Complex characteristics of advanced materials using new transmission electron microscopy techniques

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I. Introduction

The nano-structure character of advanced materials calls for their characterization with methods like transmission electron microscopy, capable of atomic level spatial resolution both for imaging and measuring local chemical composition. Aside from paring of the materials features to be described with the TEM spatial resolution, one has to produce a specimen thin enough to pass electron beam through it, i.e. well below 100nm. The non-conducting nature of nitrides or carbides of which these hard coatings are usually built require either argon ion milling or gallium focused ion beam cutting (FIB) sample preparation techniques. Both of them were devised for helping research from electronic industry, what means that they are efficient at working with silicon and alike. The application of theses methods to preparation thin foils for TEM from advanced materials like super-hard coatings, metal matrix composites or ceramic compacts is caused by lack of any other solution and in most situations will help to produce thin foils at barely acceptable quality, i.e. a possibility of introduction of sample preparation artifacts has to be taken into account. The only way out from these uncomfortable situation leads through meticulous enlarging of our limited knowledge in this field.

The hard coatings form one of the most prominent group of the advanced materials. The improvement of tools for metal forming and cutting, which wear resistance up that time relied on their nitrided or carburized surfaces, started to be of high importance especially with the advent of high strength steels, composites and other hard to work materials in mass production in the mid XX century. The application of Chemical Vapor Deposition (CVD) or Physical Vapor Deposition (PVD) TiN coatings distinguished by their characteristic gold color, which doubled or even tripled cutting plates service life-time instantly turned out a great commercial success, saved the situation for a time and showed the direction for future developments. However, it is not an easy task to simultaneously better TiN high hardness, excellent adhesion to steel substrates and relatively good resistance degradation to harsh working condition, i.e. mostly high temperature oxidation. Aside of diamond coatings giving better performance only in case of working with iron free parts, other candidates for so demanding task are layered or nano-composite coatings.

The development of the layered or nano-composite coatings - with properties acceptable for practical applications - are progressing but at much slower pace than expected. The biggest problem is connected with reproducibility of mechanical properties and especially their hardness even at a laboratory scale. Their multi-component composition requires complicated deposition equipment, which in case of PVD systems is characterized by number of variable processing parameters like partial pressure of gasses, applied power, substrate bias and may others, being different from system to system. The high stress level in these coatings needs introduction of buffer layer which helps to alleviate this situation. The other important but usually poorly controlled parameter is the coatings oxygen contamination, which in case of this advanced materials also play strong detrimental role on their properties. The above situation causes, that the coatings real microstructure, as well as chemical composition might significantly differ from the designed one. Therefore, the control of coatings microstructure is of crucial importance on the way on their improvement.

The multilayer coatings evolved in a natural way from columnar monolithic ones, i.e. by alternative stacking the hardest with either the more oxidation resistant ones like in the case of TiN/CrN or with the tougher like in case of TiN/Ti. The first type of coatings gains from presence of CrN delaying coating deterioration at high working temperatures. However, swapping columnar with pseudo-columnar microstructure produces no progress concerning cracking at crystallites boundaries. In the second case the strongly differing unit cells of both phases enforces re-nucleation of new crystallites at each inter-phase boundary. This new microstructure, together with significant plasticity of titanium, allows eliminating through coating cracking and eventually the catastrophic delamination. However, their practical application has to wait until further optimization of thickness of individual layer possibly helps to produce hardness comparable with the monolithic TiN. A lowering the TiN/CrN multilayer coating period down to nanometer range aimed at keeping the local lattice coherency and its strengthening by numerous inter-phase boundaries, i.e. producing superlattice-like coatings is promising, but also needs further investigations.

The nano-composite coatings present a completely new approach in this field. The simultaneous deposition of silicon with titanium should helped swap the columnar TiN microstructure with the eqiaxed nanometer sized TiN crystallites separated by channels of amorphous Si_3N_4. As yet, aside from TiN/Si_3N_4 also deposition of CrN/Si_3N_4 was tried. The first principle calculations indicate that the monolayer of silicon nitride shows higher binding energy to titanium nitride than bonding within the latter. The first results indicated that gain in hardness might be very high, occasionally multiplying the original values of TiN. However, the attempts to reproduce these results were rarely successful and the doubts concerning the whole idea started to mount. The biggest problem was connected with the coatings nanostructure nature, i.e. confirming presence of monolayer of amorphous material on the boundaries on nano-crystallites. The control of the deposition process at that level is a very demanding task even having nowadays technology at hand.

The results of the transmission electron microscopy observations of the TiN/Si_3N_4 or CrN/Si_3N_4 coatings published up till now, practically confirm only the presence of fine columnar or nano-crystalline microstructure. The amorphous like contrast visible among fringes from nano-crystallites lattice planes could be formed by other unfavorable oriented nano-crystallites. The above situation is aggravated by the fact, that ion thinning could easily cause its partial amorphisation starting at defects like crystallites boundaries. Therefore, the further development of these interesting materials needs detail complex control of coatings composition and microstructure.

The aim of this review was to show that with the help of carefully chosen set of techniques of the transmission electron microscopy method, like bright/dark field, selected area diffraction, high resolution electron microscopy (HREM), energy dispersive spectroscopy (EDS) or Gatan Energy Filtering (GIF) one may successfully describe both microstructure, phase and chemical composition of so demanding advanced materials as hard coatings.

IIA. Characterization – ARC coatings

The tool steel, due to presence of high density of various types of large carbides (Fig.1), is a demanding type of a substrate, i.e. the macroscopically smooth and polished surfaces contain numerous microscopic scratches and upheavals. The former accompany any mechanically polished surface, but the latter are connected with presence of WC, MoC, TiC and other carbides (Fig.1), which are much harder to wear during polishing than the neighboring martensitic matrix. The surface roughness as well as its different local properties may deteriorate the adhesion of deposited coatings and adversely affect its smoothness.

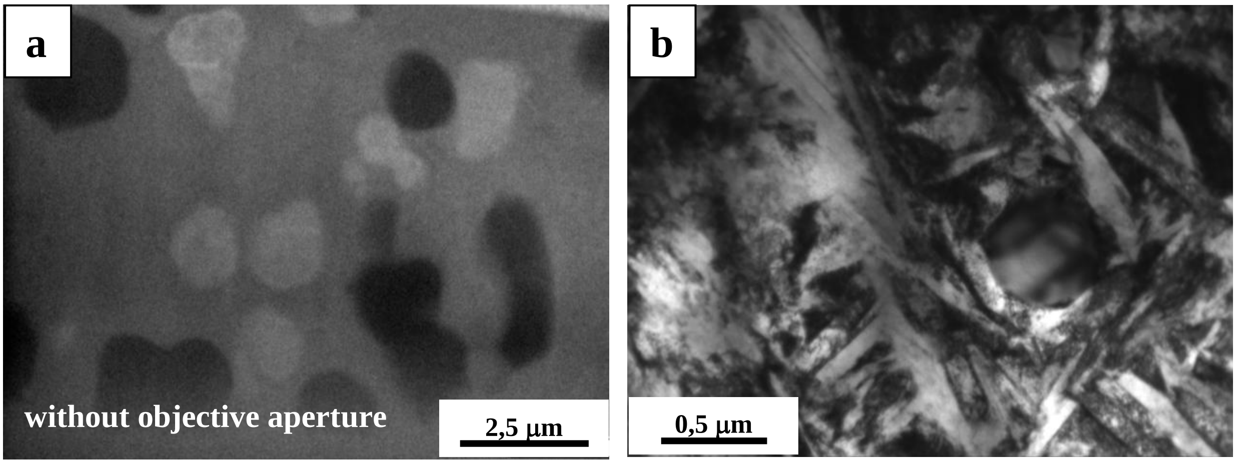

Fig. 1. Typical transmission microstructure image of tool steel presenting TiC-light and WC-dark carbides (a) and its martensitic matrix (b)

The TiNC coating was characterized by columnar microstructure (Fig.2). The crystallites close to the substrate were ~50 nm in diameter, while those higher up were from 100 to 300 nm. The analysis of selected area diffraction patterns (placed as inserts) indicate, that crystallites are of TiN-type cubic phase. Presence of small steps on the substrate evidence itself by comparable in height bumps at the coatings surface (marked wit arrow in Fig. 2a).

