

THE EFFECT OF SURFACE TREATMENTS ON THE ELECTROCHEMICAL BEHAVIOR OF TITANIUM

Adriana Elena CHIVU¹, Sorin CIUCĂ², Dionezie BOJIN³, Fedor S. FEDOROV⁴,
Annett GEBERT⁵, Jürgen ECKERT⁶

Titanul și aliajele sale sunt utilizate pe scară largă ca materiale de implant non-degradabile pentru aplicații ortopedice în corpul uman, datorită rezistenței înalte la coroziune și a biocompatibilității sale. Tratamentele de suprafață sunt de obicei necesare pentru a îmbunătăți biocompatibilitatea acestor materiale și pentru a favoriza osteointegrarea. După aplicarea tratamentelor de suprafață, toate probele arată o stabilitate îmbunătățită la coroziune, acest lucru fiind dat de mutarea potențialului de coroziune spre valori mai mari. Acest lucru se datorează formării unor straturi de oxid de tip barieră pe suprafață, dar în același timp, densitatea curentului anodic este în creștere. Acest studiu prezintă efectul diferitelor tratamente de suprafață (cum ar fi sablarea, tratamentul alcalin, tratamentul cu acizi și acoperirea titanului pur cu un strat de hidroxiapatită) aplicate titanului pur grad 2, asupra comportamentului său electrochimic în soluție Hank.

Titanium and its alloys are widely used as non-degradable implant materials for load bearing orthopaedic applications in the human body due to high corrosion resistance and biocompatibility. Surface treatments are usually needed to improve the biocompatibility of these materials and to favor osseointegration. After the surface treatment, all the specimens show improved corrosion stability as their corrosion potentials are shifted to greater values resulting from the spontaneous formation of different barrier-type oxide layers on the surface, but at the same time the anodic current density is increasing. This study presents the effect of different surface treatments such as blasting, alkaline, acid treatment and hydroxyapatite coating of commercial pure titanium on its electrochemical behavior in Hank's solution.

Keywords: Titanium; Coating; Surface treatments; Hydroxyapatite (HA); Corrosion

¹ PhD student, Materials Science and Engineering Faculty, POLITEHNICA University of Bucharest, Romania, e-mail: adrianachivu@yahoo.com

² Prof., Materials Science and Engineering Faculty, POLITEHNICA University of Bucharest, Romania

³ Prof., Materials Science and Engineering Faculty, POLITEHNICA University of Bucharest, Romania

⁴ PostDoc, Institute for Complex Materials, IFW Dresden, Germany

⁵ Head of Department, Dept. Chemistry of Functional Materials, Institute for Complex Materials, IFW Dresden, Germany

⁶ Director: Institute for Complex Materials, IFW Dresden, Germany

1. Introduction

Titanium and its alloys are among the most used metallic biomaterials in dental and orthopaedic applications because of their excellent properties, such as low density, relatively low Young's modulus and other favourable properties, corrosion resistance and biocompatibility [1, 2, 3].

Titanium and its alloys have a high corrosion resistance due to the formation of a stable, homogenous protective oxide layer. The composition, structure and thickness of the protective oxide layer on titanium alloys depend on the preparation conditions. This oxide layer is responsible for the excellent biocompatibility of titanium implants [4]. Formation of oxide films on titanium does not lead to a cessation of the corrosion process. Moreover, a titanium surface is not bioactive, and surface treatments are usually needed to enhance the bioactivity and to improve the osseointegration with bone tissues [5]. These treatments can also improve the corrosion resistance and wear resistance of the implant in the human body [6, 7].

The methods for surface modification can briefly be classified as mechanical, chemical and physical according to the formation of the modified layer on the substrate. Common mechanical surface modification methods, such as grinding, polishing and blasting [8,9] have as principal objectives the adjustment of specific surface topography and roughness, the removal of surface contaminations and the improvement of the adhesion in subsequent bonding steps [10]. The most used chemical treatments of titanium and its alloys are acid treatment [8,11], alkaline treatment[10,12,13], hydrogen peroxide treatment, heat treatment and passivation treatments.

