UDK 617.3:617.57:669.295:621.9
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 44(5)261(2010)

OSSEOINTEGRATION AND REJECTION OF A TITANIUM SCREW

OSEOINTEGRACIJA IN ZAVRNITEV TITANOVEGA VIJAKA

Grega Klančnik[1], Miro Zdovc[2], Uroš Kovšca[2], Borut Praček[3], Janez Kovač[3], Janez Rozman[4]

[1]University of Ljubljana, Faculty of Natural Science and Technology, Aškerčeva cesta 12, SI-1000, Ljubljana, Slovenia
[2]University of Nova Gorica, Material Characterization Graduate Study Programme, Vipavska 13, Rožna Dolina, 5000 Nova Gorica, Slovenia
[3]Jožef Stefan Institute, Jamova cesta 39, SI-1000 Ljubljana, Slovenia
[4]ITIS, d. o. o., Center for Implantable Technology and Sensors; Lepi pot 11, SI-1000, Ljubljana, Slovenia
grega.klancnik@ntf.uni-lj.si

Prejem rokopisa – received: 2009-12-01; sprejem za objavo – accepted for publication: 2010-04-22

In the present study, a rejected titanium implant, an orthopaedic screw removed from a patient, was investigated. The screw was implanted into the metacarpal bone for one year and was removed due to irritation. The first signs of irritation were indicated three months after the implantation. After the removal, the signs of irritation disappeared. AES and EDS analyses showed that the surface of the screw was significantly different from the bulk material. The high contamination of the surface layer was found to be caused by the screw-manufacturing process, which is considered to be the main reason for the rejection of the implant.

Keywords: orthopaedics, titanium implant, titanium screw, contamination, AES, EDS

V predstavljeni študiji smo preiskali zavrnjen titanov vijak, ki je bil odstranjen pacientu. Vijak je bil privit v dlančnico in po enem letu odstranjen zaradi razdraženosti okoliškega tkiva, ki se je pojavila v prvih treh mesecih po implantaciji. Po odstranitvi razdraženosti ni bilo več. AES analiza in EDS analiza sta pokazali, da se površina močno razlikuje od notranjosti vijaka. Odkrita je bila kontaminacija površine, ki je tehnološke narave in se zato predvideva, da je bil to glavni razlog zavrnitve implantata.

Ključne besede: ortopedija, titanov implantat, titanov vijak, kontaminacija, AES, EDS

1 INTRODUCTION

Titanium alloys are commonly used as biomaterials and, like stainless steels, are used in orthopaedics. Titanium is a superior orthopaedic material because it has a high compatibility in contact with bone tissue and is more corrosion resistant than stainless steels. In addition, because of its low tension modulus (55–100 GPa), titanium implants tend to be handling-friendly during the placement. However, one of the most common problems with titanium alloys is related to the contamination of the implant oxide surface with metal ions, which can contribute to the rejection of the implant (**Figure 1**).

Figure 1: Titanium screw – rejected implant
Slika 1: Titanov vijak – zavrnjeni implantat

1.1 Osseointegration

The term "osseointegration" describes the process of having a stable, loaded implant in direct contact with the bone. Biomaterials with the so-called osseointegrability, e.g., commercially pure (CP) titanium with a low iron content, CP tantalum and calcium hydroxyapatite (HA),[1] are widely used. Stainless steels are also widely used for orthopaedic applications. Classical 316L can, for example, provide a natural surface oxide coating like titanium and titanium alloys. If we compare titanium (CP) with 316L, exposed to physiological fluids, no reactions are usually present. However, stainless-steel implants, after a longer implantation time, release metal ions, Cr^{6+}, Ni^{2+}, Mo^{6+} and Fe^{3+}, into the surrounding tissue. A test of cytotoxicity performed on rate bone-marrow stromal cells showed the following order of toxicity: Cr > Mo = Fe > Co >Ni. All these ions can cause local inflammation by ion accumulation inside the body.[2] Because the surface of the implant is so important when it is in contact with the bone, tissue and particular cells, biochemical modification is used for a better and faster integration.[1]

