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Study of electrochemical properties of thin film materials obtained using plasma technologies for production of electrodes for pacemakers

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Abstract. Studies of thin film materials (TFM) as coatings of tips of pacemaker electrodes implanted into the human heart have been performed. TFM coatings were deposited in vacuum by arc magnetron discharge plasma, by pulsed discharge of “Plasma Focus”, and by electron beam evaporation. Simulation of electric charge transfer to the heart in physiological blood-imitator solution and determination of electrochemical properties of the coatings were carried out. TFM of highly developed surface of contact with tissue was produced by argon plasma spraying of titanium powder with subsequent coating by titanium nitride in vacuum arc assisted by Ti ion implantation. The TFM coatings of pacemaker electrode have passed necessary clinical tests and were used in medical practice. They provide low voltage myocardium stimulation thresholds within the required operating time.

Electric cardiac pacemakers implanted into human heart are used to treat heart arrhythmia. The modern pacemaker is an intellectual device that analyzes the patient condition at the lowest consumption of electric power. The pacemaker is implanted into human body inside a titanium capsule under the collarbone. The endocardiac electrode (ECE) of the pacemaker is drawn through the subclavian vein into the ventricle of the heart. The cathode tip ECE is pressed against the His-Purkinje nerve center. Due to current flow through the heart tissue, a double electrical layer (DEL) is formed near the cathode where charges of the blood electrolyte are separated. The equivalent scheme of the current flow is shown in figure 1.

The active resistance of the circuit - R_Σ is a sum of all series resistances of the human body R_{hb}, wires R_w, thin film on the electrode R_{tf} and a shunt R_s used in the current measurements. The Faraday resistance of DEL - R_f measured in experiment is approximately 10^3-10^4 Ohm and it is significantly larger than R_Σ. In this case, in conditions of direct current, the voltage drop on DEL is practically equal to the voltage of the power source.

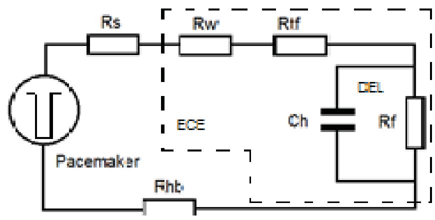

Figure 1. Schematic circuit of current flow from the pacemaker into a human body.

In the case of impulse voltage applied, electric capacitance of DEL must be taken into account. The electric capacitance of the cathode tip is much smaller than that of the anode tip ECE due to larger specific surface of the anode. During a short heart stimulating impulse (10^{-3} - 10^{-4} s), the drop of the voltage on the anode is much less than that on the cathode. Therefore, electrochemical processes near the anode can be neglected. Within a lapse time, the Helmholtz capacitance of DEL near the cathode, shorts Faraday resistance, and decreases ECE impedance significantly. Periodically repeated electric impulses of stimulation are mathematically represented in the form of super-position of harmonics with frequencies proportional to the heart frequency. For the harmonic with frequency ω, the impedance $Z(j\omega)$ of the equivalent current is: $Z(j\omega) = R_\Sigma + R_f/(1+j\omega R_f C_h)$.

At $\omega R_f C_h \rightarrow 0$, the impedance is maximum and is equal to $R_\Sigma + R_f$, and at $1/\omega R_f C_h \rightarrow 0$, it has minimal value equal to R_Σ. The above analysis shows that increase of the cathode capacitance C_h is a way to promote the charge transfer to the human body. Increase of the capacitance can be realized by increase of the specific surface of the electrode, which is in contact with the blood electrolyte. As it is shown in [1,3], vacuum PVD technologies of film deposition make it possible to produce the surface with highly developed structure of micro- and nano-sized pores (porous, columnar, fractal, etc.).

To coat tips of pacemaker electrodes, several PVD technologies were used: electron beam evaporation (EB PVD), magnetron sputtering (MS PVD), and evaporation in stationary and impulse arc (ARC PVD) produced in "Plasma Focus".

Coatings were deposited on disc samples with diameter of 9 mm. Generally, titanium nitride was deposited. The thickness of PVD coating, measured in the cross-section, varied within 3-5 µm. In the case of ARC PVD, samples were preliminary sand blasted, then titanium powder was deposited in Ar plasma torch at atmospheric pressure. In dome cases, 80 keV titanium ion beam was used for finish treatment of the coating to produce nano-sized structure.

The coating properties in physiological solution were controlled in the electrochemical cell. The cell was powered by harmonic and impulse electric signals with the maximum voltage amplitude of 5 V. The cyclic volt-ampere characteristics (CVAC), the amplitude-frequency characteristics (AFC), and the transient characteristics were measured at pulsed voltage applied. In most cases, CVAC had a form of ellipse, the main axis of which determines the active reactive components of the current flowing through the cell.

Table 1 shows the results of the transition impedance change of AFC measurement of TiN samples, not coated–Z_1 and coated–Z_2 by ARC PVD technology. Table 2 shows the Helmholtz capacitance and the impedance of samples coated using different methods.

