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MODIFICATION OF THE TITANIUM IMPLANTS SURFACE BY SILANES AND COLLOIDAL SILVER

MODYFIKACJA POWIERZCHNI IMPLANTÓW TYTANOWYCH SILANAMI I SREBREM KOLOIDALNYM

Surface modification of an implants by colloidal silver and three kinds of silanes such as Z-6020, A – 187, TRIAMO were carried out. Contact angles of the implants covered colloidal silver with different properties were examined. The change of a hydrophobic character of the surface implants was defined. DSA 100 System which allow to contact angle measure of a solid bodies in wide bounds from 4° to 122° with accuracy of measurement to 0,1° were applied. The roughness of modified implants surface was examined by profilometer WYKO NT 9300 with high optical resolution.
Keywords: colloidal silver, contact angle, implants, roughness, silanes

W pracy przedstawiono modyfikację powierzchni implantów srebrem koloidalnym oraz trzema rodzajami silanów: Z – 6020, A – 187 oraz TRIAMO. Zmierzono kąt zwilżania na implantach pokrytych srebrem koloidalnym o różnych właściwościach. Określono charakter zmian hydrofobowości powierzchni implantów. Do pomiarów wykorzystano system DSA 100, który pozwala na pomiar kąta zwilżania płynów na powierzchniach ciał stałych w szerokich granicach od 40° do 120° z dokładnością pomiaru do 0,10°. Chropowatość powierzchni modyfikowanych implantów zmierzono przy pomocy profilometru optycznego Wyko NT 9300 o dużej rozdzielczości.

1. Introduction

Materials with different and specific applications, espatially in medicine and in biology, received in the last years special attention and a considerable progress of the application of the materials still took place. The creative intellectual movement was concentrated on development of interdisciplinary connection the medicine and the technique, which in the last years develop very dynamic. In this domain all attention was concentrated on application of the methods, which develop in the physical and chemical science, and on the processes occurring in the living organism description for theirs results application in study among others new and modified the bones implants.

The restitution of complete or partial function of the tissue group is in the sphere of capabilities the reconstruction surgery and the prosthetics. The implantology play a significant role in the reconstruction and allow to reparation of the damaged structure and restitution of the lost functions.

The most important challenge of the implantology is find a solution of biotolerant and biofunction of the materials. The complete compatibility of the implant structure and his function with living organism is far to analog the organism – implant.

In the cellular level it is ensue to the osteointegration. It is a biology concept and it could be explain do an adhesion of the living bones tissue with the titanium implant surface. The effect cause integrating of implant with the bones. The influence on osteointegration process has appropriate preparation of the surface of the implant [1, 2].

The modification of the surface implant could be execute via different chemical, physical and mechanical way [3]. The usefulness of the biomaterials in implantation require the experimental verification by research works and stimulating models of the phenomena which declining in the living organism.

As a result and experiments usefulness of biomaterials for implantation can be defined [4].

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2. Material

The Implants of the Osteoplant system with biocompatibility Tytan Grade 4 in the research were used.
Along the huge group of the implants , only the Osteoplant implants were elaborated and implemented in Poland.
Results showed that the 40 % of the materials implanted in Poland there are the Osteoplant implants, elaborated and implemented by the Medical Academy Foundation of the Marcinkowski name in Poznań.
For the modification of the surface of the implants three different silanes, and the colloidal silver were used [5, 6].

TABLE 1

The silanes and the colloidal silver used to surface of the implants modification [6]

ModifiedTytan Grade 4 No. of the sample	Modificator	Chemical name
1	–	
2	3% Z-6020	γ – aminopropylotrietoxysilane $H_2N(CH_2)_3\ Si(OC_2H_5)_3$
3	3% A-187	γ – glicydyloksypropylotrimetoxysilane $H_2COCHCH_2O(CH_2)_3Si(OCH_3)$
4	3% TRIAMO	triaminofunction propylottrimetoxysilane $(CH_3O)_3Si(CH_2)_3NH(CH_2)_2NH(CH_2)_2NH_2$
5	Colloidal silver	

3. Samples

The starting sample and the samples after modification were incubated in 36° C during 6 weeks in SBF liquid with Na^+, K^+, Ca^{2+}, Cl^-, Mg^{2+}, HCO_3^{2-}, HPO_4^{2-}, SO_4^{2-} ions, for the estimating of the efficiency of the builded the hydroxyapathyte structure.

