Characterization of electro-eroded surface of Ti alloys

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Abstract. The principal materials for fabricating implants are usually metallic alloys, which have suitable mechanical and corrosion properties. Titanium and its alloys are widely used nowadays. In this work, we make a comparison of the electro-eroded surfaces of Ti, Ti6Al4V and Ti5Al2.5Fe alloys. Using the contact profilometer and confocal microscopy we obtained the roughness parameters; the differences among the samples were very small. We also studied the chemical state of the surface and the carbon-based gradient layer that was found on all the electro-eroded samples by X-ray photoelectron spectroscopy (XPS), Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection Analyses (ERDA). We obtained the depth profiles of several elements in the layer, and also the hydrogen content. The layer thickness was \( \sim 0.5 \mu m \), though it was inhomogeneous. Raman spectroscopy proved the graphitic structure of the layer with various degree of crystallinity between the amorphous and crystalline state.

1. Introduction
Titanium and its alloys are very promising materials for hard tissue implants. Generally, the biocompatibility of implants is strongly influenced by two surface properties - their roughness and their chemical state. While roughness tends to be characterized by a limited number of parameters, the definition of the chemical state of the surface, even on a defined material, has a large number of variables. An oxide layer usually forms on the surface of titanium and titanium alloys. In recent times, electro-erosion has emerged as a promising technology employing a DC discharge in a hydrocarbon atmosphere [1]. In this way, a very rough surface is produced, and this is very suitable for a strong connection with tissue, especially with bone.

Although the material and its roughness had a strong influence on cell adhesion and proliferation, our preliminary results on tissue cell growth on the electroeroded surface of Ti alloy and plasma-sprayed Ti particles on Ti alloy indicated limited dependence on surface technology [2]. The results showed that neither the number of adhered cells nor the doubling time depends significantly on the chemistry, composition and treatment of the surface. Finally a layer of unknown thickness, composition and chemistry was discovered on electro-eroded samples.

In this work, we have studied the surface state of pure Ti, Ti6Al4V and Ti5Al2.5Fe alloys, which were prepared by an industrial electro-erosion process at Beznoska Ltd., Kladno. The aim of this study was to characterize the roughness (topography) of the surface, the parameters of the layer and the chemistry of its surface on Ti alloys machined by an electro-erosion technique.
2. Materials and methods

We studied three types of sample material - pure Ti (ISO 5832-2, HWM Titan Gmbh or ZAPP Gmbh, Germany), Ti6Al4V (ISO 5832-3, ACNIS International (France)) and Ti5Al2.5Fe (ISO 5832-10, Poldi a.s., Kladno, CR), denoted as TiAlV and TiAlFe, respectively. The samples were prepared in the form of discs 2 mm in height by turning from a rod 30 mm in diameter. The discs were then electro-eroded using the AGIETRON SPIRIT 2 system in a mixture of mineral and synthetic oils with a carbon cathode under the following conditions: discharge DC current 72 A, voltage 100 V, with the distance between the electrodes automatically set by the system.

Using the JEM 5410 scanning electron microscope (JEOL, Japan), we observed the surface topography of the electro-eroded samples, using software equipped with the SCANDIUM code (OLYMPUS - Soft Imaging Solutions, Germany) for 3D reconstruction of the surface from two tilted images. The Talysurf 6 contact profilometer, (Taylor&Hobson, Ltd., UK) was used for standard roughness measurements. It is necessary to use a special very light and long cantilever for measuring electro-eroded, highly rough surfaces; the assessment length for the measurements was 12 mm. We also obtained several images of electro-eroded surfaces on the LEXT OLS 3000 confocal microscope (OLYMPUS, Japan). The images were taken at objective magnification 10x, then the roughness parameters were calculated. The field of view was ~ 1x1 mm.

