Coating multilayer material with improved tribological properties obtained by magnetron sputtering

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Abstract. This work is based on the Patent no. RO 128094 B1, granted by the Romanian State Office for Inventions and Trademarks. The goal of the work is to obtain for investigations tribological coatings with multilayer structure with improved tribological properties, deposited by magnetron sputtering process from three materials (sputtering targets). Starting from compound chemical materials (TiC, TiB2 and WC), as sputtering targets, by deposition in argon atmosphere on polished stainless steel, we have obtained, based on the claims of the above patent, thin films of multilayer design with promising results regarding their hardness, elastic modulus, adherence, coefficient of friction and wear resistance. The sputtering process took place in a special sequence in order to ensure better tribological properties to the coating, comparing to those of the individual component materials. The tribological properties, such as the coefficient of friction, are evaluated using the tribometer test.

1. Introduction

It is well known that, for the terrestrial mechanisms, friction has a strong contribution to: decreased performance; increased energy consumption; added maintenance; wear damage; shortened lives or catastrophic failure of the mechanical systems. Lubrication is indispensable for achieving reduced friction between two moving surfaces and to fulfill these requests only fluid lubricants were used in the first period. The increasing demand for low friction and wear in aircraft and other tribological applications that, involve severe sliding conditions and the limitations of fluid lubricants at extreme environmental conditions, involve the necessity for using only of the reliable lubricants that were for a long time tested and verified in real working conditions.

For a given tribological application with given working and environment conditions (temperature, pressure, contact load, sliding or rotating speed, presence of corrosive gases, etc.) it must be chosen the correct coating type in terms of deposition methods and types of materials used (that have a great influence on friction couple, for: A. working life time, respectively wear resistance...
and B. financial cost), because the response of a coated system (friction couple) depends on the following factors [1]:
1. Substrate properties (roughness, hardness, toughness, cleaning state before deposition);
2. Counterpart properties (roughness, hardness, toughness, coefficient of friction);
3. Coating properties (hardness, toughness, porosity, thermal oxidation/chemical corrosion-resistance) that mainly depends on the used materials and deposition method;
4. Properties of substrate-coating interface (adhesion).

According to the claims of above Patent, the materials for the tribological coatings must be selected by taking into account the fact that tribological coatings must fulfill (in accordance with the working conditions) the following maximal properties: 1. Low coefficient of friction; 2. High hardness; 3. High toughness; 4. Good adhesion to the substrate; 5. High thermal conductivity; 6. High corrosion resistance and high thermal oxidation resistance.

WC is a material with: very good thermal conductivity ($\lambda = 80-100$ W/m.K); good coefficient of friction ($\mu$/COF = 0.4-0.6), high hardness ($HV_0=2100$), good elasticity (E=550GPa). Coatings with carbon compounds generate tribofilms, reducing the friction coefficient. Variations in the number of layers and thicknesses, as well as the distribution within the coating are determinant to obtain the adequate mechanical properties in order to reduce the wear rate [2].

TiB$_2$ is well known as a ceramic compound with relatively high melting point, hardness, strength to density ratio, abrasion, oxidation resistance and wear resistance. Although TiB$_2$ coatings have been widely studied by many researchers, their real applications have been limited. The fact is that the adhesion of the TiB$_2$ coatings is poor for the coating-substrate system. The main reasons for this are that the TiB$_2$ coating deposited is very brittle and that it accommodates very high compressive residual stresses. These limit both the practical adhesion and the thickness of the TiB$_2$ coatings [3]. In order to enhance the TiB$_2$ coating adhesion TiB$_2$-based nanostructured engineering coatings should be developed. A possible way to obtain lower stress levels could be to utilize multilayer coatings that is, to combine the stressed material with a more ductile material in a layered structure [4].

TiC is a material that has a relatively good adhesion to the metallic substrates and allows obtaining by reactive magnetron sputtering in DC (with $N_2$ as reactive gas) of the TiCN coatings that have been used to improve wear resistance of metallic materials in a wide range of engineering applications, such as cutting and forming tools.

According to the patent claims, using TiC (material with good adhesion), TiB$_2$ (ceramic material with high hardness, high oxidation and wear resistance) and WC (material with low coefficient of friction, high thermal conductivity) deposited successively, in the above order and simultaneously at different concentrations, we obtained thin films of multilayer design with promising results regarding their hardness, elastic modulus, adherence, coefficient of friction and wear.

