

519. Surface activity of titanium alloys contacted with the simulated body fluid

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Abstract. The purpose of this study was to analyze surface chemical species deposited on various implant materials immersed in simulated body fluid (SBF). The investigated materials including pure titanium, two beta titanium alloys and stainless steel (316L) were formed into discs using cold pressing and sintering. The samples were examined using SEM and mid-IR microscopes. All the sample discs exhibited nucleation and growth of calcium phosphates, precipitated from the SBF solution containing calcium, phosphate and other ions. The results have shown that the nucleation and growth of phosphates depend on the alloy composition and become more intensive in the case of the titanium alloy with the niobium addition.

Keywords: titanium alloy, simulated body fluid (SBF), calcium phosphate, bioactive surfaces

Introduction

Pure titanium, titanium alloys and stainless steel grade 316L have been widely used in the manufacturing of dental and orthopedic implants owing to their superior mechanical properties and high corrosion resistance [1]. On the other hand, the bioactivity of metal surfaces is not sufficient to induce growth and fixation of bone tissues [2]. An ideal biomaterial for medical applications should exhibit excellent biocompatibility with no adverse cytotoxicity, excellent corrosion resistance, and a good combination of mechanical properties such as high strength and fatigue resistance, low modulus, and good wear resistance [3, 4]. Thus, intensive and thorough investigations are needed to obtain materials with properties similar to the replaced tissues. One of the prospective research directions is the application of porous metallic materials for osteointegration processes. Application of materials with appropriate porosity allows one to accomplish mechanical fixation of implants without using a bone cement. This successful result can be achieved because of spontaneous bone growth into the implants' porous structure [5]. Modern technologies, such as powder metallurgy, offer new possibilities of producing original porous alloys and composite materials.

On account of the relevance of titanium alloys for orthopedic applications, both nucleation and growth of calcium phosphates have been investigated. A simulated body fluid (SBF) with ion concentrations nearly equal to those of human blood plasma, can be used in tests of the bioactivity of investigated materials [6]. Apatite depositions on the surface of materials immersed in SBF solution have been widely used for the in-vitro assessment of the bioactivity of bone and dental implant materials [2].

The aim of the present study was to investigate the bioactivity (surface composition) of the titanium alloys immersed in SBF solution. Also, the titanium surface structure using SEM was examined. The chemical analysis of the surface layer was conducted using the FTIR method [7-10].

Materials and methods

Pure titanium, two beta titanium alloys and steel 316L were investigated. Metal discs, 7.0 mm in diameter and 1.5 mm thick, were produced of those materials using the powder metallurgy method. Two titanium alloys, Ti-15Mo-2.8Nb and Ti-7.5Mo-2Fe were prepared using commercial pure titanium powder of the particle size below 150 μm , pure molybdenum powder of the particle size 3-7 μm , pure niobium powder of the particle size 1-5 μm and pure iron powder of the particle size below 10 μm . The steel disc was prepared using the 316L powder of the particle size 125 - 250 μm .

The technological process involved cold pressing under the pressure of 500 MPa, followed by sintering. The sintering process was carried out in vacuum for 3h at 1230°C. Thus formed discs were cooled down naturally to ambient temperature inside a furnace.

Before immersing all the samples into the SBF solution consisting of KCl, NaCl, HCl, MgCl₂·6H₂O, CaCl₂, Na₂SO₄, NaHCO₃, KH₂PO₄·3H₂O and TRIS (hydroxymethyl aminomethane) [6], the surface of the discs was mechanically polished and analyzed using HITACHI S-3000N electron microscope with attachment for X-ray microanalysis. The samples were immersed for 56 days in the SBF solution (pH 7.2, 37°C) specified above and afterwards the precipitation of calcium phosphates was investigated.

The FTIR method was used to analyze chemical composition of the coating produced after immersion of the metal discs into the SBF solution. The middle-range infrared spectra were collected using a PerkinElmer Autoimage infrared microscope equipped with a digital camera and operating in the reflection mode. The background was recorded prior to the measurement of coated surfaces by reflection from an untreated surface of each studied alloy and it was automatically subtracted. All the spectra were acquired in the same conditions (aperture size 100/100 μm^2 , number of scans 500, resolution 1 cm^{-1}). The spectra did not show any derivative-like features, typical of specular reflectance, hence neither Kramers-Kronig nor Kubelka-Munk transformations were required. The spectra were processed with the GRAMS/AI 8.0 software (Thermo Scientific), which was also used for deconvolution of selected spectral regions and curve-fitting of overlapping bands.

Results

The surfaces of the tested titanium, titanium alloys and steel 316L were studied using SEM before and after immersing them for 56 days in the SBF solution (Fig. 1).

