153rd MPP meeting

Oxidation behavior of graphite in air at high temperature

A. Perillo-Marcone, M. Calviani (EN-STI-TCD)

In collaboration with EN/MME

ENGINEERING DEPARTMENT

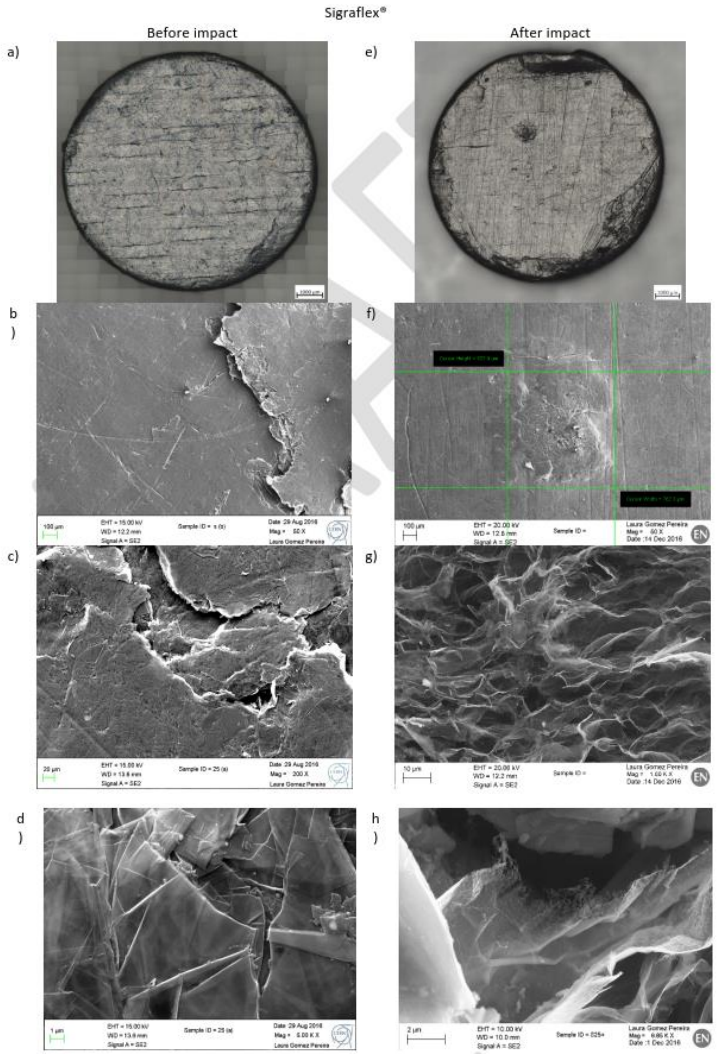
Oxidation of graphite at high temperature over milliseconds

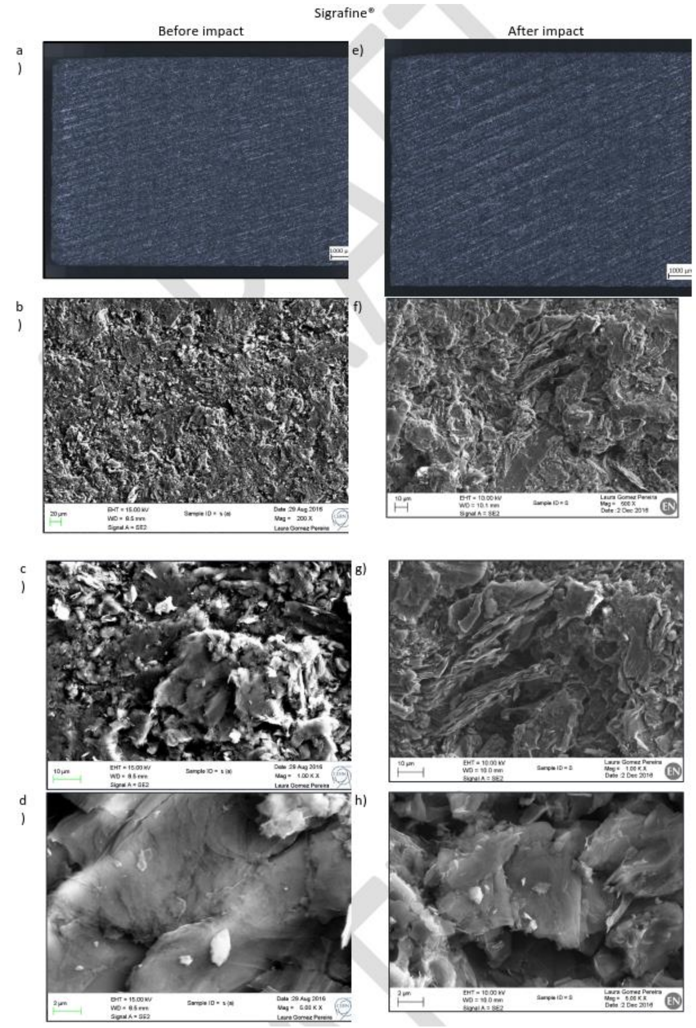
Performed at CERN by EN/MME

Methodology

- Impacting samples with laser beam in air
- Temperature reached ~900-1300 °C
- Exposition time ~10 ms
- Materials
  - Sigrafine (high density graphite in TDE)
  - Sigraflex (low density graphite in TDE)
- Examine changes in:
  - Microstructure
  - Chemical composition
  - Phase

Results


Sigraflex®
Before impact
After impact
a)
b)
c)
d)
e)
f)
g)
h)


Sigrafine®
Before impact
After impact
a)
b)
c)
d)
e)
f)
g)
h)

Laser Impact – Conclusions

- No clear indication of oxidation
- Observed damage generated by thermo-mechanical stresses (not representative of stresses from proton beams)
- Highly pessimistic conditions in comparison to TDE:
  - Exposition times ~10ms (instead of us for TDE)
  - Atmosphere 100% air

