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Strateški projekt sofinancira Evropski sklad za regionalni razvoj

PROOF-OF-CONCEPT EXPERIMENT REPORT

MORPHOLOGY AND COMPOSITION OF CR-FREE COATINGS ON METAL SUBSTRATES

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*Department of
Molecular
Sciences and
Nanosystems*

Proof-of-Concept experiment details

Main aim of the PoC experiment:

To study the morphology and layer composition, especially mapping the surface with EDX (Energy Dispersive X-rays Spectroscopy). Inspection of the critical points (defects, stains, ...) on the coating and preparation of the specimen for SEM/EDX investigation.

Characterize the coating in critical points (defects) compared with non-critical areas, in order to understand the possible reasons for defect formation. The characterization is morphological (top view and X-section when relevant) and elemental.

The company wants to verify if SEM/EDX is effective in investigating their samples and, in particular, in understanding the source of the defects.

Received samples: 4 samples (+ 1 extra sample: specimen with a new formulation) have been received for the present PoC experiment. In the following table, the list of samples and the measurements performed are reported.

| Samples | Measurements / characterization |
|------------------------------------|--|
| - Sample 124 | - SEM, EDS, EDS maps |
| - Sample 119z | - SEM, EDS, EDS maps, optical microscopy |
| - Sample 119z conc. (extra sample) | - SEM, EDS, EDS maps, optical microscopy |
| - Sample 116 PO | - SEM, EDS, optical microscopy |
| - Sample 116 PN | - SEM, EDS, optical microscopy |

Description by company: the samples consist of a Cr free coating on top of metal substrate and they have been generally described in the POC proposal submitted within Nanoregion project. More information is delivered with the samples:

- Sample 124: Zr-Al₂O₃ coating on galvanized steel substrate (mixed organic/inorganic treatment)
- Sample 119z and 119z_conc: protective layer on galvanized steel substrate.
- Samples 116 PO and PN: layer with Fe phosphate on steel substrate + organic titanates applied to the surface. Fresh new product (116 PN) and the old product (116 PO).

Planned analysis:

- Sample 124: study of the layer composition, especially mapping the surface with EDX to evaluate the distribution of zirconium. Possible cross-sectional analyzes.
- Sample 119z and 119z_conc: to verify the morphology and composition of the coating.
- Samples 116 PO and PN: evaluation of the differences between samples treated with fresh and aged products, especially with regard to coating defects. Pre-treatment: phosphate conversion (Fe phosphate) for painting. PO and PN have yellow lines aesthetic and paint problems.

Sample preparation: The samples arrived already prepared for SEM and EDX analysis. Sample 119z_conc (the extra sample) has been prepared for cross-section measurement (cut and lapping).

Measurement author, dates and place: the reported measurement has been performed by dr. Federica Rigoni in the period from 14/05/20 to 20/07/20 at Ca' Foscari University of Venice.

Observation conditions:

Imaging: beam energy 10 KeV; secondary electron detector.

EDX mapping and spectroscopy: beam energy: 20 KeV.

Results

1) SEM and EDS investigation on sample 124

Morphology and EDX analysis

See attached file: «SEM and EDS investigation on samples 124and 119z» ([ATTACHMENT 1](#))

2) SEM and EDS investigation on sample 119z

Morphology and EDX analysis

See attached file: «SEM and EDS investigation on samples 124and 119z» ([ATTACHMENT 1](#))

3) SEM and EDS on sample 119z_conc + cross-sectional measurements

Morphology and EDX analysis

See attached file: «SEM and EDS investigation on sample 119z concentrato» ([ATTACHMENT 2](#))

X-section analysis

See attached file: «SEM and EDS investigation on tilted sample 119z concentrato» ([ATTACHMENT 3](#))

4) SEM and EDS on samples 116 PO and PN

Morphology and EDX analysis

See attached file: «SEM and EDS investigation on samples POand PN» ([ATTACHMENT 4](#))

Summary

- Morphology and elemental investigation of the samples have been performed.
- On sample 124 (mixed organic / inorganic treatment), the EDS results show that Zr is detected from ZrO_2 (Zr was not observed from previous XRF measurements carried out by the company).
- The measurements on the samples 119z and 119z_conc confirm that the product gives a protective layer for galvanized material. The obtained results confirm that the company have improved the preparation system.
- PO, PN: simple system, organic titanates applied to the surface. Titanate has not been observed (no Ti detected from EDS spectra). No improvements of the PN layer with respect of the PO layer have been observed. Eventually, it has been observed that the samples subjected to a forced oxidation show rust after few months stored in a drawer.

Final remarks on the effectiveness of SEM/EDX in the investigation of coating on metal substrates

SEM/EDX investigation has been proved to be effective in the characterization of these kind of samples, giving access to information about the morphology and the composition of the coatings, which are useful in the assessment of the product properties and in their development.

Advices for future possible investigations: XPS on samples PO and PN in order to detect Ti traces on the surface.

This report has been written by Federica Rigoni (Mestre, 09 February 2021)

List of attached files:

- [ATTACHMENT 1](#): SEM and EDS investigation on samples 124 and 119z
- [ATTACHMENT 2](#): SEM and EDS investigation on sample 119z concentrato
- [ATTACHMENT 3](#): SEM and EDS investigation on tilted sample 119z concentrato
- [ATTACHMENT 4](#): SEM and EDS investigation on samples PO and PN

ATTACHMENT 1

SEM and EDS investigation on samples 124 and 119z

Nanoregion project **PoC#2**

PoC coordinator: **Federica Rigoni**

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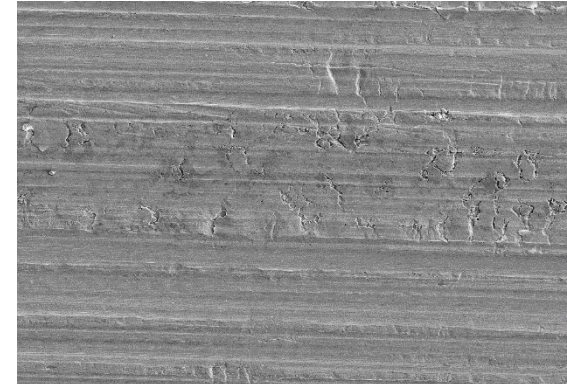
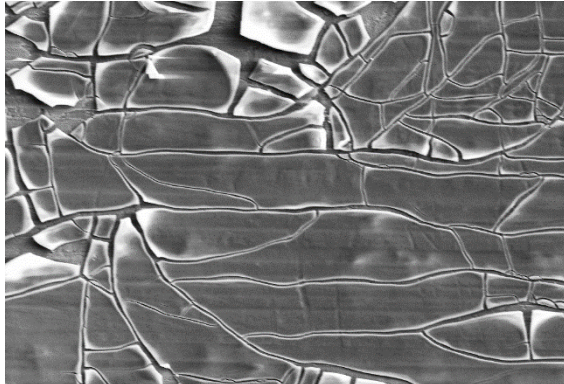
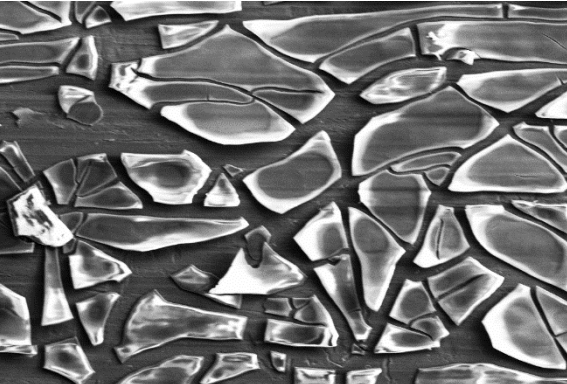
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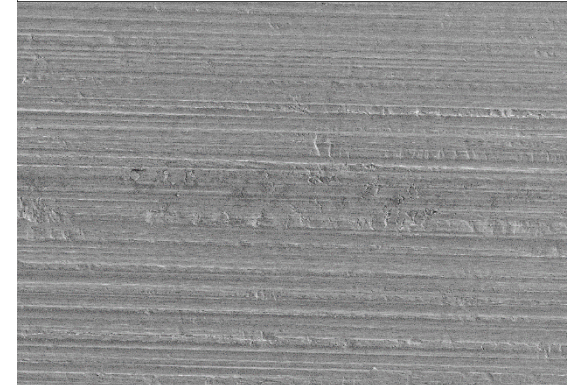
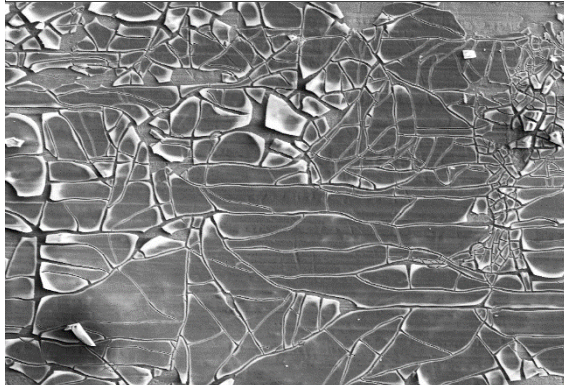
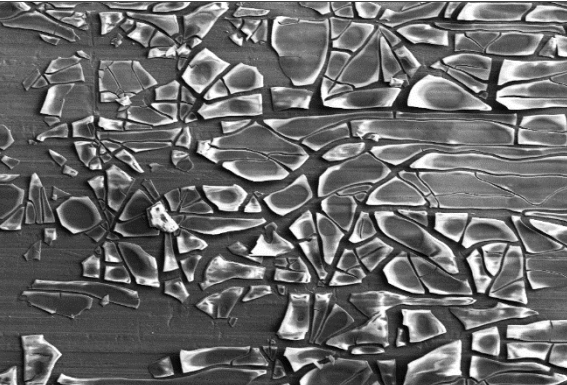
Sample 124 - SEM images

Bianco

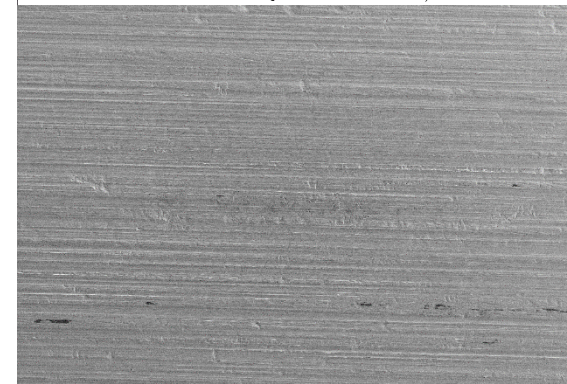
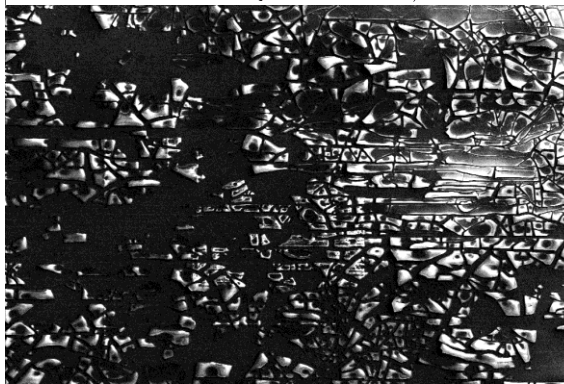
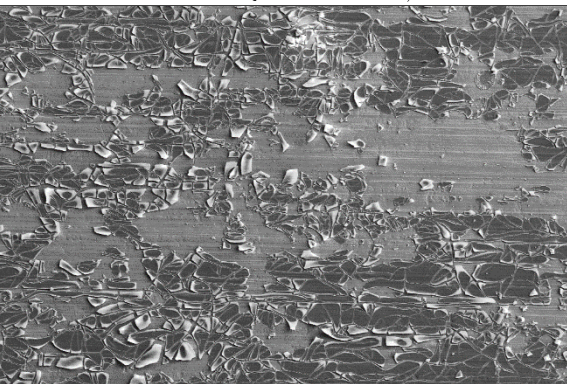
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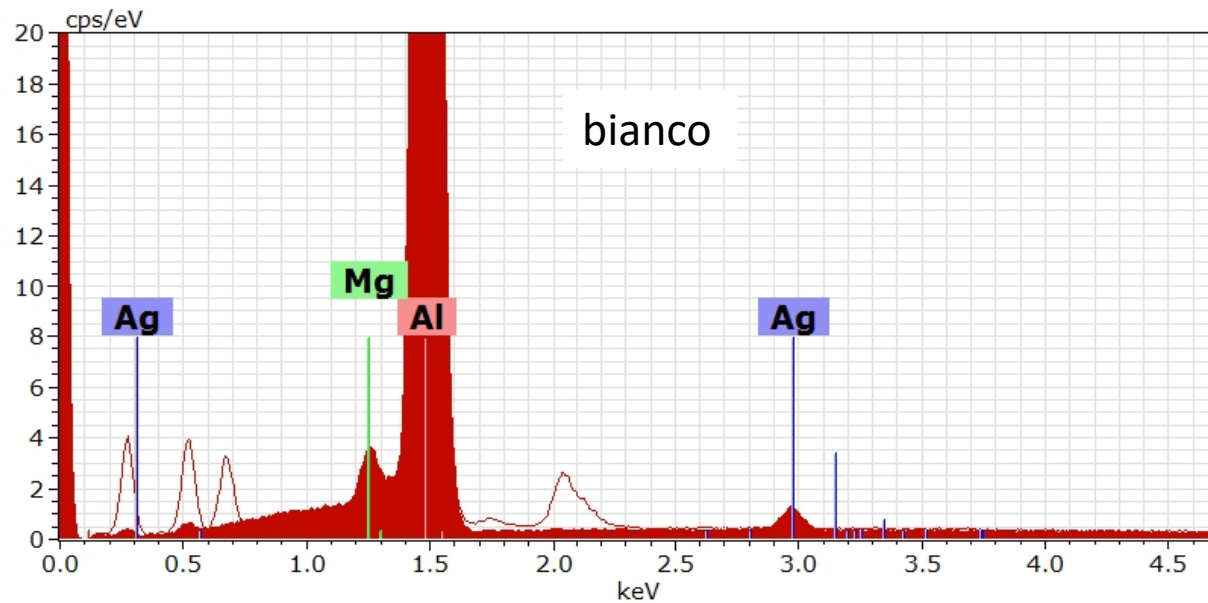
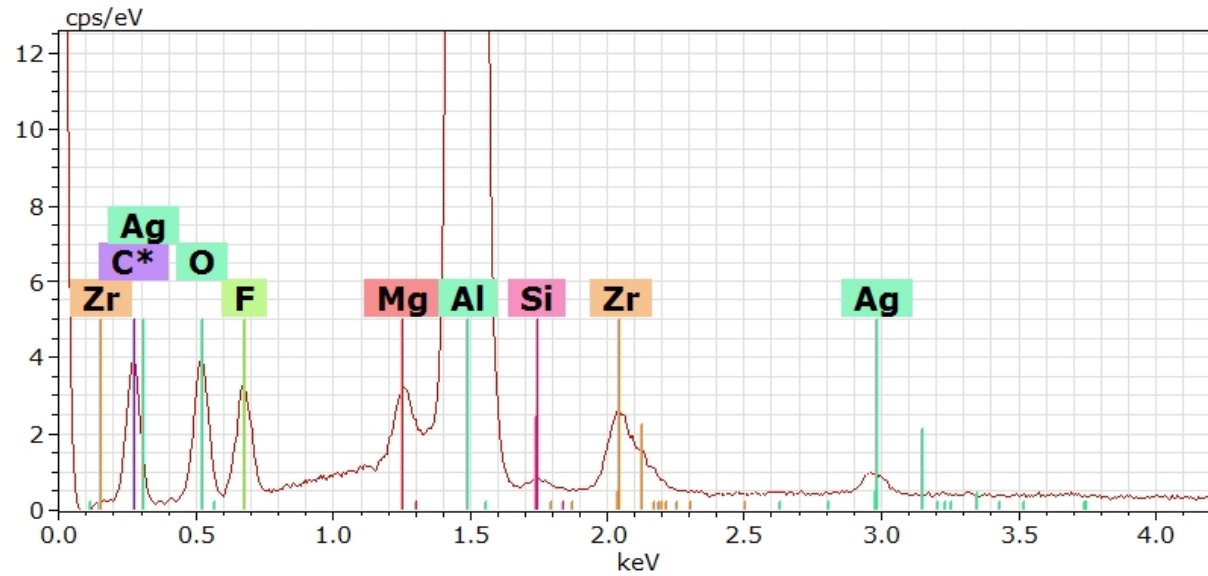


