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CUT Czestochowa University of Technology

Hybrid oxidation of titanium substrates for biomedical applications

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Hybrid oxidation of titanium substrates for biomedical applications

Abstract

Titanium oxidation for biomedical applications is still a challenge in obtaining both good mechanical and physicochemical properties of thin oxide layers as well as the required good adhesion to titanium substrates and of course bioactivity. Interesting techniques for TiO_2 layers formation are electrochemical methods (anodizing), plasma methods (PVD) and diffusive methods (Fluidized Bed FB). Each method aims to create a thin homogenous oxide layer characterized by thermal stability and re-passivation in the presence of body fluid environment. However, an important aspect here is also phase composition of thin oxide layers, essential in the processes of osseointegration. Accordingly research carried out by the Author aims to produce such a titanium substrate, where surface zone is $Ti_\alpha(O)$ solid solution formed with Fluidized Bed diffusion process (883K, 913K for 6h / 8h) and the outer layer is TiO_2 oxide produced by PVD magnetron sputtering. Effects of such hybrid oxidation on titanium physiochemical properties were investigated with TEM / EFTEM, SIMS, RS and Nanoindentation tests. Results showed that hybrid oxidation made it possible to generate favorable synergetic effect between Fluidized Bed and PVD oxide layers and to reduce the stresses at their interface. In turn, variable share of TiO_2 oxide phases (rutile + anatase mixture) obtained at the titanium surface allowed for the significant enhancement of hydroxyapatite growth which was confirmed by 7 / 14 days Kokubo tests. Hybrid oxidation processes also influenced the decrease in the surface roughness parameters, important for implant materials.

Functionalization of titanium substrates for biomedical applications – state of the art (1)

Thin layers formation: TiO_2, TiN_xO_y

PVD, CVD, Sol-Gel, PLD (single stage treatments)

Applied Surface Science 317 (2014) 986–993

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ELSEVIER

Sputtered titanium oxynitride coatings for endosseous applications: Physical and chemical evaluation and first bioactivity assays

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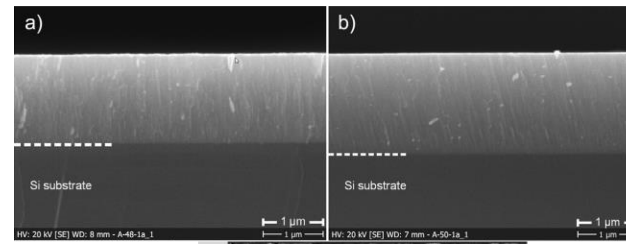
ABSTRACT

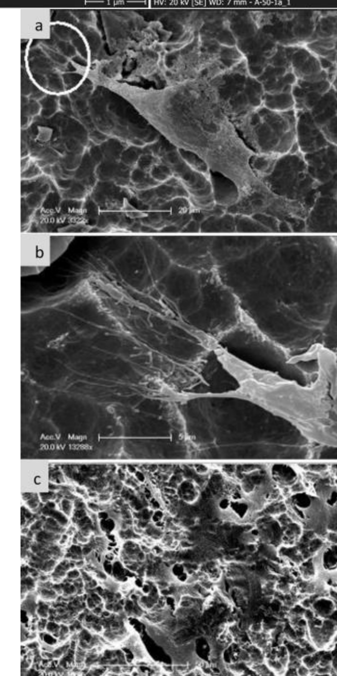
Titanium oxynitride coatings (TiN_xO_y) are considered a promising material for applications in dental implantology due to their high corrosion resistance, their biocompatibility and their superior hardness. Using the sputtering technique, TiN_xO_y films with variable chemical compositions can be deposited. These films may then be set to a desired value by varying the process parameters, that is, the oxygen and nitrogen gas flows. To improve the control of the sputtering process with two reactive gases and to achieve a variable and controllable coating composition, the plasma characteristics were monitored *in-situ* by optical emission spectroscopy.

TiN_xO_y films were deposited onto commercially pure (ASTM 67) microroughened titanium plates by reactive magnetron sputtering. The nitrogen gas flow was kept constant while the oxygen gas flow was adjusted for each deposition run to obtain films with different oxygen and nitrogen contents. The physical

Investigation of layers: Structure, Phase composition etc.



Bioactivity of the layers



Banakh, O & Moussa, Mira & Matthey, Joel & Pontearso, Alessandro & Cattani-Lorente, Maria & Sanjines, Rosendo & Fontana, Pierre & Wiskott, Anselm & Durual, Stéphane. (2014). Sputtered titanium oxynitride coatings for endosseous applications: Physical and chemical evaluation and first bioactivity assays. Applied Surface Science. 317. 986-993

Functionalization of titanium substrates for biomedical applications – state of the art

SBF, In vitro, Cell culture tests of TiO_2 thin layers
Functionalization of TiO_2 scaffolds etc.

Materials Science & Engineering C 81 (2017) 597–606

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Review

Functionalization of titanium dioxide nanotubes with biomolecules for biomedical applications

Weslley F. Oliveira[a], Isabel R.S. Arruda[b], Germana M.M. Silva[b], Giovanna Machado[b], Luana C.B.B. Coelho[a], Maria T.S. Correia[a,*]

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Biosensor
Lectin

ABSTRACT

Titanium (Ti) and its alloys are extensively used in the manufacture of implants because they have biocompatibility. The production of a nanostructured surface can be achieved by means of titanium dioxide nanotubes (TNTs) which can have dimensions equivalent to the nanometric components of human bone, in addition to increasing the efficiency of such implants. The search is ongoing for ways to improve the performance of these TNTs in terms of their functionalization through coating these nanotubular matrices with biomolecules. The biocompatibility of the functionalized TNTs can be improved by promoting rapid osseointegration, by preventing the adhesion of bacteria on such surfaces and/or by promoting a more sustained local release of drugs that are loaded into such TNTs. In addition to the implants, these nanotubular matrices have been used in the ...heir surfaces, ...techniques of ...olecules that ...veillance also ...ces, lectins.

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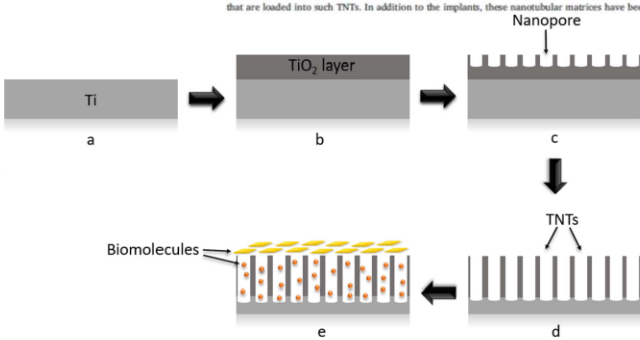

Bioactive Materials 2 (2017) 108–115

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journal homepage: http://www.keaipublishing.com/en/journals/bioactive-materials/

Bioactivation of titanium dioxide scaffolds by ALP-functionalization

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Titanium dioxi...
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Polydopamine
Surface modifi...
Bioactivity

ABSTRACT

Three dimensional TiO_2 scaffolds are receiving renewed attention for bone tissue engineering (TE) due to their biocompatibility and attractive mechanical properties. However the bioactivity of these scaffolds is comparatively lower than that of bioactive glass or hydroxyapatite (HA) scaffolds. One strategy to improve bioactivity is to functionalize the surface of the scaffolds using biomolecules. Alkaline phosphatase (ALP) was chosen in this study due to its important role in the bone mineralization process. The current study investigated the ALP functionalization of 3D titanium dioxide scaffolds using self-polymerization of dopamine. Robust titanium scaffolds (compressive strength~2.7 ± 0.3 MPa) were produced via foam replica method. Enzyme grafting was performed by dip-coating in polydopamine/ALP ... enzymatic ...ion on the ...ALP coated ...P enhances ...system for

1. Introduc...

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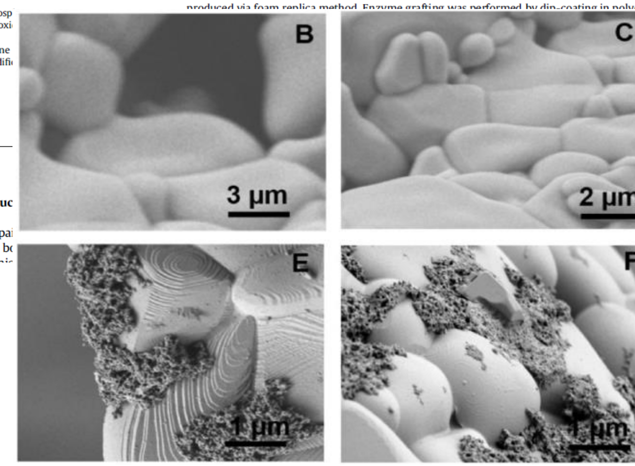


Sengottuvelan, Abirami & Balasubramanian, Preethi & Will, Julia & Boccaccini, Aldo. (2017). Bioactivation of titanium dioxide scaffolds by ALP-functionalization. Bioactive Materials. 2. 10.1016/j.bioactmat.2017.02.004.

