UKRAINIAN JOURNAL OF MECHANICAL ENGINEERING AND MATERIALS SCIENCE

Vol. 8, No. 4, 2022

Tetiana Tepla[1], Eduard Pleshakov[2], Jan Sieniawski[3], Lidiya Bohun[4]

[1] Department of Materials Science and Engineering, Lviv Polytechnic National University, 12, S. Bandery Str., Lviv, Ukraine, e-mail: tetiana.l.tepla@lpnu.ua, ORCID 0000-0002-0474-797

[2] Department of Material Science, Rzeszów University of Technology, Poland, e-mail: jansien@prz.edu.pl, ORCID 0000-0002-2229-2820

[3] Department of Materials Science and Engineering, Lviv Polytechnic National University, 12, S. Bandery Str., Lviv, Ukraine, e-mail: lidiia.i.bohun@lpnu.ua

[4] Department of Material Science, Rzeszów University of Technology, Poland, e-mail: jansien@prz.edu.pl ORCID 0000-0002-5118-2743

CAUSES OF DEGRADATION OF TITANIUM DENTAL IMPLANTS

Received: September 14, 2022 / Revised: September 28, 2022 / Accepted: September 30, 2022

https://doi.org/10.23939/ujmems2022.04.031

Abstract. Corrosion is one of the main processes that cause problems when using metal implants in the environment of the human body. Due to its properties, titanium and its alloys are currently the most widely used biocompatible materials. But the use of implants made of titanium-based alloys is not always successful. The purpose of our research was to establish the reasons for the rejection of a Swiss firm's dental implant made of Grade 5 titanium alloy. Implanted in the patient's jawbone, it worked as a support for an artificial tooth. But after 1 year of operation, inflammatory processes began at the implantation site, which ultimately led to rejection of the implant. To establish the material science reasons for this, we conducted microstructural studies using an electron microscope Zeiss EVO 40XVP. The sample was metallograpically prepared by grinding, polishing, and etching by using Kroll's Reagent. A statistical image processing program was used to estimate the quantitative ratio of the phase components of the implant alloy Image J. Elemental analysis and mapping elements were also performed to know the compositional and distribution of each element Ti, Al and V by using energy dispersive X-Ray spectroscopy coupled in SEM. The hardness value was determined using Vickers microhardness tester. The conducted studies established that the working surface of the implant suffered corrosion damage during operation. The edges of the implant are uneven with open and closed pitting. In some places, the merging of several pittings is observed, which leads to the occurrence of ulcerative corrosion. Elemental analysis established the redistribution of chemical elements in the surface layers as a result of contact with the biological environment of the human body. Unstable compounds are created on the surface, which dissolves in the human body during use. As it follows from the conducted studies, the degraded surface of the dental implant needs additional protection.

Keywords: biocompatibility, implants, titanium alloys, corrosion damage.

Introduction

Biocompatibility and durability of dental implants is an important problems in modern orthopedic dentistry. The biological environment of the human body, in which metal implants work, is a very complex system that somehow affects their degradation [1, 2]. The aggressiveness of this environment depends on a person's state of health, age, nutrition, the environment in which a person lives, and many other factors. Therefore, metals that are passive or inert in the air can be subject to various damages in the environment of the human body. Corrosion is one of the main processes that cause problems when using metal implants in the environment of the human body [3]. To understand the corrosion of metal implants and its impact on the

use of medical alloys in the human body, it is necessary to take into account the influence of the environment, the chemical and biological environment of the body, as well as the impact caused by high cyclic loads associated with human life [1]. The passivity of metals and alloys of implants is ensured by the formation of a protective film on their surface, which slows down corrosion processes and restrains the release of corrosion products. But numerous cellular and biochemical factors at the site of implant placement cause activation of redox reactions. These reactions affect the formation of the protective passivation film on the surface of the metal implant and can stimulate corrosion destruction [1].

Problem Statement

Almost all materials from which implants are made are subject to corrosion damage during operation. Corrosion types characteristic of biocompatible metals and alloys include pitting, galvanic, intergranular corrosion, corrosion cracking, corrosion fatigue, and fretting corrosion [3]. Such degradation under physiological conditions can lead to a decrease in the mechanical strength of the implant in bone or other tissues. During corrosion processes, metal implants emit unwanted metal ions that may not be biologically compatible. Corrosion products or dissolved metal ions accumulate next to the implant in the tissues of the human body, which can be accompanied by discomfort and painful sensations. This shortens the life of the implant and may lead to the need for surgical removal of the implant. It also becomes possible to lose bone around the implant [4].

Review of Modern Information Sources on the Subject of the Paper

Materials for dental implants are selected based on analysis of mechanical and chemical properties, as well as their biocompatibility [5, 6]. Implant materials should have good corrosion resistance, and biocompatibility and be free of toxic elements. Since approximately 1981, titanium and its alloys have been used for the manufacture of dental implants in global dental practice due to their biocompatibility with bone tissue, corrosion resistance in the environment of the human body, high strength, and low density, and ability to osseointegration [6, 7].

Technical titanium is available in the industry in four grades (Grade 1–4). Most often, a grade 4 medium with the highest oxygen content of about 0.4 % is used for dental implants (Table 1). Technically pure titanium has significant corrosion resistance, and biocompatibility, but insufficient mechanical strength. Therefore, titanium alloys are more widely used, but in terms of biocompatibility, they are somewhat worse than technically pure titanium [1].

