Characterization of titanium and stainless steel medical implants surfaces

Karakterizacija površin medicinskih vsadkov iz titana in nerjavnih jekel

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Abstract: Medical implants made from titanium and stainless steel have been used widely and successfully for various types of trauma and orthopaedic reconstructions. It is believed that oxide films covering implant surfaces are of crucial importance for biocompatibility and successful osseointegration. The aim of this study is to investigate the surfaces of new and used commercial medical implants made from titanium and stainless steel. The surfaces were studied by Auger electron spectroscopy (AES) and Atomic force microscopy (AFM).

Izvleček: Medicinski vsadki narejeni iz titana in nerjavnega jekla so uspešno uporabljani v kirurški praksi pri rekonstrukcijah v travmatologiji in ortopediji. Splošno prepričanje je, da so oksidne plasti, ki prekrivajo površine, bistvenega pomena pri biokompatibilnosti in uspešni oseointegraciji. Cilj te študije je preiskava površin komercialnih novih in že uporabljenih medicinskih vsadkov narejenih iz titana in nerjavnih jekel. Površine so bile preiskane z Augerjevo elektronsko spektroskopijo (AES) in mikroskopijo na atomsko silo (AFM).

Key words: medical implants, AES, depth profiling, AFM, roughness
Ključne besede: medicinski vsadki, AES, profilna analiza, AFM, hrapavost

Scientific paper

INTRODUCTION

Implants used in medicine for bone osteosynthesis have to satisfy functional demands defined by the working environment of human body. Ideally, they should have biomechanical properties comparable to those of autogenous tissues without any adverse effects. The principal requirements are corrosion resistance, biocompatibility, biofunctionality, bioadhesion, etc. Geometry, roughness and other characteristics of the implant surface also importantly influence the surface-tissue interaction, which is considered to be dynamic. In the first few seconds after the contact has been made, there are only water, dissolved ions, and free biomolecules in the closest proximity of the surface, but no cells. The composition of the body liquid changes continuously as inflammatory and healing processes precede, causing changes in the composition of the adsorbed layer of biomolecules on the implant surface until it is balanced. Cells and tissues eventually contact the surface and, depending on the nature of the adsorbed layer, they respond in specific ways that may further modify the adsorbed biomolecules[1].

Currently commercially pure (CP-Ti), titanium alloy TiAl6V4 and stainless steel AISI 316L are the most popular alloys used for the trauma and orthopaedic medical implants and are normally covered with a thin protective film, which largely determines the surface properties of an implant. On stainless steel a layer of the surface oxide is formed either during manufacturing or intentionally passivated in various media. Passivation is the spontaneous formation of a surface film on a metal which inhibits further corrosion. A metal is passive when it behaves nobler than it is in a given solution as a result of the protective surface film, usually an oxide. As the name indicates, the metal is then said to be passive to corrosion. Passivation of AISI 316L steel can be performed either thermally, electrochemically, or in nitric acid. Very good corrosion resistance of medical grade stainless steel is derived from the protective layer of chromium oxide type Cr_2O_3 that forms on the surface. If surface is damaged, e.g. scratched the oxide layer reforms almost instantly and can be referred to as "self-healing"[2]. This surface oxide provides the ultimate interface with tissue after implantation and behaves differently compared to bare metallic surface. The corrosion process is responsible for cell toxicity and stimulates fibroblast growth, protein, and platelet adhesion. Metallic implants can interact with living tissue in 3 ways: (1) by electron exchange – redox reaction, (2) by proton exchange – hydrolysis, and (3) by complex formation – metal ion-organic molecule binding. The behaviour of stainless steel is dominated by its nickel component, which induces all 3 reactions, whereas none have been observed with titanium[3]. Studies by other authors reported the surface oxide on commercially available titanium implant systems, consisted mainly of TiO_2, and the oxide structure was found to be noncrystalline[4-6]. This thin oxide film, naturally formed on a titanium substrate, is presumably responsible for the excellent biocompatibility of titanium implants due to a low level of electronic conductivity[7], a high corrosion resistance and a thermodynamically stable state at physiological pH values[8],[9].

The primary goal of this study was to investigate the difference of the surfaces chemical and physical properties on the unused and the in-vitro implanted medical device by using atomic force microscopy (AFM) to study the surface morphology and Auger electron spectroscopy (AES) to analyze the chemical composition of surface oxide layers.

