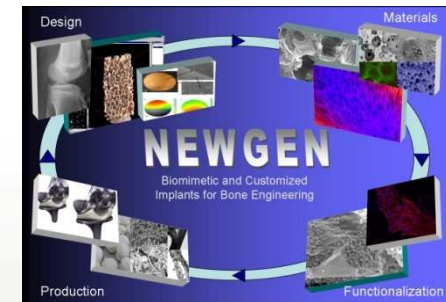




AGH UNIVERSITY OF SCIENCE  
AND TECHNOLOGY



# 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 October 2015



# International Centre of Electron Microscopy for Materials Science



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

- **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 Z0 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, acoustic emission

## Research infrastructure

### Analytical high resolution (70 pm) transmission electron microscope Titan<sup>3</sup> G2 60-300



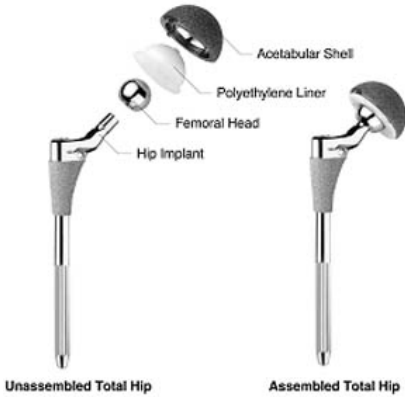
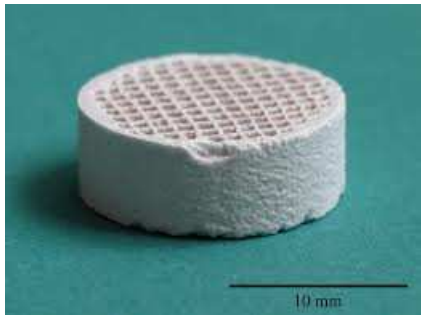
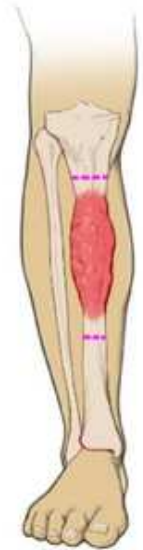
- new X-FEG Schottky high brightness source with a monochromator
- high resolution STEM-HAADF unit with a new dodecapole DCOR probe Cs corrector
- new ChemiSTEM EDX system based on a 4 windowless Silicon Drift Detectors (Super X) with enhanced acquisition efficiency and speed for low dose, high spatial (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



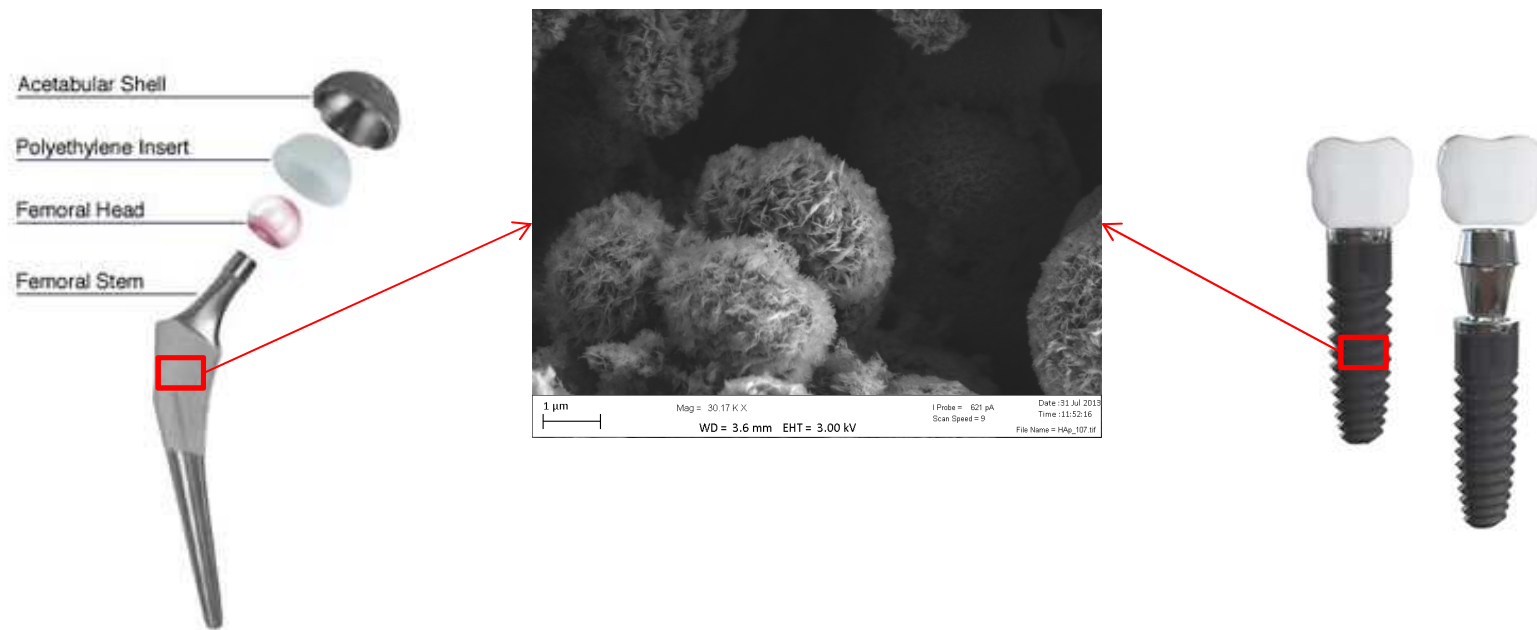
Knee joint replacements:  
13 142 procedures  
including 1 076 (7,57%)  
revision surgeries\*



