TRIBOLOGICAL STUDIES FOR COMMERCIALLY PURE GRADE 4 TITANIUM WITH DIFFERENT MICROSTRUCTURES, WITH AND WITHOUT COATING

ТРИБОЛОГИЧЕСКИЕ ИССЛЕДОВАНИЯ НА ТЕХНИЧЕСКИ ЧИСТОМ ТИТАНЕ GRADE 4 С РАЗЛИЧНОЙ МИКРОСТРУКТУРОЙ С ПОКРЫТИЕМ И БЕЗ ПОКРЫТИЯ

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Abstract. *The paper presents experimental data on the tribological properties of commercially pure titanium with different microstructures with and without coating. As a result of the conducted experiments, it was established that the integral value of the friction coefficient, as well as its adhesion component, are structurally sensitive parameters. It is noted that the ultrafine-grained structure, obtained as a result of intense plastic deformation, contributes to the reduction of the coefficient of friction, as well as to the increase of the load-bearing capacity of tribo-conjugation.*

KEY WORDS: *COEFFICIENT OF FRICTION; SHEAR STRENGTH OF ADHESION BONDS, HARDNESS, INTENSE PLASTIC DEFORMATION, MICROARC OXIDATION, ION-PLASMA SPRAYING.*

Introduction

According to the expert assessment, the use of strain-hardened commercially pure titanium in the field of medicine (as implants, tools, fasteners, etc.) is promising [1]. This is largely due to the fact that commercially pure titanium has a high biocompatibility, bioinertness, hypoallergenicity and is also non-toxic [2 - 5]. The applied deformation processing technologies make it possible to achieve a high-strength state due to the formation of ultrafine-grained (UFG) microstructure, which contributes to a significant increase in mechanical and functional properties [6, 7].

There are known works on the production of semi-products from commercially pure titanium for medical use with ultrafine-grained (UFG) structure, produced by high pressure torsion (HPT) [8 - 10], with subsequent application of a coating from titanium nitride [8, 9] and diamond-like carbon with zirconium [10]. At the same time, high strength of the material with improved tribological properties is achieved, but the samples have very small dimensions – a diameter of up to 5 - 8 mm and a thickness of less than 1 mm - which create significant limitations for their widespread use. In addition, it is difficult to conduct tribological tests on such samples.

Thus, for engineering applications, of great interest are technologies that make it possible to produce bulk (large-sized) nanostructured materials with unique physico-mechanical, performance and functional properties [1, 2, 11 - 14]. These technologies are based on the methods of equal-channel angular pressing (ECAP) [11, 14, 15], in particular, the ECAP-Conform process for the formation of UFG structures in large-sized long-length metallic materials (the principle is shown in Fig. 1).

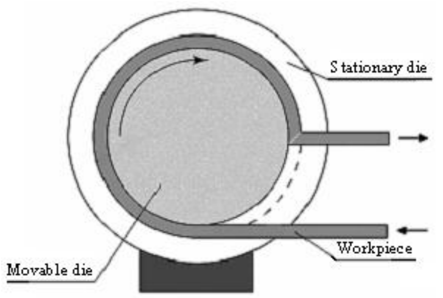

Fig. 1 *Principle of the ECAP-Conform process for producing long-length semi-finished products with ultrafine-grained structure*

For large-sized samples, many aspects related to the study of functional properties, in particular tribological ones, remain open, depending on the structural state of commercially pure titanium. In addition, comparative tribological studies of the material with different microstructures with and without coatings are of practical interest.

1.1. Methods to evaluate the integral quantity of the friction coefficient and its adhesive component

For tribological studies, the two schemes are shown in Fig. 2.

