Structure and properties of solid lubricating coatings based on the TiN-Pb system

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Abstract. This paper presents the results of comparative investigations of solid lubricating coatings of the TiN-Pb system including multi-layer coatings with layers thickness of the nanoscale range. Morphology, phase and chemical compositions and textures of the coatings are investigated, and the results of tribological tests are presented.

In the problems of tribology, the use of solid lubricating coatings is an effective and relatively inexpensive way to reduce friction and protect the surface of products against wear. The choice of a suitable coating to solve specific tribological problem is very difficult since the effect of many factors must be taken into account such as coating properties, substrate, interface, operating conditions and capabilities of deposition methods [1–4].

It is generally believed that alloying with soft metals, such as Pb, can reduce the friction coefficients of the coatings due to the effects of lubrication although they have poor wear resistance. The joint application of soft and solid metals, such as Ti [5], can reduce friction coefficient and improve mechanical properties of coatings. In this paper, the results of investigations on the capabilities of this method for the TiN-Pb system are presented.

Coatings were formed on specimens with the sizes of 20×15×10 mm made of VT9 titanium alloy. Before deposition, specimens were polished with diamond wheel over the surface with a larger area to the roughness of Ra ≤ 1.2 μm. The specimens were then cleaned in gasoline and isopropyl alcohol before deposition and placing into a vacuum chamber.

The specimen was placed into the chamber at a distance of 100 mm to the target of magnetron. After opening the shutter of diffusion pump, specimens were heated up to the temperature of 160 °C which then grew up to about 180 °C with the magnetron being turned on. The surface of the grounded substrate in the chamber was purified with Ar ions using an ion source for 20 minutes with the following process parameters: \( P_{Ar} = 5 \times 10^{-2} \) Pa, current of \( I = 0.5 \) A, ion energy of the order of \( E \approx 1.5 \) keV. After purification the ion source was not turned off when all types of coatings being formed, which thus provided ion-stimulated sputtering during the whole process. Sputtering was carried out in the pulsed medium-frequency mode of magnetron operation (50 kHz). To spray Ti + Pb, a mosaic target was used, i.e. titanium with lead inserts.

Comparative investigations of coatings with the following compositions were made: TiN (№ 1), TiPbN single-layer (№ 2) and TiPb / TiPbN multi-layer (№ 3). The TiN coating (№ 1) with 3 μm
thickness was obtained at a chamber pressure of \( P_{\text{Ar}} = 5 \times 10^{-2} \text{ Pa} \), a discharge current of \( I_d = 3.5 \text{ A} \) and a discharge voltage of \( U_d = 585 \text{ V} \), and a bias voltage on the substrate of 75 V. The TiPbN single-layer coating (№ 2) with a thin (50 nm) TiPb sublayer were obtained using the following deposition mode. First, at a chamber pressure of \( P_{\text{Ar}} = 5 \times 10^{-2} \text{ Pa} \), Ti + Pb layer with 50 nm thickness was deposited for 3 minutes at a discharge current of \( I_d = 4 \text{ A} \) and a discharge voltage of \( U_d = 525 \text{ V} \), and a bias voltage on the substrate of 75 V. Nitrogen was then introduced into the chamber, and the second TiPbN layer with 1.5 μm thickness (immobile substrate) and 1 μm thickness (rotating substrate) was deposited at a pressure of \( P_{\text{Ar}} = 2 \times 10^{-1} \text{ Pa} \) for 85 minutes under the same discharge parameters.

The TiPb / TiPbN multi-layer coating (№ 3) with 3 μm thickness was obtained using the following deposition mode. At a chamber pressure of \( P_{\text{Ar}} = 5 \times 10^{-2} \text{ Pa} \) the TiPb layer with the thickness of about 150 nm was deposited for 6 minutes at a discharge current of \( I_d = 4 \text{ A} \) and a discharge voltage of \( U_d = 629 \text{ V} \), and a bias voltage on the substrate of 75 V. Then nitrogen was introduced into the chamber, and at the pressure of \( P_{\text{Ar}} = 2 \times 10^{-1} \text{ Pa} \) the second coating layer, TiNPb, was deposited also for 6 minutes under the same discharge parameters. Thus, 20 layers each of TiPb and TiPbN alternate one after another for 240 minutes (the last layer is TiPbN) forming a multi-layer coating. Morphology of the coatings and elemental composition were studied using the EVO-40 CarlZeiss scanning electron microscope with the INCAOxfordInstruments attachment for the energy-dispersive analysis; phase compositions and textures of the coatings were determined using the DRON-4 diffractometer in filtered CuKα radiation. To estimate the values of friction coefficients and compare tribological properties of various coatings compositions, the friction test machine was used shown in figure 1.