Oxidation in air furnace

Performed at CERN by EN/MME

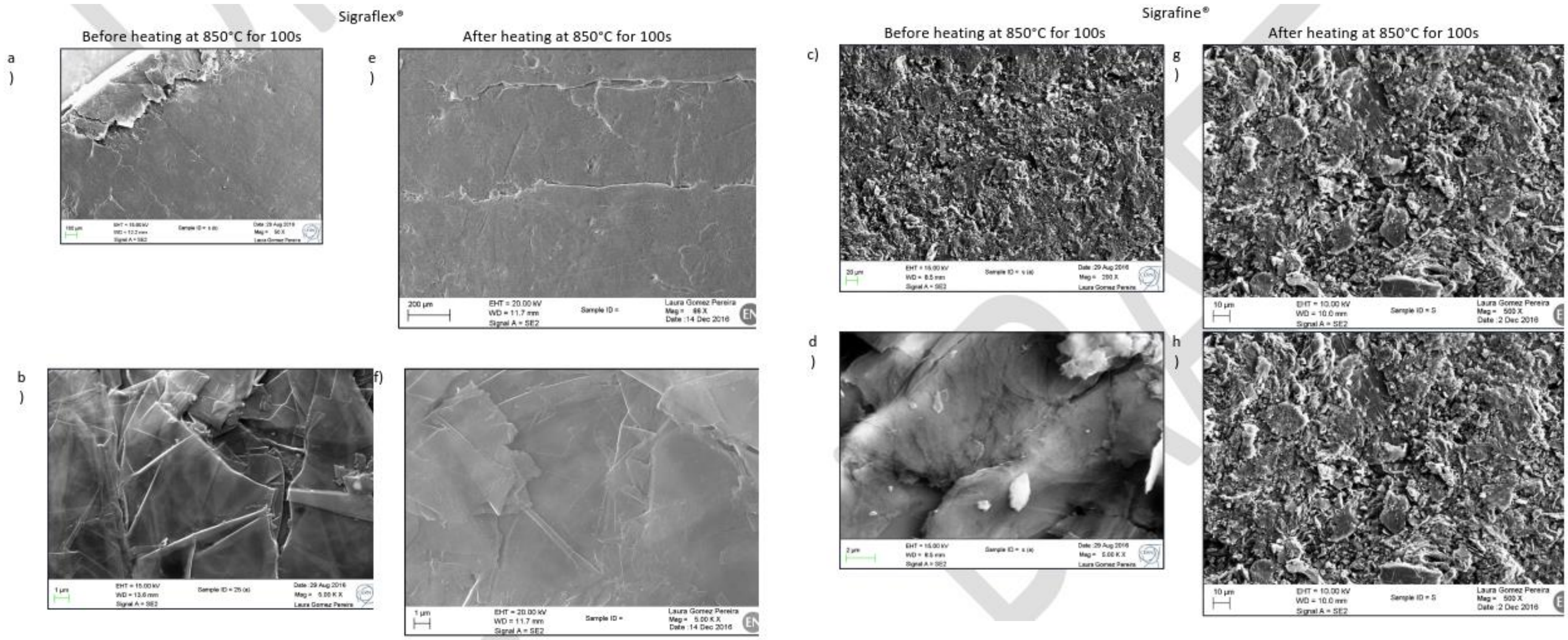
Scope

- Remove thermomechanical stresses
- Overly conservative exposition time
- Exposition to 100% air atmosphere

Methodology

- Preheating air furnace to >1100 °C
- Insertion of samples in furnace (temperature drop to ~850 °C)
- Samples maintained in furnace during 100s
- Microscopy and chemical analysis of samples

Results



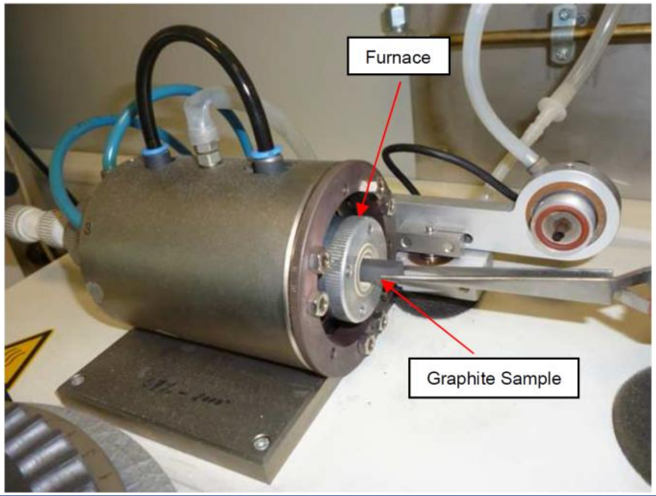
- No apparent change in microstructure
- Amount of O and Si keep constant before and after the study
- Material does not seem to be affected by oxidation
- **Further test in oven at 1100°C under way**

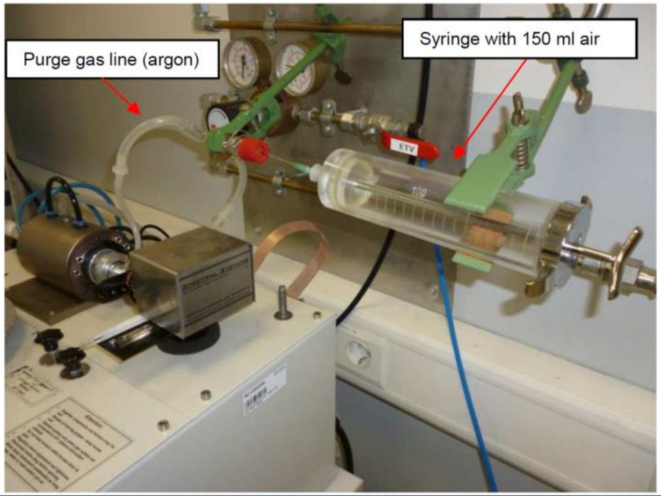
Oxidation at 2500 °C – 10s

Performed by SGL

Methodology

- Five samples of Sigrafine and Sigrafoil tested separately
- Heating up in argon to 2500 °C
- Injection of air in furnace
- Exposition time ~10s





Tested samples

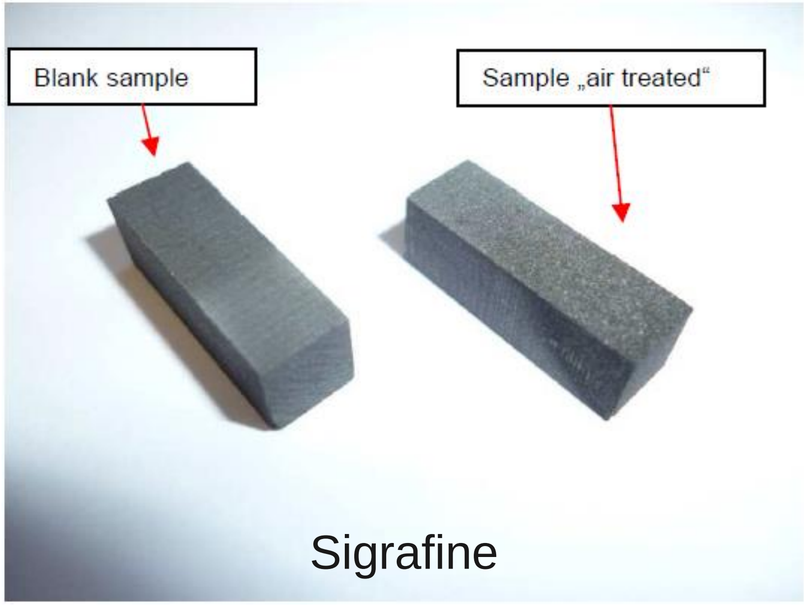
Sigraflex

Sigrafine

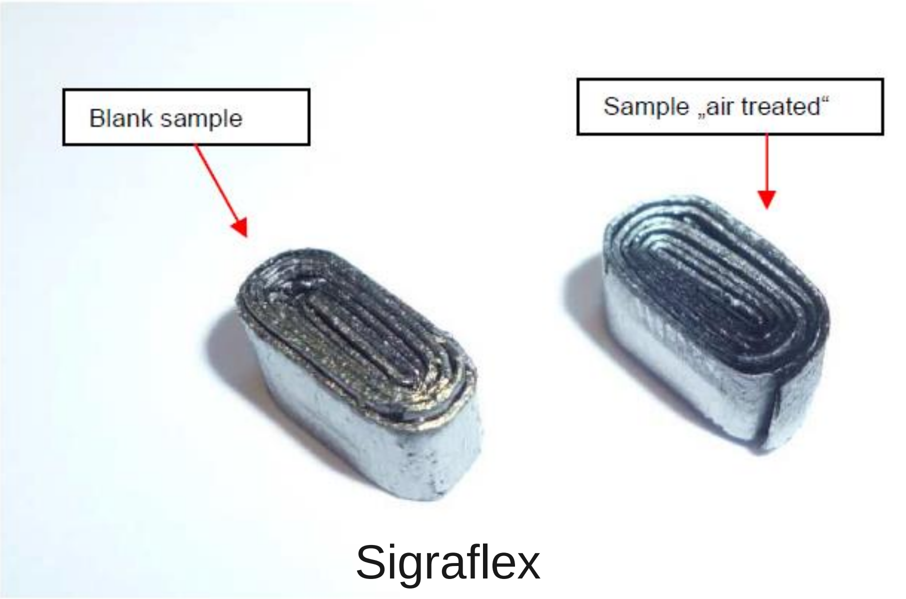
Results

After exposition to air at 2500 °C in air during 10s, there is a mass loss of:

- 0.66% in Sigrafine
- 0.99% in Sigraflex



Sigrafine



Sigraflex

Conclusions

- Attack limited to surface
  - Thermal energy too high for O_2 to penetrate/diffuse in the bulk
- Findings in line with previous studies found in literature, limited to 1500 °C
- Low temperature oxidation not located on surface → voids would appear in the bulk (longer times required for this)