Table 1

Composition (wt %) and mechanical properties of titanium alloys used as implants [7, 11]

Alloy	cpTi Grade 4	Ti-6Al-4V ELI Grade 5
Aluminium	–	5.5–6.5
Vanadium	–	3.5–4.9
Oxygen	0.4 %	< 0.13 % max
Iron	0.3 %	< 0.25 %
Nitrogen	0.05 %	<0,05
Hydrogen	0.15 %	<0.012
Carbon	0.1 %	< 0,08
Titanium	ca 99 %	Balance
UTS/MPa	550	900
Yield strength/MPa	480	850
Elongation at failure/ %	15	10

One of the most widely used titanium alloys at present is the Ti-6Al-4V ELI alloy (it is also designated as Grade 5). Its wide application is due to a good balance between mechanical properties, the ability to change shape and plastic deformation, the efficiency of heat treatment and welding, as well as biocompatibility [8, 9]. It contains 6 wt. % aluminum, and 4 wt. % vanadium, like the industrial Ti-6Al-4V alloy, but a smaller and controlled amount of impurity elements. Aluminum stabilizes and strengthens the α-phase, increases the temperature of the α+β↔β transformation, and reduces the density of the alloy. Vanadium, as a β-stabilizer, reduces the temperature of the α+β↔β transformation and facilitates hot pressure treatment (the volume fraction of the β-phase increases). Due to the lower level of impurities, Ti-6Al-4V ELI alloys have higher resistance to salt corrosion, better plasticity, and fracture toughness compared to commercial Ti-6Al-4V alloys [10].

In case of corrosion damage, Ti-6Al-4V ELI alloy can release aluminum and vanadium ions. Aluminum interferes with bone mineralization, which leads to structural deficits [12], and vanadium exhibits high cytotoxicity and can cause allergic reactions [13]. Such side effects occur if each of these elements is present in tissues in sufficient concentrations. However, the levels of their release from the alloy in the human body are too small to cause a toxic effect [6, 14].

The surfaces of both commercially pure titanium cpTi and the Ti-6Al-4V alloy are oxidized during operation, a 4–6 nm thick TiO2 oxide layer is formed on the surface, which also contains hydroxyl groups [15]. The oxide layer, as a rule, has favorable biological properties. However, the body still recognizes it as a foreign body, so in some circumstances, it can cause fibrosis around the implant [16].

Studies have confirmed that Ti-6Al-4V alloy provides satisfactory osseointegration [17]. The long-term integrity of titanium implants and their ability to osseointegration is also preserved, especially after surface treatment (Table 2) [7]. Statistical analysis performed on several hundreds of surface-treated implants proved a high level of their durability. The number of implants suitable after 10 years of use was at least 89 %.

Table 2

Results of clinical studies of surface treated titanium-based dental implants [7]

Time of observation, years	Preliminary surface treatment	Durability coefficient, %
10	Sandblasting and acid etching	98.8–99.7
20	Plasma sputtering of Ti	89.5
10	Anodizing	96.5
9–12	Oxidation	97.1

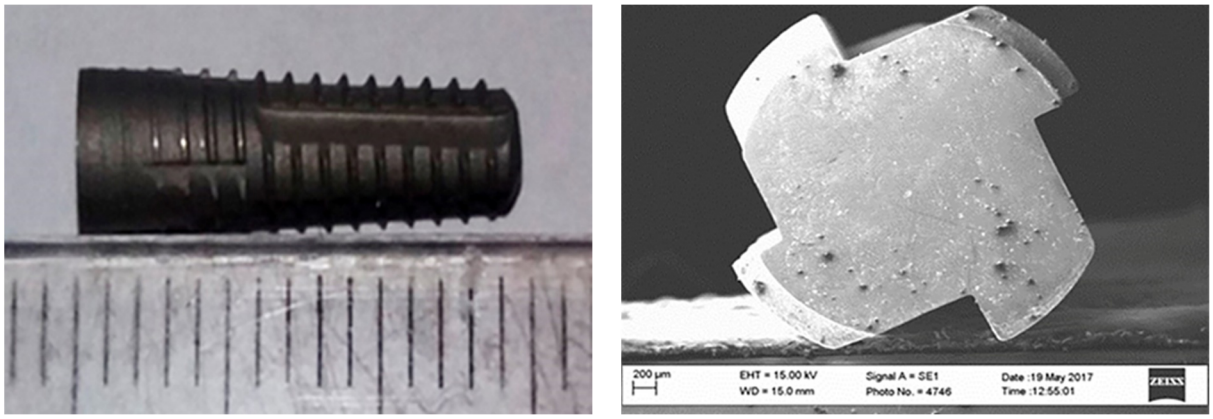
However, the use of titanium-based alloy implants is not always successful. There are rare cases of rejection of dental implants. Therefore, the goal of our research was to establish the material science reasons for such rejection, in particular, due to structural changes in the surface layer of degraded implants.

Objectives and Problems of Research

The object of the study was a dental implant of a Swiss company, manufactured by mechanical processing from a Ti-6Al-4V ELI (Grade 5) titanium alloy rod (Fig. 1, *a*). Implanted in the patient's jawbone, it worked as a support for an artificial tooth. But after 1 year of operation, inflammatory processes began at the implantation site, which ultimately led to a rejection of the implant.