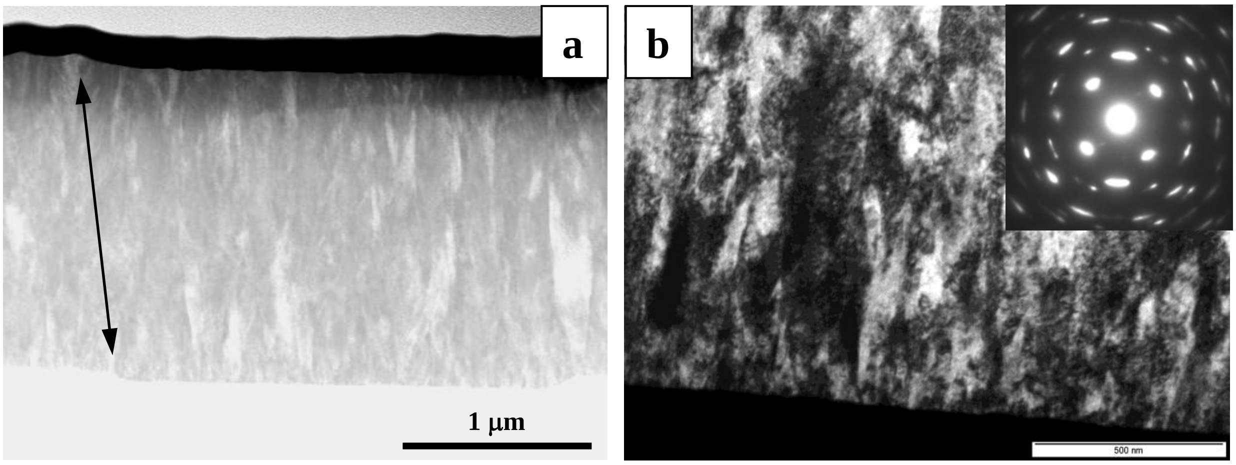

Fig.2. The scanning-transmission (a) and transmission (b) image of TiNC coating

The coatings like nACVIc® present much more comlicated microstructure, as presented in Fig. 3 and 4. It starts, with approximately ~400 nm thick buffer layer of columnar crystallites. They are of TiN-type, as ascertain by selected area electron diffraction patterns presenting two strong closely spaced rings from 111 and 200 planes and slightly farther away one more corresponding to 220 plane (insert at Fig. 4b). Next, a gradual refining of columnar microstructre is observed (Fig. 4c). Eventually, most of the coating is filled with extremely fine but still elongated in the growth direction crystallites. Additionally, a fine striation is superimposed on the image of crsyatllites. The diffractions shows similar in sequence but much more diffused rings indicating that the crystallites in this area are finer but also of TiN type (Fig. 4c-insert). The striations result from rotation of substrates with respect to titanium and aluminium-silicon targets introducing periodic changes in coating composition. The thickness of darker rich in Ti fringes vary from 3 to 5 nm, while lighter fringes corresponding to Si and Al rich ones are from 2 to 4 nm thick. Occasionaly, a light elements rich “lens – like” defects also form, as well visible on Z-sensitive images obtained using HAADF detector (Fig. 3). The measurements of local chemical composition along the line perpendicular to the substrate confirmed, that the buffer layer consist of TiN and next of (Ti,Al)N, i.e enriched in Al sublayers of ~100 and ~200 nm respectively (Fig. 5). Higher up, in the “striated area” (Fig.4c) the Al and Si level in the coating tend to increase gradually. Eventually, the Al content rougly equels that of Ti, while Si content stabilizes at much lower level. The values averaged over the several layers shows that the Ti:Al:Si remains approxymately at 4:4:1 ratio. The mappings representing chemical distribution showed, that the “lens –like”like deffects are enriched in both Al and Si (Fig. 6). Occasionally in this areas also the chromium is present.

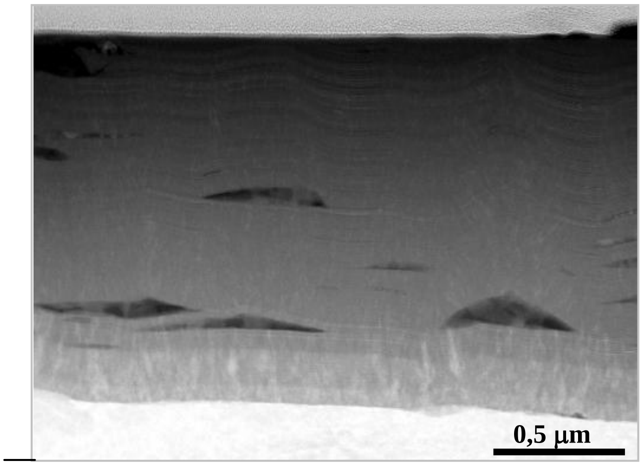

Fig.3. The scanning-transmission image of microstructure of nACVIc® coating

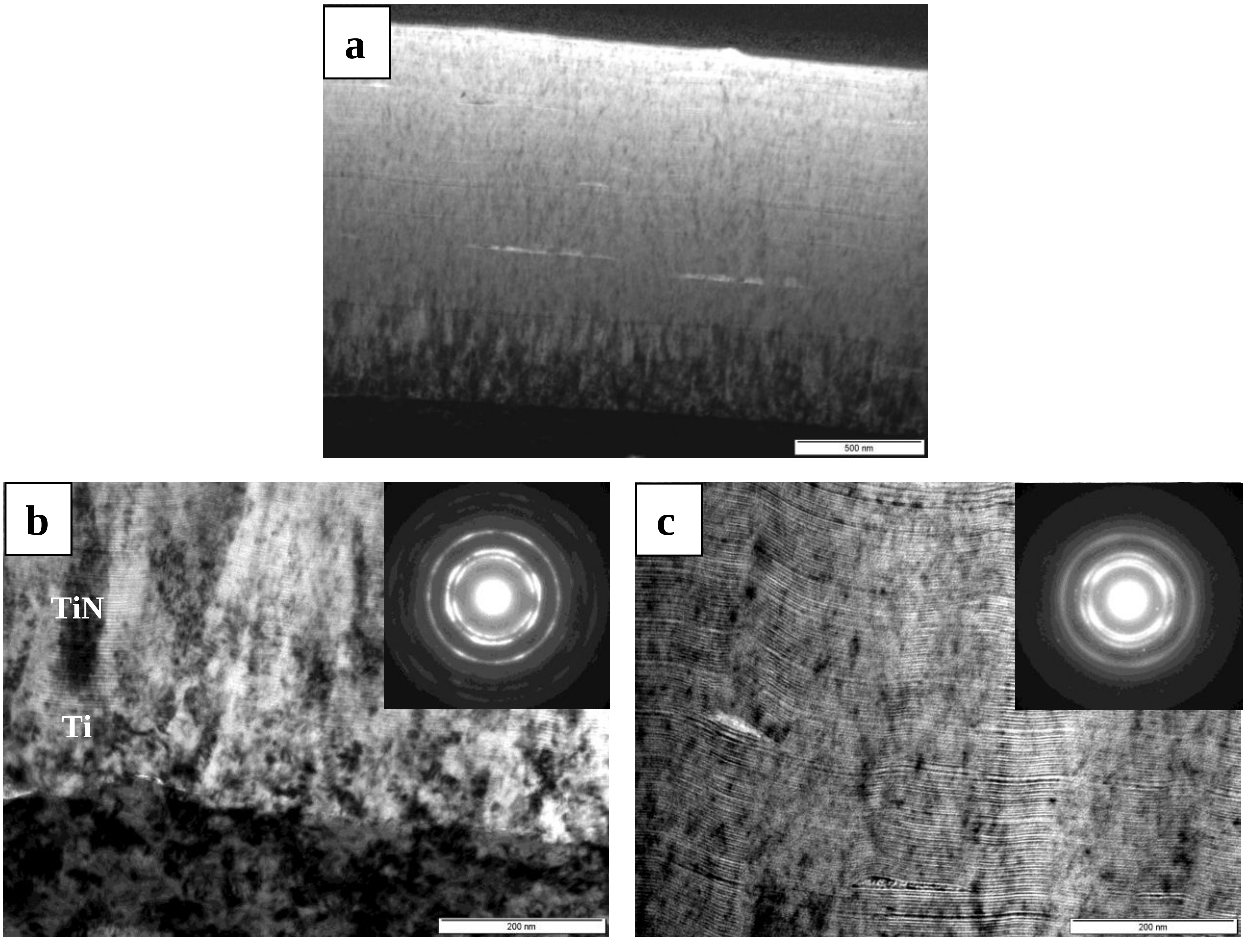

Fig.4. The transmission images presenting microstructure of nACVIc® coating (a) together with its enalrged parts from near-substrate (b) and centre (c) areas together with correcponding selected area diffractions

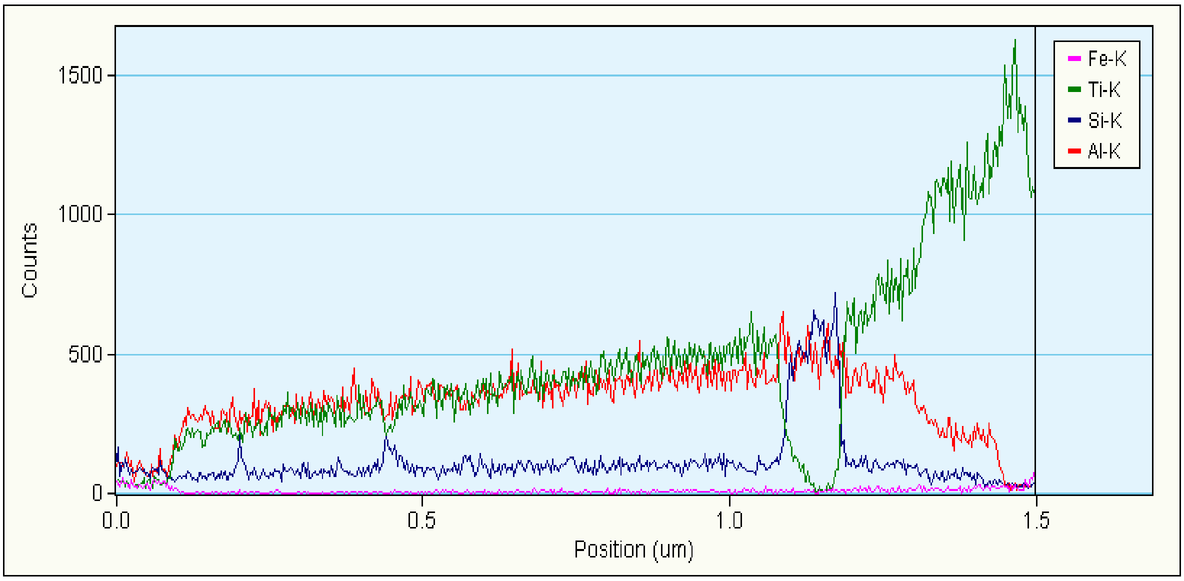

Fig. 5. The image presenting local chemical composition along the line perpendicular to nACVIc® coating substrate obtained using EDS system

