# Mechanical and tribological behaviour of the multilayer dry lubricant coatings with ternary composition from compound materials ($Ti_xN_y$; $TiB_2$/ $Ti_xB_yN_z$; WC/ $W_xC_yN_z$)

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Multilayer Coatings with ternary compositions ($Ti_xN_y$; $TiB_2$/ $Ti_xB_yN_z$; WC/ $W_xC_yN_z$) for dry lubricant applications are deposited by standard and reactive DC magnetron sputtering. Two types of samples are prepared in multilayered arrangement: First sample (1) is made of one set of three layers (*$Ti_xN_y$ / $TiB_2$/ WC).* The second sample is deposited in set of three layers *($Ti_xN_y$/ $Ti_xB_yN_z$/ $W_xCyN_z$)* repeated in five sequences *(sample 2)*. Each layer has a constant composition and all the sequences are identical. Both samples are topographically, mechanically and tribologically characterized by AFM, nanoindentation, scratching and pin-on-disk measurements. By comparison the mechanical and tribological tests prove that the hardness obtained by both testing methods is similar and the value of the friction coefficient is less than 0.2 with both measurement methods for the two investigated samples.

(Received October 24, 2014; accepted May 7, 2015)

*Keywords:* Multilayer coatings; Dry lubricant coatings; Ternary composition; Wear resistance

## 1. Introduction

The friction coefficient is strongly influenced by: roughness, molecular adhesion, surface deformation, environment characteristics (*composition, pressure, humidity, temperature, etc.)*. The solid lubricants are a new alternative to the liquid lubricants. They are used to control friction and wear under severe application conditions where conventional materials and lubricants cannot provide the desired levels of performance or durability *(such as high vacuum, aerospace, high-speeds, high loads, and very low or high temperatures)*. In the last decades new modern concepts and solid lubricants are developed targeting higher lubricity and wear life.

Recent progress in thin-films deposition techniques has shown that the solid lubricants passed from traditional metal ceramic and polymer matrix composites to multilayered architectures with adaptive self–lubricating [1]. In order to have high wear resistance and long using life of the mechanical systems the Tribological Coatings (TC) must fulfil the following essential properties: 1. High adhesion to the metallic substrates; 2. High hardness; 3. High tenacity; 4. High corrosion resistance; 5. Good resistance to the thermal oxidation; 6. Low coefficient of friction [2]. Complex monolayer with binary, ternary or quaternary composition or multilayer with repetitive sequences (packages) of 2-4 layers, depending on the working conditions of the friction couple, are recommended to be used in the composition of the dry lubricant coatings, starting from simple and compound materials that fulfil more than one of the above 6 essential properties of the TC. The dry tribological coatings can be made of complex multilayers with constant or gradual composition that contain 2-6 simple *(chemical elements)* or compound materials with complementary-cumulative properties that completely or partially fulfil the above 6 essential properties for the tribological coatings [3,4]. Using repetitive packages with „superlattice" thicknesses (**2 nm<$h_i$< 10 nm**) for the component layers, the tribological properties *(coefficient of friction, operating load, wear resistance)* of the TC are improved [5-8]. Therefore, for a given tribological application and environment conditions *(temperature, pressure, contact load, sliding/ rotating speed, presence of corrosive gases, etc.)* the appropriate coating type in terms of deposition methods and materials used must be chosen. The response of a coated system (*friction couple*) depends on the following factors: **substrate properties** *(roughness, hardness, toughness, cleaning state before deposition)*; **counterpart properties** *(roughness, hardness, toughness, friction coefficient);* **coating properties** *(hardness, toughness, porosity, thermal oxidation resistance, chemical corrosion resistance)* that mainly depends on the deposition method; **interface substrate-coating properties** *(adhesion)*; **interface counterpart-coatings** *(friction coefficient, hardness, toughness, porosity, thermal oxidation resistance, chemical corrosion resistance)* [9-11]. This contribution describes a new approaching in designing of tribological coatings based on multi-layered structures made of

$TiN_x/TiB_2/WC$, respectively $Ti_xN_y/Ti_xB_yN_z/W_xCyN_z$. Their properties and perspective for application are taken in account based on author contributions in several patents [12].

