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NANO-SCALE STRUCTURE INVESTIGATION OF VAPOUR DEPOSITED AlCrSiN COATING USING TRANSMISSION ELECTRON MICROSCOPE TECHNIQUES

The investigations concerned the structural analysis of the AlCrSiN coating deposited by arc Physical Vapour Deposition method on the X40CrMoV5-1 hot work tool steel substrate. The deposition process was carried out on a device equipped with a technique of lateral, rotating cathodes. The nano/microstructure, phase identification and chemical state of the coating were analysed by high-resolution transmission electron microscopy. It was found that the investigated coatings have nanostructured nature consisting of fine crystallites. The fractographic tests were made using the scanning electron microscope and allow to state, that the coating was deposited uniformly and tightly adhere to the substrate material. In the work is presented the nature of a transition zone between the produced AlCrSiN coating and substrate material.

Przeprowadzone badania dotyczyły analizy struktury powłoki AlCrSiN naniesionej w procesie fizycznego osadzania z fazy gazowej metodą łukową na podłożu ze stali narzędziowej do pracy na gorąco X40CrMoV5-1. Proces osadzania powłok był realizowany na urządzeniu wyposażonym w technologię bocznych, obrotowych katod. Badania dyfrakcyjne, składu chemicznego oraz nano/mikrostruktury powłok przeprowadzono z wykorzystaniem wysokorozdzielczego transmisyjnego mikroskopu elektronowego. W wyniku przeprowadzonych badań stwierdzono, że powłoki wykazują nanokrystaliczną strukturę. Wykonane badania fraktograficzne w skaningowym mikroskopie elektronowym pozwalają stwierdzić, że powłoka jest nałożona równomiernie i szczelnie przylega do materiału podłoża.

W pracy przedstawiono charakter połączenia występujący w strefie przejściowej pomiędzy powłoką AlCrSiN a materiałem podłoża.

Keywords: AlCrSiN coating; PVD; HRTEM; SEM; nano-scale

1. Introduction

Several techniques, in particular, Physical Vapour Deposition (PVD) are now available for the deposition of nanostructured films on various substrates. Many PVD technologies are more and more applicable in different branches of the industry. The required functional characteristics of tools are a result of correct structure formation, mechanical and tribological properties of hard nanocrystalline coatings [1-5].

A large number of technologies are available for the production of nanostructured coatings. The most promising methods are laser ablation, magnetron sputtering, plasma assisted chemical vapour deposition (PACVD), vacuum arc evaporation and hybrid techniques consisting of a combination of above mentioned [6]. Nowadays one of the commonly used coating equipment for large-scale industrial production is the LARC Technology. The most important advantages on this technology come from the permanent rotating cathodes and their lateral position [7, 8].

Multicomponent nanostructured coatings are indispensable in the development of a new generation of protective materials for various tribological applications. AlCrSiN coatings are recognised as one of a very interesting premium film for modification of tools surface, due to their excellent wear and oxidation resistance and high hardness [9-12]. Despite the big number of scientific investigations in the field of thin films and coatings, still some lack and scarcity of verified material knowledge occurs. Therefore, coating characterization is the inevitable and important step for ensuring of high-quality product for the intended application. Since nanoscale singularities have the enormous influence on bulk materials behaviour, the high-resolution transmission electron microscope (HRTEM) has become a powerful and irreplaceable tool for characterizing nanostructured materials [13-15].

The goal of this work was investigations concerned structural and phase analysis of AlCrSiN coating deposited by arc PVD method on the X40CrMoV5-1 hot work tool steel substrate.

