CORROSION PROPERTIES OF POROUS TITANIUM SINTERES WITH SODIUM CHLORIDE

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Abstract

Materials for long term implants must be highly corrosion resistant. Corrosion resistance of surface is closely connected to biocompatibility of particular application. Surfaces of implants can also be treated for specific biological reaction of organism. The article is focused on corrosion properties of porous titanium with different level of porosity. This material was created by sintering titanium powder with different fraction of sodium chloride. Porous surface on implants from such material ensure high level of osteointegration of the implant into bone. The surface of the implant can be also treated additionally and this material is common for manufacturing of long term implants. Electrochemical corrosion behaviour of this material was tested and observed. Isotonic solution was used for these particular measurements. Open circuit (corrosion) potentials were found, corrosion rate and polarization resistance values were determined. Pitting potentials of depassivation and repassivation were also measured. Effect of porosity on corrosion properties was compared and discussed. Surfaces of samples were observed by light and electron microscopy before and after testing. EDS microanalysis were made on surface of tested samples and inside of corrosion pits.

Keywords: Porous titanium, biocompatibility, implants, electrochemical corrosion, polarization test

1. INTRODUCTION

Metallic materials are still most common used materials in fields like surgery, implantology and other specific medical disciplines. Especially a unique combination of mechanical properties makes metallic materials only suitable for constructing most of medical instruments or applications. For most stressed parts of implants like artificial joint head only high strength materials (Co-Cr alloys) can be used, but on the other hand for less stressed parts of implant like temporary support or stabilizers even special polymers can be applied [1, 2].

Usability of biomaterial is determined by its biocompatibility, which is closely connected to corrosion properties of specific biomaterial. If material is corroded during his contact with an organism, corrosion products are released into organism tissues. If these products are toxic or became toxic after reaction with organisms environment, they can cause pathological changes of different organism tissues. In this case material corrosion properties must be improved by surface treatment, unless this material can't be used in implantology because of high risk of allergies or other diseases [1, 3]. On the other hand there are applications where corrosion damage of material is acceptable or even required. These materials are used for construction of applications, which don't have to be removed. Material of application is degraded and metabolized by organism during his lifetime. According to interaction of material and body environment is this sort of materials called bioactive [3].

Long term implant application requires high corrosion resistance and higher strength for its proper function. Also specific interaction between implant surface and surrounding tissues is necessary for fixation of application. For this case implants from bio-inert material covered by bioactive layer started to be used. As a reason of significant difference between mechanical properties (Young modulus and tensile strength) of material used for implant construction and surrounding tissue, connection between implant surface and tissue cells can be disrupted or damaged in case of extreme mechanical loading of implant. It leads to functionality decrease of whole application [4]. Materials with mechanical properties close to tissue properties were developed during last couple decades. These materials can also have different porosity level in cross-section; core of material with low porosity level and high Young modulus is surrounded by material with higher porosity level and lower elastic modulus. Whole application manufactured from this kind of material is rigid enough to

carry all mechanical load without failure but the connection between material and surrounded tissues is stable and effective [5, 9].

Porosity of material can negatively affect corrosion resistance of material, which can be easily degraded by aggressive corrosion environment of organism. Especially risk of crevice corrosion is increased as a reason of pores geometry. Residues of pore forming agent can also negatively affect localized corrosion resistance, which is typical for non-noble metallic materials protected by corrosion resistant passive layer [6]. The aim of this present research is to compare corrosion characteristics sintered titanium material with different level of controlled porosity. Specimen without addition of pore forming agent was also tested for corrosion resistance. Relation between corrosion resistance and porosity was studied in this paper. There are corrosion properties of porous titanium and other titanium alloy (Ti6Al4V) compared in this paper. Ti6Al4V is also commonly used in implantology or for other medicinal purposes.