2. Experimental procedures
According to the patent claims, for achievement of the tribological coatings with multilayer structure, we have used standard magnetron sputtering deposition process in DC. We have used 3 sputtering targets: Titanium carbide (TiC), Titanium diboride (TiB$_2$) and Tungsten carbide (WC) with the following properties:
- TiC, used for the 1$^{st}$ layer, with acceptable COF and adhesion to the metallic substrate.
- TiB$_2$, used for the 2$^{nd}$ layer, with high hardness and also with a high wear resistance.
- WC, used for the 3$^{rd}$ layer, with very good thermal conductivity and low COF.

The experiments took place in a vacuum deposition system equipped with four DC magnetrons of 600 W, having 2 targets that can be adjusted for co-focal deposition and with a controller with quartz crystals sensors for measure film thickness and deposition rates. The distance between the targets and substrates was around 15 cm. The polished stainless steel substrates were ultrasonically cleaned before introducing them in the deposition process chamber. Then they were heated up to 550°C for a better adhesion of the coated film to the metallic substrates and they were in a 20 m/s rotation motion in order to obtain coatings with high uniformity for their entire surface. We reached a pressure less than...
10\(^5\) mbar in the technological chamber in the first step and around 3\(\times10^{-3}\) mbar when we introduced 100 sccm of Ar. A deposition control ensured process controlling and in situ measurement of deposition rate and coating thickness.

In the above configuration of the deposition process we made coatings using 550°C for the heating temperature, in a multilayer design consisting in: 10 and 15 packages of three constituent layers 10x(TiC/TiB\(_2\)/WC) – Sample 1 and 15x(TiC/TiB\(_2\)/WC) – Sample 2 (Figure 1-a) and a multilayer structure of 3 constituent compound layers of 3 materials with different concentrations – Sample 3 (Figure 1-b).

Figure 1. Structure of the multilayer tribological coatings
a) multilayer structure (n = number of the repetitive packages)
b) multilayer structure made of three constituent compound layers with different concentrations

The power injected in magnetrons was the same for all the targets for Sample 1 and 2 and for Sample 3 it was double in each layer for one material than it was for the other two used (Table 1). So, in this way we made tribological coatings with multi layer structure and improved tribological properties, with quaternary composition (Ti-B-W-C), respectively with pseudo-ternary composition (TiC-TiB\(_2\)-WC), starting from the 3 sputtering targets: TiC, TiB\(_2\) and WC, by standard DC magnetron sputtering process.

The working process parameters for achievement of the 3 samples are presented in Table 1.

Table 1. Working process parameters for deposition of the samples

| Sample No. | Target | Materials | Deposited layer | Power injected in the gun's plasma [%\(\times P_{\text{max}}\)] | Deposition time [min] | Magnetron parameters |
|------------|--------|-----------|-----------------|-----------------------------|----------------------|---------------------|
|            |        |           |                 |                             |                      | Voltage [V]          |
|            |        |           |                 |                             |                      | Current [mA]         |
| 1          | TiC    | TiC/TiB\(_2\)/WC | 10x(TiC/ | 30                      | 338-339             | 84-83               |
| 1          | TiB\(_2\) | TiB\(_2\)/WC | 30              | 150                         | 466-560             | 175-174             |
| 1          | WC     | WC        | 30              |                             | 557-559             | 177-176             |
| 2          | TiC    | TiC/TiB\(_2\)/WC | 15x[Ti/ | 30                      | 338 - 303            | 84-83               |
| 2          | TiB\(_2\) | TiB\(_2\)/WC | 30              | 150                         | 580 - 454            | 175-174             |
| 2          | WC     | WC        | 30              |                             | 578 - 520            | 177-175             |
| 6          | TiC+TiB\(_2\)+WC | TiC+TiB\(_2\)+WC/ | 60+30+30     |                             | 286-280             | 25 - 24             |
| 6          | TiC+TiB\(_2\)+WC | TiC+TiB\(_2\)+WC/ | 60+30+30     |                             | 432 - 440            | 55 - 54              |
| 6          | TiC+TiB\(_2\)+WC | TiC+TiB\(_2\)+WC/ | 30+30+60     |                             | 462 - 470            | 57 - 56              |

* \(P_{\text{max}} = 600\) W
3. Evaluation methods

The relative concentration of W and Ti of the samples 1 and 2 was determined using the micro-beam X-ray fluorescence (µ-XRF) method, developed at NILPRP [5-7]. The samples were analyzed at low value excitation energies (<50 KeV). This method is optimal for thinner layers (<10 µm) due to the fluorescence auto saturation effect. As we already know the integrated area peak for the experimentally investigated bulk Ti (152970±10%) and also for the Ti contained in the ceramic compound (6737±10%), we made conversion to layer thickness. Experimental conditions for µ-XRF and source parameters were kept fixed, integration time of 30 seconds, Mo target X-ray source with current of 700 µA and a 45 kV voltage. Using bulk materials, energetic calibration of the spectrum was carried out in order to conduct area integration upon characteristic energetic line especially for W (L-line 9.67 keV) and Ti (K-line 4.5 keV).

