Journal of the Balkan Tribological Association *Vol. 27, No 1, 1–20 (2020)*

SOME WAYS TO INCREASE THE WEAR RESISTANCE OF TITANIUM ALLOYS

T. PENYASHKI[a], V. KAMBUROV[b], G. KOSTADINOV[a],
M. KANDEVA[c], R. DIMITROVA[b], A. NIKOLOV[b]

[a] *Institute of Soil Science, Agrotechnologies and Plant Protection „N. Pushkarov", Sofia, Bulgaria*
E-mail:tpeniashki@abv.bg, gdkostadinov@gmail.com

[b] *Department of Materials Science and Technology,*
Technical University of Sofia, Bulgaria
E-mail: vvk@tu-sofia.bg; r_dimitrova@tu-sofia.bg; anikolov@tu-sofia.bg

[c] *Faculty of Industrial Engineering, Tribology Centre,*
Technical University of Sofia, Bulgaria
E-mail:kandevam@gmail.com

ABSTRACT

In the present work the properties, advantages and disadvantages of titanium and its alloys and their suitability for use in various fields of application are discussed. The essence and technological features of the methods for improve the tribological characteristics of titanium and its alloys are considered.

Based on a comparative analysis of their technical parameters and technological capabilities, appropriate methods and processes for applied of wear-resistant coatings and surface modification in order to improving the abrasion resistance and performance of titanium and titanium alloys are shown. The reasons for choosing the electrical spark deposition as an effective and suitable method for improving the surface properties of titanium alloys are determined. Guidelines for selecting an effective and suitable method for improving the surface properties of titanium and its alloys in different operational applications are indicated.

Keywords: titanium alloys, surface modification, electrical spark deposition, tribological characteristics

---

* For correspondence.

AIMS AND BACKGROUND

In recent years, titanium and its alloys have become the main materials for the manufacture of various responsible parts and structures in many areas of industry – rocket- and aerospace technique, shipbuilding, automotive, biomedical, energy and chemical industries and many other industries[1÷6]. The combination of low specific weight, high strength, good corrosion resistance, manufacturability, biocompatibility, non-magnetism determines their wider application in practice.

Titanium is a light and strong metal with a very high strength-to-weight ratio, low density and quite malleable (especially in an oxygen-free environment). Industrially pure titanium[3] has a density $\rho \approx 4.5$ g/cm^3, which is significantly lower than that of steel, a tensile strength $\sigma_b \approx 540$ MPa, almost twice as high as that of aluminum and comparable to the strength of some steels, but its weight is more than 40% lower than that of steels, melting point 1 725°C, relative elongation $\delta = 25\%$, hardness HB≈195, modulus of elasticity $E = 1.078 \cdot 10^5$ MPa. The thermal conductivity of titanium – $\lambda = 15.24$ W/(m.K), its modulus of elasticity and hardness are significantly lower than those of steels and aluminum. Its specific weight, strength and operating temperature are between aluminum and steel, but its specific strength is high and has a high fatigue threshold, excellent corrosion resistance and ultra-low temperature, does not magnetize and is a weak conductor of heat and electricity. It is no longer used only in aerospace applications, but has become a high-performance material available to designers.

However, titanium has a high chemical activity and reacts with O, N, H, CO, CO_2, water vapor and ammonia in the atmosphere, forming hard but brittle oxides, nitrides and carbides[1÷6]. In addition, pure titanium has low hardness and poor machinability[2,3]. Due to its insufficient strength at high temperatures, titanium is not suitable for use in aviation, but due to its extremely high corrosion resistance, in some cases it is indispensable in the chemical industry and shipbuilding. It is used in the production of compressors and pumps, pipelines, valves, autoclaves, various types of containers, filters, etc. for work in aggressive environments such as sulfuric, hydrochloric, nitric acid and their salts, aqueous and acidic solutions of chlorine, etc.

The permanent striving for search of better efficiency, including operation at higher temperatures, pressures and speeds, together with the need in some applications for complete reliability of the equipment is the reason for the growing need to improve its properties by creating various titanium alloys.

According to their phase composition, titanium alloys are classified into the following three types[1,2,3]:

– "α" alloys – single-phase structurally stable alloy, which has a higher wear resistance than pure titanium and strong oxidation resistance;

– "β" alloys (high temperature) – high strength, composed of a solid solution of β-phase;

– (α + β) alloys – two-phase alloy with good complex properties – structural stability, strength, ductility and high temperature deformation properties.

The most commonly used of the three titanium alloys are α-titanium alloys, which have the best machinability, and (α + β) titanium alloys.

According to their properties, titanium alloys are divided into heat-resistant, high-strength, corrosion-resistant, low-temperature and medical alloys[1÷6]. According to the complex of physical and mechanical properties, titanium alloys are a universal structural material combining the cold brittleness of aluminum alloys and austenitic steels, high corrosion resistance of copper-nickel alloys and stainless steels, non-magnetism, strength and specific strength higher than that of most construction materials. Their high structural properties make them preferred materials in aircraft construction and the manufacture of various responsible parts and structures[3÷7], where the aim is to obtain the lightest design combined with the required strength. The amount of titanium alloys used in aircraft in recent years has increased rapidly, reaching 20% to 30% of the aircraft's structural mass[3]. This allows to reduce their weight by 10-25%. In this case, titanium alloys can work while maintaining the required strength at temperatures up to 500°C and more, and aluminum alloys – at temperatures below 200°C. The high cost of titanium and its alloys is in many cases offset by their greater efficiency, and in some cases they are the only raw material for creation equipment or constructions that can operate under specific conditions. Titanium alloys are promising for use in many other applications, but their high cost and low abrasion resistance significantly limit their application – they can be used mainly to lighten any load-bearing elements and structures, as well as those operating in conditions in aggressive environments.

The efforts of many researchers are aimed at overcoming the negative tribological properties of titanium in order to expand the scope of its application. In this regard, the objectives of the present work are: – to clarify the advantages, disadvantages and limitations of the use of titanium and its alloys; – to identify the main problems hindering its mass implementation in the industry; – to determine and systematize the appropriate ways and methods for improving the wear resistance of alloys; – to indicate approaches and strategies for selection of methods and materials for improvement of wear resistance of alloys.

POSSIBLE WAYS TO IMPROVE THE WEAR RESISTANCE OF TITANIUM ALLOYS

The methods of "SWOT"-analysis examine the strengths and weaknesses of titanium alloys – Table 1. From the data presented in Table 1 it is established that the advantages (strengths) are much more and more significant than the disadvantages.