A bioactive hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ (HA) coating can also be utilized to modify a titanium surface [14]. The HA coating will reduce the release of metallic ions from the implant into the body [5,15] by acting as a barrier, and at the same time it can enhance the implant bioactivity by simulation of chemical constituents of the human bone [16]. Several methods have been explored to deposit HA coatings in order to enhance implant fixation. Plasma spraying [17] is the most used method to deposit HA. Other techniques are: pulsed laser deposition [18], sol-gel processing [19], electrophoretic [20] and electrochemical deposition [21].

The electrochemical method has attracted much interest in recent years. Eliaz and Sridhar [22] have studied the advantages of HA electrodeposition and the different aspects of HA electrocrystallization.

The aim of the present paper is to demonstrate the effect of different surface treatments of the CP Ti (grade 2) on the electrochemical behavior in simulated human body fluid.

2. Experimental

2.1 Surface preparation

Commercial pure titanium CP Ti (grade 2) disks of 12 mm in diameter and 2 mm thickness were employed as substrates. The disks were polished incrementally with silicon carbide paper from 320 to 4000 grit, then the specimens were cleaned with ethanol and distilled water in ultrasonic bath for 10 minutes each. The samples were then divided into 5 groups which were subjected to one of the following surface treatments.

2.2 Surface modification

The first group (i) of the samples was grit-blasted with alumina powder, and then the samples were washed in distilled water and cleaned ultrasonically in ethanol for 10 minutes.

The second group (ii) was alkaline treated in 5 M NaOH solution for 2.5 hours at 60°C, after that the samples were rinsing with distilled water, dried and heat treated at 600°C for 1 hour. As titanium has a strong tendency to oxidation, the heat treatment was performed at a pressure of 10^{-5} Torr.

The specimens from the third group (iii) were etched in 37% HCl for 2 hours at room temperature. After etching the specimens were immersed in 15 M NaOH aqueous solution at 60°C for 24 hours, then the samples were cleaned with distilled water and dried at 40°C for 24 hours.

The fourth group (iv) represents the CP Ti specimens which were covered with a thin layer of hydroxyapatite (HA) using the electrochemical method. The electrochemical deposition of HA was carried out using a Solatron SI 1287 potentiostat connected to a glass cell with three electrode configuration. As reference electrode a supersaturated calomel electrode (SCE) was used, as counter-electrode a cylindrical platinum grid was employed and the titanium disks were the working electrodes. The electrolyte used for deposition contained 0.61 mM $\text{Ca}(\text{NO}_3)_2$ and 0.36 mM $\text{NH}_4\text{H}_2\text{PO}_4$ [22], with an pH 4.5. The deposition was carried out in the potentiostatic mode at -1 V vs. SCE for 3 hours at 80°C [22]. After deposition the specimens were rinsed in distilled water and then dried at 100°C for 24 h.

The last group (v) of samples comprised of polished CP Ti disks that were used as reference.

The microstructure analysis was performed by X-ray diffraction (XRD) using a Philips X'Pert-MRD with CuK_α radiation and a scanning electron microscope (SEM JEOL 6000), coupled with energy dispersive X-ray analysis (EDX)

2.3 Electrochemical measurements

The electrochemical measurements were conducted in a three-electrode cell using a saturated calomel electrode (SCE) as reference, as counter electrode a cylindrical platinum grid was used and the titanium disks served as working electrode. The disk was electrochemically connected in a special (home-made) corrosion holder with the surface exposed to the solution of 0.5 cm^2 .

The corrosion behavior of the treated and the untreated titanium samples was tested in Hank's solution at pH 7, with the following chemical composition (in g/l): 8 NaCl, 0.4 KCl, 0.14 CaCl_2 , 0.06 $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.06 $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 0.35 NaHCO_3 , 1.00 glucose, 0.60 KH_2PO_4 and 0.10 $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ [13]. Fresh solution was used for each electrochemical test. Time dependent open circuit potential (OCP) measurements and potentiodynamic polarization experiments were carried out at a temperature of 37°C using a Solatron SI 1287 Electrochemical interface potentiostat.

