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Short communication

Preliminary studies of creation of gold nanoparticles on titanium surface towards biomedical applications

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ABSTRACT

This paper is devoted to present the results of creation of gold nanoparticles on titanium surface. We focused on the problem how to create gold nanoparticles on the titanium surface with defined particle size and distribution, which could be interesting for several applications (e.g. providing well-defined substrates for biomedical research, etc.). To do that the sample is affected by the complex physical rout of gold nanoparticles formation: by gold ion implantation, thin Au layer deposition and thermal annealing. The effect of the technology, influence on the surface structure and its parameters were investigated by the X-ray diffraction, Scanning Electron and Atomic Force Microscopy, as well as by Secondary Neutral Mass Spectrometry methods.

Titanium is a widely used material for different applications in industry and medicine. The latter relates to implants with high stability and biocompatibility, where properties of the tissue-Ti/TiO_2 interaction are really important. Titanium itself is a biocompatible material; however its osseointegration can generally be influenced by modifying the surface structure, which is playing an important role in its successful clinical application [1,2]. Several studies show that the formation of a titanium oxide layer improves the biological compatibility of titanium and present many surface treatment methods to increasing the thickness of native oxide layer [3–5]. However, beside of this, the use of titanium implants with composite surfaces can exhibit antibacterial properties and influence cell growth processes [6,7]. These processes could be enhanced by adding gold nanoparticles (GNP), besides of that they also can easily establish special bonds to biomolecules [8]. A number of chemical and physical ways are known and used for GNP fabrication [8–13]. A preliminary study was done for surface modification of Ti by gold ions produced by electron cyclotron resonance (ECR) ion source (further called the ECR method) [14], but the created nanostructures were not analyzed deeply. In this work we present the results of structural changes investigated by different methods. One of the novelties of our works is improving the biocompatibility and osseointegration of Ti surface by gold ion beam produced by the ECR ion source (ECRIS) [15]. For the sample preparation we focused on two methods, used either separately or in combination:

(1) the nano-structurization of thin gold layer, deposited by magnetron sputtering method onto the surface of natural titanium sample kept under normal environmental conditions. We call it the physical vapor deposition (PVD) method.
(2) irradiation by Au ions provided by an ECR [15–17].

The heat treatment (annealing) of the samples also was applied in order to form GNP on the surface. Scanning Electron Microscope (SEM), Secondary Neutral Mass Spectrometry (SNMS) and Atomic Force Microscope (AFM) were used to establish the interconnection between the applied technology and the parameters of the resulted surface.

The Au ion beam was produced by the sputtering method [18], i.e. a gold pastille was bombarded by oxygen ions in the plasma. The extracted ion beam was straightly transported to the targets so all the beam components hit the samples. Before irradiation the extracted complex ion beam was analyzed by charge-to-mass ratio resulting in a beam spectrum. The peaks in the spectrum were

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identified and measured, and thus the ratios of the beam components could be exactly calculated. The composition of the beam was: Au – 2.4%, O – 78%, H – 10%, C – 8%, others 1.6%. The dose of the irradiation of gold ions was $1.5 \cdot 10^{16}$ ion/cm^2. Due to the different charges the gold ions were distributed not in a form of a thin layer, but stopped at different depth forming a density distribution in the surface layer of samples.

The 0.5 mm thick titanium plates (99.6 at%, grade 2, Spemet Co., Taipei, Taiwan) with dimension of 10 mm × 10 mm were mechanically polished to #2000 grid level, followed by 1 μm Al_2O_3 powder polishing to produce a mirror-like surface. All substrates were immersed in fresh 30% HNO_3 for 30 min at room temperature. In the next step all plates were sonicated in ethanol for 30 min, rinsing with distilled water for further 30 min and were dried in air.

Before ECR irradiation half part of the samples were covered by the stainless steel sheet. After irradiation this sheet was turned in 90 degree and the sample was covered with 15 nm thick gold layer by magnetron sputtering method. In this way we produced four different treated 5 × 5 mm parts on the same Ti sample. After preparation the samples were annealed at 550 °C for 6 h at atmospheric pressure to form gold nanoparticles from both Au components (irradiated and deposited). The following parts of the samples were investigated: 1 – pure Ti surface (Ti part), 2 – Ti surface irradiated with Au ions (ECR part), 3 – Ti surface irradiated with Au ions and covered with gold layer (ECR + PVD part), 4 – Ti surface covered with gold layer (PVD part).

Before and after annealing the samples were investigated with several different methods: SEM (Hitachi S-4300 CFE), AFM (Veeco diCaliber) and X-Ray diffraction (XRD). In order to have good statistical results all samples were investigated in 10 different places by SEM and AFM. The θ–2θ XRD measurements were carried out with a Siemens CuKα X-ray tube (λ = 1.54 Å) and a horizontal goniometer equipped with graphite monochromator. The parameters of the nanostructures were calculated using a standard image analyzing process on the SEM pictures made by National Instrument Vision Assistant. Energy dispersive x-ray spectroscopy (EDX) in the SEM system was used for checking the chemical components of the investigated samples. An INA-X type SNMS equipment (SPECS, Berlin) was used to measure the depth distribution of the elements to make a comparison with SRIM (*Stopping and Range of Ions in Matter*) simulation.

