Tribological properties of TiN-Pb system solid lubricant coatings with various morphologies

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Abstract. The paper presents the results of the investigation of the solid lubricant coatings (SLC) tribological properties of several designs based on a TiN matrix with the addition of Pb (~6% atomic). A comparison of the tribological properties is made between the TiN coating without the addition of a solid lubricant component, a monolayer coating of TiPbN with a TiPb adhesive layer and a multilayer coating with alternating TiPb / TiPbN layers. It is shown that the monolayer coating has the smallest friction coefficient (~0.2), while the friction coefficient of a multilayer coating is ~0.75, which coincides with the friction coefficient for the TiN coating. Despite the friction coefficient high level of the multilayer coating, its resistance to wear is at the level of the monolayer coating.

1. Introduction

The use of solid lubricating coatings (SLC) to protect friction surfaces is usually recommended when the use of liquid lubricants is impossible 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. Titanium nitride has been used for a long time as a wear-resistant coating, but has a high friction coefficient [7]; therefore, in order to improve this index, the present work provides a method to form a SLC based on a wear-resistant TiN matrix with solid lubrication in the form of precipitated Pb by magnetron sputtering.

2. Materials and methods

Coatings were formed on substrates measuring 20 × 15 × 10 mm, made of titanium alloy VT9 with a pre-polished surface to a roughness of Ra ≤ 1.2 μm. Before installing the substrates in a vacuum chamber, they were cleaned in isopropyl alcohol and then in deionized water and dried in hot air.
The substrate was placed in the chamber at a distance of 100 mm from the magnetron target. The surface was cleaned by ion bombarding with Ar ions for 20 minutes. The substrate heating temperature during the coatings deposition was 180 °C. A titanium mosaic target with lead inserts was used for spraying.

Three types of samples were prepared to study the effect of Pb addition and the coating structure on the tribological properties: TiN (1) monolayer coating, TiPbN (2) monolayer coating, and alternating TiPb / TiPbN (3) multilayer coating. Before the formation of the coatings main compositions, a metallic adhesive mono- and multilayer of Ti and TiPb was deposited respectively for the TiN and TiPbN. The magnetron deposition parameters for all types of samples are presented in Table 1.

Table 1. Magnetron sputtering deposition parameters.

| №  | Sample         | Gas     | U, V | I, A | f, kHz | P, mPa | t, min |
|----|----------------|---------|------|------|--------|--------|--------|
| 1  | TiN            | Ar+N₂   | 525  | 4    | 50     | 87     | 85     |
| 2  | TiPbN mono     | Ar+N₂   | 525  | 4    | 50     | 400    | 85     |
| 3  | TiPbN multi    | Ar+N₂   | 525  | 4    | 50     | 400    | 240*   |

* Deposition time was 6 min for every layer (TiPb or TiPbN). Coating consists 40 layers.

The thickness of the coatings was measured by an interferometric method using the ledge formed on a witness sample using a MicroXAM-100 3D surface profilometer. The study of the morphology of the coatings was carried out on an EVO-40 Carl Zeiss scanning electron microscope.

The friction machine shown in figure 1 was used to estimate the values of the friction coefficient and compare the tribological properties of the coatings. The tests were carried out with a normal force $F_n = 1$ N according to the sphere/plane scheme. 100Cr6 steel ball with a 12.7 mm diameter was used as a counterbody. The friction couple realized a relative reciprocating sliding. The displacement of the bodies was $D = 100 \mu m$, frequency – $f = 20$ Hz, number of friction cycles $n = 5 \times 10^4$ and the rigidity of the system $k_s = 31$ 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 (1) [8–10]:

$$\mu = \frac{E_{di}}{2DF_n},$$

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 (2):

