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EVALUATION OF SELECTED MECHANICAL AND CHEMICAL METHODS OF MODIFICATIONS OF TITANIUM

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Medical titanium produced by Titanium Wire Corporation (grade IV) was the subject for analysis. The mechanical treatment of subjected titanium pieces was carried out with the use of sand - blasting. One sand - blasted titanium cylinder was left as the control one. The others were subjected to acid – etching in different acid mixtures. The enlargement of the titanium surface area was estimated by measuring of surface roughness. This factor is described by average roughness Ra which is an internationally recognized amplitude parameter defined as an arithmetic mean of departure of the roughness profile from the mean line. After modifications all samples were soaked in Simulated Body Fluid. Adsorption of calcium phosphate on modified surface is the expression of the biological properties of this surface. The results indicate that there is no direct correlation between adsorption of calcium and phosphorus and surface roughness expressed by Ra parameter.

Key words: titanium, surface roughness, SEM, AES

INTRODUCTION

Osseointegration is a complex biological process regulated by various factors. The enlargement of the titanium implant surface area can, for instance, increase osseointegration (Bigi A. 2005, Cleries L. 2000, Martin J.Y. 1995). This enlargement can be achieved by mechanical and chemical methods, which increase the metal surface, independent of implant shape, as well as enlarge the implant/bone interface by the variation of threads and perforations. The problems relating to preparation of an

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endosseous implant surface and issues relating to the implant/bone anchorage still exist and are mainly connected with the process of osseointegration determined by the nature of implant surface, particularly by surface roughness (Arentowicz G. 2002, Cooper L. F. 1998, Hedzelek W. 2002, Martin J.Y. 1995). This factor is described by average roughness Ra which is an internationally recognized amplitude parameter defined as an arithmetic mean of departure of the roughness profile from the mean line. Surface roughness can be changed by mechanical and chemical methods as well as other methods such as the Titanium-Plasma Spray. Factories producing implants do not disclose details of production but they do aspire to optimize surface roughness.

THE AIM OF THE STUDY

The aim of this study was to utilize microscopic and profilometric analyses to estimate the size of the titanium surface area after mechanical and chemical treatment. Then to estimate biological properties of modified surfaces by finding correlation between Ra parameter and calcium and phosphorus adsorbed on modified surfaces.

An introductory study was performed to select five different titanium surfaces of different surface roughness, prepared by using four different acid mixtures and techniques. Medical titanium produced by Titanium Wire Corporation (grade IV) was the analyzed material. Titanium cylinders about 5 mm in diameter and 5 mm in length were treated. The mechanical treatment of titanium cylinders was carried out with sand - blasting. Sand – blasting involved the blasting of the end surfaces of the cylinder with Al_2O_3 particles about 100 μm in size for 3 minutes at a pressure of 6 atmospheres. One sand - blasted titanium cylinder was left as the control one. The others were subjected to acid – etching for 10 minutes in different acid mixtures at room temperature (20ºC). Then the acid–etching, titanium discs were at first rinsed in an ultrasonic cleaner in acetone for 7 minutes, and then in distilled water for 3.5 minutes until finally they were left to dry.

In the first part of the experiment, the size of the titanium implant surface area was assessed using a Scanning Electron Microscope and a profilometer. The SEM pictures of each titanium cylinder were blown up 1000x at an angle of 60º.The roughness of each cylinder was characterized quantitatively and qualitatively with a profilometer with a 2 μm diameter diamond stylus.

In the next stage of the investigation, all samples were subjected to incubation in simulated body fluid (SBF), in order to characterize the adsorption of calcium phosphate. The SBF solution contains inorganic ions of concentrations corresponding to those in human blood plasma. Adsorption of calcium phosphate on modified surface is the expression of the biological properties of this surface. Tab. 1.

Table 1. Milimolar concentrations (mM) of ions in the SBF solution and in human plasma

	Na^+	K^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^{2-}	HPO_4^{2-}	SO_4^{2-}
SBF	142.0	5.0	2.5	1.5	147.8	4.2	1.0	0.5
Human plasma	142.0	5.0	2.5	1.5	103.0	27.0	1.0	0.5

Buffer (TRIS solution): tris-hydroxymethyl-aminomethane $(CH_2OH)_3CNH_2$ 50 mM+HCl45 mM.

After the incubation, a qualitative analysis was carried out with Auger Electron Spectroscopy.

RESULTS AND DISCUSSION

The results of profilometric analysis – Ra parameter of previously sand-blasted and acid-etched titanium probes: (Table 2).

