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A. Demczuk, B. Swieczko-Zurek, A. Ossowska

Gdansk University of Technology, Faculty of Mechanical Engineering, Department of Materials and Welding Technology, Narutowicza 11/12, 80-233 Gdansk, Poland
beazurek@pg.gda.pl

CORROSION RESISTANCE EXAMINATIONS OF Ti6Al4V ALLOY WITH THE USE OF POTENTIODYNAMIC METHOD IN RINGER`S AND ARTIFICIAL SALIVA SOLUTIONS

ABSTRACT

The research results of corrosion resistance of the Ti6Al4V alloy in the simulated body fluids (SBF) are presented. The polished specimens have shown better corrosion resistance than grinded surfaces in both liquids. The artificial saliva has revealed more aggressive test solution than Ringer`s solution. The pitting tendency has been observed in Ringer`s solution for grinded specimens.

Key words: Ti6Al4V alloy, corrosion resistance, potentiodynamic methods, Ringer`s liquid, artificial saliva

INTRODUCTION

The material used for implants should be [1]: biocompatible, corrosion resistant, resistant to the static and dynamic loading and possess the good workability. Considering all these properties some specific metals and alloys have been chosen for safe use in the surgical treatment. Steady research of the materials results in improving their qualities and discovering the new ones. The largest group of those materials are the metallic biomaterials: Cr-Mo-Ni steels of austenitic structure, titanium and its alloys, alloys on Co bases, tantalum, niobium and their alloys, noble metals and shape memory alloys. Apart from them other metals such as: ceramics, carbon, polymers and composites, as well as resorbable materials are used [2].
The basic property, which enables the use of metal as an implant is its biotolerance, that is the mutual interaction between implant – tissue – body liquids. The implant reactions are different and depend on the kind of implant, the place and the way of implantation. The cooperation between the implant or the group of implants and the tissue is reciprocal [3].
The materials inserted into the body must show bioelectrical conformability, that is, should have the suitable electric and magnetic properties similar to those of the body they have been introduced into [4]. To make an implant biocompatible the following factors should be taken into consideration: the kind of the material, the characteristics of the surface, its shape and susceptibility to different kinds of destruction.
One of the major problems in the proper choice of the implant material is corrosion resulting from the aggressive character of the body liquids, which contain on: chlorine, sodium, potassium, calcium and magnesium ions and phosphates. The aggressive character of the

liquid environment stimulates the presence of organic substances like proteins [2]. Other factors and affecting corrosion are: the body temperature, the loading and the tribological conditions. They also accelerate the corrosion. Under the natural conditions the body pH is 7.4. However, after introducing an implant the pH may show the acid value. All the previously mentioned features create very demanding environment, which only some materials can satisfy [5,6].

Owing to the use of modern materials the corrosion resistance has been achieved by the formation of oxygen layer, which prevent the material from corrosion. Within a few seconds there appears a thin passive layer on the surface of the material. In the case of titanium the layer is 2-5 nm thick and it grows until it reaches 6-10 nm. The corrosion occurring on the surface is of cathodic and anodic character. Anodic reaction occurring on the surface releases the metal ions into the environment, while the cathodic reaction depends on the presence of electrolytes. The cathodic reaction causes the reduction process using the electrons created in anodic process. The higher electrochemical potential of the metal is, the more resistant it is to corrosion processes occurring in the working environment [5,7,8].

The corrosion occurring in the body may result in [6-8]:

- shortening the duration of the implant in the body, limiting the possibilities of loading transfer;
- the degradation products may cause undesirable reactions resulting in the rejection of the implant, the metal ions released into the surrounding tissues may be of toxical character;
- possibility of appearing pain as the effect of penetrating the corrosion products into the surrounding tissues (without any inflammation);

The corrosion products enter the tissue environment as metal ions. They may affect the cells or get inside them. The local impact of the metal ions or the corrosion products on the tissues has been named metalosis by Nicole [9]. The lower solubility of the corrosion products of the introduced implant has the more advantageous it is for the body. The solubility of original products of alloys most frequently used in medicine [10] is presented in Fig.1

