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Influence of bone union electrostimulation on corrosion of Ti6Al4V ELI alloy implants

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Materials

ABSTRACT

Purpose: The aim of the work was determination of influence of the selected methods of bone union electrostimulation on corrosion of Ti6Al4V ELI alloy implants.
Design/methodology/approach: In vitro tests were carried out with the use of different methods of electrostimulation – invasive, semi-invasive and non-invasive. The alternating current without constant component was applied. The influence of electrostimulation on corrosion of implants was evaluated on the basis of the mass measurements and surface observations.
Findings: On the basis of the research no significant corrosion on the samples was observed. Only local surface etching was observed, however it didn't cause measurable change of mass. The presence of metallic ions in the solution was revealed.
Research limitations/implications: Lack of visible and measurable corrosion requires the change of the methodology. Further research should be focused on the amount of metallic ions dissolved from the implants. Furthermore, it should be emphasized that the absence of corrosion of the electrostimulated implants is only one of many criteria describing the usefulness of electrostimulation parameters. The basic criterion is the biological effect obtained as the result of the electrostimulation.
Practical implications: The obtained results are the basis for selection of methods and current parameters of the bone union electrostimulation in further clinical research (for stabilizing elements made of titanium alloys). Positive results of the in vitro research confirmed in tests in animals can enable further clinical tests. Positive results of the clinical tests could enable the bone union electrostimulation applied in pathological fractures in patients allergic to Cr. Allergy to Cr and Ni limits a wide use of implants made of Cr-Ni-Mo steel.
Originality/value: The paper is a continuation of the research on determining safe parameters of bone union electrostimulation of implants made of stainless steel coated with the passive and passive-carbon layers.
Keywords: Biomaterials; Ti6Al4V ELI alloy; Corrosion; Electro stimulation; Union bone

1. Introduction

Titanium alloys due to low density and higher biocompatibility, in comparison to commonly used stainless steels and cobalt alloys, are widely used in medicine. Long-term research on titanium alloys allowed to work out standardized requirements needed to apply the alloy on short-term implants [1- 4].

Table 1.
Comparison of chemical composition of the tested Ti6Al4V ELI alloy to requirements of the ASTM F – 136 standard

Element	C	N	H	Fe	O	Al	V	Ti
According to the Standard	max 0.08	max 0.05	max 0.012	max 0.025	max 0.13	5.5 ÷ 6.5	3.5 ÷ 4,5	balance
sample	0.0013	0.001	0.001	0.021	0.011	6.07	4.05	balance

Table. 2.
Chemical composition of electrolytical polishing bath

Components	H_2SO_4	HF	Ethylene glycol	Acetanilide
quantity	20-70 % vol.	5-30 % vol.	10-20 % mass	0-40 % mass

Table 3.
Chemical composition of the Tyrode's physiological solution

Components	NaCl	$CaCl_2$	KCl	$NaHCO_3$	NaH_2PO_4	$MgCl_2 * 6H_20$
quantity, g/dm^3	8	0.20	0.20	1.0	0.05	0.10

The most often used Ti alloy is the Ti6Al4V ELI alloy. It is diphase alloy (α+β) – enhanced Ti6Al4V alloy. The alloy is characterized by wide passive range, significantly exceeding potentials in a living organism (in neutral conditions). Improvement of corrosion resistance is obtained by surface treatment including mechanical working, electrolytical polishing and anodic oxidation. The surface treatment reduces surface roughness and creates an oxide layer consisting of titanium, aluminum and vanadium oxides [5].

The external osteosynthesis is characterized by elasticity of fixation. Elastic fixation enables to use electromechanical effects that activate a bone union. The electromechanical effects are based on generation of electrical potentials as a result of loading, that enables a passage of action current through a fracture site. The passage of current causes the transportation of mineral matter that lead to the activation of the bone union. Electrical phenomena in bones (present during anatomical loading) allowed to use electrical current as the factor stimulating an osteogenesis [6]. The electrostimulation of bone union depend on the replacement of action currents with the currents generated by the electrostimulator. On the basis of many research it was observed that the electrostimulation of bone union is advisable in pathological conditions like pseudarthrosis, delayed bone union, osteoporosis caused by underload and other [7-9]. However, the electrostimulation can lead to the corrosion of implants [10].

Influence of different methods and current parameters of bone union electrostimulation on corrosion of stainless steel implants with passive and passive-carbon coatings in in vitro conditions was previously investigated by the author [11].

Due to number of patients allergic to alloying elements of stainless steel, titanium alloys are widely introduced as implants applied in bone fractures treatment. This tendency inclined the authors to research the influence of electrostimulation conditions on corrosion of titanium alloys.

