Plasma technology for surface processing of the ruthenium pacemaker electrodes

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Abstract. For pacemaker electrodes, the surface structure elements should be nanometer-sized in order to reduce the capacitive electrical resistance coupling of the electrode with the myocardium tissue. It is proposed to test several approaches. One of them is the creation of the “fuzz” nanostructure on the titanium surface accompanied by the subsequent ruthenium deposition onto this structure. Another one is the formation of the “fuzz” nanostructure on the layer of pre-deposited ruthenium. Such approaches contribute to developing new technology for manufacturing the electric cardiac pacemakers with improved characteristics.

1. Introduction

The Electric Pacemaker (EP) (a device for electrostimulation of myocardium), is widely used for the patients treatment and rehabilitation after suffering heart attacks and other heart diseases [1]. One of the most important requirements for the EP operation is the stability of pulsed energy transfer from the endocardiac electrode (ECE) of the pacemaker to the heart (Fig. 1a) and the optimal coordination of the ECE parameters. The electrical coupling of the electrode with the myocardium tissue is mainly capacitive, so it is necessary to maximize capacitance as much as possible. To stimulate the myocardium, an electrical pulse with duration of 100–300 µs and energy of 1–5 µJ is required; at the stimulation threshold of 1 V, the transient capacitance should be 2–10 µF. Since blood is an electrolyte, when a potential is applied to the surface of the electrode, there appears the double electric layer (DEL). The capacitive electrical resistance of the DEL significantly exceeds its ohmic resistance. According to modern concepts, the DEL consists of two parts (see Fig. 1b): (1) the dense layer (the Helmholtz layer) near the surface and (2) the diffuse layer.

In the Helmholtz layer, the ions are confined near the metal-electrolyte boundary. They form the condensed part of the double layer. The thickness $\delta$ of this dense layer is of the order of the hydrated ion size ($\delta = 0.3–0.4$ nm), and its dielectric constant (relative permittivity) is much lower than that in the solution volume. This is due to the rigid orientation of the solvent dipoles in the dense layer, which occurs under the effect of both the electric field of the electrode and their interaction with metal.

In the DEL outer part, the ions are distributed diffusely, and their charge density gradually decreases over the length $\lambda$ (Fig. 1b). In the Helmholtz layer, ions are confined not only by the electrostatic forces, but also by the specific adsorption. The DEL is electrically equivalent to the two series-connected capacitors, and its capacity is determined by the capacities of the inner dense and outer diffuse DEL parts. To improve efficiency, it is necessary to increase the DEL capacity. Two methods are used for this: (1) increasing the surface area of the electrode by means of creating the developed electrode surface, and (2) increasing the surface adsorption by means of applying
special coatings. Modern pacemaker electrodes have the characteristic sizes of the surface structure elements of ~1 μm, which exceeds the thickness of the DEL inner dense layer, which is approximately 1 nm thick. Therefore, for the pacemaker electrodes, the sizes of the surface structure elements should be reduced to 1 nm. In practice, the developed surface with a high specific area is formed by the coating deposition or the surface treatment using various technologies, e.g., the technology of electrolytic deposition of materials from a solution onto substrates, technologies of vacuum sputtering of materials and their deposition onto substrates, sputtering by the ion beam, and the arc method (see Refs. in [2]). The nanostructured surface with the large specific area can be obtained by the plasma processing of materials. The PLM plasma device [2] has been constructed at National Research University “MPEI” to produce roughened nanostructured surfaces on metals, including the “fuzz” type surfaces, which are discussed in this paper to be used in production of the pacemaker electrodes.

Figure 1. (a) Endocardiac electrode (ECE) of the pacemaker installed in the heart. (b) Schematic of the double electric layer (DEL): $\delta$ is the Helmholtz layer, and $\lambda$ is the diffuse layer.

2. Advantages of using ruthenium for producing the pacemaker electrodes

Nowdays, the platinum group elements (platinum Pt and iridium Ir) and titanium nitride TiN are most often used as coating materials for the pacemaker electrodes. The iridium coating has low capacitance, and it is proposed to be used in modern pacemakers. The main characteristic of the coating is the impedance of the electrode-blood contact. At high frequencies, the resistance is small for all coatings, and at low frequencies, the difference in coating resistances is very large. At frequencies less than $10^3$ Hz, the iridium coating has the lowest resistance. The titanium nitride coating resistance is slightly smaller. The main function of the coating is to increase the adhesion of positive ions. The adhesion of positive ions is determined by the electronegativity of metal. The platinum group elements have the highest electron affinity among metals (tungsten W also has large electronegativity, but it is not suitable for contact with blood). The electronegativities of platinum, iridium, and ruthenium are 2.28, 2.2, and 2.2, respectively. This property determines the prospects for using elements of the platinum group as coatings for the pacemaker electrodes.