\*Data for 2013

## Motivation

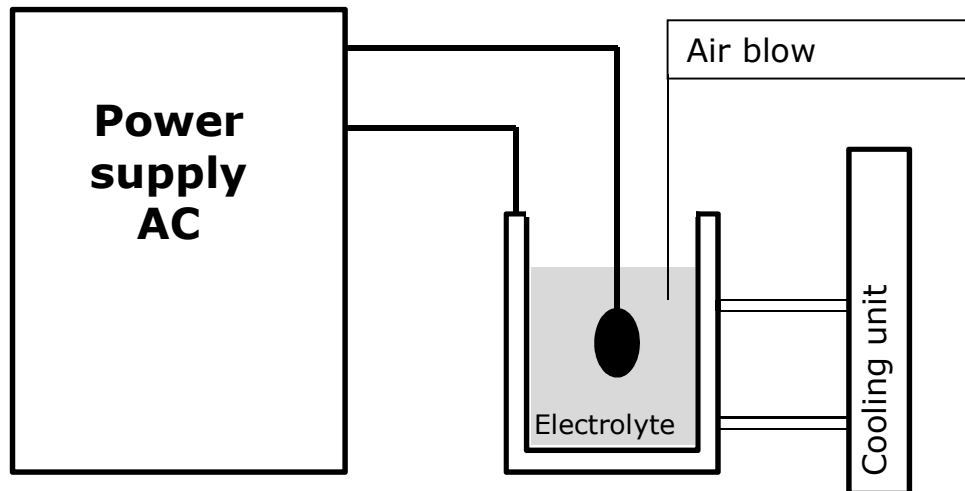
Improvement of biocompatibility of titanium based biomaterials and improvement of integration between metallic implant and bone tissue in case of long-term applications





## Micro-arc oxidation

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



Process parameters to be controlled:

- Applied voltage
- Deposition time
- Frequency
- Electrolyte composition



Setup for micro-arc oxidation

# Results

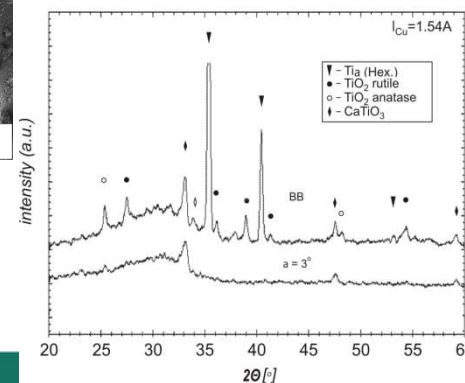
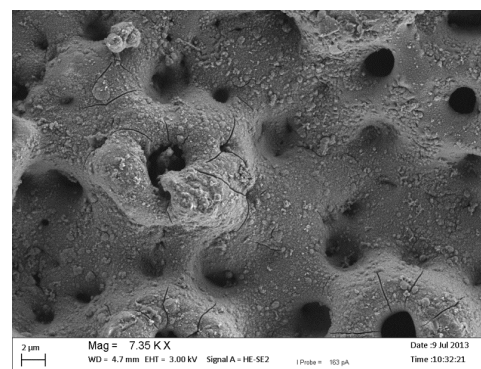
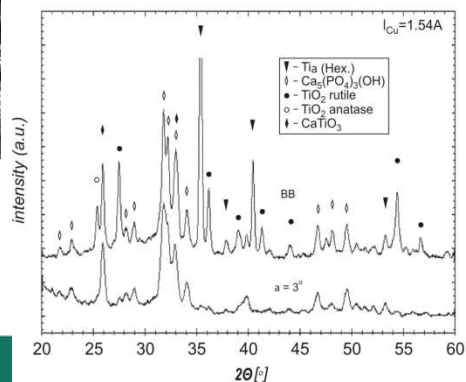
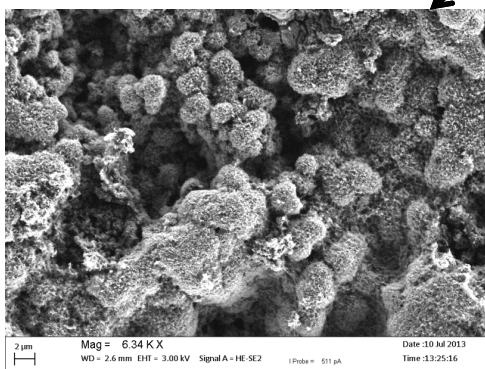
Process parameters:

