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Morphological and compositional investigations of the tribological coatings with quaternary & pentanary composition, obtained from *WC*, *TiB_2* and *Ti* by DC standard & reactive magnetron sputtering

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This work presents the first results of the morphological and compositional investigations for the tribological coatings with monolayer and multilayer-type structure with a complex composition that was not researched yet and that was deposited by standard and reactive DC magnetron sputtering, starting from 3 basic materials: WC, TiB_2 and Ti. First sample (1) is a multilayer with pentanary composition (*Ti-W-C-B-N*), deposited in one set of three successively layers *($Ti_xN_y/Ti_xB_yN_z/W_xC_yN_z$*. The second sample (2) is made of one layer of three compound materials *($Ti_xN_y+Ti_xB_yN_z+W_xC_yN_z$)* with pentanary composition by simultaneously magnetron sputtering. The third (3) sample is a monolayer with quaternary composition *(Ti-W-C-B)*, obtained by simultaneously sputtering of three materials *(Ti+TiB_2+WC)*. Surface topography, roughness and section analysis of the three coating surface layers are examined by Atomic Force Microscopy (AFM) method. Composition of the three samples is investigated by the Rutherford Backscattering Spectrometry (RBS). The AFM characterizations prove that the grain size and the roughness have lower values for the coating un-doped with N_2 than for the coatings deposited with N_2 as reactive gas. All the samples show very fine nanostructure. RBS investigations give the composition of each deposition and prove that all the coatings are non-stoichiometric complex compounds.

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1. Introduction

The essential problem of all the mechanical systems *(friction couples)* that generate noise, heating and premature failure by wear is friction, characterized by the coefficient of friction (COF), dynamic and static [1-3]. Friction is the key parameter involved in the power transfer process in mechanical systems related to the *military, energetic, automotive, aircraft, airspace, etc. industries*. The COF is the essential parameter of the tribological coatings and it is strongly influenced by the morphological and compositional properties of these coatings [4].

The energy losses due to friction in the industrialized countries are estimated at an annual cost of 5-7% of their Gross Domestic Product [5].

According to the Derjaguin Friction Theory the adhesion component of the friction force that determines the real COF is strongly influenced by the roughness of the coatings [6-7].

The roughness of TiB_2 coatings with Ti interlayer (Ti-TiB_2) deposited by magnetron sputtering, was investigated by N. Panich et al. using AFM [8] and it was shown that average roughness (R_a) was reduced from 6.95 nm to 0.81 nm with increasing of N_2 content in argon-nitrogen gas mixture from 0 to 50 %. Also, the same author shows that R_a increase from 2.33 nm – for 2 layers of Ti/TiB_2 at 20.61 nm for 12 layers of Ti/TiB_2 [9].

The influence of the annealing temperature to the grain size of the coatings with ternary (Ti-W-B) and quaternary (Ti-W-Cr-B) composition, obtained by magnetron sputtering was investigated by Al. Nevirkowez et al. [10] and it shows that lattice constant of the TiC and CrC6 phase of the coatings (and grain size, also) increase from 4.257Å at 700 ^{0}C to 4.304 Å at 1100 ^{0}C - annealing temperature.

The composition of the ternary (Ti-B-C-N) coatings *(with 1 μm TiBC single layer and with 1 μm TiBC - 15 min. /BC multilayer - 5 min.)* was investigated by V. Gorokhovsky et al. using RBS and EDS *(Energy Dispersive Spectrometry)* methods [11]. According to their results RBS and EDS techniques show similar results when coating thickness is higher than 1μm. It can be seen that RBS method provides better resolution of light elements than EDS [11].

For a given tribological application with given working and environment conditions *(temperature, pressure, contact load, sliding or rotating speed, presence of corrosive gases, etc.)* the correct coating type in terms of Deposition Methods and types of Materials used must be chosen, because the response of a coated system *(friction couple)* depends on the following factors: 1. substrate properties *(roughness, hardness, toughness, cleaning state before deposition)*; 2. counterpart properties *(roughness, hardness, toughness, friction coefficient);* 3. coating properties *(hardness, toughness, porosity, thermal oxidation resistance, chemical corrosion resistance)* that mainly depends on the used deposition method; 4. interface substrate-coating properties *(adhesion)*; 5. interface counterpart-coatings *(friction coefficient, hardness, toughness, porosity, thermal oxidation resistance, chemical corrosion resistance)* [12-15].

