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EFFECTIVENESS EVALUATION OF THE CONVERSION COATINGS APPLICATION ON TITANIUM ALLOYS IN CONTACT WITH GFRP UNDER NOMINALLY STATIONARY CONTACT CONDITIONS

Titanium products are very often used conversion coatings that are formed on the metal surface as a result of a chemical reaction with reagents or the environment. The purpose of using such coatings is to increase corrosion protection, ensure better adhesion with paint coatings, decorative aspect, and also increase wear-resistant characteristics. The paper analyzes the use of conversion coatings on titanium alloys for wear protection. Tests have shown that conversion coatings increase the wear resistance of titanium alloy Ti5Al5V5Mo1Cr1Fe for anodic coating by 10% and by 6% for phosphate coating in combination with GFRP. The shallow depth of the coating up to 20 μm and insufficient hardness only provide protection from reinforcing glass fibers of the composite material for a while and then only enhance the damage effect. When E-glass fibers come into contact with conversion coatings, deep grooves are formed at the micro level, which are located in the sliding direction. Due to shearing and setting, the products of conversion coatings, titanium oxides and glass fiber particles are mixed on the friction surface into a tribological layer that mainly has an abrasive effect. As a result of fretting processes, microcracks and areas of titanium coating delamination are formed on the surface near the grain boundaries, which increase the destruction of the titanium surface. Anodizing provides greater protection due to the formation of a film that is 40 % harder than phosphating.

Key words: *titanium alloys, coating, wear resistance, fretting, fiberglass, analysis, testing, nominally fixed contact.*

Introduction. As is known, titanium alloys have low wear-resistant properties, but despite this, the use of both titanium alloys and composite materials in modern aircraft is only increasing every year due to their high strength properties compared to their weight. The contact of these materials is increasingly common in aircraft of well-known manufacturers and design bureaus.

Nominally fixed contacts of titanium alloys and composite materials (carbon plastics and fiberglass) under the influence of vibration from aircraft operation and gas turbine engines begin to micro-move over time, which leads to slipping of surfaces and as a result the appearance of defects known as wear during fretting corrosion. Analysis of damaged parts and studies [1, 2] show that in the contact of Ti-CFRP/GFRP titanium alloys are damaged many times more than composite materials due to the high strength and abrasive action of reinforcing fibers. Thus, titanium alloys in nominally fixed contacts must always be protected with special coatings and treatments to prevent the development of fatigue cracks that occur during fretting damage.

Titanium products are often used with special coatings called conversion coatings [3-10]. This is usually a thin layer of coating (up to 10-100 microns), which is formed on the metal surface as a result of a chemical reaction with reagents or the environment. There are various types of conversion coatings on titanium alloys, including chromate, phosphate, oxide, etc., each of which has its own properties and purpose of application. The purpose of using these coatings can be increased corrosion protection, ensuring better adhesion with paint coatings, decorative aspect and they can improve the wear-resistant characteristics of titanium alloys.

The following technological solutions can be used to obtain wear-resistant conversion coatings on titanium alloys: hard anodizing [3] (in sulfuric or phosphoric acid at low temperature) allows you to obtain a dense layer of oxides with a thickness of 20-30 microns and a hardness of HV 600-1200; micro-arc oxidation (MAO) [4] (anodic process in alkaline media) allows you to obtain ceramic-oxide structures up to 20-100 microns and a hardness of HV 800-1600; blueing [5] (in hot solutions of pergamanate and nitric acid) allows you to obtain a dark oxide layer up to 1-5 microns and a hardness of HV 300-500; phosphating [6] (in a phosphate solution using Zn, Mn elements) allows you to obtain a coating of increased hardness up to 100 microns and a hardness of HV 500-900.

Analysis of the application of conversion coatings on titanium alloys for protection against fretting.

Thus, the authors of the work [7], when forming oxide structures on the surface of the VT23M titanium alloy by anodic oxidation, established that during dry friction, the wear resistance of the coating is 20-30 % higher than that of the heat-treated titanium alloy, but 8-10 times lower when rubbed with TiN and WC-Co coatings. The friction coefficient was within 0.68 compared to 0.36 for nitrided coatings. However, the authors note the highest adhesion strength of oxidized coatings compared to other types of application (detonation, PVD).