Before conducting the potentiodynamic polarization experiments the samples were immersed in Hank's solution for 1 h for stabilization and the OCP was measured during this period. Potentiodynamic polarization tests were performed at a scan rate of 0.5mV/s both in the cathodic and anodic directions from their respective OCP. In the cathodic direction, the potential scan was limited to 0.5V whereas in the anodic direction the potential was scanned up to 5V from their respective OCP. Each electrochemical experiment was conducted several times to verify the reproducibility of the results. A fresh specimen surface was prepared for each test.

3. Results and discussion

3.1. Surface state characterization

The CP Ti surfaces before and after different surface treatments were studied by SEM as well as after the corrosion tests. The surface of NaOH-treated samples shows a porous structure at high magnification (Fig 1b), the same structure was reported by Ban and Asoh et al. [12,23]. Fig. 1e shows the micrographs of a CP Ti surface after HCl etching and subsequent alkali treatment. This treatment generates micro-pits on the titanium surface but at high magnification a very porous structure is observed.

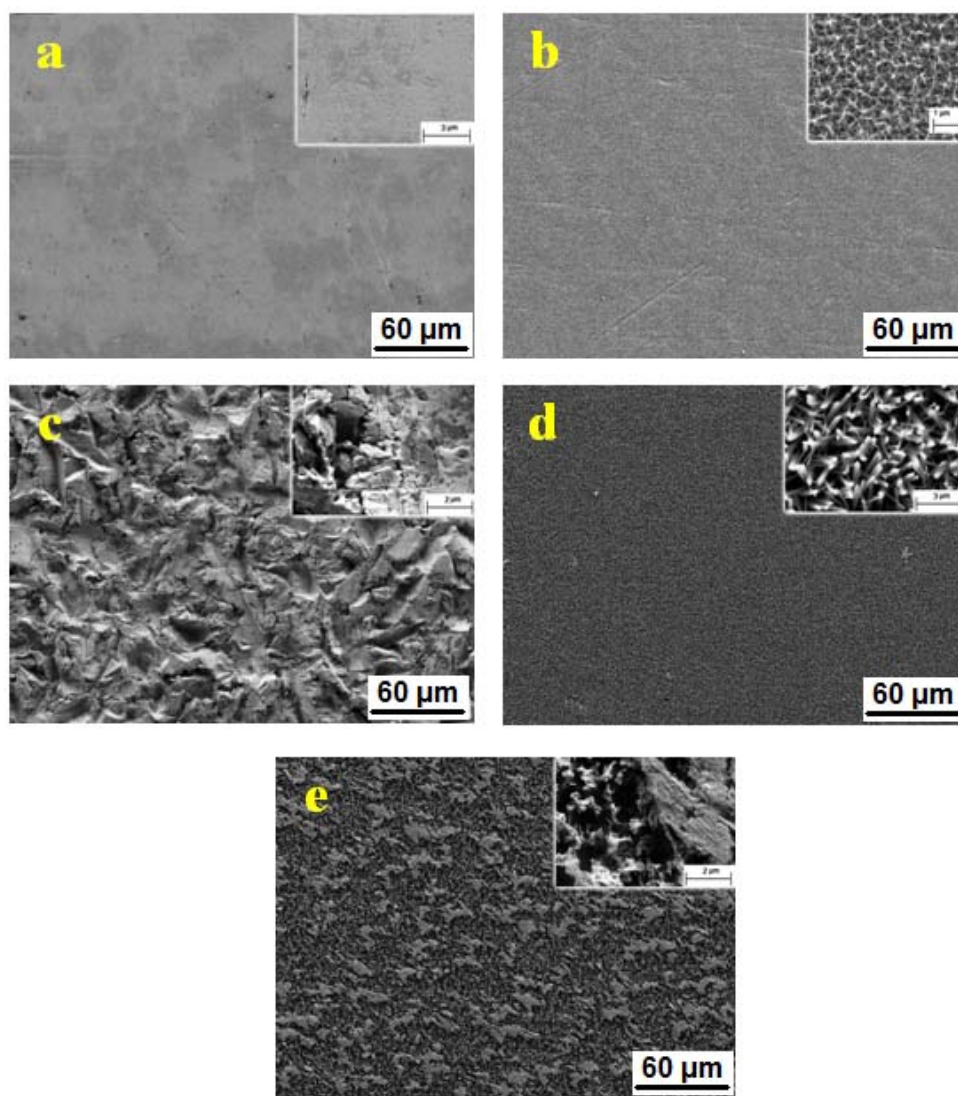


Fig. 1 SEM micrographs taken from the surface of a) CP Ti, b) alkali treated, c) blasted, d) HA/Ti, e) etched and subsequent alkali treatment, before the electrochemical measurements