## 2. Experimental procedures

### 2.1 Material and process parameters

*Deposition method*: Multifunctional vacuum thin film deposition system with three DC sputtering magnetrons *(guns)*. Reactive gases: Ar and $N_2$. This method allows the deposition of the multilayer in one working experimental cycle.

Deposition of layered structures with ternary composition: **Sample no. 1:** ***1x ($Ti_xN_y/TiB_2/WC$)***– one package of 3 layers; **Sample no. 2:** ***5x ($Ti_xN_y$/ $Ti_xB_yN_z/W_xCyN_z$)***– multilayer with five packages of 3 constituent layers.

*Substrate*: stainless steel, ultrasonic cleaned and plasma activated. The substrate was heated at 550 °C and the bias voltage was set at 0.5 kV during deposition.

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

*Table 1. Working process parameters for deposition of the samples no. 1, 2*

| Sample No. | Materials | | Working gases | | Pressure [mbar] | Power On the gun's plasma [%$P_{max}$] | Estimated sputtering rate [Å/s] | Deposition time [min] | Estimated thickness [nm] | Magnetrons/ Guns parameters | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Target/ Gun | Deposited layer | Ar sccm | $N_2$ sccm | | | | | | Voltage [V] | Current [mA] |
| 1 | Ti/<br>$TiB_2$/<br>WC/ | 1x<br>[$Ti_xN_y$/<br>$TiB_2$/<br>WC] | 150<br>150<br>150 | 40<br>0<br>0 | $3,5x10^{-3}$ | 15<br>30<br>30 | (0,4- 1,0)+<br>(0,2- 0,8)+<br>(0,8- 1,2) | 25<br>25<br>25 | 60…150+<br>30…120+<br>120...180 | 323- 315<br>542- 553<br>561-557 | 84-82<br>174-175<br>177-176 |
| 2 | Ti/<br>$TiB_2$/<br>WC/ | 5x<br>[$Ti_xN_y$/<br>$Ti_xB_yN_z$/<br>$W_xC_yN_z$] | 100<br>100<br>100 | 40<br>40<br>40 | $2,8x10^{-3}$<br>$2,8x10^{-3}$<br>$2,8x10^{-3}$ | 15<br>30<br>30 | 0,4 - 1,0<br>0,2 - 0,8<br>0,8- 1,2 | 5x5=25<br>5x5=25<br>5x5=25 | 60 …150<br>30 … 120<br>120 …180 | 338- 339<br>466 -560<br>557- 559 | 84-83<br>175-174<br>177-176 |

### 2.2. Characterization methods

The topography, microstructure, mechanical and tribological properties of the dry-lubricant coatings were investigated by the following methods: Atomic Force Microscopy Method (AFM-M), Hardness Test Method (HT-M), Scratch Test Methods (ST-M) and Pin-on-disk Tribometer.

*Topography and nanoidentation*: NanoScope IIID-atomic force microscope (*Digital Instruments Veeco Metrology Group, Santa Barbara, CA, USA); tapping mode, Tip-* TESP *(0.01-0.025 Ohm-cm Antimony (n) doped Si)* at 1 Hz scan rate, 512 pixels. Measurements are performed in ambient environment [13].

*Mechanical and tribological parameters*: CSM Table Top Platform which includes the standard Micro/ Nanoindentation head (NHT) and the standard Micro scratch tester head (MST) into a small and simple-to-use instrument [14 -16].

*Nanoidentation technique*: diamond tip mounted on a stainless steel cantilever was used in order to obtain good statistics.

The samples were indented using the option Auto Indent Mode, that allows setting up the number of the lines, columns and the space between them [17-19].

*Scratching method:* Micro scratch tester head (MST) into a small and simple-to-use instrument [16-18]. The Nanoindentation Tester *(0 - 50*0 mN) provides low loads with depth measurement in the nanometer scale. The system can be used to characterize organic, inorganic, hard and soft materials. The Micro indentation Tester *(0 - 30 N)* is suited for the measurement of thin hard coatings, thick soft coatings and bulk materials. It contains a full software package for data acquisition and analysis of the mechanical properties.

## 3. Results and discussions

### 3.1 AFM

The topography and surface roughness for both samples, deposited by using different parameters *(Table 1)* are presented in Fig. 1. Grain sizes are observed especially for ($Ti+N_2/TiB_2/WC$) sample 1 (Fig. 1a). The WC grain size was found to vary and it was not possible to distinguish the grains clearly.