1.2 Rejection of the implant

Two of the most common reasons for rejection of the implant are the mechanical damage that occurs during the procedures for implantation and the friction between the two pieces (the plates and the screw).[2] Titanium alloys have a high coefficient of friction, which can cause irritation when an implant rubs with the soft tissue or when new particles are formed during the placement. With the loss of fixation at the interface of the bone and the titanium implant, titanium splinters may be formed and influence the integration strength.[2] Because it is newly formed, the surface with titanium dioxide is very reactive with respect to contamination and this is considered to be an important variable for further storage until use. Dental titanium implants, however, failed to osseointegrate when the surface was contaminated with iron, zinc, tin and lead.[1,4]

1.3 Formation of calcium phosphate

Calcium phosphate is the name given to a family of minerals consisting mainly of Ca^{2+} with PO_4^{3-} or $P_2O_7^{4-}$ and hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$), and bone mineral is one of them. The biology of the interaction with titanium and titanium-based alloys has been studied extensively. The bone formation around the implant derives from the adjacent bone bed, which grows towards the implant. The implant surface is a highly attractive substrate for the bone cells (osteoblasts). Bone tissue is a mineralized connective tissue; it is composed of cells, called osteoblasts, that deposit a matrix of type-I collagen and also release calcium, magnesium and phosphate ions and combine with the collagenous matrix into the crystalline mineral hydroxyapatite. After a certain time of exposure of the implant to the internal environment of the body, the result is a relatively thick surface oxide layer (the natural oxidation of titanium surfaces inside the bone or body fluid) augmented with the ions, mainly calcium and phosphorous.[2,5]

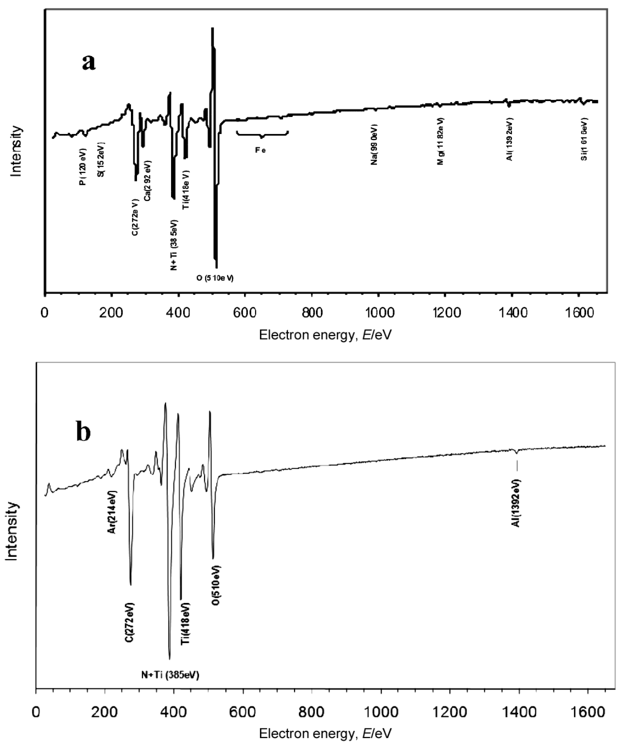

Figure 2: AES spectrum of the screw surface: (a) surface before and (b) after ion sputtering

Slika 2: AES-spekter površine vijaka: (a) površina pred ionskim jedkanjem in (b) po njem

2 EXPERIMENTAL

The investigation was aimed at the detection of possible reasons for the rejection of a titanium screw inserted into the metacarpal bone. After removal, the screw was investigated with Auger Emission Spectroscopy (AES) PHI SAM, model 545A. The first energy spectrum was recorded from the head surface of the screw and the last spectrum after ion etching with Ar^+. On a metallographically prepared sample, one AES spectrum was also recorded to detect the chemical composition under the surface of the screw. The sputtering rate was determined with a Ni/Cr reference and was found to be 2 nm/min. For the chemical analyses of possible phases, an investigation of the microstructure was made with a JEOL 5610 electron microscope and an EDS spectrometer. The investigated surface was also examined with an Olympus CX61 optical microscope and a DP70 video camera.

3 RESULTS

The AES analysis of the retrieved screw surface after one year of implantation is shown in **Figure 2a, b**.