The tribological behavior of the prepared coatings was tested using a Ball-on disc CSM, Switzerland tribometer. The following parameters were set: sliding speed: 2cm/s, bearing stainless steel 6 mm diameter, sliding radii: 2.5 mm, 3 mm and 3.5 mm respectively, loading force: 0.5 N, 1 N and 2 N respectively.

Vickers hardness was measured using a „Microhardness tester FM-700” with an indenter with rhomboidal prophile for Sample 1. The loading forces used were: 25, 10 and 50 gf. and the Dwell time was 10 sec.

4. Results and Discussions

Based on the calibration curves, we conducted also the conversion from the integrated peak area (Gaussian fit) to layer thickness of W and Ti on the investigated sample and the results are presented in Table 2. We mention that by XRF method, B concentration could be not measured due to the low atomic mass number.

| Investigated sample | Integrated peak area Ti Kα | Gaussian fit W Lβ | Calibrated thickness (nm) ± 10% relative error | Relative integral concentration (%) |
|---------------------|---------------------------|------------------|-----------------------------------------------|----------------------------------|
| Sample 1            | 6737 (Ti 33%)             | 31095            | ~700 (W), ~780 (Ti)                          | 47 (W), 53 (Ti)                  |
| Sample 2            | 6890 (Ti 33%)             | 31003            | ~720(W), ~780 (Ti)                          | 48 (W), 52 (Ti)                  |

For sample 1 the results for the coefficient of friction are presented in Figure 2.

![Figure 2. Coefficient of friction for Sample 1](image-url)
One could observe a reduction of the coefficient of friction of about 8 times ($\mu \sim 0.1$) compared with the coefficient of friction of the substrate ($\mu \sim 0.8$) in the case when the loading force was 0.5 N and a little bit higher ($\mu \sim 0.15$) when the load was 1 N or 2 N. We observe also that the deposited layer resisted without breaking 0.75 m in the case of the 0.5 N load and about 0.2 m in the case of the 1 N or 2 N loads.

After about 1.5 m sliding in dry conditions, the coefficient of friction reached the value of 0.8, the substrate characteristic. The same situation is observed for the case of 1 N loading force while in the case of the loading force of 2 N, between 0.6 m and about 3 m sliding the coefficient of friction was lower than of the substrate ($\mu \sim 0.6$ instead of $\mu \sim 0.8$) due to the rolling friction mechanism (the film debris acted as some ball bearings, and the coefficient of friction was reduced).

In the Hardness Test, a variation of the hardness with the loading force as it is presented in Figure 3 was observed. (the hardness increases with the load decreasing). The HV$_{0.01}$ was around 300 that means arround 2,94 GPa and this value was higher with 20% than the substrate hardness.

![Figure 3. Hardness of the Sample 1](image)

The coefficient of friction obtained by Ball-on-Disc-Tribometer Test for the Samples 2 and 3 is presented in Figure 4 and 5 and has the same evolution as for the Sample1.

![Figure 4. Coefficiecient of friction for Sample 2](image)  
![Figure 5. Coefficient of friction for Sample 3](image)

5. Conclusions

For the multilayer design, the deposition drastically reduces the coefficient of friction of the moving components coated with this film, as one used on sample 1. Because of the reduced thickness of the coating, the coefficient of friction for sample 1 is under 0.2 only for a sliding distance of 1 m for Ball-on Disk Tribometer Test, with loading force of 0.5 N and sliding speed of 2 cm/s.
The reduced sliding distance with low coefficient of friction (when the deposited layer resists without breaking) represents a consequence of the reduced adhesion of deposited layers to the metallic substrate and of the reduced cohesion forces between the constituent layers of the multilayer.

Multilayer from TiC/TiB$_2$/WC start from a lower value of COF (under 0.1) than the multilayer made from TiN/TiB$_2$/WC (that start at a COF around 0.3) when more deposited packages led to lower coefficients of friction [8].

Also, the wear resistance and the adherence to the substrate for TiC/TiB$_2$/WC multilayer structures is very low and this is proven by a short sliding distance (maximum 0.6 m at a loading force of 0.5N) with low coefficient of friction (under 0.2).

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