Rahimi, Nazanin & A. Pax, Randolph & MacA. Gray, Evan. (2016). Review of functional titanium oxides. I: TiO2 and its modifications. Progress in Solid State Chemistry. 44. 10.1016

Hybrid biomaterials – new approach in surface engineering

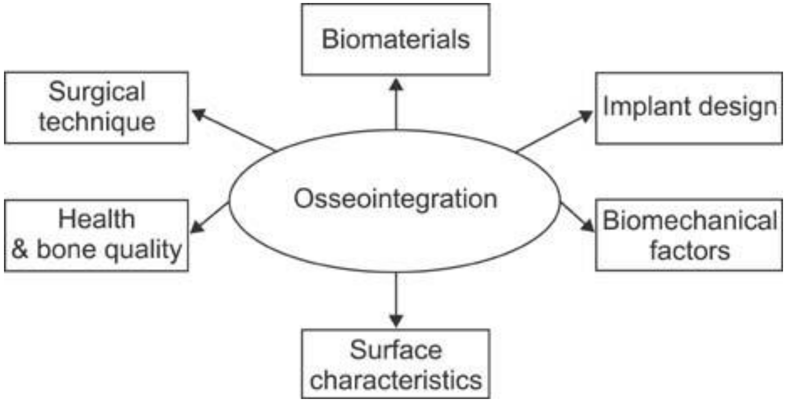
The new trend in biomaterials is to use materials that play an active role in tissue regeneration (bioactive and biodegradable materials) rather than passive and inert materials (biocompatible materials). Such class of hybrid materials has been described as the "Third Generation" biomaterials.

However in hybrid materials problem is more serious when thin layers are applied on surfaces. At the interface between the coating and the substrate considerable forces and stresses can appear that lead to inhomogeneities and cracks in the material.

Therefore to reduce this effect hybrid materials or nanocomposites are mostly formed by PVD, CVD, Sol-Gel methods

Crucial requirements for the biomaterials surfaces:

- ✓ *Composition according to the desired end application.*
- ✓ *Favourable surface morphology*
  – low roughness parameters (R_a< 1 micron)
- ✓ *Low stresses at the substrate / layer interface*
- ✓ *High bioactivity (i.e. HAp growth at the Surface after 14 days Kokubo test)*

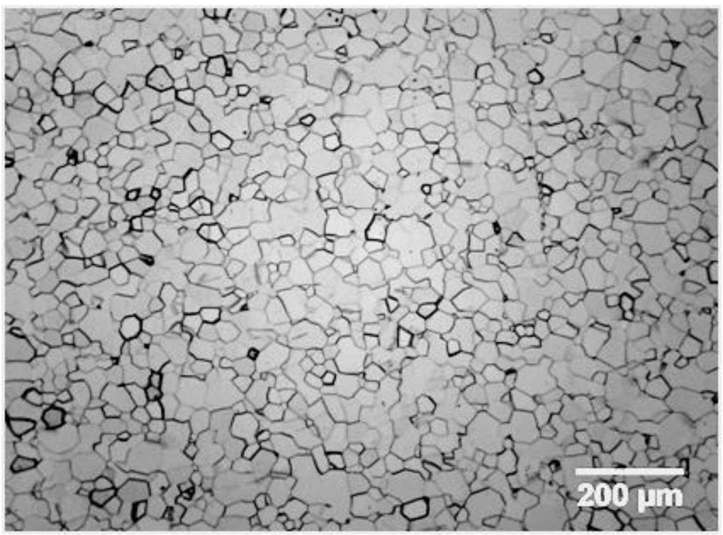


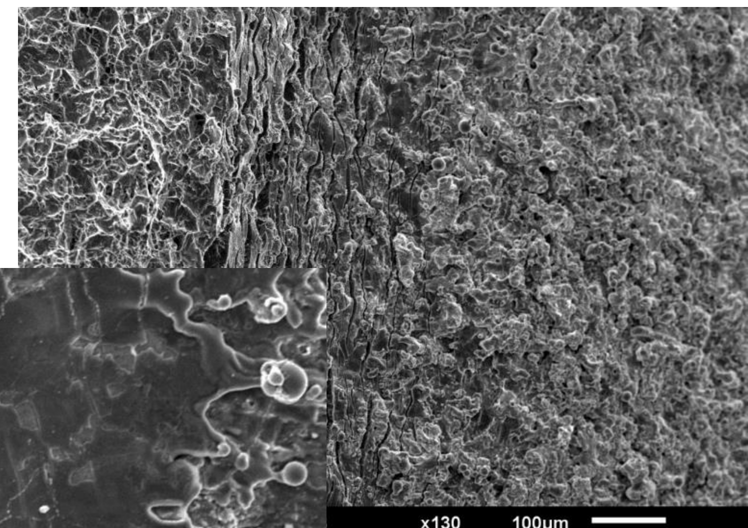
J Korean Assoc Oral Maxillofac Surg. 2014 Apr;40(2):50-60

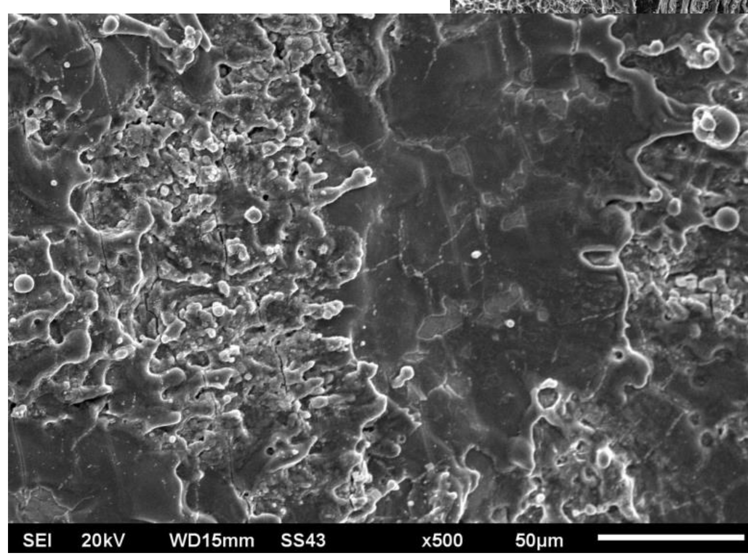
Substrate material analysis – titanium Grade 2 (LM / SEM)

Material	Chemical composition, mass %					
	O	N	C	H	Fe	Ti
Ti 99.2 / Grade 2 Certified by KOBE STEEL LTD	*0,20*	*0,03*	*0,10*	*0,015*	*0,30*	*Rest*

Microstructure: Ti_{α} – LM / SEM image, etched with 96% H_2O + 2% HNO_3 + 2% HF

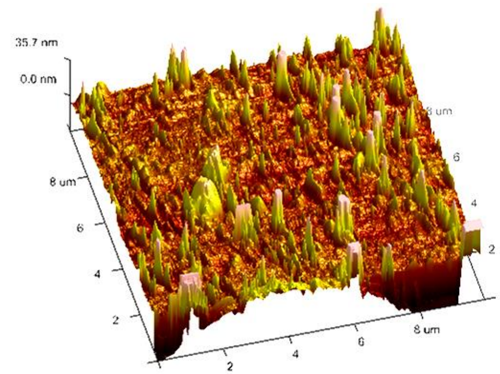




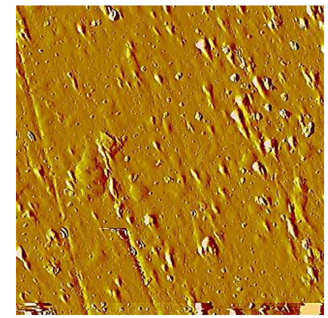


Titanium substrates preparation – SLA surface activation (SEM / AFM)

1. Mechanical activation / metallographic paper (grit 600 to 2000)



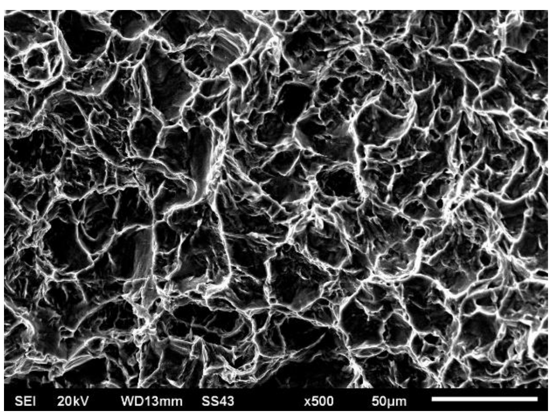
Scan area
AFM 10 x 10 µm

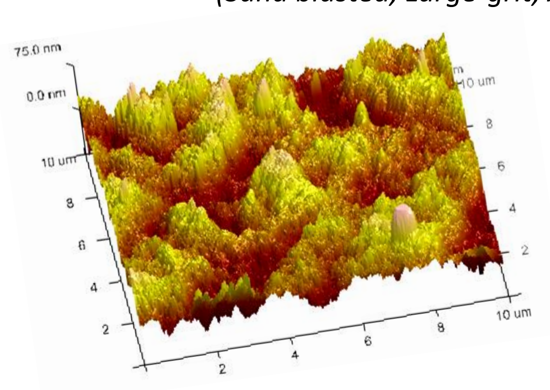


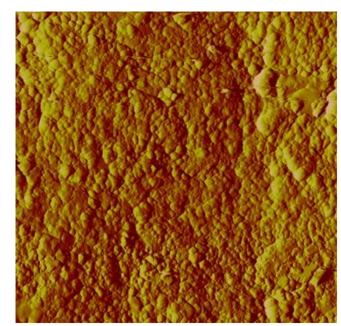
R_a = 0,463 µm ; R_q = 0,584 µm; R_{max} = 0,874 µm