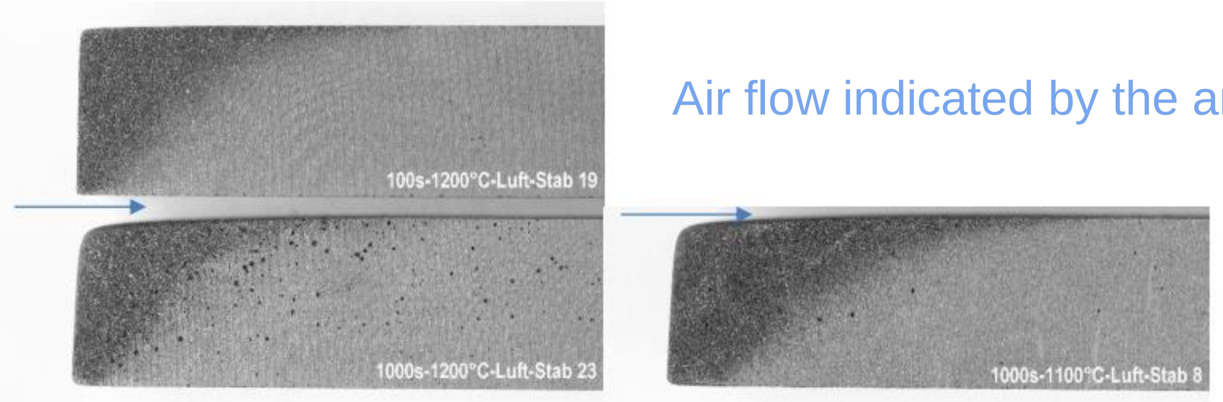
Oxidation at 1200 °C – 100s, 1000s

Performed by SGL

Methodology

- Only samples of Sigrafine investigated so far
- Furnace heated up to 1200 °C, in argon atmosphere
- Switch to air during 100/1000 s
- Switch back to argon
- Cool-down in argon
- Micro scale to measure weight
- Physical and mechanical properties measured before/after test

Results



Air flow indicated by the arrows

- Strong reaction observed after the air meets the graphite surface
- In all three cases, a pattern of the air flow around the sample observed
- After 1000s, holes observed on the surface
- Mass loss remains limited: ~1% for 100s, ~4% for 1000s
- No changes in density, electrical resistivity or dynamic modulus

General conclusions

- As well known, graphite is sensitive to oxidation at high temperature
- Oxidation highly dependent on temperature and exposition time
- At significantly high T (>1500°C) oxidation limited to surface, for exposition times of 10s
- Greater mass loss observed for longer exposition times, but still attack limited to surface
- All tests several times more pessimistic that actual conditions in TDE
- These studies allow to **exclude the possibility of graphite igniting at high temperature in the presence of air** in the TDE scenarios
- Comprehensive report including all these studies being written. Expected to be released by **end of 2017/beginning 2018**

Back-up slides

Laser heating – CERN/EN-MME

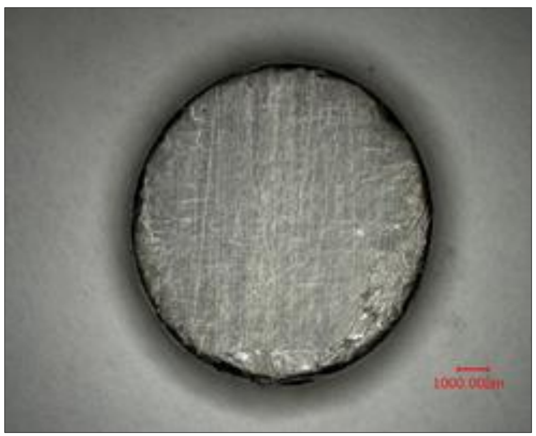
Samples

Sigraflex I (SI)

L20010

Anisotropic

Ø 10 mm x 2 mm

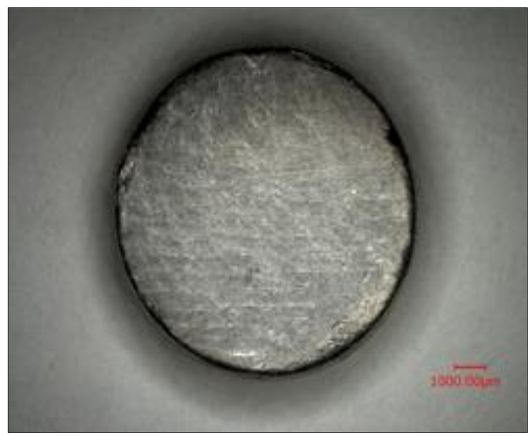


Sigraflex II (SII)

L25012

Anisotropic

Ø 10 mm x 2.5 mm

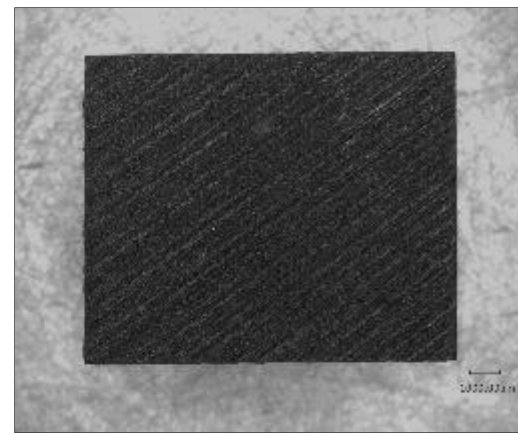


Sigrafine

R7300 P500

Isotropic

10 mm x 10 mm x 12 mm



Material supplied by SGL

Laser Parameters

Laser ≠ Proton Beam

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Less Energy density in order to minimize the thermomechanical stress on the sample

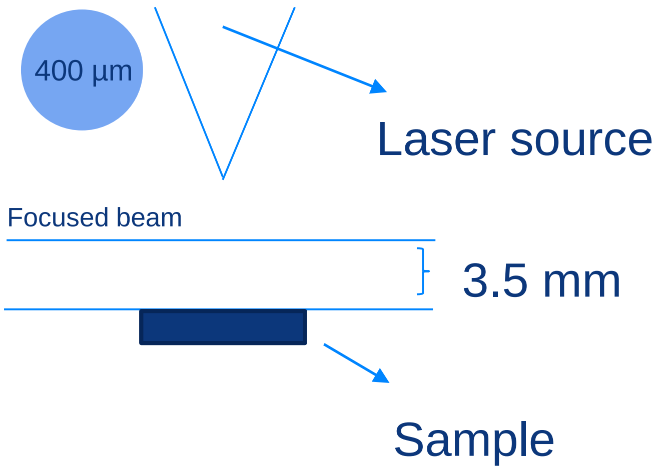
Best parameters after several trials…

Sigraflex

Energy	Frequency	Power	Wavelength	Height
1 J	1 Hz	1 W	1064 mm	Defocused beam Z – 3.5mm

Sigrafine

Energy	Frequency	Power	Wavelength	Height
4 J	1 Hz	4 W	1064 mm	Defocused beam Z – 3.5mm



Inspection procedure

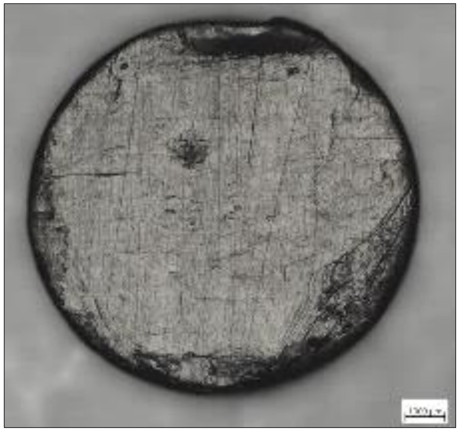
- **Microscopy observation (OM* and SEM*) → surface aspect**
  - Digital microscope KEYENCE VHX 1000
  - OM “ZEISS Axio Imager” with “ZenCore” software
  - SEM, field emission gun FEG Sigma (ZEISS)
- **Chemical Analysis → chemical composition**
  - 50 mm2 X Max Energy dispersive X-ray spectroscopy EDS detector (Oxford), INCA software
- **Phase Analysis → change in the crystalline phases after the laser impact**
  - X-ray diffraction (XRD), θ/2θ or grazing angle

