Application of AlB₁₂−Al Electric Spark Coatings to Protect Titanium Alloys During Wear Under Fretting Corrosion

A. P. Umanskyi, A. I. Dukhota*, V. E. Sheludko, M. S. Storozhenko,
V. B. Muratov, and M. A. Vasilkovskaya

I. M. Frantsevich Institute for Problems in Materials Science, N.A.S. of Ukraine,
3, Academician Krzhyzhanovsky Str.,
UA-03142 Kyiv, Ukraine
*National Aviation University,
1, Lubomir Husar Str.,
UA-03058, Kyiv, Ukraine

The article deals with the study of the possibility of using AlB₁₂−50 wt.% Al aluminium-matrix composite material electric spark (ES) coatings to protect titanium alloys during wear under fretting. Fundamental possibility of such coatings obtaining is estimated by theoretical calculation of Palatnik's criterion (1.22). Thermal conductivity coefficient and heat capacity of the composite were calculated or determined from an experiment. The coatings were deposited on ALIER-52 setup. Fretting corrosion tests were carried out on MFK-1 setup according to 'the coating−counterbody' system (counterbody− hardened Steel 45). Phase composition of the coating was studied with DRON-3M diffractometer and elemental x-ray spectrum analysis of the friction track surface was carried out using a JEOL JAMP9500F (SEM) microanalyzer equipped with an energy-dispersive x-ray microanalysis. The following phases namely TiB₂, Ti aluminides, Ti, TiO, TiO₂ and AlB₁₀ were revealed by x-ray analysis in the coating. The absence of the AlB₁₂ phase is noteworthy. It can be explained by thermal-oxidative destruction of aluminium dodecaboride under severe conditions of ES alloying (ESA). Regardless of the deposition mode, the wear of the sample with ES-coating is shown to be significantly less than that of the uncoated one. A conclusion is made about the prospect of using this electrode material for ESA of titanium alloys operating

Corresponding author: Volodymyr Yevhenovych Sheludko
E-mail: dep65@ipms.kiev.ua

under fretting corrosion.

Key words: AlB$_{12}$−Al, ES-coating, fretting corrosion, wear, titanium alloys.

Статтю присвячено дослідженню можливості застосування електроіскрових (EI) покриттів з алюмоматричного композиційного матеріялу AlB$_{12}$−50% мас. Al для захисту титанових стопів від зношування в умовах фретинґ-корозії. Оцінено теоретичну можливість одержання таких покриттів за допомогою теоретичного розрахунку критерію Палатніка (1,22). Коефіцієнт теплопровідности та теплоємність композиту були розраховані чи визначені експериментально. Покриття нанесені на установці ALIER-52. Випробування на фретинґ-корозію проводили на установці МФК-1 за системою «покриття–контртіло» (контртіло–загартована сталь 45). Фазовий склад покриття вивчено за допомогою дифрактометра ДРОН-3М, а елементну рентґеноспектральну аналізу поверхні доріжки тертя проведено на мікроаналізаторі JEOL JAMP9500F (СЕМ), обладнаному системою енергодисперсійної рентґенівської мікроаналізи. РФА в покритті виявлено TiB$_2$, алюмініди Ti, Ti, TiO, TiO$_2$ та AlB$_{10}$. Звертає на себе увагу відсутність фази AlB$_{12}$, що є наслідком термоокиснювальної деструкції додекабориду алюмінію в жорстких умовах EI-леґування (ЕІЛ). Показано, що, незалежно від режиму нанесення, знос зразка з EI-покриттям значно менший, ніж зразка без покриття. Зроблено висновок про перспективність застосування даного електродного матеріялу для ЕІЛ титанових стопів, що працюють в умовах фретинґ-корозії.

Ключові слова: AlB$_{12}$−Al, EI-покриття, фретинґ-корозія, зношування, титанові стопи.