Figure 1. Scheme of the 1401 friction test machine: 1 – electromagnetic vibrator; 2 – force sensor; 3 – displacement sensor; 4 – loading system; 5 – location of specimens contact.

The 1401 friction test machine developed in MAI allows the reciprocating relative sliding of rubbing bodies to be excited by means of the electromagnetic vibrator (1). The normal force in the contact of \( F_n = 1 \text{ N} \) was set by the lever system (4) with a plumb line; moving of rubbing bodies of \( D = 100 \mu \text{m} \), frequency equaled \( f = 20 \text{ Hz} \). Movement control was carried out by the LC-2420 laser sensor (3) with the resolution of \( \Delta = 0.01 \mu \text{m} \) and the LC-2400 controller made by the Keyence (Japan). The number of friction cycles \( n \) was limited to \( 5 \times 10^4 \) in all tests. The frictional force in the contact was recorded using the 208C02 piezoelectric force sensor (2) with the resolution of \( \Delta = 4 \text{ mN} \), and the 482A22 controller made by the PCB (USA). The rigidity of the friction test machine system with the device for fixing the samples was estimated by direct measurement and equaled \( k = 31 \text{ MN/m} \). Balls of ShH-15 material with the diameter of 12.7 mm were used as counter-bodies.

Figure 2 shows the surfaces of three coatings samples with the following composition: № 1 – TiN, № 2 – TiPbN (single-layer) and № 3 – TiPbN (multi-layered). As can be seen, the surface of sample
№ 2 (figure 2(b)) has a columnar structure, which appears in the form of spherical formations on the surface with the diameter of less than 2 μm closely adjacent to each other. The surface of sample № 3 has morphology similar to sample № 1 with TiN (figure 2(a)), but places with lens-shaped formations are observed (figure 2(c)). Considering the multi-layer construction of TiPb/TiPbN coating where the thickness of each layer does not exceed 150 nm, we can assume that the presented image (figure 2(c)) is a reflection of beginning for the columnar structure growth. At the same time the thickness of each coating layer limited to 150 nm results in an intermediate state of the surface when the columns formation is still at the initial stage.

**Figure 2.** SEM images for the surfaces of three coatings: (a) – TiN, (b) – TiPbN (single-layer) and (c) – TiPbN (multi-layer).

The elemental analysis of specimens surfaces shows that the atomic % ratio of the coating elements for TiN is 45:55, respectively. Such a relationship, as the paper [6] shows, is optimal to form a wear-resistant coating of titanium nitride.

**Figure 3.** Spectra of energy-dispersive analysis for the coatings: (a) TiPbN – single-layer (full scale 2929 imp., cursor 2.410 (538 imp.)) and (b) TiPbN – multi-layer (full scale 3576 imp., cursor 6.180 (18 imp.)).
Diffraction pattern analysis of the coatings showed that the presence of α-Ti with the HCP lattice and TiN with NaCl-type lattice was detected in coating № 1, and strong (110) texture of the substrate plane was observed. The phase compositions of coatings № 2 and № 3 are characterized by the presence of three phase reflections: α-Ti with hexagonal close-packed crystal lattice, δ-TiN titanium nitride with NaCl-type lattice, and Pb with FCC lattice. Reflections of α-Ti are the total reflections of the coating and the titanium substrate since the thickness (1–1.5 μm) of coatings is less than the penetration depth of X-rays.

Elemental analysis of the samples № 2 and № 3 (figure 3(a), (b), respectively) showed that the coatings consisted of titanium, nitrogen and lead, but had different ratios. So, the atomic % Ti:Pb:N ratio is 35:6:59 for the sample № 2, and that for the sample № 3 equals 79:0.5:20.5. Increased titanium content for the sample № 3 can be attributed to the small thickness of separate layers, their alternation of TiPb/TiPbN, and the sensitivity of the analysis method to the depth: the analyzed region is a drop-shaped volume with a characteristic size of 1 μm. Analysis of the spherical formations in the coatings of the samples № 2 and № 3 showed the elemental composition identical to that indicated above.

Figure 4. Comparative graph for friction coefficients of obtained coatings: 1 – TiPbN – single-layer; 2 – TiPbN – multi-layered; 3 – TiN.

Figure 4 shows a comparative graph for friction coefficients of obtained coatings. Friction coefficient of pure TiN with ShH-15 is approximately 0.7. The same friction coefficient is shown by the TiPb / TiPbN multi-layer coating, but irregular peaks of friction coefficient decrease to the values of 0.3 are observed. The best friction coefficient is shown by the TiPbN monolayer coating – 0.2. This value of friction coefficient was practically unchanged up to 33 thousand cycles, after which the destruction of tribological layer followed, and friction coefficient increased up to 0.7 as for the other samples.

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