4. Research methods

1. X – Ray Analysis

The analysis of the samples composition were carried out by EDS. The EDS adapter is integrating part of the scanning microscope TESCAN and allow to elementary analysis of the composition. The map of the surface composition can be made with the use of the EDS adapter and allowed also to define the changes of the contents the selected elements along the scanning line.

2. Wyko NT 9300 optical profilometric analysis

The measurements of the surface roughness of the titanium implants Tytan Grade 4 with the use of the Wyko NT 9300 optical profilometr were carried out. This equipment use for measurement an optical profilometric technique - White Light Interferometry (=VSI).

The conditions of the measurements were as followed:

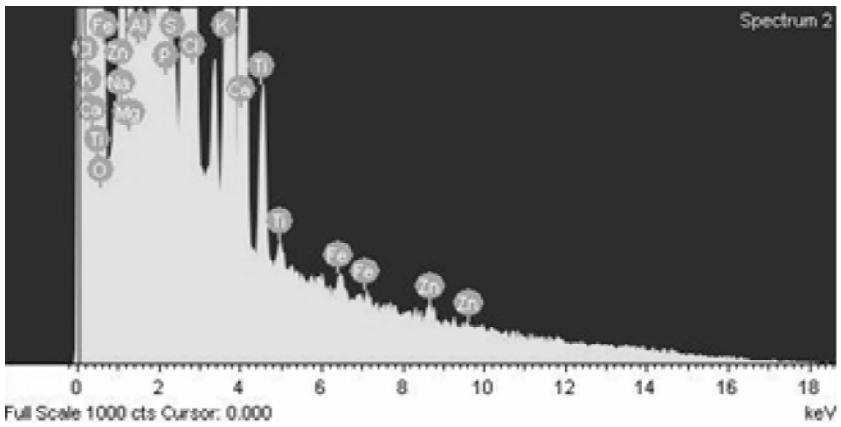
- Objective: 20x
- Field-of-View (FOV): 0,55x
- Zoom: 11,5x
- The picture size: 550 μm × 412 μm
- The pixel size: 860,72 nm

3. The contact angle researches with the use of a DSA 100 system

The Krüss measurements system is based on the drop shape analysis. The contact angle is estimate with the use of the suitable equation e.g. Young – Laplace, based on the diameter and capacity of the drop. The advantage of that measurements is possibility of the measurements automation by the digital pictures analysis. The DSA 100 allowed the measurements the contact angle of the liquid on the solid states with high bounds 40° – 120° with the accuracy of measurement to 0,10°.