2. Mechano-chemical activation: Al_2O_3+NaAl+Si_3O_8+ZrO_2+TiO_2 + H_2SO_4 90°C/HCl 60°C)

(Sand blasted, Large-grit, Acid etched – SLA)



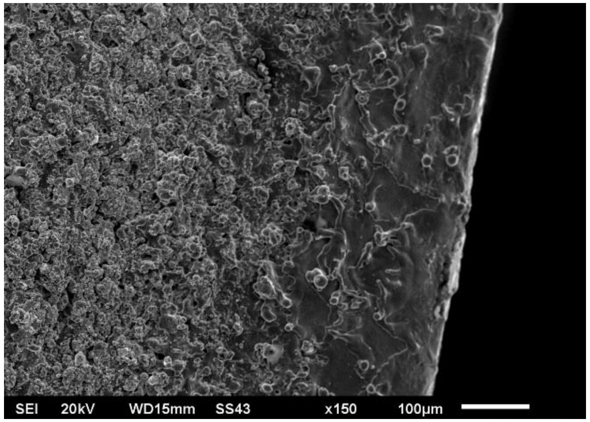




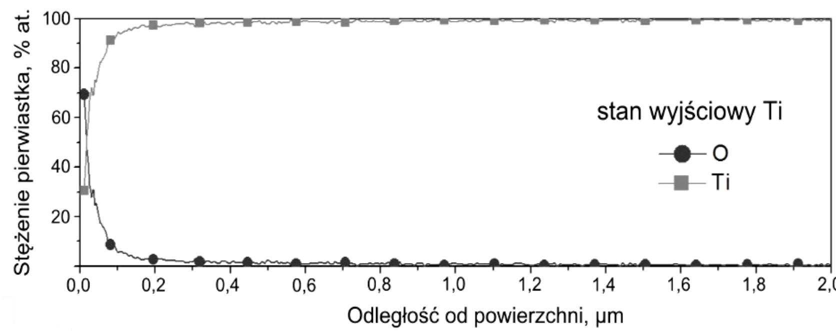
R_a = 0,937 µm ; R_q = 1,126 µm ; R_{max} = 1,386 µm

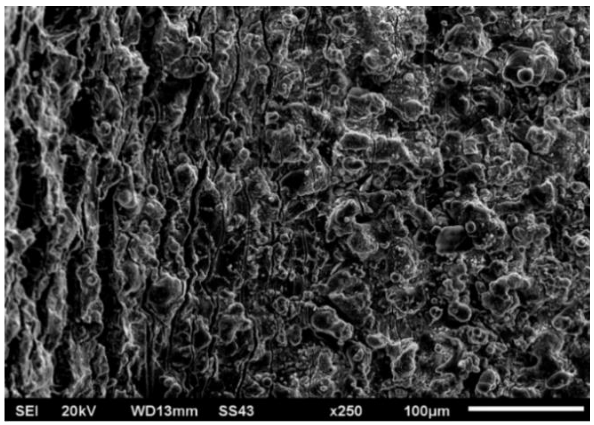
J.J. Jasiński, M. Lubas, J. Jasiński, P. Wieczorek, (2013), **Titanium oxidation effects after various surface modification methods**, Engineering of Biomaterials, Vol.16,

Diffusive oxidation (FADT) – surface layer analysis (SEM-EDX / GDEOS / HK)

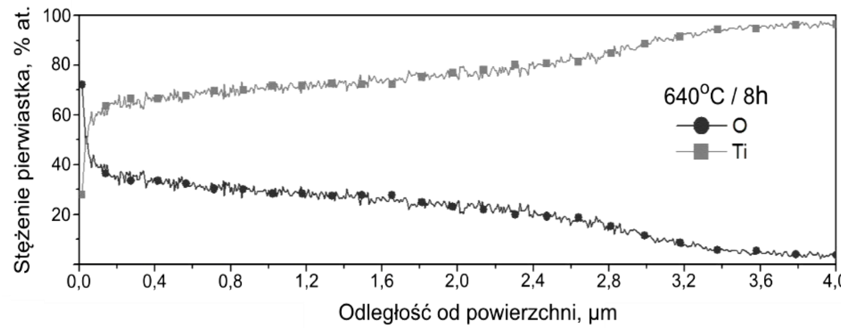


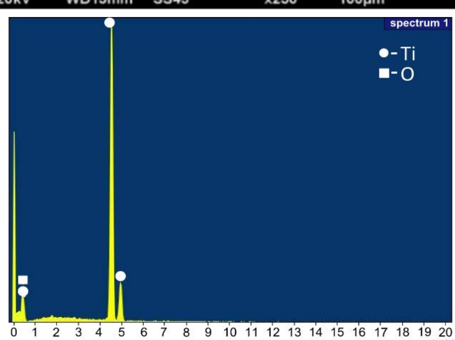
$Ti_{\alpha}(O)$ diffusive layer
9.0 – 12.0 µm

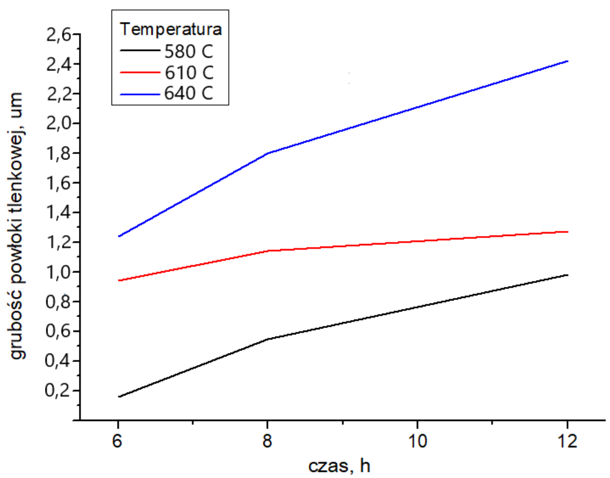




nano-porous TiO_2 layer
1.6 – 1.9 µm







<u>Ti substrates selected for hybrid oxidation</u>

T = 640°C / 8 h

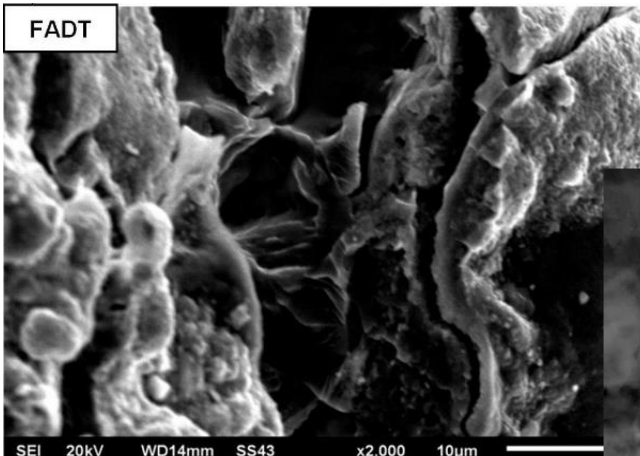
$h_{Ti\alpha(O)}$ = 9.0 – 11.0 µm

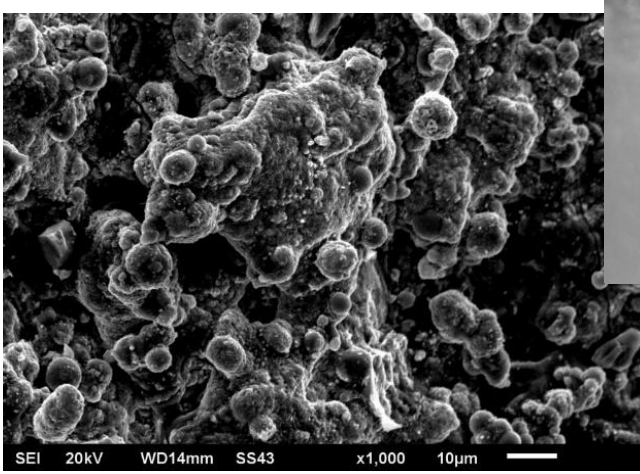
h_{TiO2} = 1.6 – 1.9 µm

H = 455 $HK_{0.01}$

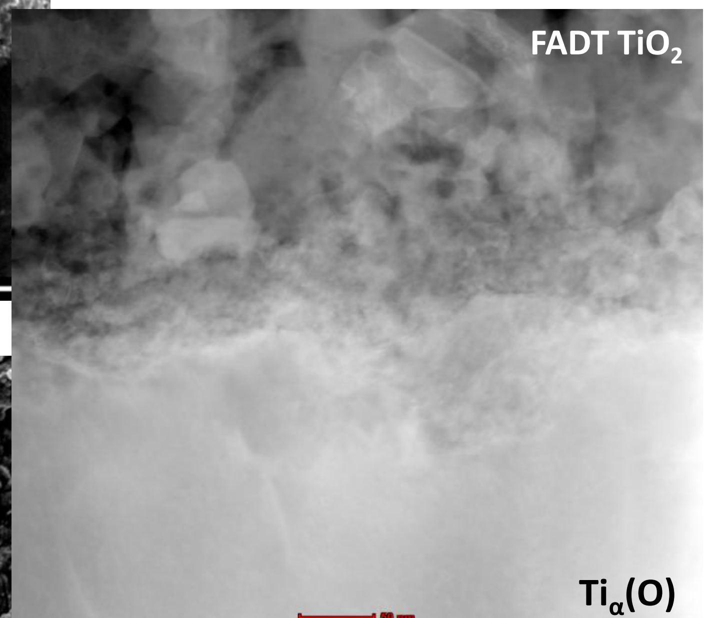
Diffusive oxidation FADT – nano-porous TiO_2 layer analysis (SEM / STEM / RS)

