Multilayered nanocrystalline CrN/TiAlN/MoS2 tribological thin film coatings: preparation and characterization

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Abstract. Nanocrystalline multilayer thin film coatings, composed of nanometer-scale thick CrN, TiAlN and MoS2 tri-layer systems, were prepared by reactive co-sputtering processes. The self-lubricated multilayer coating structures were deposited by one-fold oscillating movement of substrates in front of the sputter sources. Three independently operated direct current (dc) excited unbalanced magnetrons (UM) with rectangular cathodes of TiAl alloy (50/50%), pure chromium and MoS2 were used as sputter sources. The reactive sputtering process was performed in a mixture of Ar-N2 atmosphere. Hardened high-speed-steel (HSS) and thin oxide covered Si (100) wafers were used as substrates for tribological- and microstructure investigations, respectively. According to results of the chemical composition evaluated by Auger-electron spectroscopy (AES) and microstructure investigation by cross sectional transmission electron microscopy (XTEM), the CrN, TiAlN and the MoS2 phases form practically continuous layers with large gradient transition of composition. The as-deposited CrN/ (Al,Ti)N/MoS2 coatings have shown good friction behaviour, tested at room temperature in dry sliding condition with a ball-on-disk tribometer.

1. Introduction
In the last two decades the most of surface related properties of machine components and cutting tools were improved by application of the advanced thin film coatings. Nowadays, there is technological demand for further increase of the tribo-mechanical properties of components and for elevated lifetime of tools, which claims for new functional coatings [1]. In rolling and sliding processes these goals can be realized by improving of the wear resistance and friction behavior [2].

Development of new super-hard and ultra-hard nanocomposite coatings with hardness value exceeding 40 GPa, and 80 GPa, respectively, is a great challenge both from scientific and technological point of views [3-7]. However, it is well known that hard coatings usually are characterized with high fragility and friction coefficient ranging from 0.4 to 0.9, when they are used in dry sliding conditions [8]. Therefore, not always the very hard single layer coating materials are the best ones! In many technological applications, especially in interrupted cutting operation processes, the hardness must be supplemented with high toughness. Obviously, the hardness and toughness rather contrary characteristics are hardly to be realized in a single layer coating. Recently it has been shown
that the toughness properties of multilayer thin film coatings are greatly influenced by the morphology and structure of interfaces [9-10].

Furthermore, there is an increased technological demand toward coatings with low friction coefficient ranging from 0.02 to 0.3. In this respect inclusion of lubricious solid phase material within homogeneous hard coatings was proposed by some researchers [11-13]. The well known lubricating properties of molybdenum disulfide (MoS₂) are attributed to the lamellar structure of the hexagonal crystalline phase with very high shear ability along the basal oriented planes [14-16].

Our research activity was devoted to the development of multi-layer coatings constituted from hard nanocrystalline fcc-TiAlN, fcc-CrN metastable phases and soft amorphous or nano-crystalline MoS₂ phase, prepared under well-controlled co-sputtering conditions. This paper presents the architecture design and preparation process of nano-scale multi-layered CrN/TiAlN/MoS₂ coatings, performed in graded composition. Special references on growth morphology, microstructure and main tribological characteristics of TiAIN/CrN coatings with nano-crystalline MoS₂ interlayer, will be presented and discussed in frame of the present paper.

2. Experimental procedure: The deposition system and coating architecture design

Thin film deposition processes were performed in a laboratory-scale coater unit equipped with three independently operated unbalanced magnetron (UM) sputter sources. Details of the sputtering system used in present experiments were reported elsewhere [17, 18]. High purity planar rectangular targets (PLANSEE GmbH. products) served as cathodes of the dc excited glow discharge plasma. The targets were TiAl binary alloys composed of 50 at.% Ti and 50 at.% Al, pure chromium and MoS₂. The closely arrangement of magnetically coupled sputter sources gives opportunity to develop a gradient transition between the adjacent nano-layers in which the element composition is changing continuously.