Table 1. SWOT analysis of advantages and disadvantages of Titanium and Titanium alloys

Advantages of titanium and titanium alloys	Disadvantages of titanium and titanium alloys
Low density – helps to reduce the weight of the manufactured products while maintaining their strength characteristics.	High production costs, titanium is much more expensive than Fe, Al, Cu.
High strength at temperatures up to 500^0C – significantly superior aluminum alloys and close to steel.	Active interaction at high temperatures with atmospheric gases.
Unusually whistle forms thin (5-15 μm) continuous films of TiO_2 on the surface, firmly bonded to the metal – close and higher than that of copper alloys and stainless steels;	High tendency of titanium and many of its alloys to hydrogen brittleness and salt corrosion.
High specific strength (strength / density ratio) – in the best titanium alloys is up to twice as high as the specific strength of alloy steels.	The high chemical activity, the growth of the grains and the phase transformations at high temperature cause difficulties in welding and machining.
High biocompatibility and non-toxicity, predetermining its use as implants in surgery and dentistry, as well as TiO_2 in the composition of many drugs.	Poor machinability, similar to that of austenitic stainless steels – high temperature and cutting force, layer formation, vibration, rapid wear of machining tools.
High resistance and strength at low temperatures, high threshold of metal fatigue, which guarantees their long-term use	Low thermal conductivity, low Young's modulus and low hardness
It does not magnetize and is a weak conductor of heat and electricity.	Low friction and wear characteristics – relatively high coefficient of friction, high tendency to sticking and bonding, to the appearance of pores and cracks, intense wear

The most significant disadvantage of these alloys (Table 1) is the low surface hardness and low characteristics of friction and wear – relatively high and unstable coefficient of friction, high tendency to adhesion bonding and sticking, to the appearance of pores and cracks, severe abrasive and adhesive wear and tear. The use of conventional lubricants does not improve the sliding of the contacting titanium parts due to the complete lack of adhesion to the surface, therefore during operation there is intense wear and destruction of units of machines and mechanisms. These shortcomings prevent and severely limit their application in friction assemblies and even make their use dangerous in critical elements of machines and mechanisms. In addition, titanium alloys have low machinability and are difficult to machine by cutting. In the process of hot treatments easily absorb impurities such as hydrogen, nitrogen, nitrogen and carbon, which dramatically degrade the geometry, tribological properties and wear resistance of the surface layer.

The growing demand for new titanium materials with predetermined properties that provide better mechanical properties poses a key task for modern materials science to increase the durability of this important class of construction materials. To increase the wear resistance, fatigue strength and corrosion resistance of products made of titanium and its alloys, the world practice works in the following directions:

CREATION OF NEW ALLOYS WITH IMPROVED PROPERTIES BY ALLOYING WITH NEW ELEMENTS

Titanium alloys with different microstructures are obtained by adding suitable alloying elements and gradually changing the phase transition temperature and phase content by using the different characteristics of the two structural modifications of titanium. The elements that stabilize the "α" phase and increase the temperature of the phase transition are Al, C, O_2, N. Among them, aluminum is the main alloying element of titanium alloys, which has obvious effects on improving the normal temperature and high temperature of the alloy, reducing the specific weight and increasing the modulus of elasticity[1÷6]. The elements that stabilize the "β" phase and lower the temperature of the phase transition are "β" -stable elements and can be divided into two types: isomorphic form and eutectoid form. The first type has Mo, V, Nb, etc.; the second type has Cr, Mn, Cu, Fe, Si and similar ones. Elements that have small effect on the phase transition temperature are neutral elements such as Zr and Sn[3].

In recent years, manufacturers have been developed new titanium alloys with lower cost and high quality. The new progress in the research of titanium alloy materials is mainly reflected in the following directions:

– *High temperature titanium alloys* – The first in the world high-temperature titanium alloy is Ti-6Al-4V with simultaneous heat resistance, strength, elasticity, good machinability, weldability, corrosion resistance and biocompatibility with an operating temperature of 300-350°C. Many other titanium alloys have been developed on the basis of this alloy, which can be considered as its modification. Subsequently, high-temperature, corrosion-resistant alloys were developed, as well as those with increased strength such as IMI550 and BT3-1 with a temperature of 400°C, IMI 679, IMI 685, Ti-6246 and Ti-6242 – at a operating temperature of 450°C to 500°C. The new high-temperature titanium alloys that are successfully used in military and civil aircraft engines include alloys IMI829 and IMI834 in the United Kingdom, Ti-1100 in the United States, and alloys BT18 and BT36 in Russia. The temperature of use of the new heat-resistant titanium alloys increased to 600-650°C in the 1990's[1÷6]. In addition, shape memory alloys[5] such as Ti-Ni, Ti-Ni-Fe and Ti-Ni-Nb have emerged since the 1970's and are increasingly used in mechanical engineering.

Since the 1960’s, hundreds of titanium alloys have been developed with various designations in the direction of improving strength, ductility, modulus of elasticity, corrosion resistance, hardness and workability. The most widely used and best known are 20-30 types, such as Ti-6Al-4V, Ti-5Al-2.5Sn, Ti-2Al-2.5Zr, Ti-32Mo, Ti- Mo-Ni, Ti-Pd, SP-700, Ti-6242, Ti-10-5-3, Ti-1023; IMI829, IMI834, Ti-6%Al-5%Zr-0.5%Mo-0.2%Si – IMI 685,Ti-5.5%Al-3.5%Sn-3%Zr-1%Nb-0.3%Mo-0.3%Si – IMI 829, Ti-4%Al-4%Mo-4%Sn-0.5%Si – IMI 551, Ti-3%Al-8%V-6%Cr-4%Zr-4%Mo – Beta C, Ti-15%Mo-3%Nb-3%Al-0.2%Si – Timetal 21S[2,3,4], Ti-Al-Si alloys[8], Russian BT1-0, VT3-1 BT5, BT5-1, BT6, BT9, BT20, OT4 и OT4-1 and many others[2]. BT5- contains 5% aluminum. It has higher strength properties compared to titanium, but its manufacturability is low. BT5-1, OT4 and OT4-1 – contain Al and Mn as alloying elements. They have high technological plasticity. BT20 has been developed as a more durable sheet material compared to VT5-1. VT3-1 belongs to the Ti-Al-Cr-Mo-Fe-Si system. Class VT3-1 is one of the most widely used alloys in manufacture – heat-resistant material with high durability and strength. It is intended for continuous operation at 400-450°C. It is used for making rods, profiles, plates, forgings.