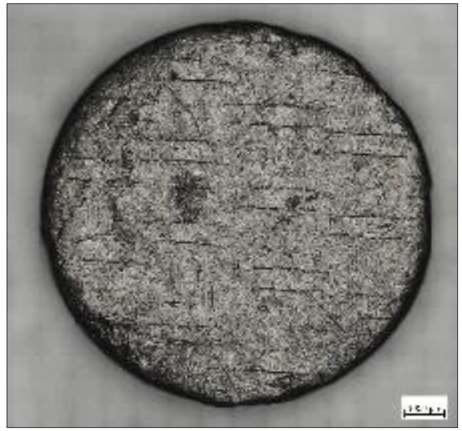
On sample as received and after impact

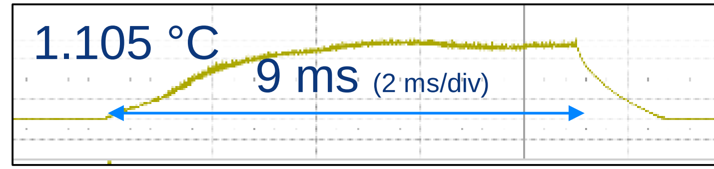
*__OM__: Optical Microscope
*__SEM__: Scanning Electron Microscope

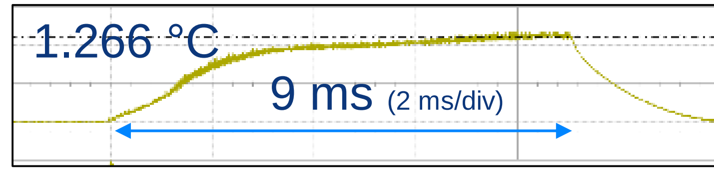
OM and SEM – Sigraflex

LVD*

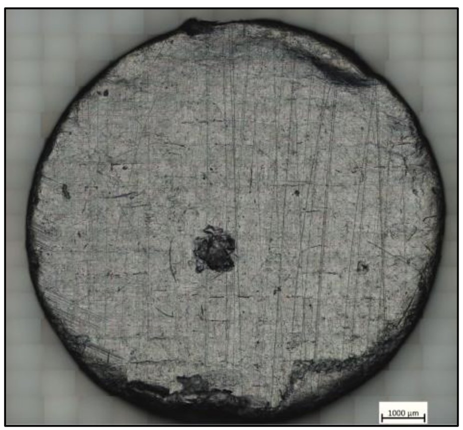


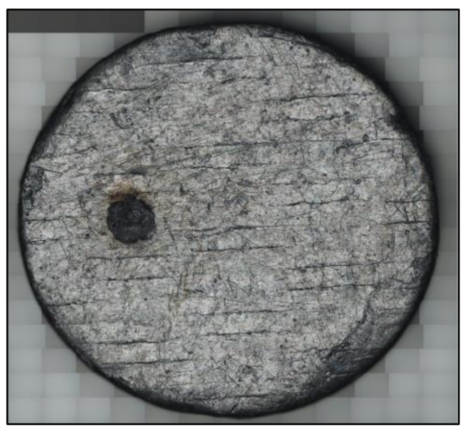


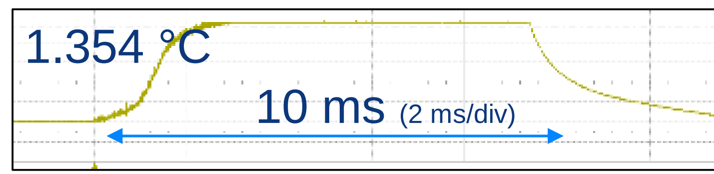


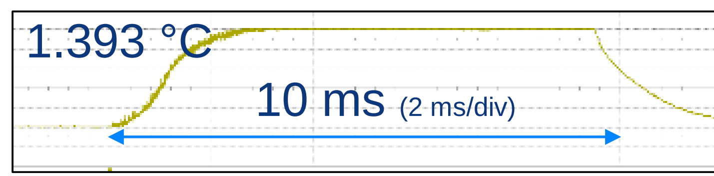


MVD*





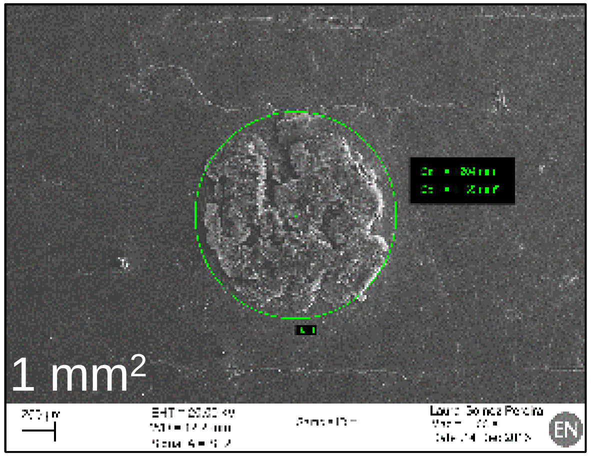


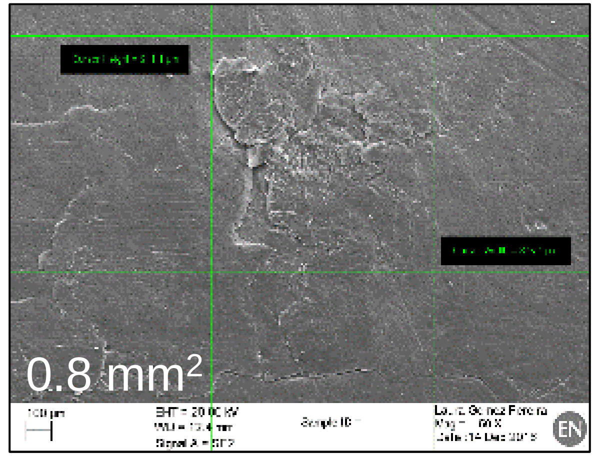


LVD = Least Visual damage
MVD = Most Visual damage

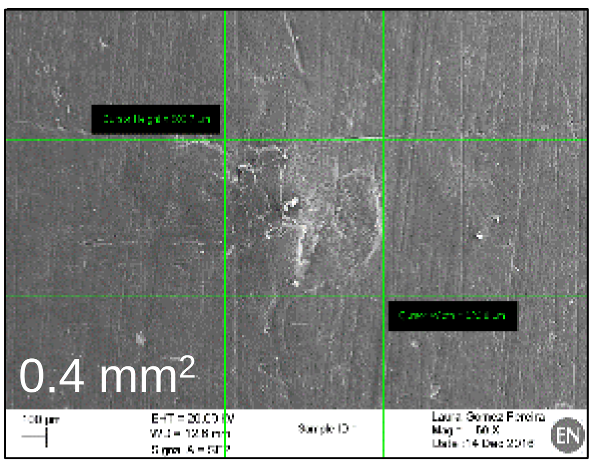
OM and SEM – Sigraflex

