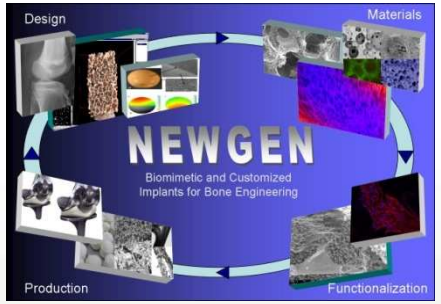
AGH UNIVERSITY OF SCIENCE AND TECHNOLOGY



Surface modifications of titanium alloys by ceramic coatings deposition

Joanna Karbowniczek, Urszula Stachewicz, Grzegorz Cempura and Aleksandra Czyrska-Filemonowicz

International Centre of Electron Microscopy for Materials Science
Faculty of Metals Engineering and Industrial Computer Science

Sofia, 14th October2015

International Centre of Electron Microscopy for Materials Science

AGH University of Science and Technology
Faculty of Metals Engineering and Industrial Computer Science

Research infrastructure

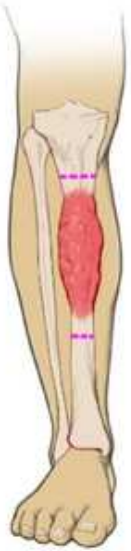
- **4 Transmission electron microscopes:**
  - **Titan Cubed G2 60-300 (FEI)** advanced probe Cs corrected (S)TEM for analytical high resolution microscopy at high (300 kV) and low (60 kV) voltage
  - **Tecnai G2 20 TWIN (FEI)** with:
    - Precession electron diffraction DigiStar and ASTAR for orientation and phase mapping
    - STEM-HAADF and EDX microanalysis system TIA
  - **JEM-2010ARP (JEOL)** equipped with:
    - STEM-ASID and EDX microanalysis system INCA
    - CCD camera Orius™ SC1000
  - **JEM-200CX (JEOL)**
- **2 Scanning electron microscopes:**
  - **Merlin Gemini II (ZEISS)** equipped with:
    - FEG and EDX microanalysis system: Quantax 800
    - EBSD: Quantax CrystAlign 400
  - **FIB-SEM NEON® CrossBeam 40EsB (ZEISS)** equipped with:
    - FEG SEM column, SE, BSE and EsB modes
    - EDX microanalysis system Quantax 200
- **Scanning probe microscope** Dimension 3100 SPM
- **2 Light microscopes (ZEISS):**
  - Axio Imager M1m
  - Stereo Discovery
  - Image analysis software
- **Comprehensive TEM sample preparation laboratory** (with NanoMill 1040)
- **Mechanical testing facilities:** MTS, Instron
- **Nondestructive testing systems**
  - Ultrasonic flaw detector
  - Eddy-current system, accoustic emission

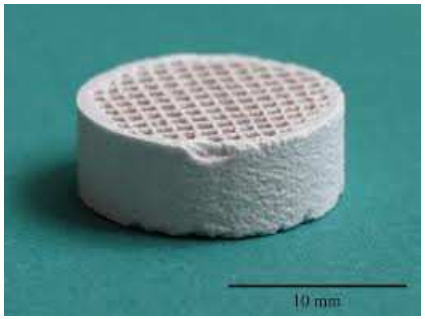
Analytical high resolution (70 pm) transmission electron microscope Titan^3 G2 60-300

- new X-FEG Schottky high brightness source with a monochromator
- high resolution STEM-HAADF unit with a new dodecapole DCOR probe Cs corrector
- new ChemiSTEM EDX system based on a 4 windowless Silicon Drift Detectors (Super X) with enhanced acquisition efficiency and speed for low dose, high spatial (atomic) resolution and fast chemical element mapping
- GIF Quantum 693 electron energy filter for EELS spectroscopy and EFTEM imaging
- new FEI precession electron diffraction
- dual-axis tomography
- off-axis electron holography, Lorentz lens
- full remote access operation (TARO)