Microstructural studies of the implant were performed on a Zeiss EVO 40XVP electron microscope. The sample was prepared by grinding, polishing, and etching using Kroll's Reagent (distilled water – 92 ml, nitric acid – 6 ml, hydrofluoric acid – 2 ml) (Fig. 1, *b*). The Image J statistical image processing program was used to estimate the quantitative ratio of the phase components of the implant alloy.

Elemental analysis and mapping element were also performed to know compositional and distribution of each element Ti, Al and V by using energy dispersive X-Ray spectroscopy (EDS) coupled in SEM. The hardness value was determined using Vickers microhardness tester.



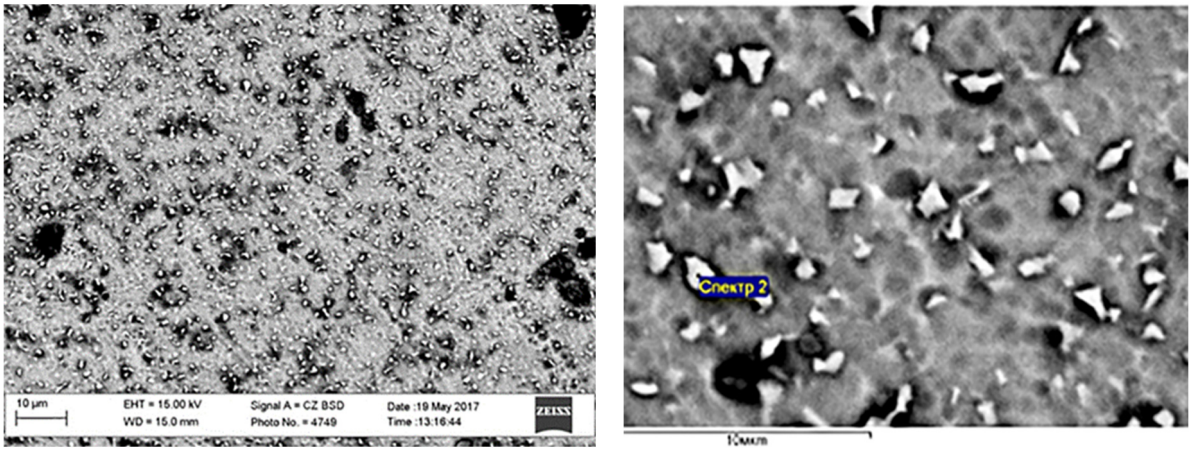
a *b*

Fig. 1. Investigated dental implant: a – outward appearance; b – cross-section

Main Material Presentation

Ti-6Al-4V alloys belong to the group of two-phase α + β titanium alloys of the martensitic class. Their properties are determined by microstructural parameters, such as morphology, size, location, and volume fraction of the two phases α and β. These parameters can be controlled by changing the technological modes of manufacturing implants. Depending on the conditions of heat treatment, it is possible to obtain an equiaxed, globular, or lamellar structure [18].

Metallographic studies established that the microstructure of the Ti-6Al-4V ELI implant alloy consists of globular grains of the α-phase (light), located mainly on the boundaries of the grains of the β-phase (Fig. 2, *a*). Such a structure was formed as a result of incomplete annealing of cold-deformed bars from a temperature slightly lower than the temperature of the (α+β) → β transition. During annealing, the primary α-plates were incompletely globalized into individual particles, the shape of which from acute to spherical depends on the completeness of their spheroidization. The structure of the investigated implant is dominated by quadrilateral and triangular particles, the size of which is from tenths of a micrometer to several micrometers (Fig. 2, *b*).



a *b*

Fig. 2. SEM micrographs showing the microstructure of the investigated Ti-6Al-4V ELI alloy dental implant at different magnification: a – x600; b – x 3000

The volume fraction of the α-phase, established based on statistical processing of images of the microstructure of the alloy using Image J software, is about 15 %.

Elemental analysis using EDS showed that the α-phase is depleted in titanium and aluminum relative to the average content in the alloy, but enriched in vanadium (~ 13 % at., which significantly exceeds the average content in the alloy of 3 % at.) and iron (Table 3).

It should be noted that hardness is one of the important properties of implant material, which determines its suitability for biomedical applications. When using dental implants, it is desirable that the hardness of the material, in this case, Ti-6Al-4V ELI, is close to the hardness of bone (~430 HV). Microhardness measurements revealed no difference in the microhardness of the surface and cross-section of the implant. The average value of microhardness of the implant at 374 ±5 HV corresponds to its heat treatment and microstructure.

The working surface of the dental implant was damaged during operation (Fig. 3). The edges of the implant are uneven with open and closed pitting. In some places, the merging of several pittings is observed, which leads to the occurrence of ulcerative corrosion. For dental implants, this type of corrosive damage is particularly dangerous, as it disrupts the contact of the implant with the bone and can initiate the initiation of microcracks and the destruction of the implant under the influence of mechanical loads. Usually, as in this case, in implants, pitting corrosion occurs on the underside of the screw heads.

