Study of the influence of the substrate material on the phase composition and thickness of Ti-Pb coatings deposited by a magnetron

A A Lozovan, S Ya Betsofen, M A Lyakhovetsky, Yu S Pavlov, I A Grushin, M A Lebedev, T S Sukhova and E P Kubatina

Moscow Aviation Institute (National Research University) (MAI), 125993, Moscow, Volokolamskoe shosse, 4
E-mail: loz-plasma@yandex.ru

Abstract. The structure of coatings deposited by reactive magnetron sputtering of Ti and Pb cathodes on substrates from Mo, 30HGSA and 304 steel was studied by X-ray diffraction. The thickness of the coatings was determined by the difference between the CTE of the coating and the substrate, which is maximum for Mo coating and minimum for 304 steel, for which the thickest coating was found, consisting of tetragonal modifications of PbO.

1. Introduction.
Thin Pb films are successfully used for solid lubrication in low-load friction units and in special aerospace devices [1]. However, the use of lead (as well as other soft materials) as solid lubricating coatings (SLC) for heavily loaded parts is ineffective due to its short service life. At present, several types of composite coatings are used for these purposes, which consist of a solid matrix and a lubricant [2–8]. This paper is devoted to the study of the composition, structure and morphology of Pb-Ti coatings obtained by simultaneous deposition of Pb and Ti on various substrates.

2. Materials and research methods
The scheme of the reactive magnetron co-sputtering process of two separate single-element cathodes (Ti and Pb, respectively) is shown in figure 1. The substrate was installed at a large distance from the magnetrons (220 mm) in order to increase the efficiency of its thermalization during transfer from the cathode to the substrate due to the large atomic weight of Pb.

Preparation of samples includes cleaning in an ultrasonic bath in gasoline and in isopropanol. After pumping air from the chamber to a residual pressure $P_{\text{res}} = 8.5 \times 10^{-6}$ mm Hg, argon was injected into the chamber to a pressure $P_{\text{Ar}}=9.0 \times 10^{-4}$ mm Hg and the sample surface was cleaned using an ion source for 15 minutes. Next, a Ti sublayer was deposited ($I = 2.5A$, $U = 342B$, $P_{\text{Ar}} = 4.0 \times 10^{-3}$ mm Hg, $\tau = 5'$), after the deposition was carried out using two Ti + Pb magnetrons (samples №. 62, 64): $P_{\text{Ar}}=9.0 \times 10^{-4}$ mm Hg and (№. 66): $P_{\text{Ar}} = 1.8 \times 10^{-3}$ mm Hg, or in a mixture of argon and nitrogen at $P_{\text{Ar} + \text{N}} = 1.2 \times 10^{-3}$ mm Hg (№. 63, 67-68), $P_{\text{Ar} + \text{N}} = 1.7 \times 10^{-3}$ mm Hg (№. 69), $P_{\text{Ar} + \text{N}} = 2.2 \times 10^{-3}$ mm Hg (№. 70). The substrate materials, current and voltage values at Ti and Pb cathodes are shown in table 1. The total time of sputtering deposition was 60 min.

X-ray phase analysis was performed on a DRON-4 X-ray diffractometer in filtered CuKα radiation with wavelengths $\lambda_{\text{CuKα}} = 1.54178$ Å.
Figure 1. Magnetron sputtering system scheme: M1 and M2 – magnetrons, IS – ion source.

Table 1. Parameters of the coating deposition.

| №№   | Substrate material | Ti I, A | Ti U, V | Pb I, A | Pb U, V |
|-------|--------------------|---------|---------|---------|---------|
| 62    | Mo                 | 3,5     | 381     | 0,1     | 385–437 |
| 63    | Mo                 | 3,5     | 388     | 0,1     | 365–381 |
| 64    | Mo                 | 3,5     | 380     | 0,1     | 395–453 |
| 66    | Mo                 | 3,5     | 332     | 0,1     | 364–422 |
| 67    | Mo                 | 3,5     | 387     | 0,1     | 396–422 |
| 68    | 304 steel          | 3,5     | 383     | 0,1     | 369–401 |
| 69    | 30HGSA steel       | 3,5     | 382     | 0,1     | 347–358 |
| 70    | 304 steel          | 3,5     | 378     | 0,1     | 332–363 |

3. Experimental results and discussion

The increase in voltage (see table 1) during the glow discharge process is associated with the reactive nature of the coating sputtering process – the supply of nitrogen to the chamber and the presence of residual oxygen in it. Figures 2–6 show X-ray patterns of coatings deposited on the Mo substrate. All 5 X-ray patterns are almost identical, they contain intense lines of a highly textured Mo substrate with a typical rolling texture of BCC metals {100} + {211} parallel to the rolling plane.