Experimental procedure

Osteosynthetic medical implants for this study have been provided by the University Medical Centre Ljubljana. Obtained osteosyntetic material have been commercial products: compression plates LCP Locking Compression Plates, screw and Philos plate system manufactured by Synthes GmbH. Titanium based samples have been coated with TiN based hard coating with two different colours (exact preparation technique of surface coatings is unknown due to the commercial nature of obtained osteosyntetic material). Details of the implants investigated are shown in Table 1. Surface analyses were performed on the central portions of the external surfaces of implants made from AISI 316L stainless steel and Ti-based alloys.

The plate shaped implants were cut in dimensions of approximately 1×1 cm and mounted into the spectrometer. Chemical composition of the samples surfaces were characterized with AES instrument SAM, PHI Model 545A, manufactured by Physical Electronics Industries Inc. The argon pressure in the chamber during depth profiling was about 10^{-5} Pa and the base pressure was about 1.1×10^{-9} Pa. A static primary electron beam of 3 keV, 1 μA and a diameter of approximately 40 μm were used. The samples were sputtered using two symmetrically inclined Perkin–Elmer-PHI Mod. 04-191 ion guns. The ion incidence angle was about 47 ° with respect to the normal of the sample surface. The samples were sputtered with 1 keV Ar^+ ion beams, rastered on area of 5×5 mm. AES depth profiles of the samples were obtained by continuous ion sputtering. The sputtering rate determined on a Cr/Ni multilayer reference sample was about 4 nm/min. The sputter rate is dependent on a number of factors such as instrumental factors (adsorption from residual gas atmosphere, impurities in ion beam, etc.), sample characteristics (original surface roughness, compounds, second phases, etc.) and radiation induced effects (primary atom implantation, atomic mixing, etc.). It is well known that metallic oxides sputter at different rates, and many at rates slower than pure metal. Although the depth profiles presented in this paper and in the literature assume constant ion sputtering rates, the rates actually increase as the oxide is removed. Absolute sputter rates are unknown because the composition of the specimen is continuously changing with depth. The Auger peak-to-peak heights of P (120 eV), Mo (186 eV), K (252 eV), C (272 eV), Ca (292 eV), N (385 eV), Ti (418 eV), Cr (446 eV), O (510 eV), Fe (703 eV), Ni (848 eV) and Na (990 eV) were measured. Concentration profiles were evaluated using relative sensitivity factors from the manufacturer's handbook[10]. The following sensitivity factors were used: P

(0.53), Mo (0.34), K (0.80), C (0.18), Ca (0.47), Ti (0.44), Cr (0.041), O (0.50), Fe (0.21), Ni (0.29), Na (0.21). The sensitivity factor of N (0.70) was determined on stoichiometric TiN thin film structure.

Surface structure was investigated with a Solver PRO-M atomic force microscope (AFM) manufactured by NT-MDT Co. in semi contact mode. The images were recorded with a resolution of 256 points per line on a 10×10 μm area using commercial Si cantilevers NSG10 series with the Au conductive coating from NT-MDT Co., with stiffness 11.5 N/m, resonant frequency 255 kHz and tip curvature 10 nm as reported by the manufacturer[11]. The roughness amplitude Ra of medical implants surfaces was measured.

Table 1. Presentation of analyzed samples
Tabela 1. Predstavitev analiziranih vzorcev

Sample	Material	Osteosynthetic system	Exposure	Analysis method
1	AISI 316L	Compression plate	Unused	AES
2	AISI 316L	Screw	Implanted	AES
3	Ti6AI4V (golden coating)	LCP plate	Unused	AES
4	Ti6AI4V (golden coating)	LCP plate	Implanted	AES
5	Ti6AI4V (blue coating)	Philos LCP system	Implanted	AES
6	Ti6AI4V (blue coating)	Philos LCP system	Implanted	AFM
7	AISI 316L	Compression plate	Unused	AFM

RESULTS AND DISCUSSION

AES depth profiles of unused and used samples made from AISI 316L stainless steel are depicted in Figure 1a,b. Elements O, C, N, Na, Fe, Cr, Mo, and Ni have been found on an unused medical implant. Characteristic depth profile of the elements distribution is exhibited in Figure 1a, where oxygen concentrated, chromium enriched and iron impaired profiles are distinguished. The depletion of iron concentration and the enrichment of chromium on the outmost surface oxide may indicate a selective dissolution of iron and a preferential oxidation of Cr metal in the depth of the passive film during the manufacturing of medical device where passivation (soaking in acids and heating at elevated temperatures) is process occurring after mechanical and electropolishing. Also a smaller extent of Ni is enriched in the oxide layer. Inner composition on depth profile is near bulk. Iron oxides such as Fe_3O_4 and Fe_2O_3 are normally reduced to FeO by ion bombardment[12] and can therefore be identified even after sputtering.

