

MILIVOJ PLODINEC

COST ACTION MP 1301

Period: 02/09/2015 to 19/09/2015

Reference code: COST-STSM-ECOST-STSM-MP1301- 020915-062807

STSM REPORT

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Boskovic Institute)**

**Title: Mechanical characterization of nanostructured composite materials for
potential applications as a bone implants**

HOST: Prof. dr. Carmen Baudin, Instituto de Cerámica y Vidrio, CSIC

1. Background:

Many used materials as implants for regeneration of bones and teeth (metals, metal alloys, and ceramics) have good biomechanical properties for applications where is needed high loading capacity. Although, these materials are biocompatible they are the most common and bioinert and therefore, they poorly or not at all grow with the surrounding tissue. In order to minimize or completely avoid the problem above, implants made of bioinert metals or ceramics were coated with bioactive calcium phosphate (CaP) prepared in various ways. The obtained biomaterials combine the advantages of good biomechanical properties of materials (basic, supporting structure of the implant) and good bioactivity of calcium phosphate (surface of the implant). Calcium phosphate can be prepared and applied to the surface of the material by various methods whereby the last decade emphasizes biomimetic process. One examples of implant material is zirconium dioxide based ceramics, whose bioactivity can be improved by coating with bioactive CaP This ceramics is commonly used as a material for bone implants due to its biocompatibility and good mechanical properties. But its bioactivity (ability fusion with bone) and the ability to ingrowth into the bone are not satisfactory for all applications. An additional problem with stabilized ZrO₂ ceramics is changes in the structure of the surface that may occur after connecting with the tissue, its poor mechanical properties. The advantages of porous ceramic as a material for making the basic structure of the implant is less specific weight, and increased surface roughness, which makes it suitable for different surface modifications, including the application of calcium phosphate. In addition, 3D porous structure mimics the structure of the bone tissue, which facilitates and promotes the adhesion and proliferation of surrounding cells. Zirconium

dioxide is commonly called zirconia. Zirconia adopts a tetragonal structure at high temperature and a monoclinic crystal at room temperature. The volume expansion caused by cooling from high temperature results in cracking. In order to stabilize the tetragonal phase, zirconia is blended with a metal oxide such as yttria (Y_2O_3). This is called tetragonal zirconia polycrystals (TZP). In particular, yttria stabilized TZP (Y-TZP) has superior biocompatibility and mechanical properties in comparison to other TZPs. Accordingly; it has been used as a material in artificial joints for a long time. Some studies on the biocompatibility of zirconia showed better results at Osseo integration than titanium [1, 2]. Due to these properties of zirconia, it is useful as a substrate for bone graft material.

On the other hand, titanium and titanium alloys are frequently used in orthopedic implants in load bearing situations because they possess favorable properties, such as a good ductility, tensile and fatigue strength, modulus of elasticity matching that of bones, low weight, and good biocompatibility. The nanotubular surface enhances adhesion, growth and differentiation of the cells. The nanotubular arrays increase the roughness of titanium implants on the nanoscale, providing the surface similar to that of a human bone. Bone-forming cells tend to adhere to the surfaces that are similar to natural bone both in chemistry and roughness. Nanotubular layers provide a high surface-to-volume ratio with controllable dimensions which are able to differentiate mesenchymal stem cells into osteoblastic cells. There is possibility to further enhance bioactivity of titanium implant with nanotubular surface by hydroxyapatite deposition into the titania nanotubes which further promotes bone ingrowth.

1. Sollazzo V, Pezzetti F, Scarano A, Piattelli A, Bignozzi CA, Massari L, Brunelli G, Carinci F. Zirconium oxide coating improves implant osseointegration in vivo. *Dent Mater* 2008; 24:357-61.
2. Schultze-Mosgau S, Schliephake H, Radespiel-Tröger M, Neukam FW. Osseointegration of endodontic endosseous cones: zirconium oxide vs titanium. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod* 2000;89:91-8.

1.1 Samples for scratch testing during STSM

In the proposed project were developed composite implant materials for solid tissue in which the main, load-bearing structure were stabilized high strength ZrO_2 porous ceramics and TiO_2 nanotubes arrays (anatase and rutile phase) grown at titanium discs. ZrO_2 ceramics were stabilized by yttria and alumina to prevent ageing and prepared either by sol-gel syntheses or by mechanochemical processing and subsequent sintering of prepared powder. All samples were coated with bioactive calcium phosphates prepared by biomimetic process.

For the scratch test measurements during were prepared 4 different series of samples:

1. Sol-gel synthesis of $ZrO_2 + 10\% Y_2O_3 + CaP$ – 14 days precipitation from solution (SG-CaP)
2. Mechanochemical synthesis $ZrO_2 + 10\% Y_2O_3 + 30\% Al_2O_3 + CaP$ - 28 days precipitation from solution (MH-CaP)
3. TiO_2 nanotubes arrays (anatase phase) + CaP - 28 days precipitation from solution (TA-CaP)

4. TiO₂ nanotubes arrays (rutile phase) - CaP - 28 days precipitation from solution (TR-CaP)

1.2 AIM

The main aim of this project was scratch testing of two ways prepared ZrO₂ ceramics and two different crystal phases of TiO₂ nanotube arrays on the titanium disc. All samples were coated with CaP. These measurements provide information about elastic-plastic deformations, formation of median, radial and lateral cracks and material failure mechanisms which occurs during scratch test. The obtained data substantially contribute to an understanding of the mechanisms involved in sliding wear and abrasion of our ceramics and nanotubes. The scratch test also provides important information about adhesion of calcium phosphate coated on the surface of all investigated samples.