The Deposition Methods and type of Materials used have a grate influence on friction couple, for: working life time, respectively wear resistance and financial cost [12].

2. Experimental procedures

2.1 Material and process parameters

Materials: Ti, TiB_2 and WC sputtering targets.

Substrate: ultrasonic cleaned and plasma activated Si. The substrate was heated at 550 °C and the bias voltage was set at 0.5 kV during deposition, in order to obtain a better adhesion to the substrate, lower values for grain size and roughness for the investigated samples.

Deposition method: Multifunctional vacuum thin film deposition system with four DC sputtering magnetrons *(guns)* of 600 W maximum power.

Reactive gas used was N_2 while Ar was used as the working gas. This method allows the deposition of the multilayer in one working experimental cycle.

For this study a set of three samples were investigated. Deposition of the structures with quaternary *(Ti-W-C-B)* and pentanary *(Ti-W-C-B-N)* composition was as it follows:

- Sample no. 1 – one package with pentanary composition, 3 layers (Ti_xN_y/ $Ti_xB_yN_z$/ $W_xC_yN_z$);
- Sample no. 2 – one layer with pentanary composition (Ti_xN_y+ $Ti_xB_yN_z$+ $W_xC_yN_z$);
- Sample no. 3 – one layer with quaternary composition *(Ti+TiB_2+WC)*.

The working process parameters of the DC magnetron sputtering deposition method used for obtaining the above samples are presented in Table 1.

Table 1. Deposition parameters of the tribological coatings.

Sample No.	Deposited layer	Working gases		Pressure [mbar]	Power injected on the plasma [%P_{max}]	Deposition time [min]
		Ar [sccm]	N_2 [sccm]			
1	Ti_xN_y/	100	40	$2.8x10^{-3}$	15	25
	$Ti_xB_yN_z$/	150	40	$3.1x10^{-3}$	30	25
	$W_xC_yN_z$	150	40	$3.1x10^{-3}$	30	25
2	Ti_xN_y+ $Ti_xB_yN_z$+ $W_xC_yN_z$	150	40	$3.5x10^{-3}$	15	30
					30	
					30	
3	Ti + TiB_2 + WC	150	0	$3.2\ x10^{-3}$	15	30
					30	
					30	

2.2. Characterization methods

The morphological and compositional characteristics were investigated by Atomic Force Microscopy *(AFM)* and Rutherford Backscattering Spectrometry *(RBS)*.

Topography and grain size were obtained using AFM. The AFM used in the present study was a MultiMode NanoScope IIIa Controller microscope *(Digital Instruments Veeco Metrology Group, Santa Barbara, CA, USA)* equipped with a 125 x 125 x 5 μm^3 piezoelectric scanner. Images were obtained in tapping mode (TM) in air using a TESP *(0.01-0.025 Ohm-cm Antimony (n) doped Si)* tip at a scan speed of 1 Hz at 512 pixels per line scan. Acquisition and offline analysis were performed using 531r1 NanoScope software and SPIP 6.0.9 software from Image Metrology. Images were processed by first order flattening to remove any background tilt [16-18].

RBS measurements were performed with a beam of $^4He^{2+}$, having energy of 3.065 MeV obtained at the 3 MV Tandetron™ accelerator from IFIN-HH [19]. The energy of backscattered particles was measured by an ORTEC silicon detector positioned at a scattering angle of 165˚ with respect to the beam direction. The detector solid angle was 1.64 $x10^{-3}$ sr and the beam spot size on the target was 1x1 mm^2. The detector resolution for 3 MeV ^4He ions was about 18 keV. The simulation of the RBS spectra was made using the code SIMNRA v6.05 [20].

3. Results and discussions

3.1 AFM results

The AFM surface topography and section analysis of the 3 samples are presented below (Fig. 1a, b and c).