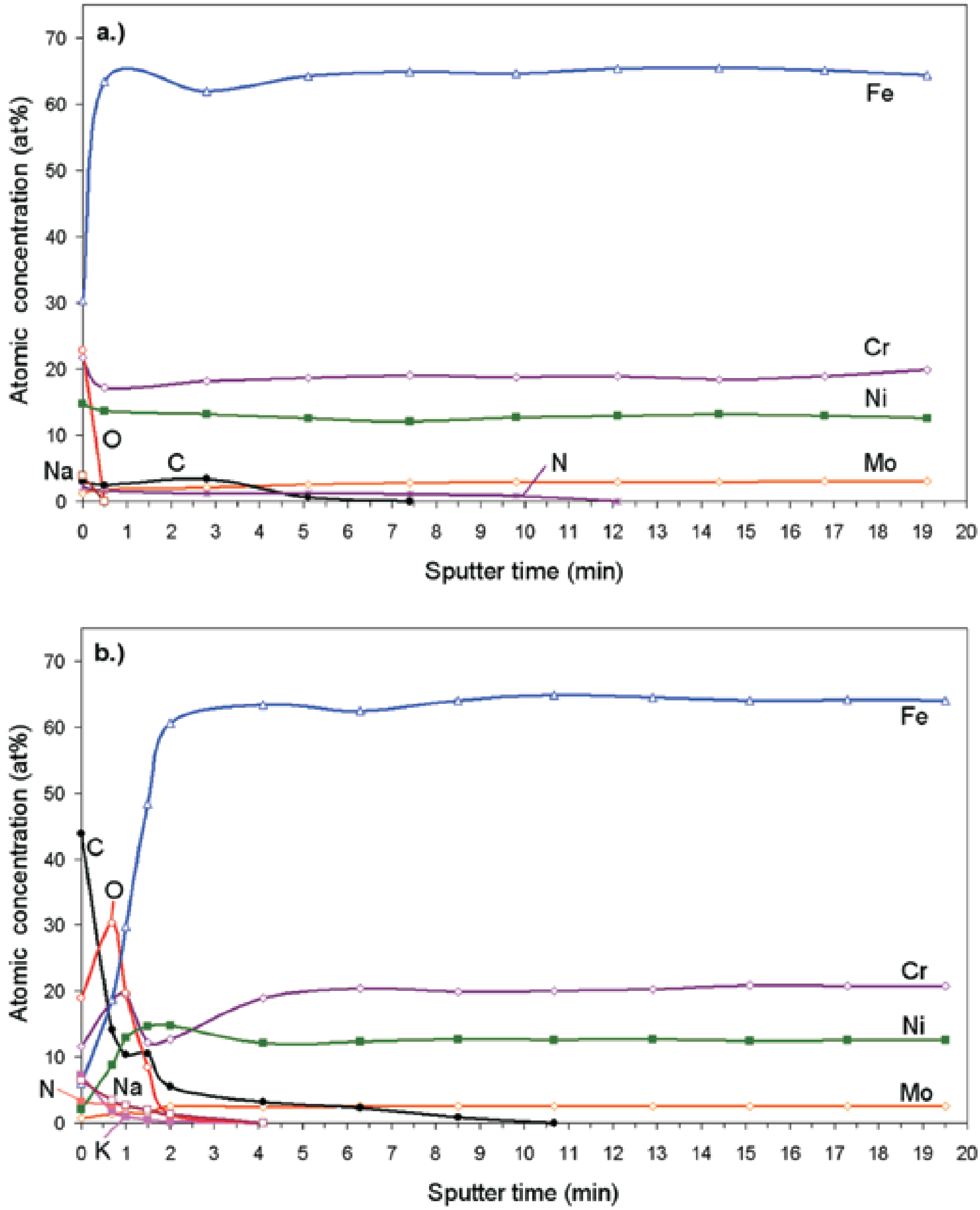


Figure 1. AES depth profile of AISI 316L sample, a.) unused medical implant, b.) used medical implant