The presence of intense substrate lines indicates that the coating is thin, especially given the ultra-high absorption index of lead, which is used as a protection against X-rays. All diffractograms have a halo in the angle range $2\theta \sim 22–35^\circ$.

Figure 2. X-ray pattern of the coating № 62 (Ti+Pb) deposited on the Mo substrate.
Figures 3–6 show X-ray patterns from coatings deposited on substrates made of 30HGSA steel with a BCC lattice (figure 8) and 304 austenitic steel with an FCC lattice (figures 7 and 9). Both steels used as substrates are also characterized by the presence of rolling textures characteristic of FCC and BCC metals, respectively \{110\} + \{311\} for 304 steel and \{100\} + \{211\} for 30HGSA steel, but in contrast to the Mo substrate, the textures of both steels are weakly expressed (figures 7–9). In addition, the absolute intensity of reflections from steel substrates (figures 7–10) is significantly lower than the intensity of reflections from the Mo substrate (figures 2–6) and X-ray patterns show distinct reflections from coatings, which indicates the presence of sufficiently thick coatings that shield reflections from the substrate.

### Figures 3–6

1. **Figure 3.** X-ray pattern of the coating № 63 (Ti+Pb+N\(_2\)) deposited on the Mo substrate.
2. **Figure 4.** X-ray pattern of the coating № 64(Ti+Pb) deposited on the Mo substrate.
3. **Figure 5.** X-ray pattern of the coating № 66 (Ti+Pb) deposited on the Mo substrate.
4. **Figure 6.** X-ray pattern of the coating № 67 (Ti+Pb+N\(_2\)) deposited on the Mo substrate.

### Figures 7–10

5. **Figure 7.** X-ray pattern of the coating № 68 (Ti+Pb+N\(_2\)) deposited on the 304 steel substrate.
6. **Figure 8.** X-ray pattern of the coating № 69 (Ti+Pb+N\(_2\)) deposited on the 30HGSA steel substrate.
In terms of substrate intensities, the thickest coating corresponds to No. 68, followed by No. 70 and the thinnest coating No. 69. Thus, the thinnest coatings are formed on the Mo substrate (figures 2–6), since the intensity of this substrate on the X-ray patterns is maximum, then the thickness of the coating on the 30HGSA steel substrate follows (figure 8), then the thickest coatings on the 304 steel substrate (figures 7, 9). This sequence of coating thicknesses can be associated with the difference in the thermal expansion coefficient for these materials and their differences, which determine the value of thermal stresses during cooling of coatings after coating deposition, show in table 2. Note that all three substrate materials have a lower coefficient of thermal expansion than the lead coating, so the thermal stress in the coating must be tensile and must have a significant effect on the adhesion of the coating to the substrate.

| Material       | $\alpha \times 10^6$, K$^{-1}$ | $\Delta \alpha_{\text{Pb}-X}$ (X=Mo, 30HGSA, 304) | $\Delta \alpha_{\text{Pb}-X} / \Delta \alpha_{\text{Pb-Mo}}$ |
|----------------|-------------------------------|-----------------------------------------------|-------------------------------------------------|
| Pb             | 29,2                          | 0                                             | --                                             |
| Mo             | 5,2                           | 24,0                                          | 1                                               |
| 30HGSA steel   | 12,3                          | 16,9                                          | 0,70                                           |
| 304 steel      | 17,6                          | 11,6                                          | 0,48                                           |

Thus, the most extended coatings are formed on substrates that have the minimum difference in the coefficient of thermal expansion with the coating (304 steel), and the least extended coatings are formed on substrates that have the maximum difference in the coefficient of thermal expansion with the coating (Mo), since the value of thermal stresses is proportional to this difference:

$$\sigma_T = E\Delta T(a_{\text{coat.}} - a_{\text{subst.}})$$  \hspace{1cm} (1)

Coatings deposited on steel substrates are characterized by different phase compositions. The X-ray pattern of sample No. 68 (figure 7) shows reflections corresponding to the tetragonal modification of PbO (PbO$_t$). In [9], a mixture of oxides from tetragonal and orthorhombic modifications (PbO$_t$ and PbO$_o$) was obtained by thermal evaporation and subsequent oxidation. In our case, the X-ray pattern shows no reflexes from the orthorhombic modification (figure 10), but there are several additional PbO$_t$ reflexes, probably belonging to other Pb oxides, of which there are several types with different stoichiometry (Pb$_3$O$_4$, Pb$_2$O$_3$, PbO$_2$, Pb$_2$O$_{19}$). Coating № 70 consists of Pb (figure 9), and № 69 consists of a mixture of Pb and an orthorhombic modification – PbO$_o$ (figure 8). It is noteworthy that the coating of all three steel samples was performed in a mixture of argon and nitrogen, but the X-ray pattern...
patterns showed oxide reflexes. EDS showed the presence of oxygen and nitrogen in the surface layers, which suggests that formed lead oxynitrides are isostructural to the corresponding lead oxides.