2. Experimental

2.1 Scratch test

Scratch tests were performed during STSM in the group of Prof. dr. Carmen Baudin at the Instituto de Cerámica y Vidrio, CSIC, Madrid, Spain on the CSM Revetest scratch tester (CSM Instruments SA, Switzerland), using a Rockwell indenter (120° diamond cone). The length of each scratch was 3 mm, speed 1.5 mm/min and the load was increased linearly from 0 to 80-100 N in case of ZrO₂ samples. In case of TiO₂ nanotubes length of each scratch was 3 mm, speed 0.9 mm/min and the load was increased linearly 0-15 N. The critical load of coatings and substrate were taken from observations of the scratch tracking with the optical microscope (Olympus LEXT, Japan), identifying the point where cracks started. During test were measured: displacement into surface (Z), lateral force (F_z), acoustic emission (ΔE), and friction coefficient (COF).

2.2 Electron microscopy

The coated and scratch tested samples were later characterized by Tabletop Microscope TM-1000, Hitachi. The micrographs of samples were compared with the results of scratch test by Rockwell indenter to determine real load where the cracks in coating and substrate appears.

3. Results

One of each samples type SG-CaP, MH-CaP, TA-CaP, TR-CaP were firstly tested to optimized proper load for the scratch test performance. On each sample were performed 5 scratch test to obtained rstatistics for the estimation of coating and substrate failure load.

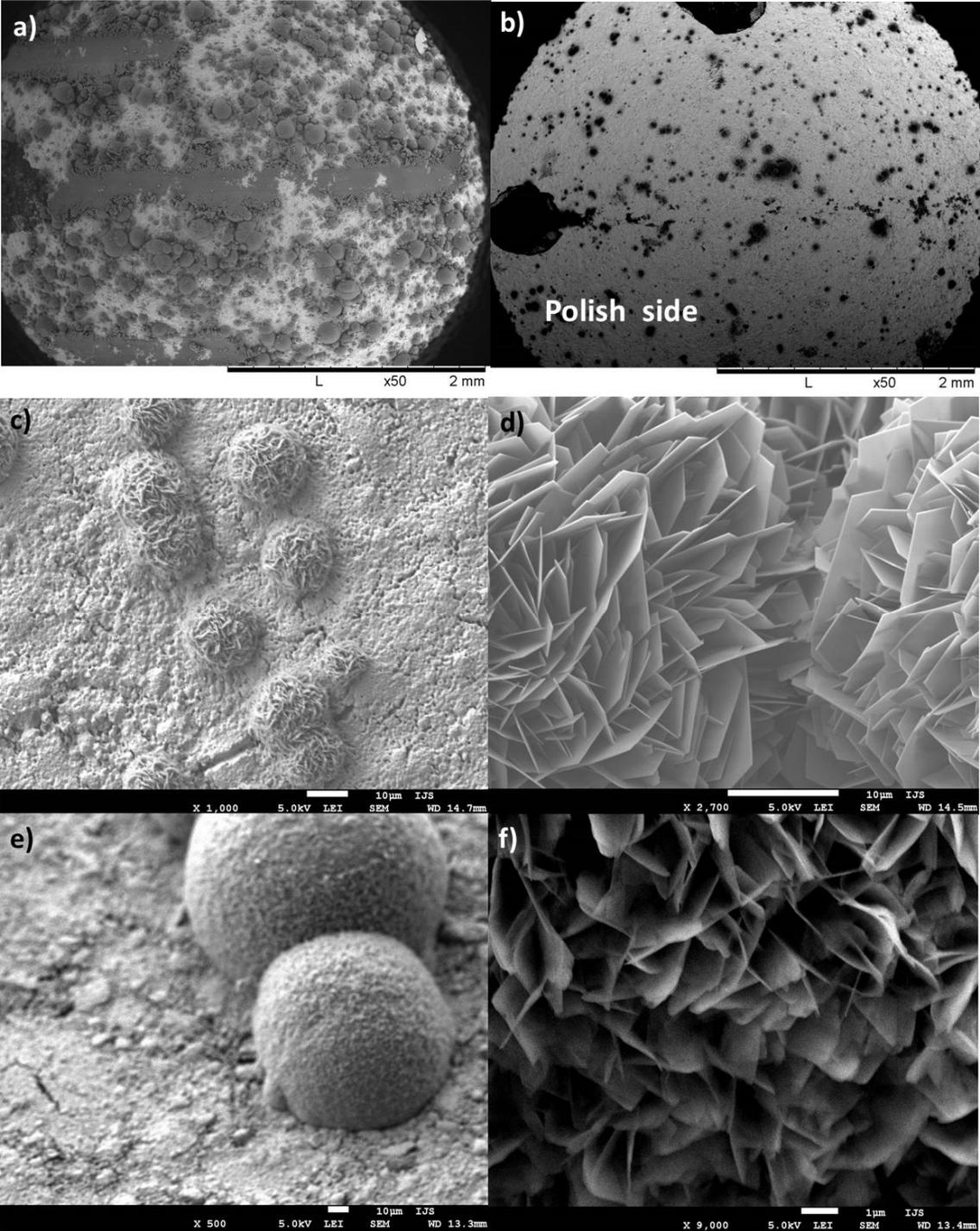


Figure 1. SEM micrograph of: a) unpolished side of ZrO_2 ceramics obtained by sol-gel synthesis partially covered by calcium phosphate (CaP); b) polished side of ZrO_2 ceramics obtained by sol-gel synthesis partially covered by calcium phosphate (CaP); c) and d) Sol-gel synthesis of $ZrO_2 + 10\% Y_2O_3 + CaP - 14$ days precipitation from solution, e) and f) Mechanochemical synthesis of $ZrO_2 + 10\% Y_2O_3 + 30\% Al_2O_3 + CaP - 28$ days precipitation from solution