Slika 1. AES profilna analiza vzorca iz AISI 316L, a.) neuporabljen medicinski vsadek, b.) uporabljen medicinski vsadek

Samples that have been implanted in the human body have surfaces which contain spots with layers of relatively thick organic material. In Figure 1b AES depth profile of stainless steel implant which has been in contact with living tissue is shown. The surface layer on the used implant changes compared to unimplanted sample, where on booth depth profiles inner composition is near bulk. Traces of S and K were additionally found on surface as depicted in Figure 2. Implanted sample consists of much thicker oxide layer compared to an unimplanted sample. All metal components are diminished on the surface and organic components are enriched. Iron and Ni concentrations increase rapidly from outermost side of the surface layer to deepness in depth profile. It can also be observed from Figure 1b that concentration of Cr increases at first and then starts to sink. This can be related to oxidation of Cr in oxide layer.

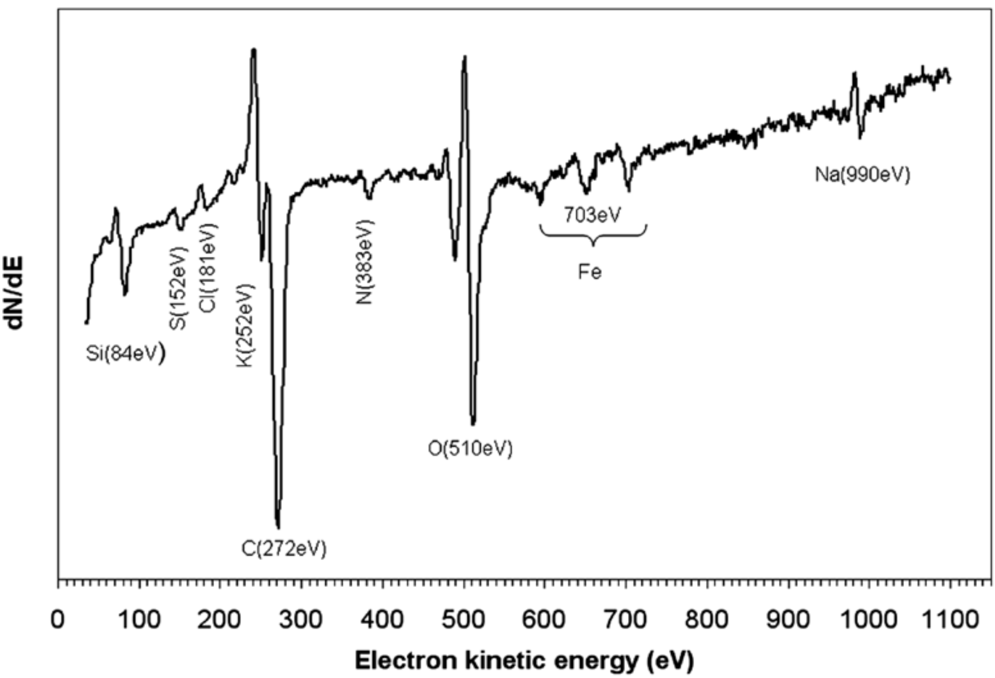


Figure 2. AES spectrum of an implanted AISI 316L sample surface
Slika 2. AES spekter na površini vsadka iz AISI 316L

According to the theory, the bipolar structure of the passive oxide film on stainless steel consists of excess metal ions or oxygen ion vacancies in the inner layer, which provide a positive fixed charge with an anion-selective property, as well as an excess oxygen ions or metal ion vacancies in the outer layer, which result in a negative fixed charge with a cation selective property. All cells and surfaces of the body carry an electrical charge, and the majority of the particles within the blood are negatively charged[13].