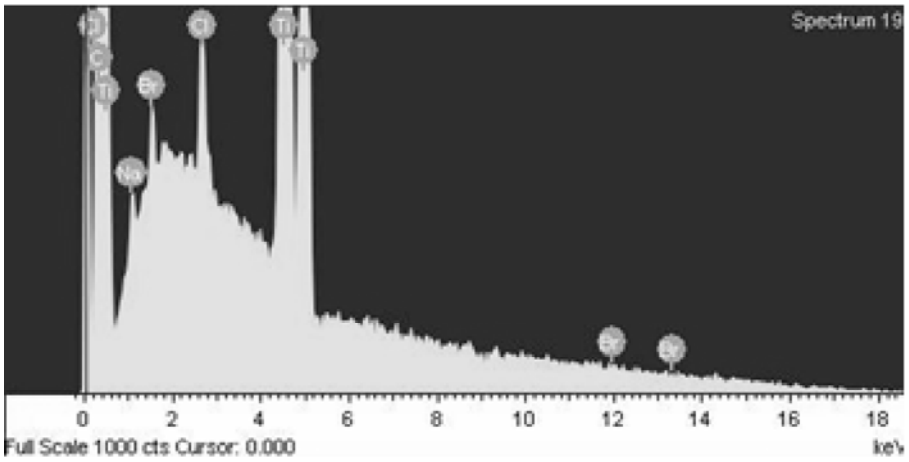
5. Results

The titanium implants (the Osteoplant system) with modified surface were investigated via the X – Ray analysis. The detailed results for the starting sample and sample modified by 3% Z – 6020 of the quality and the quantity analysis are showed in Figs. 1 and 2.



Element	Weight%	Atomic%
O K	49.96	68.84
Na K	1.41	1.35
Mg K	0.88	0.80
Al K	0.18	0.15
P K	14.45	10.28
S K	0.20	0.14
Cl K	6.95	4.32
K K	0.36	0.20
Ca K	24.28	13.36
Ti K	0.84	0.38
Fe K	0.15	0.06
Zn K	0.33	0.11
Totals	100.00	

Fig. 1. The quality and the quantity analysis- starting sample



Element	Weight%	Atomic%
C K	13.27	30.68
O K	12.18	21.14
Na K	5.82	7.03
Mg K	0.18	0.21
P K	0.23	0.20
Cl K	5.38	4.22
K K	0.19	0.14
Ca K	0.21	0.15
Ti K	62.53	36.25
Totals	100.00	

Fig. 2. The quality and the quantity analysis-titanium implant modified by the 3% Z – 6020

The scanning microscope pictures of the titanium implant unmodified and , modified by the 3% Z – 6020 are showed in Figs. 3 - 4