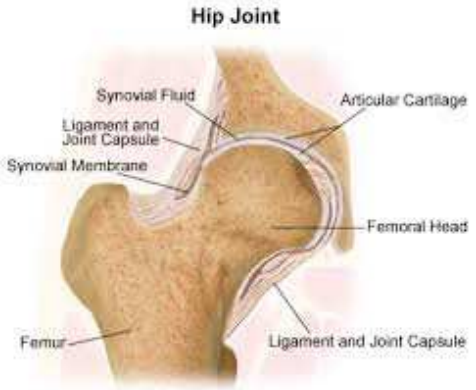
Introduction

Critical size bone defects





Osteoarthritis



Overview

Poland – population 38 mln

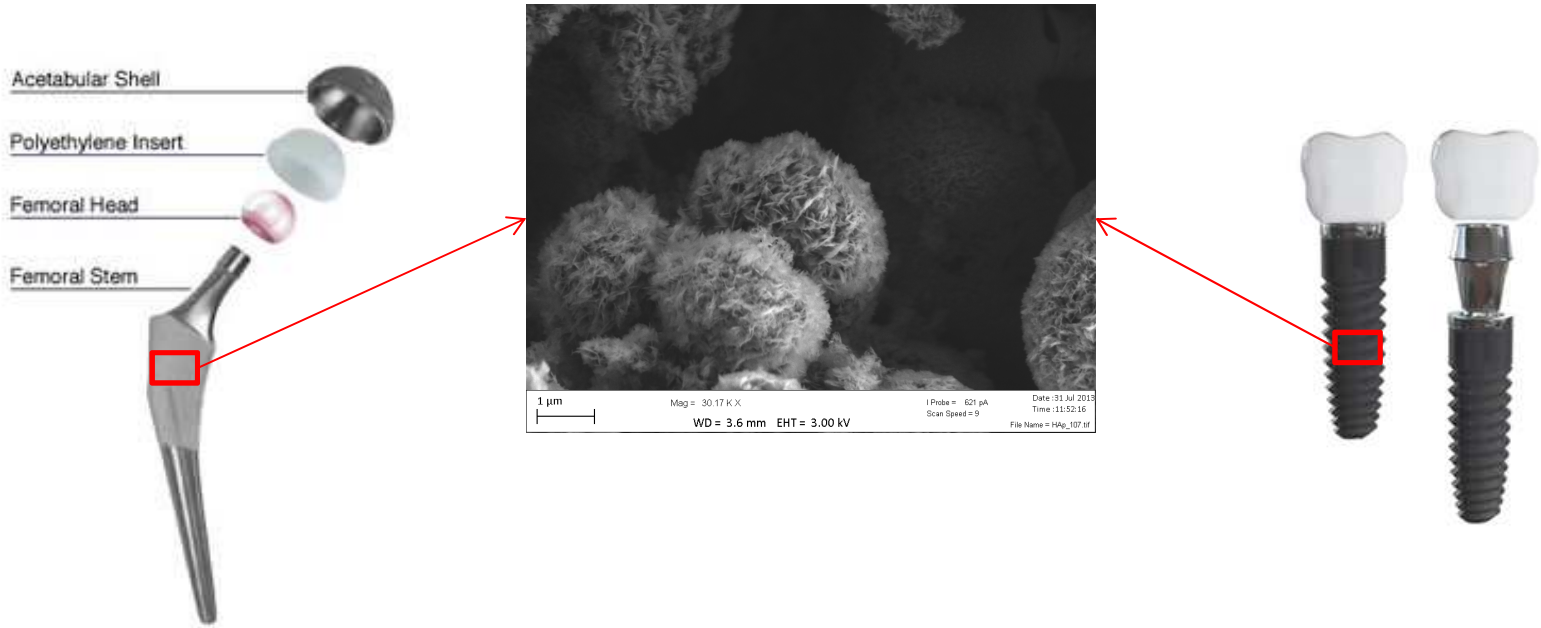
Hip joint replacements:
39 349 procedures
including 3 598 (9,14%)
of revision surgeries

Knee joint replacements:
13 142 procedures
including 1 076 (7,57%)
revision surgeries*

*Data for 2013

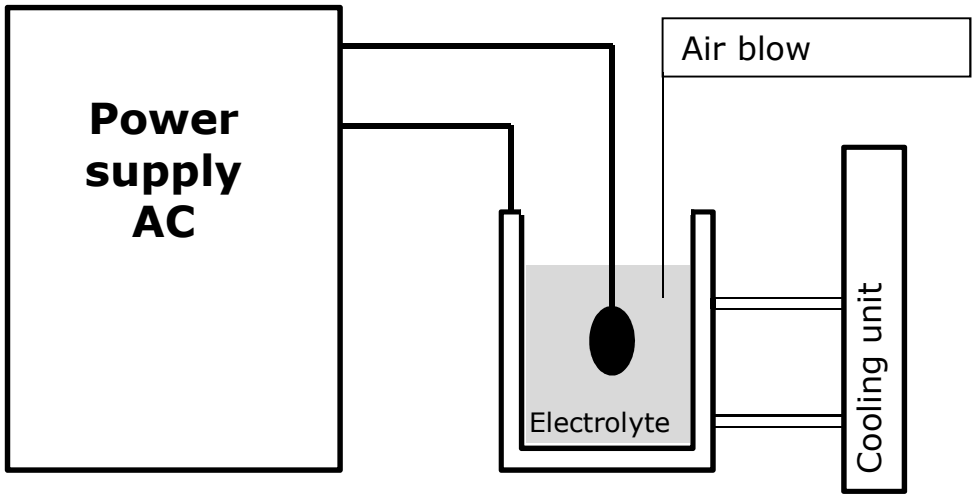
Motivation

Improvement of biocompatibility of titanium based biomaterials and improvement of integration between metallic implant and bone tissue in case of long-term applications



Micro-arc oxidation

Micro-arc oxidation (MAO) is an electrochemical surface treatment process to produce oxide coatings on aluminum, magnesium or titanium alloys.



