Nanolaminated TiN/Mo2N hard multilayer coatings

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Abstract. The paper presents results on the synthesis of hard multilayer coatings consisting of titanium nitride and molybdenum nitride thin films with thickness of several nm. The TiN and Mo2N films were successively deposited by reactive DC magnetron sputtering. These multilayer structures were investigated by Auger electron spectroscopy (AES), transmission electron microscopy (TEM), selected area electron diffraction (SAED), X-ray diffraction (XRD), cross-section scanning electron microscopy (CSSEM) and cross-section electron probe microanalysis (CSEPMA). The mechanical properties of the multilayer coatings, namely, hardness, Young’s modulus and the coefficient of plastic deformation were measured. The adhesion was evaluated by the Rockwell-C-impact test. Coatings with different total thickness were examined with respect to adhesion to substrates of tool materials.

1. Introduction
Multilayer coatings of alternatively ordered thin films of transition metal nitrides with nanoscale thickness are known to have hardness superior than that of a single film. Different physical mechanisms have been proposed to explain this effect. The decisive role has been assigned to the phenomena occurring at the interface region of the thin composing films. The dislocation blocking at this region is considered as the most important mechanism governing the properties of the coatings. The idea of composite hardness introduced in [1] may be used only as an overall suggestion for explanation of the advantageous effect observed. A deeper understanding of the nature of the processes at the interfaces is needed in order to produce better coatings and for a more complete utilization of the hard nanolaminated structures. The thickness of the interfaces usually increases at elevated deposition temperatures due to interdiffusion of the elements involved. This effect causes undesirable deterioration of the coating properties and can be avoided to a great extend by keeping the deposition temperature as low as possible. Multilayer coatings of different materials deposited at relatively low temperatures by magnetron sputtering and other physical vapor deposition (PVD) methods possess high-quality mechanical properties [2-5]. Multilayers consisting of pairs with varying thickness period showed that the best mechanical characteristics were obtained at a period of about 10 nm or more [6-8].

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The TiN/Mo₂N multilayer system has not yet been well studied although some preliminary investigations performed have shown the potential for its utilization [9]. In this work we investigated in detail the compositional, structural etc. characteristics of hard TiN/Mo₂N multilayer nanolaminated structures. The mechanical properties and adhesion of the coatings were of primary interest.

2. Experimental
The TiN/Mo₂N multilayer structures (MLS) were deposited by reactive DC magnetron sputtering. The deposition was carried out in a high vacuum system with pure Ti and Mo magnetron targets assembled on water cooled holders. Magnetron discharges in an Ar and a mixed Ar/N₂ gas atmosphere were utilized for the two process regimes: pretreatment of the substrate surface by high-pressure discharge prior to deposition and multilayer structure growth. The substrates temperature during the deposition was maintained at 360 ⁰C. Substrates of high-speed steel (marked as R18) and of a sintered hard alloy of TiC and WC with Co as a binding element (marked as KM1) were used. The process parameters are shown in tables 1 and 2.

Several deposition series of MLS with different thickness were grown: 2×5 TiN/MoN MLS (total thickness of 115 nm), 2×10 TiN/MoN MLS (total thickness of 230 nm) and 2×60 TiN/MoN MLS (total thickness of about 1300 nm).

Table 1. Substrates pretreatment parameters.

| Discharge gas | Discharge pressure, Pa | Discharge voltage, V | Discharge current, A | Substrate temperature, ⁰C | Treatment time, s |
|---------------|------------------------|----------------------|----------------------|---------------------------|-------------------|
| Argon         | 4.0                    | 1200                 | 0.1                  | 300 - 320                 | 600               |

Table 2. Film deposition parameters.

| Film Material | Process pressure, (N₂/Ar), Pa | N₂ partial pressure, Pa | Discharge Voltage, V | Discharge current, A | Deposition temperature, ⁰C |
|---------------|--------------------------------|-------------------------|----------------------|----------------------|---------------------------|
| TiN           | 1.2×10⁻¹                       | 4.5×10⁻³                | 460                  | 1.0                  | 360                       |
| Ta₂N          | 1.2×10⁻¹                       | 4.0×10⁻²                | 580                  | 0.8                  | 360                       |

Auger electron spectroscopy (AES) and X-ray diffraction (XRD) were utilized to investigate the compositional and structural characteristics of the TiN films. These investigations were performed in previous experiments in order to optimize the process parameters to achieve the strongest adhesion of the TiN films to substrates [10] as the deposition runs of MLS started with a TiN film. The AES analysis was performed in a derivative mode by a cylindrical mirror analyzer with a relative resolution of 0.6 %. A primary electron beam (3 keV, 5 µA) at normal incidence to the sample surface was used. Surface cleaning was carried out with a focused Ar ion beam (current density approx. 60 µA/cm²; ion energy of 3 keV). X-ray diffraction patterns were obtained using a Philips X-ray diffractometer in the Bragg-Brentano geometry with Cu-Kα radiation. The data were collected for different aperture sizes, scanning steps and scanning times to achieve a maximum clarity of the analysis.

The microstructure and the crystallization trend of the films were studied by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) using a Philips 400 electron microscope. The films were deposited on fresh fractured surfaces of NaCl crystals.

Cross-section scanning electron microscopy (CSSEM) and cross-section electron probe microanalysis (CSEPMA) were performed on the 2×60 TiN/MoN ML structure for qualitative investigation of the elemental content of the multilayer structure as well as to evaluate its thickness.

The mechanical properties were measured by a Fischerscope H100 nanotester loaded with 20 mN.

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The adhesion of MLS with different thickness to the substrates was measured by Rockwell-C Indentation Test.