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

Electrolyte:  
 $\text{Na}_3\text{PO}_4$  and  
 $(\text{CH}_3\text{COO})_2\text{Ca}\cdot\text{H}_2\text{O}$



Electrolyte:  
 $\text{C}_3\text{H}_9\text{O}_6\text{PO}_4$  and  
 $(\text{CH}_3\text{COO})_2\text{Ca}\cdot\text{H}_2\text{O}$



# Results

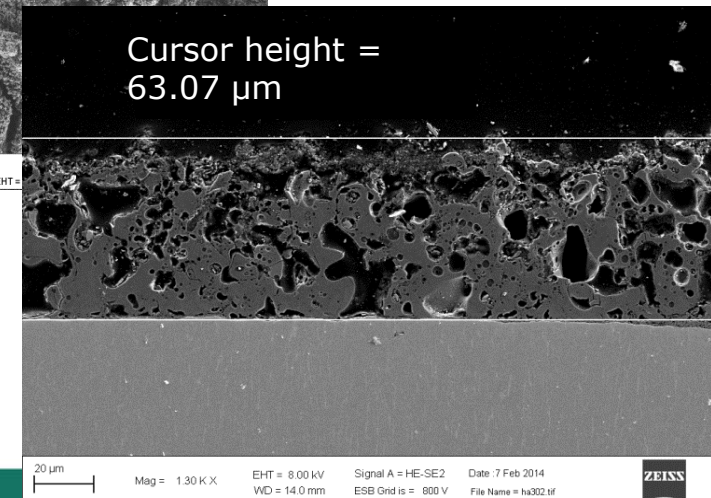
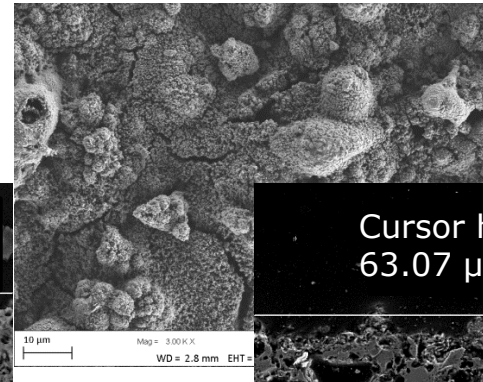
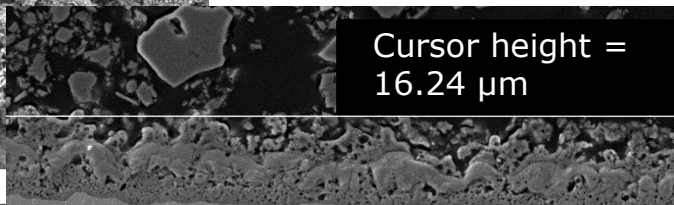
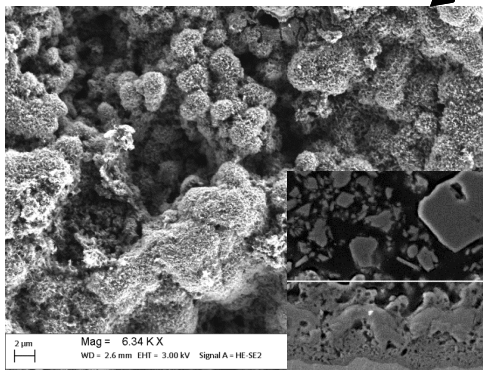
Process parameters:

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

Electrolyte:  
 $\text{Na}_3\text{PO}_4$  and  
 $(\text{CH}_3\text{COO})_2\text{Ca}\cdot\text{H}_2\text{O}$

