Plasma technology for creating highly porous titanium materials for biocompatibility testing

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Abstract. Titanium samples have been processed with plasma in PLM plasma device to obtain a highly porous nanostructured surface. Post-mortem analysis scanning electron microscopy of the samples has approved the formation of a porous stochastic nanostructured surface with the size of the pores and structure elements less than 500 nm. Such material samples will be used for biocompatibility testing using scaffold technology in support of the biomedical application of new highly porous materials.

1. Introduction

Processing of metals in modern plasma facilities leads to a significant change in the surface micro- and nanostructures \cite{1-8} under specific features \cite{9-10} of powerful plasma loads. Plasma irradiation of titanium, tungsten, molybdenum, tantalum, iron, and some other metals results in the growth of the highly porous nanostructured surface (see Refs. in \cite{11}). Such materials are characterized by new physical and chemical features never observed. The development of innovative plasma technologies for the synthesis of new nanostructured materials with the required roughness and porosity are required for nuclear, chemical and biomedical applications. \cite{11}. Metal materials have been widely used for the fabrication of the implants replacing hard human tissues or their functions, electrocardiac pacemakers etc. In biomedical applications materials of porous matrices (scaffolds) for cell and tissue cultivation must meet a variety of requirements (see \cite{12,13}) including biocompatibility, lack of toxicity, sufficient surface adhesion etc. Porous materials based on carbon compounds for medical applications have been tested demonstrating the nontoxicity, good adhesion of the cells to the surface and their proliferation capacity (see, e.g., \cite{13}). Highly porous titanium materials are attractive for medical applications. Highly porous titanium scaffolds for orthopaedic applications are of interest (see, e.g., \cite{14}). Plasma technologies for treatment of implants with roughen and porous surface are developing including the manufacture of electrocardiac pacemakers with improved characteristics \cite{15}. Highly porous titanium materials can be used as new materials for scaffolds in tissue engineering and biomedical application.
In this paper, titanium samples for scaffolds with highly porous surface produced by plasma irradiation are described.

2. Plasma irradiation of titanium samples in PLM plasma device
Four titanium (Ti) samples of 8 mm in diameter and of 2 mm thickness (Fig. 1a) with originally smooth surface were irradiated with plasma in PLM plasma device [16, 17]. The PLM plasma device is a multi-cusp linear trap with a steady-state plasma discharge that provides the powerful plasma-thermal load on test materials. In experiments, plasma parameters measured by plasma diagnostics were as follows: the plasma density was up to $3 \times 10^{18} \text{ m}^{-3}$, the electron temperature was up to 4 eV with a fraction of hot electrons of temperature up to 50 eV, the ion plasma flow onto the sample was up to $3 \times 10^{21} \text{ m}^{-2} \text{ s}^{-1}$, discharge current was up to 10 Amps, magnetic field was of 0.01 Tesla on the trap axis and up to 0.1 Tesla in the cusps. The titanium samples were irradiated with helium plasma of discharge duration up to 200 min. Incident angle between magnetic field and samples was of 90°. The samples have no active cooling, plasma heat load on Ti samples was of 0.5 - 1 MW/ m².

3. Structure of titanium sample surface after the plasma irradiation
Post-mortem analysis of four titanium samples is carried out after plasma irradiation in PLM device. Based on the micrographs of the scanning electron microscope (SEM) and X-ray analysis, it is concluded that the surface morphology of such samples was significantly changed comparing with the virgin structure. A growth of micro- and nanostructured highly porous surface was observed on all the four samples. Surface structure is shown in Fig. 1 for the first sample. The roughen surface is created on the macroscale, Fig.1c,d,e. The formation of a porous stochastic nanostructured surface with the size of the pores and structure elements less than 500 nm is observed, Fig. 1f,g. The same structure was observed on the other samples.
Elemental chemical analysis of the surface, Table 1, has revealed titanium and nitrogen on the surface demonstrating composition of material as result of a reaction with nitrogen influxed the PLM volume after plasma irradiation of the samples.

Table 1. Normalized weights of chemical elements, analyzed surface area is of ~0.04 µm², in atomic %

| Location | N  | Al | Si  | Ti  |
|----------|----|----|-----|-----|
| location 1 | 27.02 | 0.29 | 1.14 | 71.55 |
| location 2 | 27.09 | 0.28 | 1.82 | 70.81 |
| location 3 | 26.94 | 0.30 | 0.79 | 71.97 |

A metallographic study of a 1 mm thick titanium sample irradiated with plasma in the PLM device was carried out. After sectioning of the sample, polishing and chemical etching of the section surface was applied to reveal the microstructure and grain boundaries. Optic microscope micrograph of the section is shown in Fig. 2. The thickness of the heat-affected zone is 10-30 microns. The highly porous layer of 5-10 µm thickness is observed on the surface (zone 1 on Fig.2). It is characterized by a large number of defects and a porous surface relief. Under the interface (zone 2 on Fig.2), there is a layer of thermal influence (zone 3 on Fig.2), which is either recrystallized or melted titanium grains, it contains defects as intergranular cracks extending into the base metal which has a virgin coarse grain structure (zone 4 on Fig.2).
Figure 2. Metallographic section of titanium sample after plasma processing in the PLM plasma device: 1- highly porous surface layer, 2-interface non-regular layer, 3-recrystallized structure, 4-virgin crystalline structure

The titanium samples described above will be tested for a biocompatibility using scaffold technology [12,13]. Testing toxicity based on comparison of cell characteristics such as rate of proliferation, viability under oxidative stress and temperature stress will be carried out. Comparative studying of the porous titanium scaffold with reference smooth plastic surface scaffold will be done at NRU MIPT. The cell density on the surface of specimens will be accounted during experiments and statistical analysis of the data will be done to estimate efficiency of the porous titanium materials for the implants manufacturing.

4. Conclusion
Plasma processing of metals with powerful plasma loads in modern plasma facilities leads to a formation of the surface micro- and nanostructures. The growth of nanostructured surface with high porosity is observed in experiments with titanium, tungsten, molybdenum and other metals. Four titanium samples were irradiated with plasma in steady-state helium discharges in PLM device. The plasma load on the sample surface was 0.5-1 MW / m². Post-mortem scanning electron microscopy of the samples approved a formation of highly porous stochastic nanostructured surface with pores size less than 500 nm. Such material is of interest for a biomedical application. The titanium samples obtained will be tested for a biocompatibility using scaffold technology to estimate efficiency of the highly porous titanium materials for the implants manufacturing.

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