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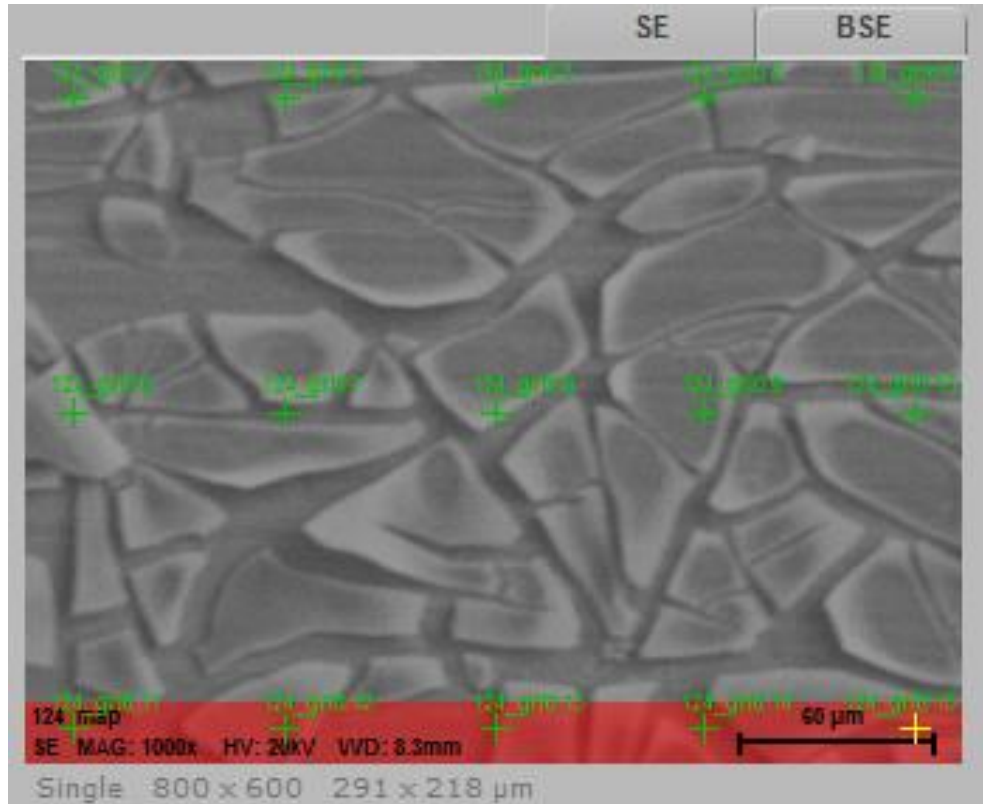
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Sample 124 – EDS analysis

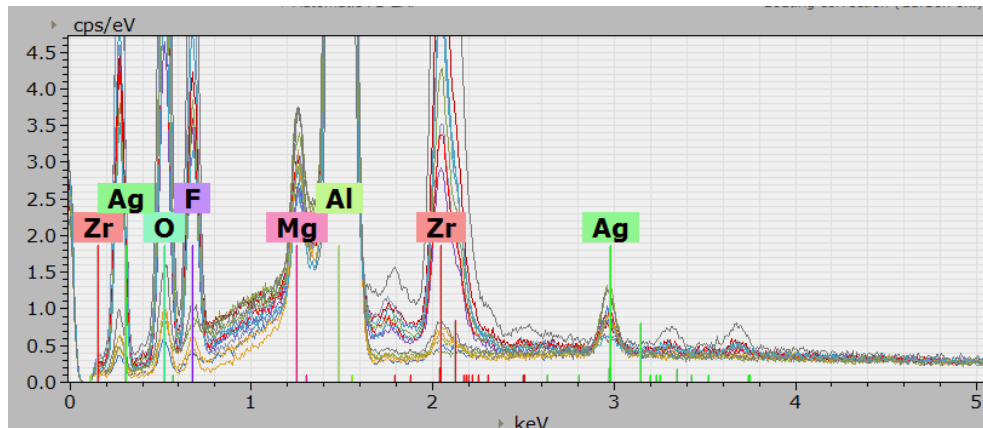


PoC#2

Sample 124 – EDS multi point spectrum (grid)

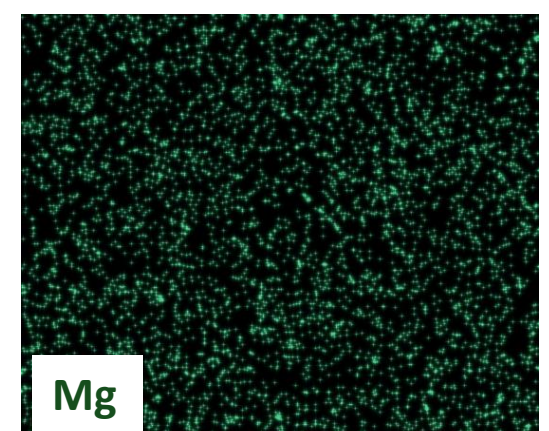
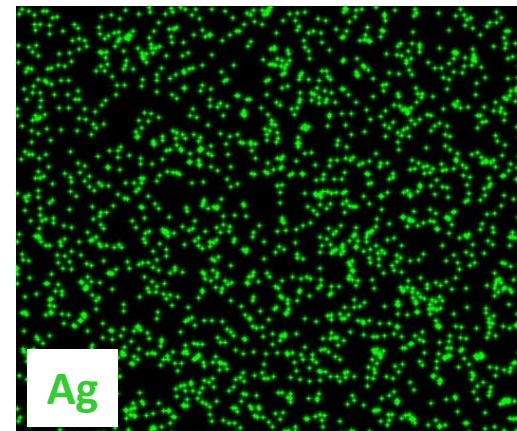
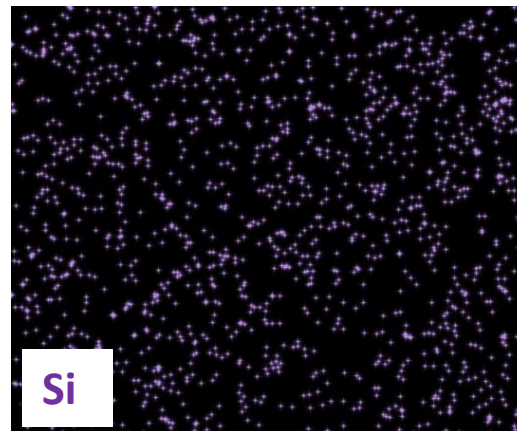
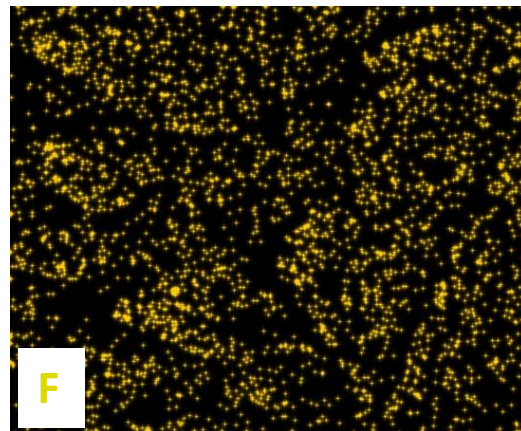
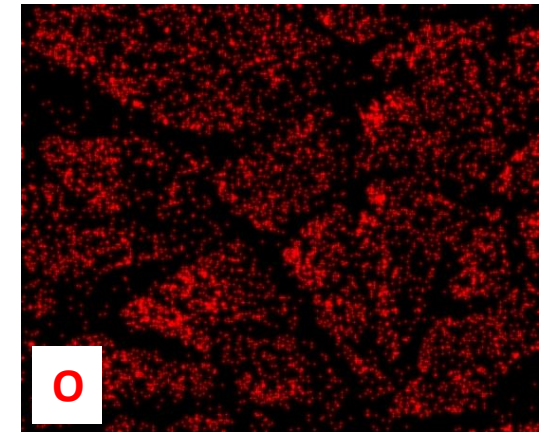
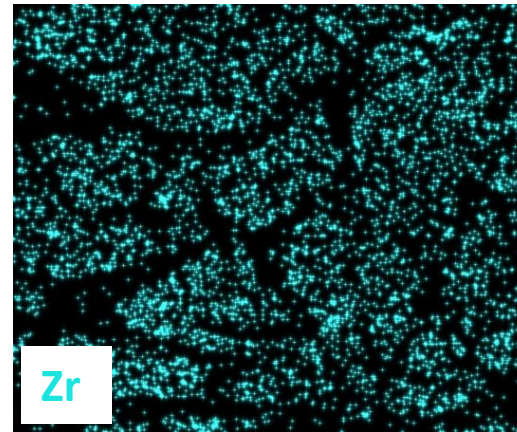
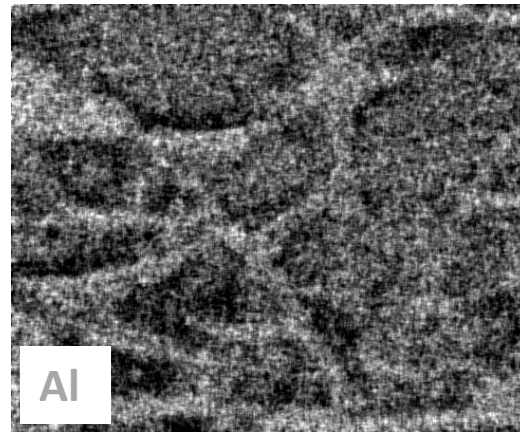
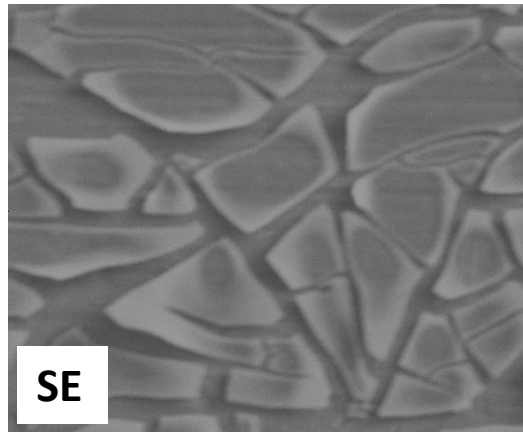