Table2. The results of profilometric analysis – Ra parameter of sand-blasted and acid-etched titanium probes

Modification	Nr of disc					Mean value	Standard deviation	Confidence level α=0,1
	1	2	3	4	5			
HF	0.93	1.19	1.14	1.11	1.23	1.12	0.116	0.0852
HF HCl/H_2SO_4	0.72	0.80	0.88	0.91	0.89	0.84	0.079	0.0582
HCl/H_2SO_4	0.73	0.72	0.74	0.60	0.61	0.68	0.069	0.0507
HF/HNO_3	0.53	0.53	0.36	0.57	0.56	0.51	0.086	0.0631
HCl/H_3PO_4	0.51	0.61	0.65	0.59	0.63	0.60	0.054	0.0397
control	0.62	0.74	0.55	0.79	0.80	0.70	0.110	0.0811
Max	0.93	1.19	1.14	1.11	1.23	1.12		
Min	0.51	0.53	0.36	0.57	0.56	0.51		

The sand-blasting and acid-etching increased surface roughness only in case of HF + HCl/H_2SO_4 and HF pickling solutions (Table 2). The other modifications revealed lower surface roughness then the control one (sand – blasted only). The titanium disc modified with HF showed the maximum magnitude of Ra parameter (1.23 μm Ra) while the modification in HF/HNO_3 showed the minimum magnitude of Ra parameter (0.36 μm). Figures 2-5 present the titanium surface area: control (sand-blasted only, Fig.1) and after mechanical and chemical modification (Fig.2-4).

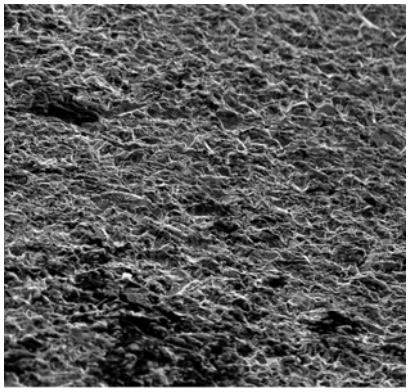

Fig. 1. Ti sand-blasted (sb) without chemical treatment.

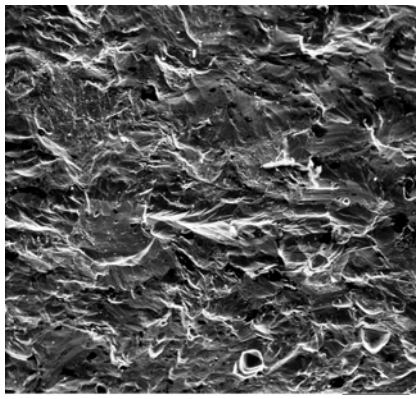

Fig. 2. Ti sb; 40% HF, ~ 1000x

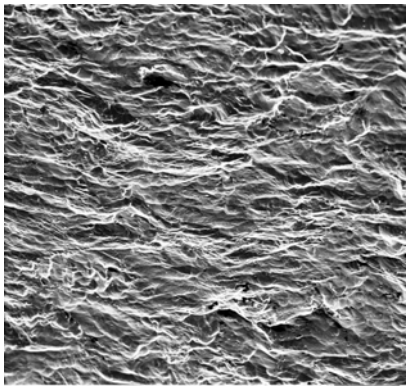

Fig. 3. Ti sb; 15%HF 36%HCl/ 96% H_2SO_4 1000x

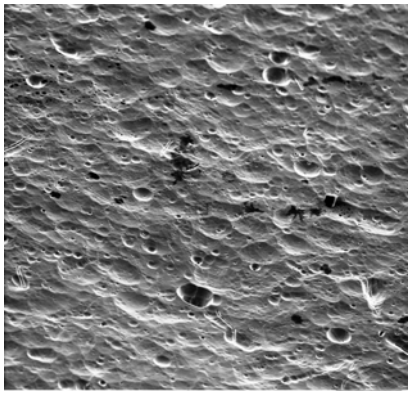

Fig. 4. Ti sb; 20% HF/ 30% HNO_3 ~ 1000x

After modifications all samples were soaked in SBF for 168 hours (Table 1). After incubation, AES analysis was performed, which showed the presence of calcium and phosphorus on sand–blasted and acid – etched surfaces. The presence of calcium and phosphorus on titanium implant surface area were also estimated with the Scanning Electron Microscope (SEM).

Fig. 5. AES pattern of the modified titanium surface after soaking in SBF.The highest amounts of calcium and phosphorus are observed for HF/ HNO_3 modification 76.5 and 15.5, respectively (Table 3).

Other modifications HCl/ H_2SO_4 and 40% HF gave contents of calcium 70.5 and 63.0 and of phosphorus 10.50 and 10.17, respectively. The calcium and phosphorus contents for control disc were 6.17 and 2.17.