1. INTRODUCTION

Among the wide range of constructional materials, the titanium alloys occupy a special place. Their low specific weight, high specific strength, and corrosion resistance are the most important advantages of these alloys. Due to this combination of properties, titanium alloys are widely used in aircraft industry, rocket science, shipbuilding, and many other branches of technology [1−3]. For example, in the PS-90A aircraft engine for the Ilyushin Il-96, Ilyushin Il-76, and Tupolev Tu-204 planes, 40.4% of the parts are made of various titanium alloys, and in the designs of aircrafts of the AN family (ANTONOV company) the mass of such parts is 8−9% of the mass of the airframe [4, 5]. The range of operating temperatures for the titanium alloys to use is in the range from very low cryogenic temperatures to 600°C, which exceeds the range of similar temperatures for light alloys based on Al and Mg [1]. At the same time, titanium alloys are characterized by low hardness, wear resistance, and scoring resistance, which causes problems when working in friction conditions.

The analysis of causes of wear and technological methods of hardening surface treatment of friction parts shows that in many cases the problem of increasing their wear resistance is solved by modifying the working surfaces by electrospark alloying (ESA) [6–11]. This method, characterized by technological simplicity and low power consumption, allows to form on metal substrate surface-strengthened layers with high wear resistance and the strength of adhesion of the deposited coating with the base. A large number of parts of modern aviation objects subjected to ESA-surface hardening are made of titanium alloys, working in conditions of fretting corrosion wear. At the same time the use of ESA-surface hardening technology does not provide sufficiently effective protection of the functional surfaces of these parts for a long service life.

The WC–Co cemented carbides, refractory compounds of transition metals, such as carbides, nitrides, aluminides, silicides, and borides are used as materials for surface ESA hardening [7, 8]. ESA-coatings deposited by WC–Co cemented carbides are distinguished by high hardness and wear resistance; however, they form a relatively thin layer due to the fast-falling in time (during the alloying process) mass transfer of the alloying electrode material to the machine part. The disadvantage of titanium-containing refractory compounds most related to titanium is the tendency to form loose surface oxide films during common atmospheric oxidation and tribooxidation. Titanium oxide has a volume 1.6 times greater than that of the base metal. According to the Pilling–Bedworth ratio [12], such films are loose, low-strength and cannot perform protective functions in the process of frictional destruction.

Among the materials to deposit protective coatings by the ESA method, aluminium dodecaboride AlB$_{12}$ is of interest. Its synthesis from Al and BN, developed at the Frantsevich Institute for Materials Science Problems of N.A.S. of Ukraine is more rational and economically efficient than direct one from Al and B [13]. AlB$_{12}$ has a low density (~ 2.52 g/cm^3) and the particularity of its crystalline structure (icosahedral boric frame) determines its high hardness (22–24 GPa) and infusibility (2070°C) [14].

However, the low crack resistance of aluminium dodecaboride significantly limits the scope of its application [14]; therefore, it is advisable to use AlB$_{12}$ in combination with plastic metal bonds. It is promising to use aluminium, which is characterized by high plasticity, low density (2.7 g/cm^3), and low melting point (660°C). Earlier Al was found to wet AlB$_{12}$ well, with the formation of contact angles ($\theta \approx 20$ deg) and the secondary phases in the interaction zone at the Al–AlB$_{12}$ interface are absent [14]. In addition, aluminium having a resistivity of 2.7 $\mu\Omega\cdot$cm, acts as a kind of additive increasing the conductivity of the AlB$_{12}$–Al composite (a resistivity of AlB$_{12}$—10^6 $\Omega\cdot$cm), which is of great importance in ESA.

So, the aim of the work is to investigate the possibility of using the aluminium dodecaboride AlB_{12}–Al composite material to obtain protective ESA-coatings on a titanium alloy operating under fretting corrosion.

2. EXPERIMENTAL DETAILS

The AlB_{12} samples were prepared from the powder synthesized at the IPMS of N.A.S. of Ukraine according to the procedure described in [15, 16]. At first a porous AlB_{12} ceramic frame was obtained. Then it was impregnated with an Al melt in vacuum ($1.33 \cdot 10^{-4}$ Pa) at a temperature of ~ 1100°C. This made it possible to obtain the aluminium-matrix composite of AlB_{12}–50 wt.% Al in the form of a bar of 50×50×5 mm in size, from which the electrodes for ESA were cut by the electro-erosion method.

The structure of the material consists of three phases: a metal matrix, AlB_{12} grains (the size of which varies in the range of 1–4 μm) uniformly distributed in the matrix, and Al_2O_3 particles (the cross-section microstructure of the electrode material AlB_{12}–50 wt.% Al, obtained with a JEOL JAMP9500F microanalyzer and the result of its micro x-ray spectral analysis at local points are given in [17]).