QUANTITATIVE ANALYSIS
HAS BEEN PERFORMED



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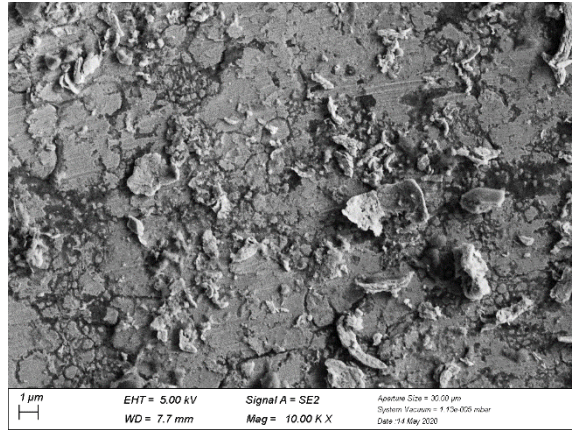
Sample 124 – EDS map



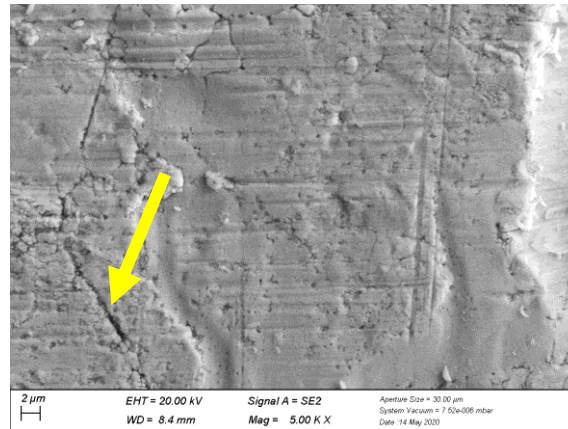
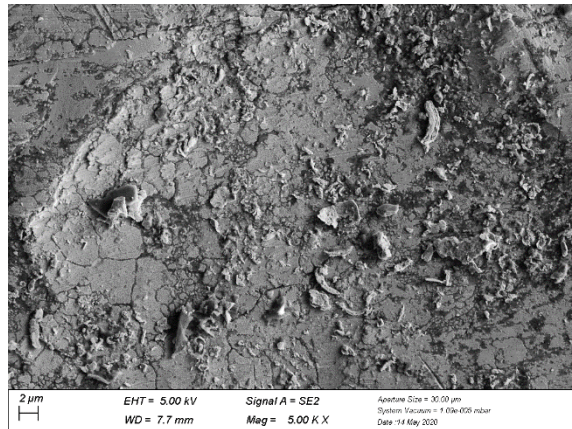
PoC#2

Sample 119z - SEM images

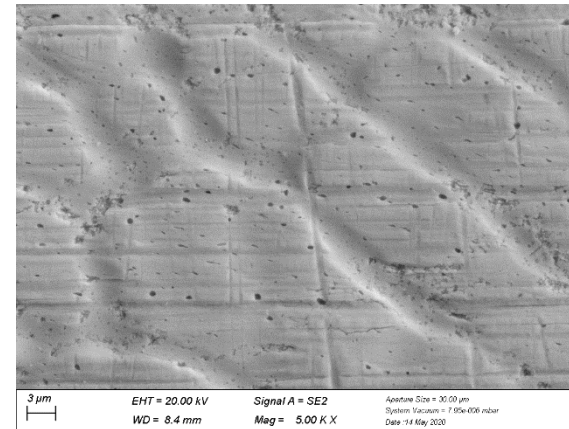
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Mag = 5K X



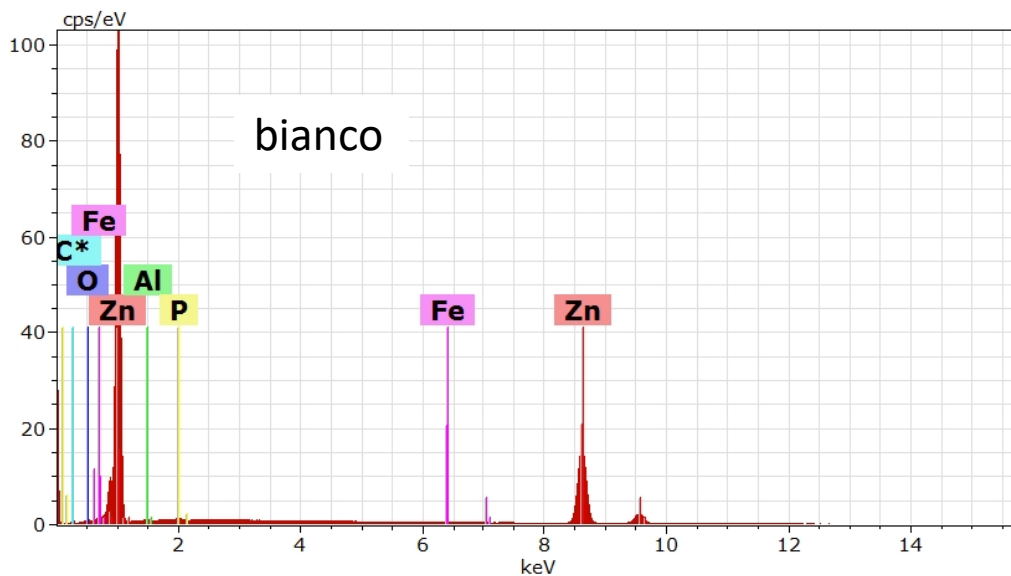
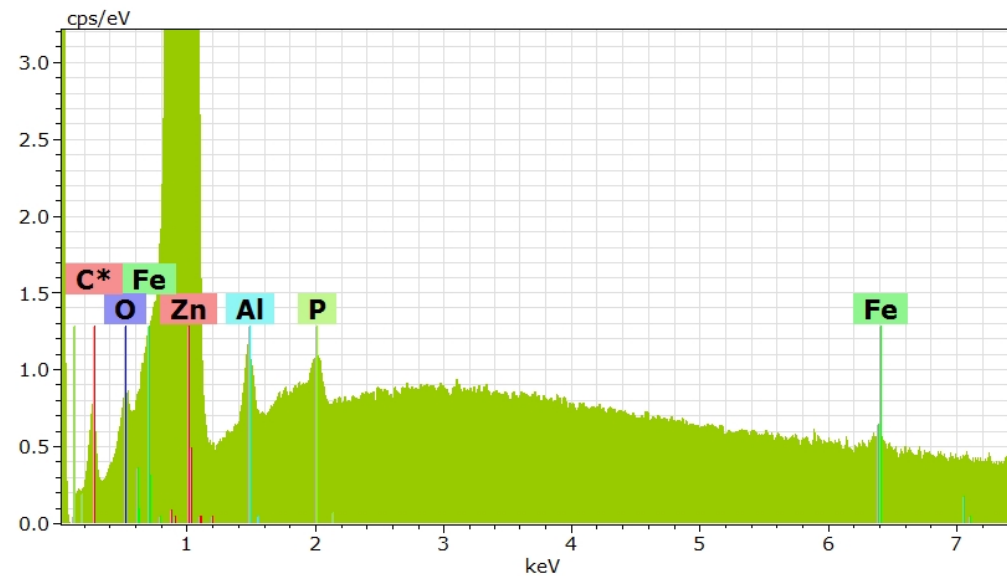
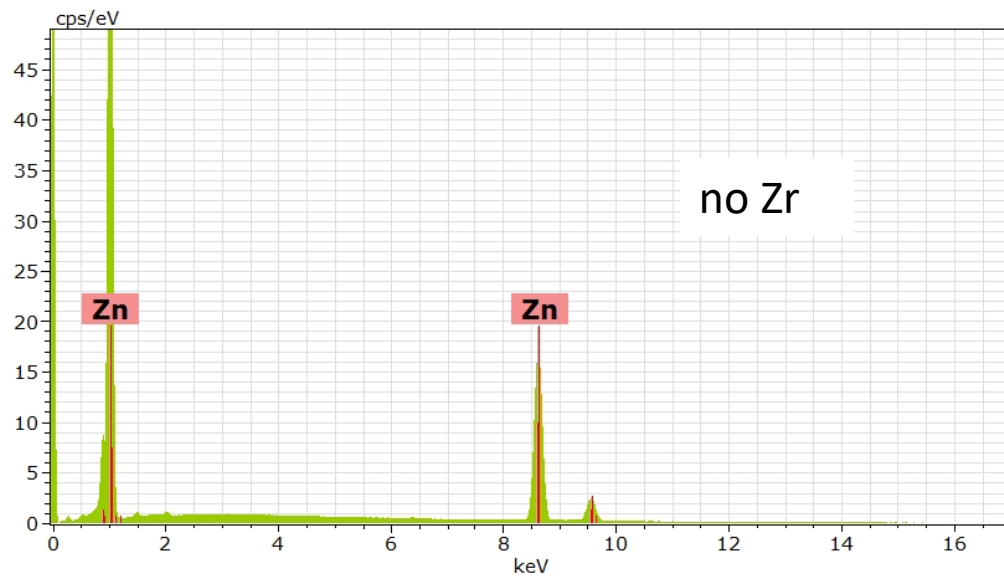
Bianco



See EDS maps (last slide of this attachment)

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Sample 119z – EDS analysis



PoC#2

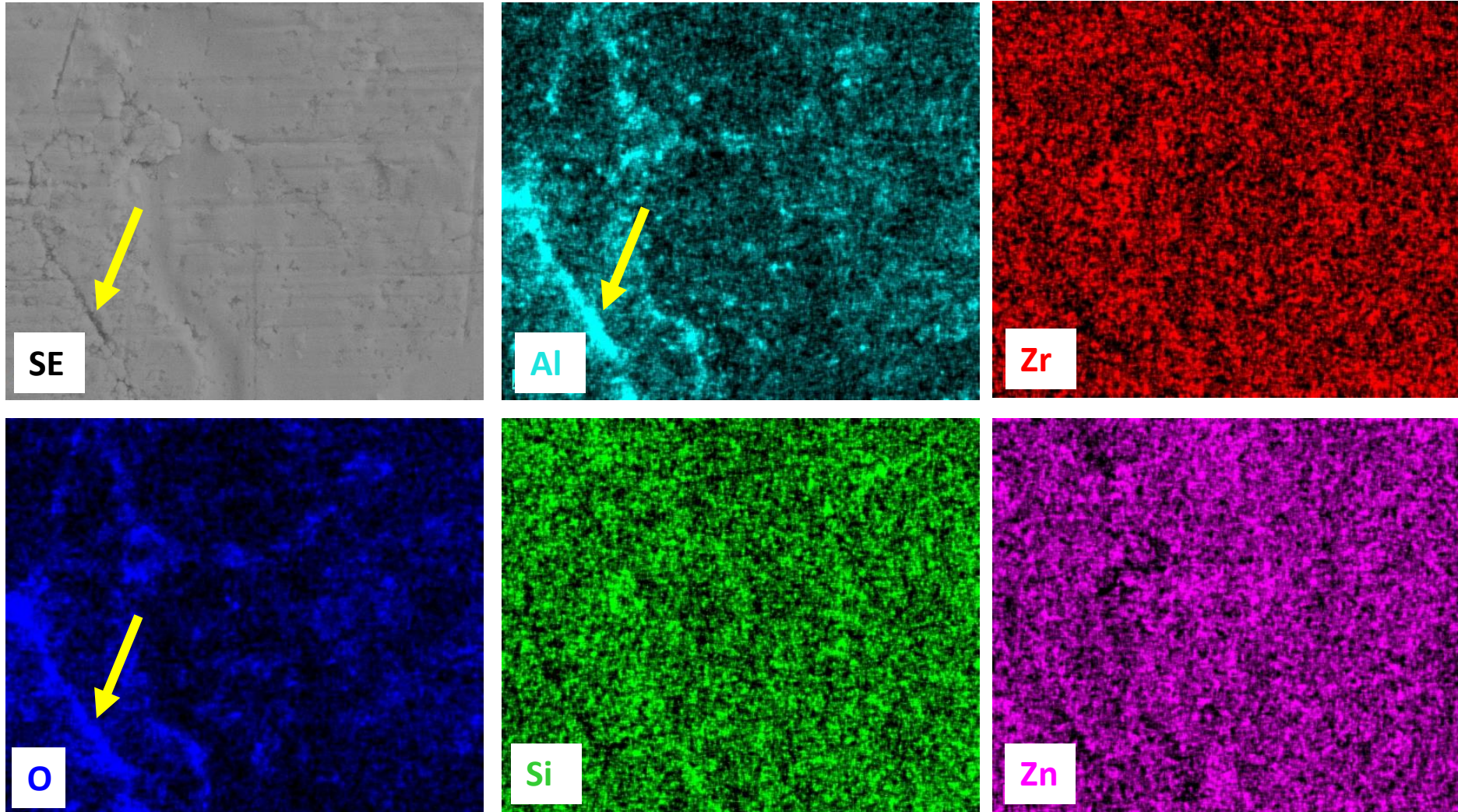
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Sample 119z – EDS map



More Al which oxidized, from the substrate.