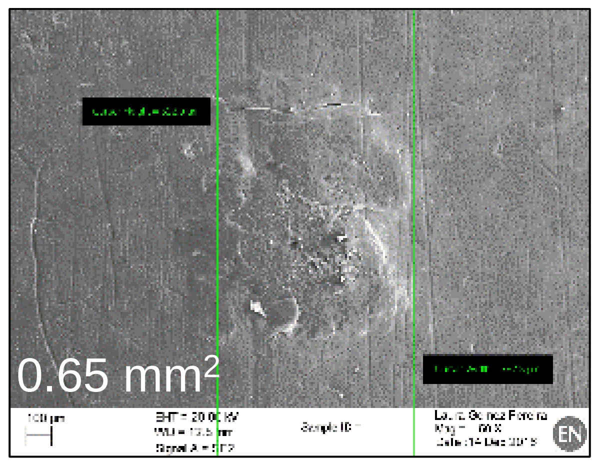
LVD*





MVD*

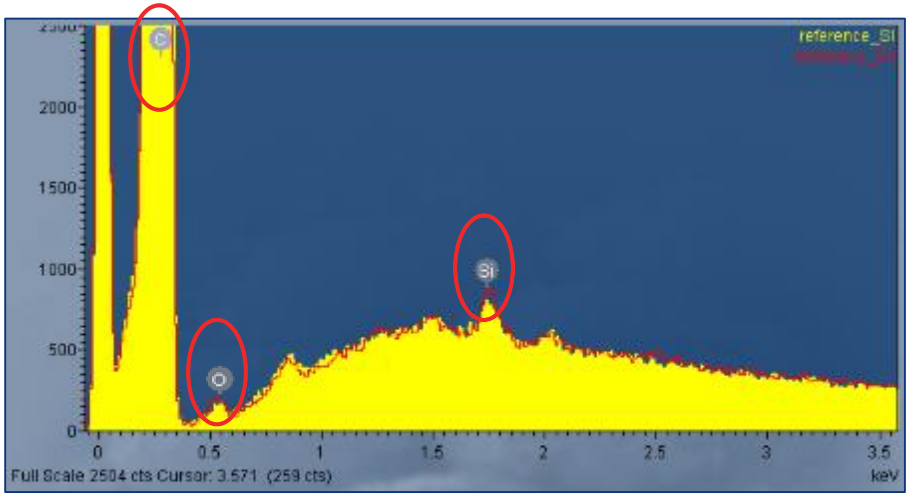


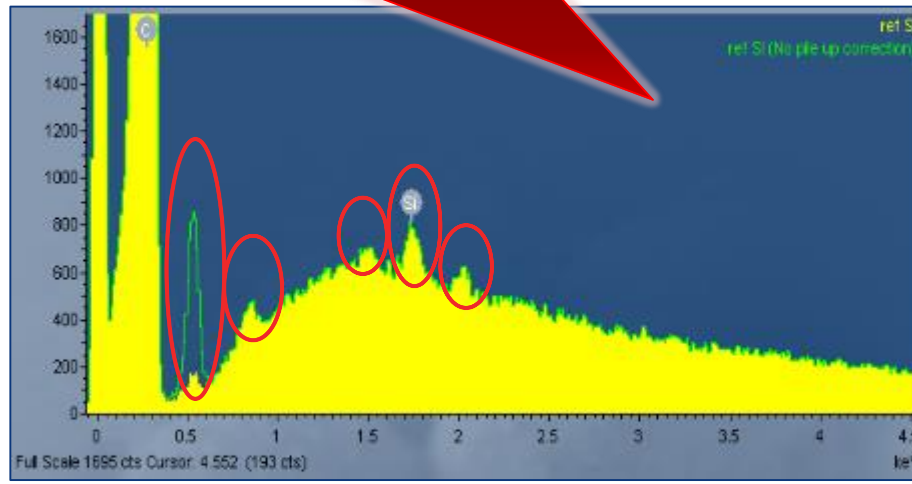


- Discontinuities
- Decohesion
- Flake like morphology
- Swelling
- Embossed Surface

EDS – Sigraflex as received

Presence and quatification of O cannot be 100% ensured





- Peak of C, O, Si
- Similar Chemical Analysis

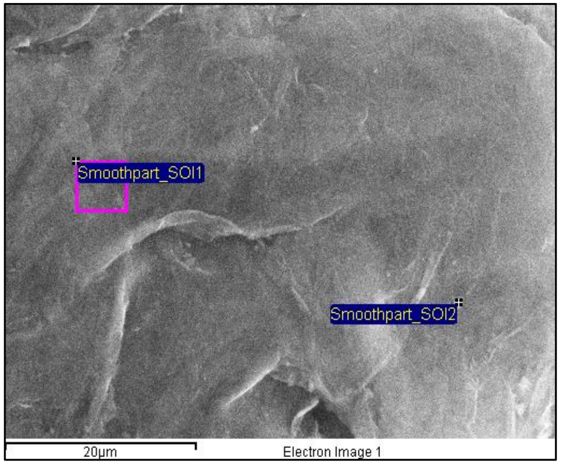
↓

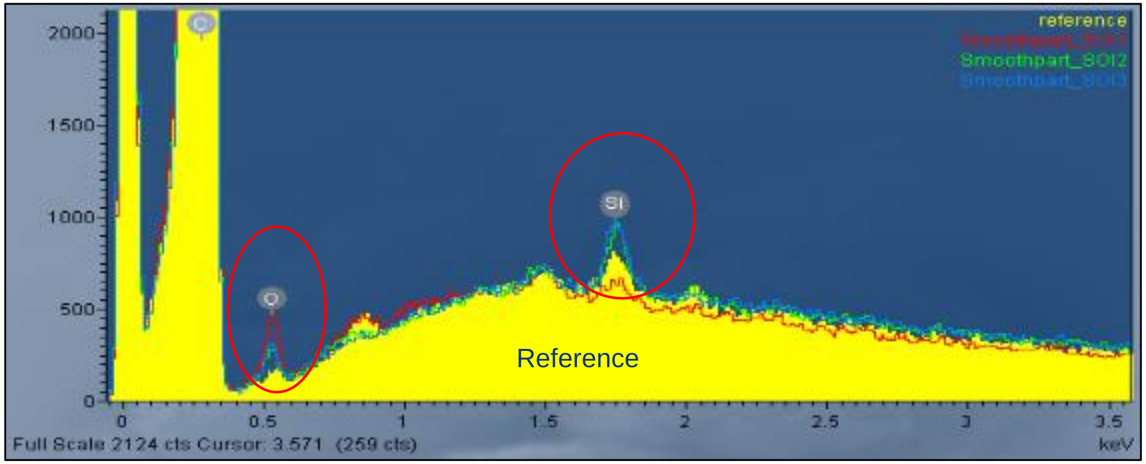
One chosen as reference

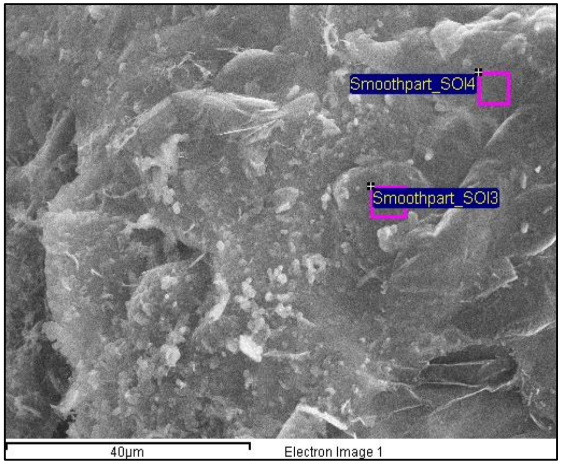
Examples:

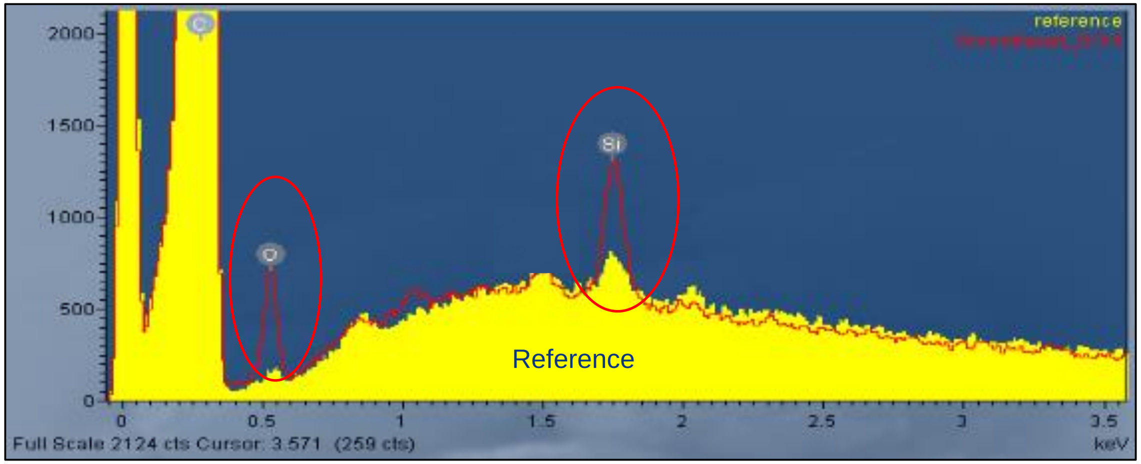
Σ peak	E (keV)	El.
C + C	0.54	O
C x 3	0.81	-
C + Si	2.02	P