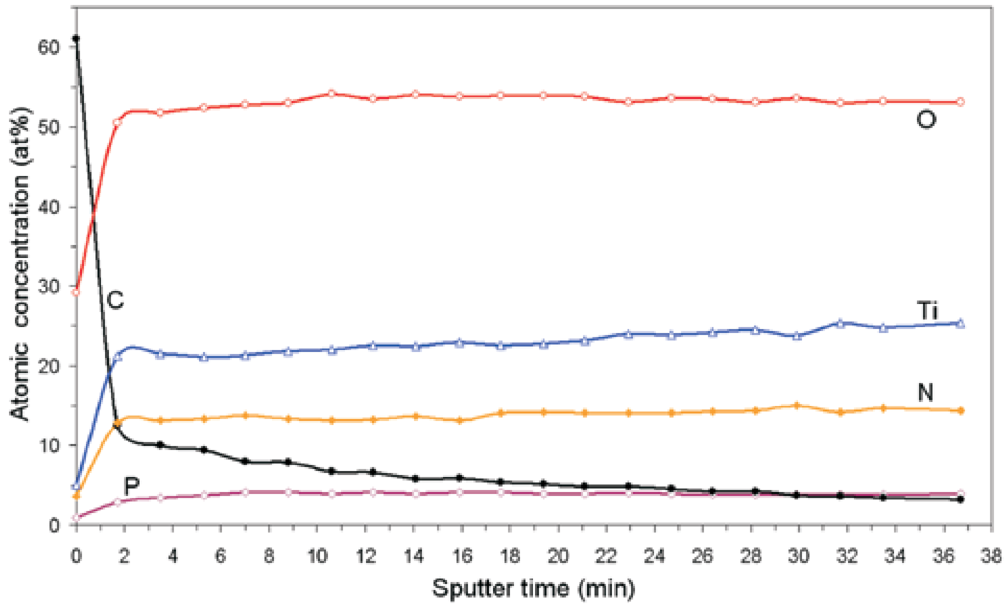
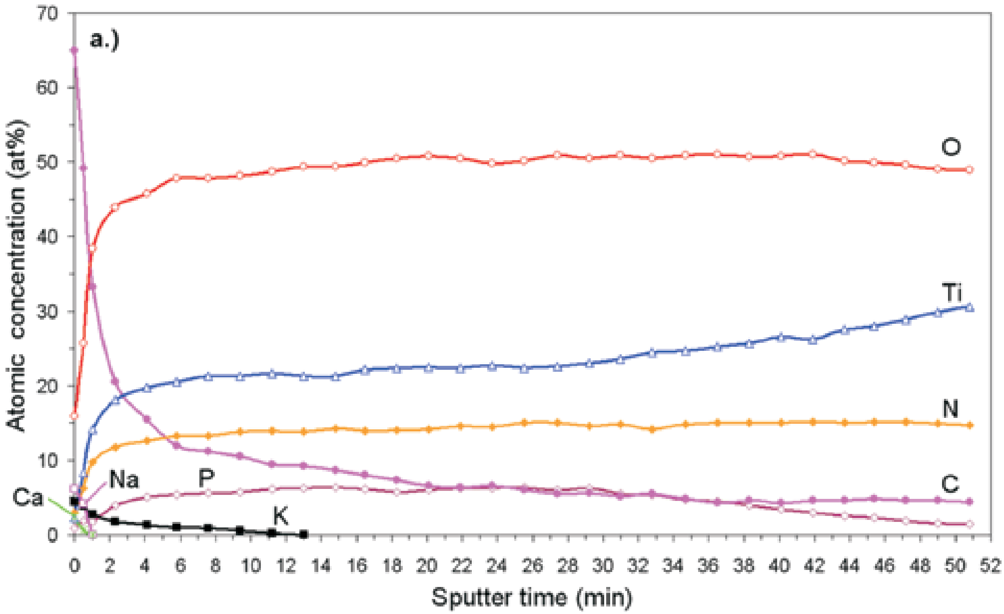


Figure 3. AES depth profile of unused titanium medical implant with golden colour protective layer
Slika 3. AES profilna analiza neuporabljenega vzorca medicinskega vsadka narejenega iz titana z zlato obarvano zaščitno prevleko

An AES depth profile of an unimplanted titanium sample with golden colour protection layer is shown in Figure 3. Elements O, Ti, N, P are compounds of an coating deposited on bulk titanium to increase biocompatibility. Carbon in the depth profile is due to surface roughness and carbon low density. It is overestimated due to the backscattering effect and preferential sputtering. High content of O, Ti and N is found due to the formation of protective layer and appears to consist of either mixture of TiO_2 and TiN_x or a Ti oxynitride (TiO_xN_y).