Setup for micro-arc oxidation

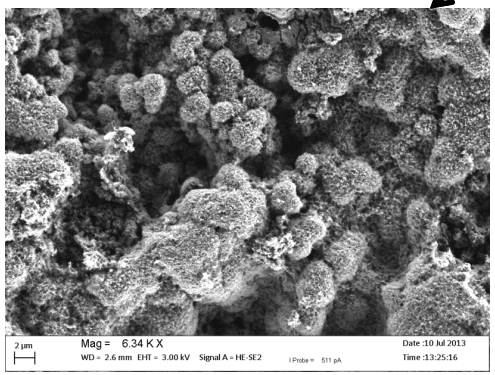
Process parameters to be controlled:

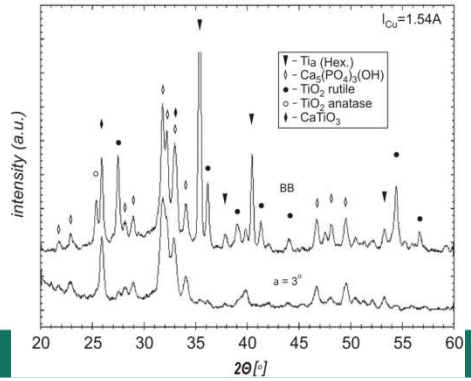
- Applied voltage
- Deposition time
- Frequency
- Electrolyte composition

Results

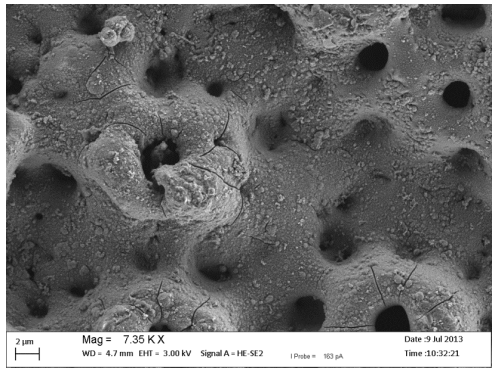
Process parameters:
-applied voltage: 400 V (positive half cycle) 80 V (negative half cycle)
-frequency: 250 Hz
-duration: 5 min
-substrate: Ti6Al7Nb

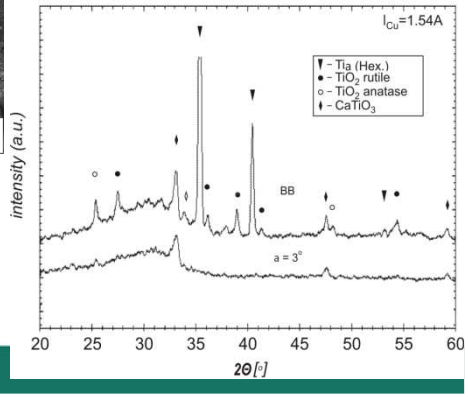
Electrolyte:
Na_3PO_4 and
$(CH_3COO)_2Ca \cdot H_2O$