– *Titanium matrix composite materials* – can reduce the weight of the constructions, increase their hardness, increase operating temperatures. They can be used as pistons for the propulsion of aircraft and engines, chassis parts, amplifiers of critically loaded constructions, compressor rotors, nozzle guide elements[6]. Of interest are fibrous composites with a matrix of titanium alloy and silicon carbide fibers[3]. Their strength reaches 5000 MPa, the modulus of elasticity is up to 900 GPa. Fibers or particles-reinforced composite materials made it possible to use titanium alloys at temperatures higher than 650°C. From composite materials it is possible to produce panels (flat or profile shapes), plates, pipes, rings, selectively (locally) hardened parts.

– *Titanium-aluminum alloys* – Compared to general titanium alloys, the most advantageous advantages of titanium-aluminum compounds Ti3Al (α) and TiAl (γ) are the high temperature characteristics (maximum operating temperatures of 816 and 982°C respectively) and the oxidation resistance and increased strength – e.g. Ti-21Nb-14Al and Ti-24Al-14Nb.

– *High strength alloys – “β” alloys* – The first titanium alloy of type β is B120VCA (Ti-13V-11Cr-3Al). The β-titanium alloy has good hot and cold characteristics, can be rolled and welded and can obtain high mechanical properties, good resistance to aggressive environments and fracture. The most representative of the new high-strength β-titanium alloys are: Ti1023, which has similar characteristics to 30CrMnSiA steel, often used in aircraft, and has excellent forging machinability; Ti153 (Ti-15V-3Cr-3Al-3Sn), whose cold workability is better than that of pure titanium, and the tensile strength at room temperature after aging can reach 1000 MPa or more; β21S (Ti-15Mo-3Al-2.7Nb-0.2Si), a new type of antioxidant, ultra-high strength titanium alloy; SP-700 (Ti-4.5Al-3V-2Mo-2Fe), which can replace Ti-6Al-4V alloy.

– *Medical titanium alloys* – Currently Ti-6Al-4V is still widely used in the medical field. However, this alloy releases very small amounts of vanadium and aluminum ions, which reduces the adaptability of cells and can cause harm to the human body. The new series of "α + β" titanium alloys have excellent biocompatibility, including Ti-15Zr-4Nb-4TA-0.2Pd superior to Ti-6Al-4V in corrosion resistance and fatigue strength.

However, among the series cast titanium alloys, there is still no material that meets the requirements for increased wear resistance at friction. Attempts to avoid the disadvantages mentioned above by creating new alloys and by introducing alloying reinforcing elements that increase the hardness have almost no effect on improving their wear resistance and do not lead to the expected results.

HEAT TREATMENT – UNSATISFACTORY DEGREE OF IMPROVEMENT

Increasing the wear resistance at friction can also be obtained by regulating the heat treatment process to obtain different phase compositions and microstructures. It is generally believed that the fine heterogeneous structure has good ductility, thermal stability and fatigue strength; the needle-like structure has high durability, creep strength and breakage strength; mixed structure – better overall performance. Commonly used heat treatment methods are annealing, solid solution preparation and aging treatment. However, heat treatment has also not yet contributed to an acceptable increase in the hardness and abrasion resistance of titanium products.

Numerous literature data confirm that heat treatment and alloying additives do not contribute to the improvement of these adverse properties[4,6,8÷11].

COATINGS AND SURFACE MODIFICATION

The use of effective surface engineering methods and technologies ensures the creation of multifunctional surface layers with high values of hardness and adhesion to the base material , high wear resistance and development of the full potential of the material. Coatings can improve many aspects of the surface properties of the material while leaving the properties of its substrate unchanged. In the literature there are diverse and numerous data on the study of the structure and properties of wear-resistant coatings applied by different methods and under different conditions[12÷54] and the results of their application, most of which report an increase in wear resistance of modified surfaces. Most of them explore the possibilities of using the numerous existing methods, technologies and materials for deposition of wear-resistant coatings and surface modification of titanium products. For materials are used mainly gases, metals, conventional hard alloys with various additives. The obtained results have a multidirectional and unsystematic character, the regularities of the processes and the influence of the technological parameters on the formation and the properties of the coatings are insufficiently studied. There is no general information for determining the modes and materials for obtaining coatings with specified thickness, roughness, composition, structure and properties. The main task of creating coatings on titanium products is to improve their resistance to corrosion and high temperatures, their surface hardness and their tribological characteristics.

The most popular and promising methods suitable for surface modification of titanium are:

– *PVD and CVD methods* – coating techniques that are completely different in chemical composition, structure and properties compared to the substrate. The PVD process involves evaporation of the coating material, chemical reactions with accompanying elements and gases with simultaneous deposition on the sample. These methods use different ways of evaporation of the material – electric arc, electronic, beam, magnetron sputtering and others. Coatings obtained on Ti-6Al-4V alloy by PVD[12÷15] show encouraging results. The method also allows for obtaining nanostructured thin coatings of different materials, low roughness, consistent tribological properties and extended service life. Obtaining a surface coating with greater thickness and high bond strength by PVD is associated with significant difficulties. Compared to PVD, CVD processes have a better deposition capacity, which allows even complex shaped parts to be covered with an even layer. The main disadvantage of the classic CVD process is the high operating temperature – over 800°C. Lower operating temperatures are possible in PACVD processes (Plasma Assisted CVD)[7,12]. The working gases and the sample are exposed to low-temperature plasma, which provides the necessary energy to activate the reactions. The temperature of the PACVD process is in the range of 450 to 650°C. The complex and expensive equipment and technology, the high temperatures and the small thickness of the coatings (up to 10-15 µm) in these processes are factors preventing their use in titanium alloys.

– *Chemical-thermal treatment* (diffusion saturation with oxygen, nitrogen, carbon, etc.) due to the diffusion penetration of the layering material at a significant depth in the base – over 200 µm are more suitable for surface modification of titanium alloys[17], but due to high process temperature 800-900°C and thermal changes in the structure, shape and size of the samples, as well as the frequent need for additional processing significantly limit the use of these so appropriate methods. The treated surfaces show significant improvements in mechanical properties, manifested by a double increase in hardness and improved corrosion resistance to the oxidation process. Carburizing demonstrates the greatest reduction in friction coefficient and wear rate[17].