Table 3

Elemental composition of the studied implant alloy

Plots of spectra		Ti, % at.	V, % at.	Al, % at.	Fe, % at.
The external surface	1	84.48	2.9	10.79	0.18
	2	83.73	3.15	10.93	0.22
	3	85.27	2.8	10.83	0.20
	Average value	84.50	2.95	10.85	0.20
Cross section	1	86.97	2.44	9.95	0.18
	2	85.70	3.14	11.16	0.18
	3	86.46	3.37	10.17	0.20
	4	87.22	3.18	9.60	0.22
	Average value	86.59	3.03	10.22	0.19
Particles of the α-phase	1	78.58	11.64	7.97	1.81
	2	77.94	14.39	6.8	2.19

For a more detailed analysis of the causes of corrosive damage to the surface of the implant, an elemental EDS analysis was carried out in order to identify a possible redistribution of chemical elements in the surface layers due to contact with the biological environment of the human body (Table 3).

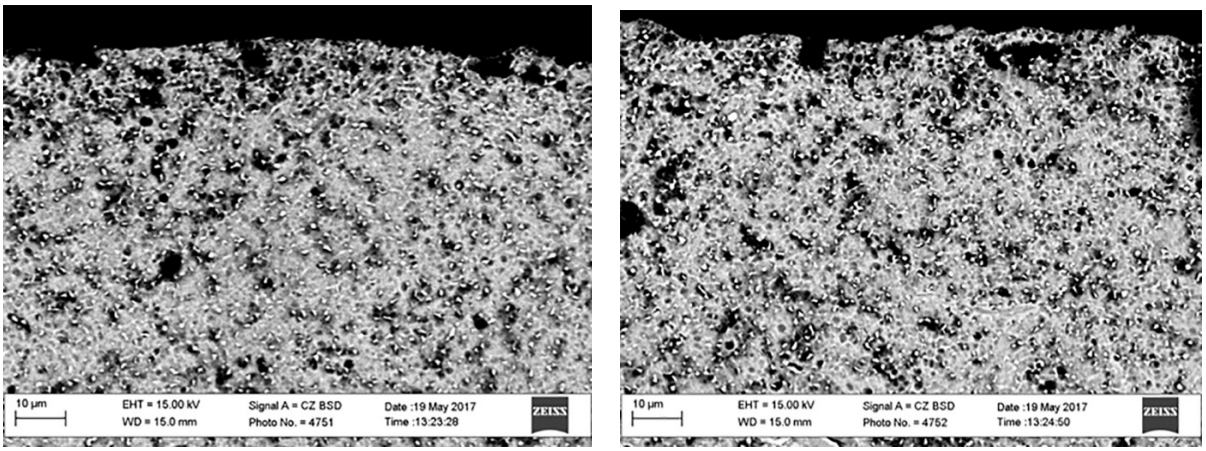
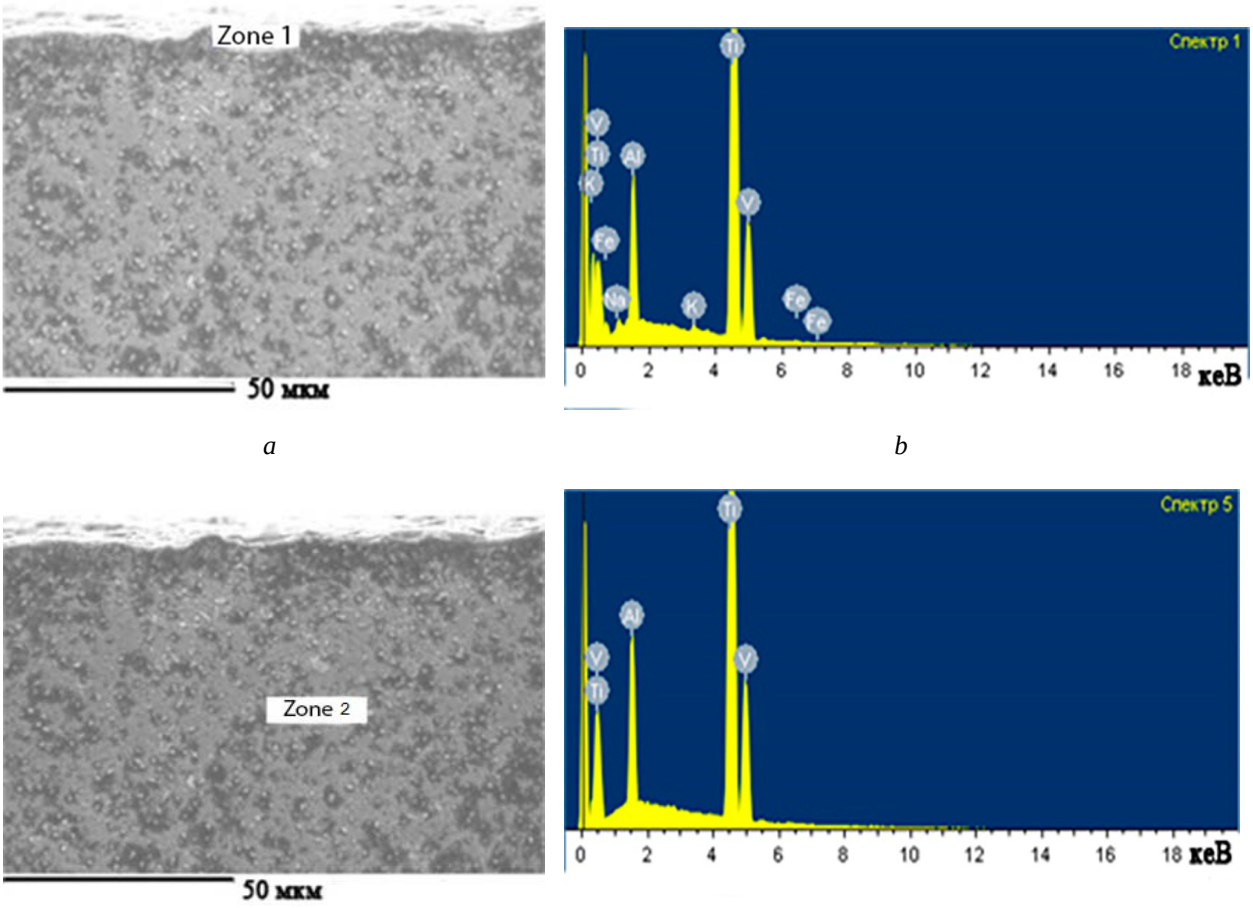


