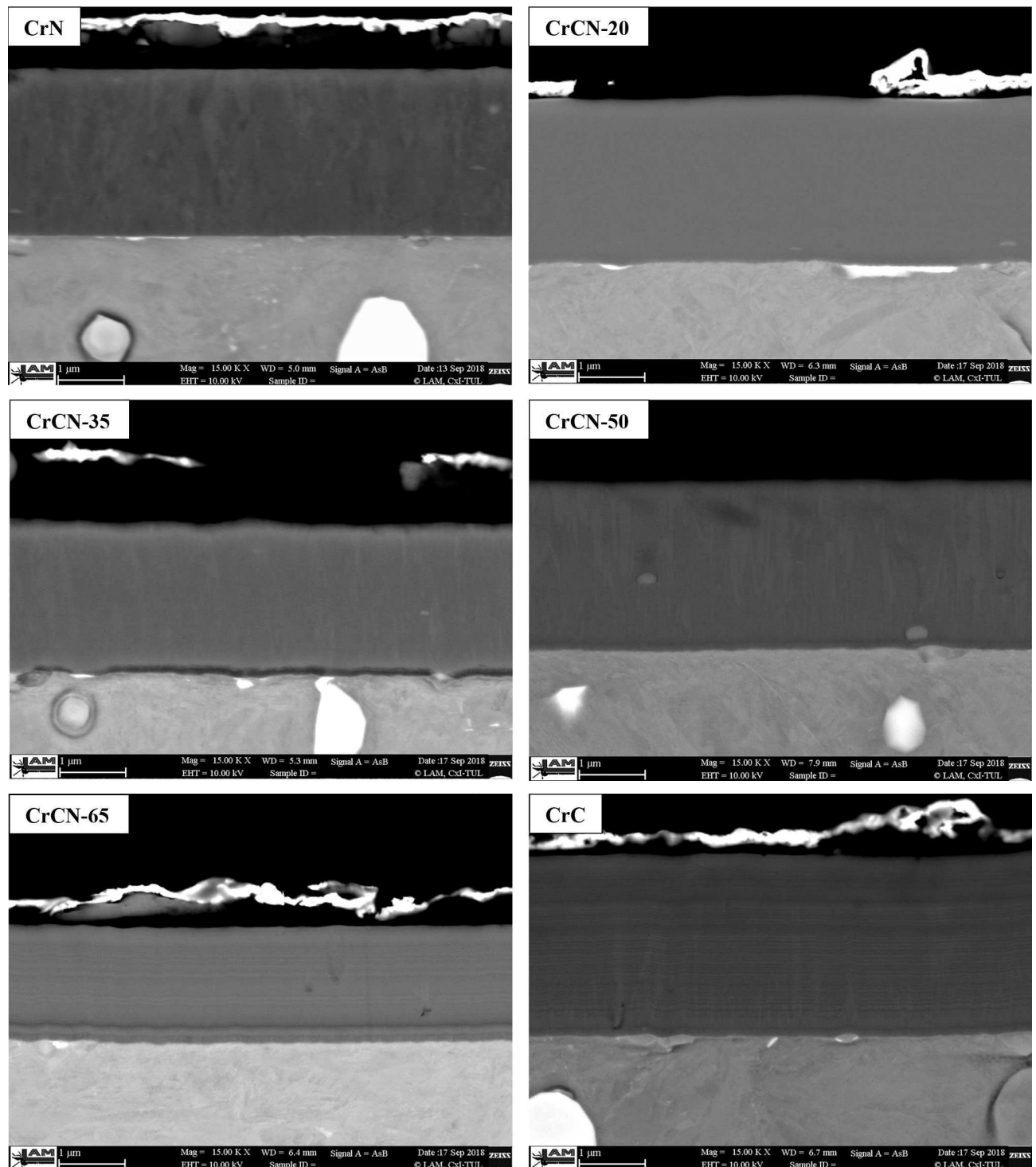
Fig. 10 The structure of thin layers seen by SEM in metallographic cross-sections.

4 Conclusion

The chemical composition, structure, thickness, and roughness of Cr(C,N) layers deposited by cathodic arc evaporation of pure Cr (99.99 % purity) in the atmosphere of reactive gasses N_2 and CH_4 where a ratio C/N was varied between 0 to 100 % were studied. Approximately linear dependence of C/N ratio of the composition on CH_4/N_2 process gas flow ratio was observed. The increase of N_2 gas flow ratio led to increasing of Cr-concentration.

The surface of all obtained layers is very smooth, Sa varies between 20 to 37.5 nm. Higher roughness was observed for layers prepared from a mixture of both reactive gasses compared to pure CH_4 or N_2 respectively. Similar results were observed from detailed 3D surface reconstruction obtained from AFM. Further research will be focused on mechanical and tribological properties like hardness, modulus of elasticity, coefficient of friction and wear resistance.

Acknowledgement

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