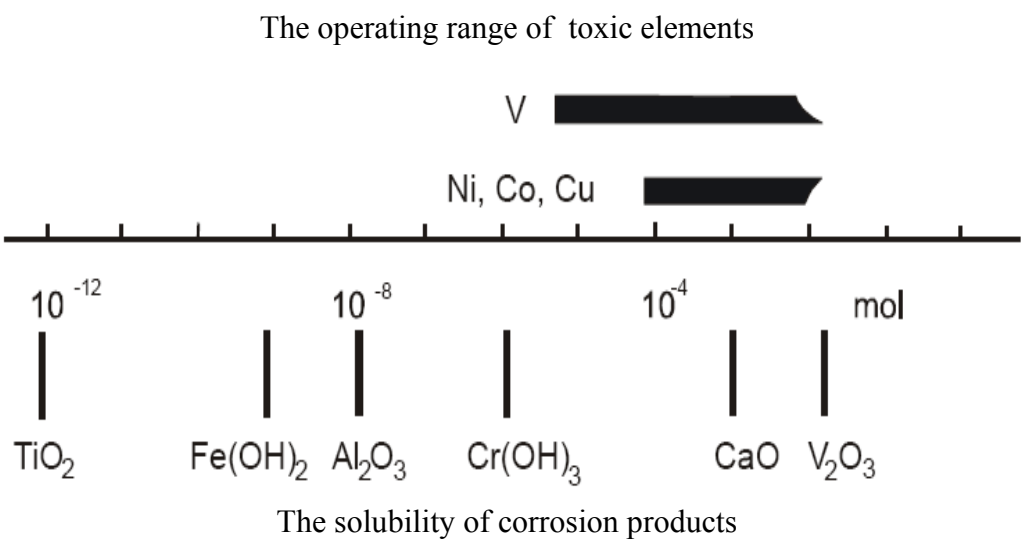

Fig. 1. The toxic operating range of corrosion products of implant alloys [10]

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High corrosion resistance is accompanied by good bioinertness. Such situation happens in case of vitality alloys accepted by the body in large amount. The toxic metals reveal the low corrosion resistance.
The proper choice of materials used in medicine means the formation of the structures, which are resistant against bioelectrochemical corrosion [9].
The corrosion occurs in strictly defined environment. The biological environment, in which the implant is placed has reactions typical of bioelectronical processes such as [1]: the biocurrent transfer, the change of the semiconductor polarization influenced by electromagnetical waves. The basic role concerns the semiconductor and piezoelectricity of the organic material in the biological environment. The transfer of the biological quantity happens on molecular level as: electrons, protons, ions or proteins movement. The electrical transfer in tissue environment is presented as electrical cells activity. It has great impact on the activity of nerve and muscle cells, and they in turn convey information. The loading can be carried together with the substance, which results in the creation of recurrent impulse as a difference in electrical potentials, for e.g.: electrodical, diffusal and cell [1].
The material introduced into the body has a direct contact with the body liquids. The pH factor ranges from 5.7 to 9.0, which depends on the duration of implants stay in the body and desirable healing process.
Every metallic implant will undergo corrosion in such environment [11]. The thickness of corrosion current ranges from 10^{-6} to 10^{-9} A/cm^2, which is equal to the corrosion rate expressed 10 to 0.01 μm/year [11-13]. The corrosion resistance of the materials used in medicine is estimated in potentiodynamic and potentiostatic research. In this way the walves of corrosion potential and the thickness of corrosion current are defined. It enables to foresee the behaviour of metals in corrosion environment.
The aim of present work is examining the corrosion resistance of Ti6Al4V alloy in the environment stimulating the body liquids.

MATERIALS AND METHODS

The electrochemical research aims at estimating the corrosion resistance of the material, which will stay in a definite corrosion environment. Owing to the research it is possible to gather in a short time the data concerning usefulness of the examined material for work in a defined environment. They also make it possible to estimate corrosion phenomena occurring on the metal, alloys or on protective surfaces.
Six specimens of Ti6Al4V alloy of 17,5x12,2x4 mm measurements were made and inserted into epoxy resin to prepare better the examined surface. All the specimens underwent polishing by the materials of different grinding powder granulation (from 150 to 1500). The surfaces prepared in this way were for three specimens (grinded), the remaining three specimens were polished using aluminium oxide and polishing (polished). After the polishing process the specimens were released from the epoxy resin. The composition of the Ringer liquid and artificial saliva is presented in tabl.1. The solutions have values of pH=3, 5 and 7.