We are the first to propose using ruthenium Ru as the coating material for the pacemaker electrodes. It was not previously used for these purposes and has several advantages. Ruthenium is one of the analogues of platinum and iridium [3]. Ruthenium is the only element of the platinum group naturally present in the human body. In medicine, ruthenium-based preparations are used as medicine and diagnostic agents. Ruthenium is much cheaper than other platinum group metals (~5.5 times cheaper than iridium).

3. Plasma method for the formation of the developed surface of the ruthenium electrodes

To improve the efficiency and reliability of pacing, the sizes of the structural inhomogeneities on the ECE surface should be reduced to the nanometer-scale sizes. Such surface morphology of materials can be obtained using plasma treatment, see [4, 5].
Recently, the formation of nanostructured stochastic surfaces of materials (see [4, 5] and references therein) has been detected in experiments on plasma facilities during the tests of materials by treating them with dense plasma with temperatures ranging from several electronvolts to tens of electronvolts. In such experiments, the porous surface morphology was registered, including the surfaces with nanostructured hierarchy. It is considered (see [4, 5]) that such stochastic clustering is the result of the collective effects occurring during the nonequilibrium plasma-surface interaction due to the high density plasma flux onto the surface. One of the effects observed in such experiments is the growth of the surfaces with a “fuzz”-like nanostructure with filament diameters of ~20–50 nm, see Fig. 2. The formation of such a structure occurs at high temperatures of the sample surface as a result of irradiation with helium ions with energies in the range of 30–200 eV. Within ~100 minutes of the sample exposure, the several-micrometers-thick layer with such a surface structure can form. The mechanism for the filamentary nanostructures formation has not been completely studied; the most realistic theoretical model for the fuzz growth [6] considers the intense motion of adatoms over the surface under conditions of high-power plasma load onto the surface.

Figure 2. Nanostructured “fuzz” on the tungsten surface formed after processing with plasma in the PLM plasma facility [7, 8]; the fibers are ~20 nm in diameter.

Experimental results show that it seems promising to develop the technology for producing the nanostructured surfaces on the pacemaker electrodes. We plan to use this technology at the PLM plasma facility [7, 8] for the ruthenium coating deposition on the ECEs by means of sputtering of the ruthenium target in plasma and further redeposition of the sprayed material on the mock-up substrate (made of materials used for ECE). Such a scheme of material redeposition in the plasma facility will provide conditions for the growth of a nanostructured surface of the “fuzz” type.

We propose the following technological methods using the plasma treatment to provide the most optimal manufacturing of the nanostructured ruthenium surface.

(i) To create the “fuzz” nanostructure on the titanium surface, and then spray ruthenium onto this structure. In this case, the thickness of ruthenium coating should not exceed the distance between the fibers (~ 30 nm) in order to preserve the “fuzz” structure on the surface.

(ii) To spray (or chemically deposit) the ruthenium layer with a thickness of more than 10 µm onto the titanium substrate; after this, the "fuzzed" ruthenium surface will be formed in the course of the plasma processing.

(iii) To create the “fuzz” structure by irradiating the substrate surface with helium ions, and to simultaneously sputter ruthenium.

Recently, it was shown [9] that the deposition of metal onto the substrate during its irradiation with helium ions leads to the decrease in time of the “fuzz” structure formation. During this process, the growth rate of the “fuzz” layer thickness increases exponentially with time, and the “fuzz” density decreases with time, reaching a density of three orders of magnitude less than the density of solid...
material. It is a result of the preferential deposition of atoms onto the exerted fibers, which results in their rapid growth. Thus, it is possible to affect the porosity of the structure and optimize it for the purpose of forming the ECE surface. The third method (3) seems to be the most promising.

The listed approaches will be tested in experiments on the PLM plasma facility. The ruthenium coatings will be applied to the titanium substrates with sizes of $5 \times 5 \times 1 \text{ mm}^3$ loaded in the helium plasma discharge. The plasma parameters are as follows: $T_e = 2\pm 5 \text{ eV}$, and $n_e = (1\pm 5) \times 10^{12} \text{ cm}^{-3}$. The samples will be studied using (1) the microscopic analysis, (2) analysis of the frequency spectrum of the complex resistance (see [2]), and (3) analysis of the electrochemical properties accompanied by the further biocompatibility testing.

4. Conclusions
In this paper, a new approach is proposed for the production of the nanostructured surface of the pacemaker endocardiac electrode. For the first time, we propose to use ruthenium Ru for covering the endocardiac electrode. Ruthenium is a chemical analogue of iridium and platinum used for the ECE production, but it has several technological advantages. Ruthenium is the only one of these elements naturally present in the human body. In the PLM facility of the National Research University “MEI”, a nanostructured ruthenium coating can be formed on the electrode by sputtering the Ru target simultaneously with plasma processing. It is proposed to test several approaches, including the creation of the “fuzz” nanostructure on the titanium surface and subsequently spray ruthenium onto this nanostructured fuzz layer; or formation of the “fuzz” structure on the pre-deposited ruthenium layer. Such experiments contribute to developing new technology for manufacturing the electrocardiac pacemakers with improved characteristics.

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