ATTACHMENT 2

SEM and EDS investigation on sample **119z concentrato**

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PoC coordinator: **Federica Rigoni**

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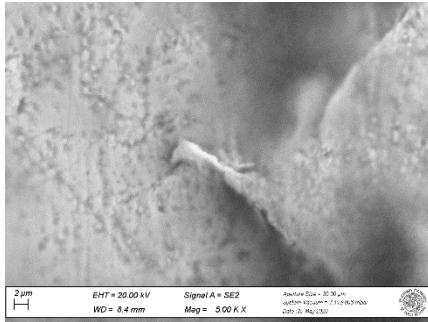
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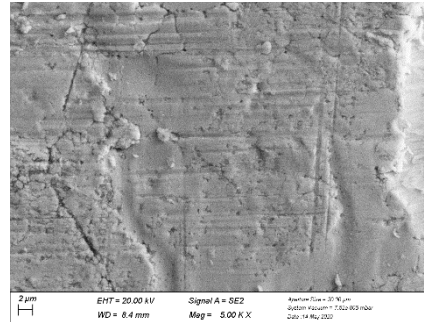
Sample 119z concentrato - SEM images

119z concentrato

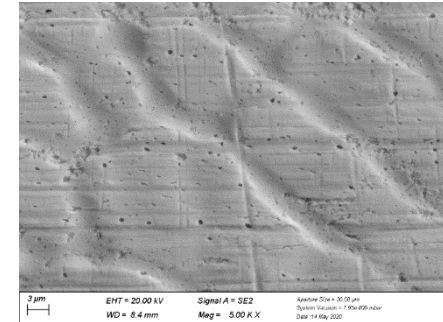
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EHT = 20 KV



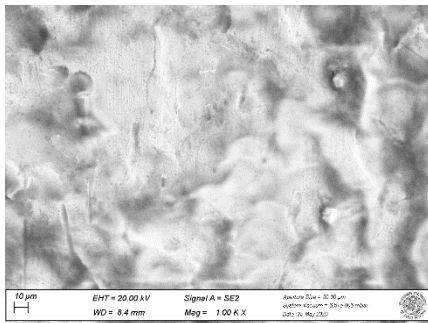
119z



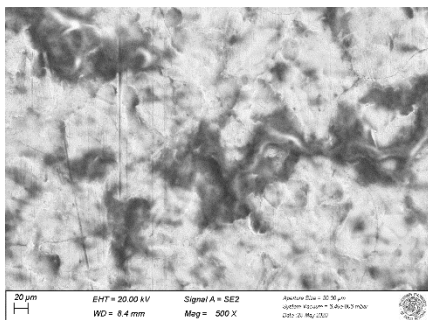
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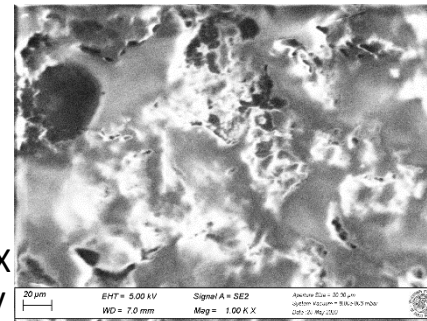
Mag = 1K X
EHT = 20 KV



Mag = 500 X
EHT = 20 KV



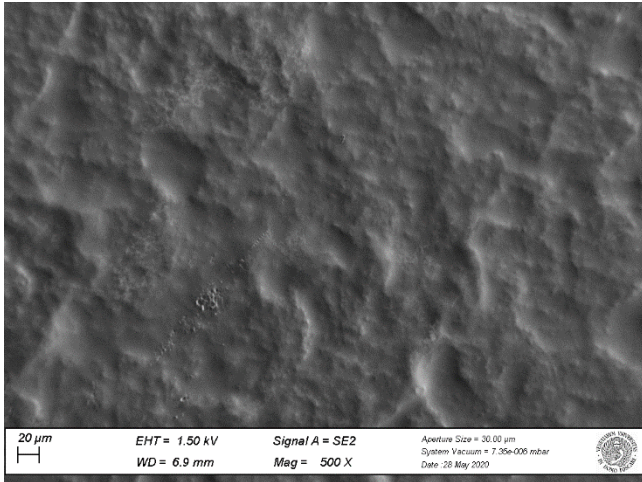
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EHT = 5 KV



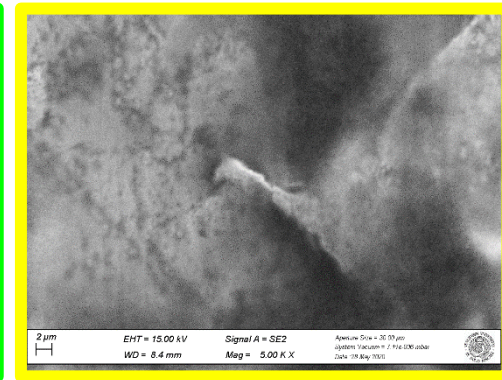
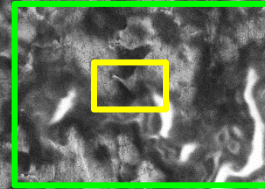
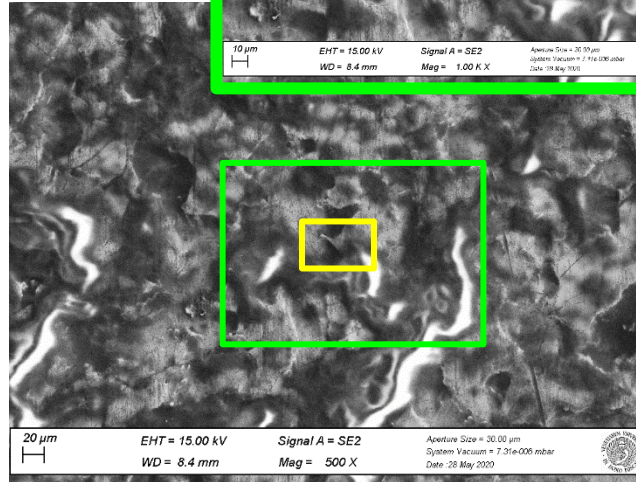
Charging effects at low EHT... probably because at higher voltage the charge can reach the metallic substrate...

PoC#2

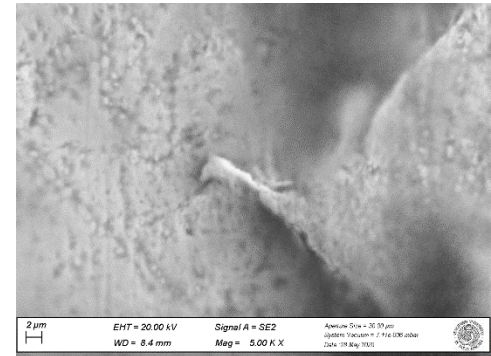
EHT = 1.5 KV



EHT = 15 KV



EHT = 20 KV



See EDX of this region
(Mag 1k X)
Last slide of this
attachment.

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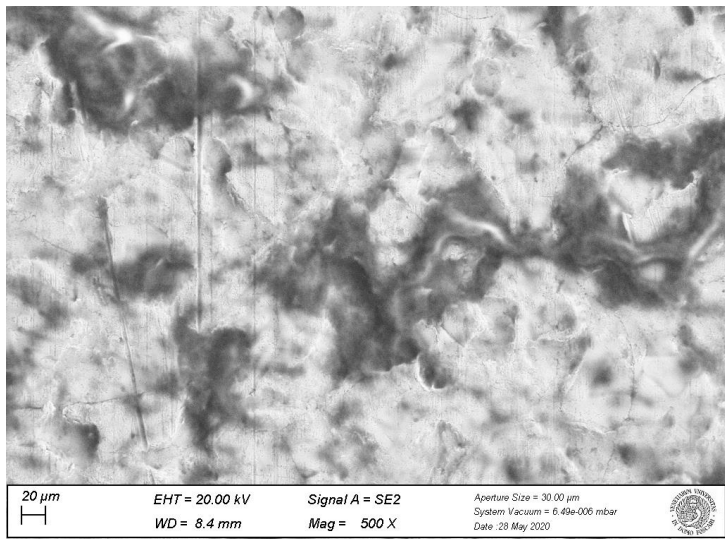
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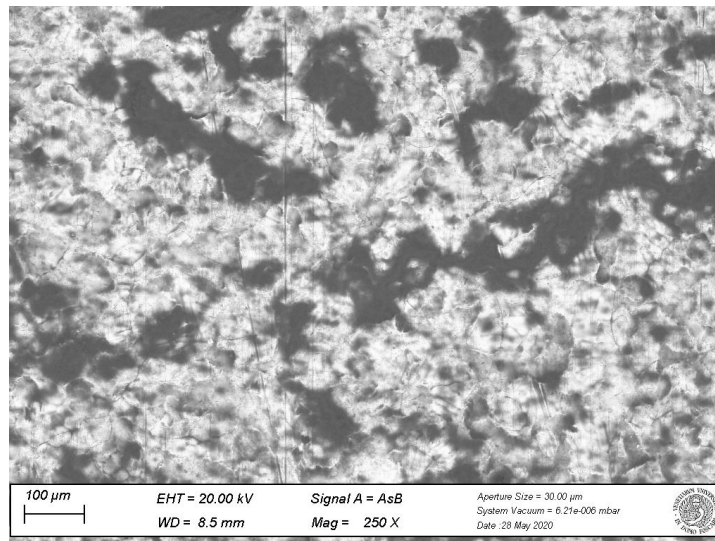
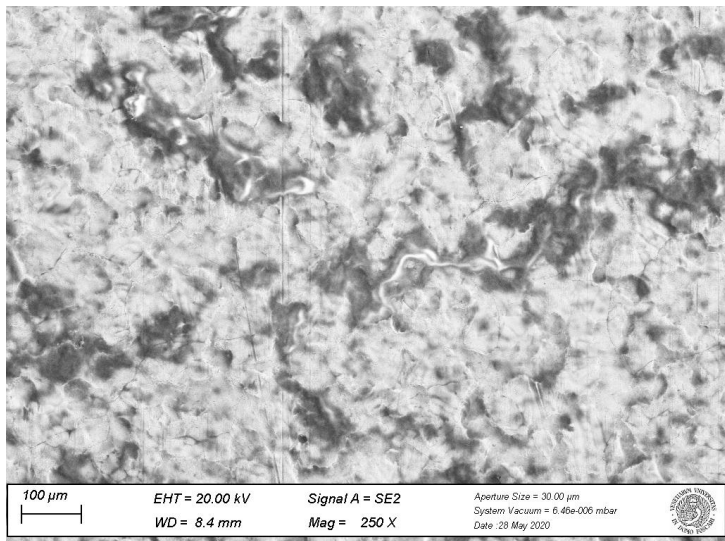
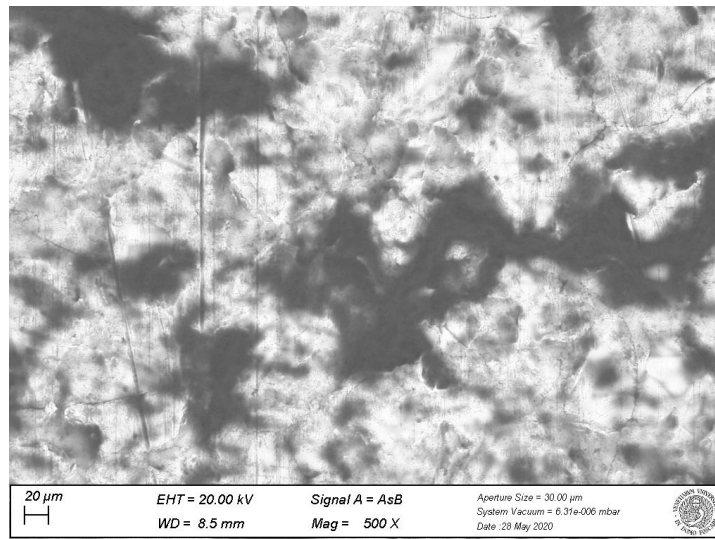
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Detector: SE

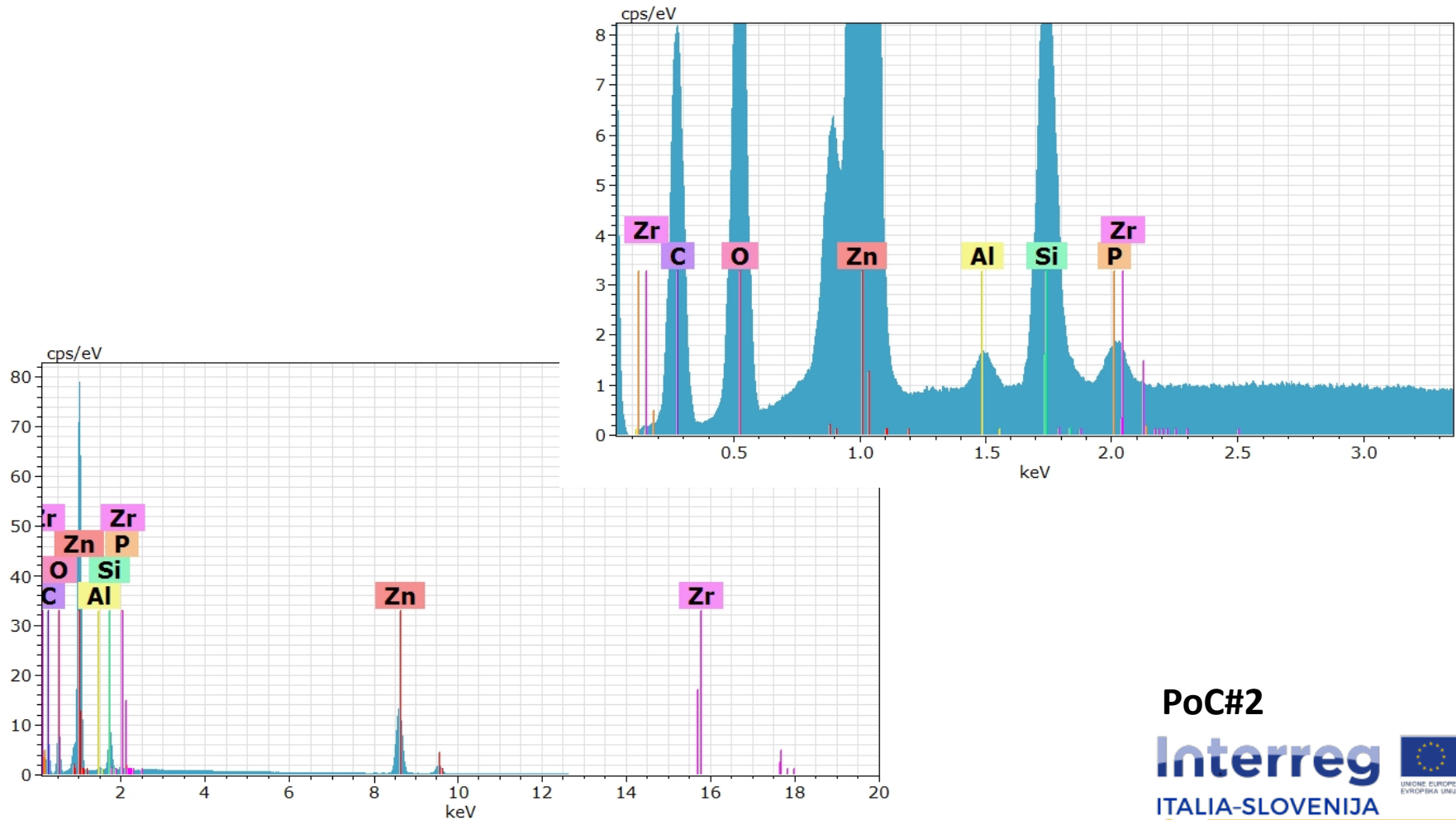


Detector: BSE



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Sample 119z concentrato - EDS analysis