An alkaline modification allows to change the surface state from hydrophobic (acid etched) to hydrophilic as it was reported by Breme et al. [24]. Fig. 1d reveals a very uniform HA coating consisting of needles. SEM images acquired at high magnification revealed that the needles are orientated in different directions. This morphology was also reported by Eliaz et al. [25]. After the sand blasting with Al_2O_3 particles a surface with high roughness is produced (Fig. 1c).

Using this method, Al_2O_3 particles are often found to be attached to the surface [8] which has been observed by EDX analysis (Fig.2).

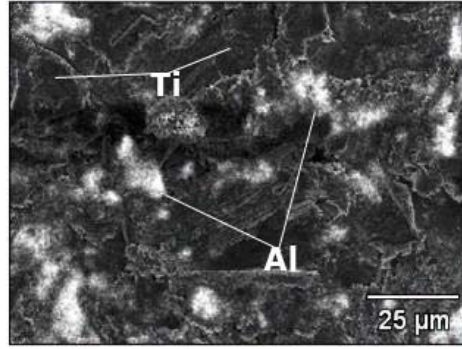


Fig. 2 EDX mapping of CP Ti blasted with Al_2O_3

XRD patterns of polished CP Ti as reference and all samples after different surface treatments are shown in the Fig. 3. For polished CP Ti the presence of α -Ti phase is observed. After NaOH treatment a second phase of sodium titanate (Na_2TiO_3) is revealed, which was also reported by Shukla et al. [13].

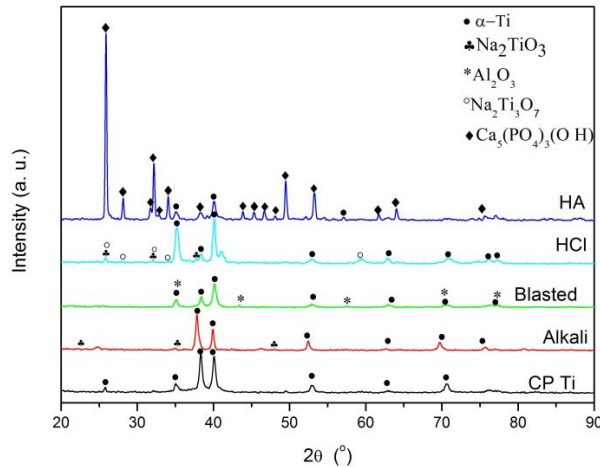


Fig. 3 XRD pattern obtained from the surface of CP Ti, alkali treated, blasted, HA/Ti, etched and subsequent alkali treatment

By immersing the HCl etched sample in alkaline solution, an additional phase consisting of sodium titanium oxide ($\text{Na}_2\text{Ti}_3\text{O}_7$), can be found in the XRD pattern. In the case of a sample blasted with Al_2O_3 particles, the XRD patterns shows that besides the α -Ti phase also aluminium oxide Al_2O_3 peaks are present.

For the samples covered with hydroxyapatite, peaks from both the deposited HA coating and the Ti substrate were observed.

Fig. 4 reveals the SEM micrographs of all the samples after the polarization tests. In all cases the surface is free from pits but there are some residual products left from the electrolyte, indicating that the samples rinsing, after the corrosion tests was not sufficient.