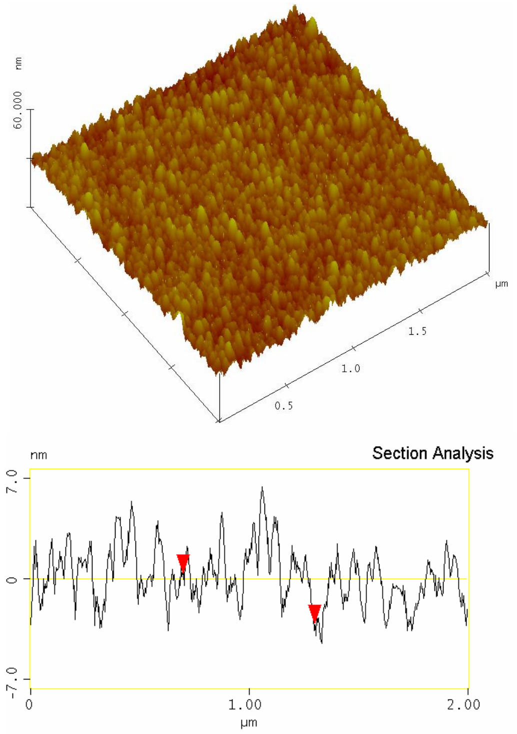

Fig. 1a. TM-AFM images showing 3D surface topography, 2x2 μm^2 and section analysis, sample no. 1

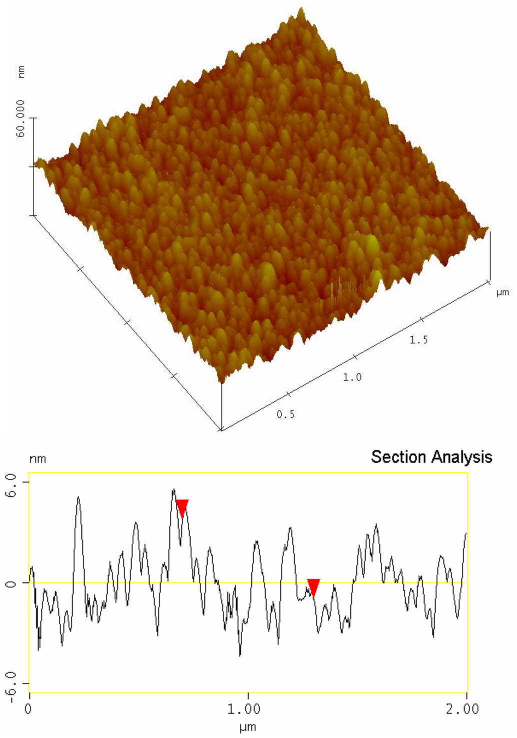

Fig. 1b. TM-AFM images showing 3D surface topography, 2x2 μm^2 and section analysis, sample no. 2.

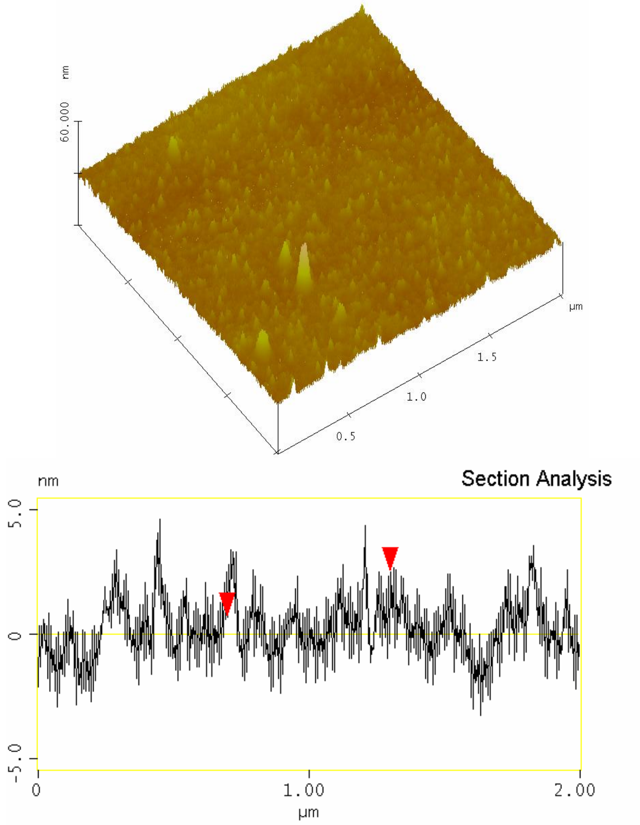

Fig. 1c. TM-AFM images showing 3D surface topography, 2x2 μm^2 and section analysis, sample no. 3

The root mean square (RMS) roughness (Rq) parameter, which represents the standard deviation of the surface heights values within a given area, was measured over the entire image using the roughness analysis option of the AFM software [21]. RMS values obtained were: 2.1 nm *(sample no. 1)*, 2.3 nm *(sample no. 2)* and 1.6 nm *(sample no. 3)*. The results show nanometer grains with various sizes and diameters as illustrated in figures below.