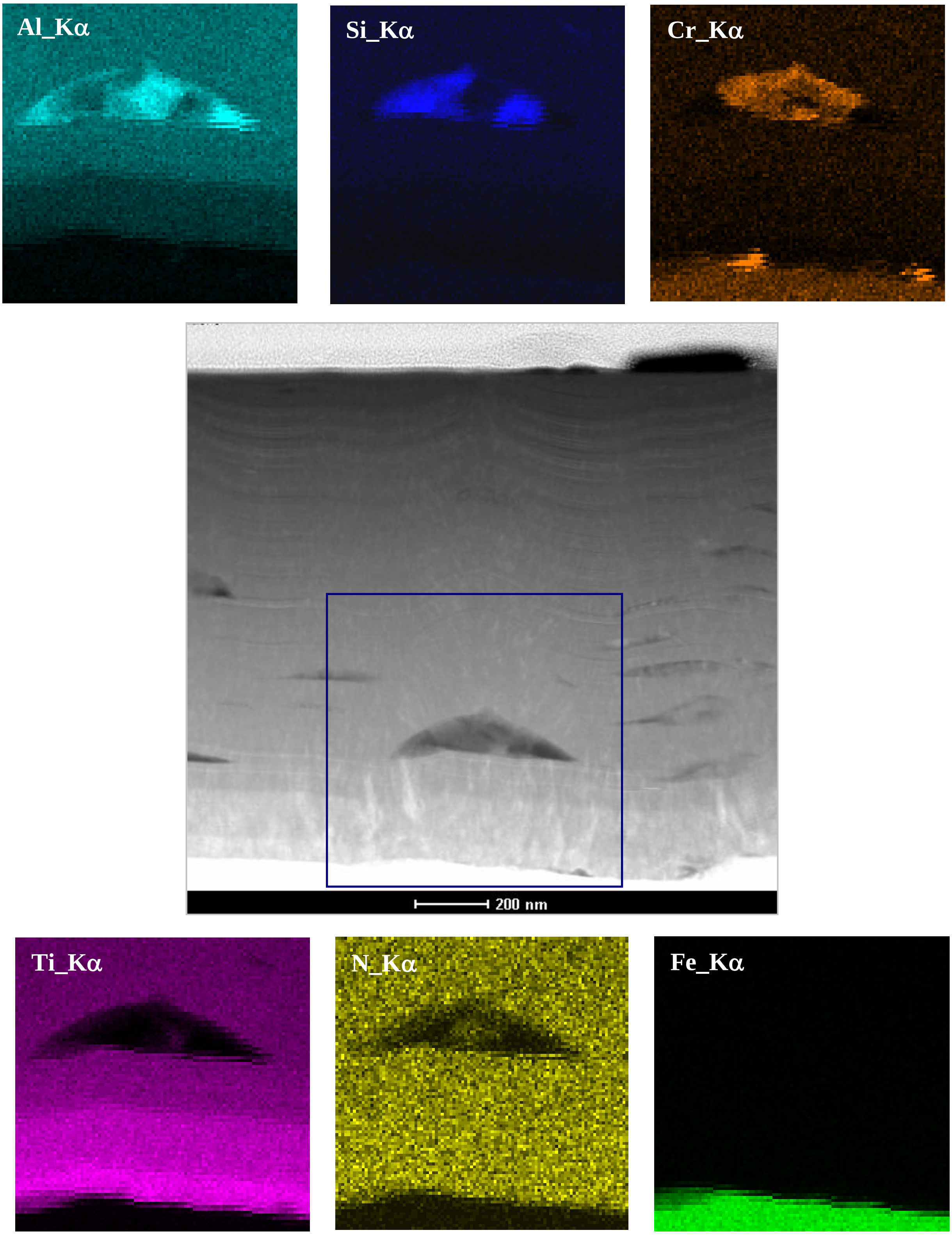

Fig. 6. The images presenting scanning-transmission HAADF image and accompanying maps of Al, Si, Cr, Ti, N and Fe distribution on a section of nACVc® coating obtained using EDS system (type of lines marked on the respective maps)

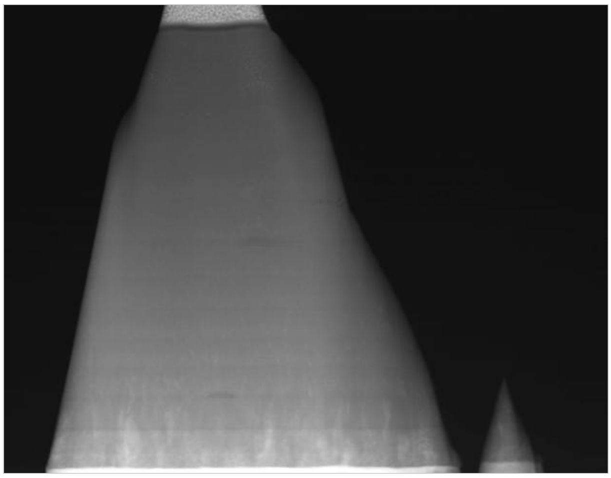

Fig. 7. The scanning-transmission image of microstructure of nACo® coating

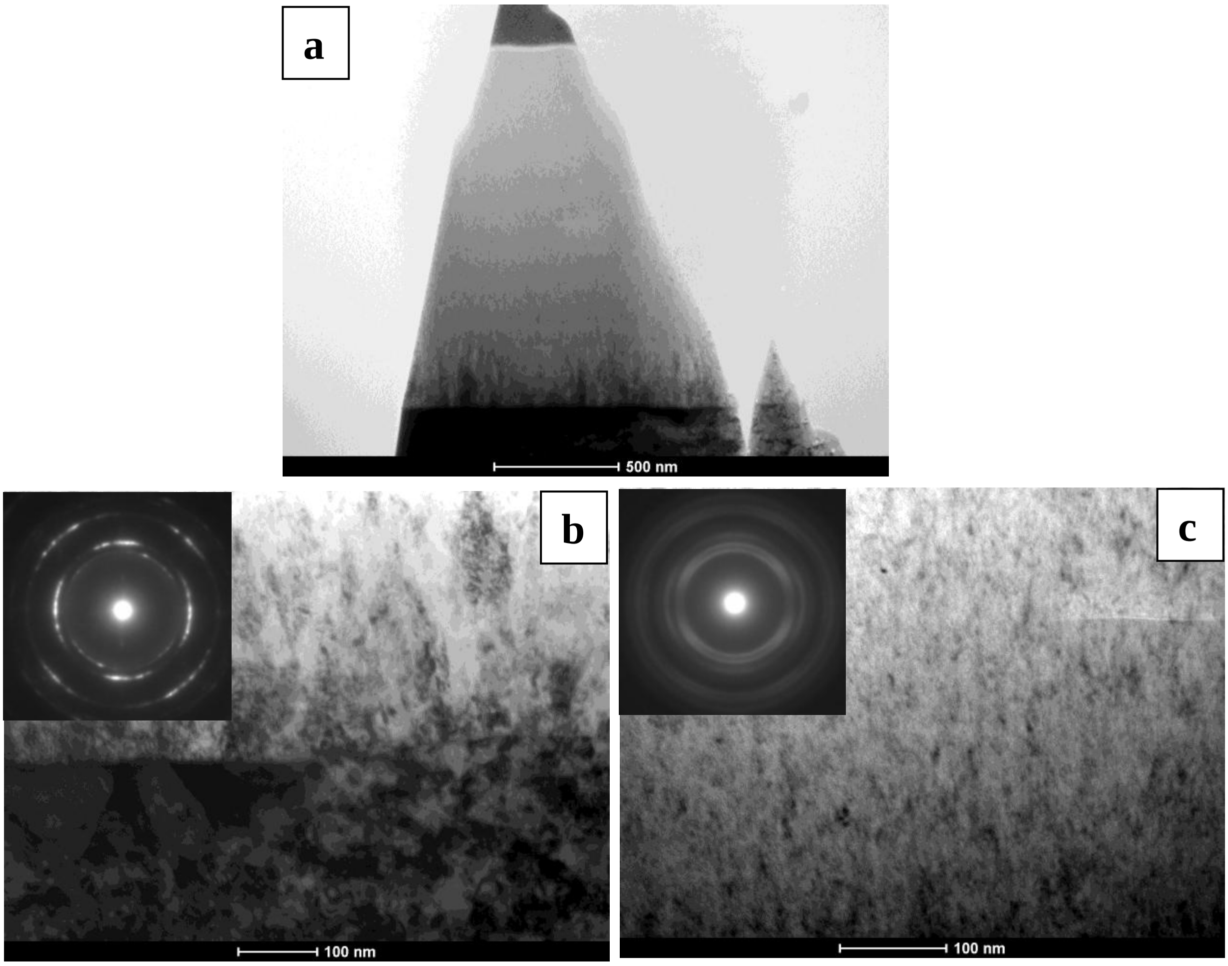

Fig.8. The transmission images presenting microstructure of nACo® coating (a) together with its enalrged parts from near-substrate (b) and centre (c) areas together with correcponding selected area diffractions

The nACo® is built in similar way to nACVc®, i.e with columnar layer close to the substrate, which gave way to an amorpous-like material higher up (Fig. 7, 8a). The observations performed with higher magnification showed that also the center and near surface part contain numerous very fine but this time more rounded crystallite (Fig. 8c). The selected area diffractions obtained both from near substrate area or coating centre again gave sets of diffraction spots arranged along the rings of diameter proper for the TiN type lattice (inserts in Fig. 8b,c). The high resolution observations confirmed that the crystallites are highly defected and in the range of several nanometer in diameter (Fig. 9).