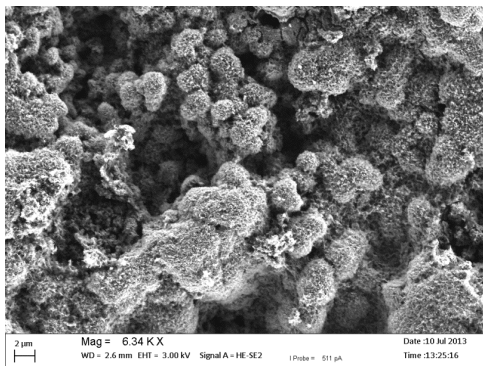
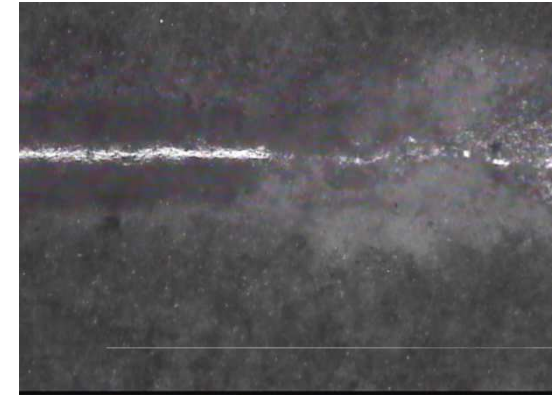
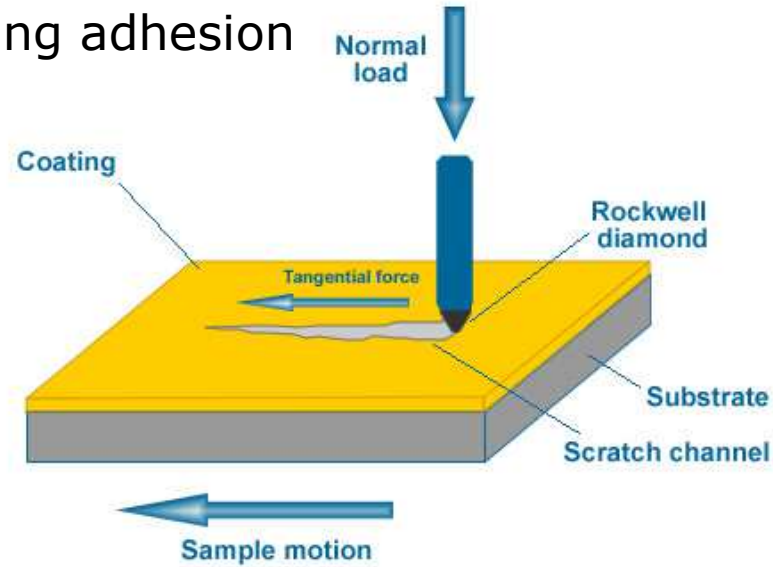


Electrolyte:  
 $\text{Na}_3\text{PO}_4$  and  
 $\text{C}_3\text{H}_7\text{CaO}_6\text{PO}_4\cdot\text{H}_2\text{O}$

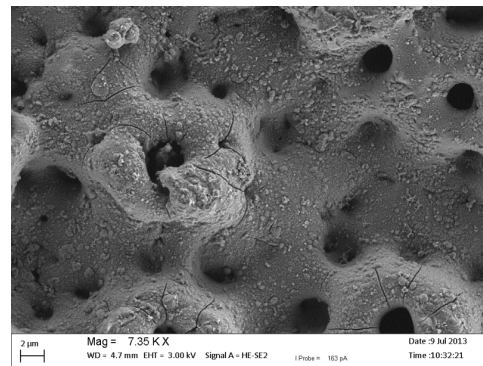




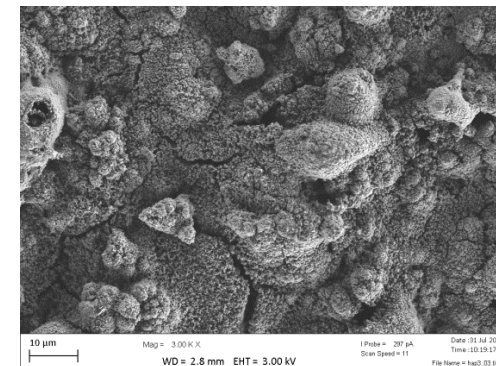
## Scratch test – coating adhesion



22 N

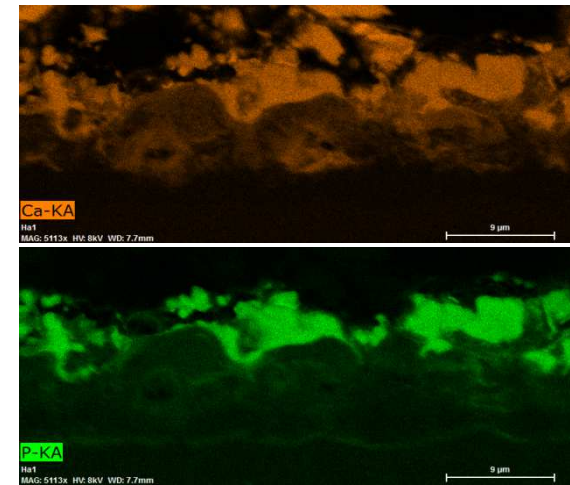
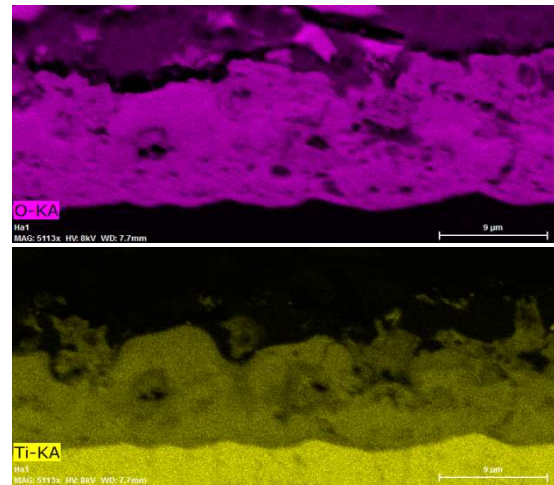
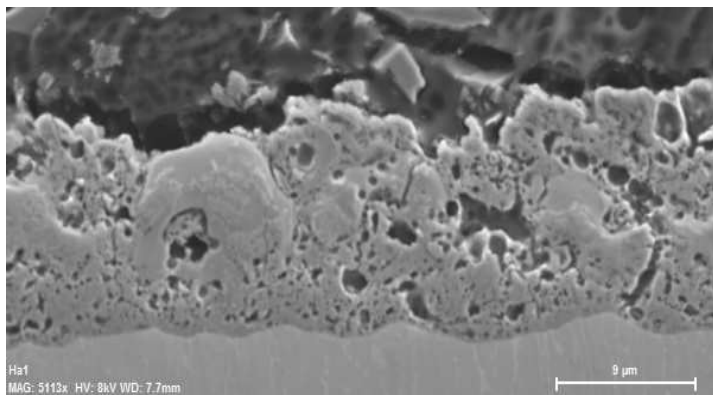