Electrolyte:
$C_3H_9O_6PO_4$ and
$(CH_3COO)_2Ca \cdot H_2O$





Results

Process parameters:
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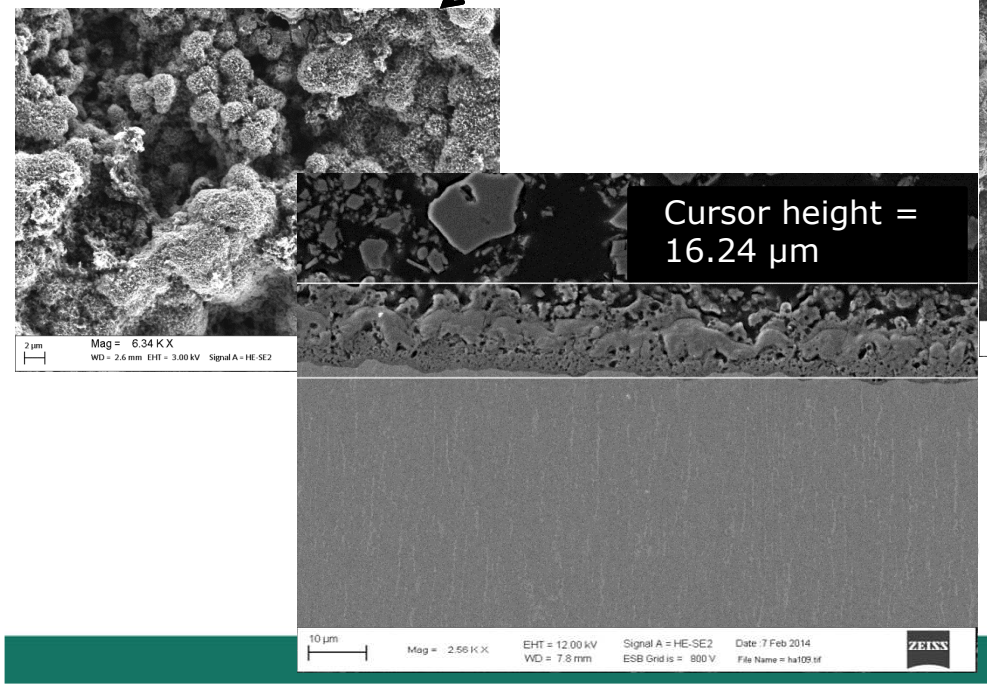
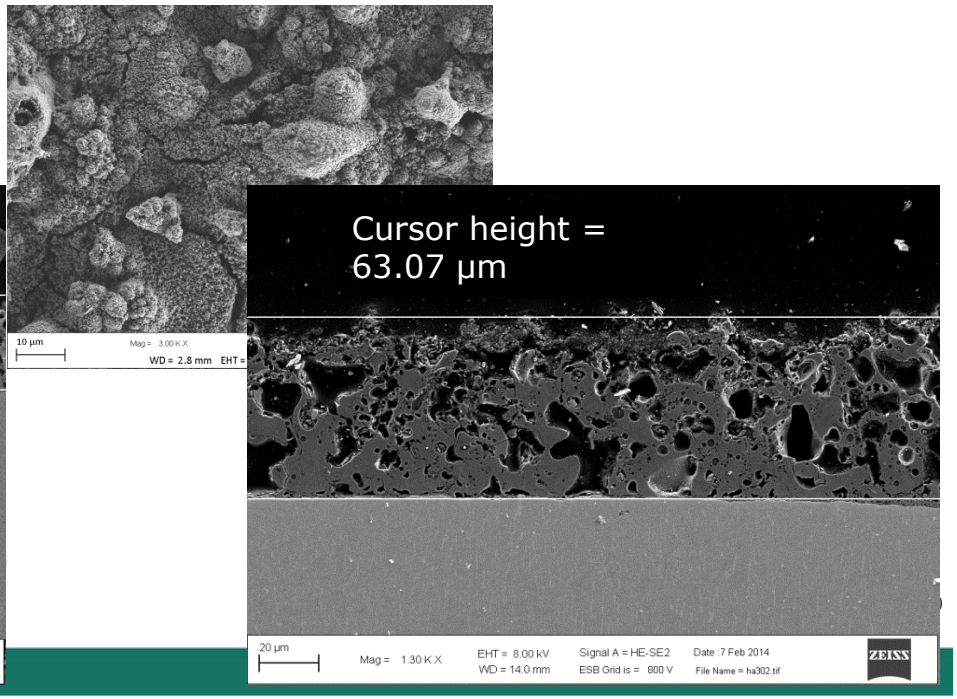
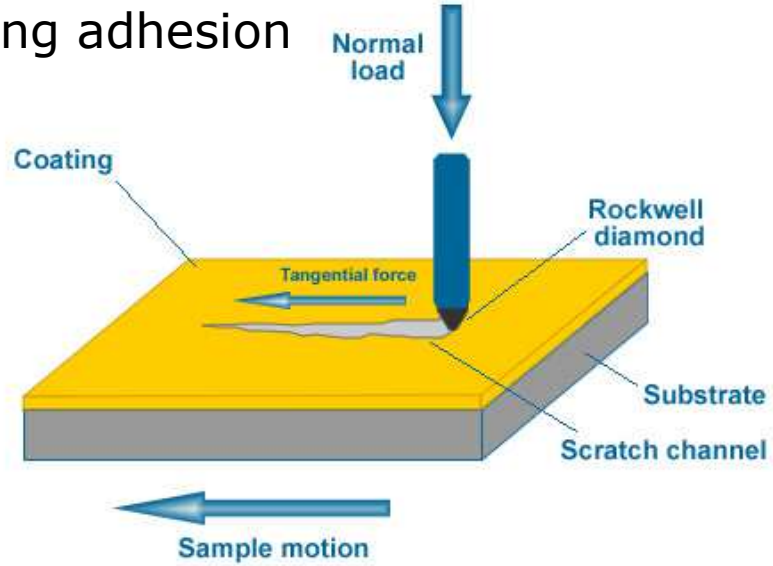


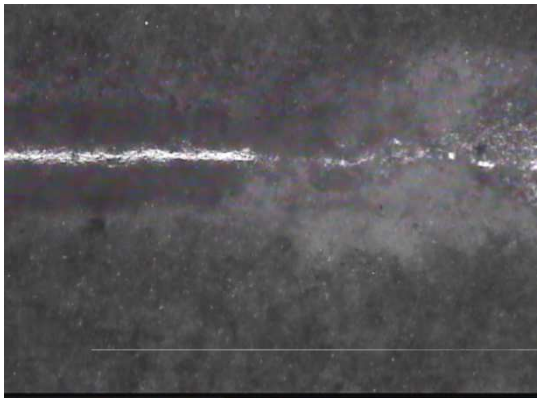
Electrolyte:
Na_3PO_4 and
$C_3H_7CaO_6PO_4 \cdot H_2O$