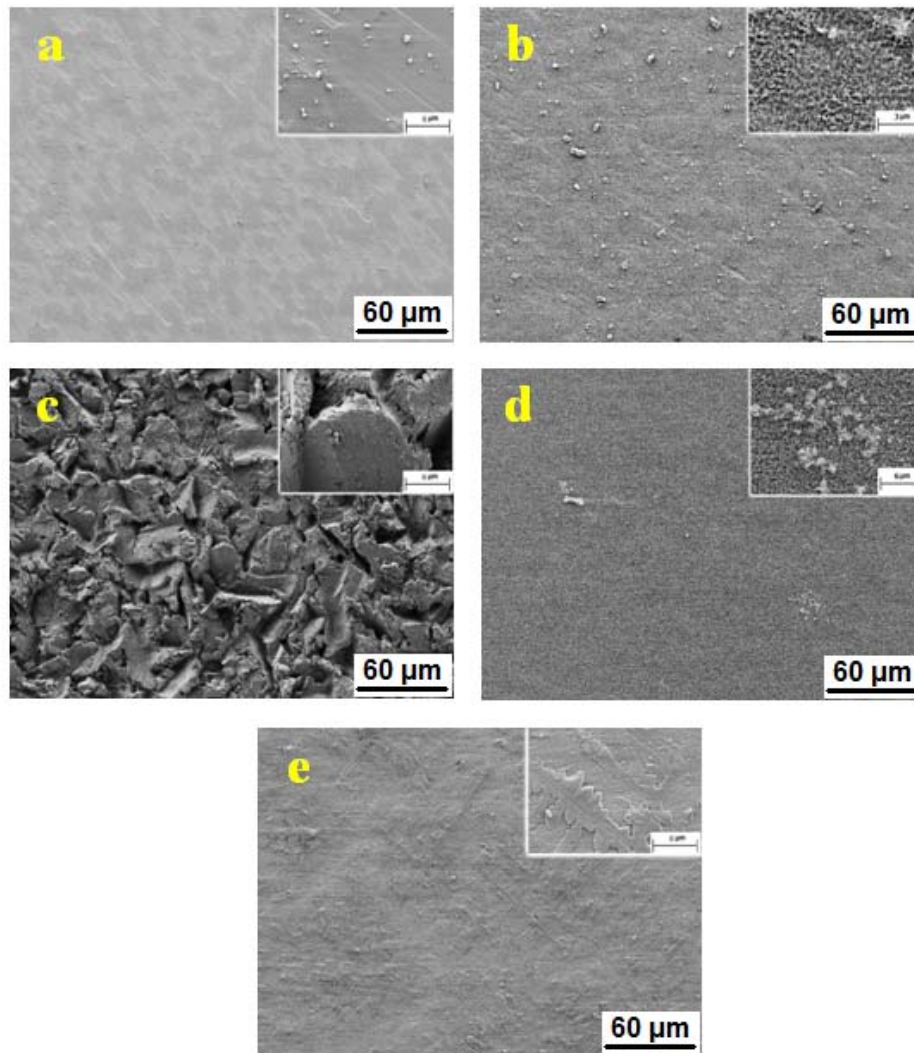


Fig. 4 SEM micrographs taken from the surface of a) CP Ti, b) alkali treated, c) blasted, d) HA/ Ti, e) etched and subsequent alkali treatment, after the electrochemical measurements.

3.2 Electrochemical characterization

The differently surface treated Ti samples were immersed in Hank's solution at 37°C for 1 h for stabilization and the open circuit potentials were measured during this period (Fig. 5). For all the studied samples except HA coating, the OCP shifts in the positive direction to more noble values, this suggests the formation of a passive film. The formed film acts as a barrier for metal dissolution and thus, can reduce the corrosion rate.

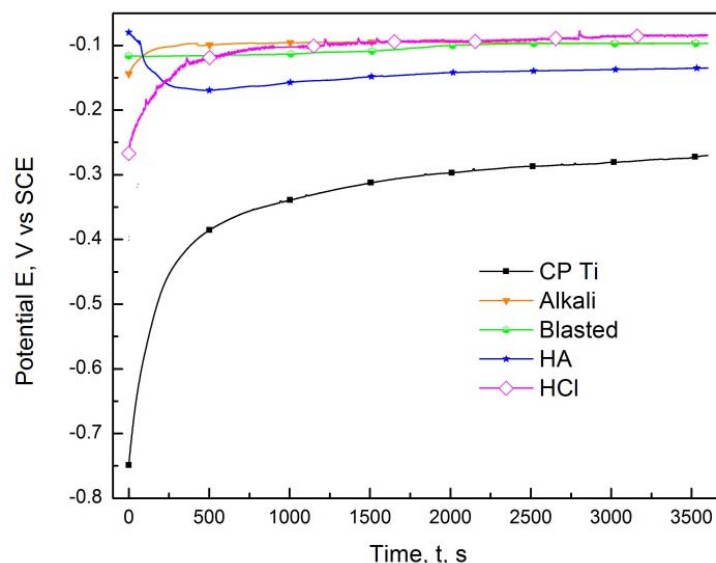


Fig 5. The open circuit potentials of CP Ti, alkali treated CP Ti, blasted, HA /Ti, etched and subsequent alkali treated CP Ti in Hank's solution at 37°C