Calcium and phosphorus were both found to be the electrolyte constituents of the body fluid, and both are related to the formation of calcium phosphate. The presence of oxygen, nitrogen, titanium, silicon, aluminium and iron was also established (**Figure 2 a**). However, the last recorded AES spectrum, at the end of the ion etching inside the oxide layer, did not reveal the presence of iron (**Figure 2 b**). A trace of argon was found, because of the ion etching with Ar^+. The presence of carbon on the screw's surface is related to the atmospheric contamination. The AES depth profile in **Figure 3 a** shows a high concentration of carbon, which is a result of backscattering.

The presence of an oxidized surface suggests a strong affinity for oxygen (Figure 3a). The AES depth profile of the titanium screw's surface revealed a surface contaminated with iron deep inside the oxide layer (**Figure 3 b**). However, the AES spectrum of the bulk material, in **Figure 4**, does not show the presence of any iron.

Oxygen is always present in trace amounts. **Figure 4** shows that inside the screw, in the titanium, an alpha structure is also present. The bulk of the screw was investigated with SEM and EDS (**Figure 5**).

EDS analysis (**Figure 5 a**) and AES spectrum of the bulk material (**Figure 4**) revealed no aluminium, silicon or iron in the bulk material. The chemical composition of

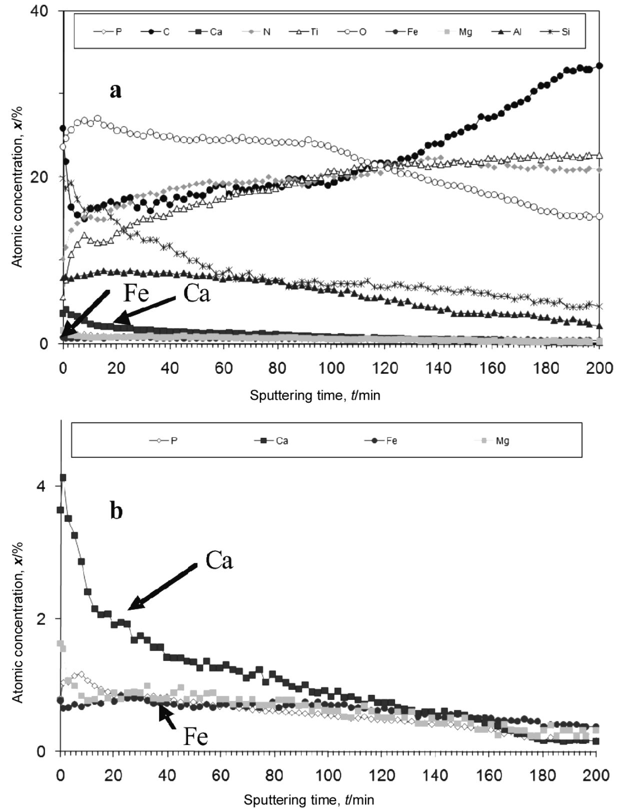

Figure 3: AES analysis: (a) depth profile of titanium screw (b) contamination with iron
Slika 3: AES-analiza: (a) profilna analiza titanovega vijaka (b) kontaminacija z železom

the titanium screw's surface strongly differs from the bulk composition.

The EDS analysis of the precipitates also revealed the presence of carbon (**Figure 5 b**). The detection of the x-ray signal with the EDS system is difficult for carbon on account of its low atomic number. The results from the EDS analyses in **Figures 5 and 6** hint at the presence of titanium carbides. The micrograph in **Figure 5** revealed a 14-μm-thick layer of titanium with a reduced presence, or absence, of precipitates. As already discussed, the absence of other elements was established.