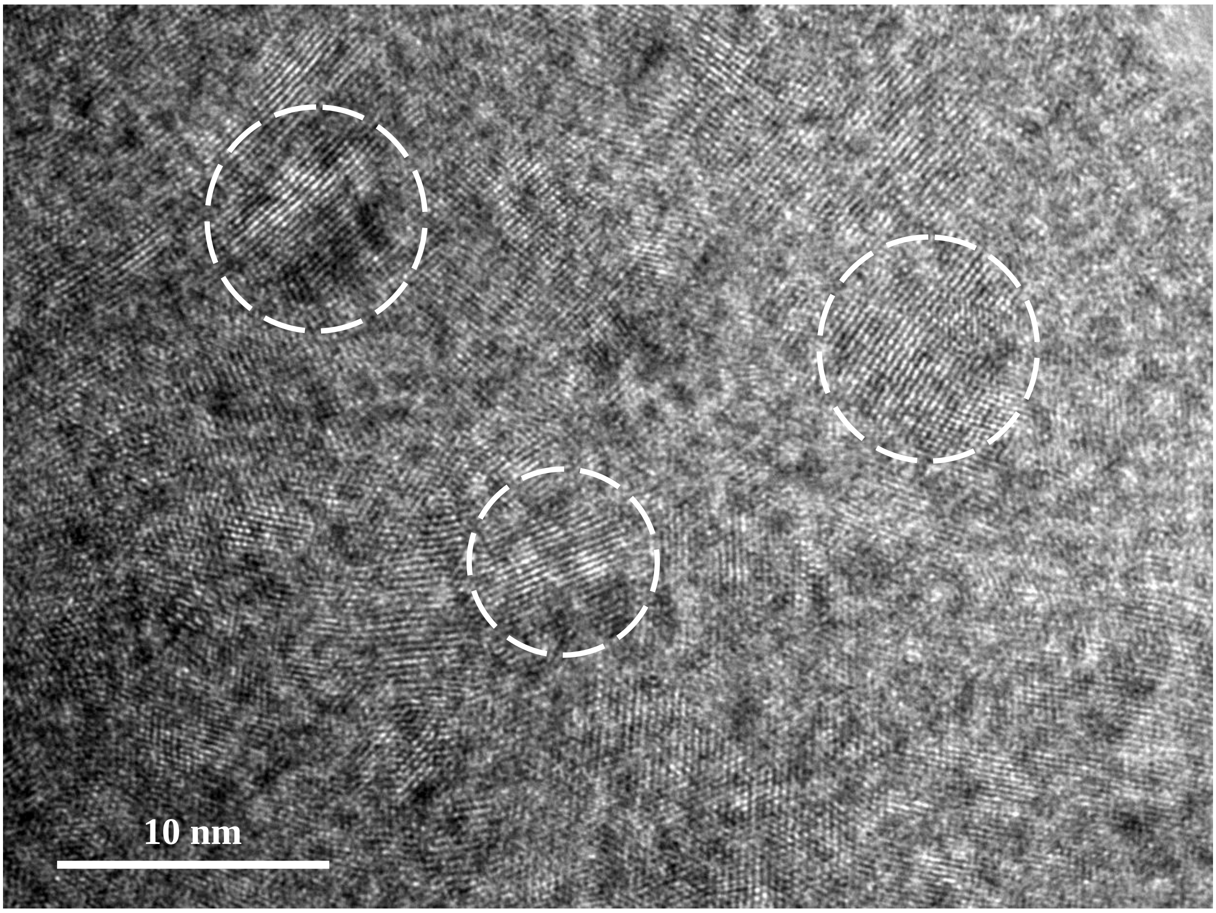

Fig.9. The high resolution image presenting nano-crystalline nature of centre of the nACo® coating

The measurements of the local chemical composition through the coating thickness showed very similar to previous one composition profile, i.e. presence of TiN near substrate (due to partial overlapping and of Ti_Lα and N_Kα line the signal corresponding to nitrogen was omitted) followed by gradual increase of aluminium and silicon content (Fig. 10). Only in the upper part of the coating, i.e. those closer to the surface the aluminium seems to dominate (previously it was approximately at a same level).

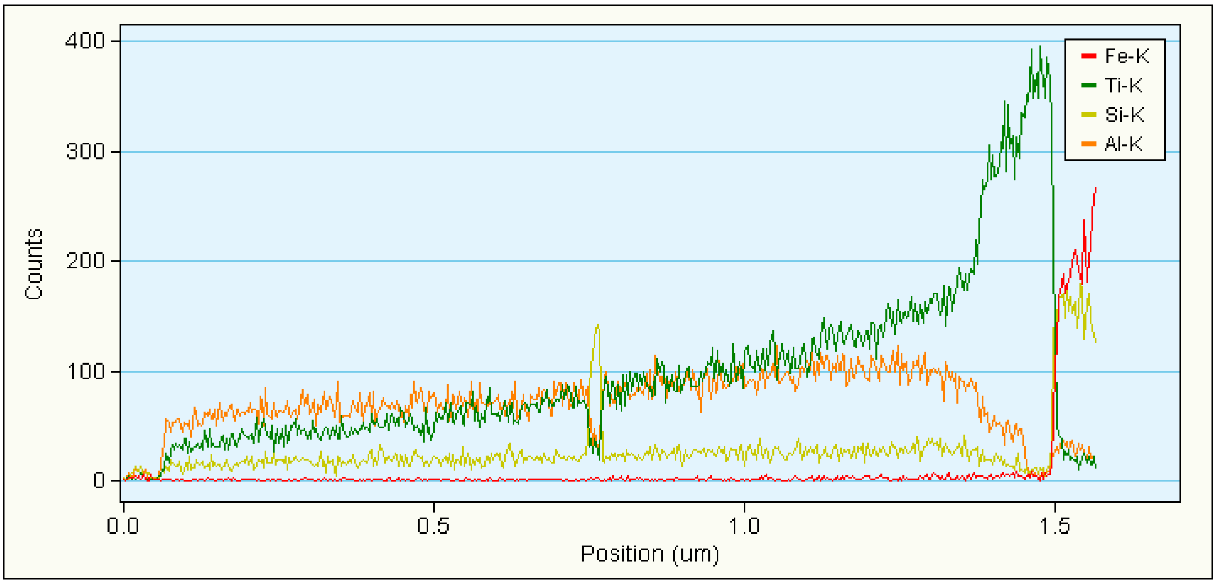

Fig. 10 The image presenting local chemical composition along the line perpendicular to nACo® coating substrate obtained using EDS system

The UniversalAl® TiAlN coating is built in different way than the previous ones. It may be roughly described as a multialyer sandwiched in between buffer and a relativly thick top columnar layer (Fig. 11, 12). The buffer of standard for present series thicknes of ~80 nm is followed by ~80 nm slightly coarser columnar crystallites layer. Only than starts an amorphous with nanocrystalites / fine colunar crystalline multilayer of Λ ~150 nm (1:2, respectively). The amorphous with nanocrystallites bears evident striation of a few nanometer spacing (Fig. 12b, 13), while the adjacent columnar shows similar, but much fainter striations (Fig. 12a). Each of the electron diffraction patterns place as inserts showed set of rings characteristic for TiN type lattice, i.e. closely spaced 111and 200 and sligly further outside 220. However, the diffraction from central par of the coating, dubbed as "multilayer" showed also a faint ring inside those described above, what suggest that it is a two phase area.