For the freshly polished CP Ti surface this potential shift is more pronounced corresponding to the most significant passive layer formed. For the pre-treated samples the potential shift is much smaller since the surfaces were already pre-passivated by these pre-processing. The shift initial negative in the potential of the HA coated sample may be indicative for a weak change in the coating chemistry caused by the immersion in the electrolyte.

The measured potentials in Hank's solution at pH ~ 7 correspond very well with the potential region of TiO₂ stabilization at the same pH value in the Pourbaix diagram [26], indicating that the surface of the studied samples is covered with a stable oxide layer.

Potentiodynamic polarization curves of the untreated and treated CP Ti in Hank's solution at 37°C are shown in Fig. 6. The corrosion potential, corrosion current density and passive current density values at 750 mV and 4.5 V are

summarized in Table 1. The potentiodynamic polarization curves for a potential region close to the free corrosion potential are additionally shown in the inset of the Fig. 6. The nature of all polarization curves indicates a low free corrosion activity and a stable anodic and transpassive behavior, without chloride induced layer breakdown.

After the polarization studies the CP Ti surfaces were free from pits as it was shown in fig. 4 and this corresponding to what was also reported by Shukla et al. [13].

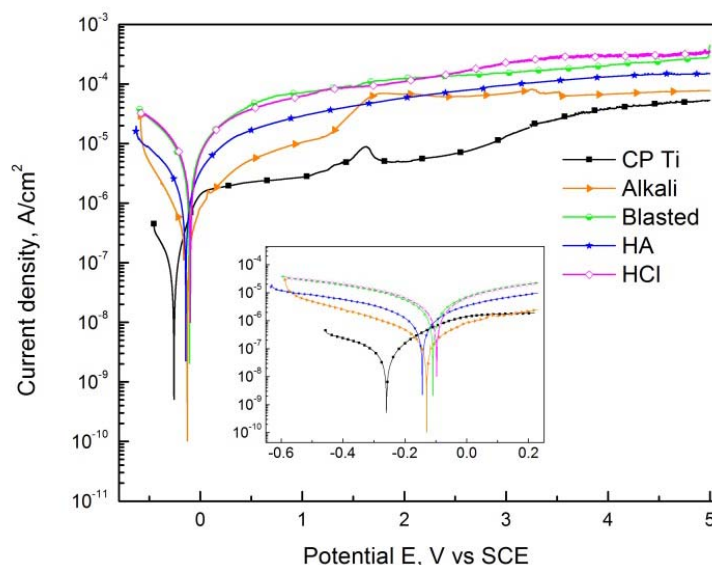


Fig. 6. Potentiodynamic polarization curves of the CP Ti, alkali treated CP Ti, blasted, HA /Ti, etched and subsequent alkali treated CP Ti at 37°C

For the freshly polished CP Ti surface the corrosion potential is ~ -0.25 V and is related with a corrosion current density of $7.1 \mu\text{A}/\text{cm}^2$, then, as the potential is increased to more positive value, the current density increased to $\sim 2.4 \mu\text{A}/\text{cm}^2$ when a stable passive plateau is revealed and occurs up to ~ 1.3 V when the decomposition of water begins, as indicated by a small anodic peak. This is followed by a transpassive region and this passive state remains stable up to 5 V.

The alkaline surface shows a more noble value of the corrosion potential of ~ -0.12 V but at the same time a higher corrosion current density compared with freshly polished CP Ti surface. This can be attributed to an effect of the interaction between chloride ions and the alkali group + alkali layer. This layer usually has a thickness of $\sim 1 \mu\text{m}$ and has a lower barrier effect compared with the nano-meter passive layer of freshly CP Ti surface. After passing the water decomposition potential range a wide stable transpassive region is observed.