However, most of the authors claim that in order to avoid recrystallization and annealing of titanium alloys, the work surface temperature in these technologies should not exceed 400°C. It is therefore necessary to create anti-wear coatings on titanium alloys that have a strong metallurgical bond with the titanium substrate, while minimizing heat input to the substrate to avoid structural and thermal deformations. In this regard, it can be argued that the widest possibilities for obtaining improved characteristics of titanium surfaces have processing methods that use concentrated energy fluxes, such as low-temperature plasma, laser, electron and ion beams, pulsed discharges, thermal spraying, electrospark deposition. In these methods, the coating-base bond is most often diffusion, which implies higher wear resistance.

– *Gas-flame, plasma and detonation coating* (thermal spraying) due to the strong diffusion connection of the coatings with the substrate, the possibility of deposition all metallic and non-metallic powder compositions, relatively inexpensive equipment, the availability of technology and the possibility of applying coatings with greater thickness – 20-500 μm are also suitable methods for the obtained increase of the hardness and wear resistance of titanium alloys with coatings of WC, TiC, etc. reported[18,19]. The high heating temperatures of the substrate and the need for subsequent surface treatment are the factors limiting the widespread use of these relatively light, inexpensive and affordable methods. Gas-flame coating, as a rule, complicates the production technology, as it includes preparatory and subsequent operations. Detonation spraying makes it possible to obtain a higher quality coating compared to flame spraying. Disadvantages of the method include the complexity of the implementation of the technological process and the difficulty in installing the part in the technological equipment. Disadvantages of plasma spraying include high temperature during remelting, which leads to deformation of the part, high quality requirements and granulating composition of self-fluxing powders, relatively large quotas for machining, careful preparation of the substrate before coating[18,19].

– *Laser surface modification and case hardening* – allows to obtain thin layers with high microhardness and good wear resistance. Laser reinforcement tools and equipment are complex and expensive, and it is difficult to achieve a coating on a titanium alloy with complex geometry[20]. Laser nitriding is a process that uses the strong affinity of titanium for nitrogen, which interacts with the surface of the sample melted by the laser beam. High process power is achieved by using CO_2 or YAG / Y3Al5O12/ lasers[21]. Among other processes, laser nitriding is proving to be a promising way to improve the poor tribological behavior of titanium alloys[21]. The main factors limiting the wide application of this method are the expensive equipment and the complex technology.

– *Ionic implantation* – The surface modification of titanium and its alloys by ion implantation with nitrogen or carbon is done in order to improve its wear resistance and anti-seizure properties. During ion implantation, accelerated ions reach the surface of the sample, the ion source being bombarded with electrons to ionize the molecules by igniting a discharge arc between the anode and cathode. If conditions are created to maintain the implantation dose at a certain level, it can have a positive effect in the direction of forming a stoichiometric balance between the implanted elements (N, C) and the primary cell (TiN or TiC) close to the surface. This leads to the transformation of the wear mechanism from adhesive to abrasive with a corresponding improvement of the wear-resistant properties of the base material. The surface layer is most often with a thickness of 100-200 nm to several microns and with increased hardness and wear resistance[22,23].

– *Plasma nitriding* – Ionic-plasma nitriding is one of the most widely used techniques to increase the surface hardness and wear resistance of titanium products. The process is characterized by the diffusion of nitrogen atoms into the metal surface in the presence of a plasma environment. It is carried out in an environment of smoldering discharge, while increasing simultaneously the current and voltage. The sample can be heated by energy transfer by ion bombardment. In this way, nitrogen reaches its surface, which diffuses into the interior[2,6]. Ionic-plasma nitriding[16,24,25,26÷31] provides a final effect that allows to obtain hardened layers with a hardness of $HV_{0.01}$ 650–1000 with a thickness of 0.07–0.20 mm in 3–6 hours[30,31], depending on the type of titanium alloy. Technological factors influencing the efficiency of ion-plasma nitriding of materials are the process temperature, saturation duration, pressure, composition and flow rate of the working gas mixture. The results of the authors cited above show that nitrided samples acquire higher surface hardness and significantly increased abrasion and adhesion wear resistance, but the corrosion behavior of untreated and nitrided samples has similar characteristics. Nitriding carried out by other known methods – ionic, gas, electrochemical, PVD, laser, electric arc, conventional gas nitriding, etc. according to the authors shows a satisfactory increase in friction, abrasion and adhesion resistance, but lower than that of ion-plasma nitriding.

– For protection of titanium alloys by many other methods such as *nitrogen* or *oxygen treatment, ion implantation, electrochemical, non-current deposition* and *anodizing* -suitable for sheet material and large details, *thermal oxidation, microarc oxidation*, etc. reported many authors[32÷36], but the applications of these surface technologies are limited due to the generation of some adverse effects on titanium alloys. For example, causing thermal deformation of titanium bases by chemical-thermal nitriding, oxidation by gas-thermal spraying, etc. A disadvantage of gas nitriding, for example, is that it is difficult to control the oxygen content, so titanium alloys tend to form brittle phases on the surface which has a negative effect on their mechanical properties[32].

– Electrical *spark deposition (ESD)* is one of the promising methods for obtaining coatings on titanium products. ESD is the lightest, simplest, cheapest, environmentally friendly and safe, universal and effective means for local application of wear-resistant coatings for various purposes on the work surface of rapidly-wearing parts and tools without special surface preparation and volumetric heating.

ESD makes it possible to form coatings with high adhesion strength to the substrate from almost all conductive materials. As a result of the spark-plasma discharges on the surface of the substrate a layer with modified structure and thickness is formed when using hard alloys 5 to 100 microns, and from plastic and lower melting materials the covering layer can reach 0.3 mm. The advantages of this method include insignificant heating of the substrate, lack of thermal deformation, low energy consumption and ease of technological operations, the possibility of layering complex surfaces[37,39,40]. The disadvantages are the small thickness of the applied coating and low productivity. Wear-resistant, anti-corrosion and other functional properties of the coatings can be obtained by selecting the appropriate electrode material or treatment medium. The short duration of the electrical pulse leads to a very fast hardening of the deposited material, which usually leads to a new structured coating, demonstrating unique tribological and corrosion efficiency.