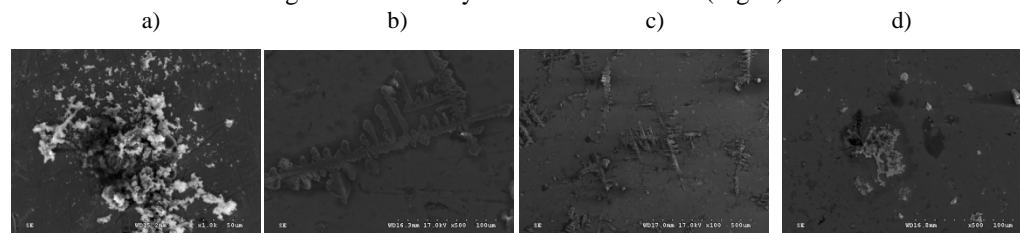


Fig. 1. SEM micrographs of the sample surfaces after the SBF treatment: a) pure titanium, b) Ti-7,5Mo-2Fe, c) Ti-15Mo-2,8Nb, d) steel 316L

Figure 1 indicates that apatite crystallites were formed on each of the sample surfaces. The SEM images showed deposition of dendrite-like particles which habit is typical of apatite crystallites. The crystallites have been further analyzed using the FTIR microscopy. Figure 2 shows a representative infrared reflectance spectrum of the studied coatings obtained for the 316L steel sample. The spectral assignment was done using IR frequencies from the literature [Thomas S. Enhanced IR-Wizard. Available from URL: <http://www.chem.uni-potsdam.de/~thomas/index.php> (follow the link to Wizards)]. All the acquired spectra are similar and contain bands originated from the SBF components. The peaks at 1658, 1561 and 1296 cm^{-1} come from the organic component (TRIS). The intensive, well resolved band at 662 cm^{-1} originates from sulphates. Carbonate bands were detected in the 1450-1400 cm^{-1} region and at 873 cm^{-1} .

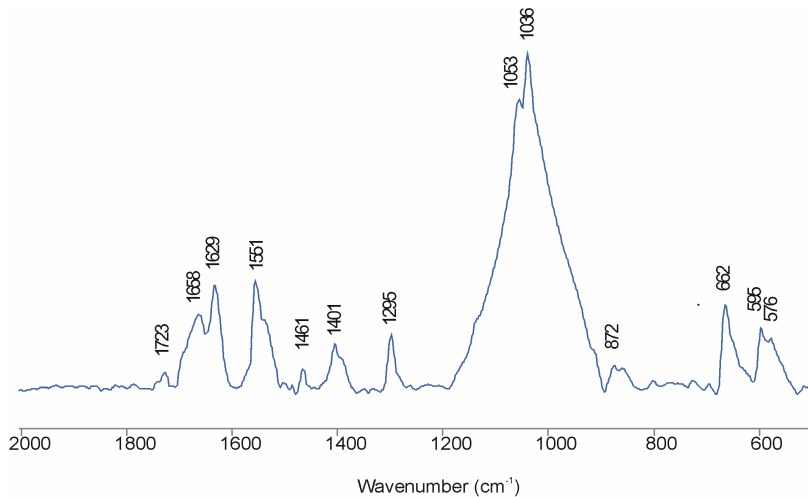


Fig. 2. The representative infrared spectrum of the analyzed coatings (steel 316L)

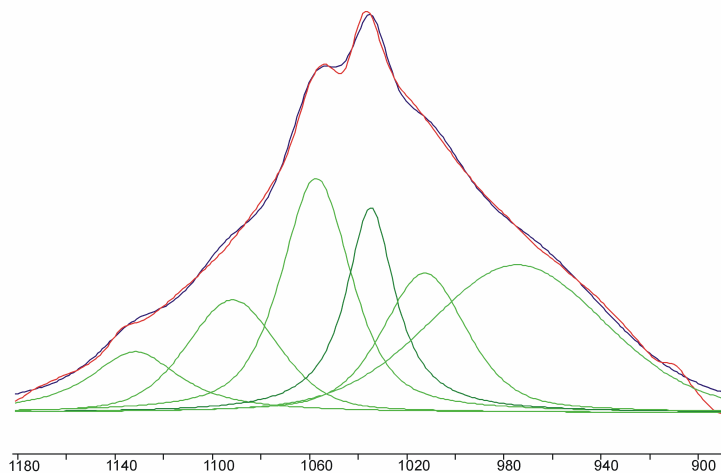


Fig. 3. Deconvolution of the 1200-900 cm^{-1} IR region (steel 316L)

The broad, complex peak in the 1200-900 cm^{-1} region comprises overlapped acidic phosphate (HPO_4^{2-}), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) bands (Fig. 3). The presence of the bands at 1053 cm^{-1} and 1036 cm^{-1} indicates that the coatings contain crystalline calcium phosphate. The bands in the 600-550 cm^{-1} spectral range confirm the presence of apatite phosphates. It may be noticed that the apatitic deposits are poorly crystalline, because the band at 630 cm^{-1} characteristic of structural hydroxyl groups is not detectable. The carbonate bands indicate that PO_4^{3-} groups from apatite crystals are partially substituted by CO_3^{2-} groups (B-type substitution).

Conclusions

Bioactivity of pure titanium, two beta titanium alloys and steel 316L was investigated using the SEM and IR microscopic methods in this work. Considering the results of the investigations, the following conclusions may be formulated:

- Bioactive precipitations were formed on the surface of each sample;
- The SEM micrographs show dendrite-like crystallites that are typical of apatite phosphates;
- The FTIR spectra confirm the presence of poorly crystalline carbonatoapatite in the deposited surface layer;
- The FTIR spectra indicate that the carbonatoapatite is of type B (PO_4^{3-} groups are partially replaced by CO_3^{2-} groups in the crystal lattice).

Acknowledgments

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