

## Abstract:

In this work, microstructure and properties of M-Al-(Si-)N nanocrystalline hard coatings and thin film nanocomposites deposited by cathodic arc evaporation (CAE) process at different positions of substrates in the deposition apparatus were investigated using the combination of electron probe microanalysis, X-ray diffraction, transmission electron microscopy with high resolution and hardness measurement. Six series of specimens that differed in the transition metal type (Cr, Ti and Zr) and in the amount of Si and Al were deposited using the CAE process in the deposition apparatus  $\pi$ -80 produced by Platit AG.

The essential microstructural parameters; the chemical and phase composition, the residual stress, preferred orientation of crystallites, crystallite size and mutual disorientation of crystallites were determined in all coatings under study. The derived microstructural parameters were correlated with the hardness of coatings. Finally, the microstructural model of the nanocrystalline hard coatings and thin film nanocomposites formation was developed.

Depending on the sample chemical composition, three regions with different phase compositions exist in the coatings. In the transition metal richest samples, a single fcc  $M_{1-x-y}Al_xSi_yN$  phase exists in the coating. With increasing Al content, wurtzitic-AlN starts to develop as a second crystalline phase, whereas in this region both phases, fcc and w-AlN, coexist. Finally, at the highest Al concentrations only w-AlN phase exists in the coatings. In samples containing silicon, the silicon atoms are dissolved in the fcc phase in coatings with low Si concentration and with increasing Si content they form a third, amorphous  $Si_xN_y$ , phase. The phase composition and the limits of the phases coexistence depends strongly on the transition metal type.

In all coatings under study, no residual stress and lattice parameter depth gradients as well as no shear stresses and only biaxial rotationally symmetrical compressive state of residual stress were observed. The elastic anisotropy of the fcc crystallites decreased with increasing Al and Si concentration for all samples, whereas in the Ti-Al-(Si-)N coatings the anisotropy decay was linear with increasing Al and Si and the elastic anisotropy factor  $A$  approached one and the fcc crystallites became elastically isotropic. In the Cr-Al-(Si-)N and Zr-Al-(Si-)N coatings a significantly higher influence of the Si addition on the elastic anisotropy factor relaxation and thus transition from the elastically anisotropic to elastically isotropic state of the fcc crystallites was observed. The elastic anisotropy of the fcc crystallites remained high in samples without Si even for coatings with higher w-AlN phase fraction, while in samples containing Si the elastic anisotropy factor approached 1 in samples with prevailing w-AlN contents and the fcc crystallites appeared elastically isotropic.

In all studied M-Al-(Si-)N coatings, a strong preferred orientation of crystallites was observed. In the fcc crystallites of the Cr-Al-(Si-)N and Ti-Al-(Si-)N coatings the  $\langle 111 \rangle$  crystallographic direction, and in the Zr-Al-(Si-)N samples the  $\langle 100 \rangle$  crystallographic direction was preferentially oriented perpendicular to the sample surface. With increasing Al and Si contents, the main texture direction of the fcc crystallites significantly inclined from the sample surface perpendicular direction. Besides, in the Cr-Al-(Si-)N and Ti-Al-(Si-)N coatings a pronounced three-dimensional preferred orientation of the fcc crystallites, described by coexistence of the out-of-plane and in-plane texture, was observed. The texture evolution in the fcc crystallites of studied coatings was described on basis of the deposition geometry, phase composition and residual stress and elastic anisotropy.

The cluster and the crystallite size of the investigated M-Al-(Si-)N coatings were determined from the analysis of the XRD line broadening and confirmed by the TEM and HRTEM investigations. The size of the clusters obtained from the XRD line broadening did not change significantly with the Al and Si contents. Increasing aluminium contents in the coatings caused a reduction of the fcc crystallites size and an increase of their mutual disorientation. More pronounced increase of the fcc crystallite disorientations was observed

after w-AlN appeared in the coatings. Moreover, the increasing volume fraction of the w-AlN crystallites accelerated the reduction of the fcc crystallites. The addition of silicon speeded up the reduction of the size of the fcc crystallites in the Cr-Al-Si-N and Ti-Al-Si-N coatings. At the Si contents higher than approximately 4 at.%, the mutual disorientation of fcc crystallites exceeded the limit of their partial coherence for X-rays both in the Cr-Al-Si-N and in the Ti-Al-Si-N coatings. The fcc crystallites in the Cr-Al-Si-N and Ti-Al-Si-N coatings were not partially coherent for the X-rays any more, contrary to the Zr-Al-Si-N coating which remained partially coherent even for such high silicon contents.

In all M-Al-(Si-)N samples under study, the hardness of the coatings increased with the addition of Al until a maximum was reached that was followed by a decrease of the hardness with further increasing Al contents. The Al contents, for which the maximum hardness was observed, decreased with increasing intrinsic lattice parameter of the respective binary transition metal nitride. The addition of silicon shifted the maximum of hardness slightly to lower Al concentration region in Cr-Al-Si-N and Ti-Al-Si-N coatings, while the Al concentration of the hardness maximum in Zr-Al-Si-N was nearly similar as in Zr-Al-N coatings. The samples with the maximum hardness consisted of two crystalline phases, fcc phase and w-AlN, having approximately the same volume ratio, which confirmed that the formation of the nanocomposites is responsible for high hardness of the M-Al-(Si-)N coatings deposited using CAE.

It was shown that the elementary and the phase composition, residual stress, preferred orientation of crystallites and the size and partial coherence of nanocrystallites significantly influence the hardness of coatings. A fundamental role play the elementary and implicitly the phase composition as we saw that highest hardness developed in coatings containing two crystalline phases (fcc phase and w-AlN) in which the fcc crystallites were partially coherent. In samples with partially coherent cubic crystallites the crystallites of the fcc phase and w-AlN phases are intertwined, which is needed for the transfer of the local crystallographic orientation in the coatings that is necessary for the partial coherence of cubic crystallites and that contributes concurrently to the development of the intrinsic lattice strain. The intrinsic lattice strain, that improves the hardness of coatings, results from a mismatch of the interplanar spacings in both structures (fcc phase and w-AlN) if the crystallites have an appropriate mutual orientation. In samples with non-coherent crystallites, the crystallites are separated by amorphous phase, which can neither transfer the crystallographic orientation between neighbouring crystallites nor assist in development of the intrinsic lattice deformation at the crystallite boundaries. However, a small amount of amorphous  $\text{Si}_x\text{N}_y$ , in the samples where the fcc crystallites are still partially coherent, is beneficial for the higher hardness of the coatings as well, since the amorphous phase can absorb the local strain changes that could otherwise lead to the creation and propagation of cracks in crystalline phases. This phenomenon was found to be responsible for increase of the hardness in the Cr-Al-Si-N and Ti-Al-Si-N coatings in comparison to samples without silicon. Finally, the influence of crystallite size on the hardness of coatings was obvious in all M-Al-(Si-)N samples under study.