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Table 1. *The Ringer`s and artificial saliva components (ISO 10271)*

SOLUTION	COMPONENT	CONCENTRATION [g/dm^3]
RINGER	NaCl	8.6
	KCl	0.36
	$CaCl_2$	0.48
ARTIFICIAL SALIVA	NaCl	0.4
	KCl	0.4
	$CaCl_2$	0.795
	NaH_2PO_4	0.78
	Na_2S	0.005
	Urea	1

RESULTS AND DISCUSSION

The figures above show the polarization curves obtained for Ti6Al4V with differently prepared surfaces in the solution of Ringer and artificial saliva.

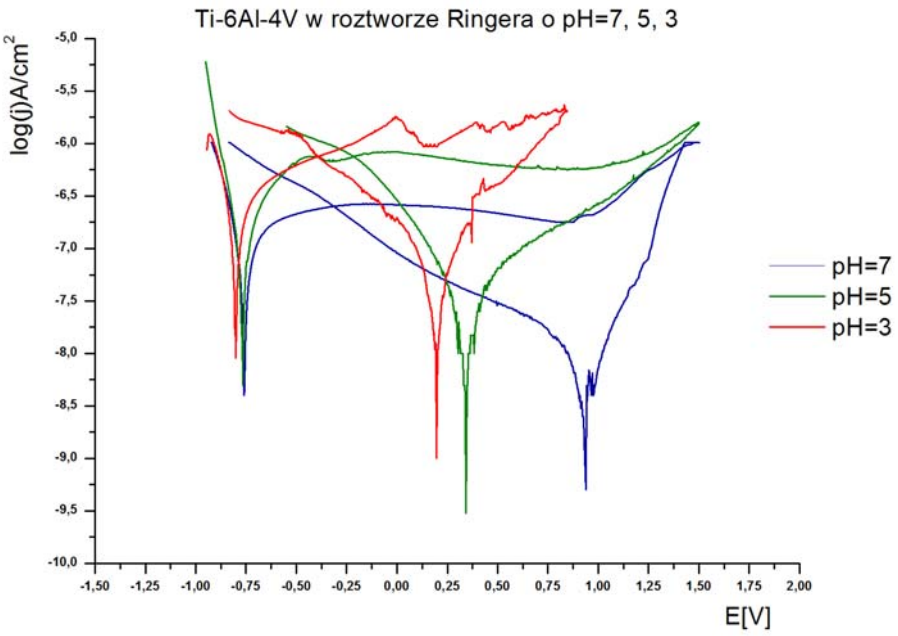

Fig. 2. The polarization curves for Ti6Al4V alloy with polishing surface in Ringer`s solution of pH=7,5,3

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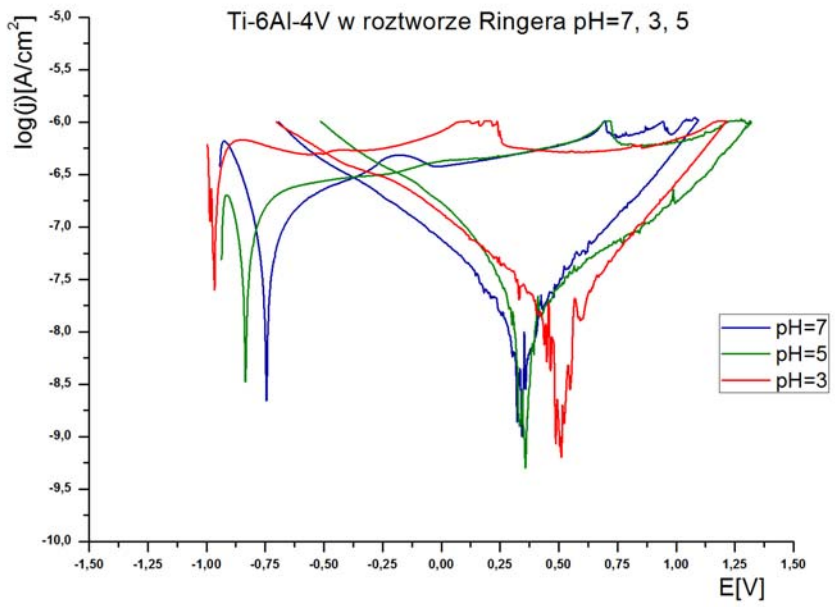

Fig. 3. *The polarization curves for Ti6Al4V alloy with grinding surface in Ringer`s solution of pH=7,5,3*