2. Methodology

Diphase Ti6Al4V ELI alloy (manufactured by President Titanium & Stell Co) was aplied in the research. Chemical composition, structure and mechanical properties met the appropriate standard. Comparison of chemical composition of the Ti6Al4V ELI alloy to requirements of the ASTM F–136 standard was presented in Table 1.

The research was carried out on cylindrical samples of diameter equal to 6 mm and length equal to 40 mm. The applied surface treatment consisted of grinding (abrasive paper 120–600), electropolishing and anodic passivation. The electrolytical polishing was carried out in a bath of chemical composition presented in Table 2. Temperature of the bath was in the range 25–50 °C and anodic current density was in the range 60–100 A/dm^2. Time of the process was 5–30 minutes. After the electropolishing the samples were passivated [12-14]. The passivation process was carried out in the bath at room temperature and voltage was in the range 20 to 80 V in 5–30 minutes. The obtained surface was characterized by roughness less than Ra < 0,16 μm.

In order to carry out the research on influence of different methods of electrostimulation on corrosion of Ti based implants a research stand, enabling electrostimulation in physiological-like conditions was used [15]. Samples were immersed in 300 ml containers filled with Tyrode's physiological solution of chemical composition presented in Table 3.

Three methods of electrostimulation were applied. In an invasive method, the samples were electrodes directly connected to the current generator. In this method 10 samples were used.
In a non-invasive method two PtIr electrodes were applied. Two variants of passage of current were applied:

1) Samples connected with a wire in order to ensure electric contact (2 samples),
2) Free samples (2 samples).

In a semi-invasive method one sample was used as electrode and another one was in the passage of current region. The second electrode was made of PtIr. In this method 4 samples were applied.

The distance between electrodes, in all methods, was equal to 40 mm. The electrostimulation was carried out in the Tyrode's physiological solution at the temperature of T = 22 °C ± 1°C and pH in the range 7.6–8.6.

In order to ensure similar current conditions for all tested variants, all electrodes were connected in series with an electrostimulator. The electrostimulator generated a run of current as an alternate pulse train A exp-(t/t_0) of amplitude 80 μA, a time constant t_0=0.2 s and frequency equal to 1 Hz.

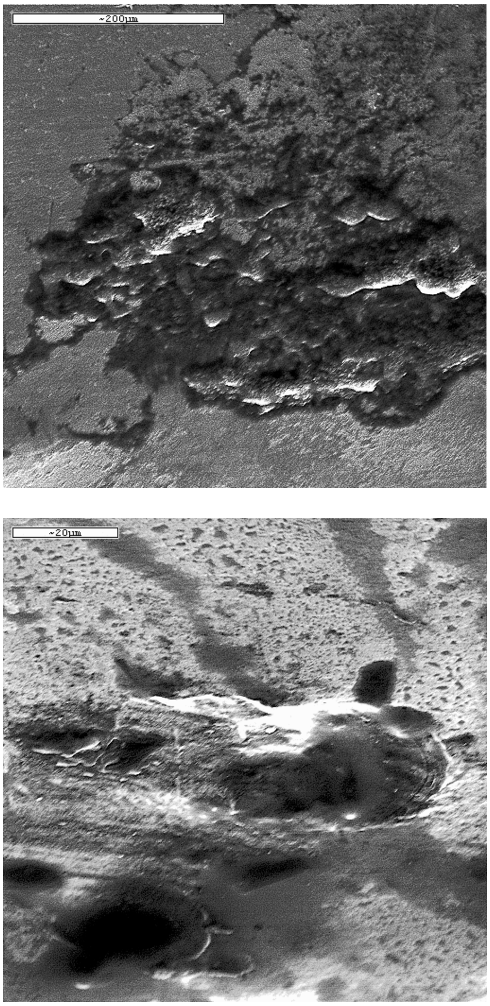

Fig. 1. Corrosion damage of the sample's surface after 28-day in vitro electrostimulation in the Tyrode's physiological solution, SEM

The samples were weighed with the use of WA34 TYPE PRL T A14 scales with accuracy $5x10^{-5}$ g. Microscopic observations were carried out with the use of the scanning electron microscope OPTON DSM 940. Before tests all samples were ultrasonically cleaned. The electrostimulation lasted 28 days and was conducted in a continuous manner (24 h/day). After the 28-day electrostimulation repeated observations and mass measurements were carried out.