Fig. 3. Cros-section SEM micrographs of the investigated dental implant surface layer: a – x600, b – x600

It was established that the content of titanium and vanadium decreases on the surface of the implant, while the content of aluminum slightly increases (Fig. 4, *a*, *b*; spectrum 1) relative to the core (Fig. 4, *c*, *d*; spectrum 5). This confirms the redistribution of elements in the surface layers when the implant is in contact with the human body.

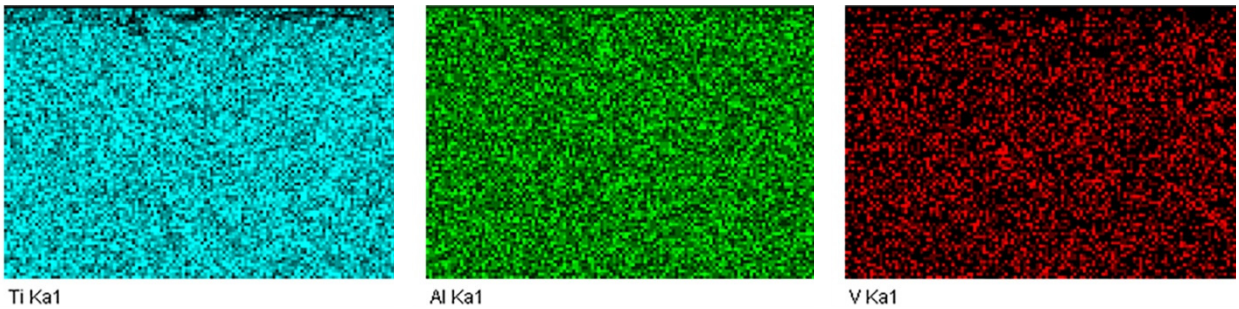


a *b*

c *d*

Fig. 4. SEM micrographs of the microstructure dental implant with zones 1(a), 2 (c) and corresponding EDS elemental analysis spectrums 1 (b), 2 (d)

The map of the distribution of elements confirms that there is an uneven distribution of titanium and vanadium in the surface layers of the implant (Fig. 5).