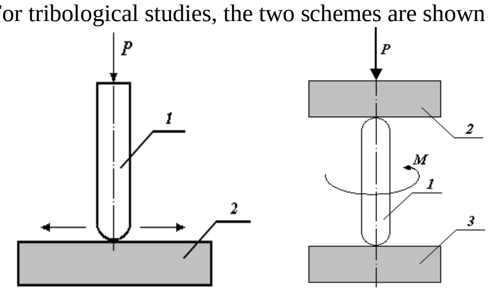

Fig. 2. *Reciprocal test scheme: a) 1 - spherical indenter; 2 - the test sample; a test scheme for determining the shear strength of adhesion bonds and the molecular component of the friction coefficient: b) 1 - spherical indenter; 2 and 3 are test samples.*

The first scheme for reciprocating motion (Fig. 2a) was used to estimate the friction coefficient in pairs "commercially pure titanium Grade 4 - chromium steel of composition Fe-1.5Cr-1.0C". This scheme was implemented on the tribometer "Nanovea TRB-1" (Fig. 3).

Fig. 3. Tribometer "Nanovea TRB-1"

For the tests we used samples in the form of a parallelepiped with a length of 25 mm and a section of 9.5 x 9.5 mm. For the indenter, we used bearing steel of composition Fe-1.5Cr-1.0C with a spherical contact surface with a diameter of 3 mm. The test conditions are as follows: temperature – room temperature; the displacement amplitude at a normal load of 5 N was 20 mm at 5000 cycles. Speed of movement was 30 cycles per min.

The second scheme (Fig. 2, b) was used to evaluate the shear strength of adhesive bonds and the molecular component of the friction coefficient. The test samples were made in the form of parallelepipeds with a section of 9.5 x 9.5 mm and a thickness of 5 mm, a spherical indenter with a sphere radius of 2.5 mm - from high-speed tool steel of composition Fe-6W-5Mo. Tests to determine the shear strength of adhesion bonds were carried out on a one-ball adhesion tester by the scheme shown in Fig. 2, b. In Fig. 4 shows a general view of the equipment for evaluating the strength of adhesion bonds.

Fig. 4. *Equipment for determining the shear strength of adhesion bonds*

The tests were carried out at a temperature of 20 ° C on a one-ball adhesion tester [16]. This method is based on the physical model, which in the first approximation reflects the actual conditions of friction at the local contact.

According to this model, the spherical indenter 1 (simulating a single asperity of the contact spot of rubbing solid bodies), compressed by two plane-parallel samples 2 and 3 (with high accuracy and cleanliness of the contacting surfaces) rotates under load around its own axis. The force F expended on the rotation of the indenter is mainly due to the shear strength of the adhesion bonds.

The initial roughness of the contact surfaces of the test samples and indenter in both test schemes was 0.06-0.16 μm on the Ra scale.

The test samples used for both schemes had a coarse-grained (CG) and ultrafine-grained (UFG) structure, obtained in the first case after annealing at 600 ° C for 1.5 hours and, in the second case, after six cycles of severe plastic deformation (SPD) processing by ECAP- Conform.

For comparative tests via both schemes, one group of samples was without surface treatment (without coating), TiC coating was applied by ion-plasma spraying (IPS) to the surface of the other group of samples, and the surface of the third group of samples was treated by micro-arc oxidation (MAO) with producing of titanium oxide TiO.

The shear strength of adhesive bonds (*MPa*) was determined from the relationship:

$$\tau_n = 0.75 \cdot \frac{M}{\pi \cdot \left(\frac{d_{1,2}}{2}\right)^3}, \qquad (1)$$

where $d_{1,2}$ are the diameters of indents on the tested samples, *mm*; *M* is the moment of the indenter's rotation, *N mm*.