Table 1

The characteristics parameters, corrosion potential, and corrosion current density, obtained from the potentiodynamic polarization curves (shown in Fig.6)

Sample	E_{corr} V (SCE)	I_{corr} A/cm ²	$I_{\text{pass}(750\text{mV})}$ A/cm ²	$I_{\text{pass}(4.5\text{V})}$ A/cm ²
CP-Ti	-0.25	7·10E-8	2.4·10E-6	4.6·10E-5
Alkali	-0.12	6·10E-8	7.5·10E-6	7.5·10E-5
HCl	-0.09	7·10E-7	4.9·10E-5	3·10E-4
Blasted	-0.1	7·10E-7	6·10E-5	2.4·10E-4
HA	-0.14	2·10E-7	2.2·10E-5	1.4·10E-4

The blasted, HCl etched and HA coated CP Ti surfaces show a higher corrosion current density and a higher anodic current density in comparison with the freshly polished CP-Ti surface. In the case of the sample etched in 37% HCl this increment in the current density may be due to the strong increased in the specific surface area. This and the mechanical defects present on the sand blasted surface may similarly induce this particular behavior. Coating of the CP Ti with a thin layer of hydroxyapatite is changing the surface chemistry due to precipitation of Ca PO₄ compounds, which may yield a lower barrier effect than a TiO₂-based passive layer which can only grow in unlimited manner on a uncoated surface.

4. Conclusion

The treated titanium surface presents a different phase constitution according to the applied surface treatment.

In this work, it was shown that thin titanium oxide films grown by different surface treatments, protect the Ti-grade 2 surface up to 5 V in Hank's solution at 37°C.

The corrosion resistance studies of the treated samples show an improvement in the corrosion stability as their corrosion potentials are shifted to more positive values.

Acknowledgements

The work has been funded by the Sectorial Operational Programme Human Resources Development 2007-2013 of the Romanian Ministry of Labour, Family and Social Protection through the Financial Agreement POSDRU/88/1.5/S/61178 and by the European Commission in the network project EC-ITN BioTiNet under contract no 264635.