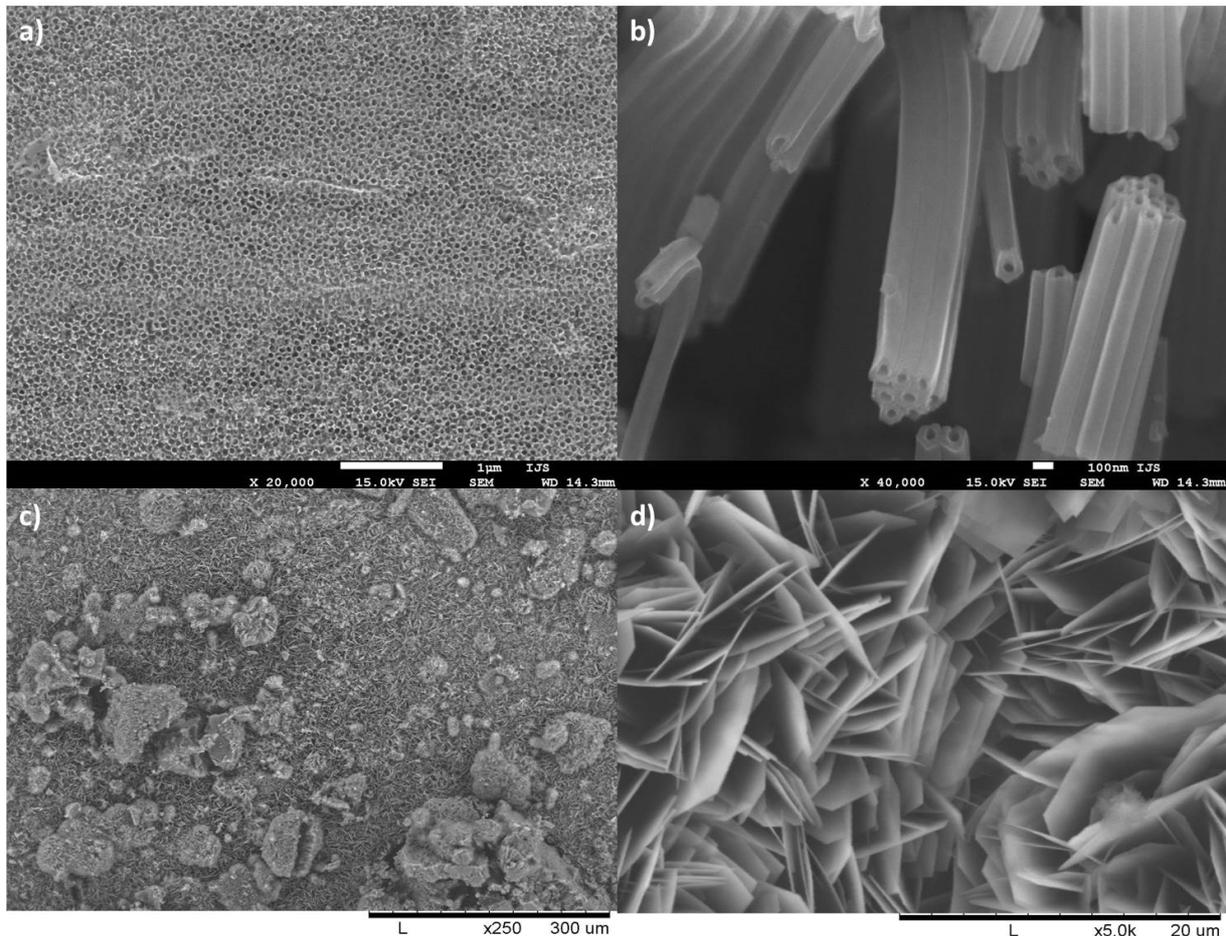


Figure 2. TiO_2 nanotube arrays obtained by anodization of Ti-disc: a) and b) Before deposition of CaP, c) and d) after 28 days in CaP solution.

On the Fig. 1 and 2 are shown the surfaces of the samples which were subjected to scratch test analysis. It was observed and later confirmed by Raman spectroscopy that samples which were in CaP solution for 14 days have mixture of octa-calcium phosphate (OCP)/hydroxyl-apatite(HAP) crystal phase at the surface of substrate ($ZrO_2 + 10\% Y_2O_3$) and samples which were 28 days have just hydroxyl-apatite (HAP) phase at the surface of substrates ($ZrO_2 + 10\% Y_2O_3 + Al_2O_3$, TiO_2 -anatase, TiO_2 rutile).