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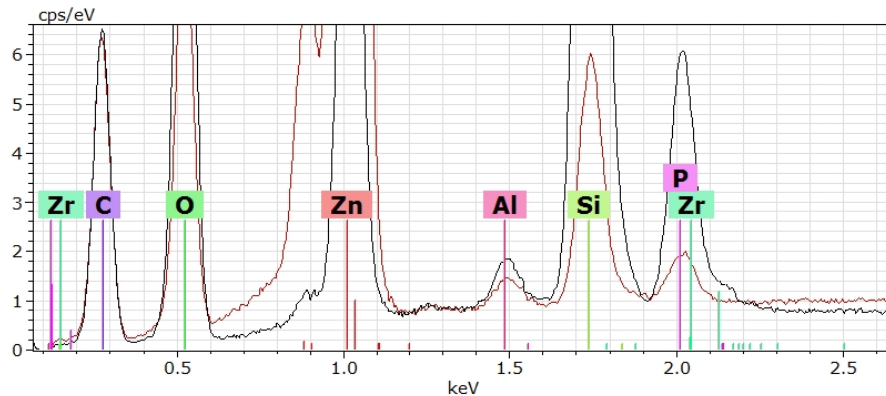
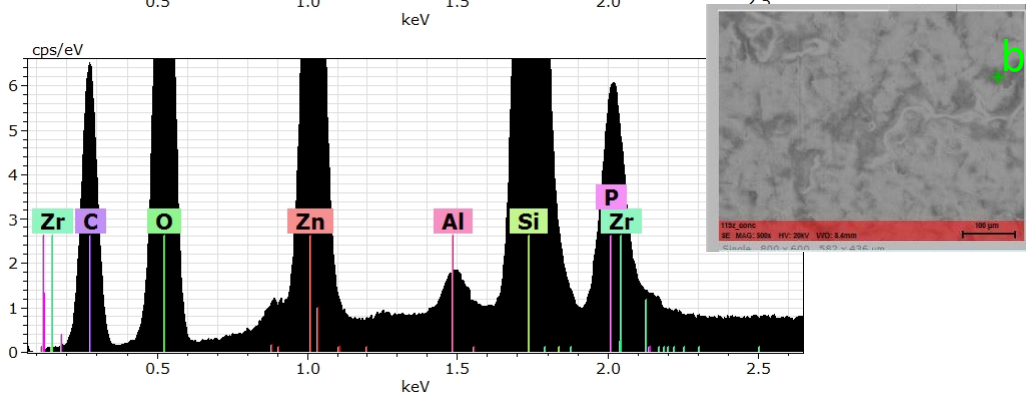
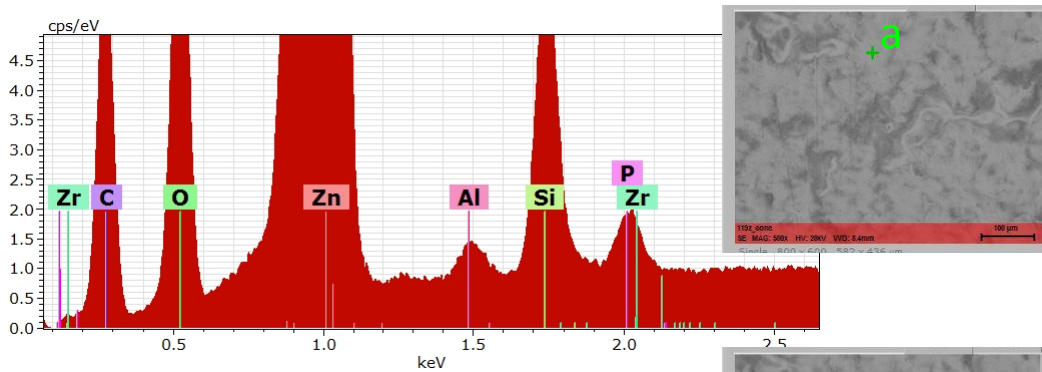
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Sample 119z concentrato - EDS analysis



Comparison between bright region (a) and dark region (b). More Zr detected from the dark region.

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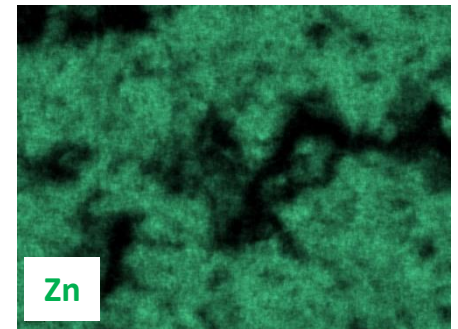
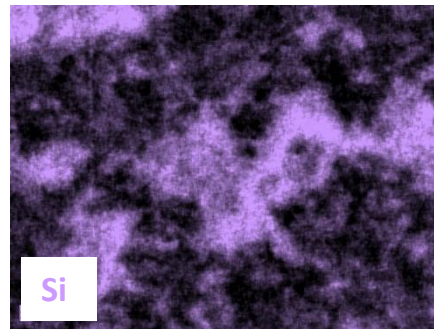
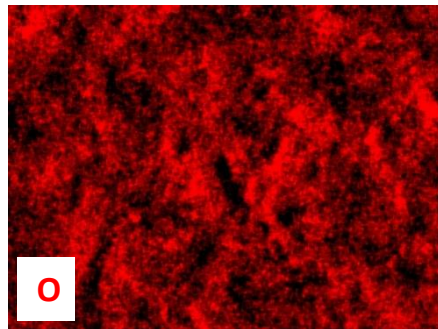
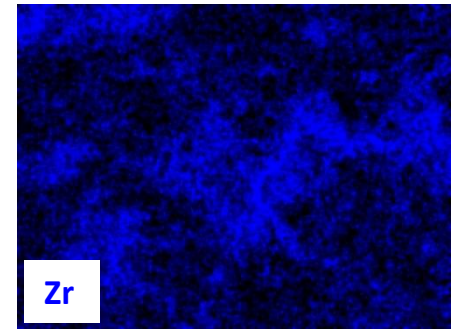
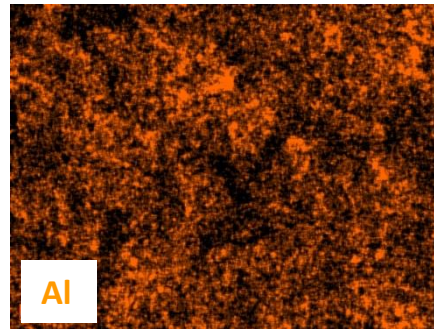
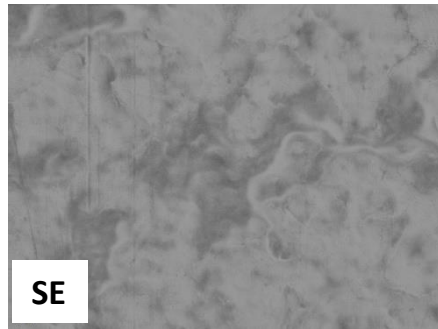
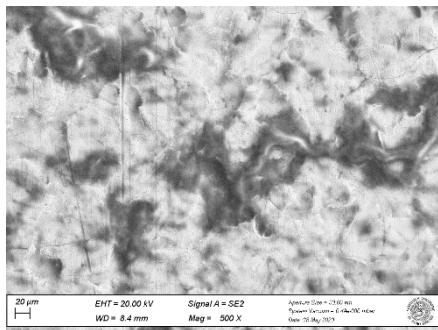


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Sample 119z concentrato - EDS map

Mag = 500 X
EHT = 20 KV



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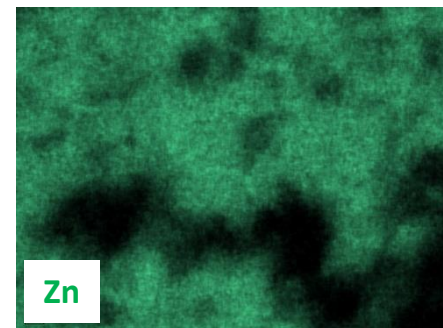
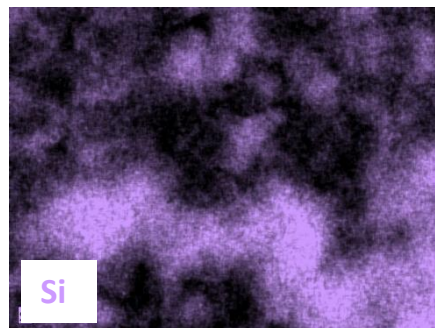
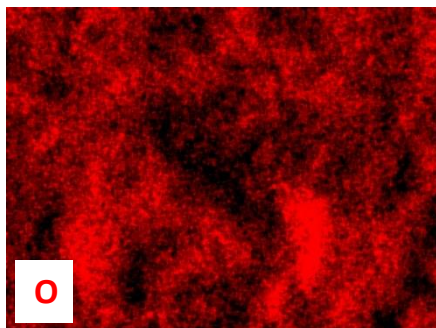
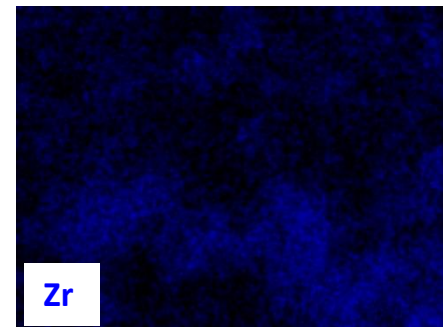
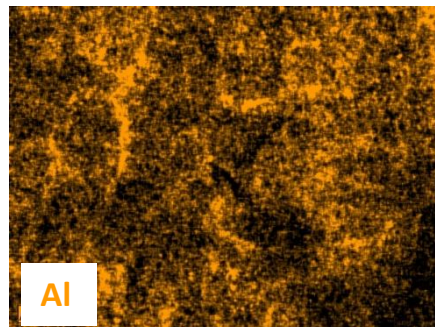
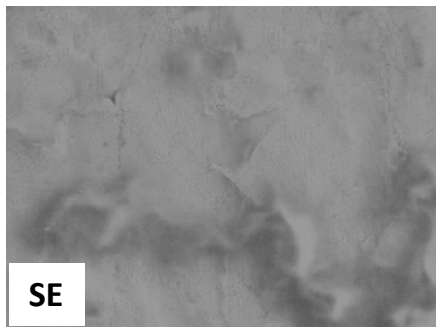
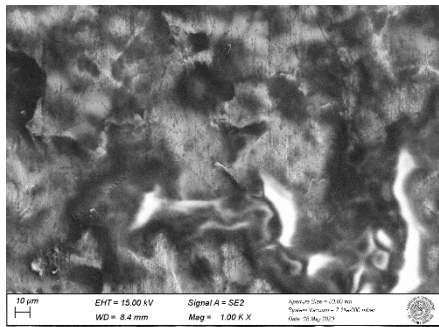
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Sample 119z concentrato - EDS map