2. MATERIALS AND METHODS

Titanium with controlled porosity level was used for corrosion testing. Titanium sponge with a purity of 99.99% was crushed in ball mill to achieve particles of proper fraction. These particles were mixed with sodium chloride in specific ratio - addition 0 %, 10 %, 15 % and 25 % of pore forming agent was realized. After that specimens were stamped and pore forming agent were discharged in hot water. In the end samples were sintered in evacuated chamber. Details of manufacturing process were published earlier in [7].

For corrosion tests special samples were prepared. Small discs (dimensions 13 x 5 mm) were cut from sintered specimens. These discs were soldered to isolated copper wire and mounted by resin. After that front side of mounted sample were grinded on abrasive SiC papers of different grain sizes (120-250-500-800 and 1200) for proper surface state without any deep scratches. No polishing or etching was applied. Structure of tested samples can be seen in **Fig. 1**. Weight ratio of pore forming agent in each sample is demonstrated in **Table 1**.

Table 1 Weight ration of pore forming agent

Sample number	Ti-1	Ti-2	Ti-3	Ti-4
Structure ration of pore forming agent (wt. %)	0	10	15	25

For corrosion testing isotonic solution was used. This solution can simulate body environment and contains 0.9 wt.% of NaCl. All corrosion measurements were performed according to ASTM F 2129 standard [8]. Solution was tempered to 37±1 °C during all measurements. Capacity of glass corrosion cell was 1000 ml of corrosion solution. Main equipment used for this experiment was potentiostat Voltalab PGZ 100 and software Voltamaster 10. Before experiments the samples were connected to potentiostat as a working electrode. Saturated calomel electrode (SCE) served as a reference electrode. In the end the platinised titanium counter electrode with surface a larger then 10 cm^2 was fixed to create consistent electric field around working electrode. Samples were immersed in saline electrolyte for 1 hour to establish a corrosion potential. After that interval corrosion potentials were measured. During next step pitting or crevice corrosion was initiated and simulated by linear polarizing of sample to potential much more noble values than corrosion potential. Polarization scan rate was 1.0 mV/s. During this polarization pitting or crevice corrosion is marked by general and large increase of current density. When current density increased to value 2.0 mA/cm^2, reverse polarization of sample has started. Experiment was finished when current density decreased to -0.10 mA/cm^2 or potential reached starting value. After corrosion tests the samples surfaces were observed by light and electron microscopy.