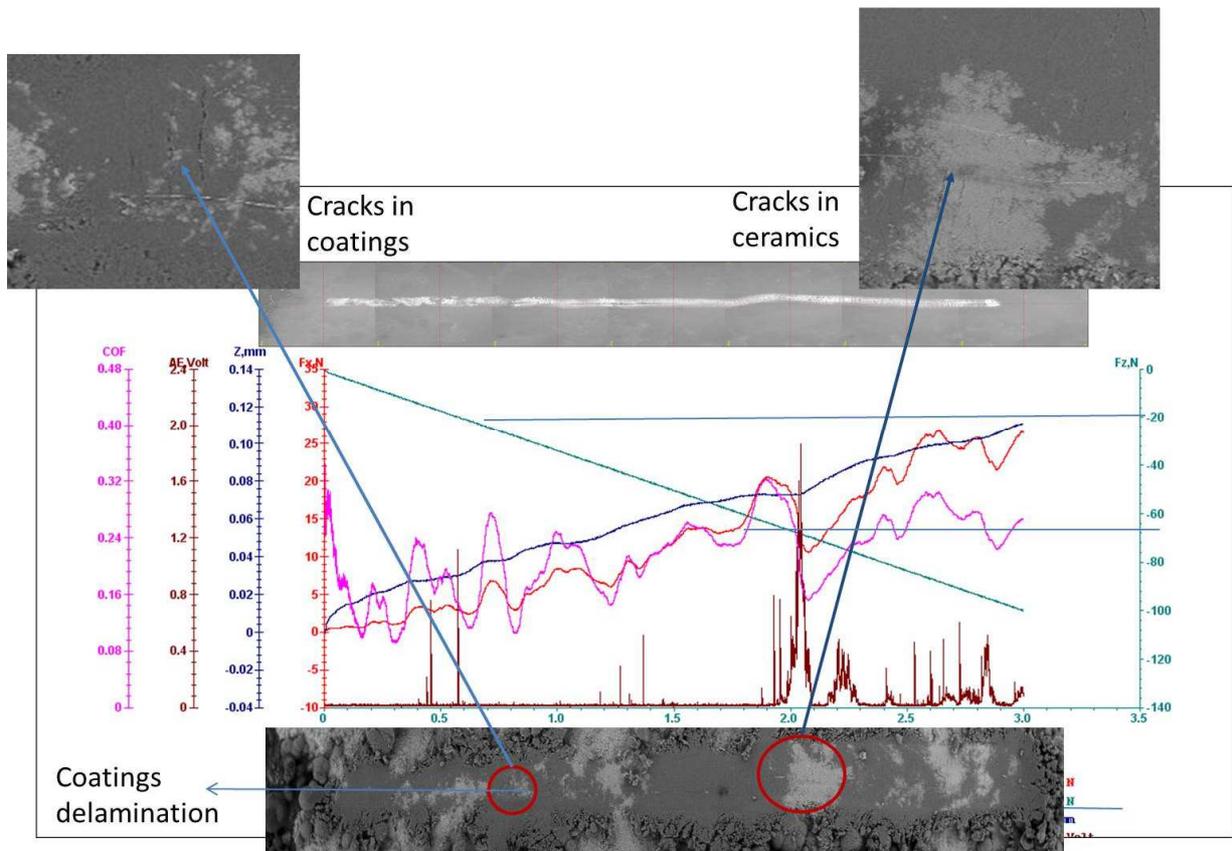


Figure 3. Scratch test results of SG-CaP sample. On the graph is shown dependency of COF, ΔE and Z over applied load and distance from starting points. SEM micrographs and optical image illustrating the major failure of coatings and ceramics in the single pass scratch test using Rockwell C diamond stylus $R = 200 \mu\text{m}$.

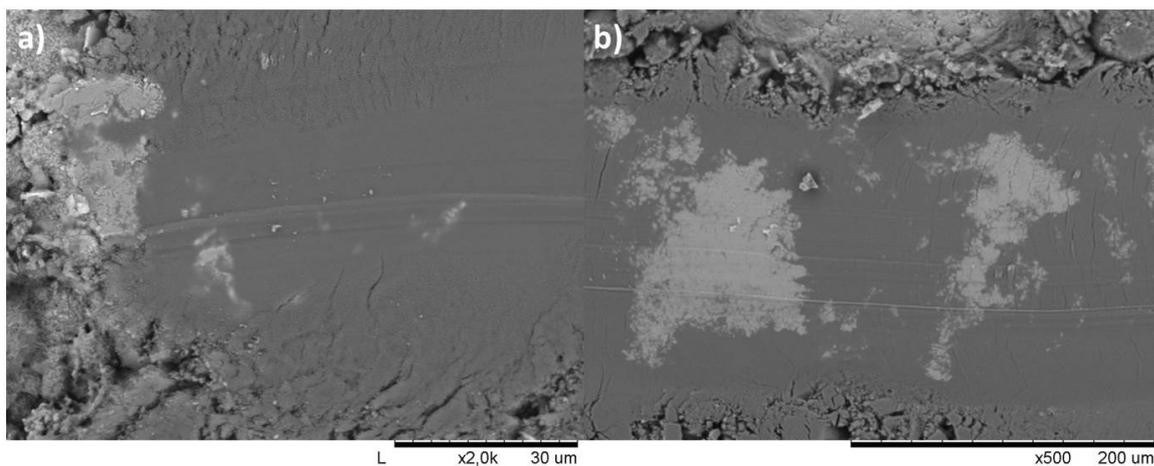


Figure 4. SEM micrographs of SG-CaP: a) Beginning of scratch line b) CaP coatings removal from substrate.

On the Fig. 4 can be observed that surface of coatings is very soft but very strongly bonded with ceramics surface, because even with load of 100 N the coatings can't be completely removed. At beginning of scratch line (Fig. 4a) densification of the coating under the indent and cracking of the densified coating edge of scratch line occurred. Excepting the cracks of coatings and ceramics, were also observed abrasion in coatings (Fig. 4a) due to moving of detached ZrO₂ nanoparticles by nanoindenter tip over the surface of specimen.

We performed 5 scratch lines (the same as on the Fig. 3) on 3 samples to obtained reliable results. The results of analysis are shown in the table 1. Some of the lines were not considered during evaluation, due to too low coatings at the surface of our disc or complete crack of sample into several pieces during test.

Table 1: Critical loads failure in the coatings and ceramics of SG-CaP samples.

	Coatings failure (Lc ₁ , N)	Ceramic failure (Lc ₂ , N)
1	20	50
2	22	55
3	17	42
4	16	48
5	20	40
6	20	60
7	17	45
8	18	50
9	18	45
10	20	50
11	18	65
12	15	55
13	20	45
14	18	40