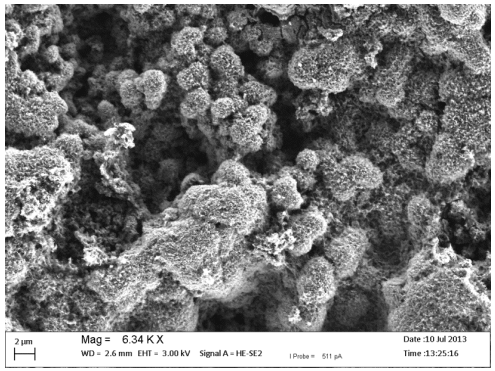


Results

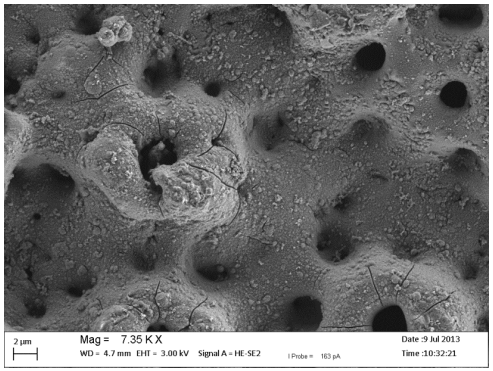
Scratch test – coating adhesion



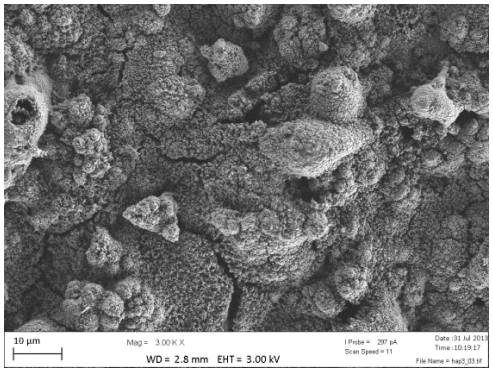




22N



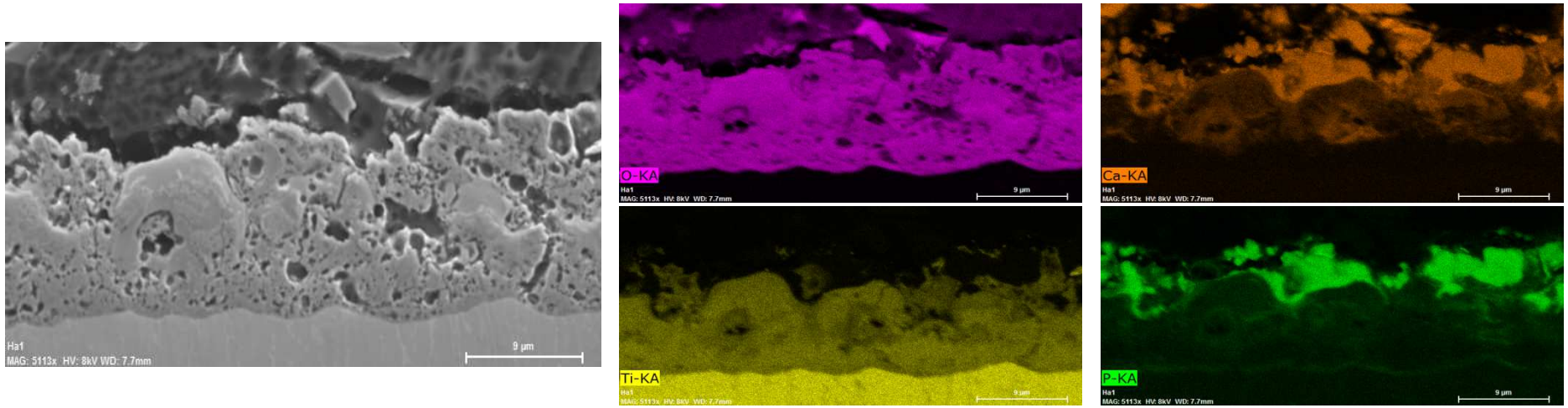
9 N



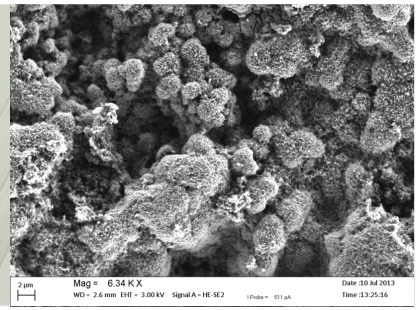
18 N

Results

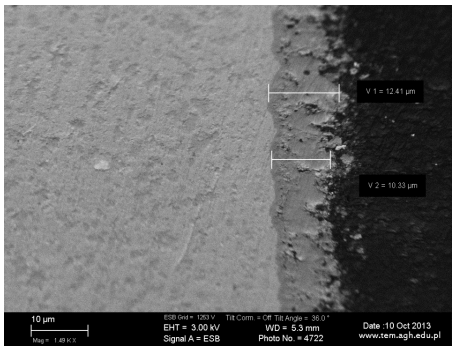
Energy dispersive X-ray spectroscopy (EDS) mapping