By changing the parameters and conditions of ESD it is possible to regulate the micrometallurgical processes in this area, to perform targeted synthesis of refractory and other chemical compounds and to form complex composite coatings of intermetallic compounds, carbides, nitrides, oxides[37,39,40]. The deposited layer consists of the substrate material, the electrode material, as well as the new phases obtained in the deposition process and the rapid cooling after deposition. This method is also suitable for surface treatment of titanium and titanium alloys and allows to increase their surface hardness and wear resistance. By varying the layering modes and the materials of the layering electrodes, coatings with predetermined quality indicators, composition, structure and properties can be obtained.

The main disadvantage of electrical spark deposition is that with an increase in the thickness of the applied coating, its roughness increases, which negatively affects its operational properties.

At present, many researchers are working to create ESD coatings on titanium alloys. Numerous coatings of different materials have been obtained and a positive effect on the hardness, wear resistance and corrosion resistance of alloys has been found[37÷48].

– *Diamond-like (DLC) and nanocomposite coatings* deposited by various methods are of considerable interest in practice[49÷54]. These coatings have both high hardness and wear resistance, high temperature and corrosion resistance.

Table 2 shows the current opportunities to improve the wear resistance of titanium alloys. An indicative assessment of the degree of applicability of the individual activities was performed. The analysis of the obtained data shows that

Table 2. Classification Assessment of the possibilities for reduction (‘mitigation’) of the imperfections

№	**Possibilities**	**Compatible with available assets (materials, machinery, resources)**	**Accordance with criteria, time and price requirements**	**Accordance with strengths, technological criteria**	**Risks**	**Ease of imple-mentation**	**Sum of points**
1	Creation of new alloys with improved properties	2	Increases production time and prices -2	Incomplete improvement-2	Incomplete improvement, high investment-3	2	**12**
2	Additional heat treatment	3	Additional surface treatment Increases time and cost -3	Incomplete improvement Need for finishing-2	Oxidation of titanium, phase and structural transformations due to high temperatures, change of shape and size -3	3	**14**
3	Surface treatment, etching, polishing, passive treatment, oxidation, etc.	3	Increases the time and cost of production -3	Incomplete improvement -2	Incomplete improvement -3	3	**14**
4	Chemical-thermal treatment oxidation, carburizing, nitriding, etc.	3	Additional surface treatment Increases the time and cost of production -3	Acceptable improvement Need for additional processing-4	Change the size and shape. Oxidation of titanium, phase and structural transformations due to high temperatures, many factors -3	3	**17**

5	Deposition of coatings by CVD, PVD methods	Expensive and complex equipment and consumables, high price-3	Increases time and cost Additional surface treatment-not always-4	Acceptable improvement-4	Change of structure and dimensions, thin coatings, risk of insufficient adhesion, Complex technology, many factors on which the process depends-4	3	**18**
6	Surface treatment Laser, electron beam, ion, etc.	Expensive equipment and consumables, high price-3	Increases time and cost -3	Acceptable improvement in some cases, need additional processing-4	Complex technology, many factors on which the process depends-3	3	**16**
7	Electrospark surface treatment	Cheap, affordable and portable equipment -5	Increases production time and cost, Cheap simple and light technology, low productivity-3	Acceptable improvement to two and more times reduced wear-4	Risks of incorrect selection of materials and regimes, oxidation and interaction of titanium with atmospheric air-4	5	**20**
8	Thermal spray – Gas flame, plasma, layering	Relatively cheap and affordable equipment – 4	Increases time and cost, need for additional processing – 3	Acceptable improvement, pre- and post-processing – 4	Risk of deformation and restructuring, Need for additional processing, low control – 2	4	**17**
9	Electrochemical deposition of metals, gases, compounds	Relatively expensive but affordable equipment – 3	Increases the time and cost, need for additional processing – 4	Acceptable, but also contradictory improvement, insufficient adhesion – 3	Risk of restructuring, need for further processing – 3	4	**17**
10	Ionic-plasma nitriding	Expensive equipment and consumables, high price – 3	Increases time and cost – 4	Significant improvement – more than twice – 4	Risk of restructuring, Need for further processing – 4	4	**19**

Legend: 1 – lowest, 5 – highest

at the present stage the electrospark deposition and the ion-plasma nitriding are outlined as the most suitable option for most cases and especially for the surfaces of the movable and contact joints of the parts.

CERTAIN GUIDELINES FOR SELECTION OF SURFACE MODIFICATION METHOD AND MATERIAL AND WEAR-RESISTANT COATING

Currently, there is no clear concept and recommendations in the literature for the use of this or another method for surface modification of specific products for certain operating conditions. The choice of method for surface modification of specific products is most often of a priori-intuitive nature, based on the experience, intuition and preferences of specialists, which does not always allow find optimal solutions. Most often, the evaluation of the effectiveness of the respective method is limited to the comparison of the durability of the modified and unmodified products.

The effectiveness of the methods for applying coatings is a function of the correct choice of coating materials determined by the use of deposition materials, which must ensure, on the one hand, a high level of physical and operational properties of the surface for the specific case and the operating conditions, and on the other – the technological and economical effectiveness of the coating process, according type and size of the loads, conjugated friction materials and so on. For each particular problem, a unique solution is needed to create a wear-resistant surface that requires a suitable selection of coating materials.

When choosing a method, it is necessary to take into account the positive and negative components of all methods, comparing the mechanical properties of the coatings required for the field of application. It is necessary to make appropriate comparative technological and economical calculations based on: requirements for the article; operating conditions; accessibility, features, capabilities of the method and the resulting coatings and their suitability for the particular conditions of use; the possibilities for the necessary increase in the durability of the product at the lowest cost of layering; the production costs and cost of modification. It should be borne in mind that a method and a material that is most effective under certain operating condition, under other conditions it may not lead to the same increase in durability and wear resistance. In addition, coatings of the same material applied by two different methods may have significant differences in their properties, for example, in the composition of a TiCN coating, obtained by plasma process there are also oxides, nitrides, intermetallic phases and compounds with the base metal, and in PVD methods – TiCN is in pure state, which makes it more resistant to abrasioarn wear, but less resistant to high and variable impact loads compared to plasma coating.