The implanted gold ions in Ti samples showed a Gaussian-like depth density distribution with a maximum around 10 nm in depth. The irradiation conditions were modeled by the well-known simulation code, SRIM [19]. Fig. 1 represents the comparison of the penetration calculation by SRIM to the data of the SNMS measurement, which was done on a sample before heat treatment. As it can be seen from Fig. 1(b) the gold ions penetrate into Ti up to about 13 nm, while oxygen strongly decreases in 3–5 nm depth showing the thickness of the oxide layer developed after ECR irradiation on Ti. The formation of this thin oxide layer (over the already existed ~25 nm thick natural titanium-oxide) probably also enhance the biological compatibility of the titanium implants [3,6]. In the SRIM simulations gold ions with realistic composition (obtained from the ECR beam spectra) were used. It was established that the model calculations are not perfect, but in good agreement with the experimental results; hence the SRIM can be used for modeling the penetration of the Au ions in the Ti samples during such a low-energy implantation. (For comparison Fig. 1(a) shows the theoretical distribution of gold ions in TiO, as well.) Fig. 1(b) shows that the implantation of Au ions was successful and the measured penetration depth corresponds with the SRIM calculation. It is also necessary to note that results of the SNMS method show that annealing (which is necessary for GNP creation) increases the thickness of the oxide layer on Ti surface up to 100÷120 nm.

Figs. 2 and 3 represent the SEM and AFM images of different parts of the Ti sample before and after heat treatment. AFM was used to measure the average roughness of the surface before and after the heat treatment. For the characterization of average roughness the root mean square (RMS) values for each samples was established from these measurements. The figures demonstrate the occurrence of nanostructures in case of the 4 areas due to annealing, whose parameters (average size and filling factor) depend on the surface treatment. The average roughness of different part of the samples, before heat treatment, was the following: Ti – 5 nm, Ti + ECR – 3 nm, Ti + ECR + PVD – 3 nm, Ti + PVD – 4 nm; while the roughness after heat treatment has changed: Ti – 11 nm, Ti + ECR – 9 nm, Ti + ECR + PVD – 17 nm, Ti + PVD – 25 nm. We can state that the heat treatment results in an increase of the roughness of the sample surface.

The structural characteristics of the pure Ti part of the sample were measured by XRD before and after annealing (Fig. 4). The spectrum of the investigated sample has changed definitely due to annealing. Appearance of TiO nanocrystals was observed after heat treatment. Characteristic peaks appeared at 35.1, 38.4, 40.2, 53.0 and 27.4, 35.9, 54.4 2θ degrees, which correspond to Ti and TiO_2 (rutile), respectively [20,21]. The size of the TiO_2 crystals has been calculated by the Scherrer-equation [22,23] and was determined in average size of 14 nm. The change of the roughness of pure Ti surface could be explained by the presence of TiO_2 nanostructures which is supported by XRD measurement. The XRD data is show –

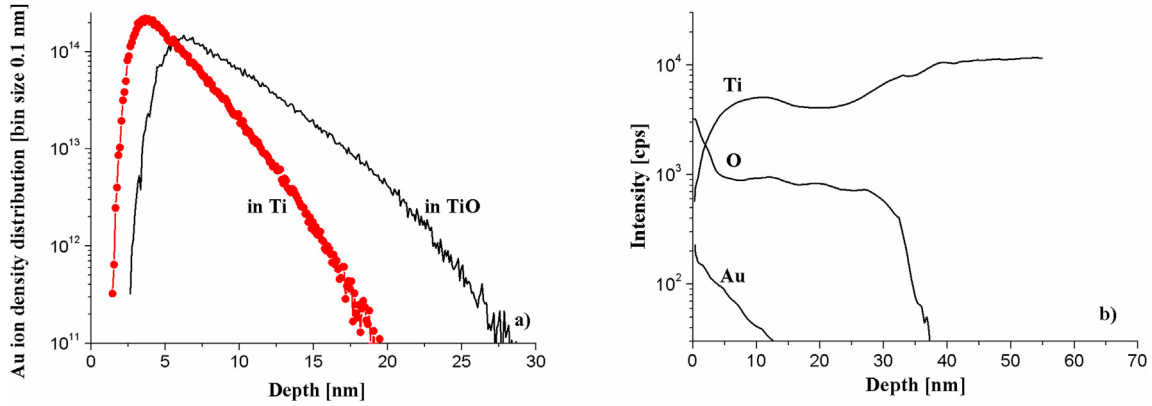

Fig. 1. a) Calculation with SRIM of the implantation of Au ions in the Ti and TiO samples. b) SNMS depth profile of the Ti sample, which was irradiated with Au ions before heat treatment.