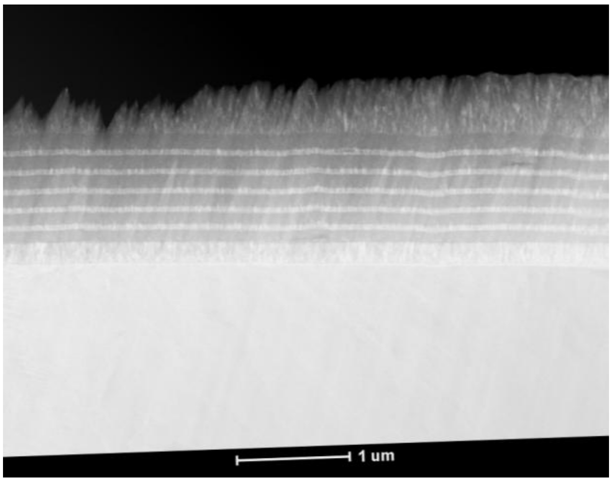

Fig. 11. The scanning-transmission image of microstructure of UniversalAl® TiAlN coating

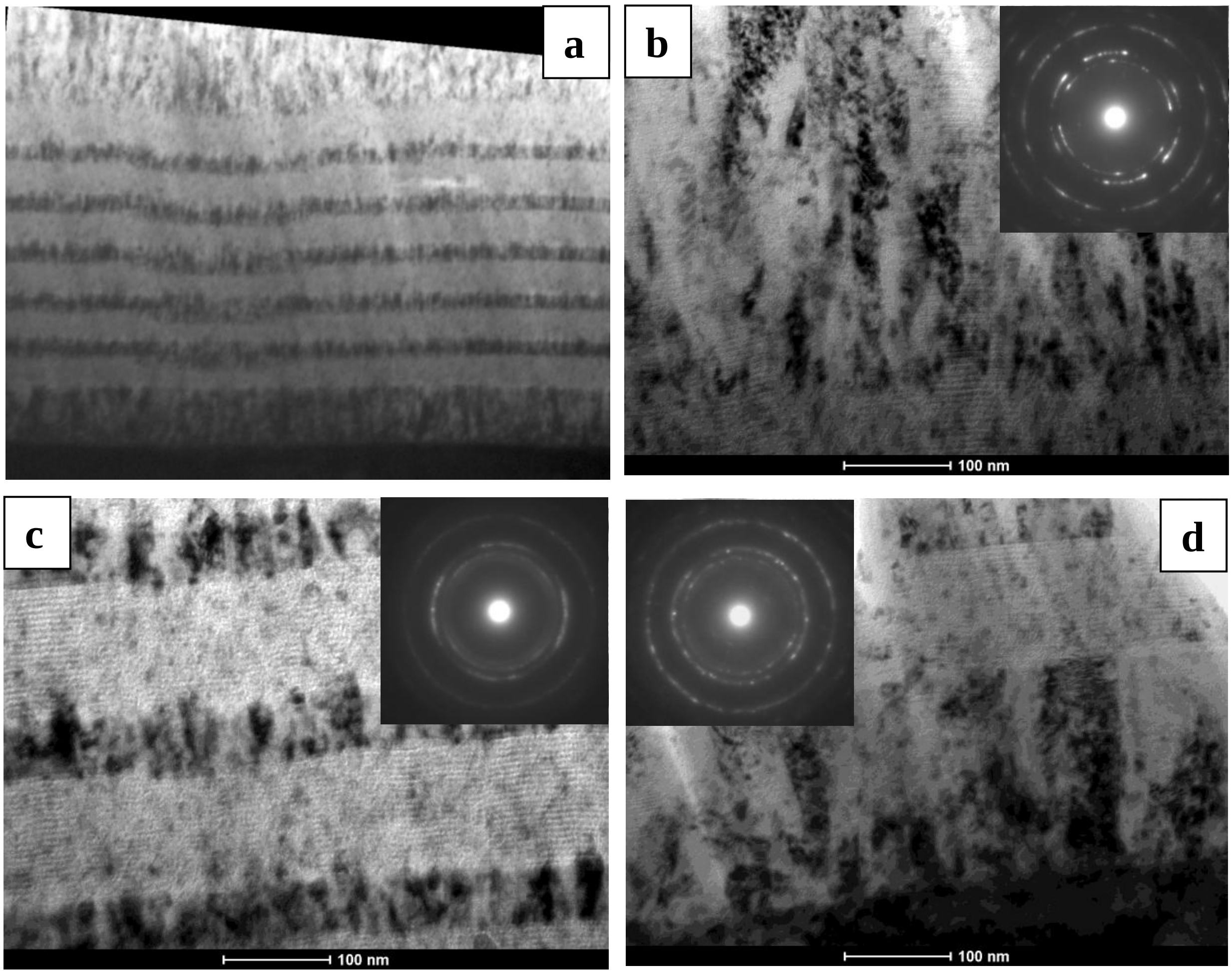

Fig.12 The transmission images presenting microstructure of UniversalAl® TiAlN coating (a) together with its enalrged parts from near-surface (b), centre (c) and near substrate areas together with correcponding selected area diffractions

The evident presence of straiations on images obtained using Z(atomic mass)-sensitive scanning-transmission techniques (Fig. 13) indicates, that they are connected with some composition variation, i.e. local periodical of “heavy” and “light element” fluctuations (in present case the “heavy” means Ti, while “light” to Al).

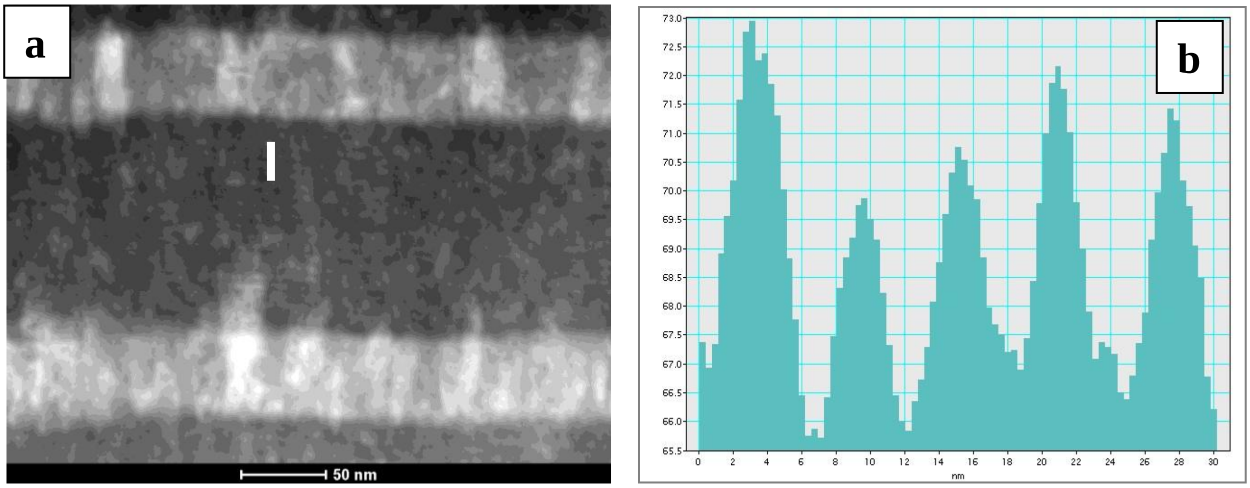

Fig. 13. The scanning-transmission image of microstructure of center part of UniversalAl® TiAlN coating (a) and accompanying intensity profile acros a line mark on it (b)

The high resolution observations proved that the amorphous-like material in the central part of this coating are rather built with extremely fine layers of nano-crystallites of size below 5 nm (Fig. 14). As the size of this crystallites match the thickness of straiations, they take form of beeds forming strings. It seems that they are separated by 1-2 nm thick sheet of amorphous material as marked by thick white arrows.