The adhesive (molecular) component of the friction coefficient was determined as:

$$f_M = \frac{\tau_n}{p_r}, \qquad (2)$$

where p_r – is the normal pressure, *MPa* (3)

$$p_r = \frac{P}{\pi \cdot \left(\frac{d_{1,2}}{2}\right)^2}$$

where *P* is the force of sample compression, *N.*

The high sensitivity of measurements is ensured by the absence of additional supports of the upper and lower samples. The standard values of the radius *(r=2.5 mm)* of the spherical specimen (indenter) and the compressive force ensure that the conditions $0.02 \le \frac{h}{r} \le 0.2$ (where *h* is the penetration depth), which mainly covers the range of the ratio of the microasperity depth to the radius at the vertex, characteristic for external friction. In this case, the pressure at the contact site can be considered as uniformly distributed (with an error of no more than 10%). The deformation of a spherical specimen that is harder than a plane sample is neglected.

1.2. Determinations of the friction coefficient under elastic contact conditions

The results of tribological tests according to the first scheme (Fig. 2, a) in the following friction pairs: "commercially pure Grade 4 titanium without coating - chromium steel of composition Fe-1.5Cr-1.0C"; "Commercially pure Grade 4 titanium with IPS coating - chromium steel of composition Fe-1.5Cr-1.0C"; "Commercially pure titanium Grade 4 coated with MAO - chromium steel of composition Fe-1.5Cr-1.0C" in Fig. 5. The material under investigation was of different microstructure: coarse (CG) after annealing and ultrafine-grained (UFG) after six cycles of severe plastic deformation by the method of equal-channel angular pressing (ECAP) combined with Conform (ECAP-Conform).

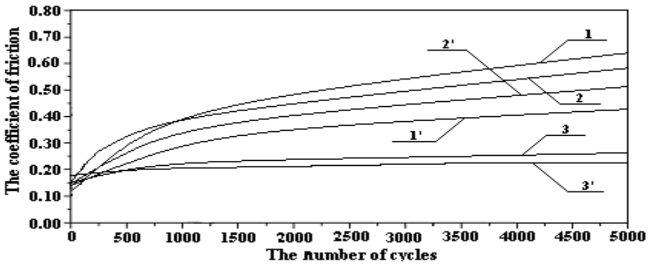

Fig. 5. *Dependence of the friction coefficient on the number of cycles (the number without a prime corresponds to the material with a CG structure, the number with a prime corresponds to the material with a UFG structure): 1 - 1 '- commercially pure titanium Grade 4; 2 - 2 '- commercially pure titanium Grade 4 with IPS coating (TiC); 3 - 3 '- commercially pure Grade 4 titanium with a coating obtained by the MAO technology (TiO).*

As it can be seen from the presented graph, the values of the friction coefficient obtained for annealed samples, both coated and uncoated, are higher (curves 1, 2 and 3) than for samples after 6 cycles of SPD processing by ECAP-Conform (Curves 1 ', 2' and 3 '). And it is noted that the greatest effect, in terms of reducing the friction coefficient from the deformation-induced increase in strength, is observed on uncoated samples (curves 1 - 1 '). For the sample with a CG microstructure, after 5000 cycles of action on the surface of the test specimen during reciprocating motion according to the scheme shown in Fig. 2, a, the friction coefficient is about 0.6, while for the UFG sample after 6 cycles of the SPD processing it decreases, approximately, to 0.4, which is an important indicator.

For samples with different microstructures with applied coatings, the effect of a sharp decrease in the friction coefficient is not observed (curves 2 - 2 'and 3 - 3'). But, nevertheless, we can see some decrease. Most probably, this is due to the fact that the coating itself has a greater effect on the tribological properties of commercially pure titanium, rather than the changes in the rheological properties of the substrate on which it is applied. It was noted that the TiO2 coating formed on the surface of commercially pure titanium by its treatment with MAO technology is most preferable from the point of view of reducing the friction coefficient (curves 3 - 3 '). In addition, it should be noted that in the case of using this coating, a much shorter run-in area is observed, especially on a material with a UFG microstructure. This property, due to the high tribological properties of the MAO coating, is very important and attractive for medical implants that are in frictional contact.

Fig. 6 shows the friction paths after testing samples with different surface preparation.