SEM

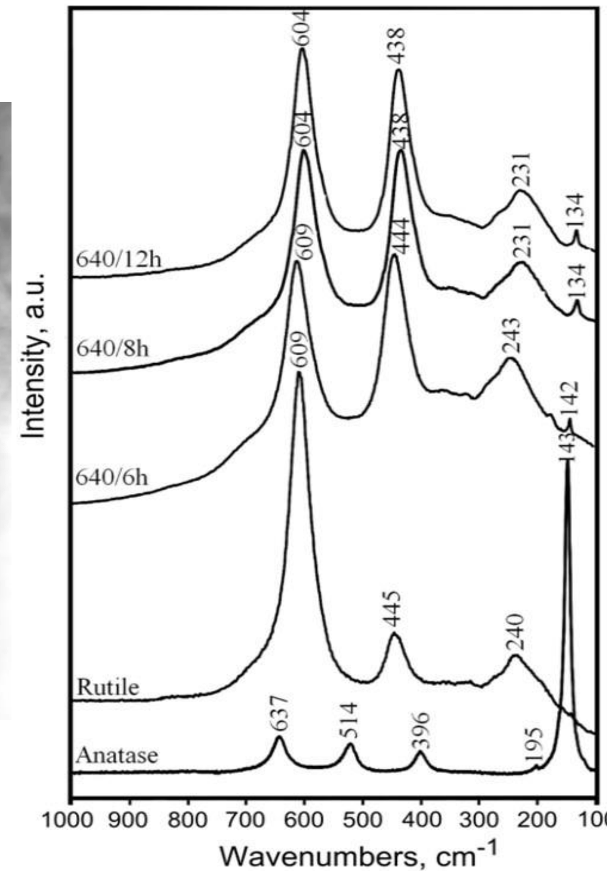




STEM



RS



M. Lubas, M. Sitarz, **J.J. Jasinski,** et al: **Fabrication and characterization of oxygen –Diffused titanium using spectroscopy method**, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy vol. 133, 2014, pg. 883-886.

Hybrid oxidation parameters

Microstructure FADT + PVD (SEM)

FADT+PVD TiO_2

PVD Magnetron sputtering

Process parameters

I. Stage: vacuum – 1 x 10^{-4} Pa

II. Stage: sputtering

Pressure: 3 Pa

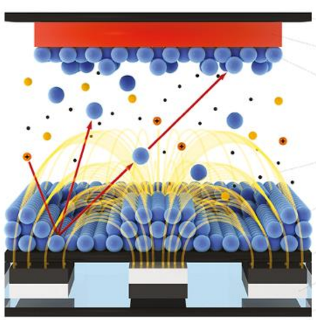
Power: 400 W

Atmosphere: 100% Ar

Target material: TiO_2

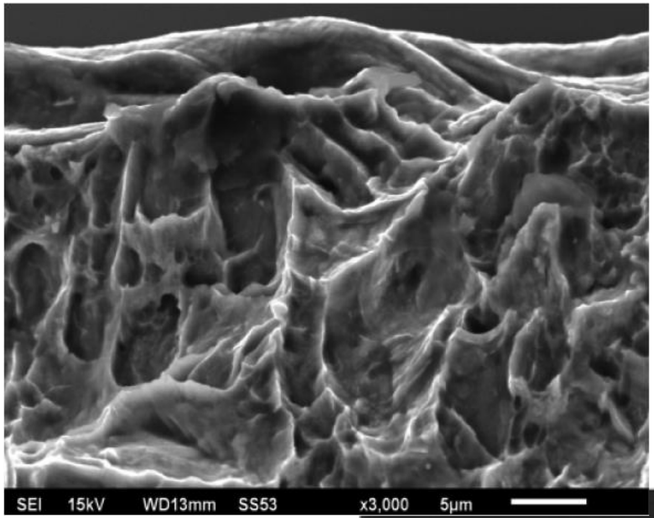
Sample – target distance: 55 mm

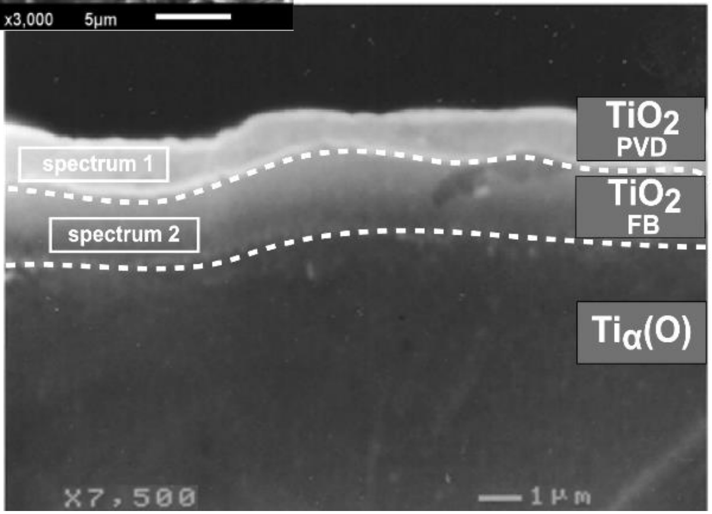
Process time: 20 min



visual-science.com

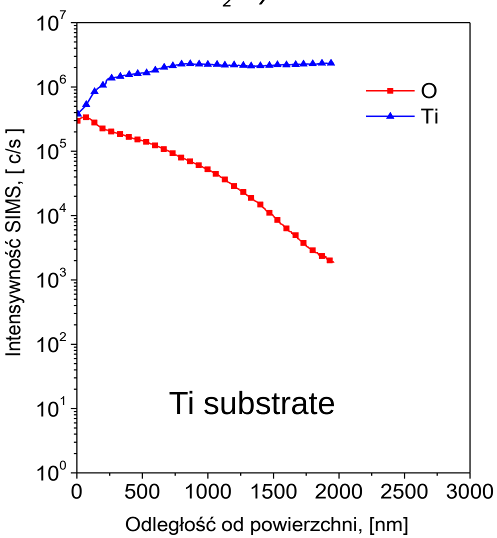
Patent application
no Pat-24/05/07/12,
Chemical heat treatment solution
of metallic alloys,
J.J.Jasiński P.Podsiad, J.Jasiński,

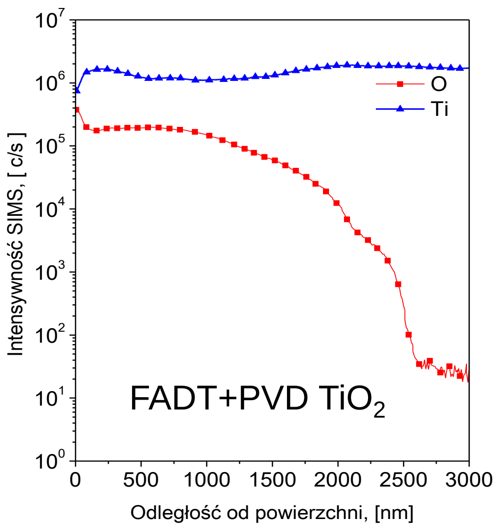




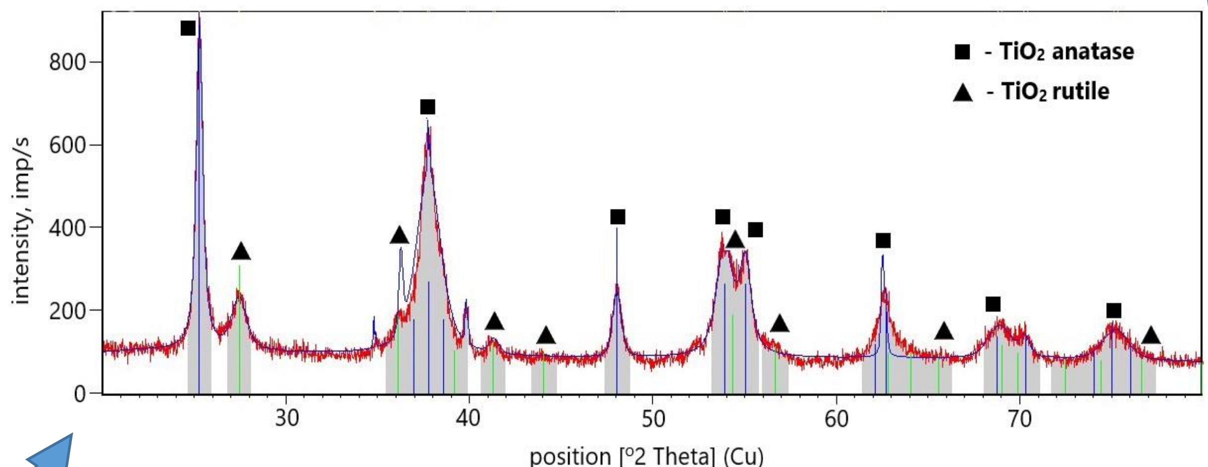
Hybrid oxidation – TiO_2 layers phase analysis (SIMS / GID-XRD)