In a monograph devoted to conversion coatings on titanium alloys, the authors [8] note the high wear resistance of coatings applied by such methods as: coating with mixed oxides, electrochemical synthesis of Mn_xO_y manganese coatings, plasma-electric oxidation and coating in diphosphate environments. Coatings applied by such methods can increase the wear resistance of titanium alloys by 5-10 times, approaching the wear resistance of TiN structures. Depending on the method, oxide coatings with different structures can be formed on the friction surfaces (Fig. 1), which allows to retain the lubricating layer during friction.

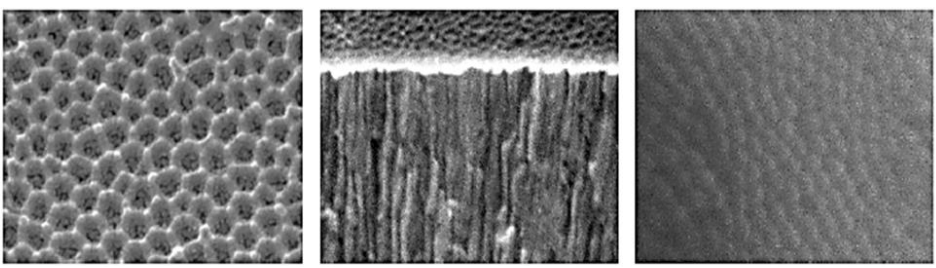

Fig. 1. Porous oxide coating on the surface of titanium to improve adhesion properties (x1000000) [8].

In works [9, 10] the authors established that the reduction of grain sizes and the formation of microglobular structures on the surface of titanium occurs with an increased content of manganese in mixed oxide layers, which is associated with electrochemical and thermochemical reactions in the surface and in the volume of the oxide layer. The reduction of abrasive wear correlates with the reduction of grain and smoothing of surface layers. The abrasive wear resistance of $Ti_xO_y \cdot Mn_xO_y$ structures in $K_4P_2O_7$ electrolytes increases by 3-5 times.

Analysis [5-10] showed high wear resistance of coatings obtained on titanium alloys during dry abrasive friction. However, the operating conditions of fretting corrosion and Ti-CFRP/GFRP contact in aircraft are somewhat different. Coatings that have proven themselves well in unidirectional wear may be unreliable in the reversible action of abrasive particles of reinforcing fibers and hard abrasive structures obtained as a result of conversion coatings. Therefore, to determine the effectiveness of the use of conversion coatings in the Ti-CFRP/GFRP contact under fretting corrosion conditions, comparative studies are necessary. Table 1 presents a comparative analysis of wear resistance and some characteristics of conversion coatings on titanium alloy Ti5Al5V5Mo1Cr1Fe taken from literature sources under dry friction [3-12].

Table 1

Comparative analysis of the characteristics of conversion coatings on titanium alloy Ti5Al5V5Mo1Cr1Fe [3-12]

№	Type of coating	Coating thickness, μm	Hardness, HV	Coefficient of dry friction	Wear rate, 10^{-6} мм^3/N·м
1	Phosphating в $Zn^{2+} + H_3PO_4$	5-15	425-550	0,4-0,6	10-30
2	Phosphating в $Zn^{2+}+Mn^{2+} + H_3PO_4$	8-18	500-650	0,35-0,55	8-20
3	Phosphating в $Mn^{2+} + H_3PO_4$	10-20	550-700	0,3-0,5	5-10
4	Phosphating в $Ca^{2+} + NH_4H_2PO_4$	3-5	300-450	0,6-0,8	20-50
5	MAO-silicate	30-50	900-1200	0,6-0,8	1,2-1,8
6	MAO+MoO_3	40-60	1100-1600	0,4-0,6	0,5-1,0
7	MAO+MoS_2	50-70	1500-2100	0,2-0,4	0,1-0,3
8	Anodizing in H_2SO_4	5-15	350-550	0,6-0,7	20-40
9	Anodizing in $H_2SO_4 + H_3PO_4 + K_2Cr_2O_7$	15-30	800-1200	0,4-0,5	10-20
10	Phosphate acid anodizing in H_2SO_4	10-20	500-700	0,3-0,5	10-30
11	Electrolytic plasma boriding in H_3BO_3 + NH_4Cl 850–900 °C	10-15	1100-1600	0,3-0,4	0,2-0,4
12	Chemical bluing in $KMnO_4 + HNO_3$	1-2	350-450	0,4-0,6	80-150
13	Thermal bluing in air aerosol, 700 °C	3-5	600-700	0,35-0,5	10-30
14	Anodic bluing in $H_2SO_4 + K_2Cr_2O_7$	10-20	500-800	0,3-0,5	5-10