EDS – Sigraflex after impact





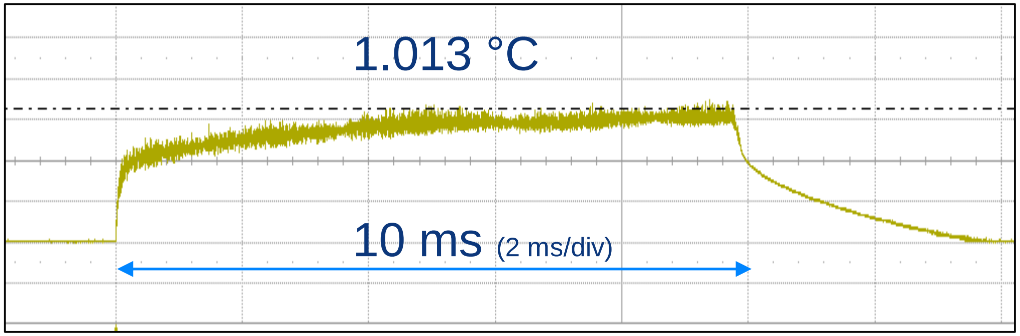


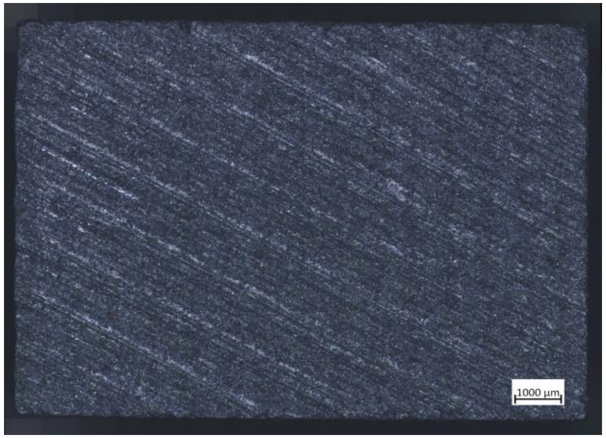


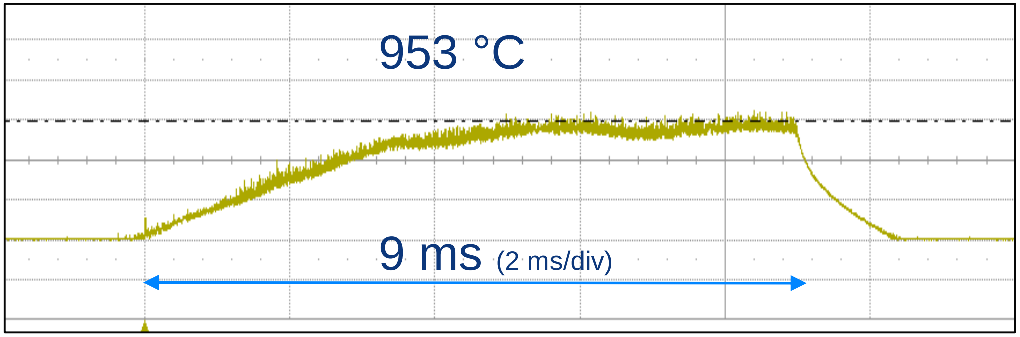
Higher amount of **O** and **Si**

Common features in all Sigraflex samples

OM – Sigrafine after impact

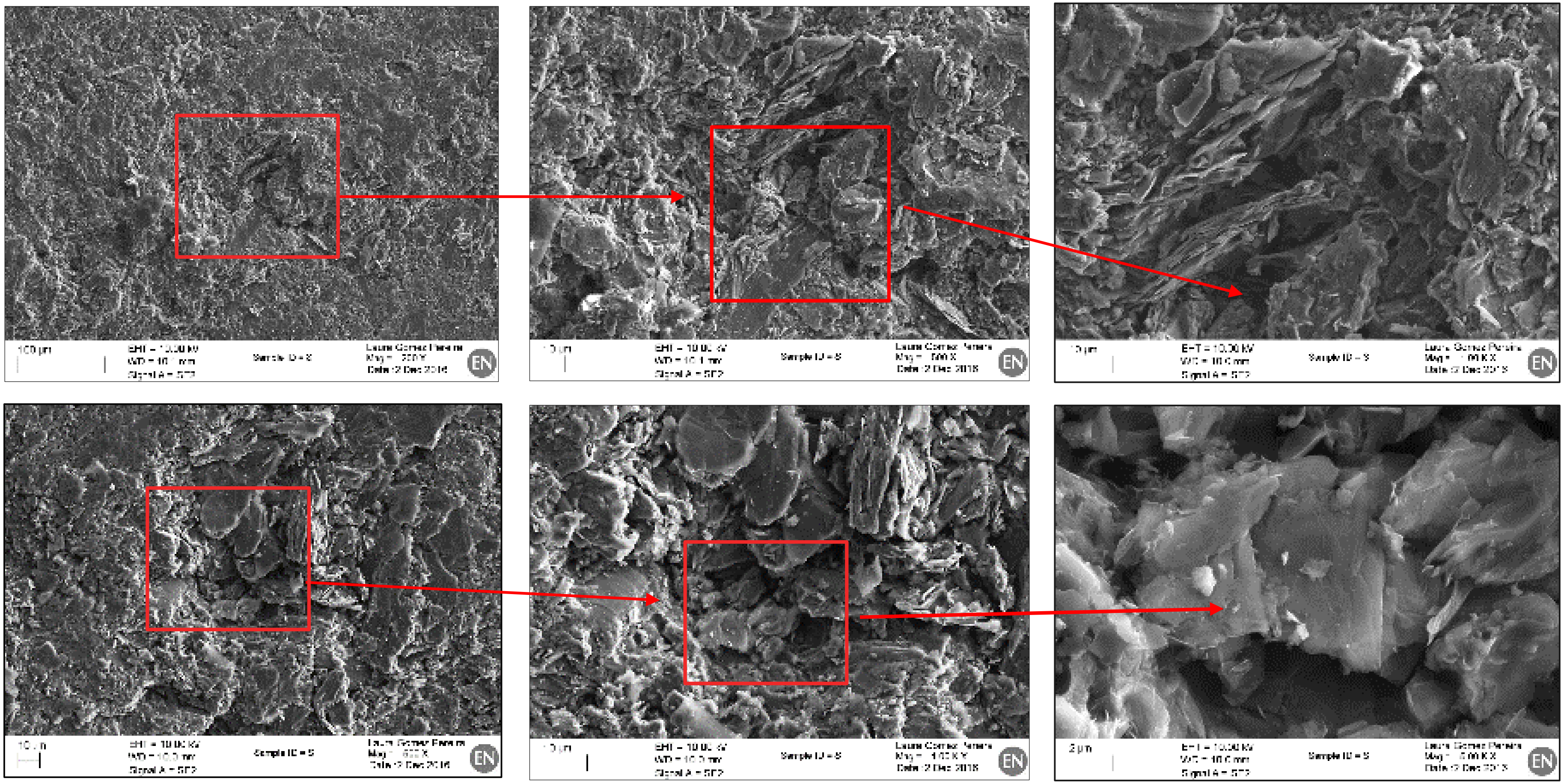






No laser impact visible with OM

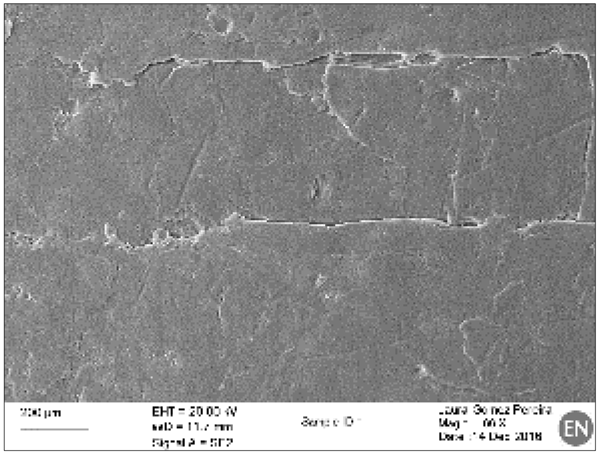
SEM – Sigrafine after impact

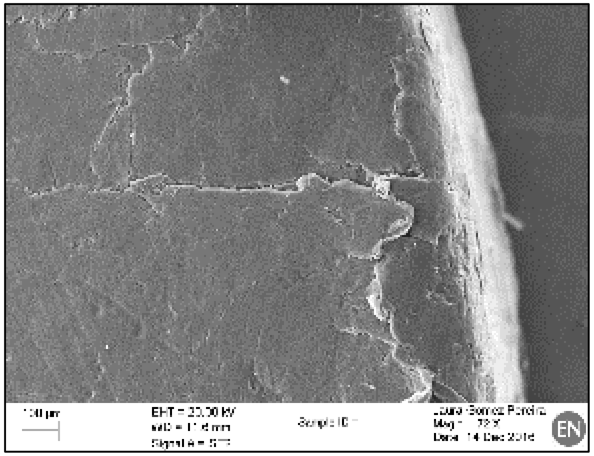


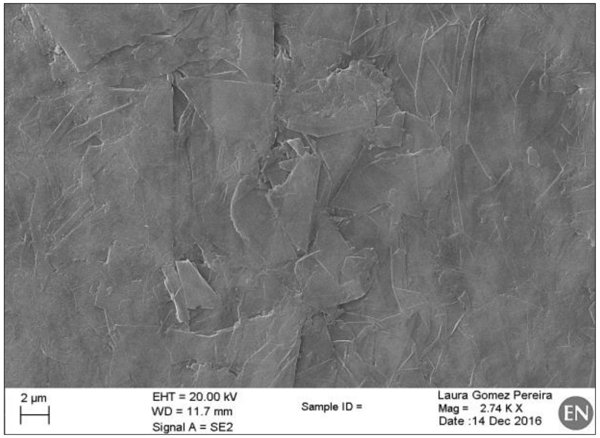
Presence of a macro-voids
No changes of Microstructure