2. Experimental details

The production process of AlCrSiN coatings was performed continuously with a π80 device by PLATIT fitted with 2 LARC (Lateral Rotating Cathodes) cathodes. High purity argon (99.99%) was used as a sputtering gas and mixtures of high purity nitrogen (99.99%) were used as reactive gasses in the deposition process. Cathodes containing pure Cr metal and the AlSi (88:12 wt. %) alloy were used for deposition of

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the coatings. After pumping the chamber to a base pressure below 5×10^{-3} Pa, the substrate was heated to appropriate the desired temperature. The temperature was controlled by thermocouples. Then the substrates were cleaned by argon ion at the pressure 2 Pa and the bias voltage of 750V/200V for 20 min. To improve the adhesion of coatings, a chromium-based metallic transition layer was applied. The coatings were deposited on the X40CrMoV5-1 hot work tool steel substrate.

The fractographic test of investigated coating was made on transverse fractures in a scanning electron microscope SUPRA 35 by ZEISS.

Diffraction investigations and coating structure investigations were conducted using a scanning-electron microscope (S/TEM) Titan 80-300 FEI, equipped with an electron field gun XFEG with a Schottky emitter with increased brightness, an energy dispersion spectrometer EDS, an external energy filter for imaging EFTEM, a system of three BF/ADF/HAADF detectors for scanning work mode. Observations were carried out within the energy range of 80-300 kV in the classical model (TEM) and in the beam surface-scanning mode (STEM). Microscope tests were performed on thin lamellas dimensioned about 20×8 μm that were next thinned to the final thickness of about 50-70 nm. Sampling was performed on the cross-section of layers with a Quanta 3D 200i dual focus ion beam (FIB) – scanning electron microscope (SEM).

3. Results and discussion

The cross-section of the investigated AlCrSiN coating is presented on Fig. 1. The coating presents a compact structure, without any visible delamination or defects. The morphology of the fracture of investigated coating is characterized by a dense microstructure. The fractographic tests made with the electron scanning microscope allow to state that the tested coating indicates a monolayer structure consisting of a hard nitride layer. It was found that a chromium-based layer exists well bound with a substrate that was produced to improve the coatings' adhesion to a steel substrate. The clear boundary line is visible between CrAlSiN and transition layer and between transition layer and steel substrate on the SEM image. The individual layers are deposited uniformly and tightly adhere to each other and to the substrate material.

Tests were carried out, using the HRTEM, to determine the nanostructure and size of crystallites in the layers deposited and to examine the character of transition zones between the coating and the substrate. For the coating characterization, the STEM and TEM modes were used (Fig. 2). The size and shape of grains in the produced layers was determined using the dark field technique and based on electron diffractions obtained signifying a nanocrystalline structure of the analysed layers.

It can be concluded already based on TEM images in the bright field that the investigated layers have a nanocrystalline structure (Fig. 3). Dark areas appearing on the BF image are crystallites that are oriented close to the axis of bands relative to an electron beam. It was found by examining thin lamellas from the cross section of AlCrSiN layer produced by the arc method that the layer features a compact structure with high homogeneity and grain size is less than 10 nm.

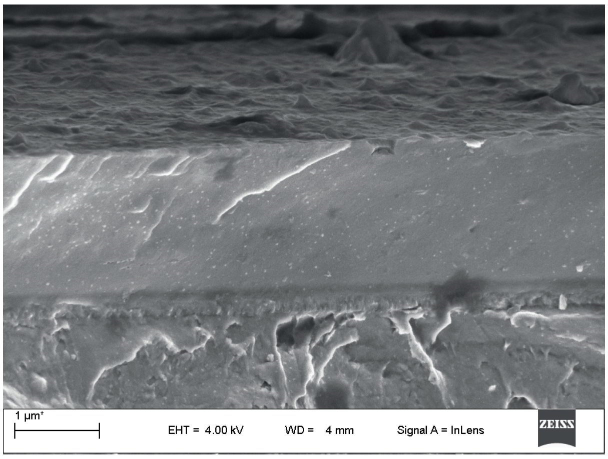

Fig. 1. SEM fracture image of AlCrSiN coating deposited onto the X40CrMoV5-1 steel substrate