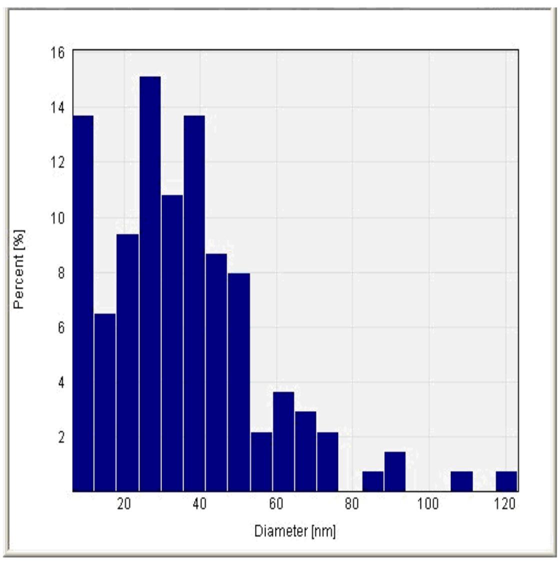

Fig 2a. Grain size distribution histogram, sample no. 1

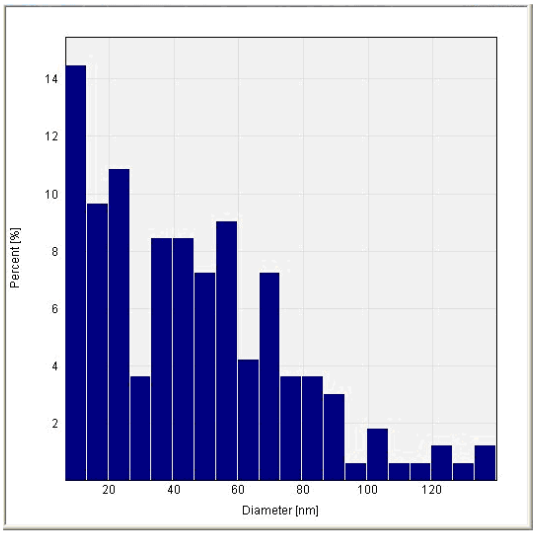

Fig. 2b. Grain size distribution histogram, sample no.2

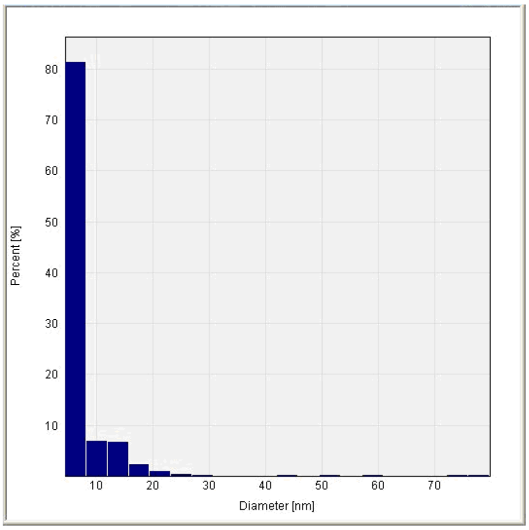

Fig. 2c. Grain size distribution histogram, sample no.3

3.2 RBS results

The results of the RBS investigations are presented in Figures 3 a, b and c. RBS natural units for the thicknesses are given by atom areal density (atoms/cm^2). We have found the following values:

- for sample no. 1, an areal density of 2.2 x 10^{18} atoms/cm^2 and the chemical composition of: $Ti_{0.3}$ $N_{0.7}$/ $Ti_{0.1}B_{0.55}N_{0.35}$/ $W_{0.43}C_{0.195}N_{0.3}O_{0.075}$.
- for sample no. 2, an areal density of 2.18 x 10^{18} atoms/cm^2 and the chemical composition of: $W_{0.31}C_{0.23}N_{0.19}Ti_{0.09}B_{0.18}$.
- for sample no. 3, an areal density of 2.06 x 10^{18} atoms/cm^2 and the chemical composition of: $W_{0.36}C_{0.225}Ti_{0.11}B_{0.255}O_{0.05}$/$W_{0.58}C_{0.225}Ti_{0.01}B_{0.145}O_{0.05}$/ $W_{0.35}C_{0.225}Ti_{0.12}B_{0.255}O_{0.05}$.