SIMS – TiO_2 layer thickness



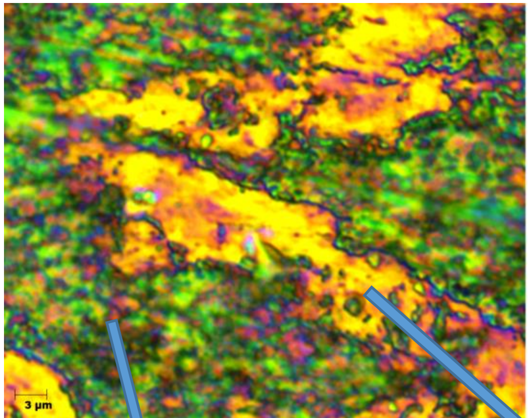


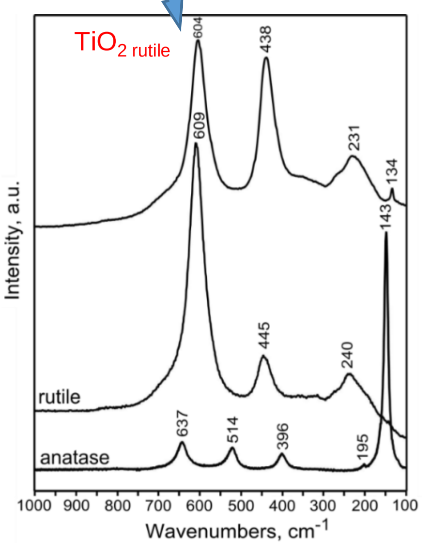
GID-XRD phase analysis of FADT + PVD TiO_2

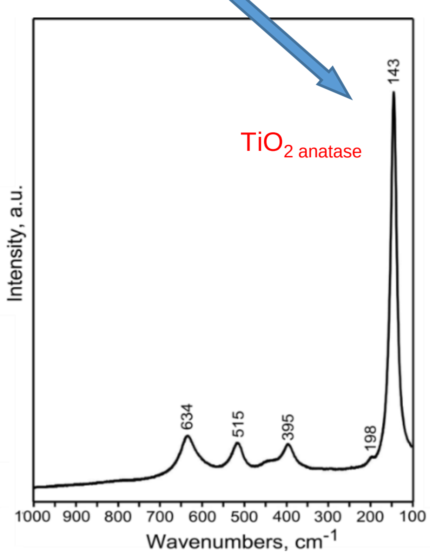


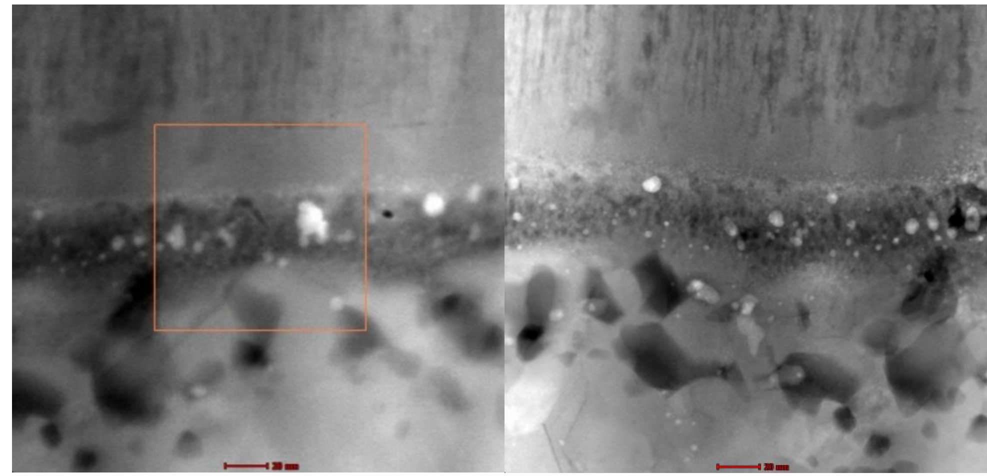
GID-XRD measurements: Cu anode / 2Θ = 20°÷80° / Ω = 1° st. 0.02, time 2.4 s/step

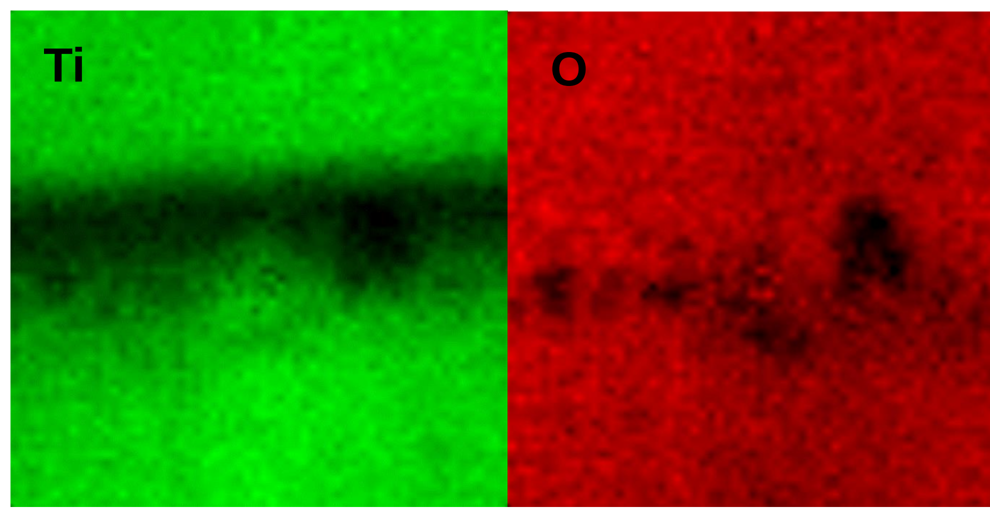
Hybrid oxidation – TiO_2 layers phase analysis (CLSM / RS / EFTEM MAPS)