Mag = 1k X
EHT = 15 KV

EHT = 20 KV



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ATTACHMENT 3

SEM and EDS investigation on tilted sample 119z concentrato

Nanoregion project **PoC#2**

PoC coordinator: **Federica Rigoni**

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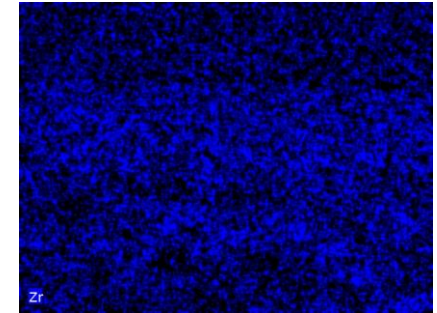
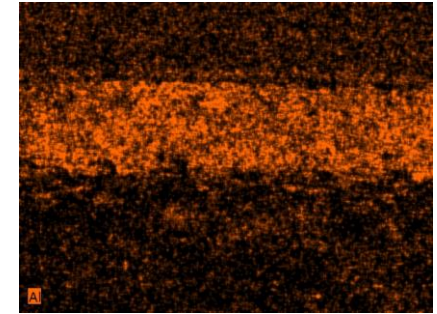
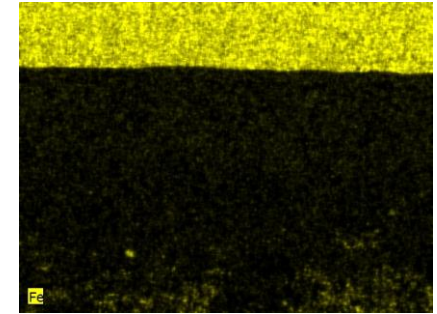
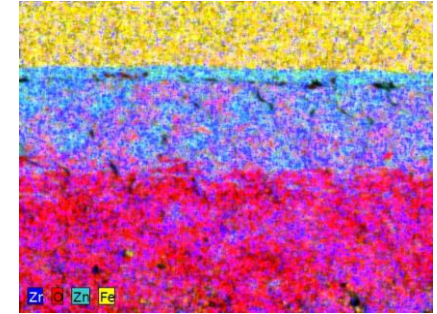
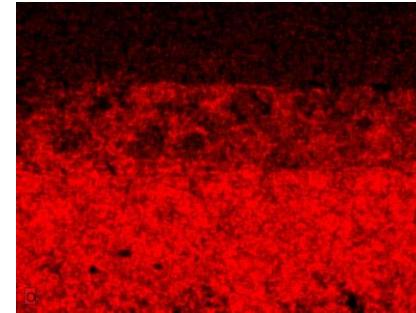
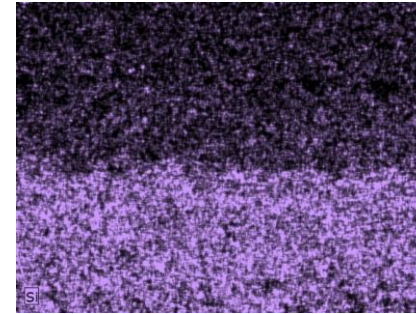
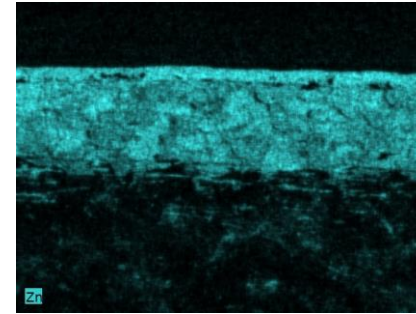
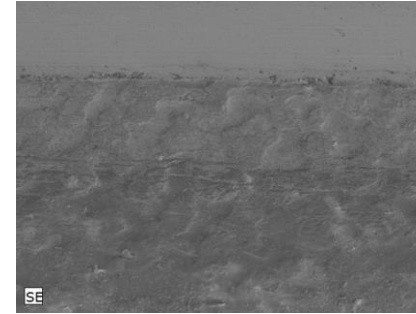
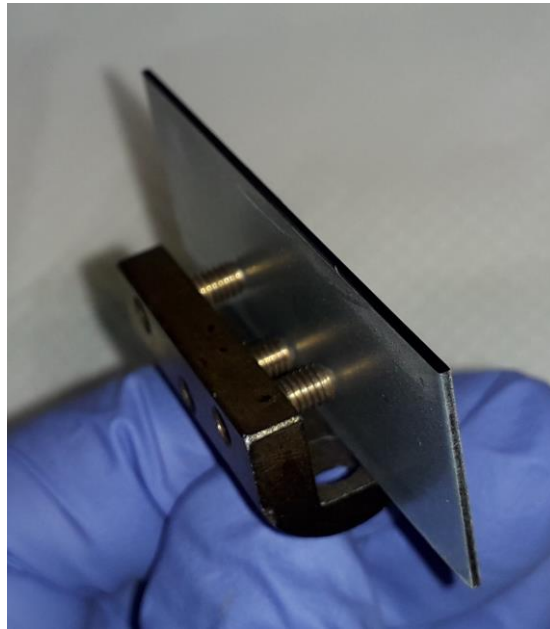
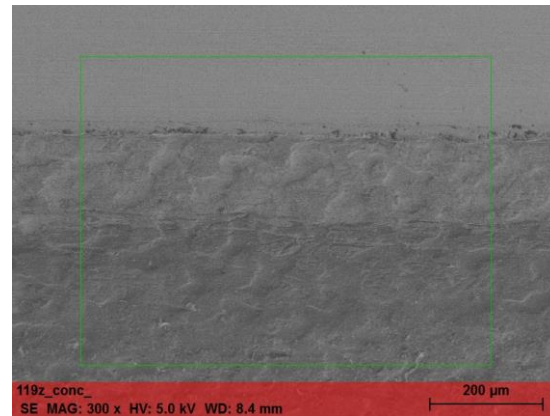
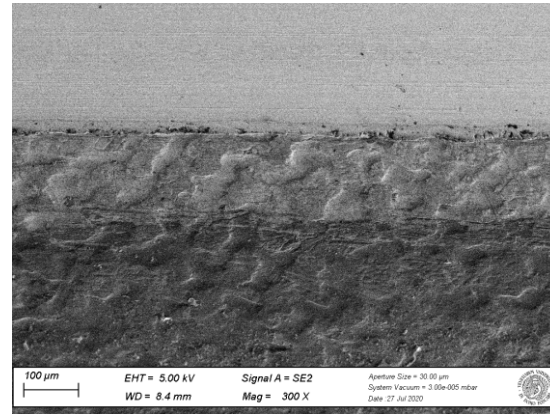
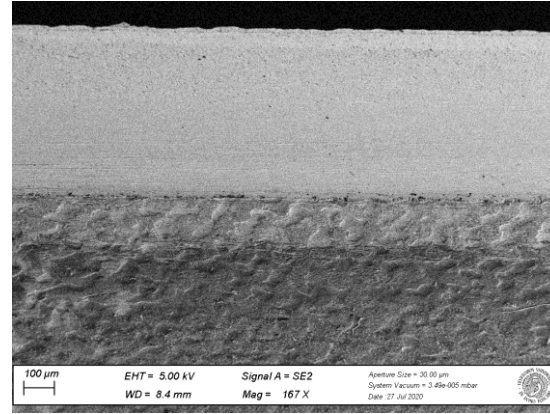
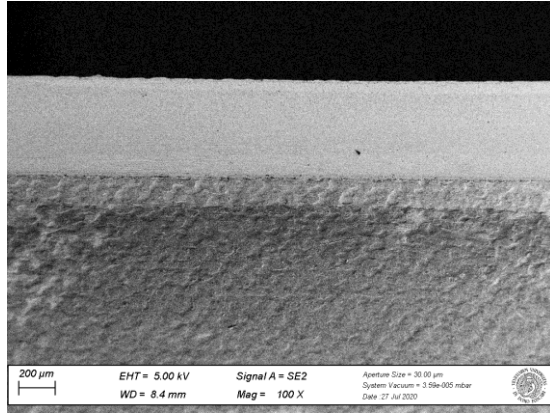
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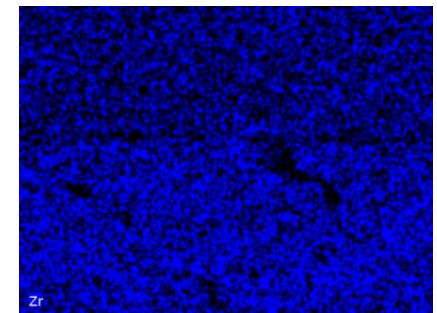
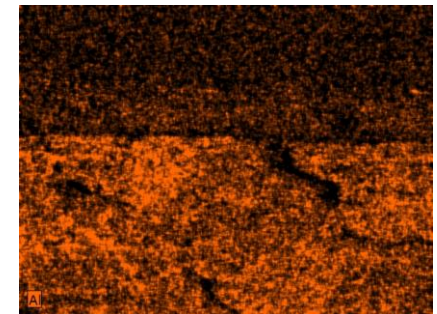
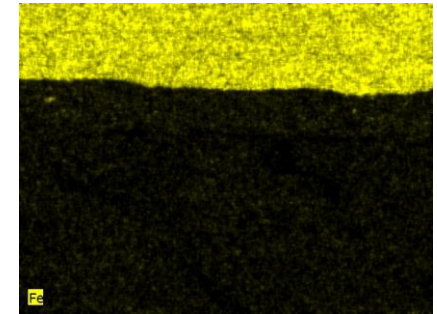
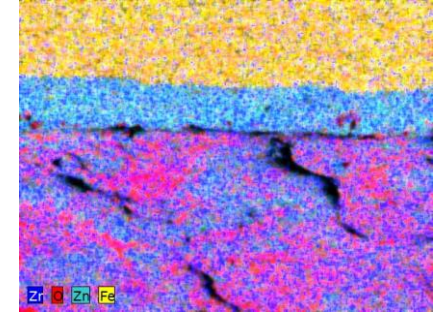
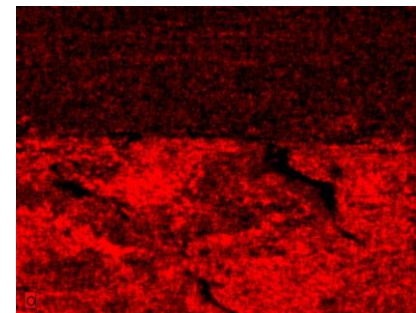
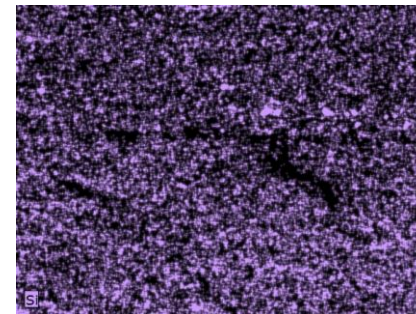
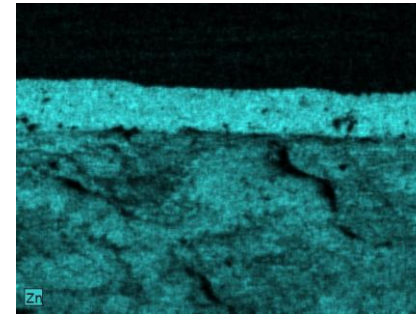
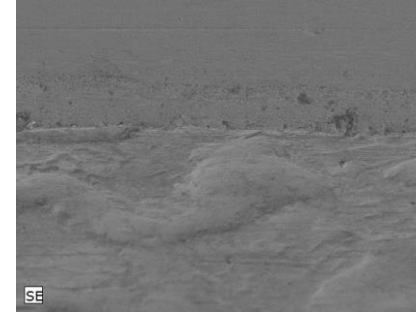
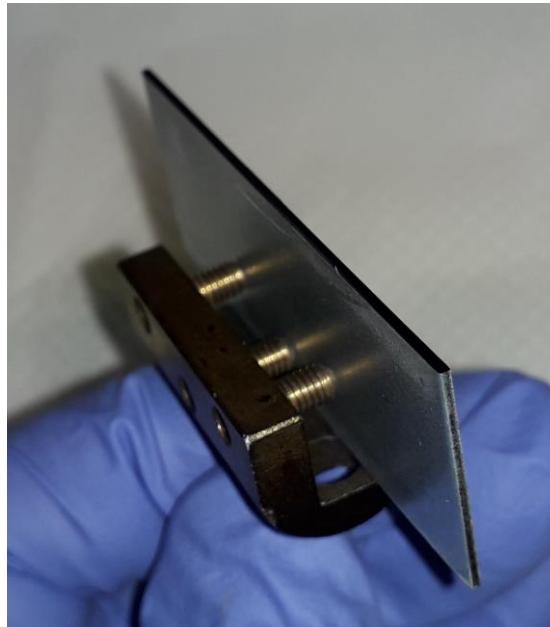
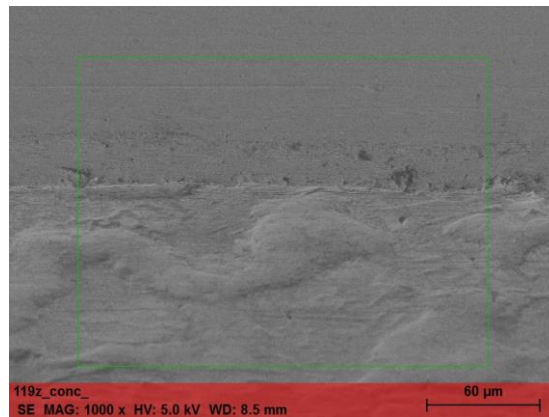
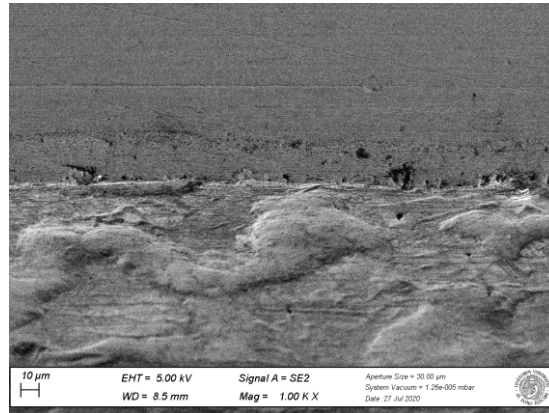
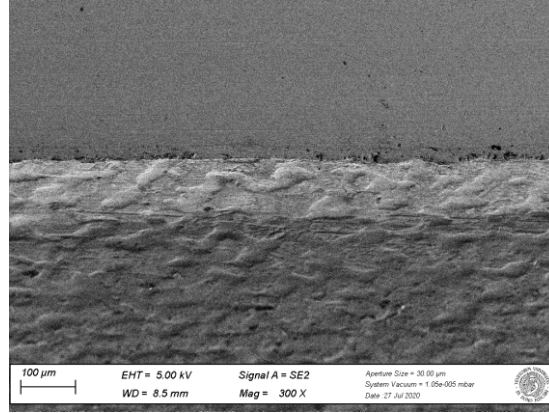
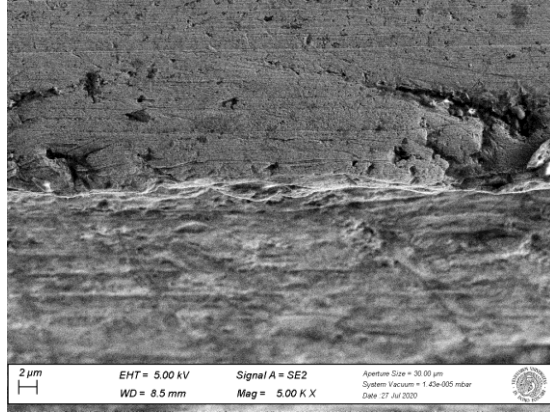
NANO-REGION