Though EB PVD technology demonstrated good capacitance, we did not use for production of pole pieces of pacemakers. We have not managed to obtain good adhesion and heterogeneity on the surface. Besides, it is difficult to coat very shapy surfaces.

Impulse ARC PVD seems can give good results, but this technology needs further research. Besides, the installations are rather complex, and the production must be expensive. There are no industrial impulse ARC PVD facilities yet.

MS PVD technology has many industrial applications, and it was used by W.C. Heraeus GmbH & Co. KG, Hanau, Germany for coating of pacemaker electrodes [3]. The drawback of this method is the high consumption of the target material. Only 30% of the target is used before its replacement, and not all sputtered material is deposited on the parts under deposition. This makes the production expensive in the case expensive materials (Pt, Ir) are used.

Table 1. Ratio of impedances of samples without coating – Z_1 and with ARC PVD coating – Z_2.

f, Hz	1	2	3	4	5	5	7	8	9	10
Z_1/Z_2	5.41	3.87	2.98	2.44	2.16	2.00	1.87	1.78	1.72	1.64

Table 2. Electrochemical properties of coatings obtained by different PVD technologies.

f, Hz	EB PVD TiN		MS PVD TiN		ARC PVD TiN		ARC PVD(impulse) “Plasma Focus”-Ti	
	C_h, μF	*Z*, Ohm	C_h, μF	*Z*, Ohm	C_h, μF	*Z*, Ohm	C_h, μF	*Z*, Ohm
2	20-25	2600-1600	7-20	1100-2400	7-18	850-1200	7-25	1600-2600
10	7-9	900-1100	2-6	700-2000	1.5-4	600-1000	3-9	700-1900
100	0.2-0.3	600-750	0.2-0.3	550-1100	0.15-0.25	570-950	0.5-1.3	500-1100

ARC PVD technology is more suitable for pacemaker electrodes production. In this case, TiN is synthesized in large volume of a vacuum chamber, the target material is used effectively (100% practically), and the production cost is low [4]. To make the adhesion better, the substrate was preliminary sand blasted to produce a coarse surface. Before TiN vacuum deposition, Ti powder coating of the thickness of 100 μm was deposited at atmospheric pressure from argon plasma torch. The roughness of such Ti layer is connected with the size of the powder particles. A 5 μm thick TIN coating with the columnar structure was deposited on this surface by ARC PVD technology. The last stage of the coating production is treatment of the surface to the depth ~ 200 nm by titanium ions with the energy of 50-80 keV. The biocompatible coating with large surface named “*Cardiocotin*” was produced by this method.

The “*Cardiocotin*” coating formed on tips of ECE are protected by [5,6]. Results of tests of ECE with “*Cardiocotin*” coating were compared with results of tests of ECE of other producers, and results are showed in figure 2. At the frequencies exceeding 5 Hz, the ratio of the capacitance current to the total current through ECE is the most high if “*Cardiocotin*” is used. Decrease of the performance for frequencies below 5 Hz is connected with formation of oxides on titanium during the anode operation cycle, which is known as the “valve effect”.

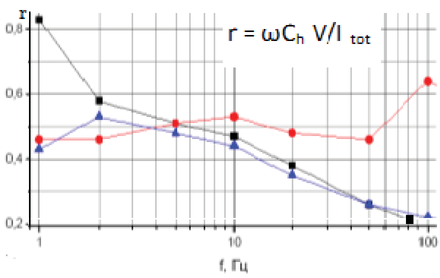

Figure 2. Ratio of ECE capacitance current to the total current as a function of frequency for ECE produced by “Cardiocotin” (red points) and ECE produced by St. Jude Medical Corp., USA (black) and Cardioelectronics Ltd., Russia (blue).

Clinic tests of electrodes with “*Cardiocotin*” coating were performed in 2007 and in 2013 and gave positive results. Figure 3 shows two basic parameters of ECE during clinic tests that determine ECE operation efficiency, namely, volt stimulation threshold (ST) of myocardium contraction stability and average for the ECE impedance impulse measured under GOST 31582-2012. The low level of ST shows stable work of biocompatible material of coating in the human body during six months. High level of impedance of ECE means high efficiency of transformation of energy and increase of the life time of pacemakers battery.

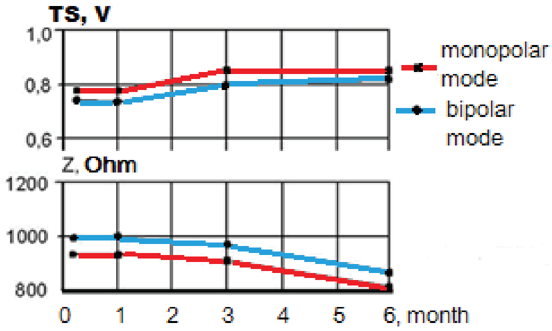

Figure 3. Results of control myocardium stimulation threshold (ST) and ECE impedance (Z) during clinic tests.

Based on clinic tests, “Cardiocotin”, produced by Cardioelectronics Ltd, Klimovsk, is used in medical practice since 2013.

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