Tribological properties of solid lubricating coatings of the TiN-Pb system at various Pb content

M A Lyakhovetskiy, A A Lozovan, I N Lesnevskiy, I A Nikolaev and Yu S Pavlov
Moscow Aviation Institute (National Research University) (MAI), 125993, Volokolamskoe shosse, 4, Moscow, Russia
E-mail: maxim.lyakhovetskiy@mai.ru

Abstract. The paper presents the results of the investigation of the solid lubricant coatings (SLC) tribological properties based on a TiN matrix with various content of Pb (13, 16 and 22 at. %) in monolayer design. The results of the study of its morphology, elemental composition and tribological properties are provided. It is shown that the increase of the Pb content from 13 to 22 at. % lead to increase of CoF and decrease the wear resistance.

The use of solid lubricating coatings (SLC) to protect friction surfaces is usually justified by the impossibility of using liquid lubricants due to extreme operating conditions: high temperature, high pressure in the contact zone, vacuum, hard radiation, etc. [1]. These extreme working conditions are typical of the aerospace systems elements (bearings, dynamic gas bearings, plain bearings, lock joints in gas turbine engines, etc.), the nuclear industry (fuel rods contacts and spacing grids), the automotive industry (cylinder wall/piston ring lubrication, arms action components), and general engineering (molding tools, cutting tools, accessories, etc.) [2–4].

Traditionally SLC (silver, graphite, molybdenum disulphide, etc.) have a low friction coefficient (~ 0.01–0.1) due to the low shear modulus value, but a short service life [5]. Therefore, to improve the tribological properties of the SLC composite coatings consisting of a solid matrix and a lubricant component are nowadays used [6]. As lubricating components of such coatings, the noble metals Ag or Au are commonly used, due to their resistance to oxidation at high temperatures. But there are a number of other plastic metals (Pb, Sn, In, etc.), whose use for friction units, in some cases is more appropriate than those mentioned before. Carbide [7], oxide [8–10], and nitride compounds [11–13] are used as wear-resistant matrices for composite coatings with plastic metals. To obtain such coatings, various methods are used [3, 5]: thermal spraying, physical and chemical vapor deposition, etc. The use of these methods is associated with their manufacturability, high adhesion of coatings to the substrate, the ability to regulate the coatings chemical and phase composition in wide ranges, etc.

Titanium nitride has been used for a long time as a wear-resistant coating, but it has a high coefficient of friction [14], therefore, to improve this thing, this paper presents a method for creating a SLC based on a wear-resistant TiN matrix with a solid lubricant in the form of Pb, deposited by magnetron sputtering.

Previously, the influence of the coatings design (mono- and multilayer) on the tribological properties of the TiN-matrix with the addition of Pb was investigated [15]. The influence of the
amount of lead in the matrix on the tribological characteristics of a monolayer coating is considered in this paper.

The coatings were applied to specimens 20 mm in diameter and 3 mm thick, made of Ti6Al4V titanium alloy with a polished surface to a roughness of Ra ≤ 1.2 μm. Before placing the samples in a vacuum chamber, ultrasonic cleaning in gasoline and drying at room temperature was carried out.

The sample was installed in the chamber at a distance of 220 mm from the magnetron targets (figure 1) and cleaned with Ar ion-beam etching for 20 minutes. The magnetrons targets were made from technical pure titanium alloy (99.9 %) and pure lead (99.99 %). Magnetron deposition modes for coatings of Samples 1, 2, 3 with various Pb content are presented in table 1.

Figure 1. Magnetron sputtering system scheme: M1 and M2 – magnetrons, IS – ion source.

| №  | Gas           | $U_{Ti}$, V | $I_{Ti}$, A | $U_{Pb}$, V | $I_{Pb}$, A | $f$, kHz | T, % | t, min |
|----|---------------|-------------|-------------|-------------|-------------|----------|------|--------|
| 1  | Ar+N₂         | 370         | 3.5         | 360         | 0.1         | -        | 100  | 360    |
| 2  | Ar+N₂         | 370         | 3.5         | 360         | 0.1         | 40       | 80   | 360    |
| 3  | Ar+N₂         | 370         | 3.5         | 360         | 0.1         | 25       | 80   | 360    |

The study of the morphology and elemental composition of the obtained coatings was carried out on a scanning electron microscope (SEM) EVO-40 Carl Zeiss with an attachment for energy dispersive analysis (EDA) INCA Oxford Instr.

To estimate the values of the friction coefficient and compare the tribological properties of the coatings, the friction machine shown in figure 2. The tests were carried out at normal contact force $F_n = 1$ N by the sphere / plane method. A sphere made of 100Cr6 steel with a diameter of 12.7 mm was used as a counterbody. Relative displacement of bodies D = 5 μm, frequency f = 20 Hz, number of friction cycles $n = 5 \times 10^5$, system stiffness $k_s = 31$ MN/m. To calculate the friction coefficient, an energy approach was used based on its assessment, as the ratio of the dissipated energy in a contact in one friction cycle to the total energy specified as the product of the total relative samples displacement and the doubled normal force [16–19]:
where $E_{di}$ – is the dissipated energy in the contact in one friction cycle. The value of the dissipated energy is calculated from the friction parameters instantaneous values:

$$
E_{di} = \sum_{i=1}^{N} \frac{\delta_{i+1} - \delta_i}{2} (F_{rpi(i+1)} + F_{rpi}),
$$

where $\delta_{i+1}$ – are the instantaneous values of the real displacement taking into account the rigidity of the friction machine system $(kc)$, $F_{rpi(i+1)}$ – are the instantaneous values of the friction force and $N$ – is the number of instantaneous measurements per friction cycle.