The following recommended areas for their use, based on the described features of the methods, could be indicated:

– *PVD methods* – are suitable for large quantities of identical or similar in size details. Extremely effective for thin coatings on assemblies, components, parts and parts at low and high speeds of friction, and low impact loads, in which there are strict requirements in terms of roughness, shape and size. The coatings also have good chemical and corrosion resistance. The coatings obtained by the different PVD installations are in principle equivalent, but their quality characteristics depend on the peculiarities of the method and the possibilities for regulating the process. For example, sputtering is more suitable for repetitive series of identical products, and evaporation processes – for products of different shapes and sizes. It must be taken into account that PVD methods are not yet the universal means of increasing durability. On the way to their mass implementation there are still many unresolved issues such as the high cost and complexity of the equipment, the necessity for preliminary and subsequent cleaning of products, relatively thin coatings, the difficult coating of complex concave shapes, the incomplete repeatability of the properties and properties of the coatings, the tendency to cracking and peeling of the coatings under more severe working conditions, etc.

– *Thermal spraying methods* – Among them with the highest capabilities are high velocity plasma and supersonic oxyfuel gas flame spraying (HVOF). The presence of portable equipment makes it possible to deposit elements and details on site. It is most appropriate to use these methods for loaded parts operating in aggressive and abrasive environments under shock, temperature and cyclic loads. When using thermal spraying methods, it must be taken into account that in most cases the coated products need additional processing to finish the micro-irregularities and possible unevenness in the thickness of the coating. Therefore, the selection of application modes and technology should provide for an appropriate addition to the thickness of the coating for subsequent treatment.

– *Electrophysical methods* – Of these, the lightest, cheapest, most affordable and most versatile is electrical spark deposition (ESD). It can be used to increase the durability of all parts made of titanium alloys, as well as for friction conditions under cyclic and low impact and mechanical loads, details under friction of various assemblies and elements. The ESD method is not suitable for large quantities and series of parts due to its low productivity, and also for details with high smoothness requirements (Ra <1 μm), due to the higher roughness of the obtained coatings. The use of other electrophysical methods – laser, electron beam layering could be effective in certain specific cases could be effective for large quantities of identical parts due to the high cost and complexity of the equipment.

Of the case-hardening methods the most appropriate and cost-effective, especially for large quantities of parts, or for single oversized titanium workpieces (eg sheet materials) are:

– *ion-plasma nitriding* – with wide areas of application;

– *ordinary nitriding, carburizing, carbonitriding* – also with extremely wide areas of application and suitable for sheet and oversized parts.

These methods are cheaper and more productive than PVD and thermal spraying methods. They can be used in products made of various titanium alloys. Although the degree of increase in durability is lower compared to PVD, plasma and electrophysical methods, and case hardening methods, are more cost-effective and efficient in many cases due to their lower price, high productivity and the ability to surface hardening of any details, even with small dimensions without rounding their edges.

– *Case hardening by diffusion saturation* with N, C, Cr, B, carbides, etc. can be used with good results for certain products. It is suitable for companies with their own thermal furnaces, as in most cases it does not require specialized equipment. However, with this method there is a risk of recrystallization of titanium and deformation of the products, therefore the saturation regimes should be combined with the regimes for heat treatment of the articles, and in the case of saturation with powders – further processing of the coated surface should be provided.

In the presence of a large number of small and medium-sized identical details, PVD and electrochemical methods are more advantageous from the point of view of productivity and price, because allow for simultaneous application of the coatings on all parts and for a lower cost of layering, as the price is determined on a “cycle” and not on a “piece”. If it is necessary to modify single or a small number of products, ESD it may be more profitable, based on the performed technological and economic calculations, although layering them with PVD, for example, can lead to a greater increase in durability.

CONCLUSIONS

1. Titanium and its alloys are promising materials that are used in different engineering fields and medicine. They have the highest ratio of strength to density, which makes them an ideal material for the construction of various engineering structures. The main disadvantages of titanium alloys are their low abrasion and adhesive wear resistance. Of the possible ways to improve the tribological characteristics of titanium, the most effective at this stage are the methods of surface modification, which allow to significantly increase the wear, temperature and corrosion resistance of titanium and its alloys by improving the properties of the surface layer.

2. The comparison of technical and technological data, results in the literature, advantages and disadvantages of existing methods of surface modification allowed to establish that the widest possibilities for obtaining improved characteristics

of titanium surfaces have methods that use concentrated low-energy fluxes, e.g. low temperature plasma, laser, pulse discharges, thermal spraying, electrical spark deposition (ESD). In these methods, the coating-base bond is most often diffusion, which implies higher wear resistance.

3. Of particular interest from the considered techniques for modification of the surface layer of titanium and its alloys are electrical spark deposition (ESD) and ion-plasma nitriding.

4. Considerations, principles and approaches are proposed, defining the main directions in the selection of the most economically and technologically advantageous methods for application of wear-resistant coatings on titanium alloys, working under different operating conditions. Each case of friction and wear needs a specific solution for the selection of economically and technologically appropriate method for applying a wear-resistant coating.

ACKNOWLEDGMENTS

The present work is based on research funded by the Bulgarian National Science Fund of the Ministry of Education and Science under the project №KP-06-H37/19 "*Technological features and regularities of creation of new high wear resistant composite coatings on titanium alloys by electrical spark deposition process*".

REFERENCES

1. C. LEYENS, M. PETERS: Titanium and Titanium Alloys, Fundamentals and Applications. Wiley-VCH Verlag GmbH & Co. KGaA, Book, 532 (2003).
2. I. V. GORYNIN, B. B. CHECHULIN: Titanium in mechanical engineering. Moscow, Mashinostroenie, 400, in Russian (1990).
3. http://m.bg.tengxintitanium.org/news/titanium-and-titanium-alloy-24972691.html, Titanium and Titanium Alloys, Editor SOPHIE WONG, in Bulgarian (2019).
4. J. C. WILLIAMS: Alternate Materials Choices – Some Challenges to the Increased Use of Titanium Alloys. Mat. Sci. Eng., A 263, 107, (1999).
5. Y. SAHIN: Wear and Friction Behaviour of Titanium-Nickel Shape Memory Alloys. J. Balk. Tribol. Assoc., **20**(4), 539 (2014).
6. http://bg.cn-nitinol.com/info/several-titanium-alloys-you-must-know-39009093.html
7. F. ZIVIC, et al: Wear Behaviour of TI6Al4V Alloy against Al2O3 under Linear Reciprocating Sliding. J Balk Tribol Assoc, **17** (1), 27 (2011).
8. N. PAVEL, K. JAN, M. ALENA, V. DALIBOR: Effect of Alloying Elements on Properties of PM Ti-Al-Si Alloys. Acta Metallurgica Slovaca, **19** (4), 240 (2013).
9. H. DONG: Tribological Properties of Titanium-Based Alloys. Surface Engineering of Light Alloys, Woodhead Publishing Series in Metals and Surface Engineering, Cambridge, UK, 58 (2010).
10. H. GARBACZ, P. WIECINSKI, M. OSSOWSKI, G. ORTORE, N. T. WIERZCHO, K. J. KURZYDŁOWSKI: Surface Engineering Techniques Used for Improving the Mechanical and Tribological Properties of the Ti6A14V Alloy. Surf. Coat. Technol., 202(11), 2453 (2008).