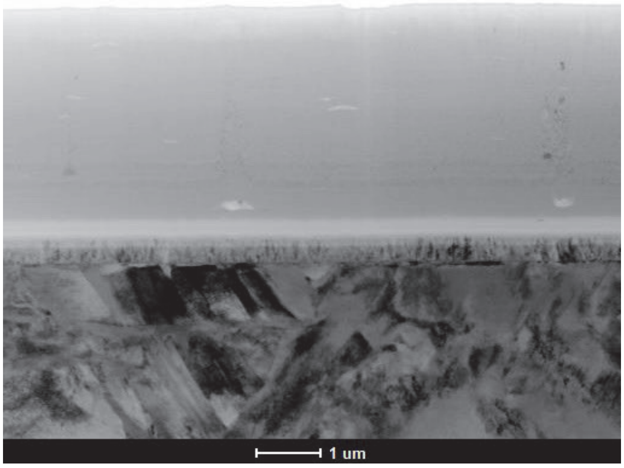

Fig. 2. BF-STEM images of AlCrSiN coating deposited on the X40CrMoV5-1 steel substrate

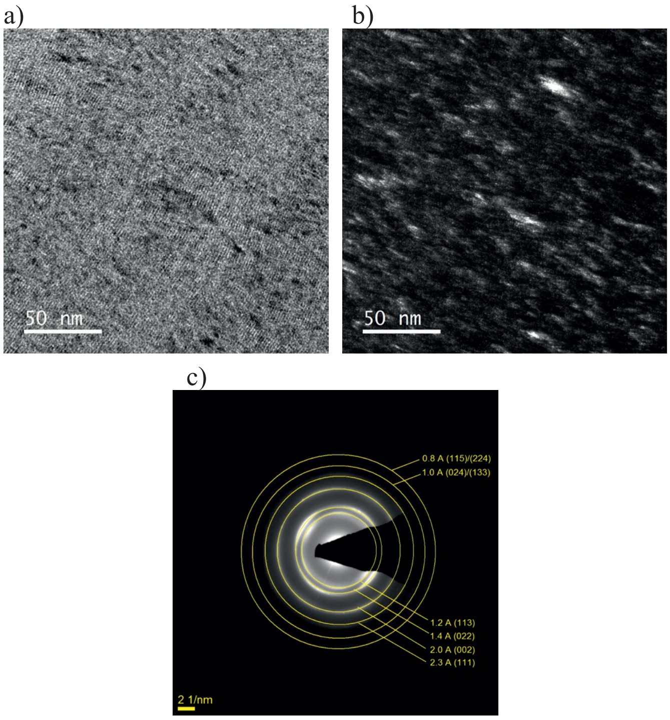

Fig. 3. Structure of the AlCrSiN coating: a) TEM bright-field image, b) TEM dark field image, c) corresponding SAED pattern

Fig. 3c presents nanocrystalline diffraction rings of AlCrSiN layer. The SAED pattern shows CrN phase and no diffraction spots of containing aluminium phase, such as AlN phase, can be found.

In additional, small crystalline grains sized several nanometers were observed in the tests of the AlCrSiN structure using the HRTEM, which may signify a nano-scale structure of the investigated layer (Fig. 4).

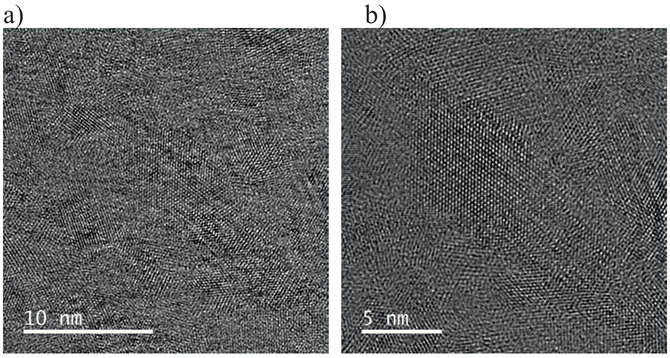

Fig. 4. High-resolution TEM images of AlCrSiN coating

Further analysis supporting the nanocrystalline structure involves electron diffraction investigations and dark-field observation. At the SAED diffraction images obtained from the BF images, there were marked points, in those the objective aperture (10 microns) was positioned for imaging in the dark field technique.