Progetto strategico co-finanziato dal Fondo europeo di sviluppo regionale
Strateški projekt sofinanciran Evropski sklad za regionalni razvoj

Tilt 45°



Tilt 30°



ATTACHMENT 4

SEM and EDS investigation on samples **PO** and **PN**

Nanoregion project **PoC#2**

PoC coordinator: **Federica Rigoni**

Interreg



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EVROPSKA UNIJA

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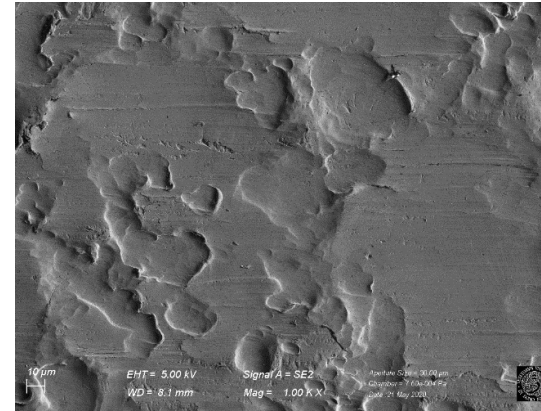
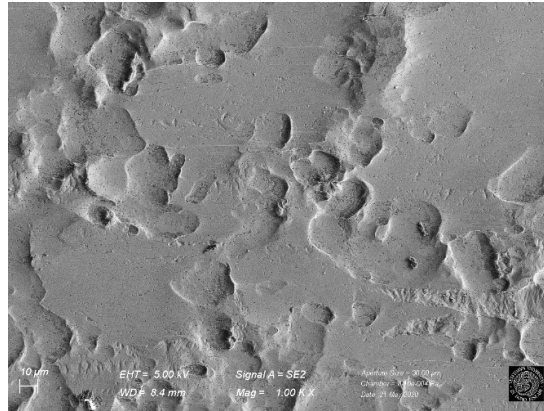
NANO-REGION

Progetto strategico co-finanziato dal Fondo europeo di sviluppo regionale
Strateški projekt sofinanciran Evropski sklad za regionalni razvoj

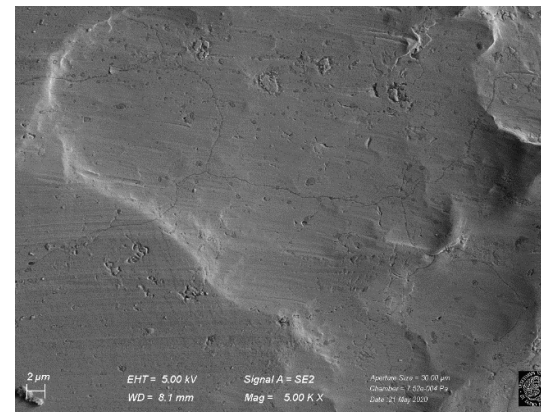
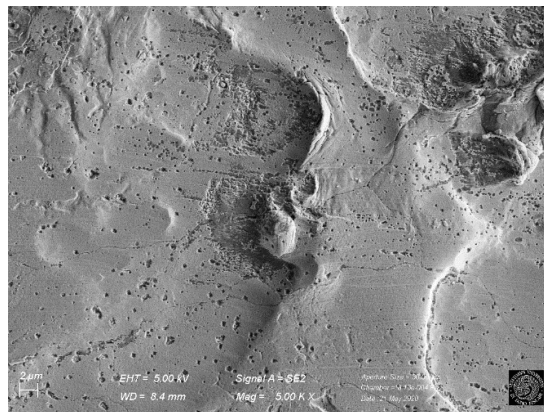
Sample PO - SEM images

Bianco

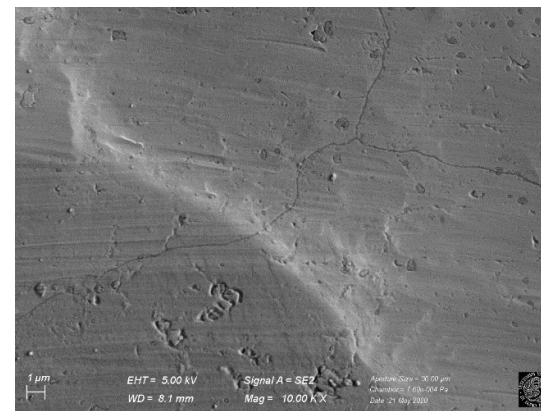
Mag = 1K X



Mag = 5k X



Mag = 10k X



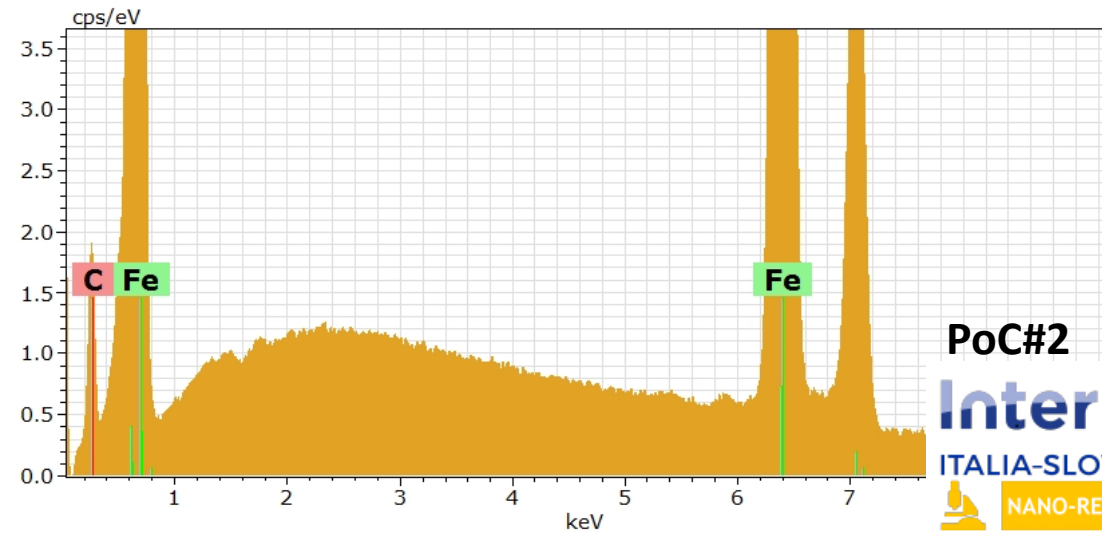
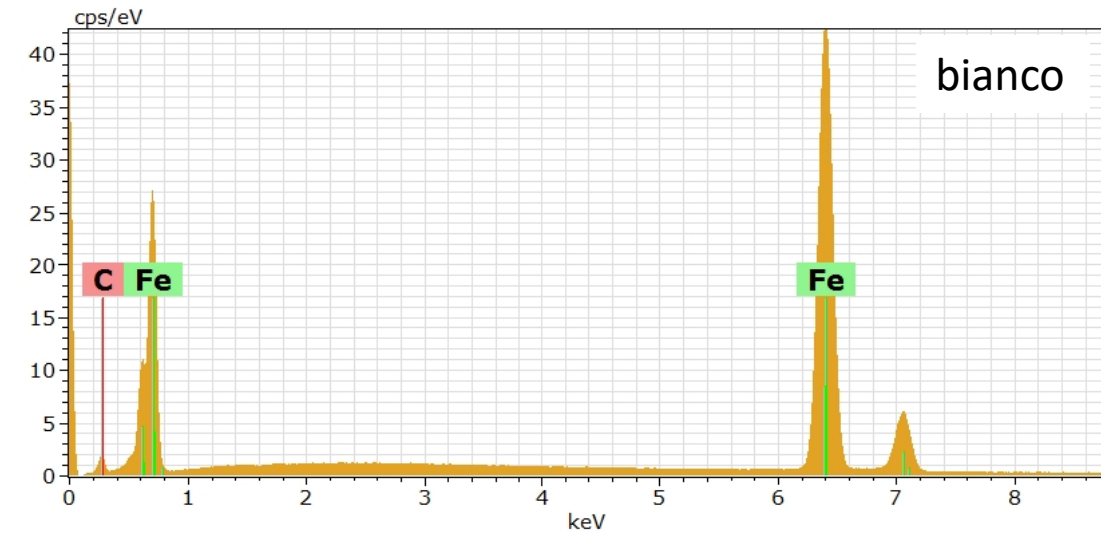
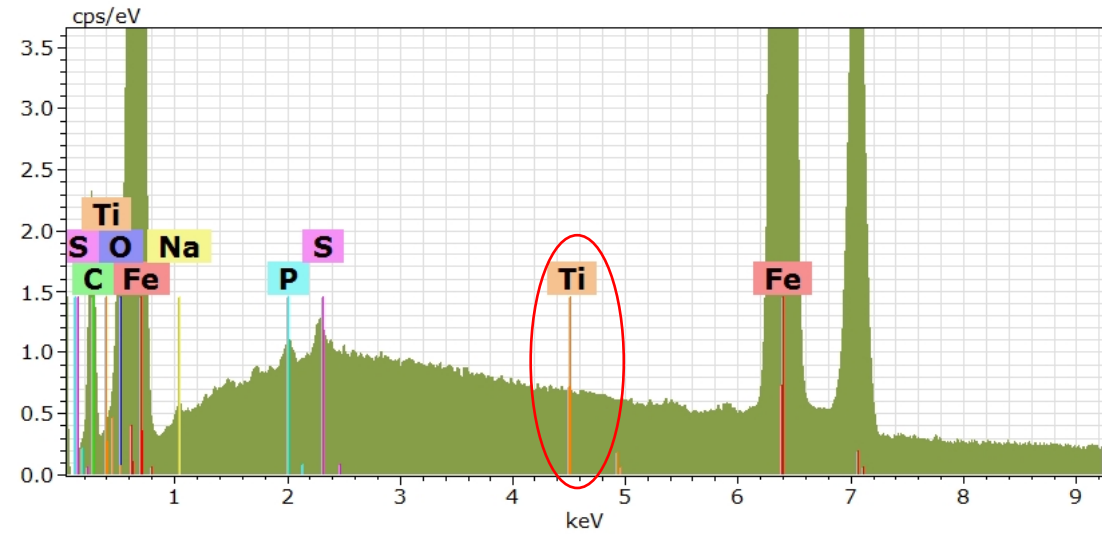
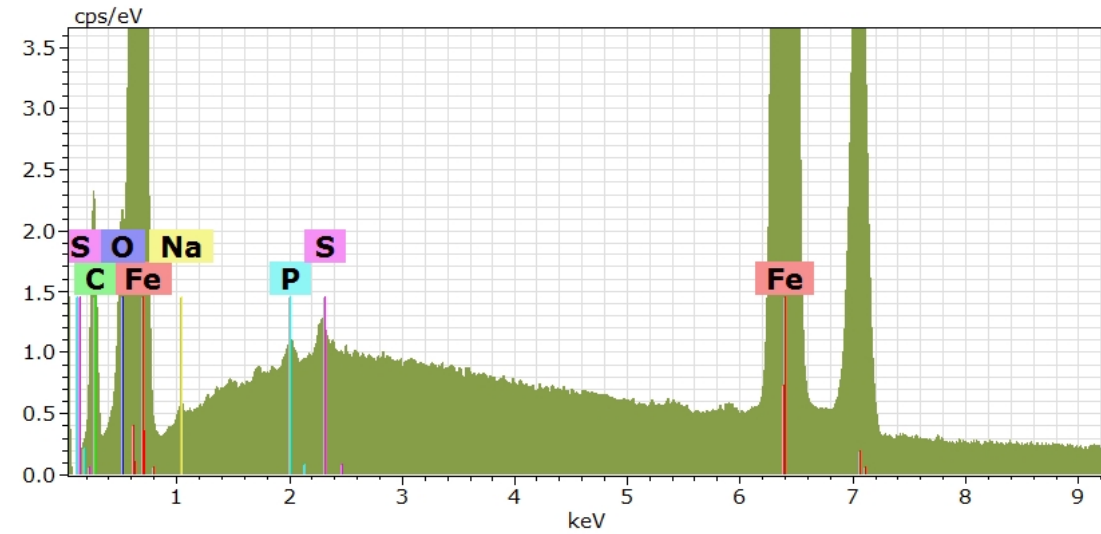
PoC#2