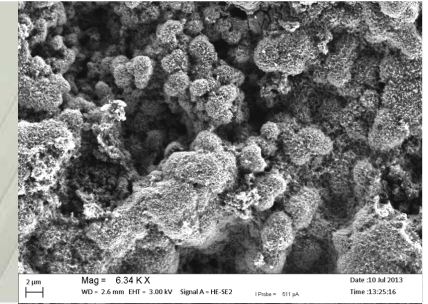
9 N



18 N

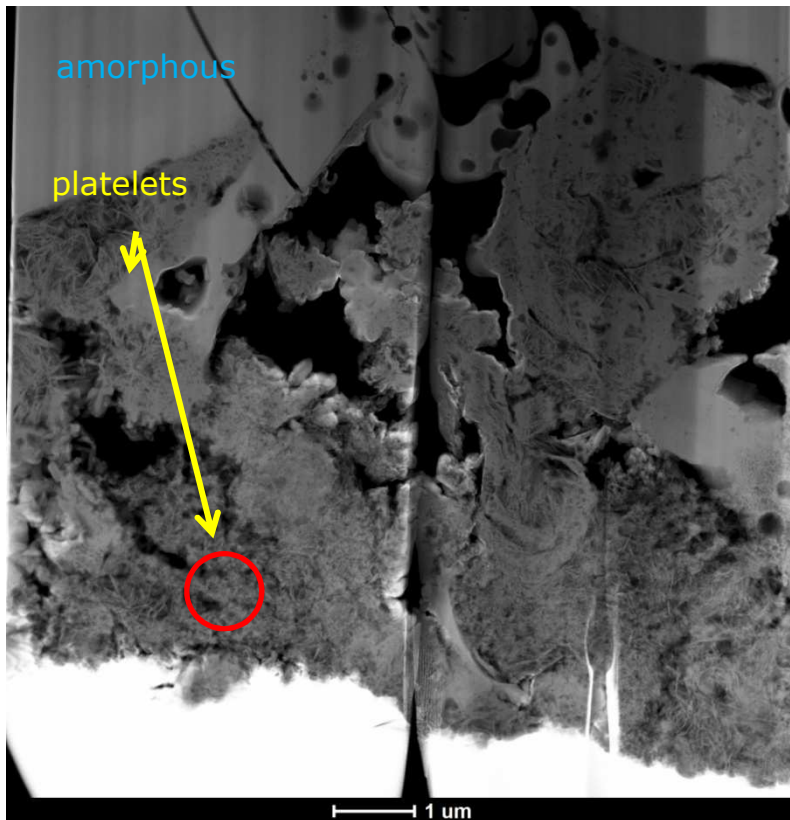
## Energy dispersive X-ray spectroscopy (EDS) mapping



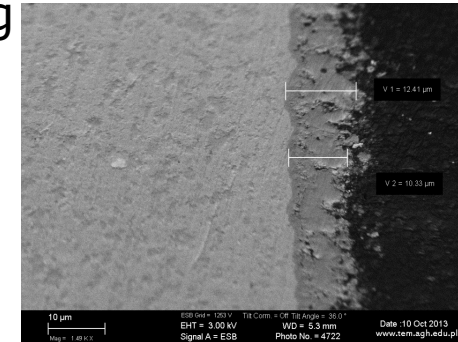
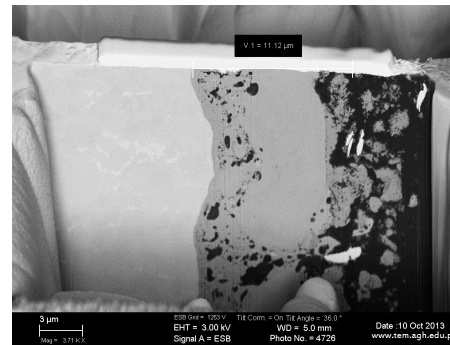