The surface roughness, which is an important parameter for the functional performance of many devices, was determined by scanning three different areas of the surface. Roughness analysis was performed over the entire image; the average value: 0.559nm *(sample 1)*, 1.047 nm *(sample 2)*.

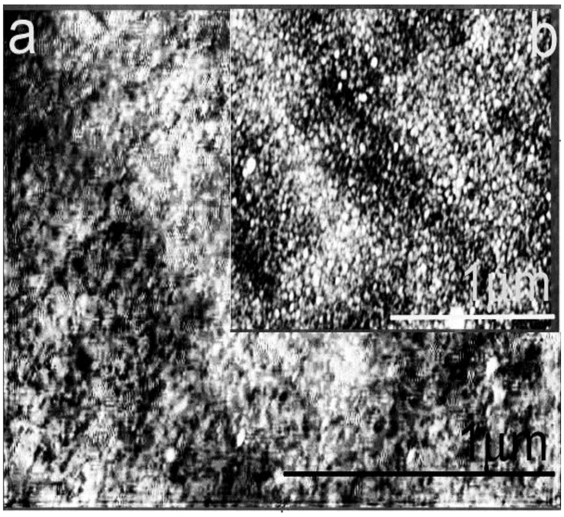
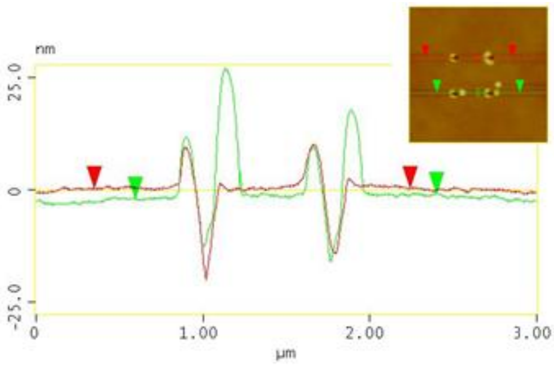
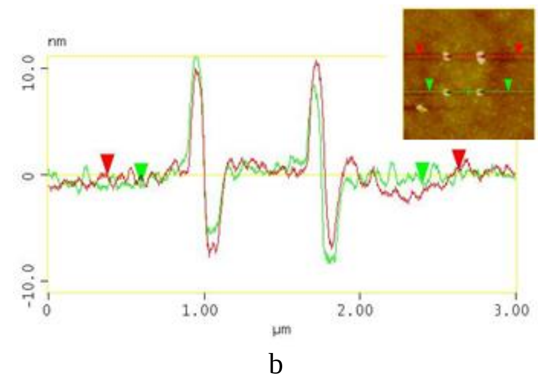



*Fig. 1. Topography recorded by AFM for sample 1(a) and sample 2(b), scale 1 micron, roughness(Rms): 0.559 nm (sample 1, a), 1.047 nm (sample 2, b)*

Both samples have the top layer made of WC *(sample 1)* respectively $W_xC_yN_z$ *(sample 2)*. The hardness of the surface layer was evaluated by AFM nanoindentation technique. A matrix consisting of four indentations was performed in two different areas of the surface using the same force (98 μN), DNISP diamond tip and operating parameters. Section analysis images show clearly the diamond tip depth and the presence of pile-up at the edges of the indentation, Figure 2.




a




b

*Fig. **2**. Section analysis and topography of tungsten carbide, top layer sample1 ( a) andsample 2 ( b)*

The hardness is expressed as the maximum load (F) divided by the projected area (A) between diamond tip and sample surface. The highest indentation depth was about 27 nm while the lowest has a value of about 6.5 nm. The bright area around of the indentation is the pile-up material. The hardness was calculated for each indentation. An average value versus indentation depth was plotted together as shown in Figure 3. The hardness increases with decreasing indentation depths. The hardness of the WC and $W_xC_yN_z$ was found to have an average hardness of: 29 GPa for sample no. 1; 18 GPa-for sample no. 2 and are synthetically presented in the Table 2 and Figure 3.