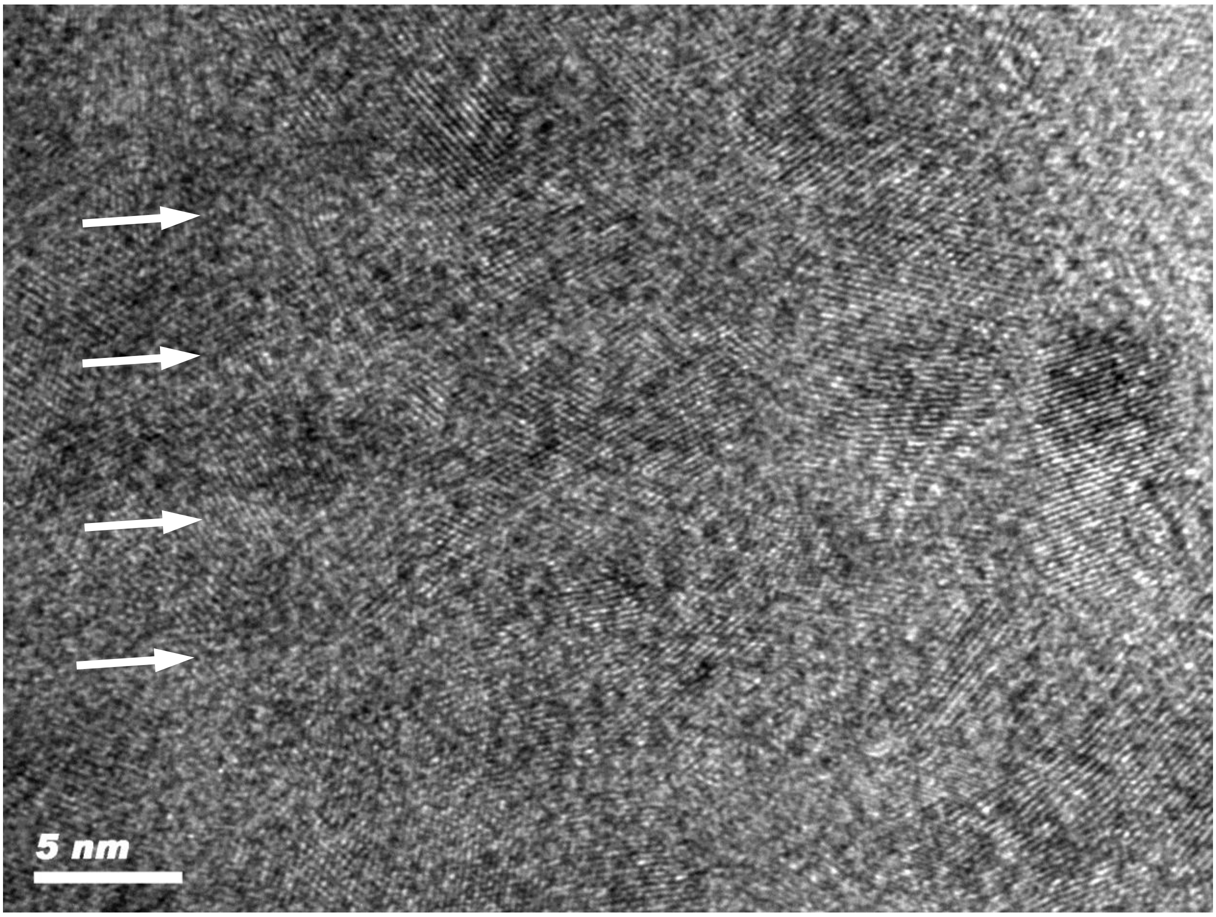

Fig.14. The high resolution image presenting nano-crystalline nature of centre of the UniversalAl® TiAlN coating

The through coating composition profile corresponds well with the complicated microstructure (Fig. 15). The TiN fine columnar buffer layer starts the stack at the first ~80nm and next a slightly thicker columnar (Ti,Al)N layer (but only with small aluminium addition) is formed. After that a multilayer character is evidence by alternating changes of aluminium and titanium levels. It is all topped with columnar (Ti,Al)N layer of approximately similar aluminium and titanium content. The set of layers which were originally dubbed “amorphous” to be reclassified after high resolution observations as strings of nano-crystallites separated by really amorphous mater indeed showed slight composition enrichment of the former (Fig. 16).

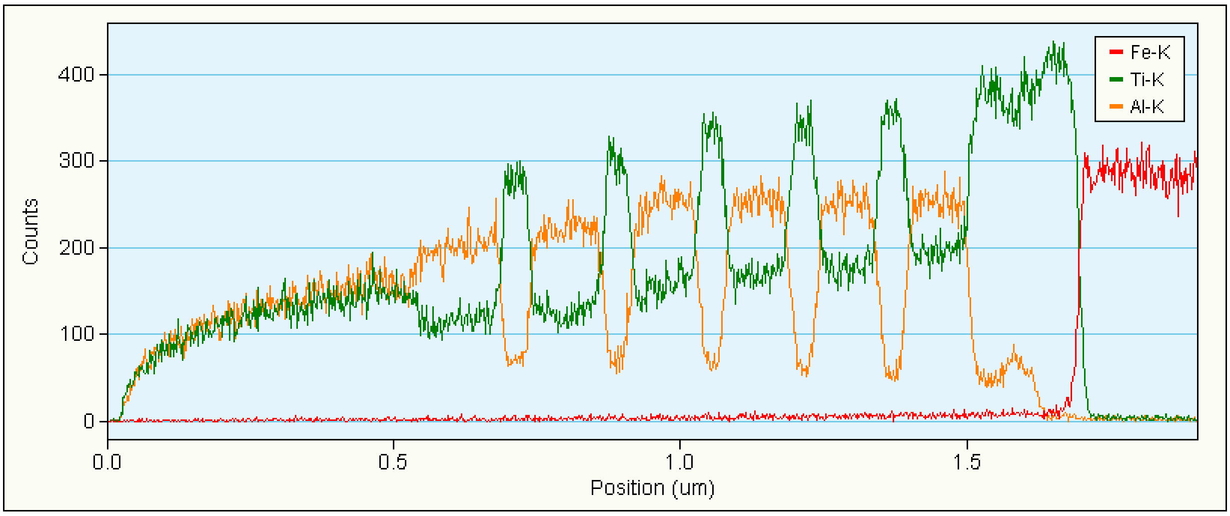

Fig. 15 The image presenting local chemical composition along the line perpendicular to UniversalAl® TiAlN coating substrate obtained using EDS system

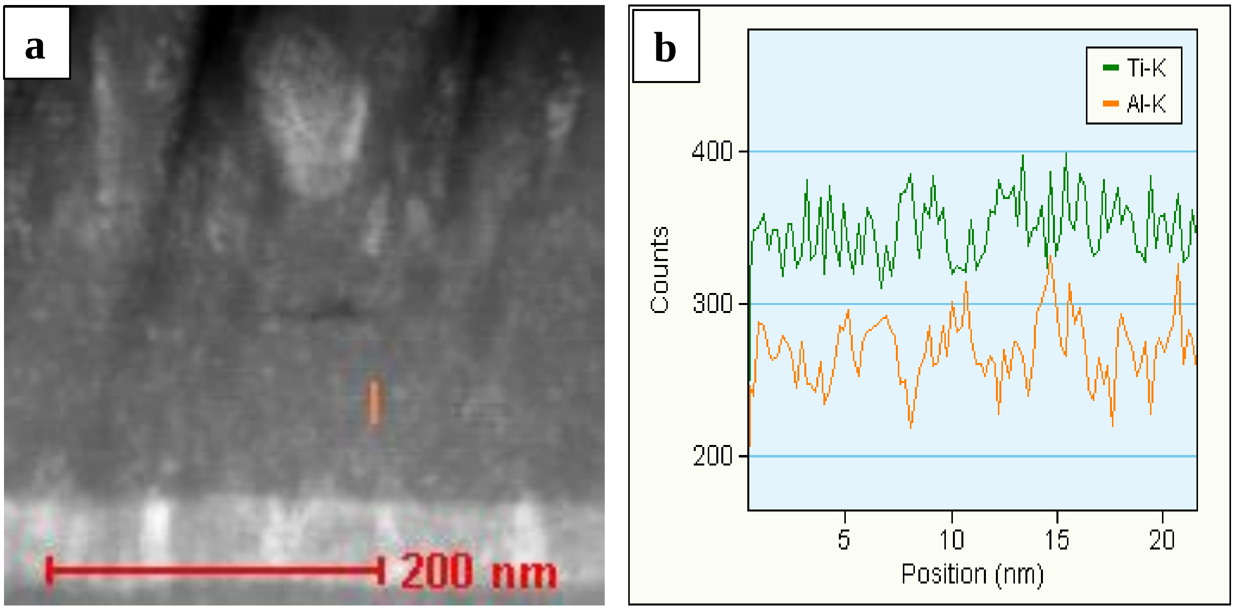

Fig. 16. The image of a cut-out of UniversalAl® TiAlN coating from the border between multilaer and capping columnar layer with marked line (a) from which the accompanying EDS spectra (b)was obtained

IIB. Characterization – magnetron coatings

The increasing of silicon additions from 10 to 20 and to 30 at. % in CrSi magnetron targets caused gradual refining of columnar microstructure of coatings deposited on substrates heated up to 600 °C (“HT”), as shown in bright and dark field images (Fig. 17). The measurements of column diameter indicated that they decreased from ~40 to ~35 and to ~25 nm respectively. The presence of 111, 200 and 220 rings in the selected area electron diffraction patterns, confirmed that all coatings are of CrN-type. The magnetron sputtering of CrSi10 target at substrates without resistive heating (“RT”) again produced columnar coating but of so fine grain that it showed close resemblance to that obtain from CrSi30 on heated substrate (“HT”).

Sputtering of CrSi20 and CrSi30 on “RT” substrates enlarged the layer of amorphous material present close to the substrate and eliminated the columnar microstructure substituting it with fine rounded crystallites immersed in amorphous matrix, i.e. allowed to produce the nano-composite microstructure (Fig. 18). The diffused intensity superimposed on rings proper for CrN-type confirmed presence of amorphous material also in upper parts of the coatings, i.e. close to the surface. The deposition using CrSi40 target produced fully amorphous coatings both on “RT” and “HT” substrates (Fig. 17g, 18e). The high addition of low grade silicon powder (oxygen contaminated) in the CrSi compacts resulted in occasional target poisoning followed by “metallic” mode visible as layer of higher density.

The measurement of chemical composition of coatings with EDS system confirmed, that their Cr:Si ratio is by 2-3 % enriched in silicon as compared with respective targets. The line profile obtain across the coatings showed that aside of Cr, Si and N, also O is present (Fig. 19). The stronger oxygen signal closer to the substrate might be connected with the preferential etching of SiO_2 contaminants present in CrSi compacts.