Table 2. *The results for polished and grinded specimens in Ringer`s solution*

RINGER	pH	POLISHED	GRINDED
E_{kor}[V]	7	-0.761	-0.743
	5	-0.765	-0.834
	3	-0.8	-0.965
I_{kor}[μA/cm^2]	7	0.004	0.0015
	5	0.005	0.002
	3	0.009	0.011
E_p[V]	7	-0.647	-0.575
	5	-0.695	-0.712
	3	-0.712	-0.875
I_p[μA/cm^2]	7	0.150	0.181
	5	0.320	0.191
	3	0.419	0.663

The obtained results show the higher corrosion resistance of the Ti6Al4V specimens with polished surfaces than those with grinded surfaces as examined in Ringer solution of different pH. The corrosion potentials of the polished specimens became more cathodic with decrease in pH and attain the difference about 0.03V. In the case of grinded specimens the decrease in corrosion potential is more pronounced being about 0.1V. Similar tendency reveals the passivation potential. Decrease in the solution density causes the shift of the passivation potential into cathodic direction. For grinded samples the change ranges from 0.15 – 0.2V whereas for polished surface the change of passivation potential is miner only about 0.02V. The corrosion current in both cases increases along with the decrease in pH and corresponds to the change of corrosion potential. The more cathodic potential, the higher corrosion current. The anodic current density corresponding to the potential -0.65V gradually increases with the acidification of solution for the polished and for grinded samples as well. The more

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aggressive the environment, the higher density of the anodic current is. This phenomenon is caused by the passive layer easier to form in the solution of higher pH. The grinded and polished samples faster undergo the passivation in acid environment and the potential range of passivity for both cases of the surface preparation is about 1V. Both polished and grinded samples didn`t show any corrosion changes. After taking out from the solution the surfaces were darker, indicating the formation of passive layer. Polished samples tended more to passivation. In the case of grinded samples passivation was lower. Bigger corrosion resistance of Ti6Al4V alloy with polished surface results from the fact of lower roughness of its surface.

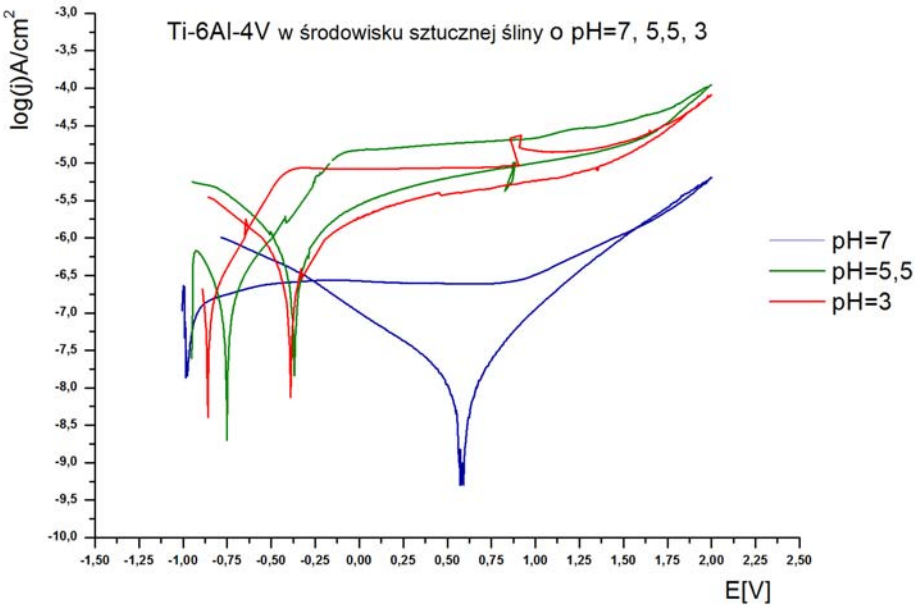

Fig. 4. The polarization curves recorded for Ti6Al4V specimens with polishing surface in artificial saliva solution of pH=7,5,3