Observations in the dark field and the diffraction images made for increasingly smaller areas confirm a nanocrystalline structure of the examined nitride layers. (Fig. 5).

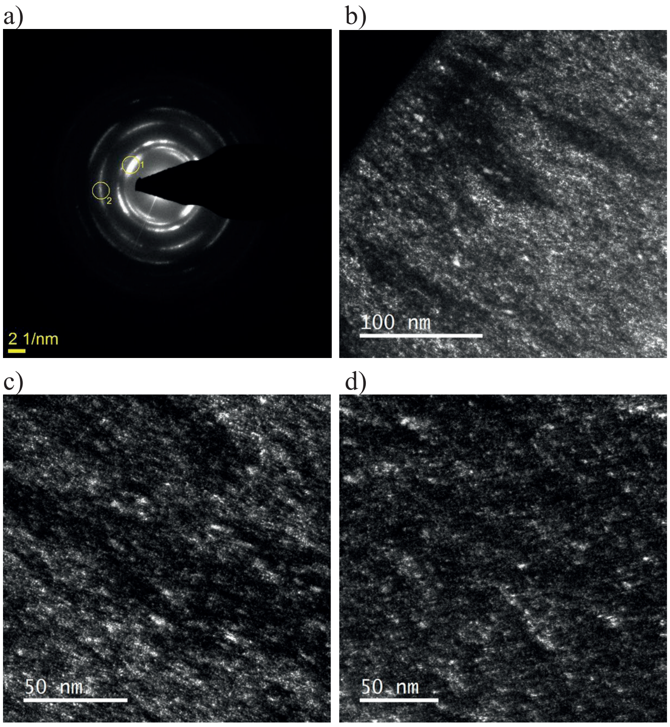

Fig. 5. AlCrSiN coating: a) SAED pattern, b÷c) TEM dark-field images based on reflex 1, d) TEM dark-field images based on reflex 2

Information about the mass and atomic concentration of individual elements in the micro areas of the AlCrSiN layer (Tab. 2, Fig. 6) was acquired as a result of a quantitative EDS X-ray microanalysis. Based on data given in Table 2 it was found that the atomic ratio of [Al+Cr+Si]/[N] is close to 1:1.

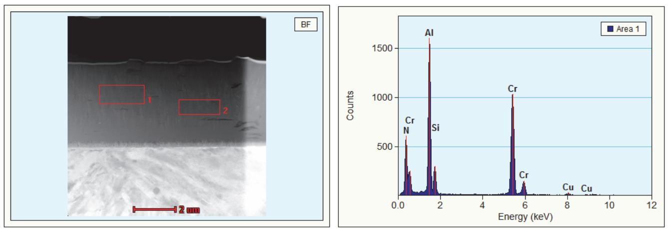

Fig. 6. STEM-BF image of AlCrSiN coating with EDS spectrum of the marked areas

TABLE

Results of quantitative analysis of chemical composition of AlCrSiN coating in Fig. 6

	Area 1		Area 2	
Element	Weight %	Atomic %	Weight %	Atomic %
Al	29.12	26.84	30.39	27.56
Cr	36.60	17.50	34.89	16.42
Si	4.49	3.97	5.29	4.61
N	28.91	51.33	29.41	51.39

Four subzones providing different contrast on TEM images in the BF (Fig. 7) can be distinguished for a transition zone between a hard AlCrSiN layer and a substrate material: proper CrAlSiN layer (designated as AlCrSiN-1), CrAlSiN quasi-amorphous structure (designated as CrAlSiN-2), CrN layer, Cr, substrate material.