Progetto strategico co-finanziato dal Fondo europeo di sviluppo regionale
Strategici progetti cofinanziati Europei (fondi per lo sviluppo)

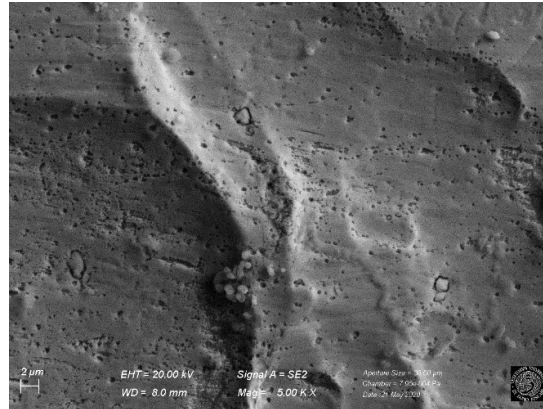
Sample PO – EDS analysis

NO Ti DETECTED

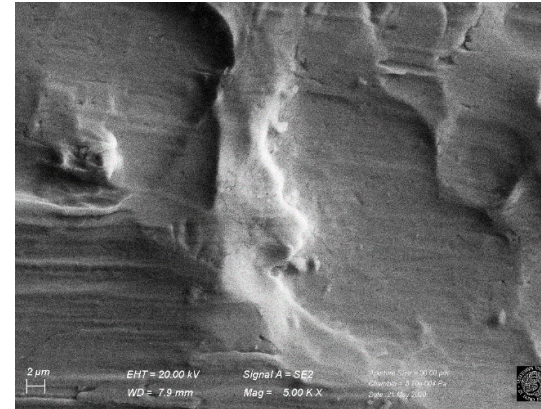


Sample PN - SEM images

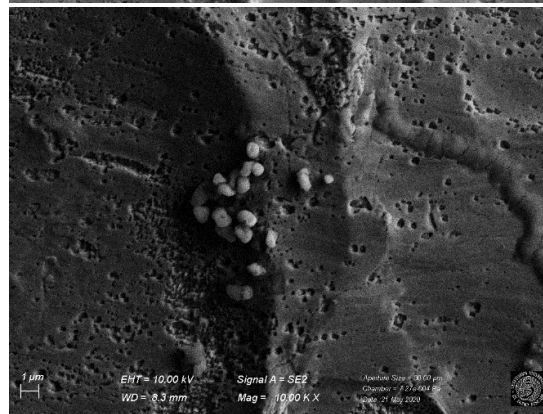
Mag = 5K X



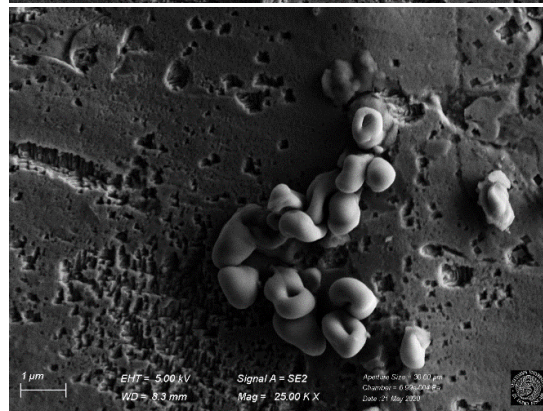
Bianco



Mag = 10k X



Mag = 25k X



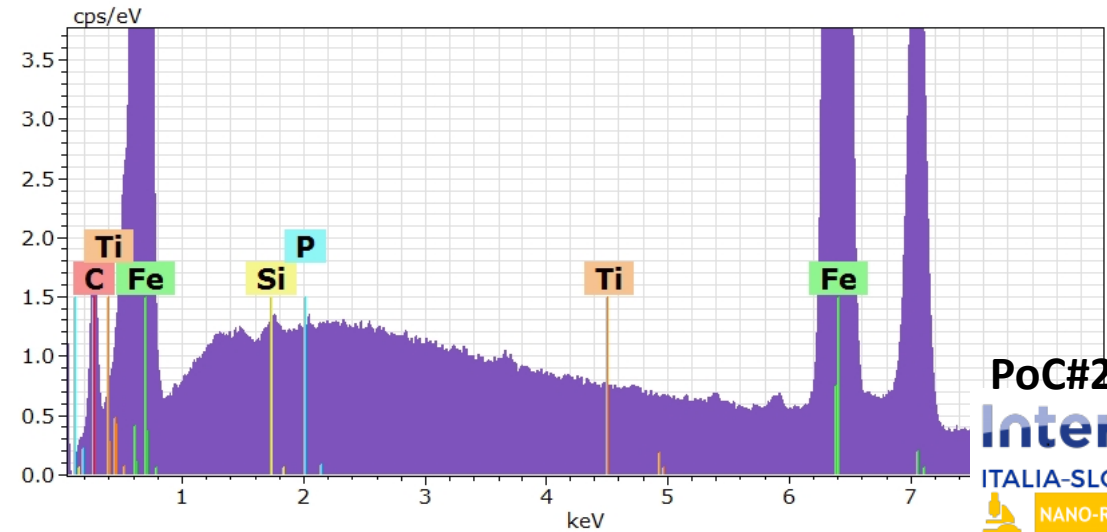
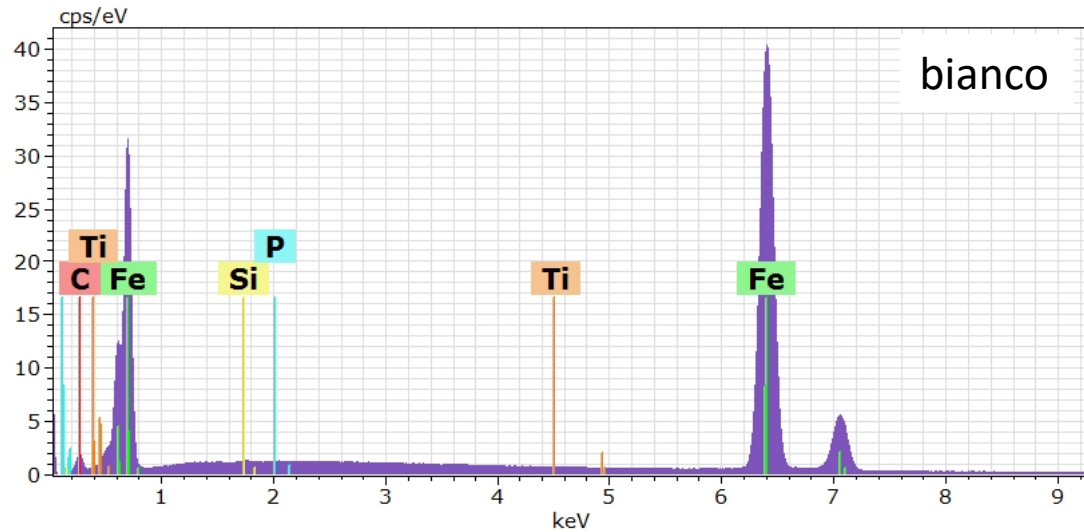
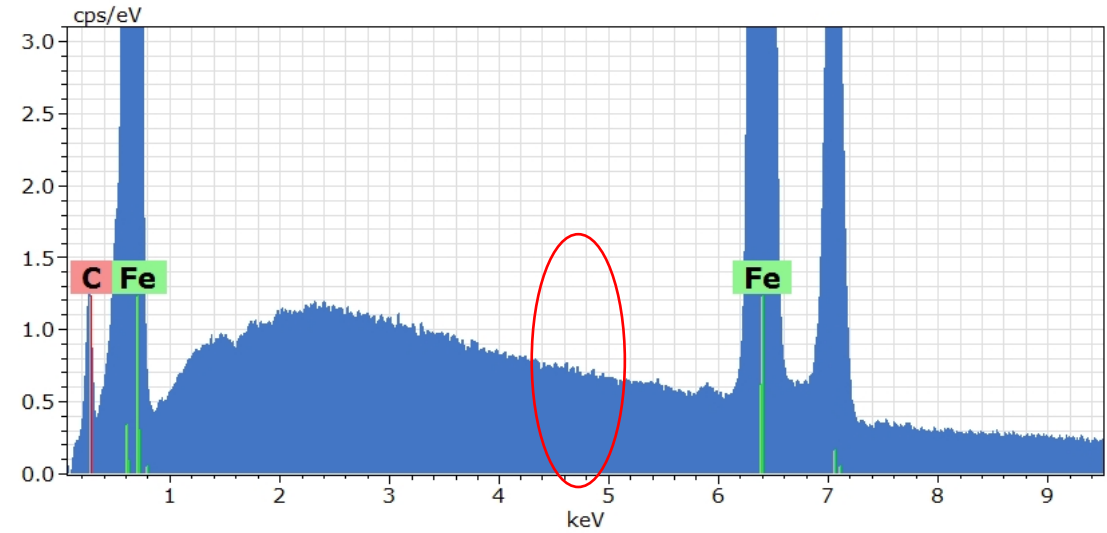
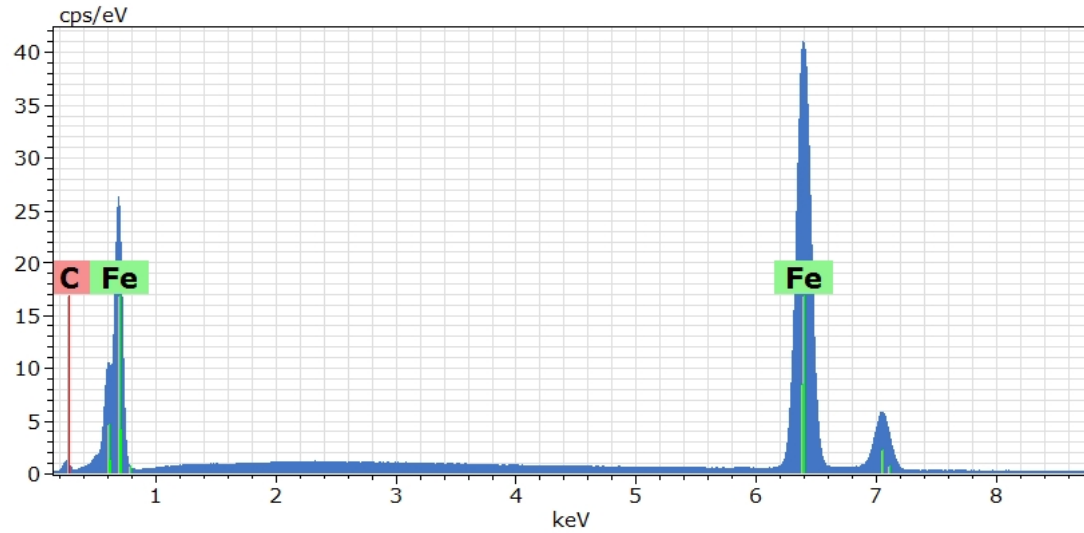
PoC#2



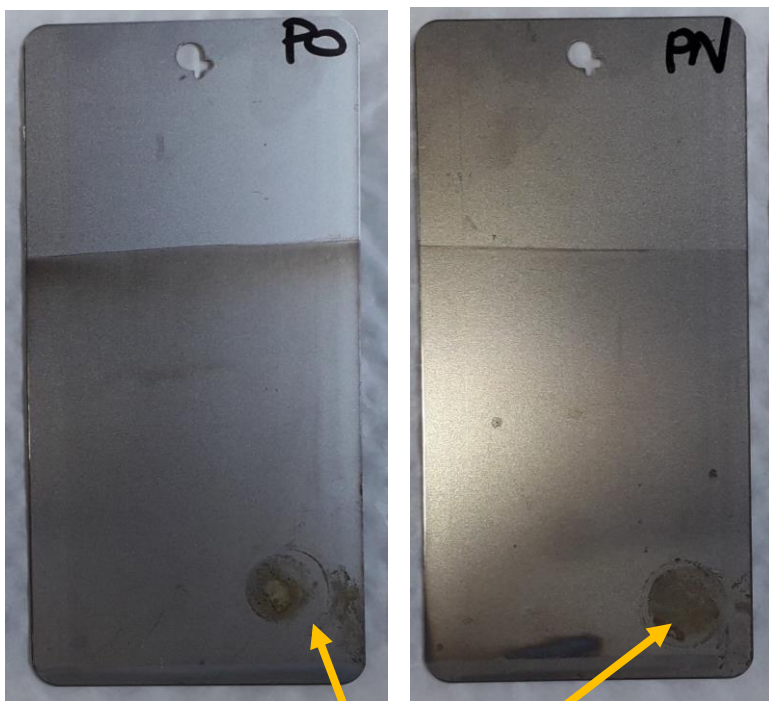
Progetto strategico co-finanziato dal Fondo europeo di sviluppo regionale
Strategici progetti cofinanziati Europei al servizio regionali e rivoli

Sample PN – EDS analysis

NO Ti DETECTED



March-April 2020



End of May 2020



End of July 2020



Forced oxidation

PoC#2

Interreg



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Progetto strategico co-finanziato dal Fondo europeo di sviluppo regionale
Strategični projekti sofinancirani Evropski sklad za regionalni razvoj