Analysis of wear resistance and functional characteristics of conversion coatings on titanium alloy Ti5Al5V5Mo1Cr1Fe shows that coatings obtained by micro-arc oxidation (MAO) technology have the highest characteristics in terms of hardness, wear resistance and thickness, and are close in these properties to nitriding technology. Coatings obtained by blueing due to their small thickness cannot be considered for Ti-GFRP contact at all, since the coating will quickly collapse under the action of fretting corrosion. Coatings obtained by anodizing and phosphating methods have approximately the same characteristics in terms of thickness and wear.

The purpose of the work is to determine the wear-resistant characteristics of some conversion coatings on titanium alloys in combination with GFRP under fretting corrosion conditions.

Testing procedure. To determine the wear resistance characteristics of conversion coatings on titanium alloys in contact with fiberglass, phosphating coatings (in the environment of solutions of Zn+Mn elements) and anodizing (in the solution of chemical elements H_2SO_4+H_3PO_4+$K_2Cr_2O_7$) were determined, which were applied to the Ti5Al5V5Mo1Cr1Fe alloy. Both coatings are black in color, 15-20 μm thick and were applied at the Antonov plant in accordance with research work No. 549-X08 (AH01-60(08). The corresponding sample was the GFRP composite material. To compare the test results and assess the effectiveness of the use of conversion coatings in fretting corrosion, the test conditions corresponded to the following [13]: amplitude of mutual displacements 175 μm, specific load 15 MPa, test base of 300 thousand cycles and frequency of 30 Hz.

Analysis of research results. The test results presented in Fig. 2 indicate unsatisfactory surface protection by conversion coatings when in contact with GFRP under conditions of nominally stationary contact, which is 10 % for anodic coating and phosphating process, the increase in wear resistance occurs only by 6 %. The small depth of the coating up to 20 microns and insufficient hardness only provides protection from reinforcing glass fiber fibers for some time and then only enhances the damage effect.

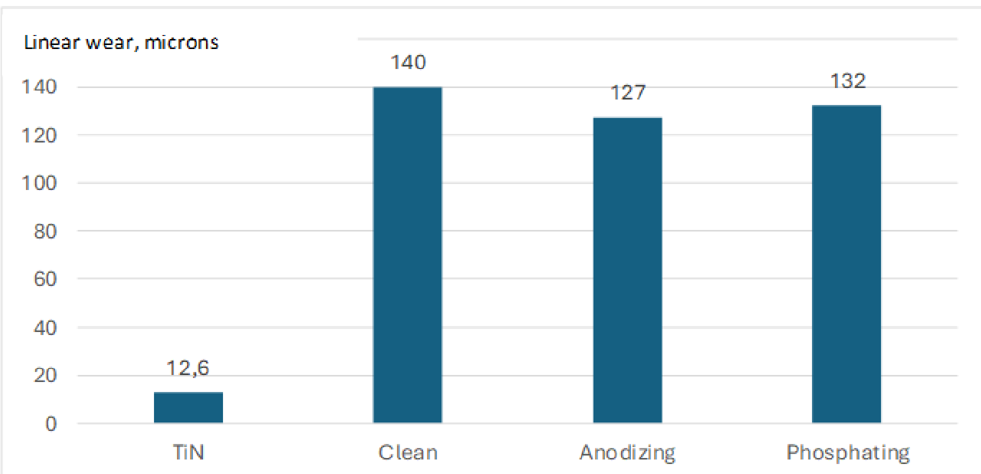

Fig. 2. Histogram of wear resistance of conversion coatings of Ti5Al5V5Mo1Cr1Fe alloy when tested under conditions of nominally stationary contact in a pair with GFRP.