A linear analysis (Fig. 8) was performed with EDS spectrometer, and a surface analysis of elements distribution (Fig. 9) using Energy-Filtering Transmission Electron Microscopy (EFTEM) was carried out to confirm the existence of a change in chemical composition of individual sublayers between a CrAlSiN layer and a substrate material. The character of changes in the intensity of the elements shows that the sublayers mentioned exist.

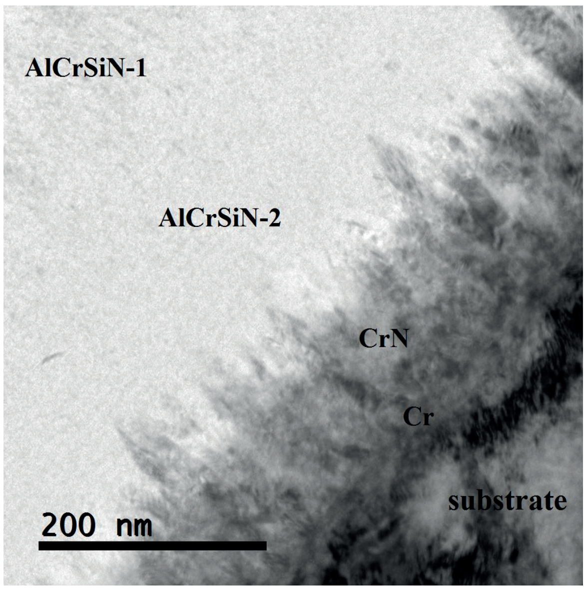

Fig. 7. Structure of the transition zones existing in AlCrSiN coatings formed on a hot-work tool steel X40CrMoV5-1 substrate

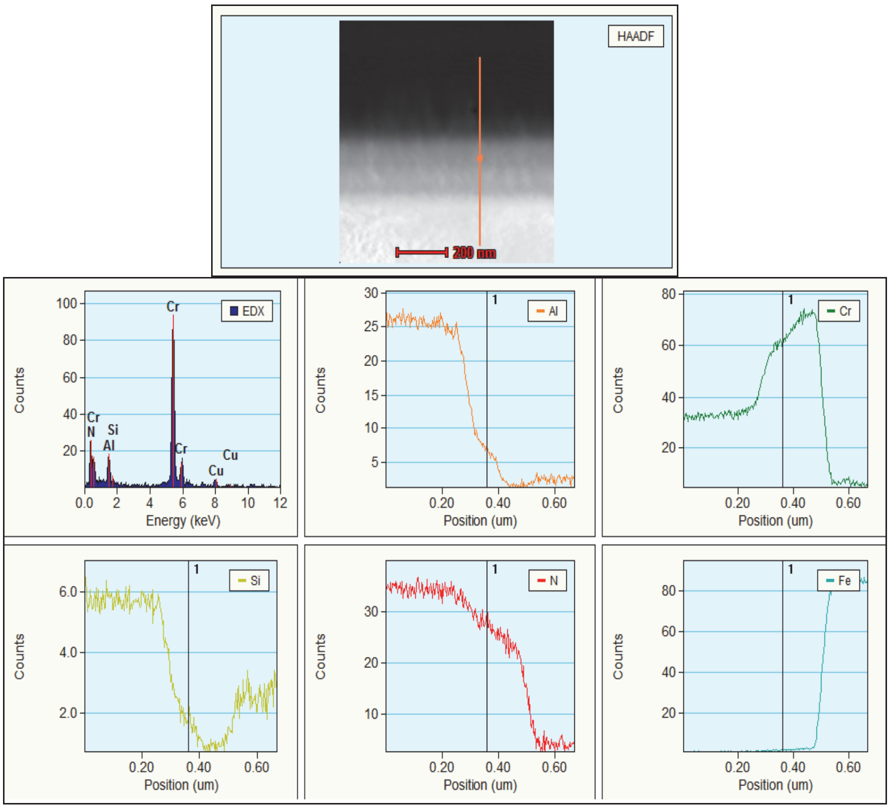

Fig. 8. STEM-HAADF image of transition zones in AlCrSiN coatings formed on X40CrMoV5-1 steel substrate with EDS spectrum of the marked line