The lowest values of the friction coefficient, as already noted above, are observed on a sample whose surface is treated with MAO technology to form titanium oxide TiO2.

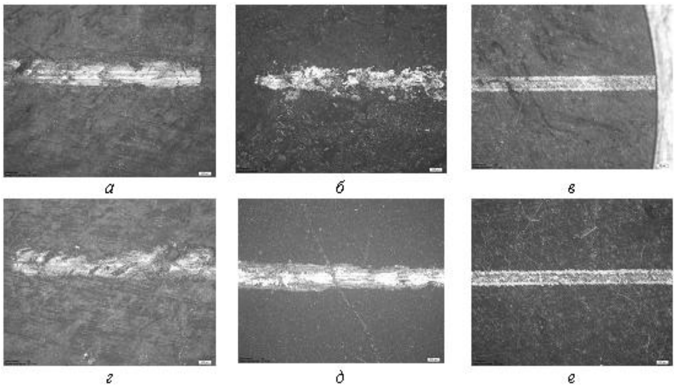

Fig. 6. *Friction paths obtained during the tribological tests according to the scheme of linear reciprocating motion: a - commercially pure titanium Grade 4 without coating with a CG structure; b - commercially pure titanium Grade 4 with a CG structure with IPS coating (TiC); c - commercially pure titanium Grade 4 with a CG structure with a coating obtained by the MAO technology (TiO); d, e, f - the same with a UFG structure (3 times magnification).*

From the analysis of Fig. 6 it can be seen that the similarity of the friction paths on samples from commercially pure titanium Grade 4 without coating (a) and with ion-plasma coating (TiC) (b) is observed. Apparently, this is due to the fact that under the accepted conditions of the physical experiment, intensive abrasion of the coating and baring of the substrate material (commercially pure titanium Grade 4) occurs. The friction path shown in Fig. 6, c and formed on a sample with TiO coating, obtained by MAO technology, is a smooth trace without any breaks. This indicates the preservation of the integrity of the investigated coating and its high strength.

The visual analysis of the friction paths during tribological tests on samples with a UFG microstructure and an applied coating (see Figure 6, d, e) provided approximately the same results as we can observe on samples with a CG microstructure (see Figure 6, b, c). The friction paths on the samples with CG and UFG microstructures without coating are somewhat different. Thus, on a sample with a UFG microstructure (Fig. 6d), the trace is more "blurred" in comparison with the friction track on a sample with a CG microstructure (Fig. 6a). Most probably, the "blurring" of the friction path on the UFG sample is associated with a higher strength obtained as a result of SPD processing by ECAP-Conform.

Thus, from the point of view of tribological efficiency, the most interesting is the TiO2 coating obtained by the microarc oxidation method, as well as the material (in this case, commercially pure titanium Grade 4) with a UFG microstructure.

1.3. Evaluation of the strength of adhesive bonds and determination of the adhesive component of the friction coefficient

Of great interest is the study of the shear strength of adhesion bonds as a function of pressure. Knowing the results of these studies, it is possible to calculate the adhesion component of the friction coefficient by formula (2). Figures 7 and 8 show the results of the evaluation of the shear strength of adhesive bonds of the material under study in the annealed state with CG and UFG microstructures, with different surface preparation.

The full-scale experiment was carried out on samples from commercially pure titanium with different microstructures and different types of surface preparation. For the indenter, we used tool steel of composition Fe-6W-5Mo. Samples with a CG microstructure were prepared by annealing at 600 ° C for 1 hour. The UFG microstructure was obtained as a result of the 6-cycle SPD processing by ECAP-Conform via route Bc with a rotation by 90 ° around the longitudinal axis of the workpiece after each processing cycle. The average grain size was about 300 nm.

In addition, samples with CG and UFG microstructures were coated with a TiC coating by ion-plasma spraying (IPS) and oxide TiO2 obtained using micro arc oxidation (MAO) technology. The tests were carried out at room temperature without lubricants.