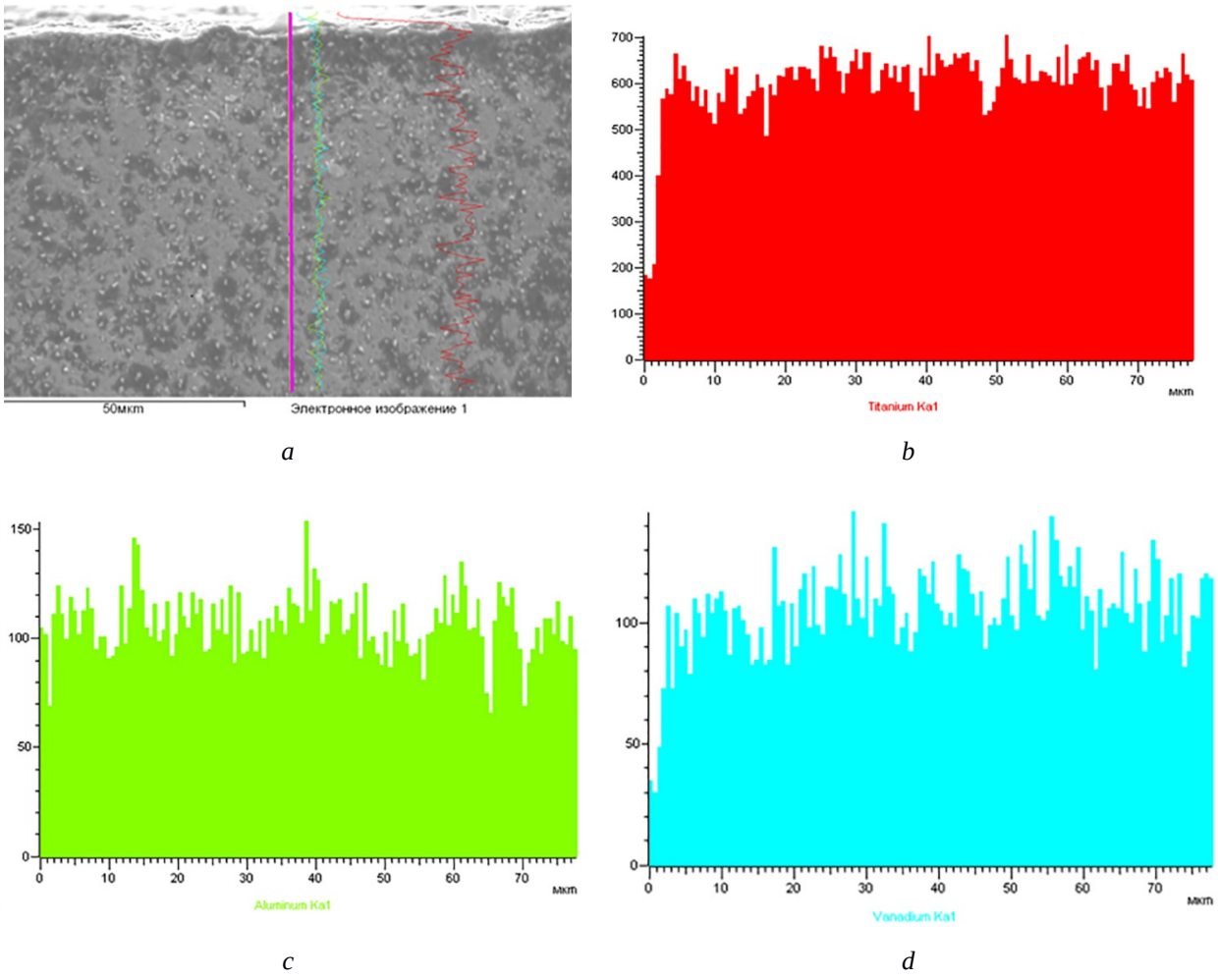


a *b* *c*

Fig. 5. Mapping images of distribution Ti (a), Al (b), V (c) in the microstructure dental implant

At the base of the implant, the distribution of titanium and aluminum is uniform, instead, vanadium is unevenly distributed, areas enriched and depleted of this element are observed (Fig. 5, *c*). Most likely, the enriched areas correspond to α-phase particles.

The energy dispersive spectral profiles by depth from the surface of the studied sample confirm these conclusions (Fig. 6).



a *b*

c *d*

Fig. 6. SEM micrograph with EDS line distribution Ti, Al, V (a) and profiles Ti (b), Al (c), V (d) along depth from the implant surface

According to the results of the research, it can be stated that the main reason for the rejection of the dental implant was the degradation of its surface due to the formation of pitting corrosion. The probable cause of this was the redistribution of alloying elements in the surface layer of the alloy under the influence of reactions with elements of the biological environment of the human body. Unstable compounds are created on the surface, which dissolves in the human body during use. As a result, the surface of the implant is depleted of titanium and vanadium, which leads to the formation of pitting. And although titanium alloy has good corrosion resistance, contact with an environment in which proteins such as albumin are present (the presence of proteins such as albumin) can increase the amount of titanium that is released into body tissues [19].

An important influence on the durability of dental implants is the oxide layer, which, in addition to the effect of passivating the metal, inhibiting corrosion, and minimizing the release of titanium ions, ensures

the development of osseointegration between the surface of the implant and living bone [20]. Coarse oxide coatings contribute to reliable and fast osseointegration.

As it follows from the conducted research, the degraded surface of the dental implant needs additional protection. An effective way to increase durability, and corrosion resistance, improve biocompatibility, and promote osseointegration of implants is a preliminary modification of their surface [9]. Modification by changing the surface topography, surface energy, and improving wettability can be a key factor for successful osseointegration, i.e., direct fixation of the implant by the growth of bone cells without the growth of fibrous tissues at the bone/implant interface [18].

Today, there are many methods of surface treatment of implants, which allow to increase the service life of implants and prevent the development of early and distant postoperative complications, to avoid repeated surgical interventions due to instability of the implant [20–36].

The most studied methods of implant surface modification are acid etching and sandblasting [22], plasma spraying (PS) [26–29], pulsed laser vapor deposition (PLD) [30, 31], femtosecond laser treatment [33, 34], ion beam technologies [32], atomic layer deposition (ALD) technology [21]. Each of these methods has its advantages and disadvantages. Therefore, for each specific biomedical application, it is necessary to select the optimal types of technologies and modes of implant surface modification.

Conclusions

Premature rejection of the studied dental implant occurred as a result of pitting corrosion of the surface under the influence of the biological environment. In our opinion, this is due to the redistribution of titanium and vanadium in the surface layer of the implant during contact with the human body. Corrosive damage caused a weakening of the mechanical fixation of the implant in the bone tissue and its degradation.

It should be assumed that if the surface modification of this implant was performed, it was ineffective and did not provide reliable protection against the negative effects of the biological environment. That is why it is so important to ensure the optimal choice of technology and mode of surface modification in the manufacture of dental implants, taking into account the conditions of use.

Acknowledgements

The authors would like to thank the dentists of the Lviv Medical College "Monada" Dr. Nazar Tepliy and Dr. Borys Shchepanskyi for the presented research materials.