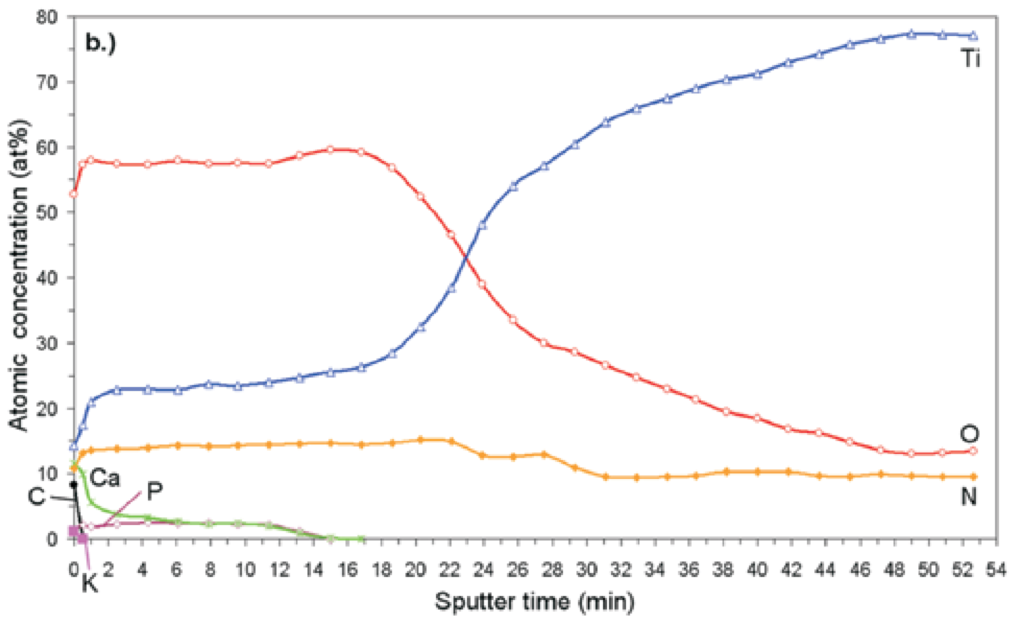


Figure 4. AES depth profile of titanium medical implants with a.) golden coloured coating, b.) blue coloured coating

Slika 4. AES profilna analiza titanovega medicinskega vsadka z a.) zlato obarvana prevleka, b.) modro obarvana prevleka

Because coating preparation technique is unknown due to commercial nature of medical products, another possible interpretation is that the surface consists of a TiO_2 layer covering the underlying Ti nitride. More detailed analysis, including angle resolved XPS, is necessary to distinguish between these interpretations. Significant change of the oxide composition in the surface region is because of contamination. Surface contamination on air-exposed samples is practically inevitable and the contamination layers on titanium oxide or oxynitride surfaces are most often dominated by oxygen and organic molecules with ingredients of Ca, Na, K and C.

Chemical properties of two used titanium medical implants with different coatings colours were examined on spectrometer by AES. Difference in the colour is due to different coating composition as can be seen in AES depth profiles of golden (sample 4) and blue (sample 5) colour coating presented in Figure 4a, and 4b, respectively. Obtained depth profiles of implanted sample 4 (Figure 4a) is significantly different compared to an unimplanted one (Figure 3). Penetration of Ca and P and also some Na was found in superficial stratum of the protective layer while K has been found relatively deeper. Sample 5 is different in composition and thickness. On its depth profile shown in Figure 4b, elements C and K were found on the surface and Ca and P in depth of the protective layer. Correlation between Ca and P can be linked to formation of calcium phosphate rich layer on its surface, very similar to hidroxyapatite which also prevents corrosion. Another advantageous property of formatted layer is that in the case of damaging the protective layer the titanium oxides and Ca-P layer regenerate[1].

This study presents surface characterization of unused and implanted biomaterial for trauma and orthopaedic medical products. A key issue in all trauma and orthopaedic medical applications of biomaterials is how the implanted material influences, and is influenced by, the biological re-

