APPLICATION OF ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY IN ANALYSIS OF SiO_2 LAYER USED FOR IMPLANTS IN BONE SURGERY

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Introduction

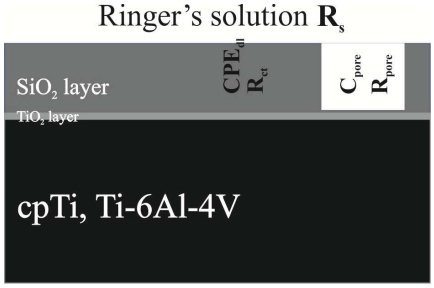
To provide the desired morphological structure and physicochemical properties of the metallic biomaterial manufacturing conditions of the surface layer involving the Si and O_2 were developed [1]. As a substrate material pure titanium cpTi (Grade 4) and Ti6Al7Nb alloy were analyzed. Tested materials met all the recommendations of the normative regarding the chemical composition, structure and mechanical properties (ISO 5832-2, ISO 5832-11), which was verified by preliminary tests [1]. Surface modification of biomaterials was carried out using a low-temperature surface treatment – sol-gel. The application of such surface treatments had no effect on the structure and mechanical properties of the substrate material. In a final step the samples were subjected to steam sterilization.

Materials and Methods

To determine the effect of SiO_2 layer to improve corrosion resistance of cpTi and Ti6Al7Nb impedance test was proposed, which was carried out in Ringer's solution (T = 37 ±1°C, pH = 6,8 ±0,2). The measurements were performed using a potentiostat AutoLab PGSTAT 302N along with a set of electrodes provided with the module FRA2 (Frequency Response Analyser). The measuring system that was used during the study enables research in the frequency range $10^4 \div 10^{-3}$Hz. The voltage amplitude of the sinusoidal excitation signal was 10 mV. In order to assess coating density of the surface layer and also the amount of ions infiltrating from metallic substrate to Ringer solution, metallic ions permeability tests were performed. The amount of ions Ti, Al, Nb and Si that infiltrated to the solution was designated. Each sample was placed for 28 days in 100ml of Ringer solution at the temperature of T = 37±1°C. Metallic ions concentrations were measured with spectrometer JY 2000, by Yobin – Yvon, applying ICP-AES method. The source of induction was plasma torch coupled with generator of frequency 40.68 MHz. When making analytical curve, diluted analytical materials by Merck were applied.

Results and Discussion

The impedance characteristics of the interface: electrode-layer-solution was established through approximation of the experimental EIS data, with the use of a pattern presented in FIG. 1, TABLE 1 and the mathematical model of an equivalent electric circuit. Such model describes drawing of two loops in Nyquist plots. The loop recorded at high frequency, where the diameter of the loop depends on the potential, corresponds to activity of the oxide layer (SiO_2/TiO_2). It is represented by C_{pore} - the capacity of the surface area material having a high degree of surface development and R_{pore} - reflecting the resistance of the electrolyte in the zone of the material. Whereas the low-frequency loop is associated with the oxide layer solution interface, where R_{ct} and CPE_{dl} sub-circuit describes the low-frequency region between 1 and 0,001 Hz.



$$Z_{CPE} = (jwC)^{-a}$$

FIG. 1. Characteristics of the system SiO_2/TiO_2 layer – metallic substrate

TABLE 1. Results of EIS.

Sample	R_s, $\Omega \cdot cm^2$	R_{pore}, $k\Omega \cdot cm^2$	C_{pore}, μF	R_{ct}, $k\Omega \cdot cm^2$	CPE_{dl}	
					Y_0, $\Omega^{-1}cm^{-2}s^{-n}$	n
cpTi	16	9	17	668	0,2587E-4	0,88
cpTi +SiO_2	17	15	29	4485	0,4879E-4	0,96
Ti6Al7Nb	16	7	28	541	0,9029E-5	0,91
Ti6Al7Nb +SiO_2	16	17	33	3369	0,5589E-5	0,92

A mathematical model of the system consisting of Ti alloy- TiO_2/SiO_2 layer-Ringer solution is expressed by the equation (1)

$$Z = R_s + \frac{1}{\frac{1}{R_{pore}} + j\omega c_{pore}} + \frac{1}{\frac{1}{R_{ct}} + Y_0(j\omega)^n} \qquad (1)$$

In turn, the results obtained from the samples bearing a layer of SiO_2 indicate a more compact construction with respect to the passive layers (TiO_2) formed on the titanium substrate. Regardless of the type of substrate, there was no change in the nature of the layer. The resistance of the oxide layer R_{ct} takes large values, reflecting the favorable properties of the samples with a SiO_2 layer. In turn, taking the amount of degradation products infiltrating a Ringer's solution, as an important criterion indicating the level of biocompatibility of a material it should be noted that the SiO_2 layer has the effect of increasing the barrier properties. It has been found that the amount of ions (Ti, Al, Nb) penetrating to a solution of the sample surface covered with a layer of SiO_2 is reduced. This is a positive phenomenon TABLE 2.

TABLE 2. Results of the tests of metallic ion penetration

Sample	Metallic ions infiltration tests, ppm (average value)						
	Ti	SD	Al	SD	Nb	SD	Si
cpTi	0,201	±0,001	-	-	-	-	-
cpTi +SiO_2	0,089	±0,002	-	-	-	-	
Ti6Al7Nb	0,104	±0,001	0,055	±0,001	0,069	±0,002	
Ti6Al7Nb +SiO_2	0,059	±0,001	0,011	±0,002	0,022	±0,001	

Conclusions

Proposing appropriate variants of surface treatment using a sol-gel method has a prospective importance and contributes to the development of technological conditions for precisely formulated parameters of the silica coatings on titanium implants.

References

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