Rectangular flat pieces of hardened high-speed-steel (HSS) specimens (15 mm x 30 mm size) were polished to surface roughness Rₐ ≤ 10 nm and were used as substrates for tribological- and mechanical tests. Thin oxide covered Si (100) mirror-like wafers were used as substrates for microstructure investigations. Prior to starting of the coating experiments the vacuum chamber was evacuated with a turbo-molecular pump to a base pressure of ≤2·10⁻⁴ Pa. The substrate surfaces were plasma-etched in argon atmosphere at 0.8 Pa pressure. The deposition processes were performed in an Ar-N₂ mixture at a constant working pressure of 0.19 Pa.

In an attempt to optimize the architecture of self-lubricated coatings, the nanometer-scaled multi-layer structure of CrN/(Ti,Al)N/MoS₂ coatings was considered. Sequences in preparation process for the development of self-lubricated tribological coating with low Cr content and high MoS₂ content (sample S₄₈), are shown in Table 1.

Table 1. The architecture design of the CrN/TiAlN/MoS₂ coating developed in nano-scale multilayer structure, prepared at pₐ=1.5x10⁻³ Torr pressure, qₐ₆=6.0 sccm, qₐ₇=7.5 sccm flow rate and substrate temperature Tₛ=350 °C.

| Sample | Sequences in coating preparation | Power of magnetron sputter sources (W) | Layer thickness (nm) | Substrate bias (V) |
|--------|---------------------------------|----------------------------------------|----------------------|-------------------|
| S₄₈    | 1. Cr (homogeneous)             | 500 Cr                                  | 500                  | -70               |
|        | 2. Cr→CrN (increasing N flow rate) | 500 Cr                                  | 200                  | -70               |
|        | 3. CrN (homogeneous)            | 500 Cr                                  | 200                  | -70               |
|        | 4. CrN→TiAlN (co-sputtered bi-layer system) | 300 Cr, 500 TiAl                     | 400 nm, with 4 nm period | -70               |
|        | 5. CrN→TiAlN→MoS₂ (co-sputtered tri-layer system) | 300 Cr, 500 TiAl, 600 MoS₂ | 4000 nm, with 8 nm period | -70               |
The sketch of the un-interrupted deposition of multilayer coating system to be evolved during of the growth process, and TEM image detail of the prepared nano-scale multilayer structure of CrN/TiAlN/MoS2 coating, shown upon cross section of the selected sample S_48, can be seen on Figure 1.

Figure 1. Top view of the magnetron arrangement and sketch for illustration of the un-interrupted deposition of CrN/TiAlN/MoS2 layer system. Cross-sectional TEM image detail of the coating microstructure is shown for the selected sample, S_48.

The main process parameters and the evaluated properties of self-lubricated multilayer coatings are listed in Table 2. In frame of this paper only the highlighted sample (S_48), characterized with moderate hardness and low friction coefficient, will be discussed in more details.

Table 2. Preparation parameters and evaluated properties of self-lubricated multilayer coatings: sputtering power $P_s$, substrate bias $U_s$, coating thickness $d$, micro-Vickers hardness $H_V$

| Sample ID | Composition of (Ti,Al) alloyed target | $P_{TiAl}$ [W] | $P_{Cr}$ [W] | $P_{MoS2}$ [W] | $U_s$ [V] | $d$ [μm] | $H_{V0.05}$ [GPa] |
|-----------|--------------------------------------|---------------|-------------|----------------|----------|----------|-----------------|
| S_33      | TiAl (50:50 %)                       | 500           | 300         | 400            | -90      | 5.7      | 7.88            |
| S_36      | TiAl (50:50 %)                       | 500           | 500         | 100            | -90      | 5.4      | 17.64           |
| S_48      | TiAl (50:50 %)                       | 500           | 300         | 600            | -70      | 5.5      | 7.84            |