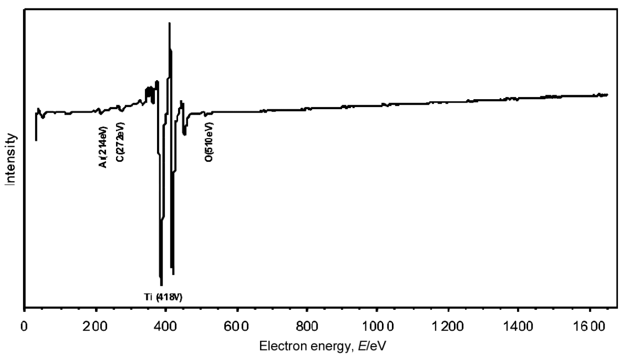

Figure 4: AES spectrum of the bulk material
Slika 4: AES-spekter osnovnega materiala

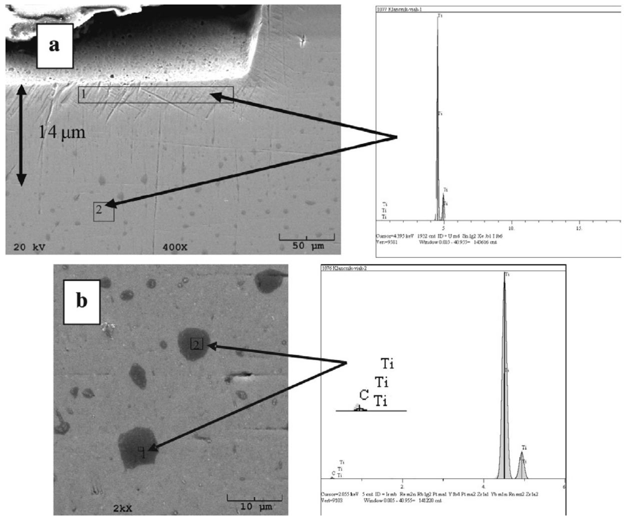

Figure 5: SEM micrograph and EDS analysis: (a) bulk material and (b) precipitates
Slika 5: SEM-posnetek in EDS analiza: (a) osnovnega materiala in (b) precipitatov

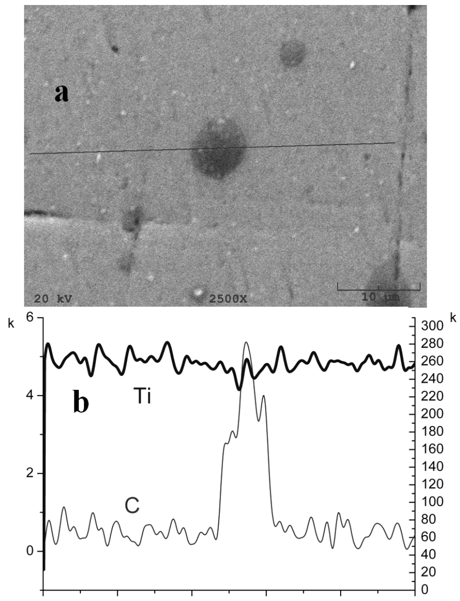

Figure 6: EDS line analysis: (a) SEM micrograph and (b) EDS line analysis
Slika 6: EDS-linijska analiza: (a) SEM-posnetek in (b) EDS-linijska analiza

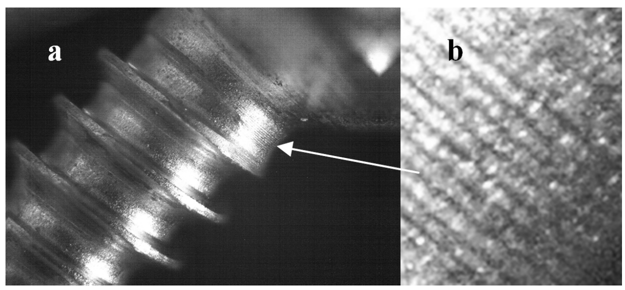

Figure 7: Macrograph of titanium screw: (a) surface and (b) turning grooves of the screw
Slika 7: Slika titanovega vijaka: (a) površina in (b) sledi obdelovalnega orodja

The evidence of the machining of the screw is represented in **Figure 7**. The shape of the grooves indicates that the screw was not polished before the implantation.