OT4 titanium alloy (GOST 19807-91) was chosen as the sample material for ESA. This is the alloy of average strength, well welded by argon-arc, contact and electron-beam welding, and also has good thermal stability and is intended for the manufacture of parts operating at temperatures up to 350°C for 2000 hours and up to 300°C—30000 hours [18, 19]. For example, in the already mentioned PS-90A aircraft engine, rings of working I–III stages of the high-pressure compressor, flanges of the thrust reverser, shells, cups, shields, *etc.* are made from OT4 alloy [4].

ESA of the samples of the aforecited alloy was carried out on an ALIER-52 setup (SCINTI, Chisinau, Republic of Moldova) at the modes indicated in Table 1.

The density of the electrode material was determined by the method of hydrostatic weighing (GOST 25281-82). Heat capacity was measured by the calorimetric method (GOST 23250-78). Thermal conductivity coefficient was obtained according to the method described in [20].

Fretting corrosion tests were carried out on an MFK-1 setup (GOST 23.211-80) in the 'coating–counterbody' system, under dry friction in air, in the following mode: oscillation amplitude—87.5 μm, frequency—25 Hz, pressure—19.8 MPa, number of fretting cycles $N = 5 \cdot 10^5$. Hardened Steel 45 (*HRC* 48–52) was used as a counterbody.

The wear resistance of the tribocouple material was evaluated by the gravimetric method by the difference in the mass of the sample before and after testing on an analytical laboratory balance with an accuracy

TABLE 1. Technological parameters of ALIER-52 setup.

Mode	Pulse duration, μs (± 20%)	Pulse current amplitude value, A (± 20%)	Pulse energy E, J
2	40	125	0.09
4	170	200	0.61
6	700	200	2.52

of 10^{-4} g. The volume wear was determined taking into account the density of the coating material.

X-ray analysis of the coating surface was carried out on a DRON-3M diffractometer in CuK_α-filtered radiation. The microstructure of the friction track surface was studied using a JEOL JAMP9500F (SEM) microanalyzer equipped with the system of energy-dispersive x-ray microanalysis.

3. RESULTS AND DISCUSSION

To evaluate theoretically the interaction between the electrode and the substrate and, to some extent, predict the composition of the coating is possible using the Palatnik criterion [21, 22], which connects only the physical constants of electrode materials as follows:

$$\frac{\tau_a}{\tau_c} \cong \frac{c_a \rho_a \lambda_a (T_a - T_0)^2}{c_c \rho_c \lambda_c (T_c - T_0)^2},$$

where τ_a and τ_c are the characteristic times of erosion (formation of melting centres in the discharge zone) of the anode and the cathode, respectively; c_a, c_c—heat capacity, J/(kg·K); ρ_a, ρ_c—density, kg/m^3; λ_a, λ_c—coefficient of thermal conductivity, W/(m·K); T_a, T_c—melting point, K; T_0 is the ambient temperature.

This ratio does not take into account a large number of factors affecting ESA process, but, it can be used for a quantitative evaluation of 3 types of interactions between anode and cathode made of various materials, namely:

− at $\tau_a/\tau_c \ll 1$ a coating is formed on a cathode surface;

− at $\tau_a/\tau_c \sim 1$ it is possible to form a coating in the form of an anode-cathode alloy;

− at $\tau_a/\tau_c \gg 1$ the substrate is eroded; the formation of a coating is unlikely (but the transfer of material from the cathode to the anode is possible [21]).

The data required for calculations according to the Palatnik criterion in our conditions are given in Table 2.

TABLE 2. Physical characteristics of the electrode materials and the value of the Palatnik criterion.

| Characteristic	Anode (AlB$_{12}$−50 wt.% Al)	Cathode (OT4) [23, 24]	The value of the Palatnik criterion τ_a/τ_c
λ, W/(m·K)	72.58	10	
C_p, J/(kg·K)	918.88	~457	1.22
T_m, K	933*	1941	
ρ, kg/m³	2616	4550	

*T_m of the most low-melting phase (Al) was used for the calculation.

It follows from the calculation that a mixed layer (from the materials of the substrate and the deposited electrode) of the ESA-coating with high adhesion to the substrate can be obtained with the AlB$_{12}$−50 wt.% Al material.