In order to increase the coating adhesion to the substrate surface about 500 nm thick pure chromium adhesion-layer was deposited by ion sputtering in Ar atmosphere of the chromium target at a controlled discharge power of 500 W. In the next step about 200 nm thick Cr(N) transition layer was reactively deposited with the same sputtering power of the Cr target, while N2 flow rate was continuously increased up to 7.5 sccm and the argon gas flow rate was kept constant at 6.0 sccm. As a next sequence of the deposition process, a 400 nm thick CrN/TiAlN nano-scaled bi-layer system with 4 nm period was deposited by oscillating movement of the substrates in front of both Cr and TiAl sputter sources, respectively. During the deposition of about 4 μm thick top-coating composed of
hundreds of nano-scale CrN/TiAlN/MoS$_2$ tri-layer system with 8 nm period, the substrate holder was continuously oscillated in front of each of three active sputter sources (Figure 1). In the experiments the discharge plasmas have been independently excited by automatic power control of each sputtering sources.

3. Results and discussions

3.1. Coating morphology and microstructure
The as-deposited thin film coatings were investigated in microstructure by using of a conventional 100kV JEOL 100U and a 200kV CM 20 Philips transmission electron microscope (TEM). The specimens were prepared for cross-sectional imaging by using of a high energy ion beam thinning unit (Technoorg-Linda IV/H/L). All samples listed in Table 2 displayed a dense and homogeneous surface morphology for top-coatings, when were studied in transmission electron microscope (TEM). Microstructure TEM investigation of the selected sample S$_{48}$ clearly shows the well distinguishable layer regions (Figure 2).

![Figure 2](image)

**Figure 2.** Transmission electron microscope cross-sectional image of sample S$_{48}$, showing up the microstructure morphology of the nano-scale layered CrN/TiAlN/MoS$_2$ coating. The enlarged inset picture shows the ordered crystalline domains of MoS$_2$ nano-lamellae separated by a dense nanocrystalline structured TiAlN/CrN layers.

The bright-field (BF) TEM image indicates that microstructure of the nano-scale layered CrN/TiAlN coating is columnar. The structure morphology of CrN/TiAlN bi-layer system with about 4 nm period could be observed only at a higher magnification of the XTEM image. The top of columns are pyramidal faceted, which results a wavy-like surface topography for the later deposited nano-scale layered CrN/TiAlN/MoS$_2$ tri-layer system.

The wavy-like ordered domains of the solid lubricious MoS$_2$ phase with nano-lamellar crystals are clearly seen on the enlarged cross-sectional TEM image (inset picture of Fig. 2). The lamellae of ordered MoS$_2$ nano-crystals are normally oriented to the growth direction, while they locally follow the surface topography of the nanocrystalline CrN/TiAlN under-layer system.

The length of the slightly curved nano-lamellae is in the order of lateral distances limited by the boundaries of adjacent columns. The distance of adjacent lamellae in the ordered MoS$_2$ nano-crystals is 0.68 nm, corresponding to the (002) lattice spacing of 2H-MoS$_2$ crystals. Selected area electron diffraction pattern (SAED) taken from B zone of the coating with CrN/TiAlN/MoS$_2$ tri-layer system, displays diffuse diffraction rings. The segments on the slightly diffuse continuous rings originate from
the very fine grains found in the dense nanocrystalline structured TiAlN-CrN compound layers. These layers are sandwiched between two ordered domains of nanolayered MoS\(_2\) crystalline layers. The two bright spots on SAED pattern, closely situated in the near vicinity of the main spot of the centrally incident electron beam, indicate that the directionally ordered wavy-like lamellar nanocrystalline MoS\(_2\) domains are the main structural components of the coating.

In-depth distribution of the chemical components of the CrN/TiAlN/MoS\(_2\) tri-layer system deposited in a dedicated model experiment was evaluated by Auger electron spectroscopy (AES) analyses. Measuring results of the AES analysis demonstrated experimentally that the adjacent layers were strongly interconnected with compositionally graded large interfaces (not shown here).