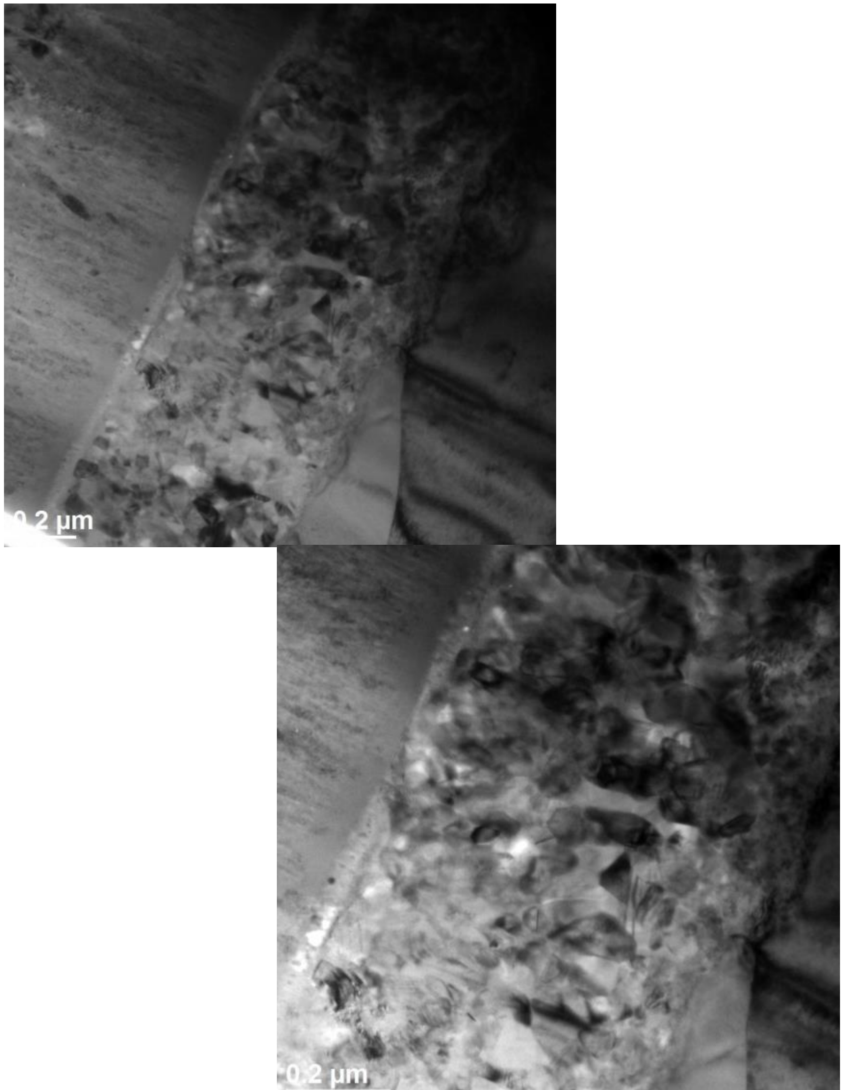


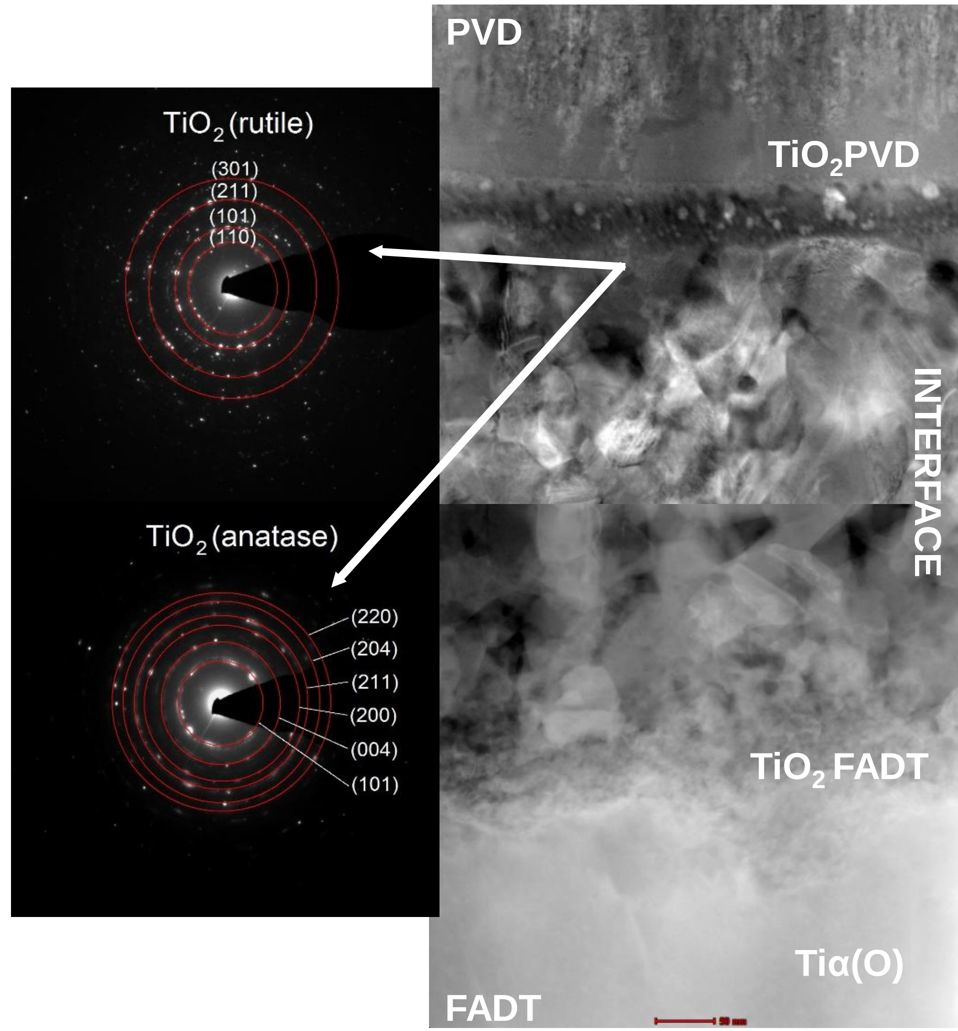


M. Lubas, **J.J.Jasiński**, M.Sitarz, Ł.Kurpaska, P.Podsiad, J.Jasiński, (2014), **Raman Spectroscopy of TiO2 Thin Films Formed by Hybrid Treatment for Biomedical Applications**, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, Vol.133, 867÷871

Hybrid oxidation – FADT TiO_2 / PVD TiO_2 interface analysis (STEM)

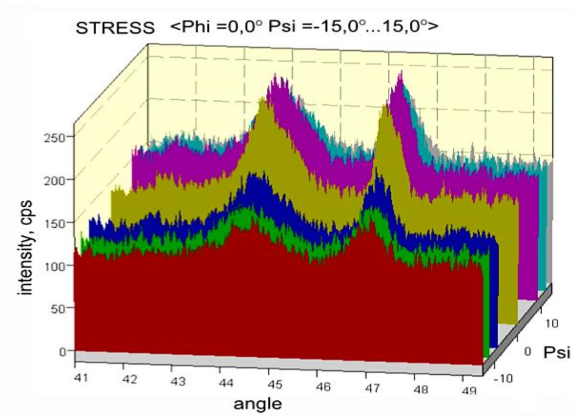
TEM Microscope S/TEM FEI Titan 80-300

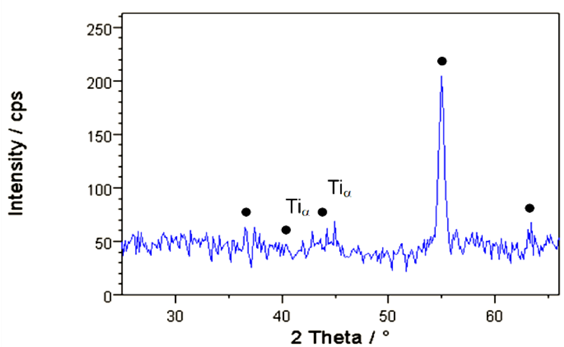


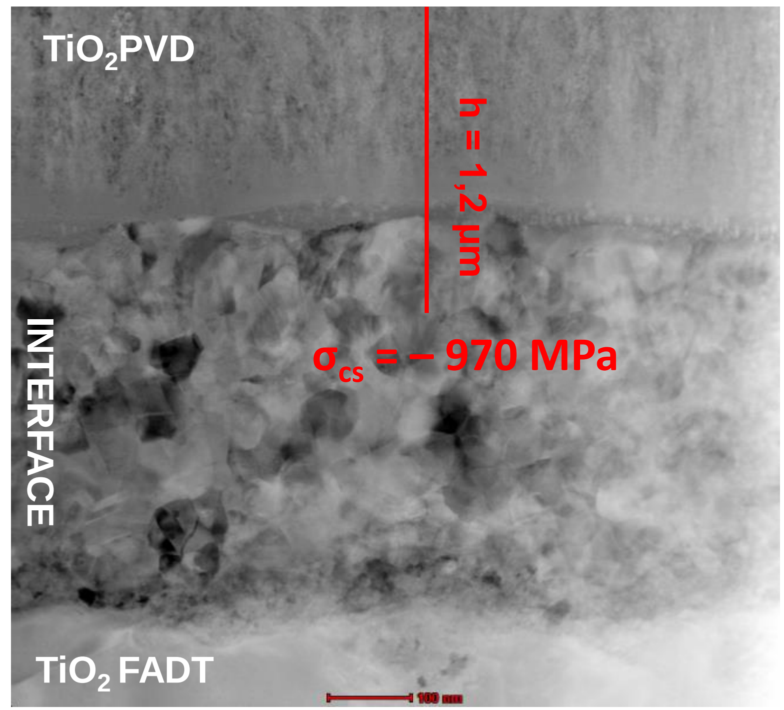


Hybrid oxidation – FADT TiO_2 / PVD TiO_2 interface analysis (Stresses, $sin^2\Psi$)

Seifert 3003TT, Bragg-Brentano geometry, K_aCo=0,17902 nm. Database Rayflex i PDF4+
$sin^2\Psi$ method, (101) reflex, 2Θ = 46,99°.
3 symetrical Ψ angle rotation.
E=112 GPa i v=0,33, reflex maximum analysis (Parabola Fit).





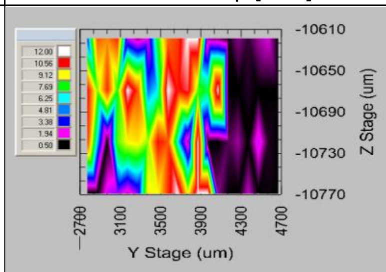
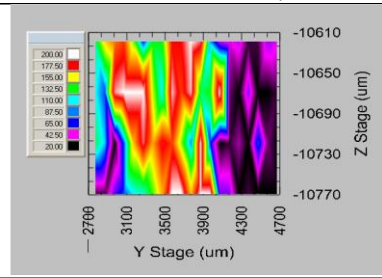
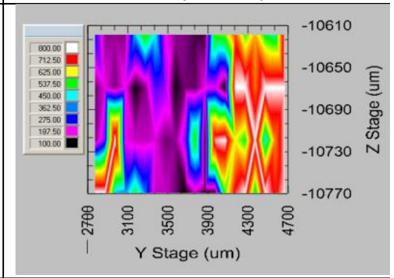
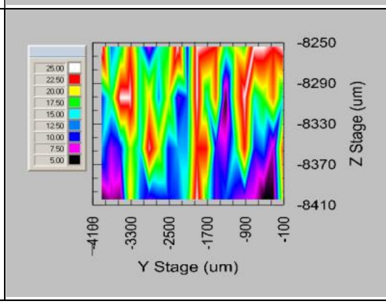
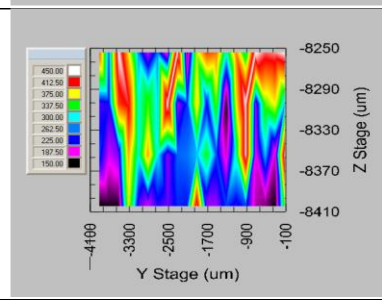
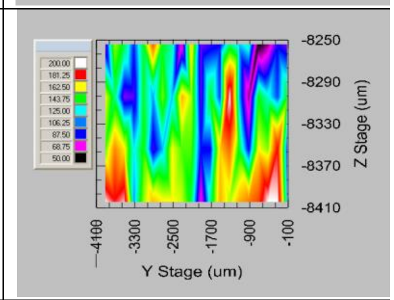