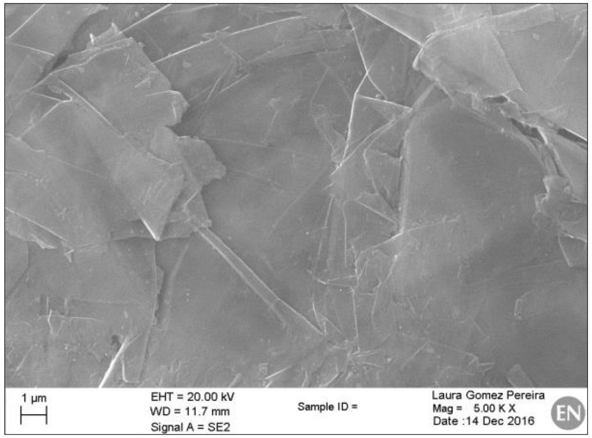
Furnace heating – CERN/EN-MME

SEM – Sigraflex









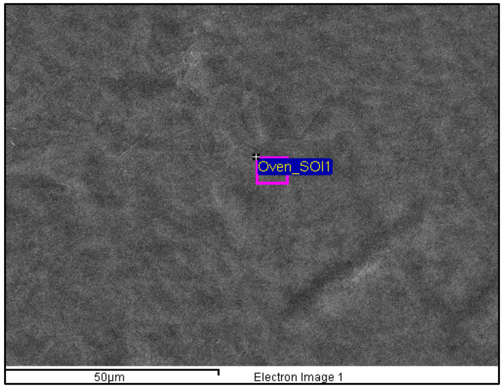
Discontinuities

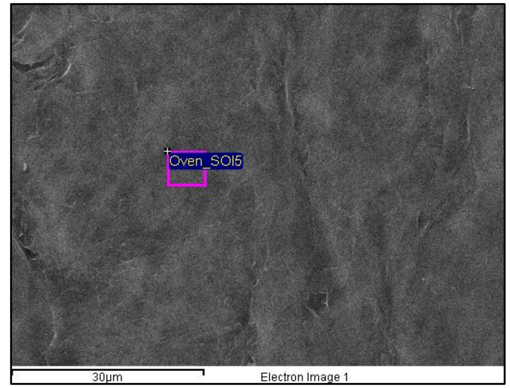
Decohesion

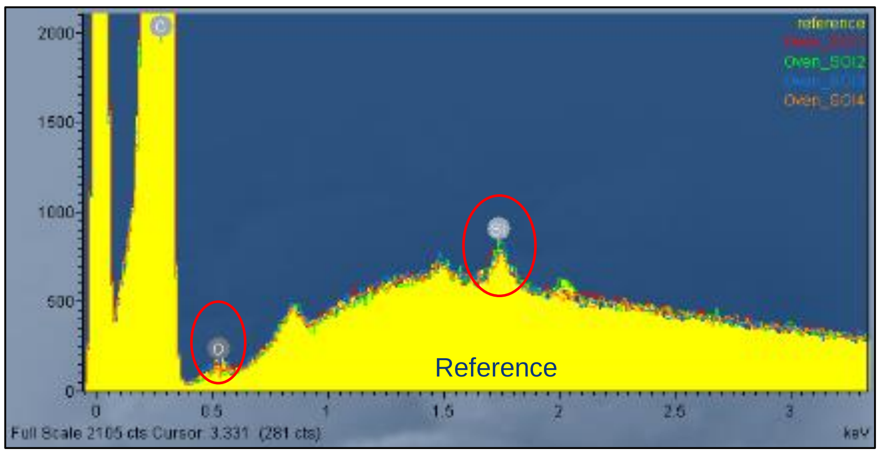
Flake like morphology

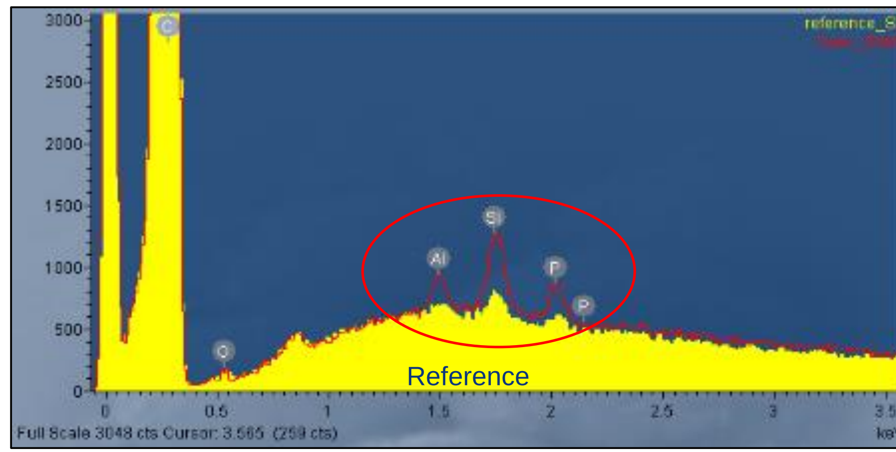
No apparent change in Microstructure

EDS – Sigraflex





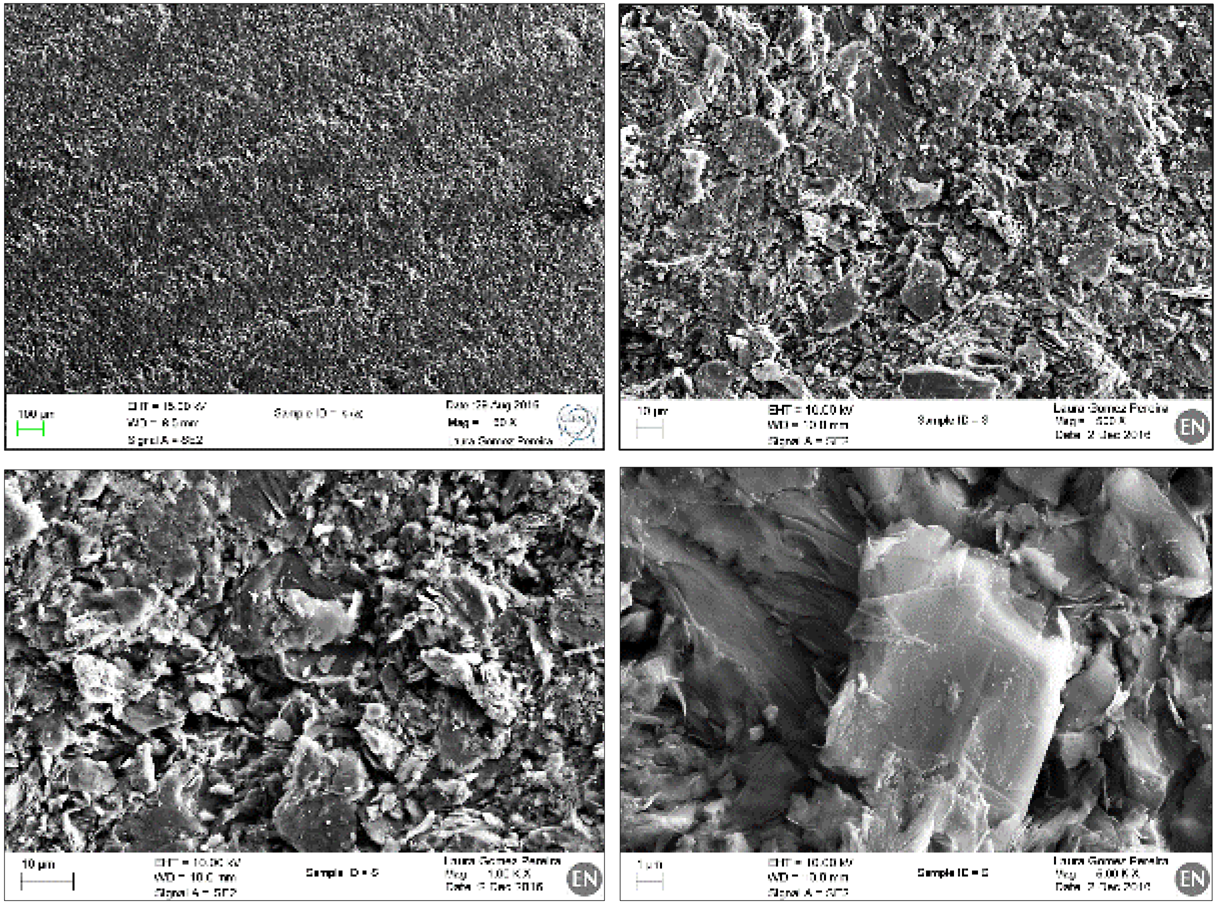




No changes in **Si** and **O** content

Pollution: **Al, Si, P**

SEM – Sigrafine



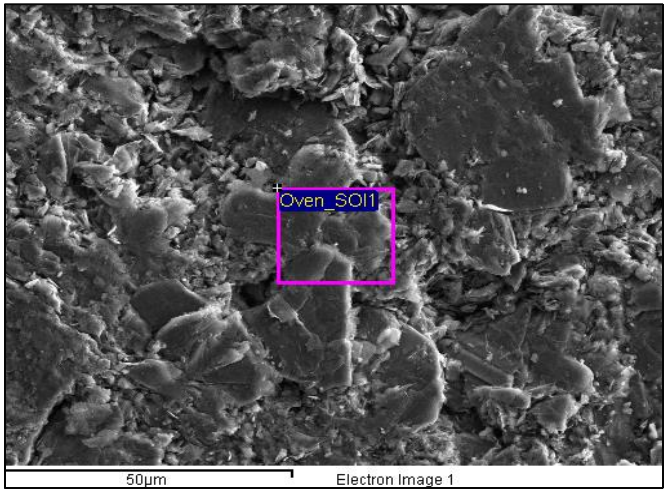
Production marks

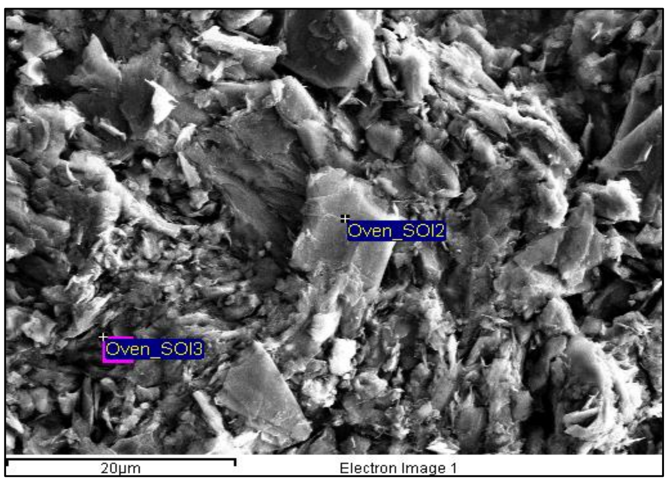
Roughness

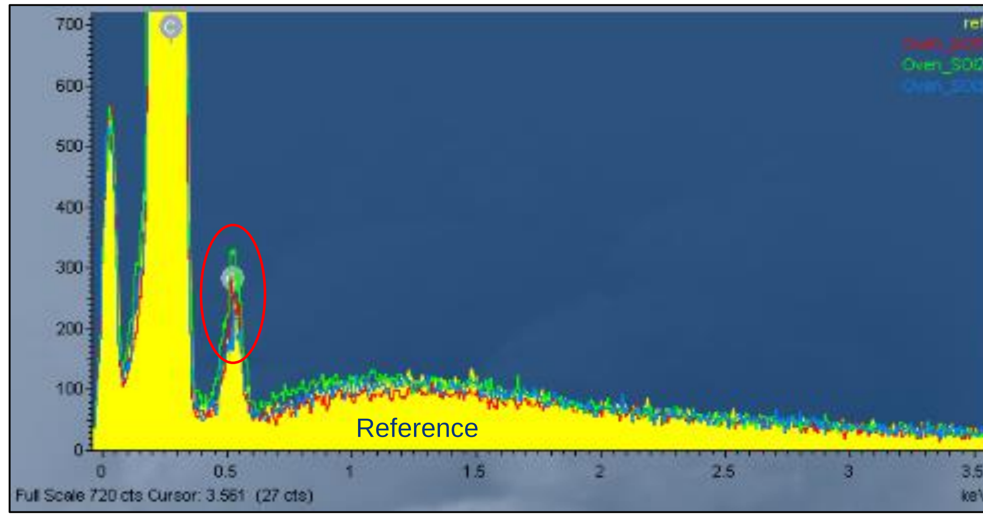
Irregular

No apparent change in Microstructure

EDS – Sigrafine



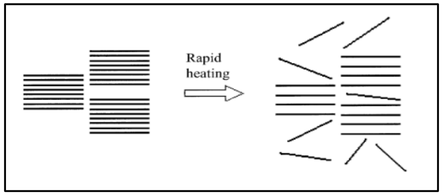




Same amount of **O**

Summary of observations

Laser Impact



Microstructure:

- Embossed surface and Expansion of graphite → **Swelling**
- Degradation of material → **Evaporation of material**

Chemical Analysis:

- Higher amount of O and Si
- Presence of pollution → probably due to manipulation

Phase Analysis: no apparent change

Oven Studies

Microstrucure:

- No apparent change in microstructure

Chemical Analysis:

- Amount of O and Si keeps constant before and after the study

↓

The graphite does not seem to be affected thermally

Further study on-going in oven at 1100°C