Cross-section of the sample

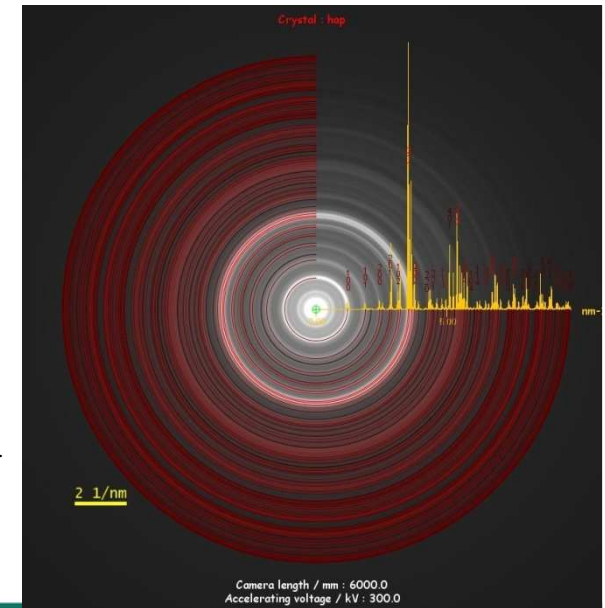
TEM investigation



FIB lamella cutting



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







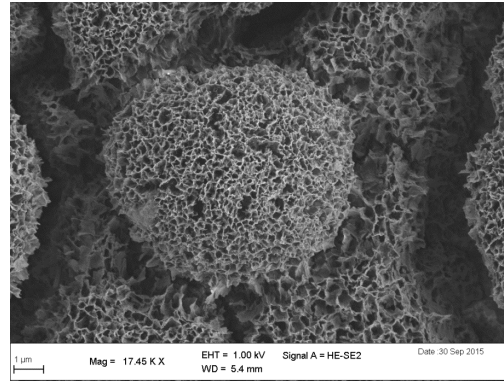
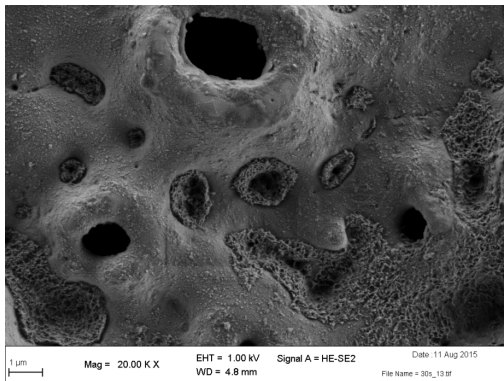
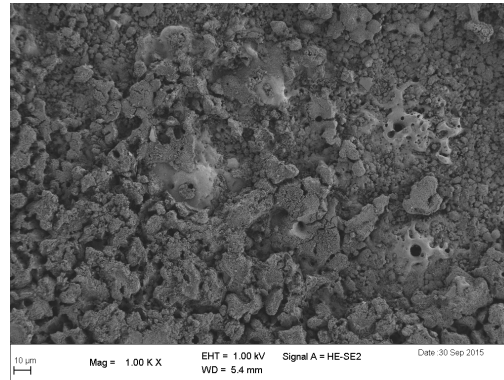
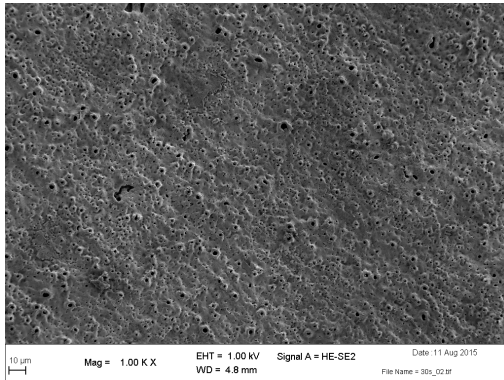
# Results

Process parameters:

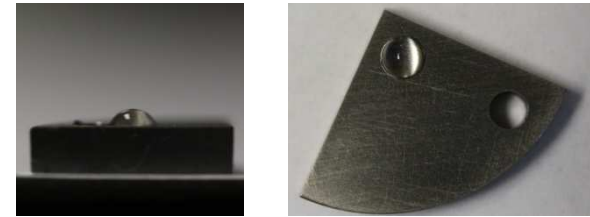
- applied voltage: 400 V (positive half cycle) 80 V (negative half cycle)
- frequency: 200 Hz
- electrolyte:  $\text{NaH}_2\text{PO}_4$  and  $(\text{CH}_3\text{COO})_2\text{Ca}$
- substrate: Ti6Al7Nb

Deposition time 30 sec

Deposition time 7 min



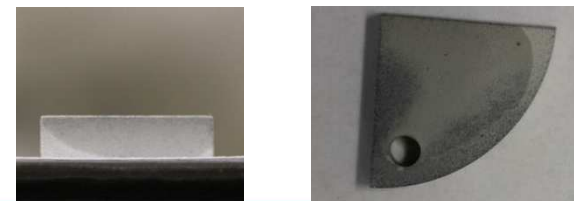
Ti6Al7Nb (untreated)  
Contact angle  $62^\circ \pm 2$