When E-glass fibers come into contact with conversion coatings, deep grooves are formed at the micro level, which are located in the direction of sliding. Wear products in the form of oxide and phosphate compounds form areas at the bottom of the grooves due to adhesion. Due to cutting and setting, the products of conversion coatings, titanium oxides and glass fiber particles are mixed on the friction surface into a tribological layer, which mostly has an abrasive effect. In turn, abrasive particles are introduced into the rougher surface of composite materials and during friction, an abrasive-adhesive type of wear occurs in contact. As a result of fretting-corrosion processes, microcracks and areas of titanium coating delamination are formed on the surface near the grain boundaries, which increase the destruction of the titanium surface (Fig. 3). Anodizing provides greater protection due to the formation of a film that is 40 % harder than phosphating.

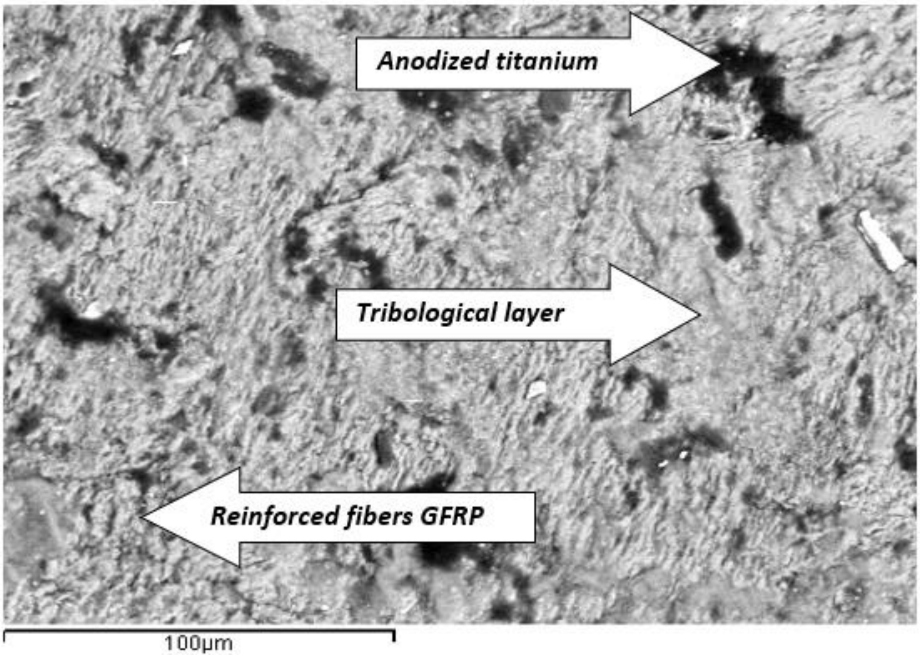

Fig. 3. Tribological layer on the surface of anodized titanium alloy Ti5Al5V5Mo1Cr1Fe during tests with GFRP under fretting corrosion conditions.

Thus, the effect of conversion coatings on the wear resistance of the Ti-GFRP contact under the action of fretting corrosion is, but not significant in comparison, for example, with chemical-thermal treatment, where the increase in wear resistance occurs more than 11 times. Thus, it can be concluded that only the coating using the MAO technology is able to create a coating that is close in its characteristics to the chemical-thermal treatment of nitriding. Also, to protect the contact of composite materials with titanium alloys with conversion coatings, they can be used in combination with other methods [14-16] (polymer composite materials, addition of solid lubricants, plastic metals).