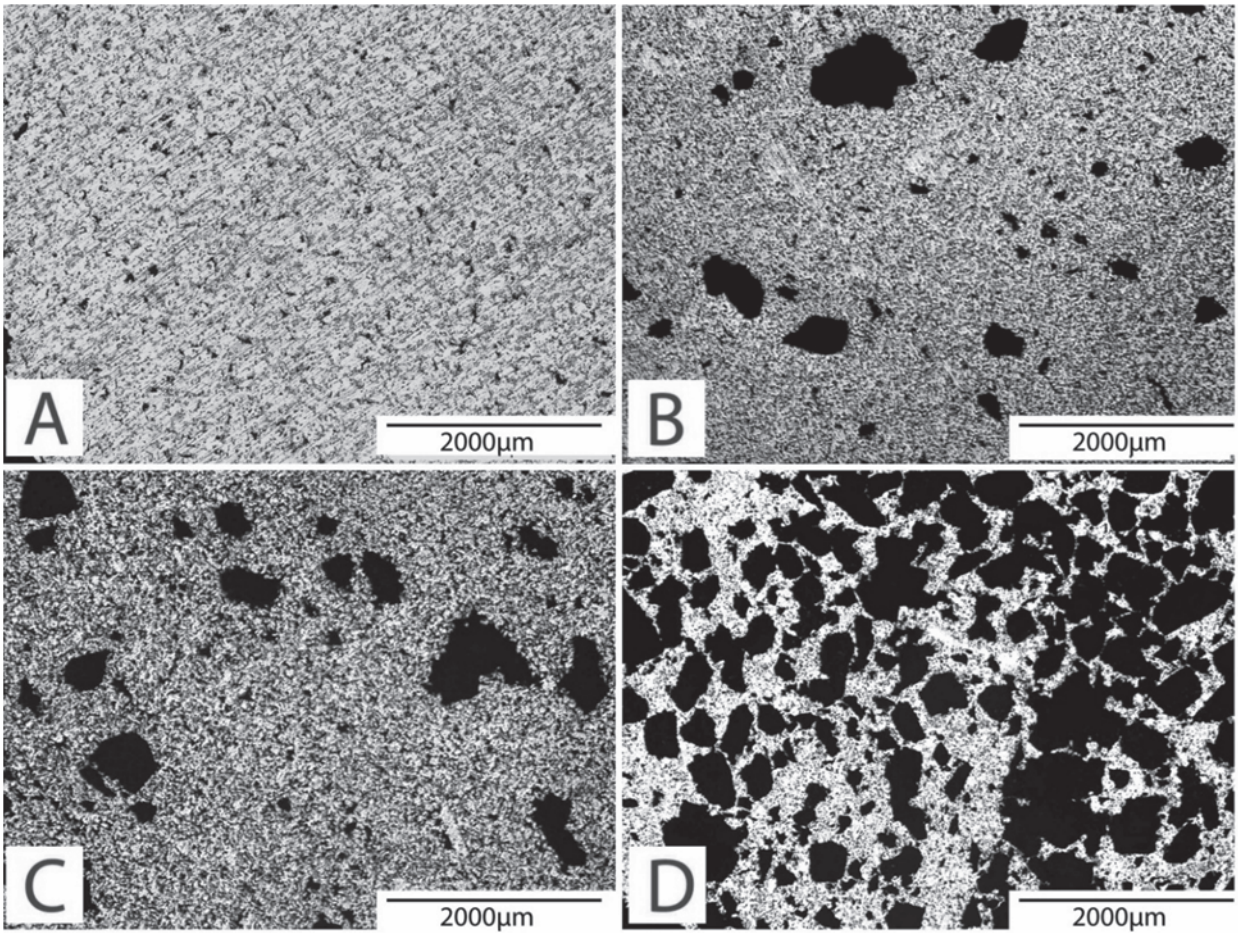

Fig. 1 A - structure of sample Ti1; B - structure of sample Ti2; C - structure of sample Ti3; D - structure of sample Ti4

3. RESULTS AND DISCUSSION

The main result of experiment is a polarization curve for each sample. From this curve certain corrosion properties can be determined. Corrosion potential, corrosion rate and polarization resistance were determined by Taffel and Stern methods and results are demonstrated in **Table 2**. Potentials of depassivation and repassivation *(E_{dep}, E_{rep})* were found out by intersection method (extrapolation of polarization curve and its intersection with X axis). Also conventional method were used: the values of depassivation potential were found by polarization curve where the current density reaches the value of 10^{-4} A/cm^2 and potential of repassivation was found on curve when current density decreases to 10^{-5} A/cm^2. These results are compared in **Table 3**.

Note: Size of exposed surface was calculated for nominal diameter 13 mm. But the size of exposed surface is also affected by porosity of the sample. With increasing porosity real size of exposed surface is also growing, but the current density was defined for nominal size of surface, which was calculated for nominal diameter of the samples. The deviation or variance of measurement could be increased with increasing of porosity.

Table 2 Chosen corrosion properties of tested materials

Sample	Corrosion potential E_{cor} (mV) vs. SCE		Corrosion rate r_c (nm/year)	Polarization resistance R_p (kΩ/cm^2)	
Ti-1	-457	-450	16750	20	21
Ti-2	-302	-307	2	7410	6820
Ti-3	-281	-272	2	79750	72330
Ti-4	-264	-264	3	153000	179000
Ti6Al4V	-518	-519	1131	104	106

Table 3 Characteristic (pitting) potentials of tested materials

Sample	Potential values (mV), SCE			
	E_{dep}	$E_{dep-con}$	E_{rep}	$E_{rep-con}$
Ti-1	2200	2150	2740	2720
Ti-2	1410	1390	1750	1800
Ti-3	1360	1290	1450	1480
Ti-4	1380	1350	1510	1490
Ti6Al4V	1790	1820	1650	1730

Just for comparison corrosion properties of Ti6Al4V alloy, which is commonly used for implant manufacturing, were added into previous tables. The surface of sample from this alloy was prepared by the same way as porous titanium samples. Also corrosion behavior was tested by the same methods as porous titanium samples. Comparison of polarization curves for sample Ti-1 and Ti-4 is demonstrated in **Fig. 2**.

