Study of the ion assisted sputtering process parameters influence on the structure and morphology of TiPb coatings

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Abstract. The paper presents the study's results of the composition, structure and morphology of Ti-Pb coatings formed by magnetron co-bombarded with the help of ions. The effect of the relationship between magnetron currents on the structure of Ti and Pb coatings is shown.

Recently, thin Pb films have been gaining popularity for solid lubrication in lightly loaded friction pairs and in special aerospace devices [1–2]. However, the use of lead (as well as other soft materials) as solid lubricant coatings (SLC) to protect the friction surfaces of highly charged parts is inefficient due to the short service life. Currently for these purposes, several types of composite coatings consisting of a solid matrix and a lubricant are used [3–8].

Titanium nitride is used as a wear-resistant coating, but has a high coefficient of friction [9], therefore, to improve this indicator, this work describes a method to form SLC based on a wear-resistant TiN matrix with solid lubricant in the form of Pb deposited by magnetron sputtering system. Another promising application of Pb could also be the alloy of certain lead coatings along with other metals. The effectiveness of this process was demonstrated in a recent work [10], in which the composite coatings of Pb-Ti / MoS2 were successfully manufactured by co-deposition using a magnetron sputtering system. In this work, the synergistic effect of applying an alloy of a MoS2 coating with two metals (Pb and Ti) was obtained by determining the optimum rate for the simultaneous sputtering of all the composite coating elements. However, a detailed study of the co-deposition process of only Pb and Ti using a magnetron sputtering system has not been found in the literature.

This work is dedicated to the study of the composition, structure and morphology of the Pb-Ti coating obtained by the simultaneous deposition of Pb and Ti in various proportions of the coating components.

The coatings were formed in 50×15×0.15 mm samples of the NCX750 alloy with a pre-polished surface at a roughness of Ra ≤ 1.2 μm. Before installing the samples in a vacuum chamber, they were washed in an ultrasonic bath with gasoline and rubbed with isopropyl alcohol. The chamber was pumped out at a pressure of 5×10⁻⁴ Pa. Then, the samples were purified by Ar ions using an ion source at argon pressure in the chamber of 7×10⁻² Pa, current I = 0.5 A and ionic energy of the order of 1.5 keV. After cleaning, the ion source was not turned off during the formation of all coatings types, which provided the ion-assisted deposition throughout the process.

The co-deposition of Pb and Ti was carried out by two direct current magnetrons located at an angle of 90° to each other. The distance of the magnetron target substrate was 100 mm. The argon
pressure in the chamber during the coating deposition was $1 \times 10^{-2}$ Pa. The deposition was carried out at different magnetron currents, limiting the maximum current to the lead target to 0.4 A due to the low melting temperature of Pb. Coating modes are presented in table 1.

| Sample | $I_{Pb}$, A | $U_{Pb}$, B | $I_{Ti}$, A | $U_{Ti}$, B | Sputtering time, min |
|--------|-------------|-------------|-------------|-------------|---------------------|
| 1      | 0.1         | 440         | 1.0         | 440         | 10                  |
| 2      | 0.2         | 512         | 1.0         | 440         | 10                  |
| 3      | 0.3         | 567         | 1.0         | 440         | 10                  |
| 4      | 0.4         | 614         | 1.0         | 440         | 10                  |
| 5      | 0.1         | 480         | 2.0         | 460         | 10                  |
| 6      | 0.1         | 400         | 3.0         | 483         | 10                  |
| 7      | 0.1         | 400         | 3.0         | 483         | 40                  |
| 8      | 0.2         | 395         | 3.0         | 483         | 10                  |

$I_{Pb}, I_{Ti}$, $U_{Pb}, U_{Ti}$ – currents and discharge voltages of the corresponding magnetrons.

Figure 1. X-ray diffraction patterns of Pb-Ti coatings on an NCX750 substrate for various sputtering conditions (see table 1): (a) – sample 2, (b) – sample 4, (c) – sample 5, (d) – sample 7.
The thickness of the coatings was measured by the interferometric method with the MicroXAM-100 3D on the ledge formed on the witness sample. The coatings morphology and elemental composition were studied using a Tescan Vega 3 scanning electron microscope with an Oxford instruments x-ray attachment for EDS analysis. X-ray diffraction analysis was performed on a DRON-4M diffractometer in filtered CuKα radiation.