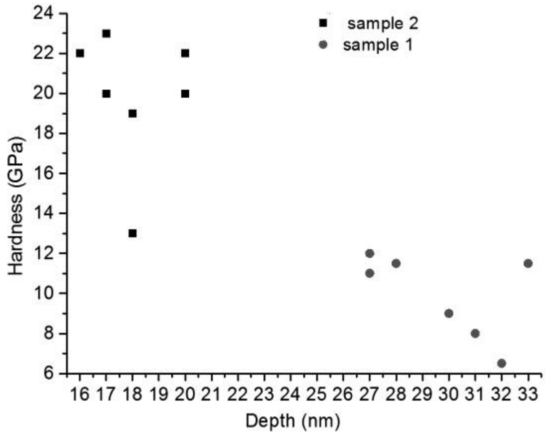



*Fig. 3. Plots of hardness versus indentation depth, (● -Sample 1; ■-Sample 2 )*

**Nanoscratch hardness.** The topography and the section analysis of the 2 samples by using of the same force (98 *μN)* are presented in Figure 4 a and b.

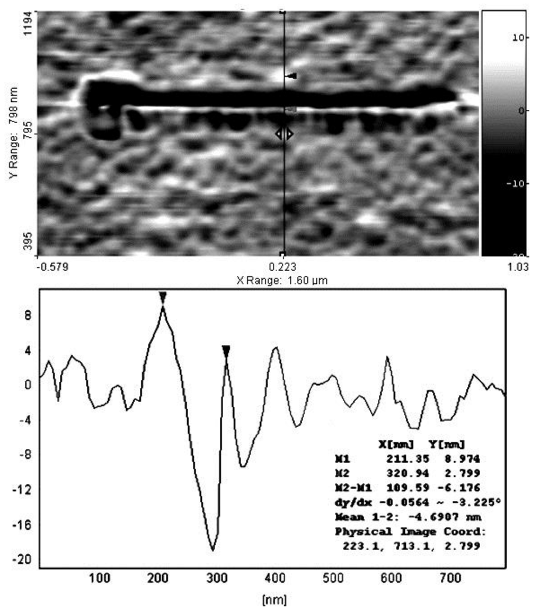



*Fig. 4a. Topography and section analysis, sample 1, scratch force (98 μN), diamond tip*

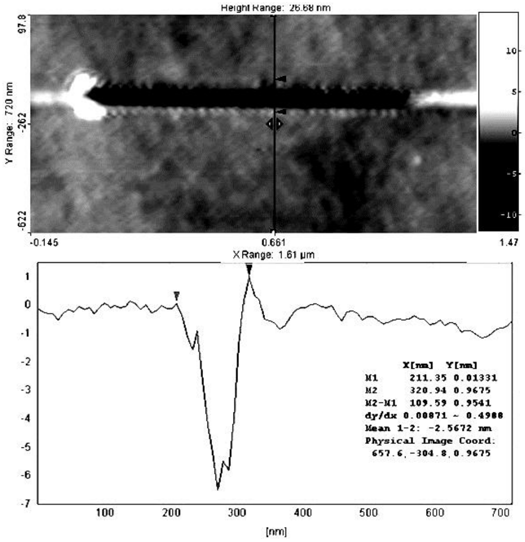



*Fig. 4b. Topography and section analysis, sample 2, scratch force (98 µN), diamond tip*

Nanoscratch hardness values were calculated with :

$$H_s = \frac{8F_N}{\pi W^2}$$

where, $F_N$ is the normal load and W is the width of the groove.

*Table 2. Hardness of the samples no. 1, 2*

| Sample No. | $F_N$ [µN] | W [µm] | $H_S$ [Gpa] |
|---|---|---|---|
| 1 | 98 | 0.109 | 29 |
| 2 | 98 | 0.109 | 18 |

### 3.2 Mechanical and tribological tests

#### 3.2.1 Hardness/indentation test results

The load used in the indentation tests is at the lowest limit of the testing apparatus in order to ensure a penetration depth, less than 10% of the film thickness that has values *lower than 500 nm*. Six hardness tests for each sample were performed. The results are presented in decrescendo order of the hardness in Tables 3, Figure 5 *(sample no. 1)* and Figure 6 *(sample no. 2)* showing the dependence of the normal force versus. penetration depth.

The hardness test results are presented in the Table 3. It can be seen that the Hardness of the surface layer of the coating is between 12.262 GPa and 9.3946 GPa and the Elasticity Modulus EIT is between 523.72 GPa and 139.66 GPa for the sample no.1; 5.655 GPa and 5.1271 GPa and the Elasticity Modulus EIT is between 179.12 GPa and 474.83 GPa for the sample no.2.