4 DISCUSSION

Due to the golden-like colour of the surface of the screw and the nitrogen found with the AES analysis, it can be concluded that the surface of the screw was nitrided (**Figure 1, 3 a**). This titanium nitride provides a relatively stable surface (better wear resistance and hardness). The presence of aluminium and silicon could be assigned to the technology of the production (blasting the surface with alumina and silica particles, contamination with silicon oils, etc.). Furthermore, the high concentration of silicon on the surface of the screw could possibly result from an unintentional deposition during the manufacture. This fact was confirmed by the corresponding concentration gradient over the sputtering time. Siliconization increases the resistance of titanium to oxidation because it dissolves in the TiO_2 surface layer and reduces the diffusion rate of the oxygen atoms through this layer.[6] Nevertheless, silicon increases the activity of osteoblasts and favours the formation of the appatite layer.

The presence of aluminium and silicon in the TiO_2 coating lowers the friction coefficient of the surface and becomes more compatible in terms of orthopaedic practice.[7] The presence of aluminium in the oxide layer, however, confirms the existence of stable Al_2O_3 oxide. Aluminium is capable of forming the most stable oxide; it can also form at room temperature and could form the piece of necrotic bone that has detached from the sound bone (the toxic response of the body). From the AES spectrum of the oxide layer it seems that a relatively high concentration of aluminium is present. Aluminium particles on the surface could weaken the stable position of the implant and cause irritation. It can be concluded from the AES analysis (**Figure 4**) that the presence of aluminium on the surface was not correlated with the bulk material.

The penetration depth of the calcium and phosphorous was determined to be over 400 nm and shows the quality of the osseointegration. From the AES spectrum in **Figure 3 b**, the presence of iron was not detected deeper than 0.4 μm, and iron was not detected in the basic (inner) material (**Figure 4**).

5 CONCLUSIONS

From the results of the AES and EDS analyses, several conclusions can be drawn. The retrieved titanium implant is unalloyed (alpha) titanium strengthened with titanium carbides. The presence of calcium and phosphorous was also established, 0.4 μm deep into the oxide surface layer, which confirms the quality of the osseointegration of the bone with the screw, and the bone as the source of calcium and phosphate ions involved in the metabolic functions. The nucleation of the growth of calcium phosphate started from the bone and from the implant surface. With interconnected pores the osteoblast cell adhesion, differentiation, proliferation as well as biomineralization were possible, relatively deep inside the oxide surface. Aluminium and silicon were found in higher concentrations and can influence the friction factor. A lower friction factor can strongly reduce the possibility of inflammation when an implant is rubbing against soft tissue. The existence of an ideal friction coefficient is impossible because it would differ from patient to patient. The aluminium contamination is relatively high when we consider that the bulk material is commercial titanium. Aluminium and iron oxides should be considered as being in the group of capsule-forming metal surfaces and the reason for retrieving the implant. Iron was found deep inside the oxide layer. The screw surface was examined with a stereo microscope and machining grooves were observed. The AES depth profile revealed that the screw surface was contaminated with iron, which could be the result of using an iron-containing steel tool. The accumulation of iron as well as the high contamination with aluminium at the interface of the implant and soft tissue can cause inflammation and irritation, which can form splinters at the implant–bone interface.

6 REFERENCES

[1] D. M. Brunette, P. Tengvall, M. Textor, P. Thomsen; Titanium in medicine; Springer, (**2001**)

[2] J. W. Nicholson; The Chemistry of medical and dental materials; The Royal society of Chemistry, (**2002**)

[3] M. G. Choi, H. S. Koh, D. Kluess, D. O'Conner, A. Mathur, G. A. Truskey, Janet Rubin, D. F. Zhou, K. L. P. Sung; PNAS; 102 (**2005**) 12, 4578–4583

[4] G. A. A.Castilho, M. D.Martins, W. A. A. Macedo; Surface characterisation of titanium based dental implants; Brazilian journal of physic; 36 (**2006**), 1004–1008

[5] E. R. Hitzky, K. Ariga, Y. Lvov; Bio-inorganic Hybrid Nanomaterials; Willey-Vch Verlag, (**2008**)

[6] D. Vojtěch, T. Kubatik; Siliconizing as a method for improving the resistance of titanium to oxidation; Mater. Tehnol., 37 (**2003**), 381–384

[7] E. A. Levashov, D. M. Shtansky, N. A. Gloushankova, I. V. Reshetov; Biocompatible multicomponent nanostructured coatings for medical implants; Avalible from world wide web: http://www.faqs.org/patents/app/20090050017