W and Ti peaks can be seen clearly from the below figures along with the Si peak corresponding to the substrate material.

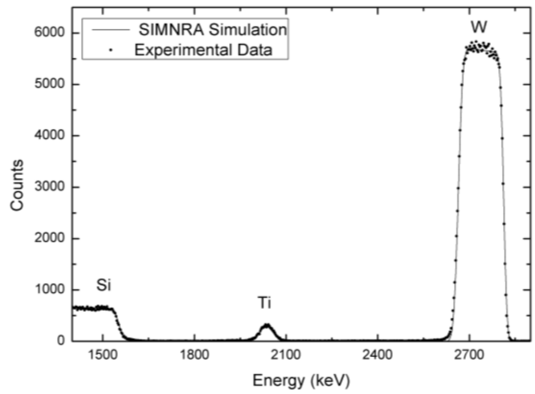

Fig. 3a. 3.065 MeV $^4He^{2+}$ backscattered at 165° from a three layer structure of $Ti_xN_y/Ti_xB_yN_z/W_xC_yN_z$ on silicon, sample no. 1. Dots: Experimental data; Solid line: Simulation.

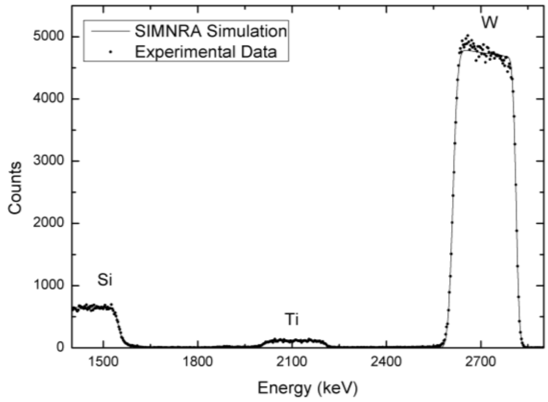

Fig. 3b. 3.065 MeV $^4He^{2+}$ backscattered at 165° from a single layer structure of TixNy+TixByNz+WxCyNz on silicon, sample no. 2. Dots: Experimental data; Solid line: Simulation.

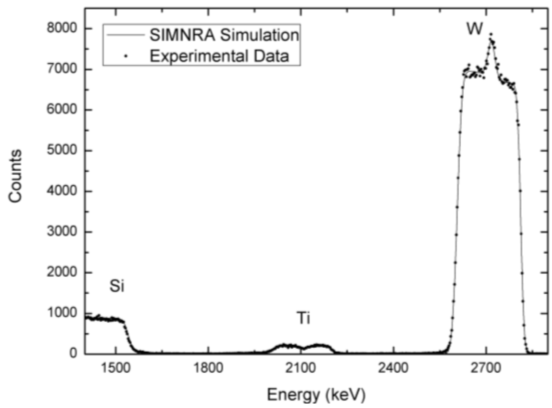

Fig. 3c. 3.065 MeV $^4He^{2+}$ backscattered at 165° from a single layer structure of $Ti+TiB_2+WC$ on silicon, sample no. 3. Dots: Experimental data; Solid line: Simulation.

4. Conclusions

Tribological coatings with monolayer and multilayer-type structure were successfully obtained by standard and reactive DC magnetron sputtering, starting from 3 basic materials: WC, TiB_2 and Ti.

AFM measurements have shown that grains are uniformly deposited on the silicon substrate. Coatings without N_2 had lower values of the roughness and grain size.

RBS gave composition information for these structures with quaternary *(Ti-W-C-B)* and pentanary *(Ti-W-C-B-N)* structure and prove that all the coatings are non-stoichiometric complex compounds.

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