Also, it can be seen that the penetration depth is lower than the estimated thickness of the surface layer *(WC for sample 1 and* $W_xC_yN_z$ *for sample 2)*.

RMS roughness measurements were performed over the entire image and the obtained values were: 2.119 nm *(sample no. 1)* and 2.318 nm *(sample no. 2)*.

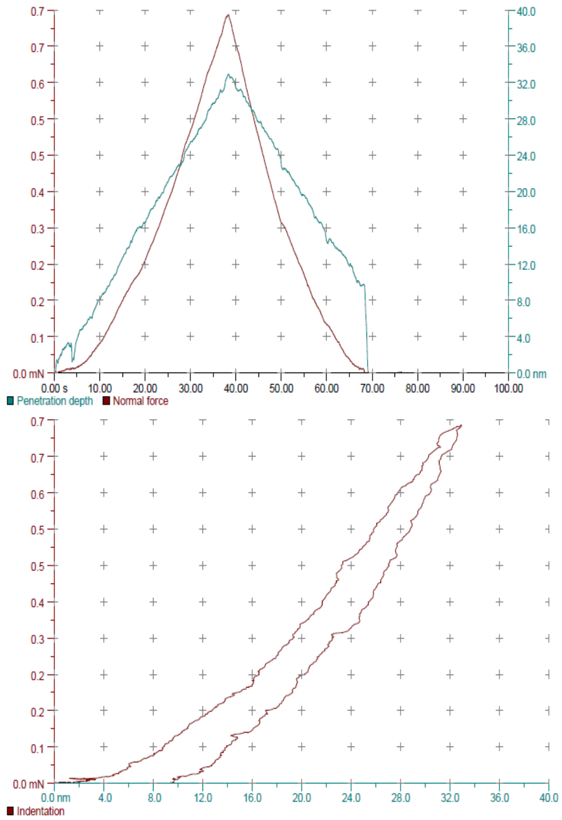



*Fig. 5. Hardness test, sample no. 1 (see text)*

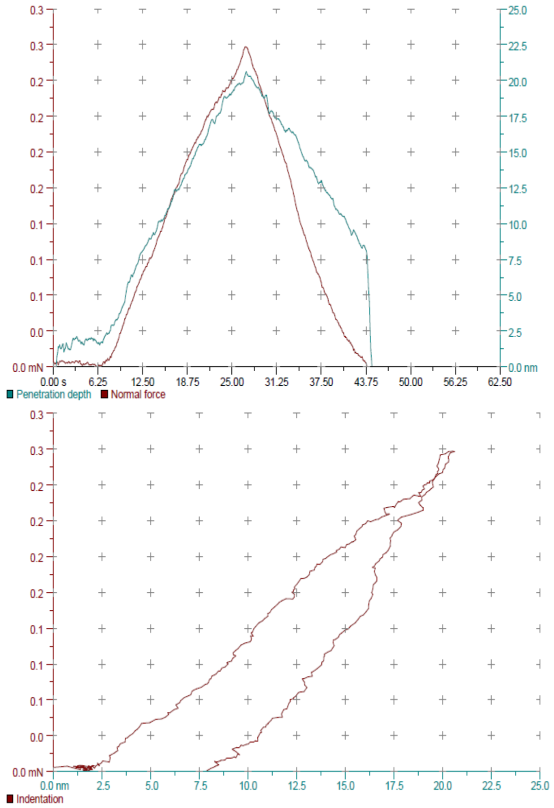



*Fig. 6. Hardness test, sample no. 2 (see text)*

*Table 3. Hardness tests*

| Sample No. | Hardness | | Elasticity | | | Additional results | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | HIT | HV | EIT | Er | $E^*$ | $F_{max}$ | $h_{max}$ | S | $h_c$ | $h_r$ | $h_p$ |
| | [GPa] | Vikers | [GPa] | | | mN | nm | mN/nm | nm | nm | nm |
| 1 | 12.262 | 1135.6 | 179.12 | 168 | 196.83 | 0.74 | 32.89 | 0.0482 | 21.41 | 17.52 | 8.93 |
| 2 | 5.655 | 523.72 | 110.62 | 109.91 | 121.56 | 0.30 | 22.93 | 0.0297 | 14.82 | 12.71 | 10.06 |

### *3.2.2. Micro scratch test results*

The micro scratch test of the sample no. 1 and 2 are presented bellow *(Table 4 and Figure. 7).*

The friction coefficient of the 2 samples obtained by micro scratch test is between 0.08 and 0.22.