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

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

3. Results and discussions

The thickness of the adhesive transition layer for monolayer coatings of TiN and TiPbN is 50 nm and 150 nm, and for the base layer is 3 μm and 2.5 μm, respectively. For a TiPb / TiPbN multilayer coating, the total thickness was 3 μm, with a ~75 nm thickness for each layer, with the first adhesive layer of TiPb being 2 times larger than ~150 nm. The surface morphology of pure titanium nitride (figure 2(a)) is a uniform surface with traces of mechanical processing during polishing, thus, the formed coating inherits the roughness obtained after polishing.
The surface morphology of the TiPbN monolayer coating is formed by lenticular formations (figure 2(b)) with a characteristic size of ≤ 2 μm. An analysis of the TiPb / TiPbN multilayer coating surface (figure 2(c)) showed that its morphology is similar to that of titanium nitride. At the same time, separate lens-shaped nucleus is clearly visible on the surface of the multilayer coating. It can be assumed that due to the small thickness of the layers, their growth does not occur in the same way as can be observed in the monolayer coating.

**Figure 1.** Friction machine scheme: 1 – electromagnetic vibrator; 2 – force sensor; 3 – displacement sensor; 4 – load system; 5 – samples contact place.

**Figure 2.** Image of the surface of the formed coatings: (a) – TiN; (b) – TiPbN monolayer; (c) – TiPbN multilayer.

The figure 3 shows a graph comparing the friction coefficients (CoF) for all types of coatings under investigation. The CoF of the TiN coating remained almost constant at ~0.75 throughout the test period. The values recording for the multilayer coating of TiPbN showed that its level was approximately in the same range of values as the TiN coating. But there was also a peculiarity associated with a strong short-term decrease in the CoF value to ~0.4–0.6 (the peaks are marked with blue arrows). This can be confirmed by the fact of the coating multylayering effect caused by changing the TiPb/TiPbN layer on the periodic decrease in the friction coefficient. It is necessary to remark that the used multilayer coating design did not allow a reduction of the friction coefficient general level.

**Figure 3.** Comparison of the coatings friction coefficients: TiN; TiNPb – monolayer; TiNPb – multilayer (blue arrows – periodic decrease of CoF for the multilayer coating; dotted line – start of sharped changing of CoF for the monolayer coating).
The friction coefficient of a monolayer TiPbN coating at the initial stage slowly increases from 0.18 to 0.23, and after 33,700 cycles (dotted line in figure 3), the sharp growth is observed. After 39,000 cycles, the friction coefficient is stabilized at a value of ~0.75.

Figure 4 shows photo of the wear points of the three samples with coatings after $5 \times 10^4$ test cycles. The obtained images show that for all the samples, when the end of the test was reached, there was a complete wear of the substrate coatings (titanium alloy). Also noteworthy is the fact that the area of the worn surfaces of the samples with Pb additive (figure 4(b), (c)) is half the size of the sample coated with TiN (figure 4(a)). It should also be taken into account that despite the fact that the average friction coefficient level of a multilayer coating compared to a monolayer was higher up to 33,700 cycles almost 4 times, their overall wear resistance was of a comparable level.

Figure 4. Image of the worn surface of the formed coatings: (а) – TiN; (b) – TiPbN monolayer; (c) – TiPbN multilayer.

The fact noted above may indicate that a high level of the CoF of a multilayer coating is associated with the presence of the TiPb layer, which, given the prevalence of Ti over Pb in it, leads to a significant increase in the coating friction coefficient as a whole. This is indirectly confirmed by the fact that the CoF practically does not change after the complete destruction of the coating (figure 3), i.e. the friction coefficient of the counterbody with the Ti substrate is identical to the friction coefficient of the counterbody with the TiPb layer. On the other hand, the wear resistance of a multilayer coating under such adverse conditions was higher than that of a monolayer (figure 4(b), (c)), which may indicate a better durability of the multilayer coating structure compared to the monolayer one.

The coatings tribological tests were carried out in the full reciprocating sliding regime, i.e. the displacement amplitude was much higher than the diameter of the contact spot. The test and diagnostic equipment used allowed the instantaneous values of the frictional force ($F_{fr}$, N) and the corresponding coordinate ($\delta$, µm) of the displacement to be fixed continuously during the experiment (n, cycles). Measuring these values allows calculating the work of the frictional force, i.e. dissipated energy in contact in one cycle. The obtained values and graphs allow to more accurately estimating the friction coefficient of the surfaces under study and the features of the operation of hard-to-use solid lubricating coatings and materials.