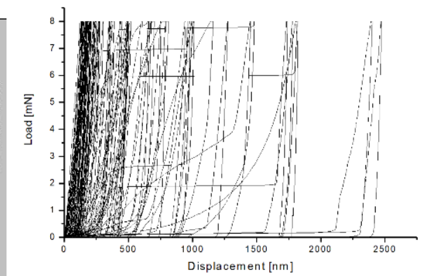
Stresses at the FADT TiO_2 / PVD TiO_2 interface, h = 1.2 µm, σ = – 970 MPa

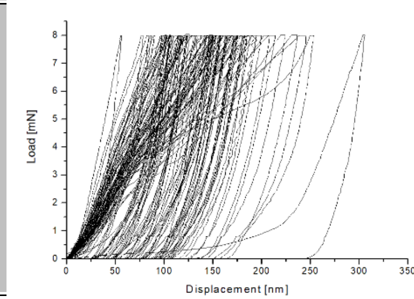
J.J. Jasinski, L. Kurpaska, M. Lubas, et al.:***Effect of hybrid oxidation on the titanium oxide layer's properties investigated by spectroscopic methods***, Journal of Molecular Structure, vol. 1126, 2016, pg. 165-171

Hybrid oxidation – TiO_2 layer mechanical tests (Nanoindentation)

MICROMATERIALS LTD. NANOTEST VANTAGE

	Hardness map [GPa]	Reduced Modulus map [GPa]	Plastic depth map [nm]
Ti 99.2			
HYBRID OX FB+PVD Ti 99.2			





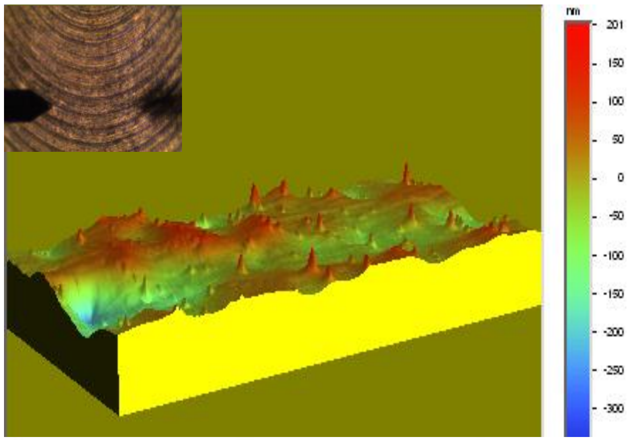
	Sample name	H, Hardness [GPa]	St. Deviation	E_R, Reduced Young modulus [GPa]	St. Deviation	E, Calculated Young Modulus [GPa]	St. Deviation	Maximum depth [nm]	St. Deviation	Plastic depth [nm]	St. Deviation
1.	**Ti99.2 – TiO_2**	9.33	4.14	160.00	60.30	148.34	55.91	204.08	57.41	167.17	54.36
2.	**Ti99.2 FADT+PVD TiO_2**	15.21	6.04	281.83	87.79	261.28	81.39	144.90	28.87	119.20	27.37

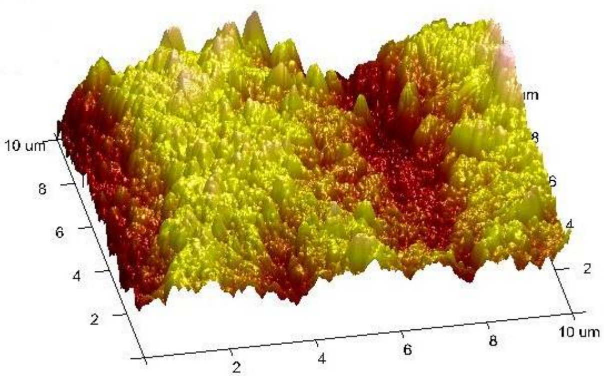
Poisson's ratio υ_{Ti} = 0.33

CIWC-2 2020

Hybrid oxidation – surface morphology (AFM)

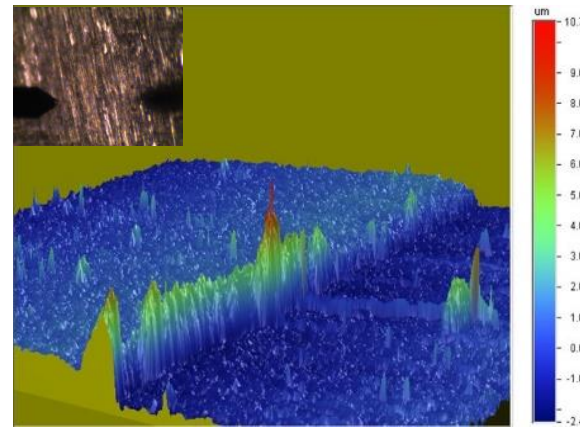
FADT

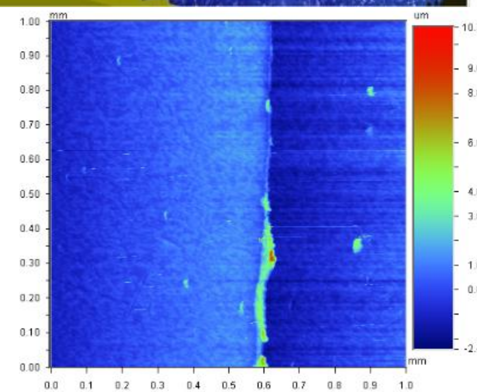




	Surface roughness [µm]
Ra	1.384
Rq	1.702

FADT+PVD TiO_2





	Surface roughness [µm]
Ra	0.741
Rq	0.922

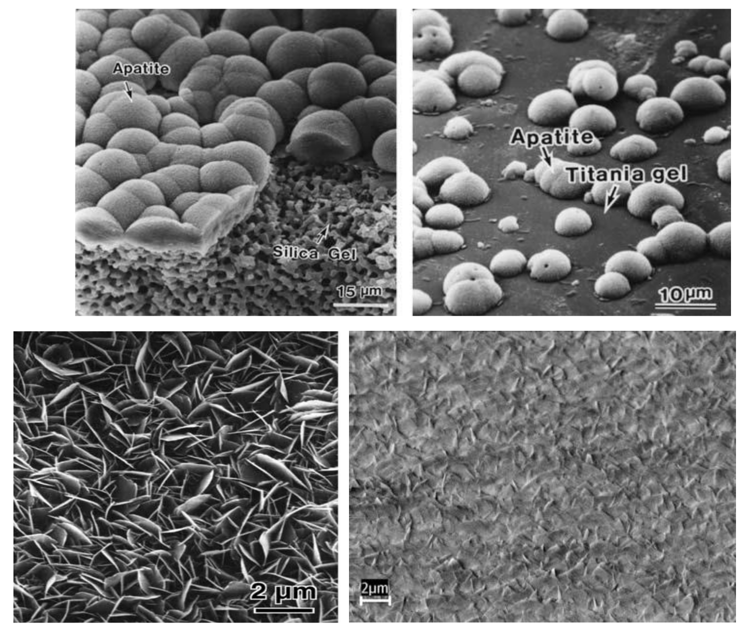
J. I. Rosales-Leal, M. A. Rodríguez-Valverde, G. Mazzaglia, et al. Effect of roughness, wettability and morphology of engineered titanium surfaces on osteoblast-like cell adhesion. Colloids and Surfaces A: Physicochemical and Engineering Aspects vol. 365(1–3), 2010, pg. 222-229

Bioactivity tests of Ti substrates after hybrid treatment (Kokubo test, 14 days)

„A bioactive material is defined as a material on which bone-like hydroxyapatite (HAp) forms selectively when it is immersed in a serum-like solution SBF (i.e. a material that accelerates heterogeneous HAp crystallization on its surface in a solution supersaturated towards HAp)".

Tadashi Kokubo, (2006)

Ion	Ion concentrations [mM]			
	c-SBF2	*c-SBF3*	*SBF-JL1*	*SBF-JL2*
Na^{+}	142.00	142.00	142.00	142.00
K^{+}	5.00	5.00		
Mg^{2+}	1.50	1.50		
Ca^{2+}	2.50	2.50	2.50	2.31
HCO_3^{-}	4.20	35.23	34.90	34.88
HPO_4^{2-}	1.00	1.00	1.00	1.39
SO_4^{2-}	0.50	0.50		
Cl^{-}	147.96	117.62	111.00	109.90