11. Y. ALEMDAG, R. COOPER, H. LIANG: Friction and Wear Behaviour of Intermetallic Ni60Ti40 Alloy Modified with Aluminium. J. Balk. Tribol .Assoc., **19** (4), 558 (2013).
12. C. MARTINI, L. CESCHINI: A Comparative Study of the Tribological Behaviour of PVD coatings on the Ti–6Al–4V Alloy. Tribology International, **44**, 297 (2011).
13. W. GAO, Z. LI: Nano-Structured Alloy and Composite Coatings for High Temperature Applications. Materials Research, **7** (1), 175 (2004).
14. J. L. LI, G. Y. CAI, H. S. ZHONG, Y. X. WANG, J. M. CHEN: Tribological Properties in Seawater for Ti/TiCN Coatings on Ti6Al4V Alloy by Arc Ion Plating with Different Carbon Contents. Rare Metals, **36**, 858 (2016).
15. A. Z. A. DJAFER, N. SAOULA, N. MADAOUI, A. ZERIZER: Deposition and Characterization of Titanium Carbide Thin Films by Magnetron Sputtering Using Ti and TiC Targets. Appl. Surf. Sci., **312**, 57 (2014).
16. I. L. POBOL, I. G. OLESHUK, A. N. DROBOV, G. SUN FEN: Investigation of Formation of Hardened Layer on Titanium Alloys by the Method of Ion-Plasma Nitriding. Proc. of the National Academy of Sciences of Belarus Physical-Technical Series, **64** (1), 25, DOI: 10.29235/1561-8358-2019-64-1-25-34 (2019).
17. J. GRABARCZYK, D. BATORY, W. KACZOROWSKI, P. NIEDZIELSKI: Comparison of Different Thermo-Chemical Treatments Methods of Ti-6Al-4V Alloy in Terms of Tribological and Corrosion Properties Materials. Publisher: MDPI, **13**, 5192 (2020).
18. Y. LUO, L. YANG, M. C. TIAN: The Friction and Wear Behavior of WC Coating on Medical Grade Titanium Alloys. Proc. IMechE, Part J: J Engineering Tribology, **227** (8), 845 (2013).
19. A. ANAND, M. DAS, B. KUNDU, V. K. BALLA, S. BODHAK, S. GANGADHARAN: Plasma-Sprayed Ti6Al4V Alloy Composite Coatings Reinforced with in Situ Formed TiB-TiN. Journal of Thermal Spray Technology, **26**, 2013 (2017).
20. P. SCHAAF: Laser Processing of Materials – Fundamentals, Applications and Developments. **139**, 234 (2010).
21. P. SCHAAF, D. HÖCHE: Laser Machining and Surface Treatment, in Comprehensive Materials Processing, **9**, 607 (2014).
22. I. ZUMBILEV, A. ZUMBILEV: On the Influence of Ion Carbonitriding on the Wear Resistance of Materials. J. Balk. Tribol. Assoc., **26** (4), 653 (2020).
23. P. VLCAK, J. SEPITKA, J. DRAHOKOUPIL, T. HORAZDOVSKY, Z. TOLDE: Structural Characterization and Mechanical Properties of a Titanium Nitride-Based Nanolayer Prepared by Nitrogen Ion Implantation on a Titanium Alloy. Journal of Nanomaterials, Art. ID 9214204 (2016).
24. F. YILDIZ, A. F. YETIM, A. ALSARAN, A. ÇELIK: Plasma Nitriding Behavior of Ti6Al4V Orthopedic Alloy. Surf. Coat. Technol., **202**, 2471 (2008).
25. A. C. FERNANDES, F. VAZ, E. ARIZA, L. A. ROCHA, A. R. L. RIBEIRO, A. C. VIEIRA, J. P. RIVIÈRE, L. PICHON: Tribocorrosion Behaviour of Plasma Nitrided and Plasma Nitrided+Oxidised Ti6Al4V Alloy, Surf. Coat. Technol., **200**, 6218 (2006).
26. Z. X. WANG, H. R. WU, X. L. SHAN, N. M. LIN, Z. Y. HE, X. P. LIU: Microstructure and Erosive Wear Behaviors of Ti6Al4V Alloy Treated by Plasma Ni Alloying. Appl. Surf. Sci., **388**, 510 (2016).
27. D. BATORY, W. SZYMANSKI, M. PANJAN, O. ZABEIDA, J.E. KLEMBERG-SAPIEHA: Plasma Nitriding of Ti6Al4V Alloy for Improved Water Erosion Resistance. Wear, **374-375**, 120 (2017).

