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# THE STUDIES OF THE STRUCTURE AND PROPERTIES OF NANOSCALE MULTILAYER COATINGS BASED ON THE NITRIDES OF REFRACTORY METALS

# ŠTÚDIE ŠTRUKTÚRY A VLASTNOSTÍ NANOČASTÍC VIACVRSTVOVÝCH POVLAKOV NA BÁZE NITRIDOV NA ŽIARUVZDORNÝCH KOVOCH

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**Abstract:**
The studies of the structure and properties of nanoscale multilayer coatings based on the nitrides of refractory metals are summarized in a brief review. By the example of TiN/MoN, TiN/ZrN, CrN/MoN, obtained by vacuum-arc deposition of cathode, the dependences of their hardness, wear resistance, friction, corrosion, and oxidation on conditions of the deposition and layers thickness are investigated and analysed. There gularities of the structure and behaviour properties of such nanoscale multilayer coatings depending on the size of nanograins, textures, and stresses arising in these coatings are described.

**Key words:**
nanoscale, nanocomposite coatings, structure, wear, corrosion resistance, hardness.

## Introduction

Titanium nitride coatings have been widely accepted in a range of industrial applications with high demands on wear resistance and adhesion to the substrate. One of the most promising applications of nanomaterials is the creation of protective coatings for products and tools with different functional purposes. The increasing demands of modern engineering have spawned the development of new advanced materials for use [1, 2].

The development of advanced materials can be considered to be a typical problem of engineering optimization. Such material characteristics as hardness, elasticity, adhesive and cohesive strength, durability, thermal and chemical stability and others are particularly important in this regard. Results of scientific researches show the tendency of active use of nitrides and borides of transition metals and their combination in the development of protective materials [1].

While nitrides of single elements are studied well enough, their multilayer modifications need study that is more detailed. Therefore, the study of features of structure, elemental and phase composition of multilayer coatings depending on the deposition conditions is an important task in solid-state physics and materials science. By the example of TiN/ZrN, MoN/CrN obtained by vacuum-arc deposition of cathode, the dependences of their hardness, wear resistance, friction, corrosion, and oxidation on conditions of the deposition and layers' thickness are investigated and analysed. The regularities of the structure and behaviour properties of such nanoscale multilayer coatings depending on the size of nanograins, textures, and stresses arising in these coatings are described.

The multilayer structures called super lattices demonstrate entirely different behaviour than one layer solid films [2]. The studies of the tribological behaviour of such coatings demonstrate that they are superior in wear resistance, cracking and strength as compared with the one layer films. These novel physical properties of super lattices open new possibilities of their application where very important is wear resistance of rubbing elements. They could be deposited using different techniques and are still one of the most popular hard coatings in industry. The presented research work is focused on fabrication and examination of tribological nanocrystalline TiN/ZrN and MoN/CrN multilayer coatings.

**Research methodology**

Development methods of multicomponent nanocomposite coatings properties evaluating is based on application of different physical models. Comprehensive studies of the tribo-films (dissipative structures) formed on the friction surface were made using a number of advanced surface characterization techniques such. The study of the morphology of the samples is possible using a scanning electron microscope JEOL JSM -7000 F (Field Emission Scanning Electron Microscope) and EDX analysis in Institute of Materials Research of Kosice.

**The preliminary results**

We have observed the microstructure and chemical composition of the investigated coatings after impulse-plasma processing (table 1). The images of the investigated multilayer coatings demonstrate that the surface structure of the film depends on the material being deposited. The superlattices MoN/CrN characterize with better flatness of the surface than TiN/ZrN. It was recognized also the effect of the substrate/underlayer on the structure of the superlattice. The same superlattice films (TiN/ZrN) deposited on different substrates/underlayer have different topographies. This reflects on the hardness of the tested superlattices. The superlattice TiN/ZrN with distinctly larger grains exhibits better uniformity of the hardness distribution than superlattice TiN/ZrN.

The researches made it possible to represent the change in the structure of complex engineered coating. The coating was a complex multilayered structure with nano-grain intergrowth within the alternating nano-layers. We clearly see layers with cubic TiN and ZrN phases (of the NaCl structure type) without preferred orientation of crystallites in the surface layers. Increasing of the $\lambda$ period led to increasing of the TiN layers specific contribution. It is seen from the changes in the intensity of the peaks of TiN and ZrN phases. Increasing of the deposition time and, as a result, bilayer thickness as well as total period of the multilayer system led to changes of the lattice period of nitride phases in the layers. Lattice period decreased with increasing of the TiN-layers’ thickness from 0.4241502 nm (deposition time was 20 sec, $\lambda \approx 70$ nm) to 0.4238870 nm (deposition time was 40 sec, $\lambda \approx 250$ nm). Changes for ZrN layers were not so large: from 0.4581055 nm (deposition time—20 sec) to 0.4581046 nm (deposition time was 40 sec).

This coating had a number of tuned characteristics, such as improved micro-mechanical properties and high oxidation stability which were integrated in a way to work in synergy. This complex nano-multilayered coating structure results in improvement of some micromechanical properties and promotes beneficial tribo-chemical reactions on the friction surface.