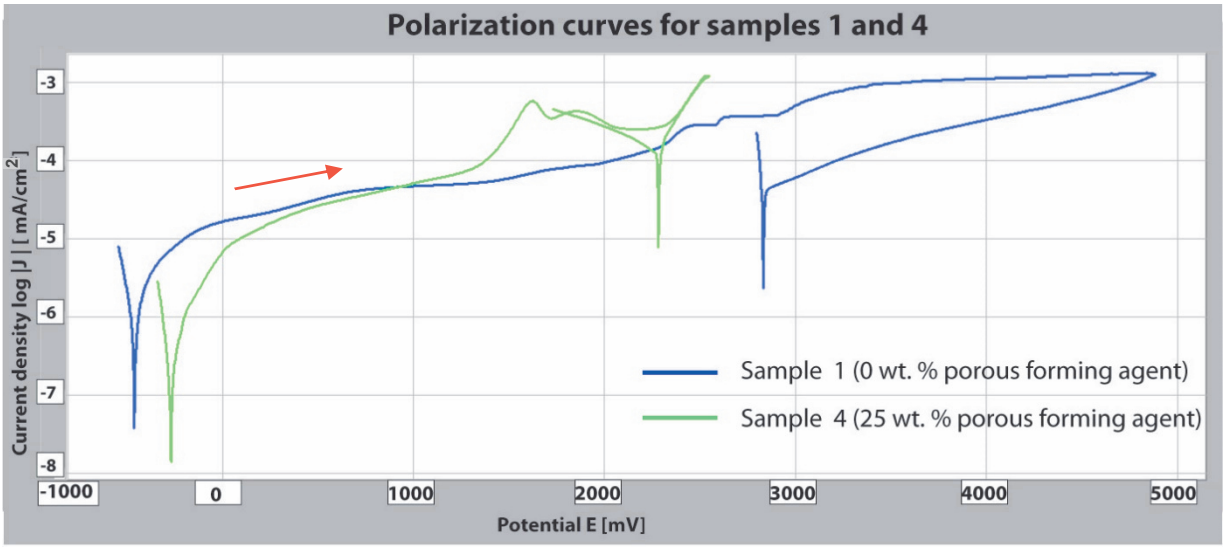

Fig. 2 Polarization curves for samples Ti-1 and Ti-4

Similar curves were registered for other samples. (Other curves are “hidden” for better lucidity in the figure). The difference between values of corrosion potential and potential of depassivation or repassivation are clearly visible. Potentials of repassivation were higher than potentials of depassivation. This was probably affected by polluted surface of sintered titanium particles-during corrosion were the particles of pollutant corroded and during reversed polarization uncontaminated surface were repassivated easily. Also sample Ti-1 have lower corrosion potential and highest corrosion rate. On the other hand potential of repassivation was highest for this sample; it means that this sample is most pitting corrosion resistive. Samples with addition of pore forming agent have higher (more noble) corrosion potential and also their corrosion rate was significantly lower. On

the other hand their pitting corrosion resistance was inferior. Corrosion pits were observed especially on surface of sample Ti-1, where the porosity was least and pitting corrosion was preferred. On the surface of samples Ti-2 - Ti-4 marks of crevice were also observed. Character and shape of polarization curves indicated crevice corrosion as well. Because of that, common level of smoothing was applied on corrosion curves. During polarization color of exposed surface was changed completely (golden shade). Complex oxides with different chemical composition or crystallographic modification were formed on the surface of titanium material in relation to applied potential-shade of oxide layer was determined by applied potential and time of exploitation. Character of corrosion pit and shade of oxide layer on the sample Ti-1 surface is shown in **Fig. 3**.