X-ray analysis showed the following phases namely TiB$_2$, Ti aluminides, Ti, TiO, TiO$_2$ and AlB$_{10}$ were revealed by x-ray analysis in the coating (Fig. 1). Attention is drawn to two aspects.

Firstly, the absence of the AlB$_{12}$ phase. ESA process occurring at plasma temperatures (2·10^4 K) in air is known to be accompanied by thermo-oxidative destruction of an anode and a cathode materials [25]. Such severe conditions aid in destructing of aluminium dodecaboride to constituent elements at $T = 2300$ K [26].

Secondly, the appearance of the Al$_5$Ti$_3$ phase, which is non-equilibrium and is absent in the Al−Ti phase diagram [27]. The formation of non-equilibrium intermetallic phases Al$_2$Ti, Al$_5$Ti$_3$, Ti$_{3.3}$Al was noted by [28] in the contact zone of Ti and Al during their explo-
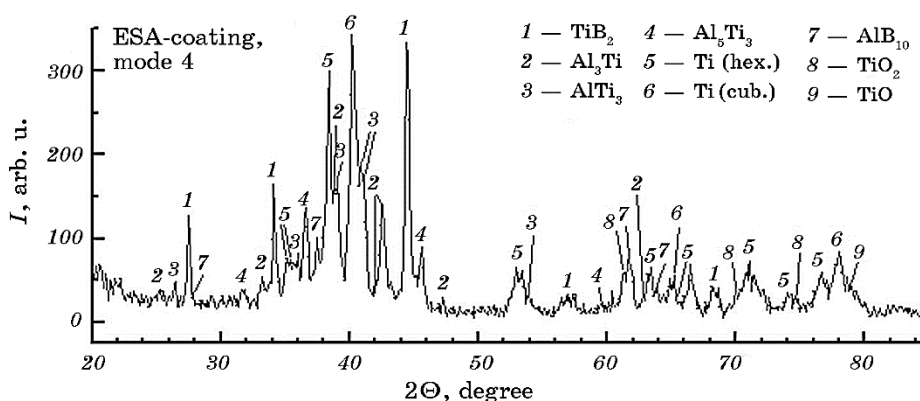
Fig. 1. Diffraction pattern of ES-coating of AlB$_{12}$−50 wt.% Al on OT4 titanium alloy (mode 4).
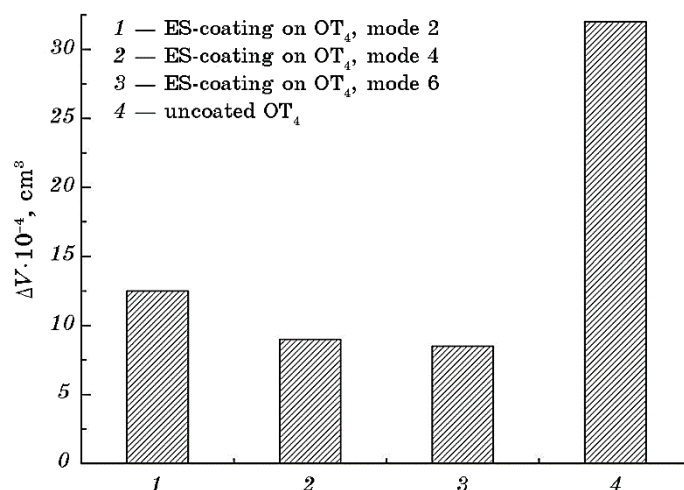
Fig. 2. Dependence of volume wear ΔV on the mode of coating deposition.

sion welding. This fact is explained from the standpoint of anomalously fast directional mass transfer under stress conditions creating the curvature of the crystal lattice. In our case, the appearance of the Al$_5$Ti$_3$ phase can be explained by the characteristic features of the ESA process, namely: the spark discharge consists of a sum of short (10^{-8}–10^{-9} s) current pulses that lead to microexplosions of cathode spots. During such microexplosions, the pressure reaches 10 GPa at a plasma temperature of $2 \cdot 10^4$ K [25]. This can lead to the appearance of processes initiating the redistribution of atoms, which, in turn, can accelerate the appearance of any new phases.