Mean value	18	49
error	2	7

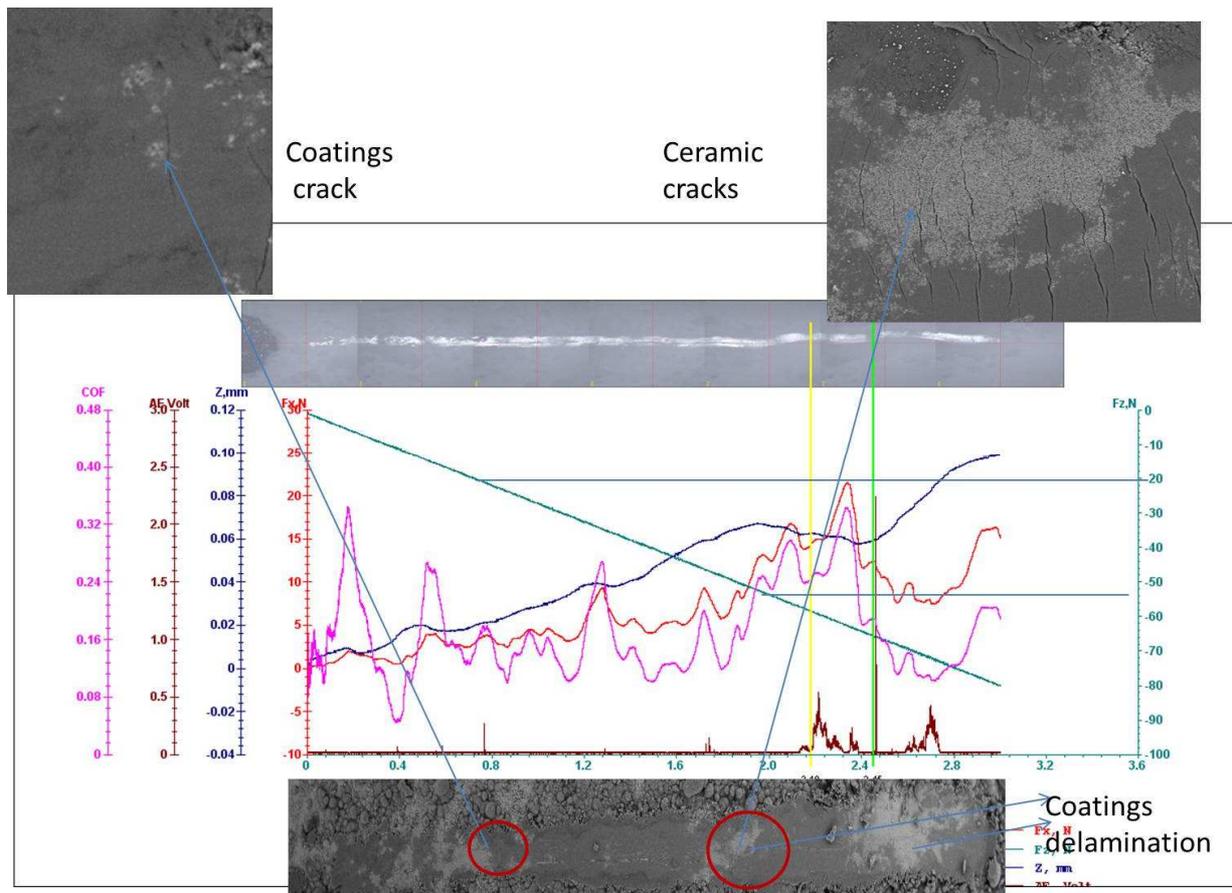


Figure 5. Scratch test results of MH-CaP sample. On the graph is shown dependency of COF, ΔE and Z over applied load and distance from starting points. SEM micrographs and optical image illustrating the major failure of coatings and ceramics in the single pass scratch test using Rockwell C diamond stylus $R = 200 \mu\text{m}$.

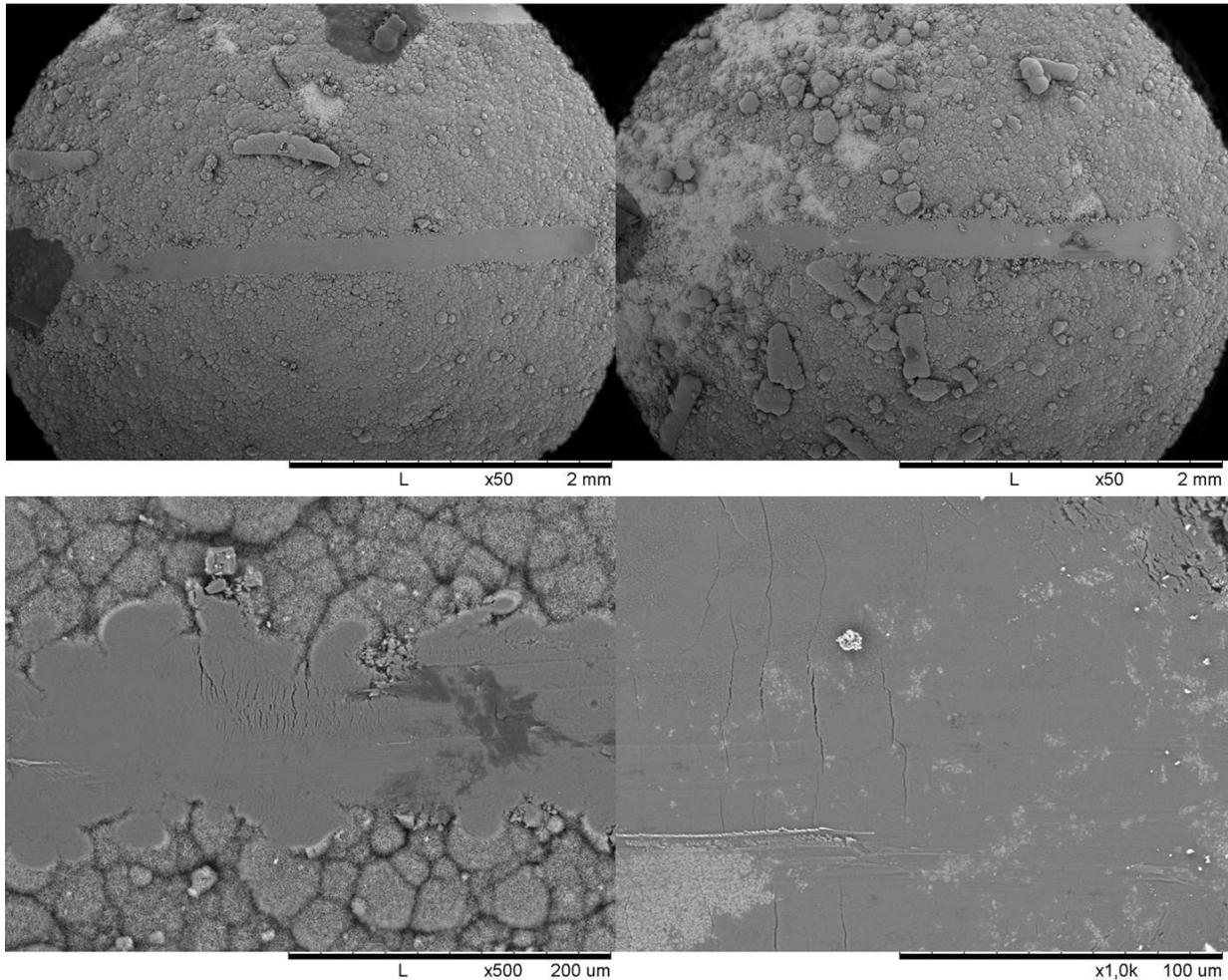


Figure 6. SEM micrographs of scratch lines of MH-CaP sample.