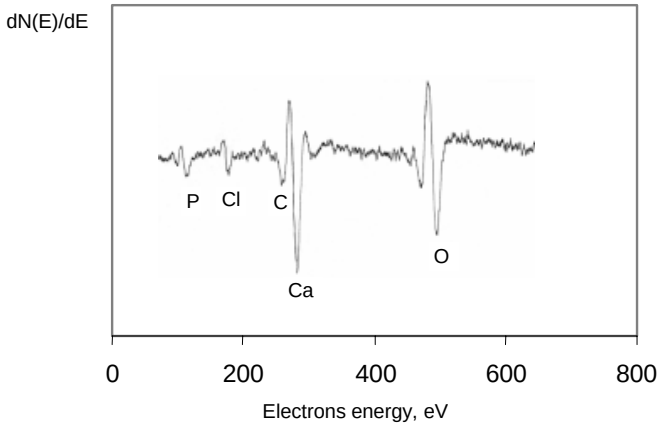

Fig. 5. AES pattern of the modified titanium surface after soaking in SBF

Table 3. The magnitude of correlation coefficient for sand – blasted and acid – etched samples ([p-p] peak-peak)

Modification	Surface roughness Ra	P [p-p]	Ca [p-p]
20%HF/30%HNO_3	0.51	15.50	76.50
36%HCl/85%H_3PO_4	0.60	3.67	7.33
36%HCl/96%H_2SO_4	0.68	10.50	70.50
control	0.70	2.17	6.17
15%HF 36%HCl/96%H_2SO_4	0.84	1.50	6.67
40%HF	1.12	10.17	63.00
Correlation coefficient		-0.139	0.032

The results indicate that there is no direct correlation between adsorption of calcium and phosphorus and surface roughness expressed by Ra parameter. In the sand – blasting trial and after modifications of titanium samples the correlation coefficient indicates total absence of dependence between surface roughness and adsorption of calcium and phosphorus.

CONCLUSIONS

- The mechanical method of sand-blasting was seen to cause the big increase in surface roughness.
- Acid–etching can rise and reduce surface roughness, as well.
- No direct correlation was found between Ra parameter and adsorption of calcium and phosphorus on modified titanium surfaces.

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Hędzelek W., Sikorska B., Domka L., *Ocena wybranych metod mechanicznej i chemicznej modyfikacji tytanu,* Physicochemical Problems of Mineral Processing, 39 (2005) 149-154 (w jęz. ang).

Zwiększenie tytanowej powierzchni wszczepu jest jednym z podstawowych problemów w implantologii, bowiem jakość i wielkość tej powierzchni decydują m.in. o wytrzymałości wiązania kość /implant i możliwości wczesnego obciążenia wszczepu. Stosując wszczepy o różnych kształtach, których gwinty czy perforacje zwiększają obszar wzajemnego kontaktu, uzyskuje się lepsze i trwalsze wyniki osteointegracji. Ważnym czynnikiem mającym wpływ na powyższe procesy jest chropowatość powierzchni tytanu.

Celem badań była ocena za pomocą analizy mikroskopowej i profilometrycznej chropowatości powierzchni tytanu po opracowaniu metodami mechanicznymi i chemicznymi. Celem szczegółowym było określenie właściwości biologicznych powierzchni poprzez wyznaczenie korelacji między współczynnikiem chropowatości powierzchni Ra, a zaadsorbowanymi na powierzchniach pierwiastkami fosforu i wapnia. Analizie poddano tytan, z którego wykonywany jest element wewnątrzkostny implantu.

W pierwszym etapie badań powierzchnie próbek wzorcowych oraz próbek poddanych wytrawieniu obserwowano przy użyciu Skaningowego Mikroskopu Elektronowego (SEM) oceniając strukturę powierzchni oraz zachodzące zmiany po wytrawieniu w stosunku do próbek wzorcowych. Pomiarów średniej arytmetycznej odchylenia profilu chropowatości Ra (wyrażonej w μm) dokonywano profilometrem.

W drugim etapie badań przeprowadzono inkubację zmodyfikowanych prób tytanu na składniki roztworu symulującego płyn ustrojowy (SBF) w celu zbadania czy nastąpi adsorpcja fosforanów wapnia na powierzchni. Ostatecznym wynikiem badań była ocena zajścia procesu przy wykorzystaniu metod Spektroskopii Elektronów Augera oraz Skaningowej Mikroskopii Elektronowej.

Z przeprowadzonych badań inkubacji modyfikowanych prób w SBF wynika, że proces wstępnego piaskowania lub piaskowania i wytrawiania jest korzystny dla zaadsorbowania się na tak przygotowanych powierzchniach jonów fosforu i wapnia.

W ocenie właściwości biologicznych modyfikowanych powierzchni nie wykazano korelacji pomiędzy współczynnikiem chropowatości Ra, a zaadsorbowanymi na powierzchni pierwiastkami fosforu i wapnia.