The figure 5 is a graph showing the change in the form of the hysteresis loop ($F_{fr}$ vs $\delta$) from the number of cycles for the TiN coating. As can be seen, the shape and nature of the hysteresis loops are almost identical throughout the test cycle. Oscillation processes in the horizontal parts of hysteresis loops are apparently associated with a high friction coefficient caused by the adhesion mechanism of the interaction of metals at high speed.

The figure 5(b) shows a graph for a monolayer TiPbN coating, from which the change in the friction character is clearly seen: from a uniform one, at which the value of the energy dissipated in the contact is significantly lower than in the TiN coating, to a similar TiN coating in character (oscillation process in the horizontal parts of hysteresis loops) and value (CoF ~ 0.75).

Unlike a monolayer coating (figure 5(c)), the shape of the loops and their area turned out to be close to the TiN-coating. This can be due to both its rapid wear at the beginning of friction and further
friction of the metal surfaces, and with a periodic decrease in the work of friction during the experiment due to the change of layers.

Figure 5. Change of the hysteresis loops shape for: (a) – TiN; (b) – TiPbN monolayer; (c) – TiPbN multilayer.

Due to the fact that in the conducted study was only possible to adequately record the transition between the coating’s work to fracture for a monolayer coating, it was only possible to evaluate the coating durability for this case. A numerical estimation of the frictional force work value (dissipated energy) per cycle for a monolayer coating on an interval when the friction coefficient is in a range between 0.18–0.23, gives a value of $E_{di} = 75 \, \mu J/\text{cycle}$. Therefore, hypothetically taking the SLC coating service life as 33,700 cycles, the value of the coating total destruction energy from the substrate is $E_t \sim 2.5275 \, J$, i.e. to destroy 1 $\mu$m of the coating nominal thickness, an energy $E_{th} \sim 0.8425 \, J/\mu\text{m}$ is required. The calculated value can be used to compare the tribological properties of the SLC coating during the development of the deposition regimes, as well as to determine the optimum thickness of the coating, provided that the same test parameters are used.

Thereby, the study showed that the addition of Pb as a solid lubricant to the TiN matrix composite coating at 6% allows improving its tribological properties: reduce the friction coefficient to 0.2, and increase the service life of such coating. It is shown that the structure and construction formed by a SLC with a similar chemical composition has a decisive role for the tribological properties of a SLC. The use of special diagnostic equipment during the tests made it possible to calculate the total destruction energy of a TiPbN monolayer magnetron coating.

4. Conclusions

Studies have shown that adding a lead matrix (~6 atomic %) to the TiN-based coating significantly improves its tribological properties, reducing the friction coefficient from 0.75 to 0.2 and increasing the wear resistance of the coating.

With the selected design parameters considered in the solid lubricating coatings work (monolayer / multilayer, number of layers of a multilayer coating, layer thickness, composition of layers, etc.), the TiPbN monolayer coating (~0.2) has the best friction coefficient, while the multilayer coating has a friction coefficient comparable to the friction between the VT9 substrate and the 100Cr6 counter body. This may be due to the presence in the multilayer coating arrangement of a TiPb layer with a predominance of Ti, which leads to an increase in the overall level of the friction coefficient of a solid lubricant coating during the adhesion interaction between friction bodies in this layer. This fact requires more research for the proper selection of the composition of this layer. In addition, the favorable indicators obtained from the friction coefficient of a monolayer coating should be applied in a multilayer, but this also requires further studies on the selection of its optimum thickness.

It should also be noted that, despite the very unsatisfactory results on the friction coefficient for a multilayer coating, in general, its wear resistance was at the level of a monolayer coating, which
should also be applied with an additional improvement of the design of a solid lubricant coating for this system.

The adequate evaluation of the coatings destruction energy indicators was possible only for the monolayer coating, this due to the possibility of tracking its operation time until its destruction. The obtained energy required value necessary for the wear of 1 μm of a TiPbN monolayer coating \( E_{th} \sim 0.8425 \text{ J/μm} \) will allow us to further evaluate the success of certain measures to improve this composition.

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