30 sec MAO process  
Contact angle  $32^\circ \pm 4$



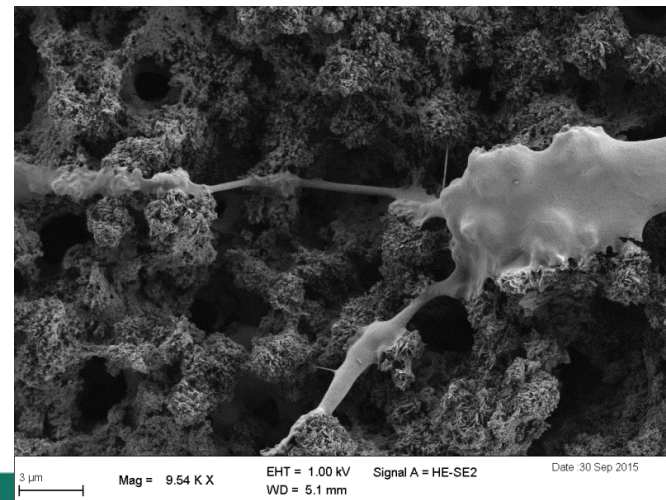
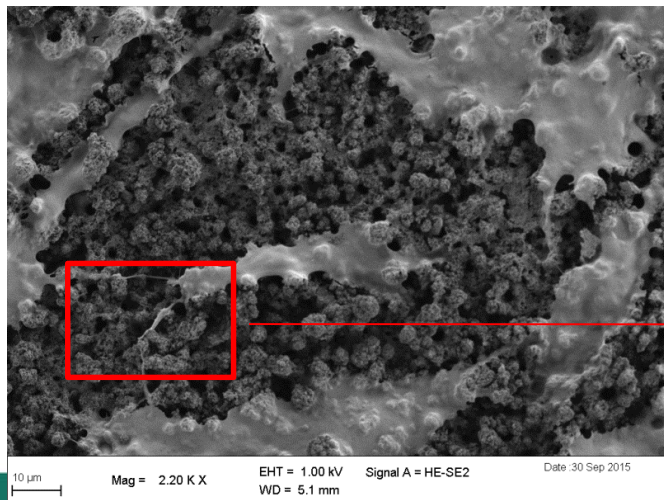
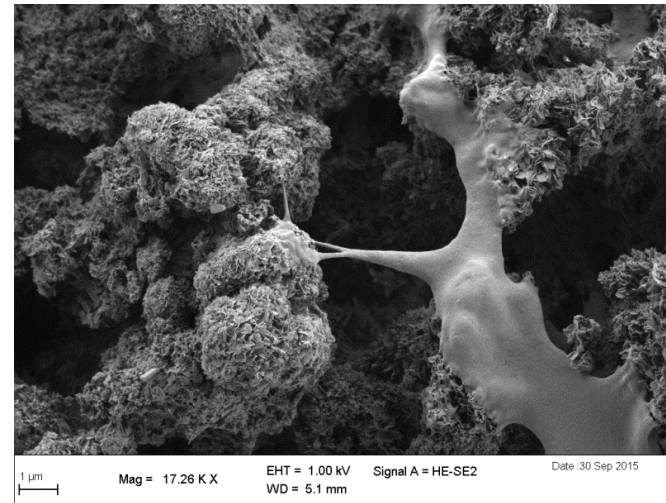
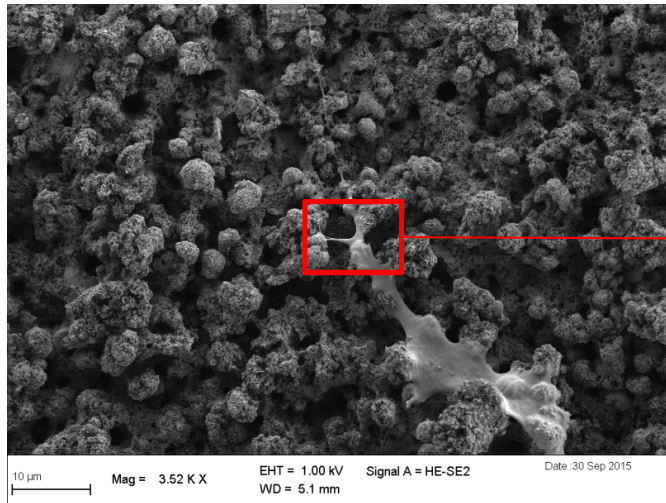
7 min MAO process





# Results

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



# Summary



Micro-arc oxidation:

- is a cost efficient and fast 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