REFERENCES

- [1] *M. Navarro, A. Michiardi, O. Castaño and J.A. Planell*, Biomaterials in orthopaedics, J. R. Soc. Interface 2008 5, 1137-1158
- [2] *J. van Drunen, B. Zhao, G. Jerkiewicz*, Corrosion Behavior of Surface-Modified Titanium in a Simulated Body Fluid, J Mater Sci (2011) 46:5931–5939
- [3] *C. Zhao, X. Zhang, P. Cao*, Mechanical and Electrochemical Characterization of Ti-12Mo-5Zr Alloy for Biomedical Application, Journal of Alloys and Compounds 509(2011) 8235-8238
- [4] *C. E. B. Marino and L. H. Mascar*, Electrochemical Tests to Evaluate the Stability of the Anodic Films on Dental Implants, International Journal of Electrochemistry, Vol. 2011
- [5] *C.T. Kwok, P.K. Wong, F.T. Cheng, H.C. Man*, Characterization and Corrosion behavior of Hydroxyapatite Coatings on Ti6Al4V Fabricated by Electrophoretic Deposition, Applied Surface Science 255(2009) 6736-6744
- [6] *M. Browne, P.J. Gregson*, Effect of Mechanical Surface Preparation on Metal Ion Release, Biomaterials 21(2000) 385-392
- [7] *G. Manivasagam, D. Dhinasekaran and A. Rajamanickam*, Biomedical Implants: Corrosion and its Prevention, Recent Patents on Corrosion Science, 2010, 2, 40-54
- [8] *L. Le Guehennec, A. Soueidan, P. Layrolle, Y. Amourig*, Surface treatments of titanium dental implants for rapid osseointegration, dental materials 23 (2007) 844–854
- [9] *A. Alves de Almeida-Jr, R.G. Fonseca, I. G. Haneda, F. de Oliveira Abi-Rached, G.L. Adabo*, Effect of Surface Treatments on the Bond Strength of a Resin Cement to Commercially Pure Titanium, Braz Dent J (2010) 21(2): 111-116
- [10] *X. Liu, P. K. Chu, C.Ding*, Surface modification of titanium, titanium alloys, and related materials for biomedical applications, Materials Science and Engineering R 47 (2004) 49–121
- [11] *H.C. Hsu, S.C. Wu, C. L. Fu, W. F. Ho*, Formation of calcium phosphates on low-modulus Ti–7.5Mo alloy by acid and alkali treatments, J Mater Sci (2010) 45:3661–3670
- [12] *S. Ban*, Effect of Alkaline treatment of pure titanium and its alloys on the bonding strength of dental veneering resins, Journal of Biomedical Materials Research, 66A (2003) 138-145
- [13] *A.K. Shukla, R. Balasubramaniam*, Effect of surface treatment on electrochemical behavior of CP Ti, Ti–6Al–4V and Ti–13Nb–13Zr alloys in simulated human body fluid, Corrosion Science 48 (2006) 1696–1720
- [14] *T. Hanawa*, Biofunctionalization of Titanium for dental implant, Japanese Dental Science Review (2010) 46, 93-101
- [15] *S.R. Sousa and M.A. Barbosa*, Effect of Hydroxyapatite Thickness on metal ion release from Ti6Al4V Substrates, Biomaterials, 17(1996) 397-404
- [16] *M.V. Popa, J.M. Calderon Moreno, M. Popa, E. Vasilescu, P. Drob, C. Vasilescu, S. I. Drob*, Electrochemical deposition of bioactive coatings on Ti and Ti–6Al–4V surfaces, Surface & Coatings Technology 205 (2011) 4776–4783
- [17] *Y.C. Tsui, C. Doyle, T.W. Clyne*, Plasma sprayed hydroxyapatite coatings on titanium substrates Part 1: Mechanical properties and residual stress levels; Biomaterials 19 (1998) 2015-2029;
- [18] *C.F. Koch, S. Johnson, D. Kumar, M. Jelinek, D.B. Chrisey, A. Doraiswamy, C. Jin, R.J. Narayan, I.N. Mihailescu*: Pulsed laser deposition of hydroxyapatite thin films; Materials Science and Engineering C 27 (2007) 484–494;
- [19] *M. Cavalli, G. Gnappi, A. Montenero, S. Bersani, P.P. Lottici, S. Kaciulis, G. Mattogno, M. Fini*, Hydroxy-and Florapatite Films on Ti alloy substrates: Sol-gel Preparation and Characterization, Journal of Materials Science 36 (2001) 3253-3260

- [20] *M. Wei*, Electrophoretic Deposition of Hydroxyapatite Coatings on Metal Substrates: A Nanoparticulate Dual-Coating Approach; *Journal of Sol-Gel Science and Technology* 21, 39–48, 2001;
- [21] *N. Eliaz, M. Eliyahu*, Electrochemical processes of nucleation and growth of hydroxyapatite on titanium supported by real-time electrochemical atomic force microscopy; *Journal of Biomedical Materials Research Part A* DOI 10.1002;
- [22] *N. Eliaz and T. M. Sridhar*, Electrocrystallization of Hydroxyapatite and Its Dependence on Solution Conditions; *Crystal Growth & Design* VOL. 8 (2008) 3965–3977;
- [23] *H. Asoh, T. Kawame, W. Shibata and S. Ono*, Electrodeposition of Hydroxyapatite on Alkali Treated Titanium, *Journal of the society of inorganic Materials, Japan*, Vol.16 (2009) 28-36
- [24] *J. Breme, C. J. Kirkpatrick, and R. Thull*, *Metallic Biomaterial Interfaces*; 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
- [25] *N. Eliaz, S. Shmueli, I. Shur, D. Benayahu, D. Aronov, G. Rosenman*, The effect of surface treatment on the surface texture and contact angle of electrochemically deposited hydroxyapatite coating and on its interaction with bone-forming cells; *Acta Biomaterialia* 5 (2009) 3178–3191
- [26] *M. Pourbaix*, *Atlas of Electrochemical Equilibria in Aqueous solutions*, Pergamon Press Ltd, 1966.