<u>c-SBF2 bioactivity test parameters</u>

Ionic strength = 140 mM,

$C_{0\ Ca2+}$ = 2.5 mM,

pH = 7.4,

Temperature = 37°C,

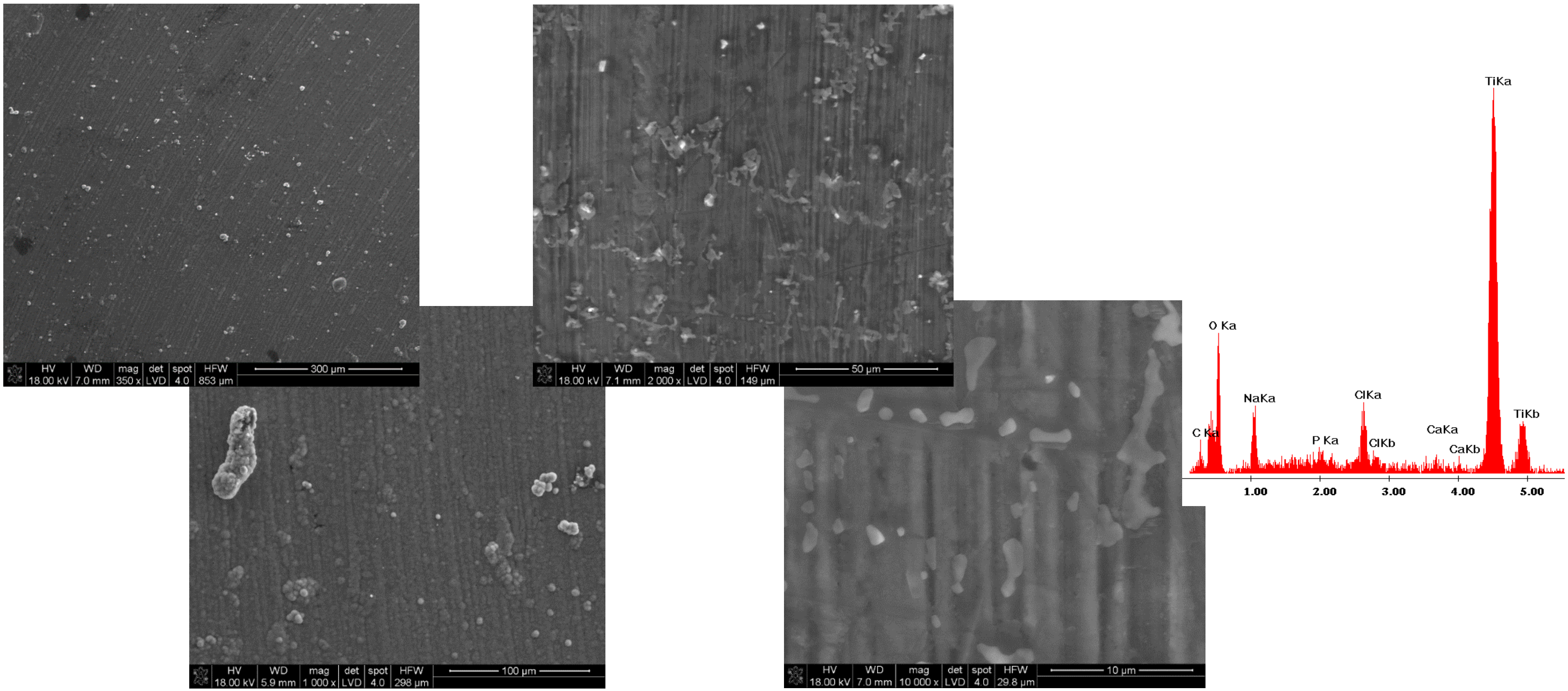
CO_2 partial pressure = 0.05 atm

T. Kokubo et al.: How useful is SBF in predicting in vivo bone bioactivity, Biomaterials vol. 27, 2006, pg. 2907–15

T. Kokubo, H.M. Kim, M. Kawashita, T. Nakamura, Bioactive metals: preparation and properties, Journal of Materials Science: Materials in Medicine Vol. 15, 2004, pg. 99-107

Bioactivity tests of Ti substrates after FADT treatment (Kokubo test, 14 days)

Ti substrates after FADT – nano-porous $TiO_{2\ rutile}$



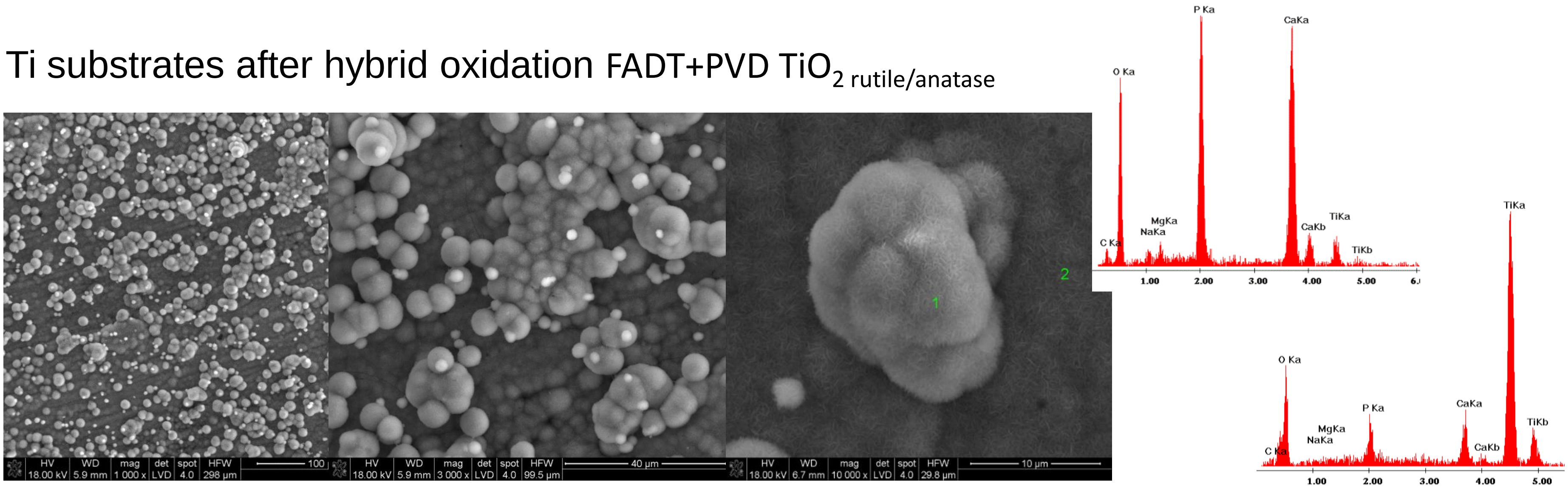
„On the microscopic level, the heterogeneous crystallization of HAp on existing surfaces is a process that involves electrostatic interactions of the surface with the calcium and the phosphate ions in SBF via sequential formation of metastable intermediates (i.e. Ca-rich and Ca-deficient phases of amorphous calcium phosphate, ACP)"

Tadashi Kokubo, (2006)

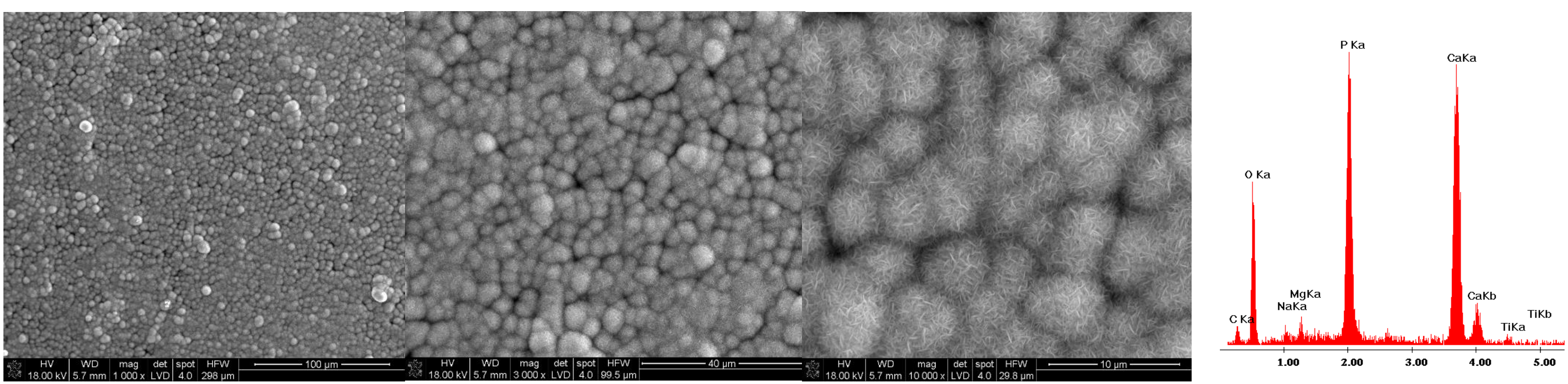
Bioactivity tests of Ti substrates after hybrid treatment (Kokubo test, 14 days)

Ti substrates after hybrid oxidation FADT+PVD $TiO_{2\ rutile/anatase}$

7 days



14 days



Jasinski J.J., Kurpaska L., Lubas M., et all, **Effect of hybrid oxidation on the titanium oxide layer's properties investigated by spectroscopic methods,** Journal of Molecular Structure, 2016 *1126*, 165-171

Conclusions

1. *The modification of titanium substrates by oxidation in a fluidized bed (FADT) leads to formation of a highly defected diffusion zone ($Ti_{\alpha}(O)$ solid solution) and the nano-porous TiO_2 which plays a role of foundation for a subsequent deposition of TiO_2 thin oxide layer by PVD magnetron sputtering.*

2. *Titanium hybrid oxidation leads to smoothing the surface as a result of the formation of a homogeneous TiO_2 PVD top layer. This is especially important in the subsequent intensified growth of globular form hydroxyapatite compounds.*

3. *In hybrid oxidation, the interface between porous TiO_2 and PVD TiO_2 with a favorable state of stress has an influence on the formation of a highly bioactive top surface oxide layer with a phase composition of rutile and anatase mixture.*

4. *Hybrid oxidation process has a significant impact on HAp growth in the first stage of vascularization of the tissues at the bioactive implant surface and finally improves the rate of osseointegration.*

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THANK YOU FOR YOUR ATTENTION

Questions ?

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