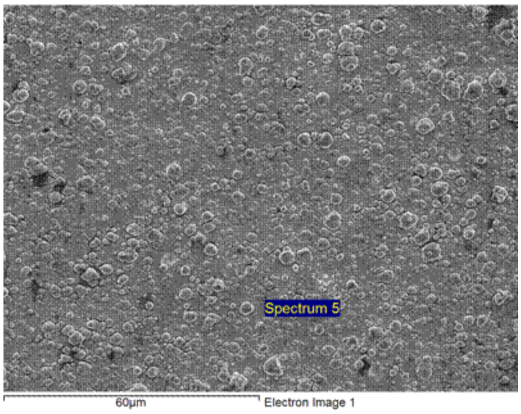
**Table 1** SEM images of coated sample and chemical composition of the investigated

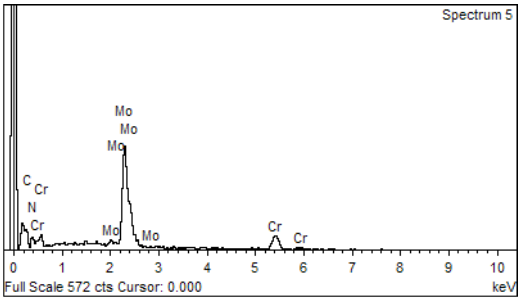
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :
C CaCO3 1-VI-1999 12:00 AM
N Not defined 1-VI-1999 12:00 AM
Cr Cr 1-VI-1999 12:00 AM
Mo Mo 1-VI-1999 12:00 AM

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 12.07 | 36.21 |
| N K | 10.67 | 27.45 |
| Cr K | 23.09 | 16.00 |
| Mo L | 54.17 | 20.35 |
| Totals | 100.00 | |



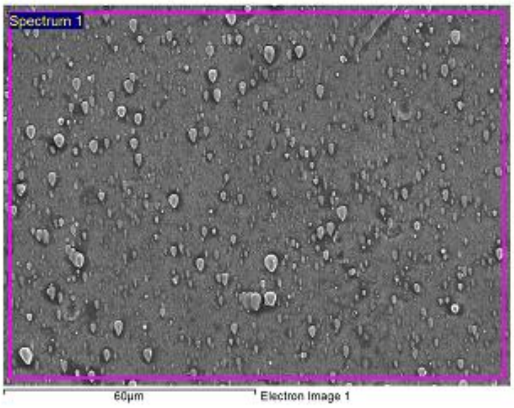

EDX spectrum of MoN/CrN coating

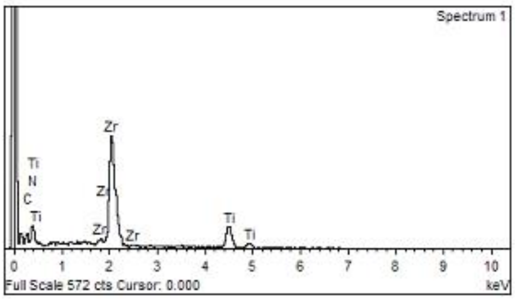
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 4

Standard :
C CaCO3 1-VI-1999 12:00 AM
N Not defined 1-VI-1999 12:00 AM
Ti Ti 1-VI-1999 12:00 AM
Zr Zr 1-VI-1999 12:00 AM

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 9.63 | 27.78 |
| N K | 14.40 | 35.62 |
| Ti K | 22.52 | 16.29 |
| Zr L | 53.45 | 20.31 |
| Totals | 100.00 | |



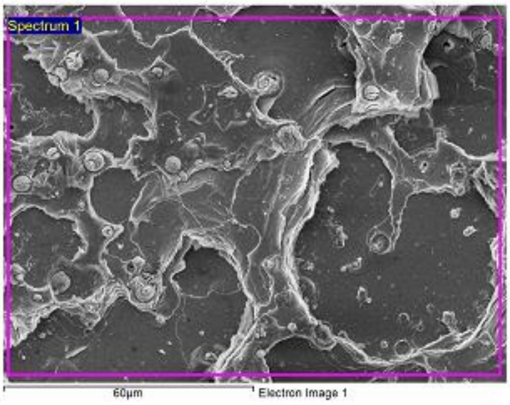

EDX spectrum of TiN/ZrN coating

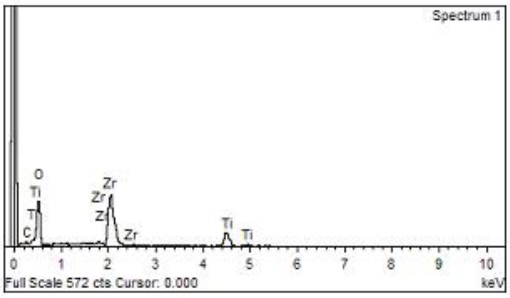
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 3

Standard :
C CaCO3 1-VI-1999 12:00 AM
O Wollastinite 27-VIII-2009 11:36 AM
Ti Ti 1-VI-1999 12:00 AM
Zr Zr 1-VI-1999 12:00 AM

| Element | Weight% | Atomic% |
|---|---|---|
| C K | 3.70 | 10.33 |
| O K | 27.03 | 56.76 |
| Ti K | 22.21 | 15.57 |
| Zr L | 47.07 | 17.33 |
| Totals | 100.00 | |




EDX spectrum of TiN/ZrN coating

## Conclusion

The results obtained show that it is possible to control tribo-films evolution during self-organization by means of increase in structural complexity and the non-equilibrium state of the surface engineered layer with simultaneous tuning of its integrative behaviour.

This information could be of critical importance for further advances in nano-structured adaptive coatings design for extreme tribological applications. The major feature of these coatings is the formation of the tribo-films on the friction surface which possess high protective ability under operating temperatures of 1000 °C and above. These tribo-films are generated as a result of a selforganization process during friction. This data was related to the micro-mechanical characteristics of the coating layer and its wear resistance.

Presented results are an intermediate stage of our work in the field of development and study of nanoscale multilayer coatings formed from refractory metals. The present results suggest the prospect of obtaining and studying such nanoscale nitride multilayer nanostructured coatings in the near future.

**References**

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