Furthermore, in order to asses the amount of Ti, Al, V and Fe ions released to the Tyrode's solution after the 28-day electrostimulation, the inductively coupled plasma atomic emission spectrometry (ICP- AES) was applied. The investigations were carried out in Spectrometric Laboratory of Institute of Applied Geology of the Silesian University of Technology. The JY 2000 (Yobin – Yvon) emission spectrometer was used. Source of induction - plasma torch (argon) connected with the generator of frequency 40.68 MHz.

Optical system of the spectrometer enabled to determine many elements simultaneously. Evaluation of heavy metals with the use of the ICP- AES is a typically comparative method. Therefore, the crucial stage following the analysis is calibration with the use of model samples of known chemical composition.

In order to obtain a calibration curve, appropriate diluted model materials (Merck) of certified chemical composition were applied. The curve was obtained on the basis of 8 points from model samples for analyzed elements: 0.2 ppm; 0.5 ppm, ppm, 1.5 ppm, 2 ppm, 3 ppm, 5 ppm, 10 ppm. The obtained calibration curve was the basis for further analyses.

In order to remove matrix effects (ei. interference of analytical lines of "non-interesting" elements) the background removal method was applied (software option of the JY 2000 spectrometer).

The length of characteristic emission lines for Ti, Al., V and Fe was equal to 336.121 nm, 257.51 nm, 202.03 nm, 238.204 nm respectively.

Results of concentration of respective elements are average values of 10 measurements and are given with relative standard deviation.

3. Results

Mass measurements after 28-day in vitro electrostimulation in the Tyrode's physiological solution revealed no change of the samples' mass.

Macroscopic observations revealed no corrosion damage on surfaces. However, microscopic observations carried out with the use of the scanning electron microscope revealed small corrosion damage. The corrosion damage was characterized by small dimensions and was similar to local etchings (Fig. 1). The damage was observed for all the samples (independently of the applied method).

Investigations of the Tyrode's physiological solution with the use of the ICP- AES method revealed the presence of Ti, Al., V and Fe ions. The presence of the ions was observed both in a new physiological solution and the solution used in the investigation of influence of different methods of electrostimulation on corrosion of the Ti6Al4V ELI alloy. The presence of metallic ions in the new physiological solution shows the poor quality of distilled water used in the investigation. Results of ion concentration in the Tyrode's solution before and after the investigation, taking the applied method into consideration, are presented in Table 4.

4. Discussion

The results of 28-days electrostimulation, stating the presence of only local surface etchings and lack of measurable mass changes suggest that the bone union electrostimulation with alternating pulses is safe for patients (form the point of view of possible implants' corrosion). However, the investigations of the chemical composition of the solution after the electrostimulation showed that amount of infiltrated metallic ions, in every method, was equal about 3 mg.

The obtained, divergent results of the mass measurements and concentration of metallic elements in the physiological solution suggest that the electrostimulation is accompanied with deposition of chemical individuals. This indicates the necessity of additional investigation of the samples' surfaces both before and after the electrostimulation. The total concentration of metallic ions after

Table 4.
Concentration of metals In the Tyrode's solution (ICP- AES)

		Ion concentration [ppm] and relative standard deviation [%]								Total concentration
		Ti		Al		V		Fe		
Tyrode's sloution	1	0.01	0.1	0.4	1	0.002	0.16	0.5	0.72	0.912
Electrostimulation method										
Invasive	1	5.60	0.22	4.11	0.26	0.24	0.08	0.85	1.80	10.83
	2	5.50	0.36	4.10	0.63	0.28	0.25	0.84	0.88	10.71
	3	5.45	0.42	4.90	0.77	0.27	0.22	0.85	0.38	11.50
	4	5.47	0.15	4.17	0.99	0.28	0.09	0.85	0.61	10.78
	5	5.43	0.26	4.91	0.81	0.28	0.21	0.85	0.02	11.48
Semi-invasive	1	5.34	1.20	4.28	2.40	0.28	0.16	0.84	0.45	10.73
	2	5.64	0.24	4.14	0.31	0.24	0.06	0.84	0.33	10.89
Non-invasive										
-Electric contact	1	5.22	0.56	4.19	0.41	0.28	0.20	0.82	0.31	10.51
-No electric contact	2	5.23	0.49	4.27	0.57	0.24	0.29	0.83	0.46	10.58

the electrostimulation was higher than 10.5 ppm and the values were similar for all the applied methods and variants of electrostimulation. The obtained results were more than 10 times higher than the ones obtained in the new prepared Tyrode's solution. Unambiguous estimation of the obtained results needs further research. It is also necessary to determine admissible amount of metallic ions that can infiltrate from implant to organism.

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