The XPS spectra were measured using the Omicron Nanotechnology ESCAProbeP spectrometer. The AlKα X-ray source was monochromatized at 1486.7 eV. The analyzed area had dimensions of 2 x 3 mm². The spectra were measured at pressure ~ 10⁻⁸ Pa. A qualitative analysis of the surface of the Ti and TiAlV samples was performed by comparing the estimated values of the binding energy Eₖ with standard values [5]. The concentration of the elements constituting the surface was evaluated from the line integral intensities normalized to the probability of photoemission [6]. For the Eₖ values and integral intensities, the photoelectron spectra were evaluated by a curve-fitting procedure, using the set of pseudo-Voight functions.

In the RBS method, the particles (protons 1.74 and 2.38 MeV, α-particles 3.04 MeV) impinging perpendicularly on the sample surface were detected under a scattering angle of 170 deg. The diameter of the analyzed area was ~0.3 mm. The RBS spectra were evaluated by GISA 3 code [3]. The ERDA with an incident beam of 2.75 MeV α-particles at an angle of 75 deg to the surface normal were measured in the same area. The hydrogen atoms recoiled below an angle of 30 deg were detected, the spectra were evaluated by the SIMNRA code [4].

Room temperature Raman spectra were measured in the backscattering geometry employing the Renishaw Ramascope system (model 1000), using the 514.5 nm (2.41 eV) Ar+ laser beam. To avoid possible material damage under laser illumination, the incident power density was kept typically below 500 W/cm². To test the actual material stability, the power density was varied in some experiments up to 1.8x10⁴ W/cm². No sample damage was observed even at the highest power used, whereas some annealing effects were observed even at the lowest power. The spectra were scanned in the region 250 – 3600 cm⁻¹, to cover also the second order of carbonaceous materials. The analyzed area was 1µm². Several different sites on the samples were analyzed.

3. Results and discussion

The characteristic SEM image of an electro-eroded surface is shown in figure 1. The main habit of the surface topography is created by deep holes (200 - 400 µm in size) and grooves with relatively smooth surfaces. Also SEM with 3D reconstruction gives us mainly qualitative and similar information. The results of the roughness measurement are shown in table 1. The parameters in the table are mean roughness Ra, quadratic roughness Rq, skewness Rsk, kurtosis Rku and mean spacing of peaks Sm. The values are the averages of three measurements. Measuring the roughness of an electro-eroded surface with a confocal microscope is a very quick and simple process. The measured values of the main parameters agree relatively well with the values obtained using the contact profilometer. However, there are some limits to the validity of the
measured roughness values, because they are taken from a relatively small place on the surface.

**Figure 1.** SEM image of the surface of TiAlV.

Using XPS the titanium Ti2p, oxygen O1s and carbon C1s core level lines of photoelectron spectra were measured. The surfaces are composed partially from titanium carbide (TiC). This finding follows from binding energy $E_b$ of carbidic C1s line (281.9 eV) present in the spectrum, and from the estimated stoichiometry of TiC ($\text{Ti}/\text{C} \sim 0.9$). Further carbonaceous phases are present in C1s lines at energies $E_b = 285.9$ eV (Ti) and 286.2 eV (TiAlV), respectively. From the line shape of C1s results the part of surface C is present in oxidized form. Further discussion of XPS results will be presented elsewhere ([7]). Vanadium is not present on the surface of the TiAlV sample in measurable concentration ($> 0.1$ at.%). The results are summarized in table 2.