Figures 1a–d show the X-ray diffraction patterns obtained from the NCX750 alloy samples, on which Pb and Ti were sputtered under various sputtering conditions. Figure 2a shows the concentrations ratios of Pb and Ti obtained by the spectral method. In the X-ray diffraction patterns (figure 1), in addition to the coatings reflections, we observe reflections of the hcp structures (111), (200) and (220) substrate, whose intensity varies according to the coatings thickness. To measure the thickness of the coatings used the effect of absorption of X-ray radiation in the coating:

$$T = \ln(I_0/I_T) \sin \theta / 2\mu$$

where $I_0$ and $I_T$ are the x-ray intensities recorded by the uncoated and coated materials counter, respectively; $\theta$ is the diffraction angle; $\mu$ is the coating material absorption coefficient in CuKα radiation.

In the calculations, we use the absorption coefficients calculated according to the Pb and Ti ratio shown in figure 2a. For the samples for which the magnetron current with a Ti target was 1 A, and the magnetron current with a Pb target was 0.1–0.4 A, the thickness of the coating was 0.4–0.6 μm. For samples for which the magnetron current with a target of Pb was 0.1 A, and for a magnetron with a target of Ti 2–3 A, and the deposition time $\tau = 10'$ the thickness of the coating was 0.6–0.9 μm, and for $\tau = 40'$ he thickness of the coating is 2.1 μm (figure 2b).

![Thicknesses of the Pb + Ti coatings on the substrate made of NCX750 - a) and the ratio of Pb and Ti concentrations (C_Pb / C_Ti) - b) for various variants of the deposition process](image_url)

**Figure 2.** Thicknesses of the Pb + Ti coatings on the substrate made of NCX750 - a) and the ratio of Pb and Ti concentrations (C_Pb / C_Ti) - b) for various variants of the deposition process

In the X-ray diffraction patterns for samples with coatings deposited at currents of 0.1 and 0.2 A (figure 1a), the Pb diffraction is pseudo-amorphous, indicating a deposition process low temperature. In the X-ray diffraction patterns, only traces of titanium diffraction lines with diffraction angles of 20–38° are visible, corresponding to the reflection from the basal planes (002), while the amount of titanium in these coatings represents a 40–45%. The weak diffraction lines of Ti compared to those of Pb can be explained by the fact that the diffraction intensity of Pb with Z = 82 is considerably of a magnitude greater than that of Ti with Z = 22. The structure of Pb in coatings deposited at higher currents (0.3 and 0.4 A – figure 1b) has a crystalline character and the line width is similar to the line width of the substrate, while the relative intensities of the reflections differ a little from the relative intensities of the standard without texture, indicating the absence of a pronounced Pb texture in the coatings. In these radiographs there are not even traces of titanium reflections, although their quantity in these coatings represents 30 and 23%. This is explained by the competition between the particles of Pb and Ti, which is determined by the relation between the currents of the corresponding magnetrons.
For a current in the titanium magnetron of I = 1A (figures 1a, b), lead ions dominate in the coating formation, and this effect increases with an increase in the lead magnetron current from 0.1 to 0.4 A.

The 4 coatings deposited with Ti magnetron currents of I = 2–3A (figures 1c, d) have a pronounced texture; in this case, when the coatings are sputtered for 10' a basal texture is formed (figure 1c), and when the sputtering time increases to 40' there is a little blur in the basal texture with the formation of the reflections (103) and (102) away from the basal plane at angles of 30–40° while the basal distant orientations at angles of 60–90° and the reflections (101) and (100) are practically absent indicating low intensities of the corresponding reflexes.

An analysis of sample 8 shows that, at a high current of the titanium magnetron, an increase in the current of the lead magnetron did not lead to an increase in the intensity of the lead.

The results of the coatings' thicknesses measured by the profilometer are largely consistent with the calculations of the X-ray diffraction patterns.

**Figure 3.** SEM image of the PbTi coating sample 7 at a magnification of ×8000.

An SEM image of the Pb-Ti coating in sample 7 is shown in figure 3. The granular structures and the presence of voids are visible. Perhaps this is due to the fact that the coating growth process is strongly associated with the physical properties of the grown material [11].

**Acknowledgements**

The financial support for the research was provided by a grant from the President of the Russian Federation MK-2019 (Project 075-15-2019-320).

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