The similar behavior as on the SG-CaP sample, of coatings and ceramics under scratch test was occurred here. On the beginning we observed densification of the coating under the indent and cracking of the densified coating. Moreover, minor cracking on edge of scratch line appeared (Fig 5. and 6.) .Also, the ceramic substrate was almost completely covered with CaP coatings, what was not the case in SG-CaP sample. At the end of the line was observed chipping and detached coating material, appearance of cracks in ceramics. The values for critical load failure of coatings(L_{c1}) and ceramics(L_{c2}) are lower than in case of SG-CaP (table). What indicate that mechanochemical prepared substrate have more defects and pores than SG-CaP sample.

Table 2. Critical loads failure in the coatings and ceramics MH-CaP

	Coatings failure (Lc ₁ , N)	Ceramic failure (Lc ₂ , N)
1	20	52
2	18	32
3	15	42
4	16	50
5	18	42
6	15	32
7	15	42
Mean value	17	35
error	2	38
	Mean value	41
	error	7

In second part of STSM we investigated by scratch test the adhesion of CaP coatings and TiO₂ nanotube arrays prepared by electrochemical etching on the Ti-. As it is shown on Fig. 6 the values for critical load failure of coatings nanotubes in case of TA-CaP sample are much lower than for ZrO₂ based ceramics. The complete failure occurred around 6 N load. Due to much weaker bonding of TiO₂ nanotubes with Ti-disc. Coating detachment started around load of 3N, what could be observed as a brighter part in the scratch line (Fig. 7). All TA-CaP samples were fully covered with coatings (Fig 7.).

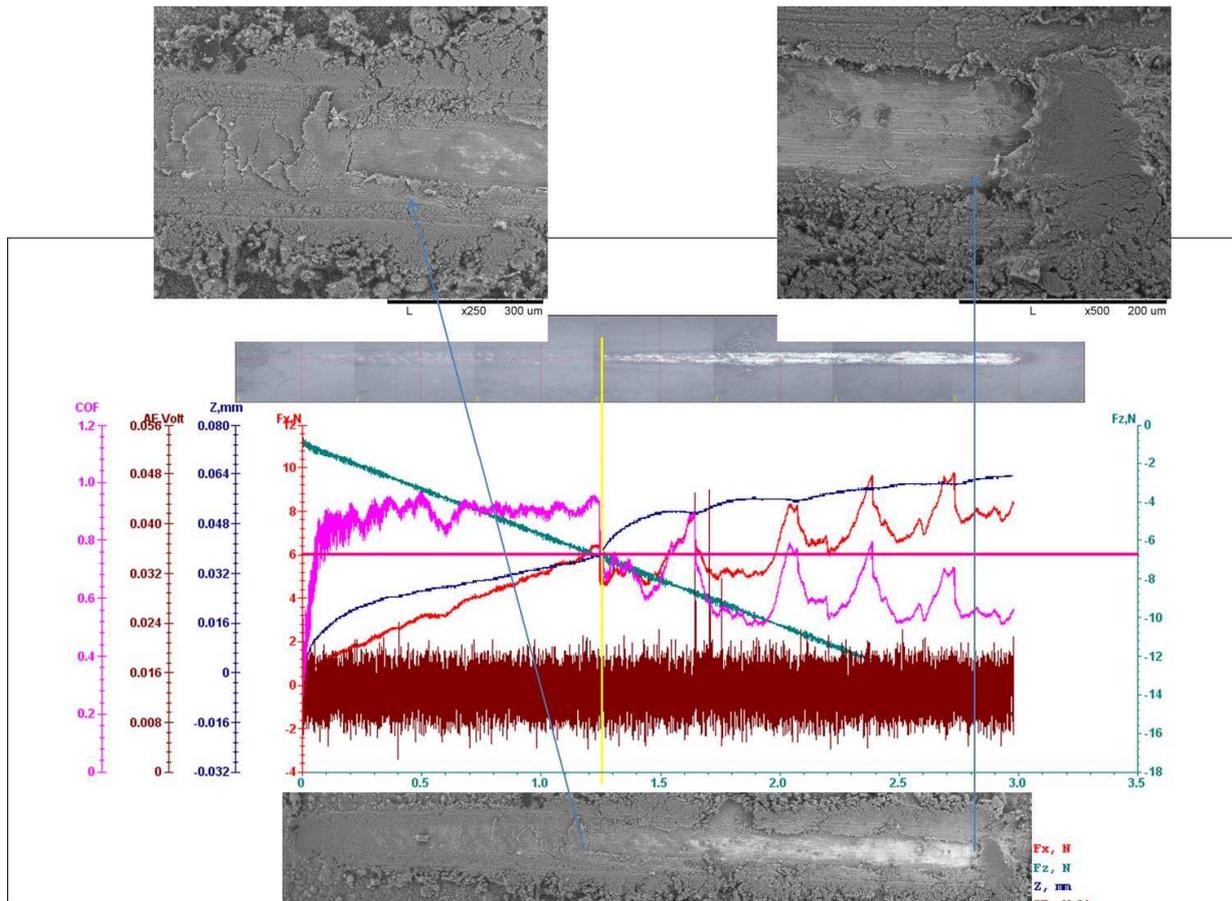
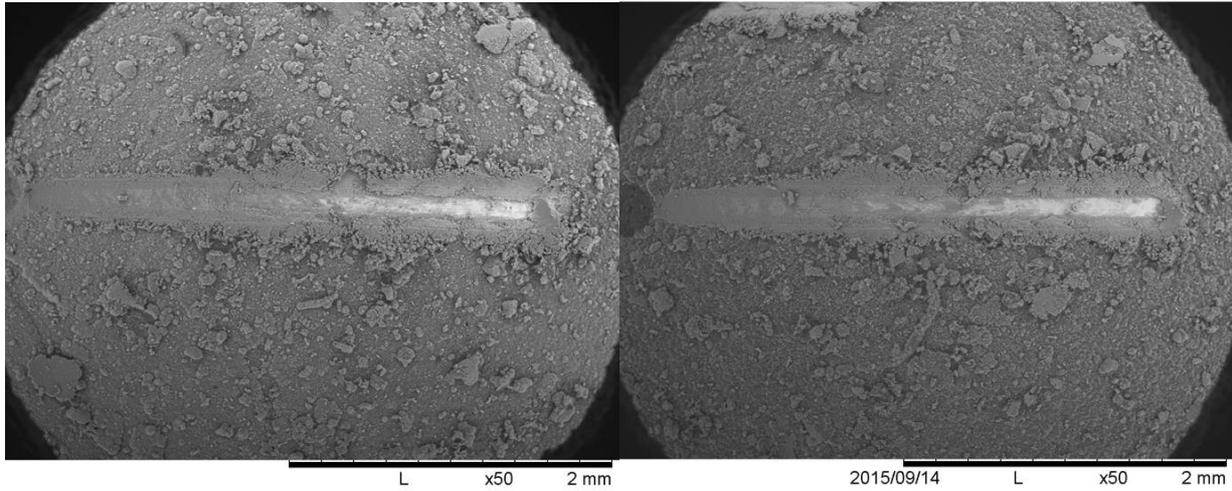