**Table 1.** Comparison of line values obtained by contact profilometer and confocal microscope.

|        | Contact profilometer | Confocal microscope |
|--------|----------------------|---------------------|
| $\mu\text{m}$ | Ti | TiAlV | TiAlFe | Ti | TiAlV | TiAlFe |
| Ra     | 17.9 | 16.3 | 15.3 | 11.89 | 11.68 | 15.79 |
| Rq     | 22.0 | 20.4 | 19.3 | 15.25 | 15.16 | 19.67 |
| Rsk    | 0.3  | -0.2 | 0.1  | 1.16  | 0.04  | 0.63  |
| Rku    | 2.7  | 3.0  | 3.4  | 4.72  | 3.39  | 4.24  |
| RSm    | 414  | 372  | 332  | 169   | 144   | 73    |

**Table 2.** Concentration of elements in the layer $\sim 3$ nm on electroeroded Ti and TiAlV by XPS [at.%].

| Sample | C   | O   | Ti | Al | Ca | N |
|--------|-----|-----|----|----|----|---|
| Ti     | 79.29 | 14.91 | 2.06 | 0  | 1.80 | 1.95 |
| TiAlV  | 77.92 | 16.56 | 1.63 | 2.68 | 1.21 | 0  |

From the RBS measurement we can conclude that the total number of atoms in the layer is about $3 \times 10^{18}$ atoms of C/cm$^2$ and about $0.8 \times 10^{18}$ atoms of O/cm$^2$; they are distributed in a layer of one half of $\mu$m with an unsteady gradient (the total number of atoms in this layer is $\sim 10^{18}$ atoms/cm$^2$). The Ti, O and C concentration profiles are shown in the figure 2. From the ERDA measurement of the TiAlFe sample, the calculation of the hydrogen content results in 11 at.% at the surface (until a depth of $6.5 \times 10^{17}$ atoms/cm$^2$) and about 4.5 at.% in greater depths.

Typical Raman spectra are shown in figure 3. On the photoluminescence (PL) background, increasing monotonously with increasing (relative) wavenumbers, there are two bands at about 1350 and 1590 cm$^{-1}$ typical of disordered carbon [8]. On the Ti and TiAlV samples there are also rather weak bands at frequencies $\sim 300$ and 600 cm$^{-1}$, which are characteristic for TiC [9]. These features were never observed on TiAlFe. In some cases, some additional features also appeared between 2600 and 2700 cm$^{-1}$. The origin of these peaks remains unclear at present. We may assign it tentatively to the residue of the oils used for electro-erosion. The broad and weak hump around 3000 cm$^{-1}$ on the TiAlV trace in figure 3 is the second order spectrum of carbon. On the Ti trace, the second order becomes stronger, more structured and down-shifted ($\sim 2700$ and 2900 cm$^{-1}$). It is an indication of the better ordering of carbon on this site.

All the samples investigated here were inhomogeneous. This is seen by comparing the spectra from the same sample and different sites. There are just peaks corresponding to the first and second order Raman spectra of polycrystalline graphite (lower trace of TiAlFe). It is evident from the widths of the peaks that the ordering on this site is more advanced. It should be noted that there are also sites where the spectra were featureless, displaying only the monotonous PL curve. Its intensity and slope decreased with increasing time of illumination.

The surface films may be classified as a multicomponent heterogeneous system. One component is the well-known polymer-like a-C:H (PLCH), characterized by high concentration of
hydrogen and strong PL [8]. The slope of the PL background decreases as the time of illumination increases, indicating a decrease in hydrogen concentration [8] together with a decrease in the amount of polymeric component (cf., e.g., [10]). Other components are polycrystalline graphite and TiC. TiC is probably not present in the case of TiAlFe. Finally, there is probably a fourth component related tentatively to the residue of the oils used for electro-erosion.

4. Conclusions
In electro-erosion the temperature of metallic electrode reaches the melting temperature and material is teared out. The chemical state of the surface is given by appearing of carbonaceous layer; part of the layer is formed by titanium carbide, but the main part of carbon has probably a form like the DLC structure, with a large degree of disorder. Consequently, the layer surface is able to create a large number of free bonds, enabling the bonding sites of proteins to connect. Very small differences were found between the studied materials. Finally, the samples have very rough surface. In conclusion, the electro-erosion can stay a prospective method of preparation of surfaces, suitable for incorporation of tissue cells and their good adhesion to the material.

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