References

[1] Gilbert J. L., Mali S. A. “Medical implant corrosion: Electrochemistry at metallic biomaterial surfaces. Degradation of Implant Materials”. Editor Eliaz, Noam. *Springer Science + Biseness Media,* 2012, 510 p. https://doi.org/10.1007/978-1-4614-3942-4_1

[2] Yatsun E. V., Chornyi V. M., Golovakha M. L. “Perspektyvy zastosuvannia biodehraduiuchykh splaviv na osnovi mahniiu v osteosyntezi (literaturno-analitychnyi ohliad)” [“Prospects for the use of biodegradable alloys based on magnesium in osteosynthesis (literature and analytical review)”], *Problemy viiskovoi okhorony zdorovia [Problems of military health care],* vol. 36, pp. 141–148, 2013. [In Ukrainian].

[3] Kamachi Mudali U., Sridhar T. M., Raj B. “Corrosion of bio implants”, in *Sadhana* Vol. 28, 2003, pp. 601–637, https://doi.org/10.1007/BF02706450

[4] Manam N. S., Harun W. S. W., Shri D. N. A., Ghani S. A. C., Kurniawan T., Ismail M. H., Ibrahim M. H. I. “Study of corrosion in biocompatible metals for implants: A review”, *Journal of Alloys and Compounds*, 701, pp. 698–715, 2017, https://doi.org/10.1016/j.jallcom.2017.01.196

[5] Gepreel MA-H., Niinomi M. “Biocompatibility of Ti-alloy for long term implantation” *J Mech Behav Biomed Mater*, 20, pp. 407–15, 2013, https://doi.org/10.1016/j.jmbbm.2012.11.014

[6] Elias C. N., Lima J. H. C., Valiev R. Z., Meyers M. A. “Biomedical applications of titanium and its alloys”, *The Journal of The Minerals, Metals*, vol. 60 (3), pp. 46–49, 2008, https://doi.org/10.1007/s11837-008-0031-1

[7] Nicholson J. W. “Titanium Alloys for Dental Implants: A Review”, *Prosthesis*, vol. 2, pp. 100–116, 2020, https://doi.org/10.3390/prosthesis2020011

[8] Sieniawski J. (Eds.) “Microstructure and Mechanical Properties of High Strength Two-Phase Titanium Alloys In: Titanium Alloys”, *Advances in Properties Control*, 2013, https://doi.org/10.5772/56197

[9] Jemat A., Ghazali M. J., Razali M., Otsuka Y. “Surface Modifications and Their Effects on Titanium Dental Implants”, in *BioMed Research International*, Hindawi Publishing Corporation, 2015, 11 p., http://dx.doi.org/10.1155/2015/791725

[10] Leyens C., Peters M. “Titanium and Titanium Alloys. Fundamentals and Applications”, Wiley-Vch Verlag GmbH & Co. KGaA, Weinheim, 2003, 499 p.

[11] Damisih I., Nyoman J., Sah J. “Characteristics Microstructure and Microhardness of Cast Ti-6Al-4V ELI for Biomedical Application Submitted to Solution Treatment”, *Proceedings of the International Seminar on Metallurgy and Materials (ISMM2017) AIP Conf. Proc.*, 2018, pp. 020037-1 – 020037-8, https://doi.org/10.1063/1.5038319

[12] Klein G. L. “Aluminium toxicity to bone: A Multi-System effect”, *Osteoporosis and Sarcopenia*, issue 1, vol. 5, pp. 2–5, 2019, https://doi.org/10.1016/j.afos.2019.01.001

[13] Thyssen J., Jakobsen S. S., Engkilde K., Johansen J. D., Søballe K., Menné T. “The association between metal allergy, total hip arthroplasty, and revision”, *Acta Orthopaedica*, vol. 80, issue 6, pp. 646–652, 2009, https://doi.org/10.3109/17453670903487008

[14] Elias C. N., Fernandes D. J., De Souza F. M., Monteiro E. D. S., De Biasi R. S. “Mechanical and clinical properties of titanium and Titanium-Based alloys (Ti G2, Ti G4 cold worked nanostructured and Ti G5) for biomedical applications”, *Journal of Materials Research and Technology*, vol. 8, issue 1, pp. 1060–1069, 2019, https://doi.org/10.1016/j.jmrt.2018.07.016

[15] Effah E. A., Bianco P. D., Ducheyne P. “Crystal structure of the surface oxide layer on titanium and its changes arising from immersion”, *Journal of Biomedical Materials Research*, Vol. 29, iss. 1, pp. 73–80, 1995, https://doi.org/10.1002/jbm.820290111

[16] Sittig C., Textor M., Spencer N. D., Weiland M., Vallotton P.-H. “Surface characterization of implant materials cpTi, Ti-6Al-7Nb and Ti-6Al-4V with different pre-treatments”, *J. Mater. Sci. Mater. Med.*, Vol. 10, pp. 35–46, 1999.