Figure 6. Scratch test results of the TA+ CaP sample. On graph is shown dependency of COF, ΔE and Z over applied load and distance from starting point. SEM micrographs and optical image illustrating the major failure of coatings and ceramics in the single pass scratch test using Rockwell C diamond stylus R = 200 μm .



.Figure 7. Surface and scratch test lines of TA+CaP sample

Table 3. Critical load failure of TA+ CaP

	Coating and nanotubes failure and delamination (Lc, N)
1	6,6
2	6,2
3	7,2
4	6
5	6,2
6	6,2
7	5
8	6,2
9	4,8
10	5,2
11	5,70
12	4,40
13	5,2
14	4,7
15	5
Mean value	5,6
error	0,8

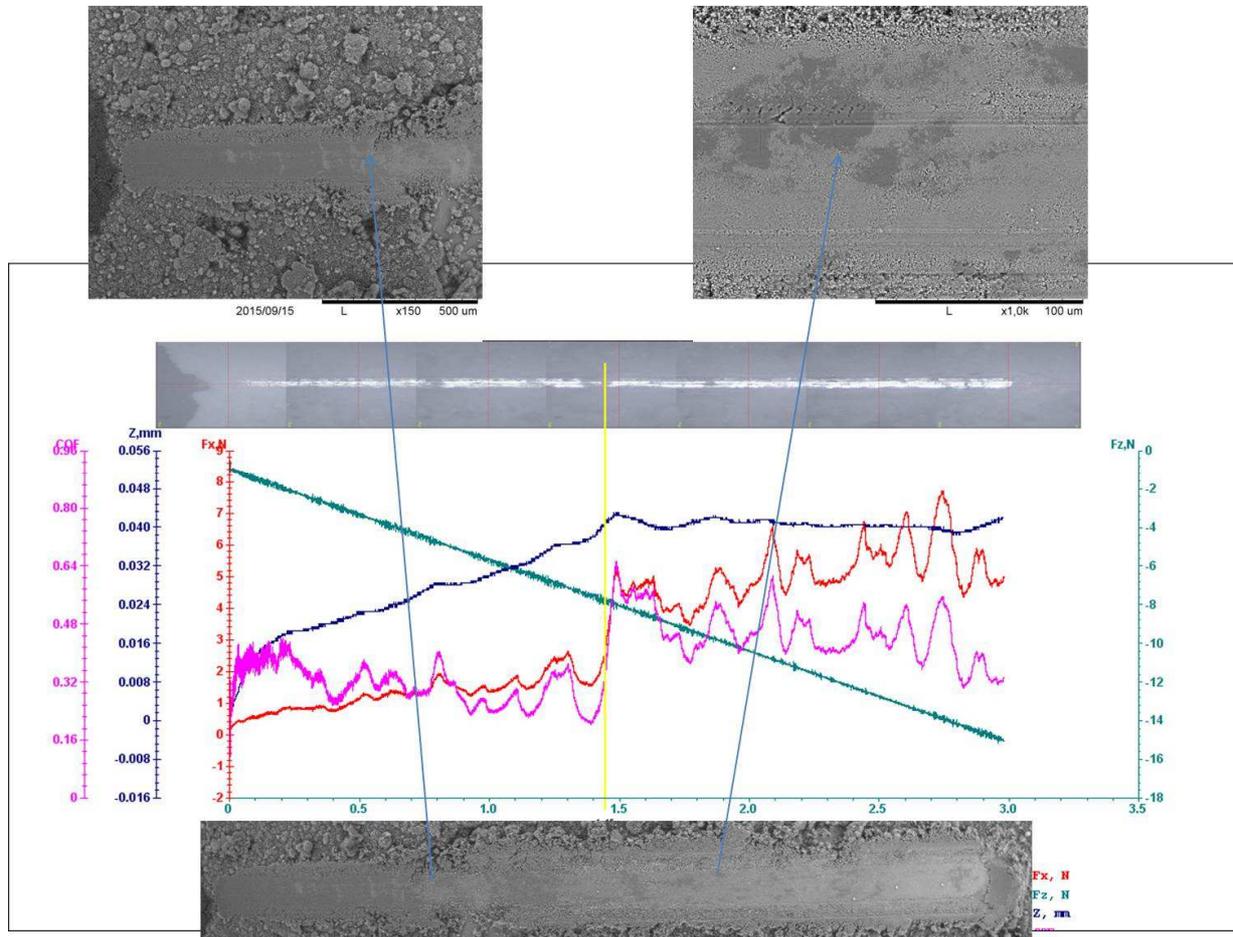


Figure 8. Scratch test results of the TR+ CaP. On the graph are shown dependence of COF, ΔE and Z over applied load and distance from starting point. Inset corresponding optical micrograph and images obtained by SEM show characteristic failure points.