Fig. 7 shows the imprints after exposure to the indenter on the samples.

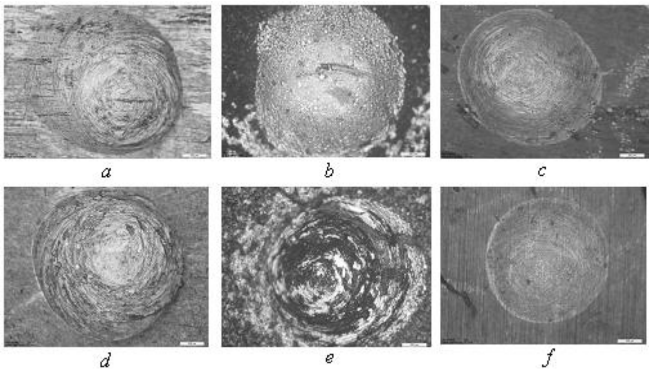

Fig. 7. *Imprints from the indenter after its impact on CG samples from commercially pure titanium Grade 4 with different surface treatments: a - without coating; b - with TiC coating deposited by ion-plasma spraying; c - with TiO2 coating, obtained by MAO technology; and on UFG samples: d - without coating; e - coated with TiC; f - with TiO2 coating, obtained by the MAO technology. (10 times magnification)*

From the figures shown, it is seen that in the indentation craters on the surface of the sample without coating (a), exposed surfaces are observed due to the formation of adhesive bridges with the indenter material. On the surface of the sample with TiC coating deposited by ion-plasma spraying, (b) there can also be seen exposed areas (light fragments in the photo) caused by the adhesive interaction of the materials of the sample and indenter. The most even and clean impression was obtained on a sample with TiO coating (c) obtained by MAO technology. For samples with a UFG microstructure (see Fig. 7, d, e f), under the same surface treatment of commercially pure titanium approximately the same effects are observed, as for samples with a CG structure. The main difference between these samples is only the smaller diameters of the craters under the same normal load, which is due to the greater hardness of the material under study after SPD processing by ECAP. As a consequence, a higher hardness determines the greater load-bearing capacity of the tribocoupling.

As a result of the tribological tests and processing of the obtained data using formulae (1) and (3), the shear strength of adhesion bonds was plotted versus normal pressure, as shown in Fig. 8.

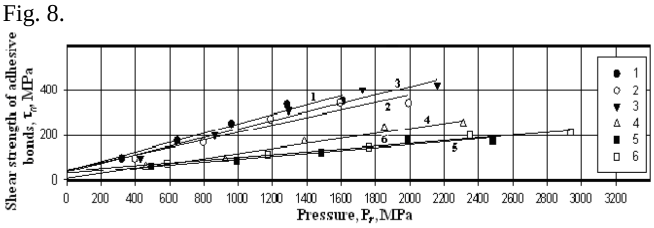

Fig. 8. *Effect of pressure on the shear strength of adhesive bonds for samples with different microstructures: 1 - CG (without coating); 2 - UFG (without coverage); 3 – CG with TiC; 4 - UFG with TiC; 5 – CG with TiO2; 6 - UFG with TiO2.*

Table 1 presents the results of a comparative evaluation of the tribological characteristics in the friction contact "steel indenter from tool steel of composition Fe-6W-5Mo - commercially pure titanium" with different microstructure and surface preparation.