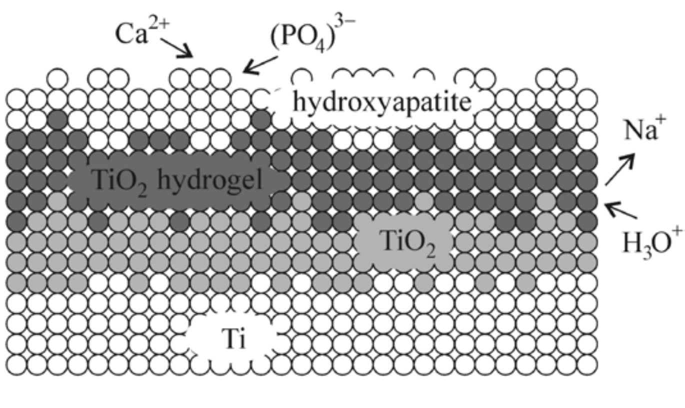


Figure 5. A formation of calcium phosphate rich layer on titanium oxide film
Slika 5. Nastanek obogatene plasti kalcijevega fosfata na substratu titanovega oksida

sponse resulting from the contact between the biological system and the biomaterial. Understanding the surface phenomena of changes when the biomaterials are used in the biosystem can improve the knowledge about material - biosystem interactions. Several scenarios have been proposed for the events that may occur when a material surface is placed in contact with a biological system. The initial events in such scenarios are adsorption of water molecules, hydrated ions, and biomolecules, which form a so-called "conditioning film" on the biomaterial surface. Cells of the host tissue interact in this hydrated biomolecule coating, therefore the original surface properties of an implanted biomaterial constitute an important starting condition for the dynamics of the interface[14]. In Figure 5 formation of calcium phosphate rich layer similar to hidroxyapatite on hydrated surface is shown[1].

Furthermore the titanium with different coatings and deposition techniques show a wide range of chemical and physical properties, depending on how they are prepared and handled, and by using different surface preparation methods it is possible to control and vary selected surface properties of titanium over a relatively wide range. Different chemical properties of protective layer of used titanium base implants analysed in this study show different behaviour of deposed layer. On one formation of Ca-P rich layer was found on sample 5 while on sample 4 on such layer was found.

The observed differences can be attributed mainly to the different textures of the surfaces, where chemical surface analyses of samples gave only a limited picture of their surface characteristics. It is equally important to characterize the structural properties also, as they influence the biological function of biomaterials as well. The topography and roughness of polished AISI 316L stainless steel (Figure 6) and blue coated titanium (Figure 7) medical implants were analyzed with AFM.

The roughness amplitude of electropolished and passivated medical implant of AISI 316L measured with AFM over area 10×10 μm and the maximum Z-range of 120 nm, resulted in Ra value of 6.5 nm. Electropolishing produces surfaces which have a mirror like appearance with smooth corrugation on the scale of 10×10 μm surveyed with AFM. In Figure 6 the individual granular structure is shown, with granule sizes of a few nanometres.

AFM roughness measurements on blue colour coated titanium over areas of 10×10 μm give Ra values of 68.6 nm, with maximum Z-range of 400 nm respectively. Higher roughness compared to polished AISI 316L samples can be explained with implantation of molecules on coating when implant was in contact with bodily fluids. 3D topography of wavy surface of blue coloured implanted sample is depicted in Figure 7, where raised and descended regions can be seen. In comparison to topography of stainless steel sample we can see fewer apexes which are nicely rounded and measured distance from highest to lowest point is increased.

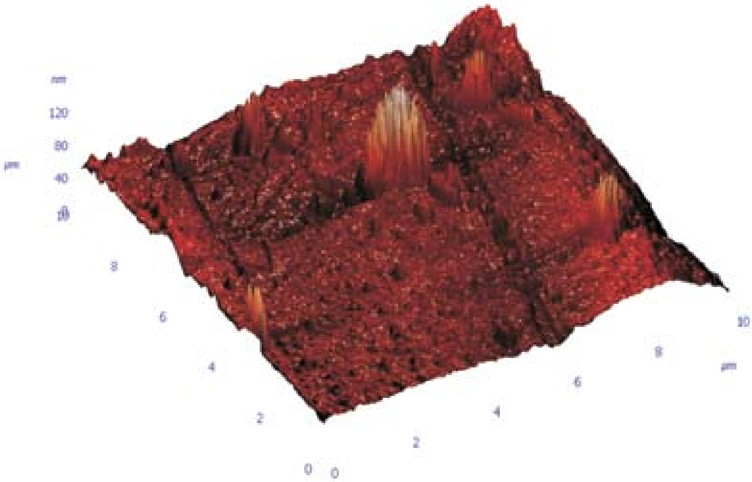


Figure 6. AFM 3D topography of unused AISI 316L medical implants (10×10 µm)
Slika 6. AFM 3D prikaz topografije površine jeklenega neuporabljenega vsadka iz AISI 316L (10×10 µm)