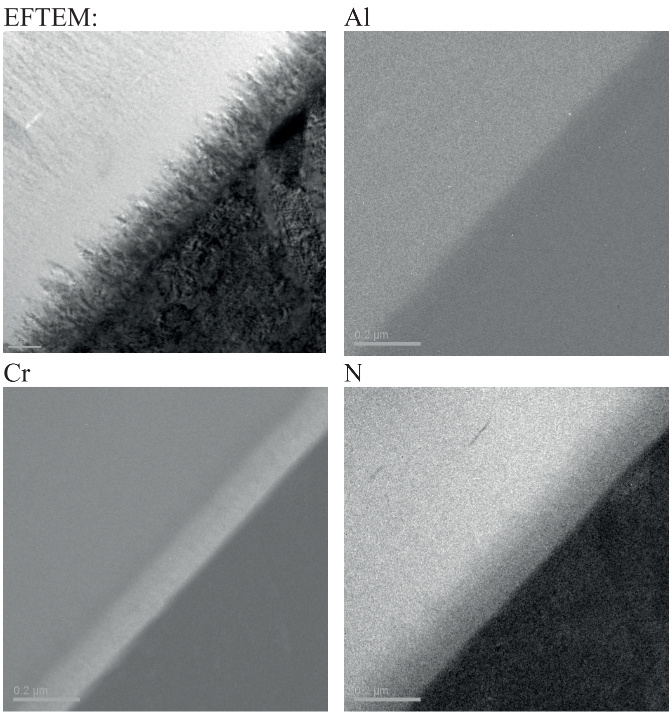

Fig. 9. Structural EFTEM images with elemental sensitivity obtained for transition zones existing in AlCrSiN coatings formed on the X40CrMoV5-1 steel substrate

Fig. 10 presents AlCrSiN sublayer structure, while Fig. 11 shows a structure of a CrN and Cr sublayers which form a transition zone between the AlCrSiN layer and the substrate material. It could be observed in Fig. 10b amorphous diffraction rings of AlCrSiN layer. In the case of CrN layer, the interplanar distances marked in Fig. 11b correspond to the CrN phase. It was found, based on electron diffraction examinations, that the AlCrSiN layer has an amorphous or quasi-amorphous structure while the CrN layer has a crystalline structure.