Conclusions. Thus, it was found that conversion coatings increase the wear resistance of titanium alloy for anodic coating by 10 % and by 6 % for phosphate coating. The shallow depth of the coating up to 20 microns and insufficient hardness only provide protection from GFRP reinforcing fibers for some time and then only enhances the damage effect. When E-glass fibers come into contact with conversion coatings, deep grooves are formed at the micro level, which are located in the direction of sliding. Wear products in the form of oxide and phosphate compounds form areas at the bottom of the grooves due to adhesion. Due to shearing and setting, the products of conversion coatings, titanium oxides and glass fiber particles are mixed on the friction surface into a tribological layer that mostly has an abrasive effect. In turn, abrasive particles are introduced into the rougher surface of GFRP and during friction, an abrasive-adhesive type of wear occurs in contact. As a result of fretting corrosion processes, microcracks and areas of titanium coating delamination are formed on the surface near grain boundaries, which increase the destruction of the titanium surface. Anodizing provides greater protection by forming a film that is 40 % harder than phosphating.

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ОЦІНКА ЕФЕКТИВНОСТІ ЗАСТОСУВАННЯ КОНВЕРСІЙНИХ ПОКРИТТІВ НА ТИТАНОВИХ СПЛАВАХ В КОНТАКТІ ІЗ GFRP В УМОВАХ НОМІНАЛЬНО НЕРУХОМОГО КОНТАКТУ

Титанові сплави володіють низькими зносостійкими властивостями, але незважаючи на це в сучасних повітряних суднах з кожним роком лише підвищується використання, як титанових сплавів так і композиційних матеріалів, завдяки їх високим властивостям міцності в порівнянні із їх вагою. Контакт цих матеріалів все частіше зустрічається в повітряних суднах відомих виробників та конструкторських бюро.

Номінально нерухомі контакти титанових сплавів та композиційних матеріалів (вуглепластиків та склопластиків) під дією вібрації від експлуатації повітряних суден та роботи газотурбінних двигунів з часом починають мікропереміщуватись, що призводить до просковжування поверхонь і як наслідок появі дефектів відомих як фретинг-корозія. Аналіз пошкоджених деталей показує, що в контакті Ti-CFRP/GFRP титанові сплави пошкоджуються в рази більше ніж композиційні матеріали завдяки високій міцності та абразивній дії армуючих волокон. Таким чином титанові сплави в номінально нерухомих контактах необхідно завжди захищати спеціальними покриттями та обробкою для попередження розвитку втомних тріщин які виникають під час пошкоджень в результаті фретинга.

Існують різні варіанти конверсійних покриттів на титанових сплавах кожен із яких володіє своїми властивостями та метою застосування. В роботі представлено аналіз застосування конверсійних покриттів на титановому сплаві Ti5Al5V5Mo1Cr1Fe з метою захисту контакту від зношування. Випробуваннями встановлено, що конверсійні покриття підвищують зносостійкість титанового сплаву для анодного покриття на 10 % та на 6 % для фосфатного покриття. Мала глибина покриття до 20 мкм та недостатня твердість зумовлює лише захист від армуючих волокон GFRP на деякій час а потім лише підсилює ефект пошкодження.

При контакті E-glass волокон із конверсійними покриттями утворюються глибокі борозни на мікрорівні, що розташовані по напряму ковзання. Продукти зношування у вигляді оксидних та фосфатних з’єднань за рахунок адгезії утворюють ділянки на дні борозень. За рахунок зрізування та схоплювання відбувається перемішування на поверхні тертя продуктів конверсійних покриттів, окислів титану та часток скляних волокон в трибологічний шар який здебільшого має абразивну дію. В свою чергу абразивні частки впроваджуються в більш шорстку поверхню GFRP та при терті відбувається абразивно-адгезійний вид зношування в контакті. В результаті фретинг-корозійних процесів утворюються мікротріщини та ділянки відшарування титанового покриття на поверхні біля границь зерен які підсилюють руйнування поверхні титану. Більший захист дає покриття анодування за рахунок утворення плівки яка на 40 % має більшу твердість в порівнянні із фосфатуванням.

Ключові слова: *титанові сплави, покриття, зносостійкість, фретинг-корозія, скловолокно, аналіз, випробування, номінально нерухомий контакт..*

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