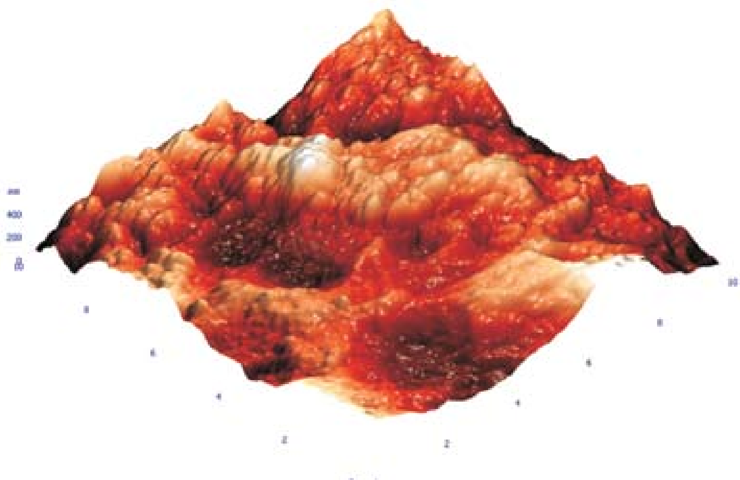


Figure 7. AFM 3D topography of used blue coated titanium trauma plate (10×10 µm)
Slika 7. AFM 3D predstavitev topografije rabljene modro prevlečene titanove plošče (10×10 µm)

The techniques utilised in this study were effective in the characterisation of the chemical composition, morphology and surface quality of the analysed surfaces. Analysed sample surfaces show a wide variety of structural and chemical properties. By using a combination of different experimental and analytical techniques it is possible to characterize the surface properties at a relatively high level of detail.

Further studies using carefully prepared and systematically varied samples surfaces are necessary, and are likely to lead to an increased understanding of the biocompatibility of materials in question. This development is dependent on thorough surface characterization of the materials by a broad range of surface spectroscopic and microscopic techniques.

Conclusions

Detailed information about changes in the composition of a medical implant's surface can be obtained by AES and AFM. A comparison of depth profiling results between unused and implanted commercial medical devices used for bone osteosynthesis using AES depth profiling with 3 keV Ar^+ ion beams and physical properties examined by AFM showed that:

- Oxides grow when implant is contact with bodily fluids on both stainless steel and titanium devices.
- Type of changes in chemical composition depends on used protective coating as has been shown on titanium implants with different coatings.
- Main factor for the colour change seems is the oxide thickness which has been confirmed by the ion sputtering of golden coated sample.
- Backscattering effect and preferential sputtering increase concentration of carbon especial on rougher titanium surfaces.
- Surfaces of stainless steel implants are much smoother, where average roughness Ra = 6.5 nm has been measured, while on coated titanium average roughness Ra was 68.6 nm, since titanium surfaces are coated with hard coatings.

Povzetki

Karakterizacija površin medicinskih vsadkov iz titana in nerjavnih jekel

Podrobne informacije o spremembah v sestavi površine medicinskega vsadka lahko dobimo z metodama AES in AFM. Primerjava globinskih profilov novega in že uporabljenega komercialnega medicinskega vsadka za oseosintezo kostnega tkiva z AES globinsko profilometrijo s 3 keV Ar^+ ioni in fizikalne lastnosti preiskane z AFM so pokazale:

- Površinski oksidi rastejo pri kontaktu vsadka s telesnimi sokovi, tako na vsadkih iz nerjavnega jekla, kot tudi na vsadkih iz titana.
- Vrsta spremembe v kemijski sestavi je odvisna od vrste zaščitne prevleke, ki je bila nanesena na vsadek iz titana.
- Barva zaščitne prevleke je odvisna od re-

ferenčne debeline oksida, kar je bilo potrjeno pri ionskem jedkanju zlato obarvane prevleke.

- Na zasenčenih površinah, ki jih pri ionskem jedkanju ne dosežemo izmerimo višjo koncentracijo ogljika, še posebej na bolj hrapavih površinah.
- Površine vsadkov, narejenih iz nerjavnega jekla so bolj gladke, s povprečno vrednostjo Ra = 6.5 nm. Na površinah titanovih vsadkov je bila izmerjena večja povprečna hrapavost Ra = 68.6 nm, kar je posledica nanosa zaščitne prevleke.

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