Reactive magnetron sputtering of TiN-Pb coatings using two metal targets

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Abstract. One of the promising areas of application of the magnetron co-sputtering method using two separate targets in a reactive atmosphere is to increase the tribological properties of friction pairs by applying composite solid lubricant coatings consisting of a solid matrix and a soft lubricant. In this paper, we study the dependence of the parameters of TiN-Pb coatings obtained by co-spraying of separate Ti and Pb targets in a mixture of Ar and N gases on pressure. The factors that have a significant impact on the process of coating deposition were also determined.

1. Introduction
Magnetron co-sputtering using two separate targets in a reactive atmosphere has become a very powerful method for applying various functional coatings [1–3]. One of the promising areas of application of this method is to increase the tribological properties of friction pairs by applying composite solid lubricant coatings consisting of a solid matrix and a soft lubricant [4]. As such a coating, our group studies the deposition of TiN-Pb obtained by co-spraying of two separate targets (Ti and Pb) in a mixture of Ar and N [5, 6].

Reactive magnetron sputtering has been intensively studied for about four decades, both experimentally and theoretically – by numerical and analytical methods. However, the problem of obtaining an accurate analytical solution for controlling the reactive sputtering process using two separate targets has not yet been solved due to its great complexity. An interesting simulation of this process was carried out in [7], which considered the co-sputtering of individual Ti and Cr targets. However, the authors of [7] assumed that the entire titanium + chromium system is divided into two separate systems, which made it possible to independently consider the equilibrium of the reactive gas and the consumption for each metal target. In this paper, we show that the acceptance of this assumption for a certain geometry and parameters of the process may not correspond to its adequate description.

2. Materials and methods of research
Figure 1 shows the scheme of the reactive magnetron sputtering process used in this work for two separate monoelement cathodes (Ti of grade VT1-0 and Pb, respectively). Extended planar magnetrons with the size of both targets 273×112×10 mm are vertically installed in the chamber at a...
distance of 100 mm from the substrate and at an angle of 90° to each other. To reduce the possible transfer of atomized atoms to another magnetron, screens made of 304 grade steel were installed. The size of the screen part parallel to the vertical axis (see figure 1) is 55 mm, so the screens only partially separate the magnetrons. The Ar and N gases were fed into the vacuum chamber through an ion source.

![Figure 1. Sputtering scheme (top view): M1 and M2 – magnetrons, IS – ion source.](image)

The coatings were deposited on 20×15×1 mm samples made of polished 304 grade steel. Before coating and placing in a vacuum chamber, the samples were cleaned in an ultrasonic bath in gasoline and isopropyl alcohol for 10 minutes.

Then the sample was placed into the vacuum chamber and it was pumped out by diffusion and rotary pumps to a pressure of 9×10⁻⁴ Pa, after which argon was fed and the surface of the chamber walls and the inner-chamber equipment was cleaned using a glow discharge. Next, the chamber was pumped to a pressure of 7×10⁻⁴ Pa and the grounded substrate was cleaned with Ar⁺ ions using an ion source for 20 minutes with the process parameters: \( P_{Ar} = 5×10^{-2} \) Pa, the ion current density \( J = 2 \) mA/cm², and the ion energy of the order \( E \sim 1.5 \) keV. After cleaning, the ion source was turned off and the Ti sublayer was sprayed at \( P_{Ar} = 1.2×10^{-2} \) Pa for 5 minutes, the TiN sublayer for 5 minutes and TiN-Pb for 50 minutes at 3 different pressures in the chamber \( P_{Ar+N2} : 0.173 \) Pa, 0.252 Pa, 0.306 Pa, keeping the argon flow rate constant and changing the nitrogen flow rate. Both magnetrons operated in the current stabilization mode at discharge currents \( I_{Ti} = 3.5 \) A and \( I_{Pb} = 0.1 \) A.

The elemental composition of the obtained coatings was studied using an EVO-40 Carl Zeiss scanning electron microscope with an INCA Oxford Instruments energy dispersive analysis (EDS) attachment. The thickness of the coatings was measured by interferometric method on the ledge formed on the witness sample on MicroXAM-100 3D surface profilometer.

3. Experimental results and their discussion
The typical coating spectrum for all three deposition modes is shown in figure 2. The content of Ti and N in all three coatings is approximately the same, while the content of Pb in the coatings varies randomly with a multiplicity of up to 3.

Figure 3 shows the dependence of the coating thickness on the ratio of nitrogen and argon consumption \( Q_{N2}/Q_{Ar} \) at a constant argon consumption \( Q_{Ar} \). Thus, it can be seen that an increase in
nitrogen consumption led to a decrease in the thickness of the coatings. In addition, slightly lower values of coating thicknesses were obtained (based on the results of separate TiN and Pb deposition). The analysis of these results, as well as the very significant specifics of the TiN-Pb coating formation process, requires additional research. This specificity lies in the simultaneous influence of the following factors:

- the presence of two separate metal targets;
- significant difference in the sputtering coefficient of Ti and Pb;
- a very large difference in the atomic masses of Ti and Pb;
- quite low pressure in the chamber during deposition process;
- reactive gas in the chamber;
- possible migration of the sputtered atoms on the opposite target;
- the presence of screens that capture part of the atomized atoms;
- significant limitation of the current density of the Pb target due to the low melting point;
- simultaneous bombardment of the substrate by ballistic and diffuse flows of atomized atoms;
- the inclined position of the targets relative to the substrate ($\alpha = 45^\circ$).

![Figure 2. Spectrum of TiN-Pb coating deposited at 0.252 Pa.](image)

![Figure 3. Dependence of the coating thickness on the ratio of nitrogen and argon consumption $Q_{N_2}/Q_{Ar}$ at a constant argon consumption $Q_{Ar}$.](image)
Briefly assessing these factors, the following processes can be noted:

- a significant (6–7 times) excess of the sputtering coefficient of Pb over Ti ($Y_{Ti} \sim 0.3$ under experimental conditions) makes it possible to obtain the necessary fluxes of atomized lead atoms by spraying the target at low currents and not overheating it;
- a large difference in the atomic masses of Ti and Pb leads to different conditions for the transport of atomized atoms: Ti atoms that are close to Ar in mass will be effectively dispersed and significantly thermalized, and for Pb atoms under these conditions, ballistic transport to the substrate will prevail; however, the free path of thermalization estimated by us according to the method [8] significantly exceeds the target–substrate distance for atoms of both metals in our conditions;
- the presence of reactive gas leads to well-studied processes of “poisoning” of targets;
- an attempt to possibly eliminate the transfer of atomized atoms to the opposite target by installing screens gave only a partial effect – our experiment to determine the effectiveness of screens when spraying only Ti targets showed that the strip of Mo fixed in the center and across the Pb target was completely covered with titanium, which confirms the above doubts about the accuracy of considering the process with completely independent targets;
- it should be taken into account that as soon as the atomized Ti particle reaches the screen surface, it is removed from the discharge almost completely [9];
- bombardment of the substrate with ballistic energetic atoms causes secondary processes that affect the growth of the coating.

4. Conclusions
The article presents a study of the dependence of the parameters of TiN-Pb coatings formed by reactive magnetron sputtering on the pressure. The factors that significantly affect the process of coating deposition are presented. The need for a more detailed study of the multifactorial process to achieve a consistently high quality of coatings is shown.

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