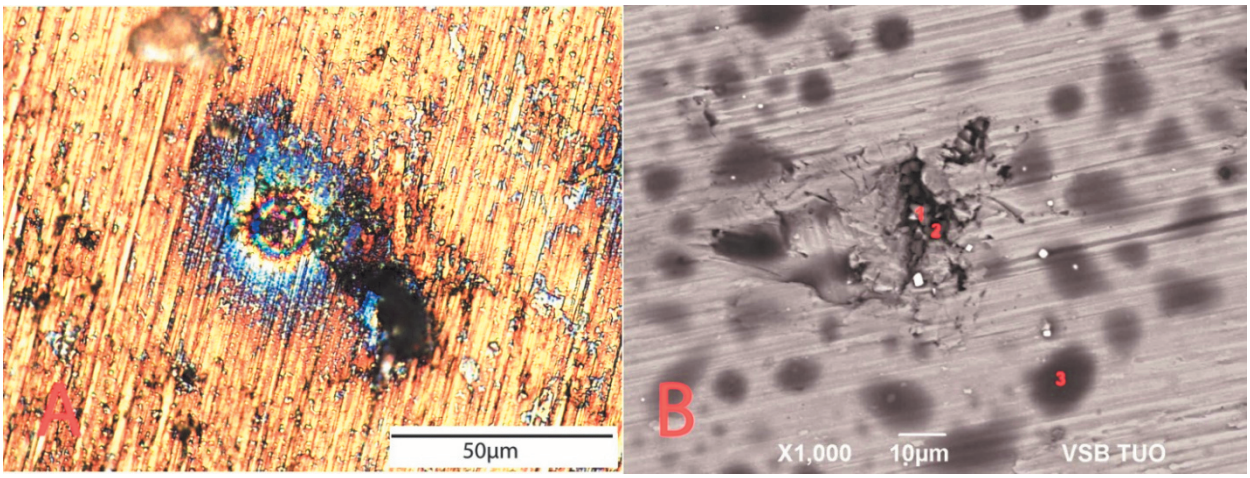

Fig. 3 Corrosion pit on surface of sample 1 observed by A light microscopy; B electron microscopy

In **Fig. 3** B are also marked areas (points 1, 2, 3) where EDS analysis was used for identification of approx. chemical composition of each area. Different chemical composition is clearly visible due to material contrast. Chemical composition of each area is shown **Table 4**.

Table 4 Chemical composition of selected areas from **Fig. 3 B**

Area	Chemical composition of each area (at.%)					
	O	Na	Si	Cl	Ca	Ti
1	39.88	24.53	0.19	14.16	1.81	19.44
2	25.10	37.12	0.23	22.27	1.77	13.51
3	55.03	0.56	n	13.97	7.85	22.58

EDS analyses of area 1 and 2 denotes, that particles at the bottom of the corrosion pits were formed during corrosion by interaction of material with corrosive solution (particles are rich for elements from physiological solution). Surrounding area of corrosion pit contains mainly oxidized base material with addition of elements from solution.

4. CONCLUSIONS

In this article porous titanium materials with different fraction of pore forming agent were tested for pitting or crevice corrosion by ASTM F2129 standard. Corrosion properties like values of corrosion potentials or corrosion rates were determined. Also potentials of depassivation and repassivation were found out during measurements. It was proved that addition of pore forming agent slightly decrease pitting or crevice corrosion resistance but relation between amount of this agent and pitting or crevice corrosion resistance wasn't found out. Corrosion properties of porous titanium were compared with Ti6Al4V alloy as well. Character of corrosion damage was observed by light and electron microscopy and EDS analysis was used for specification of

corrosion products. Feature research will be focused on in vitro and in vivo testing of bioactivity of this advanced material.

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