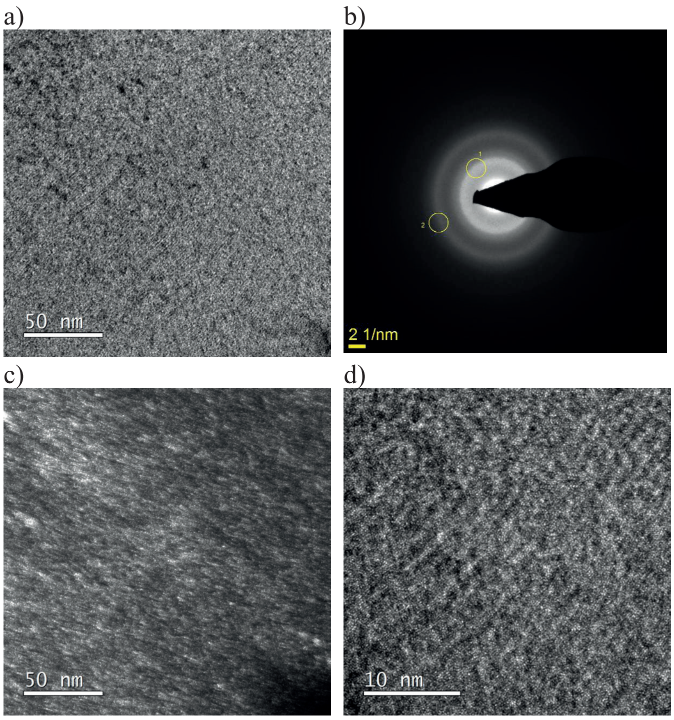

Fig. 10. Structure of the AlCrSiN-2 sublayer: a) TEM bright-field image, b) SAED pattern, c) TEM dark-field image based on reflex 1, d) HRTEM micrograph

It has been reported that nanocrystalline coatings showed excellent tribological and mechanical properties as well as oxidation resistance and thermal stability in comparison to conventional coatings [16]. The appropriate formation of the structure and properties of above mentioned coatings, their fabrication conditions and material properties must be optimised. Transmission electron microscopy (TEM) examination of the AlCrSiN coatings showed that they consisted of fine crystallites, what corresponds to the results achieved by former investigations [17].

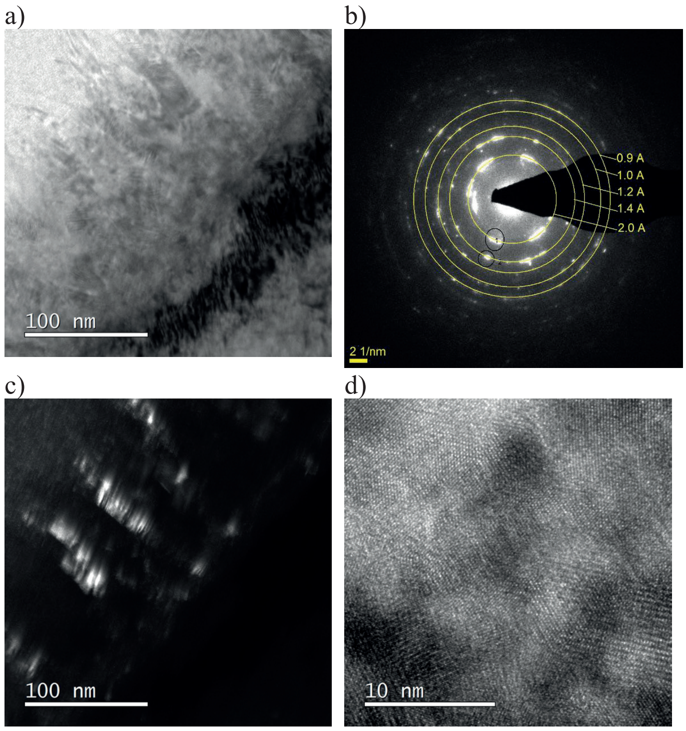

Fig. 11. Structure of the CrN sublayer: a) TEM bright-field image, b) SAED pattern, c) TEM dark-field image based on reflex (point) 1, d) HRTEM micrograph

4. Summary

AlCrSiN coating has been successfully deposited by arc-evaporation technique and investigated in detail as to their nano/microstructure. The dense microstructure of the coating without any visible delamination was observed in the scanning electron microscope. HRTEM investigation shows a nanostructure nature of AlCrSiN layer with fine crystallites while their average size is less than 10 nm. However there are also areas present in the investigated layer of quasi-amorphous nature, what was confirmed by a mind of the electro diffraction investigation. Such type of structure is difficult to determine unequivocally due to the lack of possible Bragg equation appliance, further investigation should follow using the imaging technology of high-resolution transmission electron microscope. Moreover, the investigation indicates also the occurrence of a transition zone between the substrate material and the coating, which affects the improved adhesion. A chemical composition analysis revealed an equilibrium concentration of nitride and metallic elements forming the AlCrSiN layer.

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