3. Results and discussion
The composition of the TiN films was evaluated by AES analysis. Problems of peak overlapping of the N(KLL) and Ti(L\textsubscript{3}M\textsubscript{23}M\textsubscript{45}) Auger transitions as well as Auger peak shape changes due to chemical effects make the interpretation of the Auger spectra difficult. In this study we used a comparative analysis with data obtained from a previous AES analysis of titanium nitride films implemented in direct and derivative modes [11]. The composition of the films was evaluated with an uncertainty of about 10%. Figure 1 presents an AES spectrum recorded after the removal of contaminants, mainly carbon, from the film surface. The composition of the film was evaluated as near stoichiometric.

The phase composition and crystallographic features of the Ti\textsubscript{N} films were investigated by XRD. Figure 2 shows the diffraction pattern of a film deposited at optimized conditions over a broad range of 2\textdegree\textsubscript{θ}, from 5 to 95 degrees, using a Ni filter, a step of 0.03 degrees and a scanning time of 0.5 s/point. This spectrum reveals the presence of \(\delta\)-Ti\textsubscript{N} (as a dominant phase) and \(\varepsilon\)-Ti\textsubscript{2}N phases in the film (together with peaks originating from the substrate). This XRD analysis also shows that the films grow preferentially along the (200) crystallographic direction of the fcc (face-centered cubic) \(\delta\)-Ti\textsubscript{N} phase. The lattice parameter of the \(\delta\)-Ti\textsubscript{N} phase evaluated from the main \(\delta\)-Ti\textsubscript{N} (200) peak is 0.425 nm which is slightly higher than that of bulk stoichiometric titanium nitride (0.424 nm [12]).

The TEM observations show that the Ti\textsubscript{N} films are relatively homogeneous with a certain tendency for agglomeration and chain formation. This appears in combination with the uniformly distributed nano-crystals with size varying in the narrow range between 30 and 50 nm. This mono disperse structure corresponds to a polycrystalline character (figure 3). As revealed by the SAED patterns, there exists some tendency towards texturing that could be assigned to the chain formation registered. The Mo\textsubscript{2}N films are more homogeneous and also possess a polycrystalline mono-dispersed structure. In this case, the size of the uniformly distributed nano-crystals vary from 50 to 100 nm (figure 4). The SAED patterns confirm the presence of a crystalline Mo\textsubscript{2}N phase.

Figure 5 presents the scanning electron microscopy image of cross-section of the 2\times60 Ti\textsubscript{N}/Mo\textsubscript{2}N MLS deposited on a Si substrate together with the electron probe microanalysis of the same cross section. The thickness of the nanolaminated structure was precisely measured. The EPMA pictures give a quantitative idea for the elemental content of the structure, namely, X-ray emission from a Si substrate and from Ti and Mo atoms superimposed on a large background.

The mechanical properties of the nanolaminated multilayer structures grown on substrates of tool materials are shown in table 3. The same characteristics of the substrates are presented in the table for comparison. The MLS coatings hardness is about 30 % higher than that of single Ti\textsubscript{N} films and 20 higher than that of bulk Ti\textsubscript{N}. 

![Figure 1. AES spectrum of TiN film.](image1)

![Figure 2. XRD spectrum of TiN.](image2)
The adhesion was measured for MLS coatings with different thickness, from 100 to 1350 nm. The test shows that for thicknesses of at least 250 nm the adhesion is strong. Figures 6 and 7 present pictures of the test for coatings on steel R18 and hard sintered alloy KM1 with thickness of 120, 240 and about 1400 nm respectively for 5, 10 and 60 pairs of TiN and Mo$_2$N films.

**Figure 3.** TEM micrograph and SAED patterns of TiN thin film.

**Figure 4.** TEM micrograph and SAED patterns of Mo$_2$N thin film.

**Figure 5.** SEM & EPMA Images of Cross Section of 60x2 TiN/MoN Nanolaminated multilayer structure.

**Figure 6.** Rockwell-C Indentation Test of adhesion: TiN/Mo$_2$N MLS on R18.

**Figure 7.** Rockwell-C Indentation Test of adhesion: TiN/Mo$_2$N MLS on KM1.
Table 3. Mechanical properties of nanolaminated 60x2 TiN/Mo2 MLS on R18 and KM1.

| Sample                        | Hardness, GPa | Indentor penetration depth, μm | Young’s modulus, GPa | Full energy, nJ | Energy of plastic deformation, % | Loading force, mN |
|-------------------------------|---------------|--------------------------------|----------------------|-----------------|----------------------------------|------------------|
| 60×2 TiN/MoN MLS on R18       | 24.1          | 0.181                          | 224                  | 2.08            | 37.4                             | 20               |
| 60×2 TiN/MoN MLS on KM1       | 25.9          | 0.178                          | 366                  | 1.82            | 43.3                             | 20               |
| R18 without coating           | 10.3          | 0.295                          | 172                  | 2.53            | 63.15                            | 20               |
| KM1 without coating           | 13.4          | 0.243                          | 237                  | 1.91            | 59.04                            | 20               |

4. Conclusions

Hard multilayer coatings consisting of successively deposited TiN and Mo2N films with nanoscaled thickness were deposited at relatively low temperatures on substrates of tool materials. This two-step PVD process was successfully utilized to grow structures with high mechanical characteristics. Thick multilayer structures with thickness of 1.3 μm of cubic TiN and cubic Mo2N films showed much higher hardness compared with that of the substrate tool materials (twice as high) as well as to that of single TiN and Mo2N films (more than 40%). These favorable features of the synthesized TiN/Mo2N nanolaminated multilayer coatings make them very promising for application as hard and wear resistant coatings, biocompatible coatings etc.

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