*Table 4. Results of micro scratch test*

| Sample No. | Critical load (Adhesion) Lc1=First fissure Lc2=First delamination | Normal force | Friction force | Penetration depth | Coefficient of friction |
|---|---|---|---|---|---|
| | N | N | N | nm | - |
| 1 | Lc1= 0.2, Lc2= 1 Lc3= 3.02 | 0 – 5 | 0 -1.2 | -50 … 1750 | 0.08 … 0.22 |
| 2 | Lc1= 0.35, Lc2= 0.75 Lc3= 2.39 | 0 – 5 | 0 -1.2 | 200 … 2500 | 0.07- 0.225 |

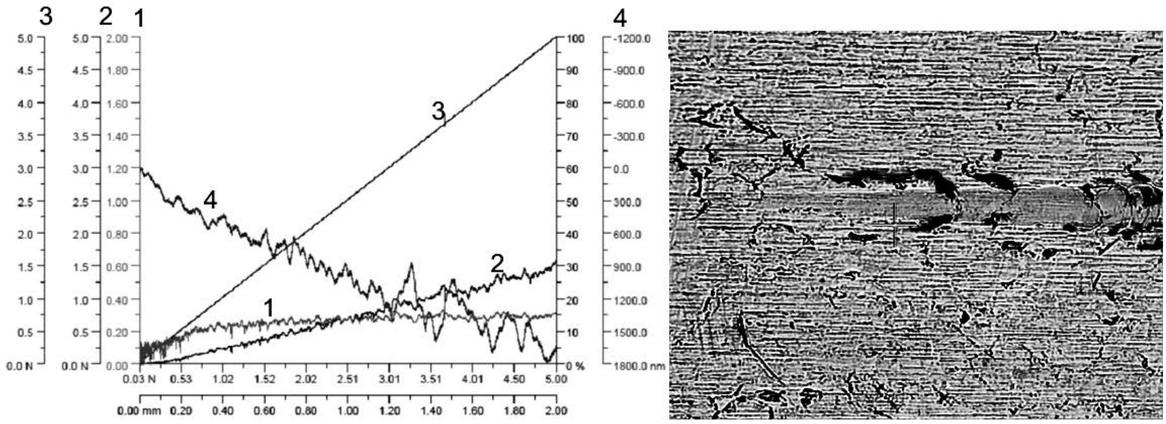



*Fig. 7a. Scratch test for sample no. 1,*
*1-Friction coefficient, 2-Frictional force, 3-Normal force, 4-Penetration depth*

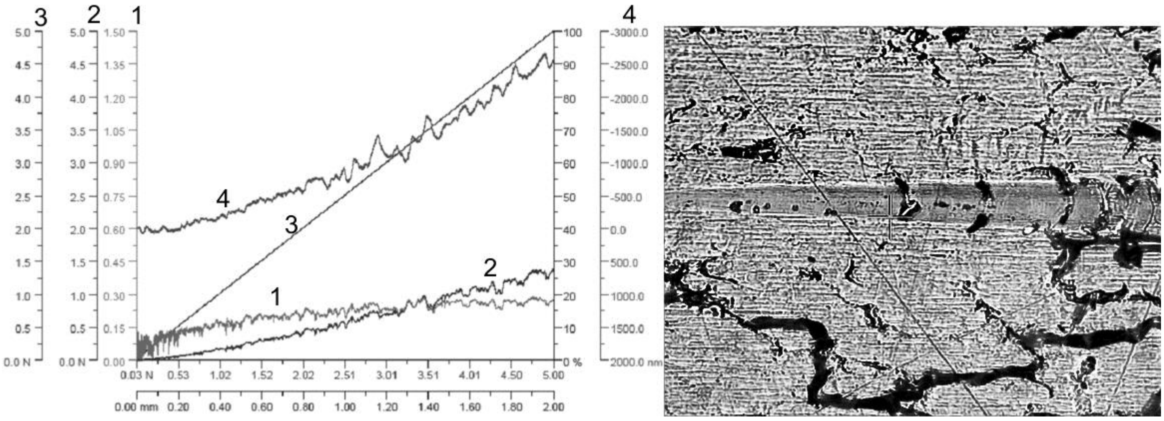



*Fig. 7b. Scratch test for sample no. 2,*
*1-Friction coefficient, 2-Frictional force, 3-Normal force, 4-Penetration depth*