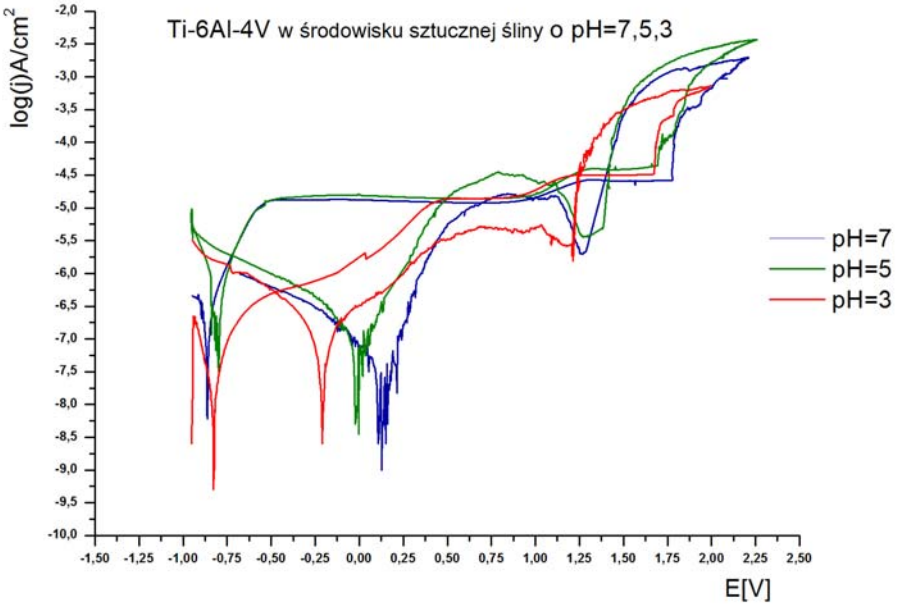

Fig. 5. The polarization curves recorded for Ti6Al4V specimens with grinding surface in artificial saliva solution of pH=7,5,3

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Table 3. *The results for polished and grinded specimens in artificial saliva solution*

ARTIFICIAL SALIVA	pH	POLISHED	GRINDED
E_{kor}[V]	7	-0.985	-0.862
	5	-0.751	-0.802
	3	-0.86	-0.827
I_{kor}[μA/cm^2]	7	0.014	0.006
	5	0.003	0.04
	3	0.004	0.005
E_p[V]	7	-0.886	-0.681
	5	-0.691	-0.693
	3	-0.848	-0.755
I_p[μA/cm^2]	7	0.21	4.63
	5	0.32	4.855
	3	1.01	0.2505

The obtained results indicates that the polished samples show the higher corrosion resistance in the environment of artificial saliva of different pH than the grinded ones. In the case of grinded as well as polished samples the corrosion potentials first tend to shift into anodic direction and then to the cathodic one at the pH=3. The change of corrosion potentials for polished samples equals 0.1 to 0.2V and for grinded samples it is about 0.02 to 0.06V. The passivation potential of grinded samples in more acid environment shifts for about 0.02 – 0.06V. The tendency of changing the passive potential for samples with polished surfaces is similar to that for corrosion potentials, that is at first it shifts to anodic direction, when pH decreases and than it becomes more cathodic. The corrosion current of grinded specimens rises along with the decreasing of pH, however, in acid environment sudden fall can be perceived. With the polished samples it is otherwise. The corrosion current initially falls down, while with the pH=3 some rise can be noticed. The density of anodic current with the potential -0.65V for polished specimens show the increasing dependence, while the solution is becoming more acid. The more aggressive the environment is, the higher density of anodic current results, which is caused by quicker formation of the passive layer. The polished and grinded specimens quicker undergo passivation in acid environment. The duration of the passivation process for grinded and polished surfaces in the potential unit is about 1-2V. After taking out of the liquid both surfaces were darker, which points to the formation of the passive layer. In case of grinded specimens the layer wasn't diversified. The polished specimens in Ringer liquid mostly tended to self-passivation. The analysis of the relevant literature indicates that in the passive range the passive layer consists of Ti_2O_3 and TiO_2 . In the polished specimens observed after the experiments, only the formation of the uniform layer has been observed. On the other hand, in grinded specimens the process of pitting corrosion occurred. The size of the pits depends on the environment in which they are in. In acid environment the pits were more numerous and deeper. In solution of pH=7 the pits are scarce, smaller and more shallow. There is no microdestruction of the surface. The Ti6Al4V alloy specimens with polished surfaces examined in Ringer`s liquid were more resistant to corrosion, which resulted from slight roughness of the surface.

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CONCLUSIONS

The studies of corrosion resistance of Ti6Al4V alloy by means of potentiodynamic method in the Ringer`s liquid and in the artificial saliva proved that:

- in both solutions polished specimens were more resistant to corrosion than the grinded ones;
- the artificial saliva causes more corrosion than Ringer`s liquid;
- the grinded specimens undergo pitting corrosion in the artificial saliva environment, but in Ringer`s liquid they are only covered with the passive layer;
- the materials used for implants should have the polished surfaces or have the additional covers;

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