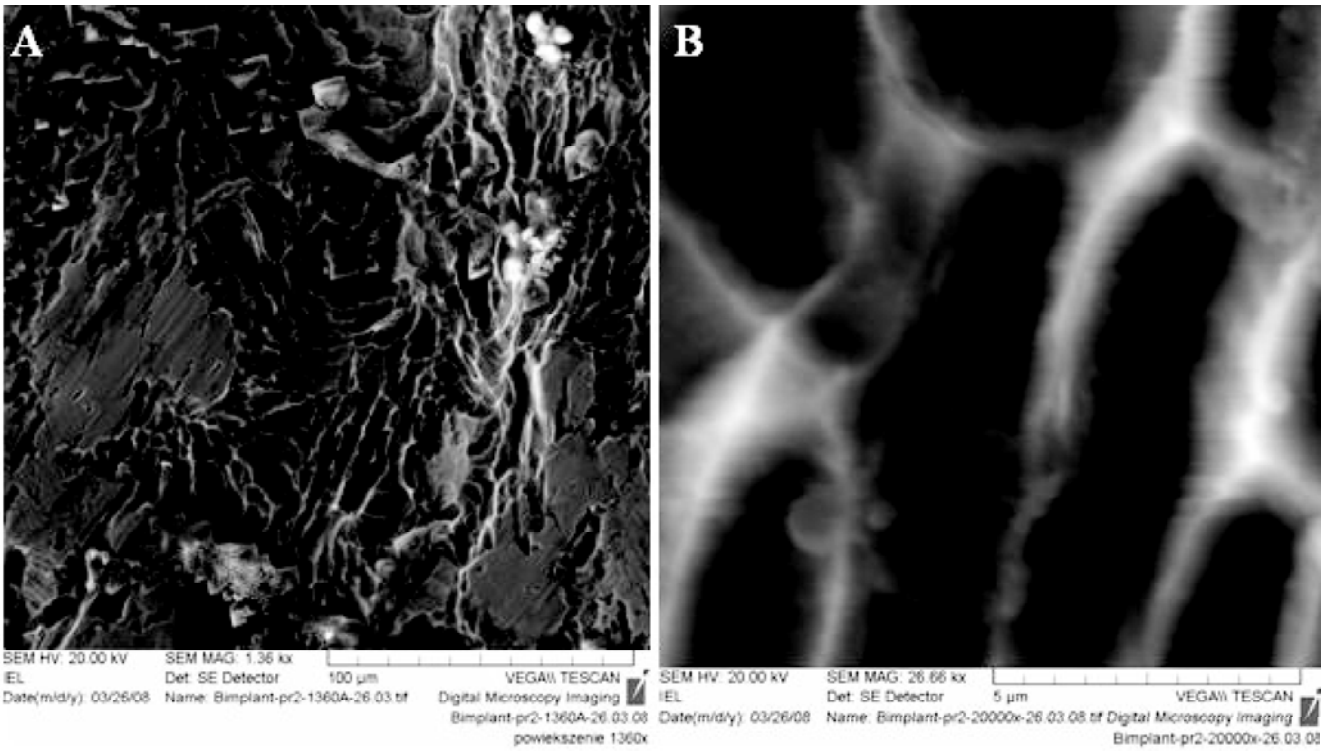


Fig. 3. The picture of the titanium implant – strating sample

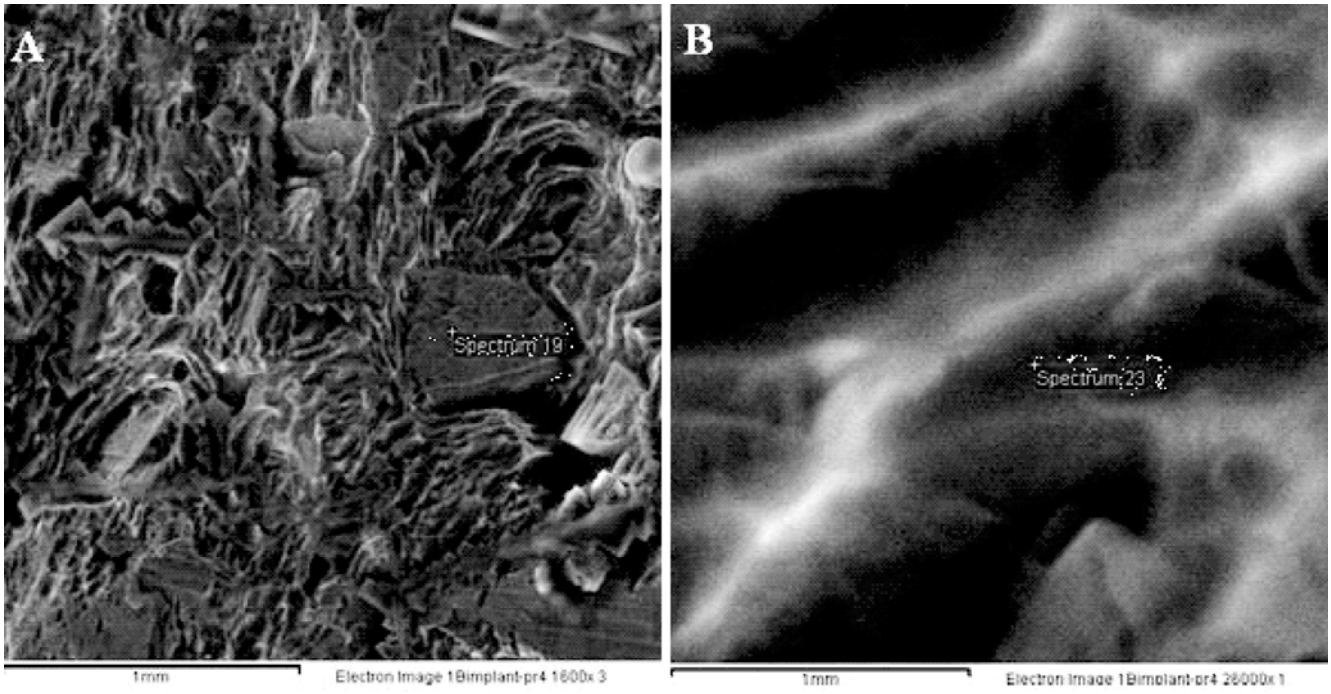
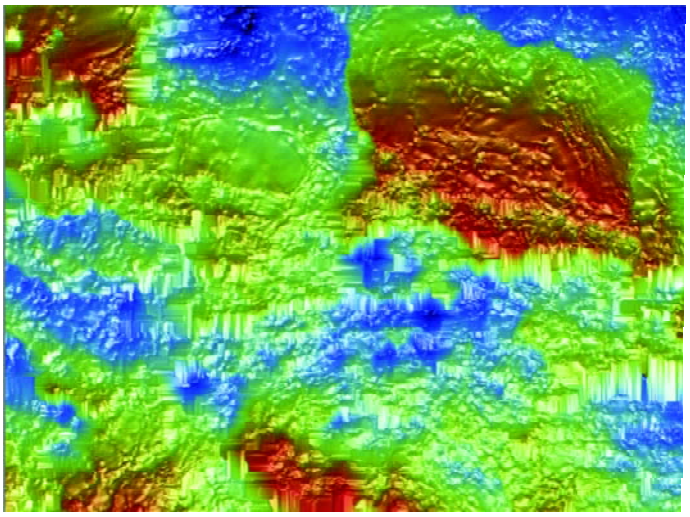