The results of wear tests during fretting corrosion (Fig. 2) indicate that, regardless of the deposition mode, ESA-coatings from the electrode material of the composition AlB$_{12}$–50 wt.% Al, formed on the OT4 titanium alloy, have significantly less volume wear, than uncoated OT4 alloy. The coatings deposited in modes 4 and 6 are the most wear-resistant. The decrease in their wear, in relation to the OT4 alloy, is approximately the same and amounts to 72 and 73.5%, respectively.

In Figure 3, *a*, *b* is shown the microstructure of the friction track of ES-coated (mode 4) sample and the results of its elemental analysis are presented in Table 3.

The data in the Table 3 indicate that oxide phases of titanium, possibly Ti$_3$O and (or) Ti$_6$O, are present in the friction track (spectra 5, 6, 7, light areas). In addition, judging by the content of elements in spectra 1–4 (dark areas), there are predominantly oxides of titanium and iron. Such structures are obviously formed from compressed powdery products of wear of the coating material and the counterbody. Their formation on a harder and stronger sublayer of the coating material cre-
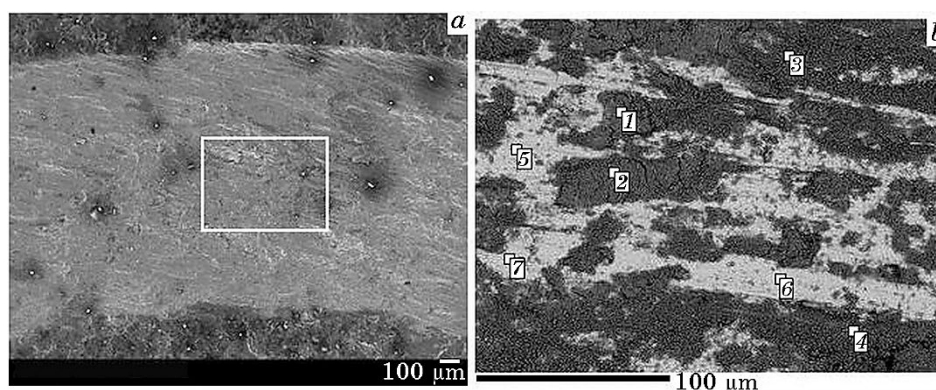
Fig. 3. Microstructure of the friction track: *a*—general view; *b*—enlarged fragment with elemental analysis data.

TABLE 3. Elemental analysis of the surface of the friction track in the AlB_{12}–50 wt.% Al ESA-coating (Fig. 3, *b*).

Spectrum	Element, wt.%						Total
	B	C	O	Al	Ti	Fe	
1	0.28	1.43	42.25	0.88	38.93	16.21	100.00
2	0.42	1.70	39.70	0.91	41.23	16.04	100.00
3	0.81	2.71	40.14	0.89	41.20	14.24	100.00
4	1.21	2.56	38.98	0.90	40.34	16.00	100.00
5	–	0.80	7.18	1.57	89.20	1.25	100.00
6	–	0.71	3.77	1.80	92.70	1.01	100.00
7	0.21	1.10	4.55	1.83	91.53	0.78	100.00

ates a positive gradient of mechanical properties in the friction contact zone, which is one of the conditions for ensuring increased antifrictionality and wear resistance of materials in friction pairs [29].

This reduces frictional loading of surface layers in real contact areas and together with the presence in the coating of such high-strength structural components as titanium diboride and titanium aluminides (Fig. 1), may be factors determining the increased wear resistance of the coating in study.

4. CONCLUSIONS

1. Composite material AlB_{12}–50 wt.% Al can be used to obtain protective ESA-coatings on a titanium alloy operating when wearing under

fretting corrosion. Theoretical estimation of the interaction between the anode and the cathode materials by the Palatnik criterion showed that in the process of ESA it is possible to obtain a mixed layer from the components of the substrate material and the electrode material with high adhesive strength.

2. Regardless of the deposition mode, ESA-coatings exhibit significantly less wear than uncoated OT4 titanium alloy. The increased wear resistance of the coatings in study under conditions of fretting-corrosion wear is explained by the formation of protective structures of wear products (which are mainly oxides of titanium and iron) on the surface of the friction track, and the presence of high-strength structural components such as titanium diboride and titanium aluminides in the coating.

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