The measurement of the samples wear volume after tests was carried out on an interferometric 3D microscope-profilometer LEXT OLS 5000 (Olympus).

![Figure 2. Friction machine scheme: 1 – electromagnetic vibrator; 2 – force sensor; 3 – displacement sensor; 4 – load system; 5 – samples contact place.](image)

Photos of the sample surface after coating are shown in figure 3 obtained on SEM using a SE detector, as well as spectrograms of energy dispersive analysis (figures 3b, d, f) of the coating composition. All coatings contain elements of titanium, nitrogen, lead and oxygen. The surface morphology of Sample № 1 (figure 3a) differs from Samples № 2 (figure 3c) and № 3 (figure 3e) in the large size of lenticular structures ~ 3–4 μm in diameter, which also has a more porous structure.

The lenticular structures of Samples № 2 and № 3 have a characteristic size of ~ 2 μm and a denser arrangement. Figure 4 shows comparative graphs of the percentage ratio of the number of atoms in the coatings obtained from the spectrograms. The number of lead atoms in the coating of Sample № 1 ~ 22 at. %, Sample № 2 ~ 16 at. %, Sample № 3 ~ 13 at. %. It should be noted that, based on the presence of oxygen atoms in the spectrum, lead is apparently in the coating in the form of an oxide.

The graph of the friction coefficient versus time is shown in figure 6. As can be seen from the graph, the smallest friction coefficient corresponds to coating № 3 with a lower lead content and is equal to ~ 0.03. On sample № 1, the friction coefficient is ~ 0.045, and on Sample № 2, a jump in the friction coefficient from 0.05 to 0.035 is observed after 2500 seconds of testing.

It should be noted that a decrease in the proportion of lead content in the coating to 13 at. % has a positive effect on increasing its wear resistance. This is due to an increase in the proportion of the influence of the matrix on the wear process.

2D and 3D images of wear worn are shown in figure 5, obtained with an 3D optical microscope.
**Figure 3.** SEM images of the surface of the samples using a SE mode at 5000x magnification and elemental analysis spectrograms: a), b) Sample № 1, c), d) Sample № 2, e), f) Sample № 3.

**Figure 4.** The ratio of the number of atoms in the sample coatings, obtained by the method of energy dispersive microanalysis for Samples № 1, № 2, № 3.
Figure 5. Image of the surface of the samples with wear spots, obtained in an optical microscope, and the measured relief: a), b) Sample № 1, c), d) Sample № 2, e), f) Sample № 3.

The obtained results of measuring the wear volume of Samples and counterbodies (figure 7) confirm an increase in the tribological properties of coatings with a decrease in the content of lead in the coating: the wear volume of the coating of Sample № 3 is more than 10 times lower than the wear volume of Sample № 1.

Morphological and elemental analysis of products and wear spots by the method of energy dispersive analysis showed that there was a destruction of the coating of sample № 1 in the process of wear (zone A, figure 5a). For specimens with Sample № 2 and № 3, no destruction is observed, but
there is a transfer of wear products to the surface from the counterbody in the form of iron oxide (zone A, figure 5c, e).

**Figure 6.** The graph of the change in the coefficient of friction versus time for Samples № 1, № 2, № 3.

**Figure 7.** Comparative graph of the wear volume of Samples № 1, 2, 3 and counterbodies.

**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] Heredia-Cancino J A, Ramezani M and Álvarez-Ramos M E 2018 Trib. Int. 124 230–7
[2] DellaCorte C 1996 Surf. and Coat. Technol. 86-87 486–92
[3] NASA Technical Memorandum 107249, Chapter 1. Solid Lubrication Fundamentals and Applications Introduction and Background, Kazuhasa Miyoshi Lewis Research Center Cleveland, Ohio June 1996
[4] Hogmark S, Jacobson S and Larsson M 2000 Wear 246 20–31
[5] Semenov A P 2007 Trenie i iznos (Friction and wear) 28 525–38
[6] Muratore C and Voevodin A A 2009 Annual Review of Materials Research 39 297–324
[7] Voevodin A A, Zabinski J S and Muratore C 2005 Tsinghua Sci. Technol. 10 665–79
[8] Wang W 2004 Surf. Coat. Technol. 177–178 12–7
[9] Endrino J L, Nainaparampil J J, Krzanowski J E 2002 Surf. Coat. Technol. 157 95–101
[10] Muratore C, Voevodin A A, Hu J J and Zabinski J S 2006 Wear 261 797–805
[11] 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
[12] Aouadi S M, Bohnhoff A, Sodergren M, Mihut D, Rohde S L, Xu J and Mishra S R 2006 Surf. Coat. Technol. 201 418–22
[13] Mulligan C P and Gall D 2005 Surf. Coat. Technol. 200 1495–500
[14] Kondratiev V A, Lesnevsky L N, Tyurin V N and Ushakov A M 2004 *Problemy mashinostoeniya I nadezhnosti machin (J. of Mach. Manuf. and Reliab.)* 2 49–54

[15] Lesnevskiy L N, Lyakhovetskiy M A, Lozovan A A and Nikolaev I A 2019 *IOP Conf. Series: Journal of Physics: Conf. Series* 1281 012049

[16] Fouvry S, Kapsa P, Zahouani H and Vincent L 2009 *Wear* 203 393–403

[17] Fouvry S, Kapsa Ph and Vincent L 1996 *Wear* 200 186–205

[18] Mohrbacher H, Celis J-P and Roos J R 1995 *Tribol. Int.* 28 269–78

[19] Lesnevskiy L N, Lyakhovetskiy M A and Savushkina S V 2016 *Journal of Friction and Wear* 37 (3) 268–73