It can be assumed that the halos in diffraction patterns from coatings on a Mo substrate (figure 2–6) correspond to the location of the amorphous halo from the orthorhombic or tetragonal modification of PbO, which is usually located in the region of reflections from planes with maximum interplanar distances (figure 10), i.e. e. in the range of angles 2Θ = 28–30° (figures 2–6). Coating on a Mo substrate for samples No. 63 and No. 67 was performed in a mixture of argon and nitrogen. In this case, by analogy with coatings on steels, the halos in the corresponding X-ray diffraction patterns (figures 3 and 6) are presumably formed from amorphous oxynitrides. The position of these halos does not differ from the analogous halos in figures 2, 4, 5, which correspond to X-ray diffraction patterns from coatings deposited in an argon atmosphere in the absence of nitrogen. Nevertheless, it can be noted that the halo intensity for coatings obtained in a mixture of argon and nitrogen is noticeably higher (figures 3 and 6) than in figures 2, 4 and 5, which correspond to coatings deposited in the absence of nitrogen.

In [9], the crystal structure of lead oxides was investigated as a possible replacement for gallium diselenide and cadmium telluride with cheaper photovoltaic materials. In this regard, lead oxides seem promising, but their efficiency is determined by the ratio of lead and oxygen atoms, on which the band gap depends. The maximum theoretical energy conversion efficiency is estimated at ~ 20 % for PbO, oxide, which has a band gap of 1.4 eV. The production of films by thermal evaporation and subsequent oxidation in [9] forms a mixture of oxides from the tetragonal and orthorhombic modifications of PbO, which is characterized by the band gap values of 2.2–2.4 eV, which is between 1.9 and 2.8 eV, respectively for PbO and PbO2. In [10], the authors consider that magnetron sputtering with the production of multilayer films is one of the possible alternative methods for the deposition of lead oxide films, which makes it possible to expand the range of available materials with advantageous properties and to make it possible to manufacture multi-junction devices.

Our coating №68 showed an almost single-phase PbO structure, which should be closer (1.9 eV) to the optimal value (1.4 eV) compared to [9], which allows us to count on the possibility of obtaining an optimal result in the implementation of targeted work.

Acknowledgements
The work was carried out according to the state project of the Ministry of Education and Science of Russia, topic number FSFF-2020-0014.

References
[1] Scharf T W and Prasad S V 2013 J. Mater. Sci. 48 511–31
[2] Muratore C and Voevodin A A 2009 Annual Review of Materials Research 39 297–324
[3] Voevodin A A, Zabinski J S and Muratore C 2005 Tsinghua Science and Technology 10 665–79
[4] Muratore C, Voevodin A A, Hu J J and Zabinski J S 2006 Wear 261 797–805
[5] Basnyat P, Luster B, Kertzman Z, Stadler S, Kohli P, Aouadi S, Xu J, Mishra S R, Eryilmaz O L and Erdemir A 2007 Surf. Coat. Technol. 202 1011–6
[6] Lozovan A A, Lesnevsky L N, Betsofen S Ya, Liakhovetsky M A and Usakov A M 2018 IOP Conf. Series: Materials Science and Engineering 387 012048
[7] Lozovan A A, Betsofen S Ya, Liakhovetsky M A and Alexandrova S S 2018 IOP Conf. Series: Materials Science and Engineering 387 012049
[8] Lozovan A A, Betsofen S Y, Lyakhovetskiy M A, Lesnevsky L N, Bespalov A V, Nikolaev I A, Pavlov Y S and Aleksandrova S S 2019 Journal of Physics: Conference Series 1396 012029
[9] Droessler L M, Assender H E and Watt A A 2012 Materials Letters 71 51–3
[10] Venkataraj S, Geurts J, Weis H, Kappertz O, Njoroge W K and Jayavel R 2001 Journal of Vacuum Science and Technology Part A. 19 2870–8