Table 1. *Influence of the structural state of commercially pure titanium and coatings on the tribological characteristics under extreme loading conditions*

Structural state and surface treatment type	**Tribological characteristics**				
	p_{rn}, **MPa**	τ_{nn}, **MPa**	τ_{nn}/p_{rn}	β	τ_0, **MPa**
1. CG microstructure (without coating)	1605	376	0,235	0,208	43
2. UFG microstructure (without coating)	1988	376	0,189	0,166	47
3. CG microstructure with TiC	2158	447	0,207	0,189	39
4. UFG microstructure with TiC	2311	266	0,115	0,112	8
5. CG microstructure with TiO_2	2480	189	0,076	0,064	31
6. UFG microstructure with TiO_2	2937	221	0,075	0,061	42

where β is the coefficient of molecular bond strengthening under the action of compressive stresses, τ_0 is the shear strength of adhesive bonds in the absence of normal load.

Analyzing the tabular values and graphical dependences shown in Fig. 8, it was established that the lowest shear strength of adhesion bonds is observed on samples with both CG and UFG structures coated with titanium oxide using MAO technology. In this case, the bearing capacity of the UFG material is higher than that of the material with a CG microstructure (see Fig. 8, curves 5 and 6). As it can be seen from the presented results, the greatest shear strength of adhesion bonds is observed on a coarse-grained material without coating (curve 1). The TiC coating on the substrate with a CG structure (curve 3) demonstrates slightly lower shear strength of adhesive bonds and a higher load-bearing capacity.

Under the considered conditions, the lowest shear strength of adhesive bonds is in the contact pair "steel indenter from tool steel of composition Fe-6W-5Mo - commercially pure titanium Grade 4 with oxidized surface using MAO technology" (curves 5 and 6). Moreover, in all variants of the test samples, a high load-bearing capacity is observed for a material with a UFG microstructure (curves 2, 4 and 6) compared to a similar surface treatment on samples with a CG microstructure (curves 1, 3, and 5). This observation is associated with the deformation-induced increase in the strength of the material under study - commercially pure titanium Grade 4.

Correlating results were obtained both in the determination of the integral value of the friction coefficient and in the evaluation of the adhesion component of the friction coefficient.

Thus, it can be stated that, from the considered options, the most acceptable type of surface treatment for commercially pure titanium, from the point of view of obtaining high tribological properties with relatively low shear strengths of adhesive bonds and high load-bearing capacity of the tribocoupling, is TiO2 oxide coating deposited by microarc oxidation in combination with severe plastic deformation processing, in particular, by ECAP-Conform.

CONCLUSIONS:

1. The coating itself has a greater effect on the tribological properties of commercially pure titanium, and not the change in the rheological properties of the substrate on which it is applied. It was noted that the TiO2 coating formed on the surface of commercially pure titanium by its treatment with MAO technology is the most preferable from the point of view of reducing the friction coefficient. It is established that in the case of using this coating, a much shorter run-in area is observed, especially on a material with a UFG microstructure. This property, conditioned by the high tribological properties of the MAO coating, is very important and attractive for medical implants that are in frictional contact;
2. The friction path formed on a TiO2-coated sample obtained using MAO technology is a smooth trace without any breaks. This indicates the preservation of the integrity of the investigated coating and its high strength;
3. The most acceptable type of surface treatment of commercially pure titanium Grade 4, from the point of view of obtaining high tribological properties with relatively low values of shear strength of adhesive bonds and high load-bearing capacity of tribocoupling, is TiO2 oxide coating deposited by microarc oxidation in combination with severe plastic deformation by ECAP-Conform;
4. The correlation dependence between the values of the complex parameter of plastic frictional contact and the strength of adhesive bonds is established for the friction pairs "material under study - tool steel of composition Fe-6W-5Mo", which is described by a single dependence in a temperature range of 20-450 °C;
5. The temperature range of frictional interaction is defined for a number of investigated materials;
6. A regression formula is obtained, reflecting the analytical dependence of the experimentally obtained results;
7. The dependence between the adhesion component of the friction coefficient and the structural state of the deformed material in friction pairs "commercially pure titanium - steel of composition Fe-6W-5Mo" in plastic contact is established. From this dependence, it follows that the strength of adhesion bonds and the molecular component of the friction coefficient are structurally sensitive characteristics.

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