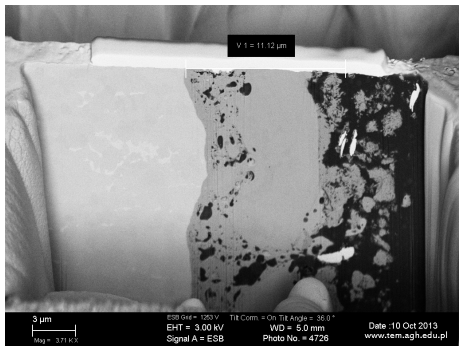
Results



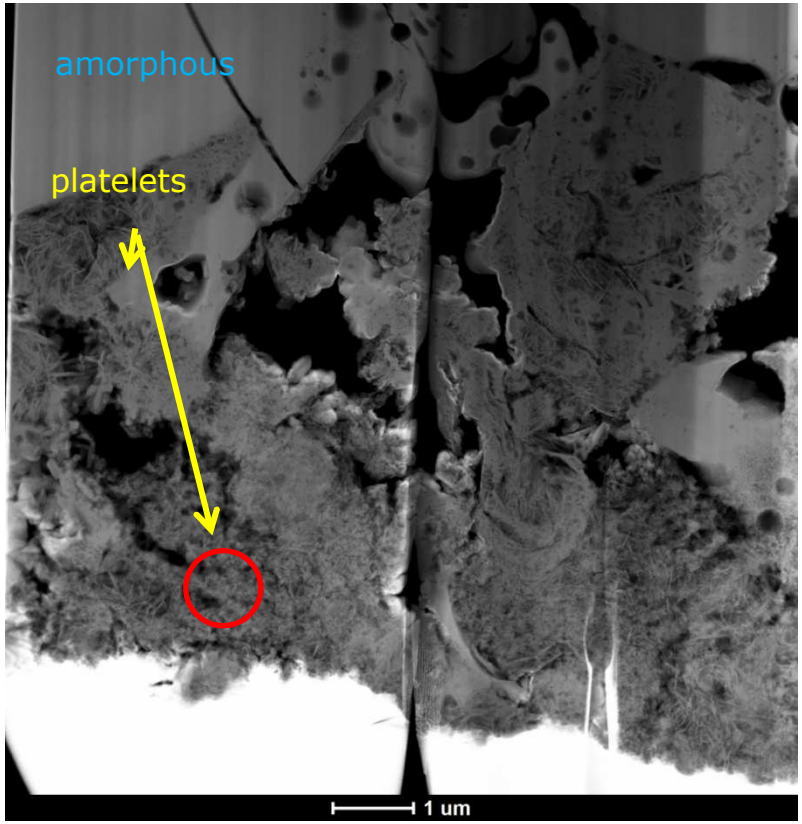
Cross-section of the sample



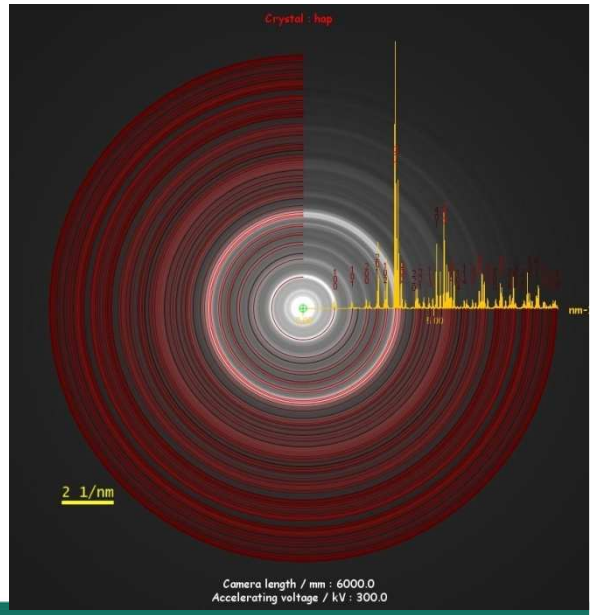
FIB lamella cutting



TEM investigation



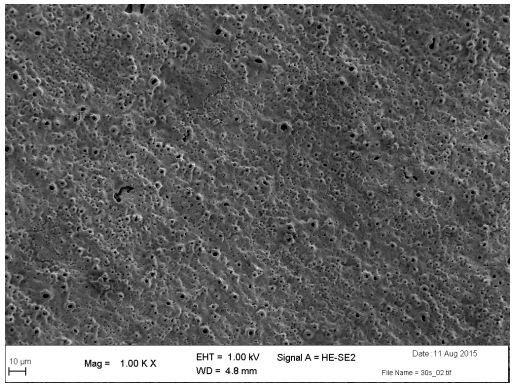
SAED (from marked area);
JAMES software matched with HA

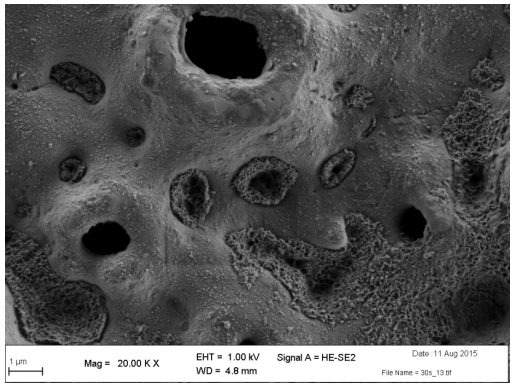


Results

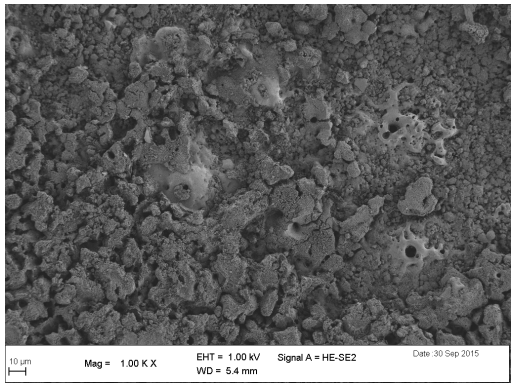
Process parameters:
-applied voltage: 400 V (positive half cycle) 80 V (negative half cycle)
- frequency: 200 Hz
- electrolyte: NaH_2PO_4 and $(CH_3COO)_2Ca$
-substrate: Ti6ALlNb