Similar effects occurred like in case TA-CaP sample chipping of coatings starts at around 4N load, but almost complete delamination happened at 7 N load. After this point it could be still seen some darker place on the scratch line (Fig. 8.and 9.) which correspond to the coating material. At these place was strongly bonded with TiO_2 rutile nanotubes. TiO_2 rutile nanotube arrays are more scratch test resistant than anatase. Because even at 15 N load the nanotubes were not completely removed from Ti-disc. (Fig. 8 c) and d)).

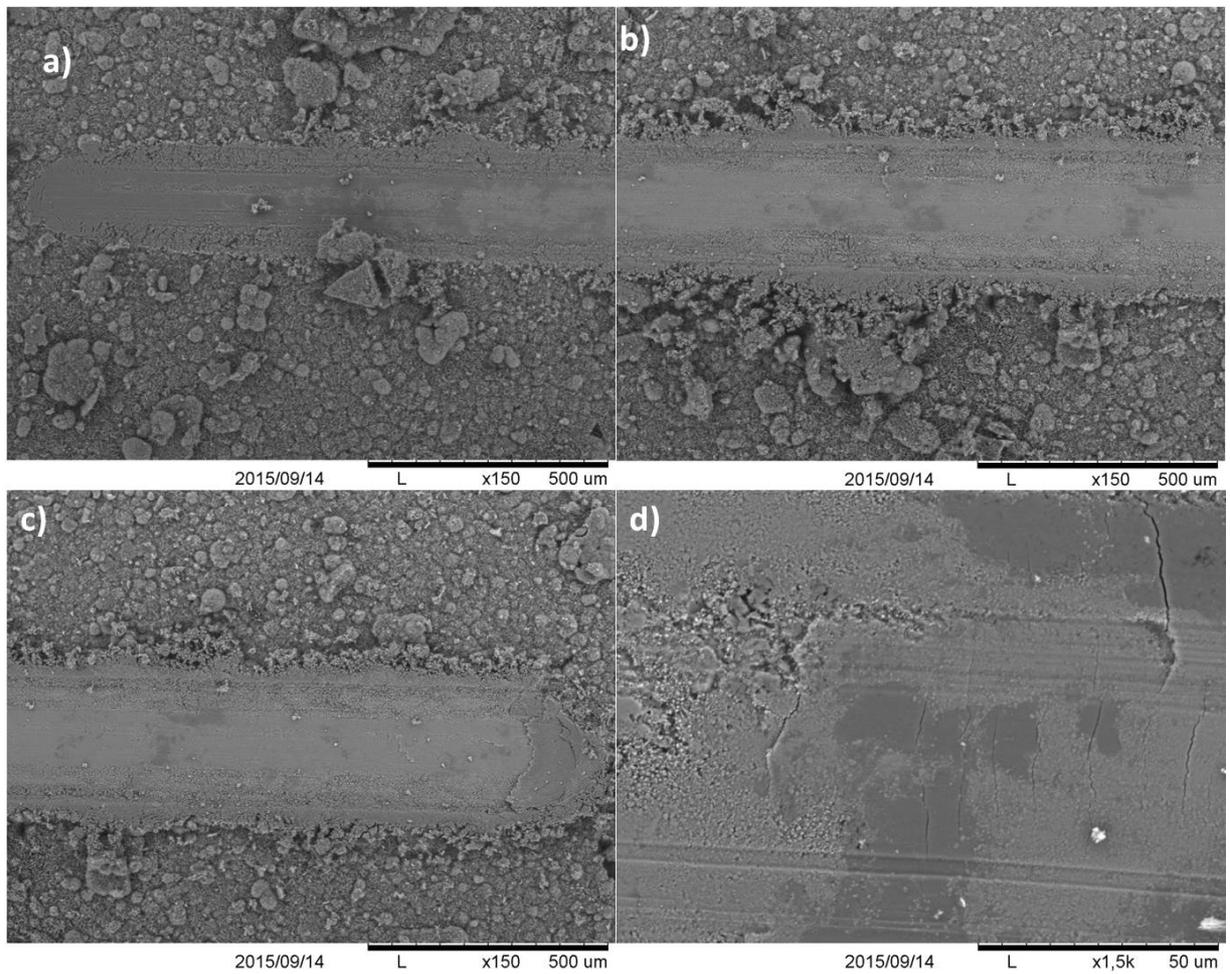


Figure 9. Different part of scratch line TR-CaP sample: a) beginning, b) middle, c) end, d) end at higher modification

	Coating and nanotubes failure and delamination (Lc, N)
1	6,2
2	6,6
3	5,2
4	7,1
5	4,8
6	7,5
7	5,1
8	10,3
9	6,7
10	6,1

11	5,5
12	7,8
13	7,5
14	7,6
Mean value	7
error	1

The scratch test results obtained on coated porous ZrO₂ (SG-CaP MH-CaP) and TiO₂ nanotube arrays (TA-CaP, TR-CaP) provide us very important information about adhesion of calcium phosphate coated on the surfaces of all substrate. Obtained results during this STSM project will be used for further developments, processes optimization and improvements of proposed biomimetic material for application as a bone implants. This STSM has inspired a collaboration between Rudjer Boskovic Institute and Instituto de Cerámica y Vidrio and it will continue in future on development and testing of biomaterials for the bone implants and application for grants on EU project open calls. Also, the results obtained in this STSM will be used in joined publications.