Fig. 4. The picture of the titanium implant – modified by the 3%

The parameters of the surface roughness such as:

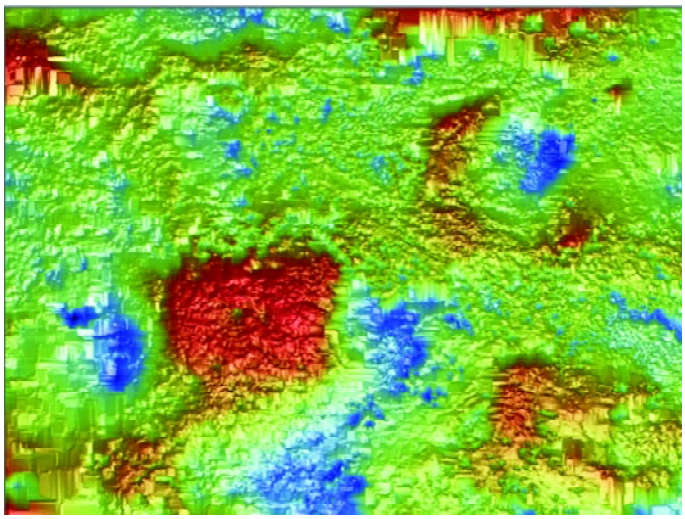
- Ra: the average roughness estimated in relation to all matrix of the picture,
- Rq: the average square (RMS) estimated in relation to all matrix of the picture and
- Rt: the distance peak- valley estimated in relation to all matrix of the picture,

of the boundary surface the titanium samples in the roller shape, which evaluate the roughness in X and Y axles and level the curve of this roughness, were estimated. The results for the starting sample and sample modified by the 3% Z – 6020 are showed in Figs. 5 and 6.



	Ra	Rq	Rt
Starting sample	µm	µm	µm
	2,30	2,78	16,17

Fig. 5. The general, 3D projection view on the measured surface the titanium implant – starting sample



	Ra	Rq	Rt
Samplc modifiedec by 3% Z-6020	µm	µm	µm
	2,38	3,08	22,38

Fig. 6. The general, 3D projection view on the measured surface the titanium implant – sample – modified by 3% Z – 6020

The contact angle for the starting samples and the samples modified by different silanes and colloidal silver are showed in Tables 2 – 5.