[17] Xiaotian L., Chen Sh., Tsoi J. K. H., Matinlinna J. P. “Binary titanium alloys as dental implant materials—a review”, *Regenerative Biomaterials*, pp. 315–323, 2017, https://doi.org/10.1093/rb/rbx027

[18] Hench L. L. “Bioactive materials: The potential for tissue regeneration”, *J. Biomat. Mater. Res*., Vol. 41, No. 4, pp. 511–518, 1998, https://doi.org/10.1002/(SICI)1097-4636(19980915)41:4<511::AID-JBM1>3.0.CO;2-F

[19] Yu F., Addison O., Davenport A. “A synergistic effect of albumin and H2O2 accelerates corrosion of Ti6Al4V”, *Acta Biomaterialia*, Vol. 26, pp. 355–365, 2015, https://doi.org/10.1016/j.actbio.2015.07.046

[20] Blumenthal N. C., Cosma V. “Inhibition of apatite formation by titanium and vanadium ions”, *J. Biomed. Mater. Res.*, Vol. 23, Iss. S 13, pp. 13–22, 1989, https://doi.org/10.1002/jbm.820231305

[21] Solovyev A. A., Ovchinnikov D. V., Korostelev E. V., Markeev A. M. “Correlation between structural and bioactive properties of titanium dioxide formed by atomic layer deposition”, *Nanotechnologies*, Vol. 8, Issue 5–6, pp. 388–391, 2013, https://doi.org/10.1134/S1995078013030178

[22] Ban, Y. Iwaya, H. Kono, H. Sato, “Surface modification of titanium by etching in concentrated sulfuric acid,” *Dental Materials*, Vol. 22, No. 12, pp. 1115–1120, 2006, https://doi.org/10.1016/j.dental.2005.09.007

[23] Chauhan P., Koul V., Bhatnagar N. “Critical Role of Etching Parameters in the Evolution of Nano Micro SLA Surface on the Ti6Al4V Alloy Dental Implants”, *Materials*, Vol. 14, 6344, 2021, ttps://doi.org/10.3390/ma14216344

[24] Juodzbalys G., Sapragoniene M., Wennerberg A. “New Acid-etched Titanium Dental Implant Surface”, *Stomatol. Baltic Dent. Maxillofac J.*, Vol. 5, pp. 101–105, 2003.

[25] Wennerberg A., Albrektsson T. “Effects of titanium surface topography on bone integration: A systematic review”, *Clin. Oral Implant. Res.*, Vol. 20, pp. 172–184, 2009, https://doi.org/10.1111/j.1600-0501.2009.01775.x

[26] Family R., Solati-Hashjin M., Nik S. N., Nemati A. “Surface modification for titanium implants by hydroxyapatite nanocomposite”, *Caspian journal of internal medicine*, Vol. 3(3), pp. 460, 2012.

[27] Sobieszczyk S. “Surface modifications of Ti and its alloys”, *Advances In Materials Science*, Vol. 10, No. 1 (23), 2010.

[28] Tas A. C. "Formation of calcium phosphate whiskers in hydrogen peroxide (H_2O_2) solutions AT 90°C", *J Americal Ceramics Society*, Vol. 90, No 8, pp. 2358–2362, 2007, https://doi.org/10.1111/j.1551-2916.2007.01768.x

[29] Bosco R., Van Den Beucken J., Leeuwenburgh S., Jansen J. "Surface engineering for bone implants: a trend from passive to active surfaces", *Coatings*, Vol. 2, pp. 95–119, 2012.

[30] Cotell C. M., Chrisey D. B., Grabowski K. S., Sprague J. A., Gossett C. R. "Pulsed laser deposition of hydroxylapatite thin films on Ti-6Al-4V", *J. Appl. Biomater*, Vol. 3, pp. 87–93, 1992, https://doi.org/10.1002/jab.770030204

[31] Dinda G. P., Shin J., Mazumder J. "Pulsed laser deposition of hydroxyapatite thin films on Ti-6Al-4V: Effect of heat treatment on structure and properties", *Acta Biomater*, Vol. 5, pp. 1821–1830, 2009, https://doi.org/10.1016/j.actbio.2009.01.027

[32] Liu X. Y., Paul K. C., Ding C. X. "Surface Modification of Titanium, Titanium Alloys, and Related Materials for Biomedical Applications", *Materials Science Engineering Report*, pp. 47–49, 2004, https://doi.org/10.1016/j.mser.2004.11.001

[33] Duriagina Z., Tepla T. "Effect of nitrogen ion implantation on properties of the vanadium alloys", *Laser Technologies. Lasers and their Application: Materials of International Scientific and Technical Conference*, June 17–19, Truskavets, Ukraine, pp. 128–133, 2015, https://doi.org/10.1016/j.surfcoat.2010.10.042

[34] Roy M., Bandyopadhyay A., Bose S. "Induction plasma sprayed nano hydroxyapatite coatings on titanium for orthopaedic and dental implants", *Surf. Coatings Technol*, Vol. 205, pp. 2785–2792, 2011.

[35] Duriagina Z. A., Tepla T. L., Kulyk V. V., Kosarevych R. Y., Vira V. V., Semeniuk O. A. "Study of structure and morphology of surface layers formed on TRIP steel by the femtosecond laser treatment", *Journal of Achievements in Materials and Manufacturing Engineering*, Vol. 93 (1–2), pp. 5–19, 2019, https://doi.org/10.5604/01.3001.0013.4137

[36] Rotella G., Orazi L., Alfano M., Candamano S., Gnilitskyi I. "Innovative high-speed femtosecond laser nano-patterning for improved adhesive bonding of Ti6Al4V titanium alloy", *CIRP Journal of Manufacturing Science and Technology*, Vol. 18, pp. 101–106, 2017, https://doi.org/10.1016/j.cirpj.2016.10.003