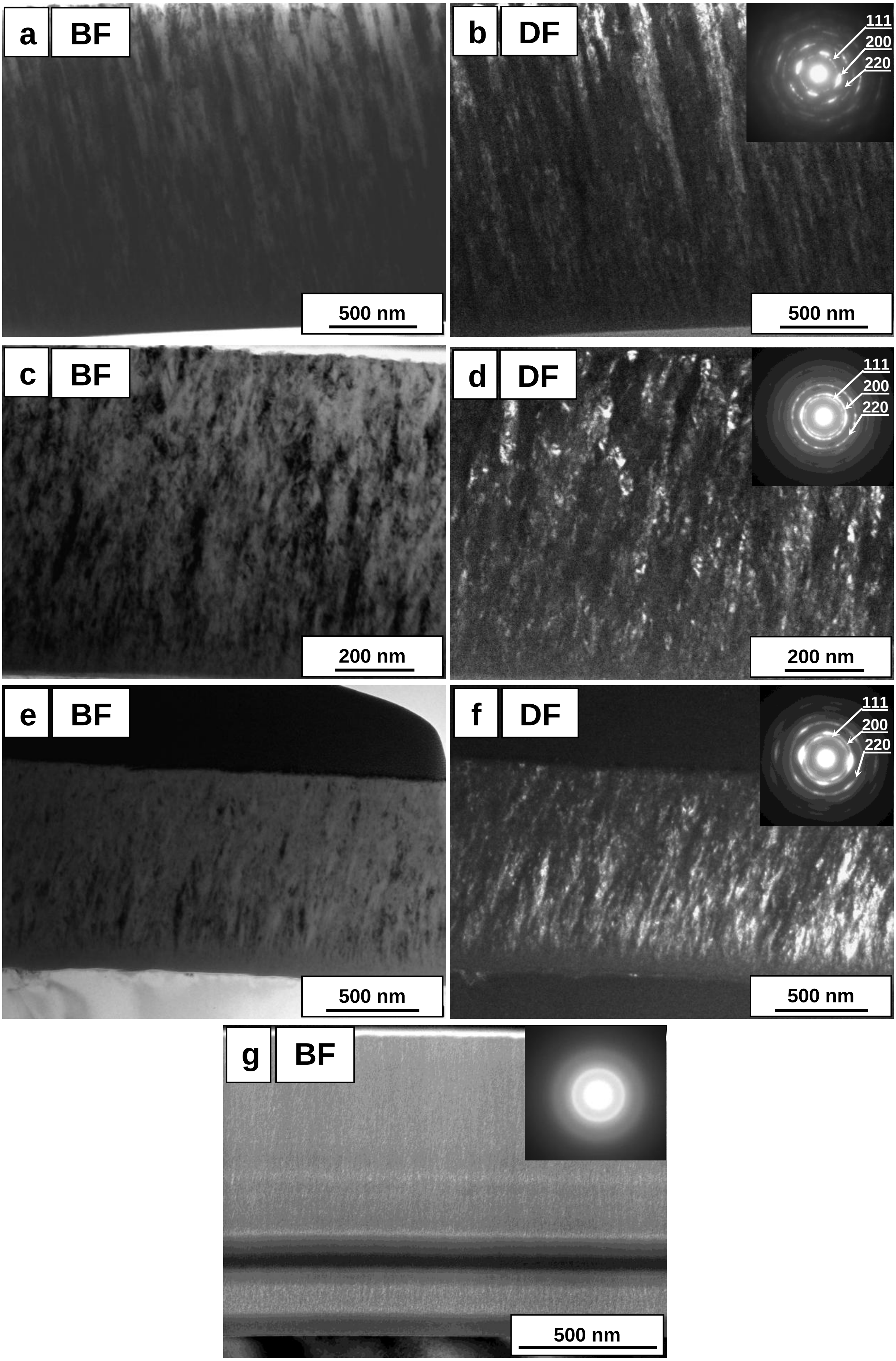

Figure. 17 Transmission microstructures of coatings obtained from CrSi10 (a, b), CrSi20 (c, d), CrSi30 (e, f) and CrSi40 (g) targets deposited at "HT"

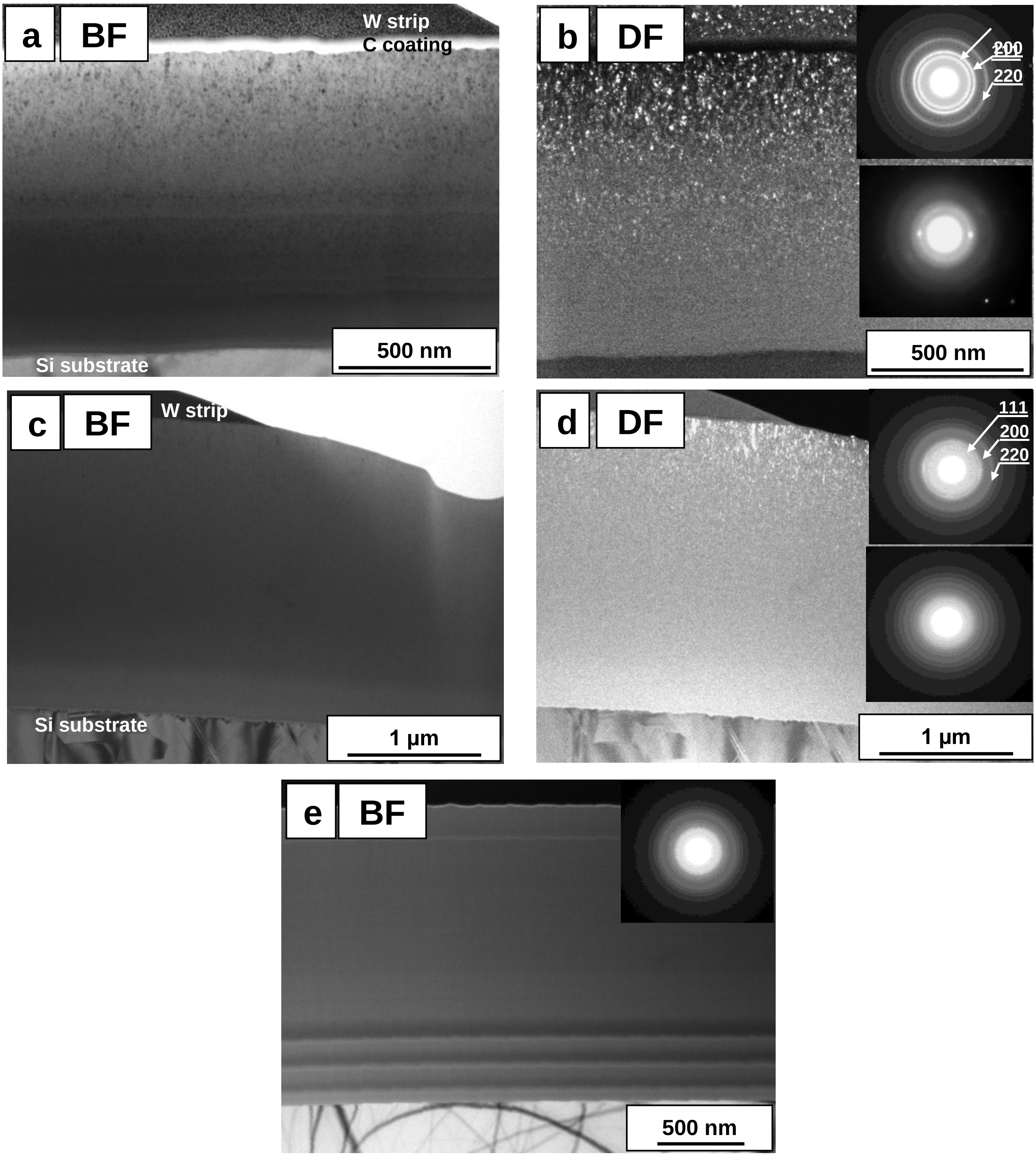

Fig. 18. Transmission microstructures of coatings obtained from CrSi20 (a, b), CrSi30 (c, d) and CrSi40 (e) targets deposited at “RT”

The high resolution observations performed on thin foils cut in *plan-view* orientation indicated, that the crystallites in coatings deposited using CrSi30 targets at “HT” substrates are fully crystalline, i.e. the lattice fringes in individual grain met at their grain boundaries (Fig. 20a). The nano-crystallites in coatings deposited at “RT” are much smaller, i.e. ~5 nm and practically always separated by amorphous-like channels (Fig. 20b).