#### *3.2.3. Tribological measurements*

The tribological tests performed with pin-on-disk tribometer at minimal load *(1N)* with small speed rotation and for a short time *(22 seconds)* in order to not induce the total coating deterioration.

The results of the tribological measurements for the 2 samples are presented below in the Fig. 8 *(for the samples 1 and 2)*.

The friction coefficient obtained by pin-on-disk tribometer is higher than the values obtained by scratch test method *(Figure 7, table 3)*. The experiments are performed at ball of 6 mm radius, linear speed- 5 cm/s, normal load- 1N, environment at 24 $^0$C, relative humidity at 32%.

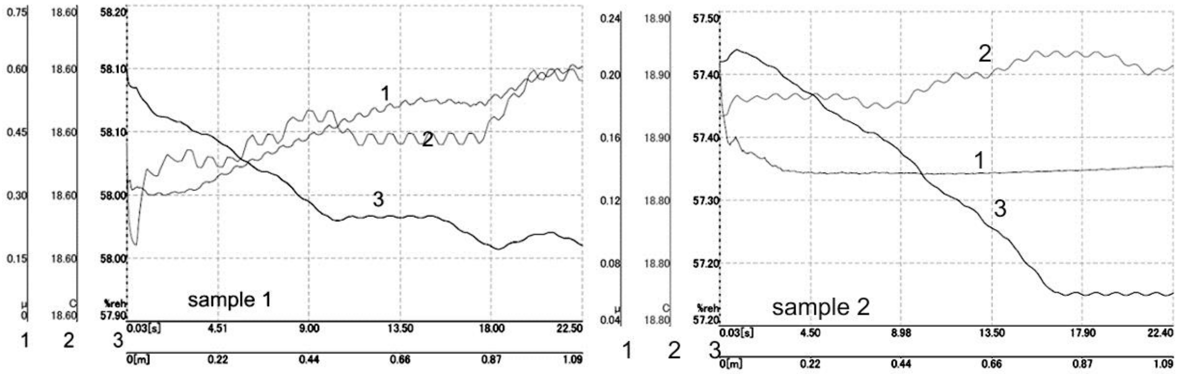



*Figure 8. Pin-on-disk tribometer test for sample no. 1 and 2. 1-Friction coefficient (sample 1:0,30 .. 0,60; sample 2: 0,20…0,14), 2-Temperature ($^0$C), 3- Relative humidity (%reh)*

## 4. Conclusions

The dry-lubricant coatings of ternary composition from three compound materials *(*$Ti_xN_y$; $TiB_2$/ $Ti_xB_yN_z$; WC/ $W_xC_yN_z$*)* were deposited as multilayer with: one package of three constituent layers- **sample no. 1**, five packages of three constituent layers with constant composition for each layer- **sample no. 2,** using standard and reactive magnetron sputtering in DC, starting from Ti; $TiB_2$ and WC targets. The friction coefficient obtained by the scratch test method was very low for the both samples *(between 0.08 and 0.225)*, but with the pin-on-disk tribometer method the friction coefficient for the sample no. 1 is much higher than for the sample no. 2 *(see Fig. 7 and Fig. 8)*. The hardness of the surface layer for the sample no. 1 and 2, evaluated by AFM nanoidentation method was found to be 18 GPa, respectively 29 GPa. The values of the friction coefficient obtained by pin-on-disk tribometer are higher than those obtained by scratch test method. It increases fast due to the reduced thickness of the coating and its destruction process for sample no. 1 and it has a constant value *(around 0,14)* for the entire testing period for sample no. 2.

**Acknowledgements**

The authors acknowledge the financial support from R&D Nucleu Programme PN 09 37 01 03. Also, this paper is supported by the Sectoral Operational Programme Human Resources Development (SOP HRD), financed from the European Social Fund and by the Romanian Government under the project number POSDRU/159/1.5/S/134378.

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