Oxidation behavior of graphite in air at high temperature

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In collaboration with EN/MME
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
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
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

- 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

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

Best parameters after several trials...

**Sigraflex**

<table>
<thead>
<tr>
<th>Energy</th>
<th>Frequency</th>
<th>Power</th>
<th>Wavelength</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 J</td>
<td>1 Hz</td>
<td>1 W</td>
<td>1064 mm</td>
<td>Defocused beam Z – 3.5mm</td>
</tr>
</tbody>
</table>

**Sigrafine**

<table>
<thead>
<tr>
<th>Energy</th>
<th>Frequency</th>
<th>Power</th>
<th>Wavelength</th>
<th>Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 J</td>
<td>1 Hz</td>
<td>4 W</td>
<td>1064 mm</td>
<td>Defocused beam Z – 3.5mm</td>
</tr>
</tbody>
</table>
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

*OM: Optical Microscope
*SEM: Scanning Electron Microscope
OM and SEM – Sigraflex

LVD*  
- 1.105 °C  
- 9 ms (2 ms/div)

MVD*  
- 1.354 °C  
- 10 ms (2 ms/div)

LVD = Least Visual damage  
MVD = Most Visual damage
OM and SEM – Sigraflex

**LVD***

Discontinuities

Decohesion

Flake like morphology

Swelling

**MVD***

Embossed Surface

1 mm²

0.8 mm²

0.4 mm²

0.65 mm²
EDS – Sigraflex as received

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

Presence and quantification of O cannot be 100% ensured

Examples:

<table>
<thead>
<tr>
<th>(\Sigma) peak</th>
<th>E (keV)</th>
<th>El.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C + C</td>
<td>0.54</td>
<td>O</td>
</tr>
<tr>
<td>C x 3</td>
<td>0.81</td>
<td>-</td>
</tr>
<tr>
<td>C + Si</td>
<td>2.02</td>
<td>P</td>
</tr>
</tbody>
</table>
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

No apparent change in Microstructure

Discontinuities
Decohesion
 Flake like morphology
EDS – Sigraflex

No changes in Si and O content

Pollution: Al, Si, P
SEM – Sigrafine

No apparent change in Microstructure

Production marks
Roughness
Irregular
EDS – Sigrafine

Same amount of O
Summary of observations

**Laser Impact**

- 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

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**Oven Studies**

**Microstructure:**
- 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