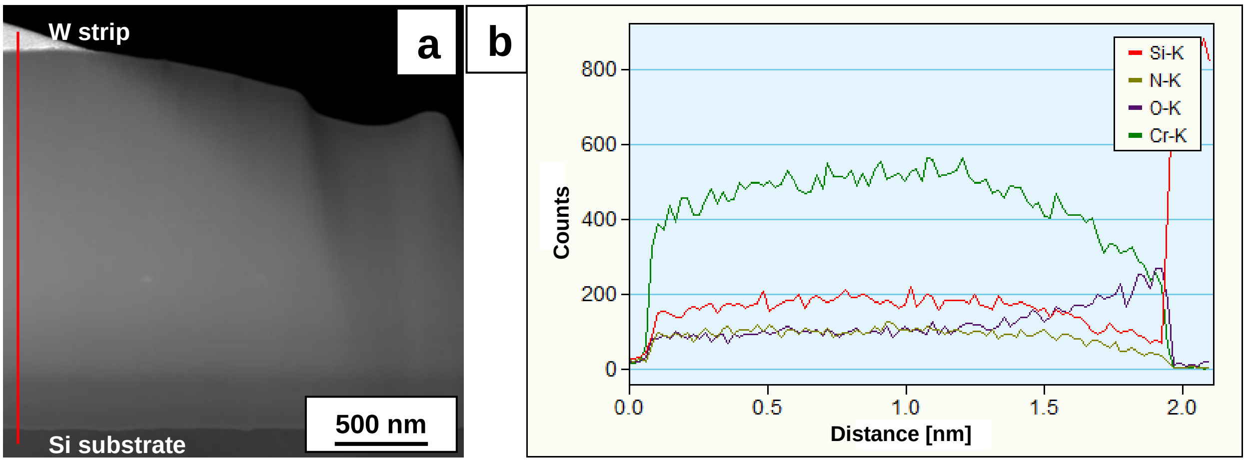

Fig. 19. Scanning-transmission microstructure of coatings (“RT”) obtained from CrSi30 target (a) and distribution of Cr, Si, N and O across it (b)

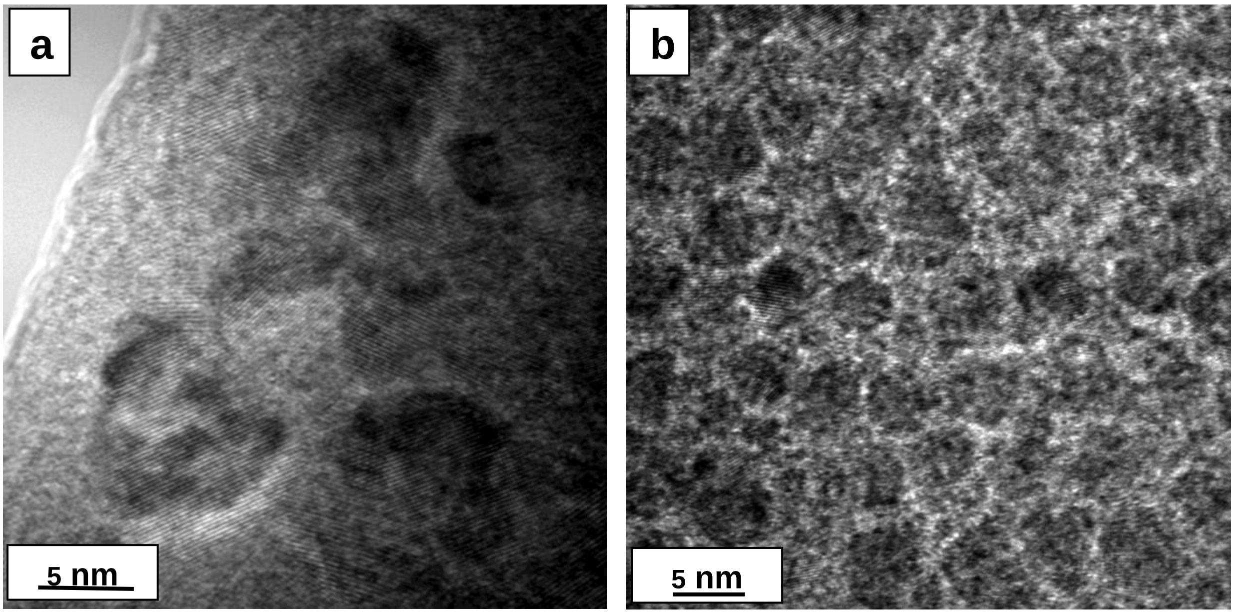

Fig. 20. *Plan-view* high resolution transmission microstructure of “HT” (a) and “RT” (b) coatings obtained from CrSi30 target

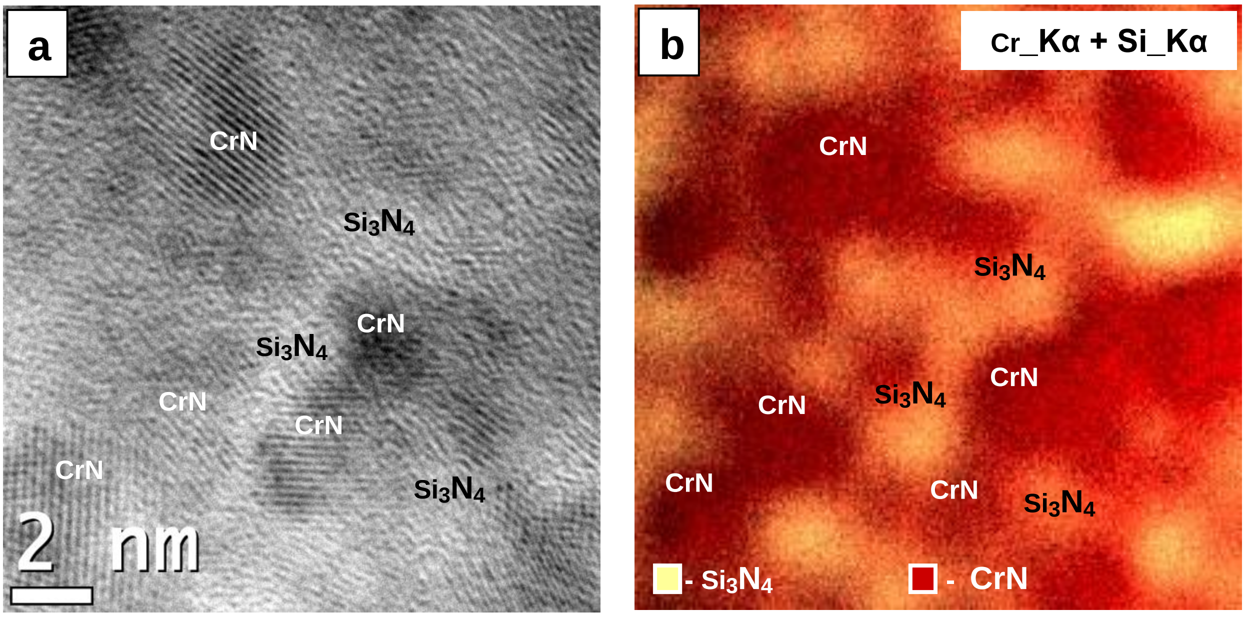

Fig. 21 *Plan-view* high resolution transmission microstructure of “RT” coating obtained from CrSi30 target (a) and accompanying GIF composite map presenting distribution of Si and Cr

The GIF energy filtered "composite" map, i.e. with superimposed intensities of Cr and Si matched with high resolution images confirmed, that the nano-crystallites are either CrN or at least strongly enriched in chromium, while amorphous channels contain dominant silicon fraction (Fig. 21). The fit between crystalline and chromium enriched areas is good, but far from perfect. The observed mismatch results from the fact, that the thickness of thin foil exceeds most of CrN size. Therefore, in some cases small well oriented CrN crystallites might produce well visible lattice fringes, but the thickness averaged thin foil composition might produce image of local enrichment in silicon. Additionally, large unfavorably oriented for high resolution imaging crystallite might produce local contrast similar to the amorphous material, while the averaged chemical composition in that area will show dominant chromium presence. Preparing the thin foil in *plan-view* orientation helped to gain advantage of the "fibrous" nature of some CrN nano-crystallites in this coating, i.e. their slight elongation in growth direction.

III. Summary

The microstructure observations at micro- (including BF and DF mode) and nano-scale (high resolution microscopy – HREM and Gatan Image Filtering – GIF) backed with selected area diffraction (SAD) studies together with measurements of local chemical compositions obtained using X-ray Energy Dispersive Spectroscopy (EDS) attachment proved that a successful characterization of either several component multilayer or even nano-composite coatings produced with the LAteral Rotating ARC-Cathodes® or magnetron techniques is possible.

The ARC TiNC® coating showed fully columnar microstructure, while the nACVIc® and nACo® ones were built of rounded 10-50nm nano-crystallites. The UniversAl® TiAlN showed the microstructure being closest to nano-composite type coating, i.e. the nano-crystallite size was pushed below 10nm, while amorphous material was found between strings/layers of such crystallites. The formation of "lens-like" makro-defects inherently connected with ejection of molten material from aluminium-silicon targets pose a serious problem, but not an unavoidably one. All investigated ARC coatings with admixture of aluminium or aluminium and silicon carried on them a unique for the arc deposition technique nano-spaced striations, which from microstructure point of view seem neutral as it concerns it mechanical properties.

The reactive magnetron sputtering of CrSi compacts with increasing silicon additions from 10, 20 and 30 at. % fraction on substrates kept at 600 °C resulted in diminishing their average column diameter from 40 to 35 and 25 nm, while similar processes performed on substrates warmed up to 100 °C - due to contact with plasma - produced gradient amorphous-crystalline coatings with an increased amount of the latter phase in coatings with higher silicon content. The profile of chemical composition obtained with EDS system indicated, that coatings obtained by sputtering of CrSi compacts are contaminated with oxygen increasing in the zone close to the substrate. The maps of local chemical composition using GIF system matched with high resolution observations proved that the crystallites are highly enriched in chromium and amorphous channels in silicon confirming presence of CrN/Si_3N_4 amorphous-crystalline composite.