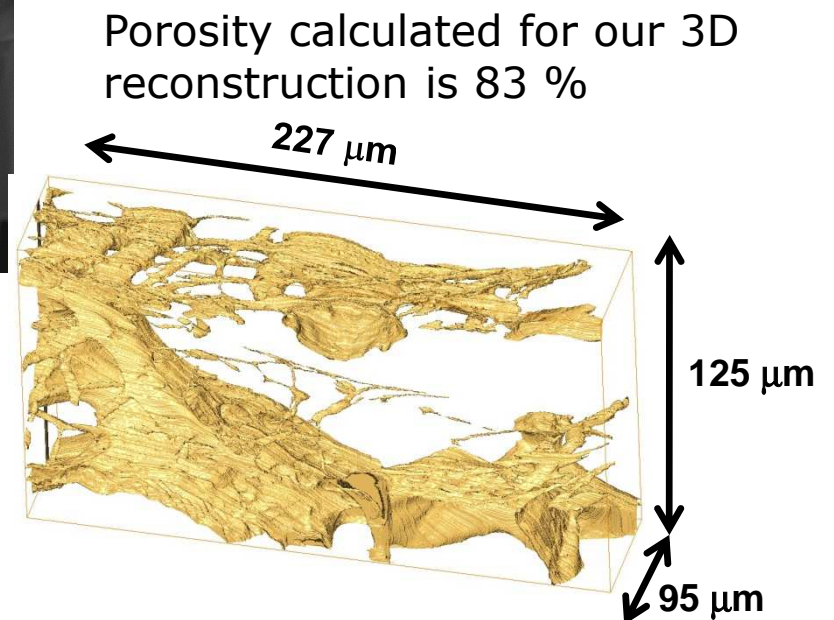
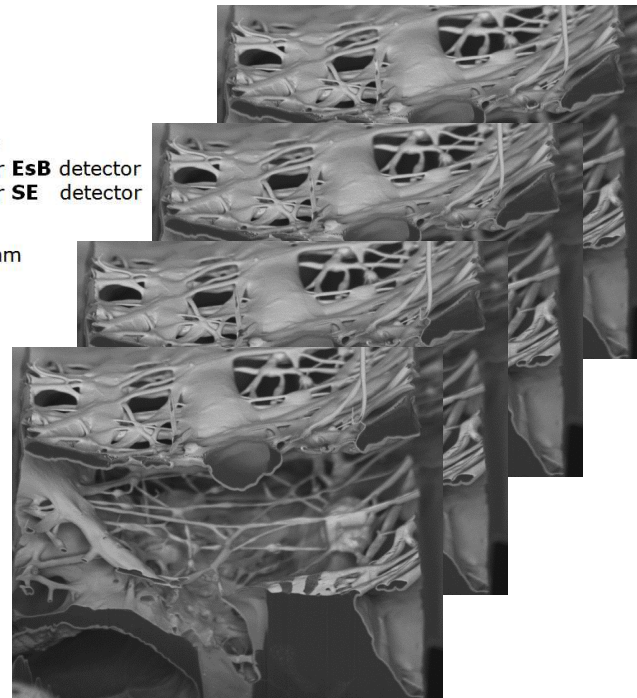
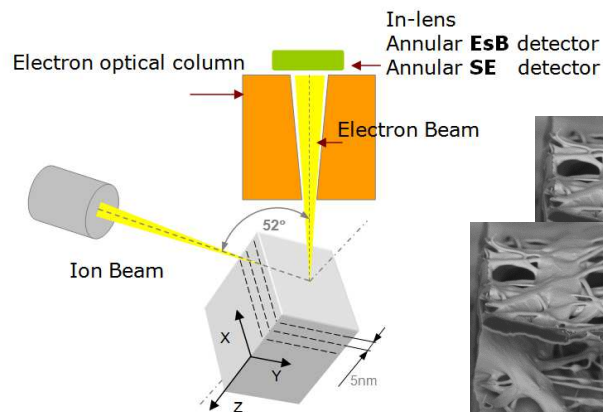




# Summary

- 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





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

The screenshot shows the ESTEEM 2 website interface. At the top, the logo for ESTEEM 2 (European Network for Electron Microscopy) is displayed. Below the logo is a navigation menu with options: Home, Project, Microscopes, Outputs, Intranet, and Contact. A sidebar on the left contains several menu items: Publications, Workshops, Software, Sample Prep, Job opportunities, and 'Apply for access!', which is highlighted with a red box. The main content area is titled 'Consortium' and lists various research institutions. A map of Europe with yellow stars is visible in the bottom left corner. The institution 'Akademia Gorniczo-Hutnicza Krakow • Poland' is circled in red.

Home Project Microscopes Outputs Intranet Contact

Publications  
Workshops  
Software  
Sample Prep  
Job opportunities  
**Apply for access!**

Overview

Consortium

Joint Research Activities

Networking activities

Project management

CEMES-CNRS  
Toulouse • France

LPS-CNRS  
Paris • France

University of Oxford  
Oxford • UK

Universiteit Antwerpen  
Antwerp • Belgium

University of Cambridge  
Cambridge • UK

Ernst Ruska-Centre  
Jülich • Germany

Max Planck Gesellschaft  
Stuttgart • Germany

Technische Universiteit Delft  
Delft • Netherlands

Chalmers Tekniska Högskola  
Chalmers • Sweden

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Krakow • Poland**

Technische Universitaet Dresden  
Dresden • Germany

NanoMEGAS  
Brussels • Belgium

CEDS  
Heidelberg • Germany





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Dr inż. Grzegorz Michta

Dr inż. Bogdan Rutkowski

Dr inż. Kinga Zawadzka

Dr inż. Maciej Ziętara

Mgr inż. Adam Gruszczyński

Mgr inż. Joanna Karbowniczek

Mgr inż. Sebastian Lech

Krystyna Płońska-Niżnik



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



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STSM – Istanbul Technical University



**Thank you for your attention!**