3.2. Mechanical and tribological characteristics

Our developed CrN/(Al,Ti)N/MoS\(_2\) multilayer coatings offered well controllable mechanical and tribological characteristics. The influence of the substrate was negligible at a relative indentation depth of RID=0.2 - 0.3. The measured hardness values, shown in Table 2, indicate a well correlated dependence with MoS\(_2\) contents of the CrN/TiAlN multilayered coatings. The micro-hardness values of the CrN/(Al,Ti)N/MoS\(_2\) multilayer coatings were obtained by using a CV-400 AAT type hardness tester unit equipped with pyramidal Vickers-type diamond indenter tip. By optical imaging of the residual plastic imprint area measured at 50 g loading and 10 s holding time, a hardness value of HV\(_{\text{pl}}\)=7.84 GPa was determined for the CrN/(Al,Ti)N/MoS\(_2\) multilayer coating of sample S\(_4\,8\). The moderate hardness value evaluated for the coating prepared with low chromium (300W) and high MoS\(_2\) content (600W) can be associated to very low intrinsic hardness value of the crystalline MoS\(_2\) phase (∼0.58 GPa), as the main phase component in the multilayer coating of sample S\(_4\,8\).

Nano-hardness and elastic modulus of CrN/TiAlN/MoS\(_2\) coating were calculated from the recorded load-displacement nano-indentation curves. Berkovich-type diamond tip indenter was used and indentation hardness value of \(H = F_{\text{max}} / A_p\) =5300 N/mm\(^2\) was experimentally found. Assuming that deformation upon unloading is purely elastic, and following the Oliver and Pharr data analysis method [19], the elastic indentation modulus, defined as \(E/(1-v^2)\), has been calculated with a Poisson’s ratio of 0.23. The Young’s modulus evaluated for the CrN/TiAlN/MoS\(_2\) coating, \(E\)=125 GPa, is much reduced as compared with Young’s modulus of the hard nanocrystalline CrN and (Al,Ti)N phases, \(E\)=340 GPa and \(E\)=460 GPa, respectively.

Sliding friction coefficient was evaluated for CrN/TiAlN/MoS\(_2\) coatings, following the ball-on-disc test method. In the wear processes the as-deposited coatings prepared on HSS substrates and hard counter materials of 100Cr6 steel balls with 6 mm in diameter and Si\(_3\)N\(_4\) balls of 4.8 mm in diameter were used, respectively. The friction tests, by using a ball-on-disk tribometer (DTHT70010 type CSM Instruments), performed at 5N normal load for 50 mm/s continuous sliding speed at room temperature and dry sliding condition, have shown friction coefficient values ranging from 0.08 to 0.2.

It is noteworthy that faceted columns of the CrN/TiAlN bi-layer system results a roughened surface topography that is going to be covered by the condensing CrN/TiAlN/MoS\(_2\) tri-layer system. The solid lubricant MoS\(_2\) phase will be trapped on the uneven surface in the groves of the column boundaries. Thereupon it will be released slowly as wear-reducing lubricant material, contributing to significant decrease of the friction coefficient between the sliding surfaces.

4. Conclusions

In the present arrangement of the sputter sources the growth surface of the coating continuously receives material flux and growth process is never interrupted. A nano-scale multilayer CrN/TiAlN/MoS\(_2\) coating structure was successfully developed, where the interface between the individual stacking layers was not sharp due to a large intermixing of co-deposited atoms. The developed transition zone could promote the better matching between the lattices of the sequentially deposited triple-layer structure. The growth of the columnar CrN and TiAlN crystals is interrupted by the co-deposition of MoS\(_2\) species. The nano-crystalline CrN and TiAlN phases of the coating are
sandwiched by hexagonal crystalline phase of MoS$_2$, where the 002 basal planes are mainly surface oriented. The platelets nature of the MoS$_2$ phase follows the growth surface locally, with a growth tendency for evolution of inorganic fullerene-like structures. This is a requirement for a low friction condition due to the effectiveness of surface oriented shear forces. A steady-state friction coefficient was established after a run-in sliding whilst a “transfer film” of MoS$_2$ layer has to control the friction behavior at the interface due to its low-shear planes terminated in sulfur atoms. The detailed analyses of the crystallographic structure of the presented multilayer systems and their dependence on the deposition parameters are in progress.

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