28. A. BLOYCE, P.Y. QI, H. DONG, T. BELL: Surface Modification of Titanium Alloys for Combined Improvements in Corrosion and Wear Resistance. Surf. Coat. Technol., **107**, 125 (1998).
29. İ. ÇELIK, M. KARAKAN: Effect of Plasma Nitriding Treatment on Structural, Tribological and Electrochemical Properties of Commercially Pure Titanium. Proc. of the Institution of Mechanical Engineers, Part H: Journal of Engineering in Medicine, **230** (2), 145 (2015).
30. E. ROLINSKI: Surface-Properties of Plasma-Nitrided Titanium-Alloys. Mat Sci Eng A, **108**, 37 (1989).
31. H. SKULEV, S. MALINOV: Phase Composition and Microstructure of Titanium Alloys after Surface Plasma Gas Nitriding. Proceedings of Second International Scientific Congress on Mechanical and Electrical Engineering and Marine Industry – MEEMI, Varna, Bulgaria, 192 (2005).
32. B. JANUSZEWICZ, L. KLIMEK: Nitriding of Titanium and Ti6Al4V Alloy in Ammonia Gas under Low Pressure. J. Mater. Sci. Technol., **26**, 586 (2010).
33. G. KARA, G. PURCEK, Y. ATASOY, E. BACAKSIZ: Microstructure and Tribological Properties of Ti Borided by Electron Beam Evaporation Technique. Journal of the Balkan Tribological Association, **17** (1), 27 (2011).
34. I. G. ZHEVTUN, P. S. GORDIENKO, V. G. KURYAVYI: Influence of Arc Discharge Time on Microstructure of the Ti–TiC Composite Surface Engineering and Applied Electrochemistry, **50** (6), 491 (2014).
35. I. CELIK, M. KARAKAN, F. BÜLBÜL: Investigation of Structural and Tribological Properties of Electroless Ni-B Coated Pure. Proc IMechE, Part J: J Engineering Tribology, **230** (1), 57 (2015).
36. C. HU, P. CHIU: Wear and Corrosion Resistance of Pure Titanium Subjected to Aluminization and Coated with a Microarc Oxidation Ceramic Coating. Int J Electrochem Sc, **10** (5), 4290 (2015).
37. A. E. GITLEVICH, V. V. MIKHAĬLOV et al: Élektroiskrovoe legirovanie Metallicheskikh Poverkhnosteĭ, Kishinev, Shtinitsa, (in Russian) 198 (1985).
38. T. PENYASHKI, G. KOSTADINOV, I. MORTEV, E. DIMITROVA: Improving the Surface Properties of Steel 210CR12 by Non-Contact Electrical Spark Deposition with Electrodes Based on WC and TiC. J. Balk. Tribol. Assoc., **23** (1-I), 69 (2017).
39. T. PENYASHKI, G. KOSTADINOV, I. MORTEV, E. DIMITROVA: Investigation of Properties and Wear of WC, TiC and TiN Based Multilayer Coatings Applied onto Steels C45, 210Cr12 and HS6-5-2 Deposited by Non-Contact Electrospark Process. J. Balk. Tribol. Assoc., **23** (2), 325 (2017).
40. V. V. MIKHAILOV, E. A. PASINKOVSKY, K. A. BACHU, P. V. PERETYATKU: On the Issue of Electrospark Alloying of Titanium and Its Alloys. Electronic Material Processing, (3), (in Russian) 106 (2006).
41. J. KOVÁČIK, P. BAKSA, Š. EMMER: Electro Spark Deposition of TiB_2 Layers on Ti6Al4V Alloy. Acta Metallurgica Slovaca, **22** (1), 52 (2016).
42. XIANG HONG, YEFA TAN, CHUNHUA ZHOU, TING XU AND ZHONGWEI ZHANG: Microstructure and Tribological Properties of Zr-basedamorphous-nanocrystalline Coatings Deposited on the Surface of Titanium Alloys by Electrospark Deposition. Applied Surface Science, **356**, 1244 (2015).

43. T. PENYASHKI: Investigation of the Wear of Steels with Coating Laid by Local Electric Spark Deposition. J Balk Tribol Assoc, **6** (2), 66 (2000).
44. YOU TAO, ZHANG CHUNHUI, SU GUIQIAO, YAN PING: Research on Depositing Ni45 Alloy on Titanium Alloy Surface by Electrospark Deposition, China Foundry, **5** (4), 244 (2008).
45. A. A. BURKOV, E. R. ZAYKOVA, M. I. JANITOR: Deposition of Ti-Ni-Zr-Mo-Al-C Composite Coatings on the Ti6Al4V Alloy by Electrospark Treatment in a Granular Environment. Electronic Proc. of Materials, (in Russian), **53** (6), 18 (2017).
46. B. R. LAZARENKO, A. E. GITLEVICH, S. P. FURSOV, V. V. MIKHAILOV, M. M. MARKUS: Some Features of Electrospark Alloying of Titanium with Aluminum and Nickel, Electronic Processing of Materials, (in Russian), **1**, 29 (1974).
47. YU. I. MULIN, A. D. VERKHOTUROV, V. D. VLASENKO: Electrospark Alloying of Titanium Alloy Surfaces. Prospective Materials, (in Russian), **1**, 79 (2006).
48. A. E. KUDRYASHOV, ZH. V. EREMEEVA, E. I. ZAMULAEVA, A. V. STRELETS, E. A. LEVASHOV, T. A. SVIRIDOVA: Influence of Secondary Electrospark Treatment with Carbon-Containing Materials on the Properties of Titanium Alloys. Hardening Technologies and Coatings, (in Russian), **5**, 17 (2010).
49. S. RAMAN, P. NAVANEETHAKRISHNAN, R. GNANAMOORTHY: Influence of Counterbody Material on Fretting Wear Behaviour of Uncoated and Diamond-Like Carbon-Coated Ti-6Al-4V. Proc. I Mech E, Part J: J Engineering Tribology, **223** (J2), 227 (2009).
50. C. A. LOVE, R. B. COOK, I. L. HARVEY, P. A. DEARNLEY, R. J. K. WOOD: Diamond Like Carbon Coatings for Potential Application in Biological Implants – a review. Tribol. Int., **63**, 141 (2013).
51. R. K. SINGH, M. T. TILBROOK, Z. H. XIE, A. BENDAVID, P. J. MARTIN, P. MUNROE: Contact Damage Evolution in Diamond Like Carbon Coatings Ductile Substrates, J. Mater. Res., **23**, 27 (2008).
52. J. GRABARCZYK, J. GAJ, B. PAZIK, W. KACZOROWSKI, B. JANUSZEWICZ: Tribocorrosion Behavior of Ti6Al4V Alloy After Thermo-Chemical Treatment and DLC Deposition for Biomedical Applications. Tribol. Int., **153**, 106560 (2021).
53. W. PAWLAK, K. J. KUBIAK, B. WENDLER, T. G. MATHIA: Wear Resistant Multilayer Nanocomposite WC1x/C Coating on Ti–6Al–4V Titanium Alloy. Tribol. Int., **82** (B) 400 (2014).
54. T. MOSKALEWICZ, B. WENDLER, S. ZIMOWSKI, B. DUBIEL, A. CZYRSKA-FILEMONOWICZ: Microstructure, Micro- Mechanical and Tribological Properties of the nc-WC/a-C Nanocomposite Coatings Magnetron Sputtered on Non-Hardened and Oxygen Hardened Ti-6Al-4V Alloy. Surf. Coat. Technol., **205** (7), 2668 (2010).

Received 20 December 2020
Revised 6 January 2021