TABLE 2

The contact angle with the use a water for the samples: starting and modified by 3% Z – 6020

Measurement for 10s 5μl	Parafilm	Sample 1		Sample 3	
Metod		Starting sample		Z – 6020	
Contact angle theta [deg]					
Tangent Metod-1	112,4	58,5	62,9	55,1	58,4
Tangent Metod-2	112,2	74,9	–	58,7	–
Circle Fitting	108,3	58,9	60,9	47,5	56,1
Laplace-Young Fitting	114,0	61,6	60,9	52,6	59,3
Height/Width Method	107,9	59,0	61,9	47,8	57,2
Averange contact angle	110,96	62,6	61,7	52,3	57,8
		62,1		55,0	

TABLE 3

The contact angle with the use a salt body fluid (SBF) for the samples: starting and modified by 3% Z – 6020

Measurement for 10s 5μl	Parafilm	Sample 1		Sample 3	
Metod		Starting sample		Z – 6020	
Contact angle theta [deg]					
Tangent Metod-2	107,6	56,1	54,0	48,3	40,8
Circle Fitting	107,4	52,8	50,0	43,7	42,1
Laplace-Young Fitting	11,5	54,3	54,2	46,7	45,8
Height/Width Method	107,0	52,9	49,9	44,0	42,2
Averange contact angle	108,78	54,2	52,3	46,0	43,1
		53,3		44,6	

TABLE 4

The contact angle with the use a water for the samples: modified by 3%Λ – 187, 3% TRIΛMO and the colloidal silver

Measurement for 10s 5μl	Sample 5		Sample 7		Sample 9	
Metod	A – 187		TRIAMO		Silver colloid	
Contact angle theta [deg]						
Tangent Metod-1	73,7	66,9	55,2	54,4	47,0	45,5
Tangent Metod-2	74,2	66,1	46,6	56,4	41,7	38,6
Circle Fitting	71,0	63,9	44,8	56,3	43,1	40,6
Laplace-Young Fitting	71,9	66,7	47,7	54,7	49,5	–
Height/Width Method	71,4	64,0	45,7	53,5	43,1	40,0
Averange contact angle	72,4	65,5	48,0	54,5	44,9	41,0
	69,0		51,2		43,0	

TABLE 5

The contact angle with the use a salt body fluid (SBF) for the samples: modified by 3%A – 187, 3% TRIAMO and the colloidal silver

Measurement for 10s 5μl	Sample 5		Sample 7		Sample 9	
Metod	A – 187		TRIAMO		Silver colloid	
Contact angle theta [deg]						
Tangent Metod-1	63,5	59,8	46,1	54,9	43,5	43,1
Tangent Metod-2	62,4	54,3	44,5	61,2	42,2	37,7
Circle Fitting	62,8	59,5	44,6	51,9	42,8	39,2
Laplace-Young Fitting	63,4	60,2	46,6	56,5	43,0	41,4
Height/Width Method	62,9	59,2	44,7	52,3	42,9	39,7
Averange contact angle	63,0	58,6	45,3	55,4	42,9	40,2
	60,8		50,3		41,6	

6. Conclusions

The research of the contact angle confirm the increase the hydrophobicity of the implants after modification [9]. The consider the possibility of the influence of the designed monolayer function group on titanium surface on the osteointegration process of the salt body fluid (SBF) ingredients, can suppose that the known influence between hydroxyapatite and metal ions can be decisive factor of the builded hydroxyapatite. In the other way the publications show that the silanes - with amines group – are not toxic for the living organisms, if they are used in small concentration [7, 8].

In our work was showed the possibility of the Osteoplant system modification also via the colloidal silver, with the object of the bacteriostatic implants autoprotection. The silver occurring is not favourable for the increase the implant roughness in the SBF liquid, but much more detailed observation of this kind of modification will be the subject of the another publication.

Roughness of the surface and microgeometry of titan by silanes modification was obtained. Roughness and micromechanical connection improve the implant stabilization. Tests have showed (Hebrew University in Jerusalem JADR – 13 august 2004) that the optimal implant surface connection can be obtain with the roughness about 5 - 10 μm, that roughness with the use of silane A – 187 was obtained. Simultaneously as a result of microscopy investigation by scanning electron microscope (SEM) it was found the most uniform shape of the surface.

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