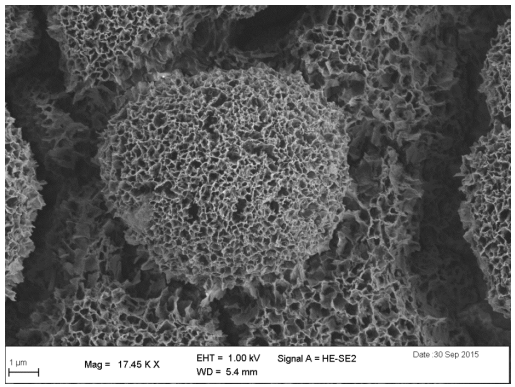
Deposition time 30 sec



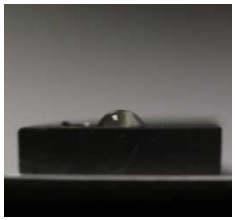


Deposition time 7 min



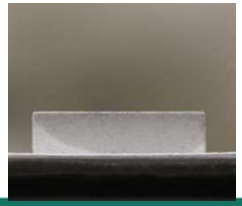


Ti6Al7Nb (untreated)
Contact angle 62° ± 2



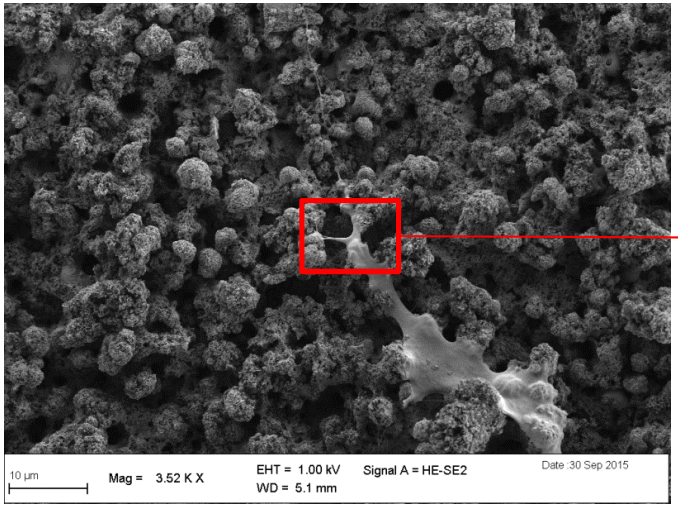
30 sec MAO process
Contact angle 32° ± 4

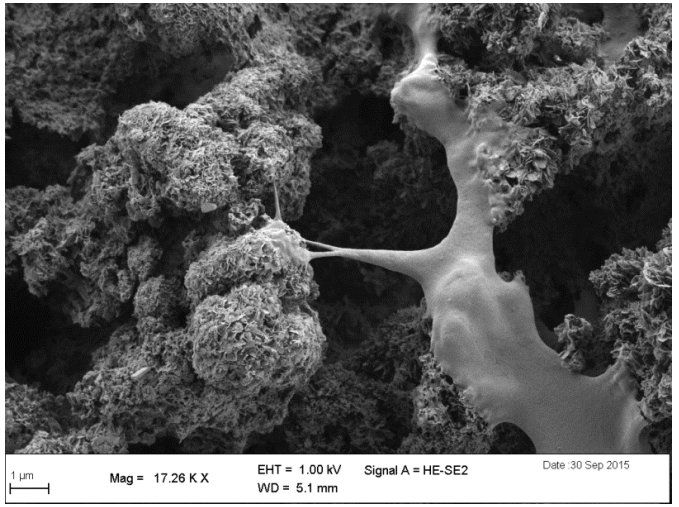
7 min MAO process

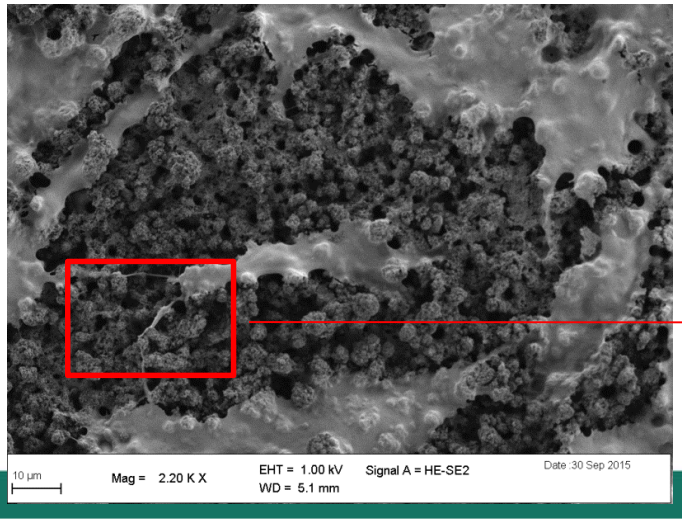


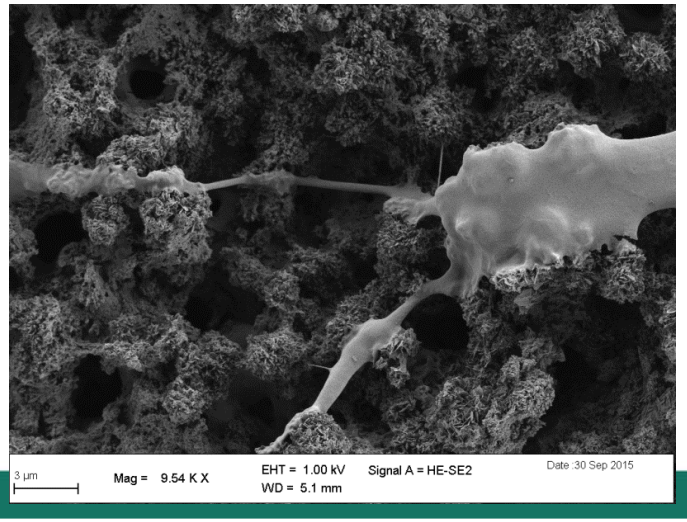
Results

Preliminary in vitro studies:
MG-63 cells after 3 days culture









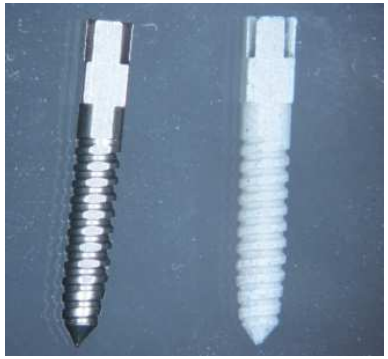
Summary

Micro-arc oxidation:

- is a cost efficient and fats method to modify Ti alloy surface

-It allows to change: chemical composition; roughness; wettability of titanium substrate by deposition of ceramic well adherent coatings

- It is possible to coat complex shape materials

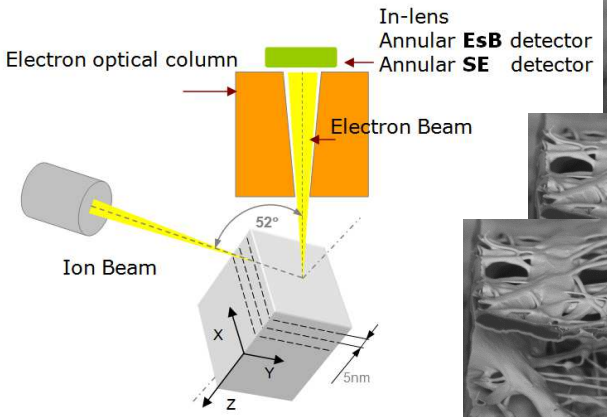


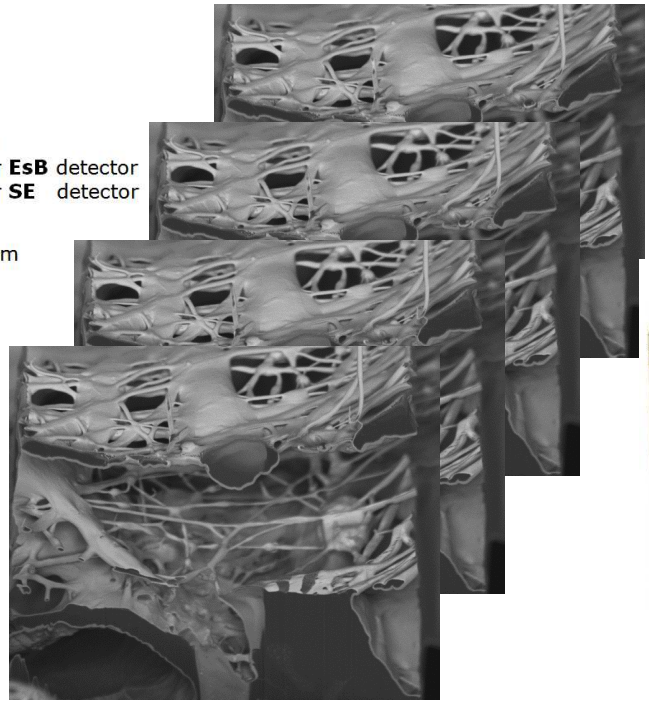
Summary

- We are looking for the cooperation in vitro studies (possibly in vivo)

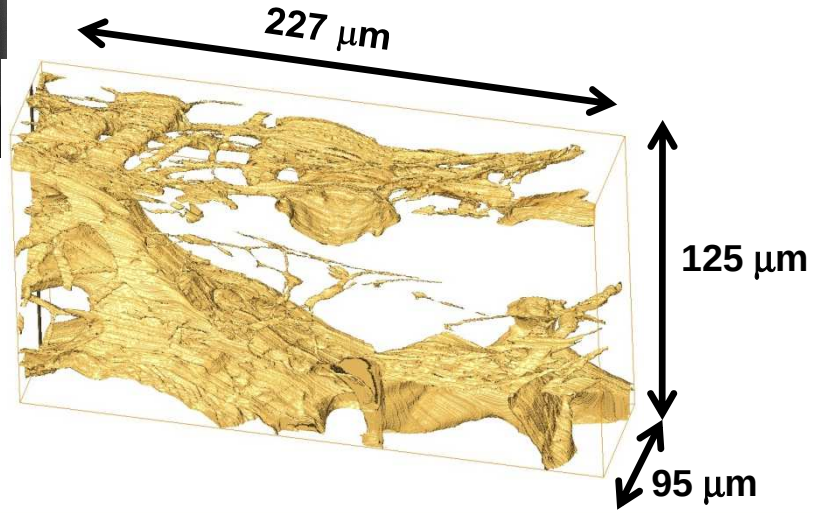
- We are open for the cooperation in materials characterization by means of advanced electron microscopy techniques

FIB-SEM tomography





Porosity calculated for our 3D reconstruction is 83 %



ESTEEM 2 project – September 2016 (http://esteem2.eu/)

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Mgr inż. Joanna Karbowniczek
Mgr inż. Sebastian Lech
Krystyna Płońska-Niżnik

http://www.tem.agh.edu.pl

NATIONAL SCIENCE CENTRE POLAND

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NAMABIO

STSM – Istanbul Technical University

Thank you for your attention!