LPBF of Ceramics - graded porosity, self healing FUORCLAM impact
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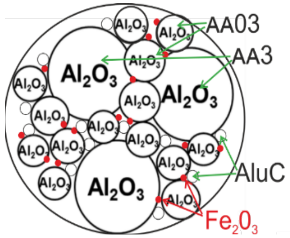
Konrad Wegener, Thomas Graule, Stefan Pfeiffer, Fabrizio Verga

IWF
Institut für Werkzeugmaschinen und Fertigung
Institute of Machine Tools and Manufacturing

FUORCLAM - Fundamental Understanding of Oxide Refractory Ceramics in Laser Additive Manufacturing

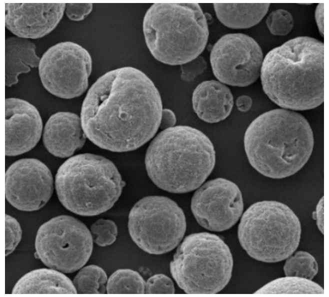

Empa
Materials Science and Technology

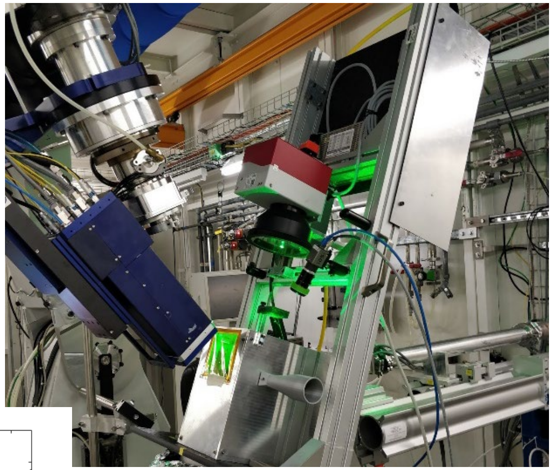
Thomas Graule
Pfeiffer Stefan



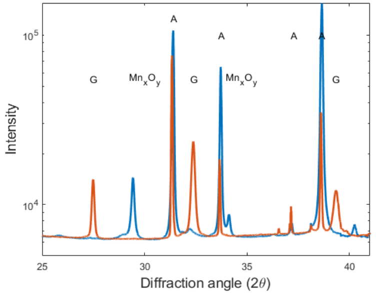
Powder preparation

- Spray granulation to increase powder flowability and packing density
- Addition of metal-oxides nanoparticles for improving **laser absorption**
- Development of new material system for **crack reduction**



Intercept of competences



Material characterization

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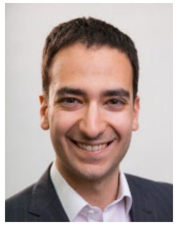
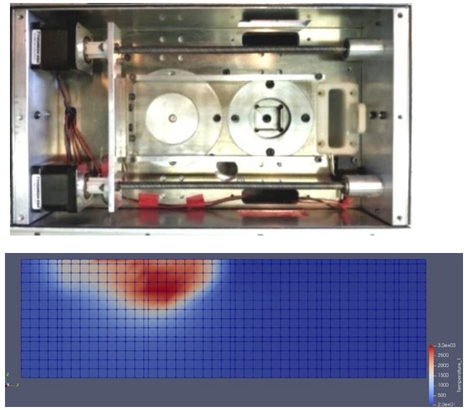
PSI

- Characterization of the starting powder
- Characterization of the SLM alumina parts
- Operando studies of SLM of alumina

Helena Van Swygenhoven
Makowska Malgorzata


Konrad Wegener
Fabrizio Verga
Florio Kevin



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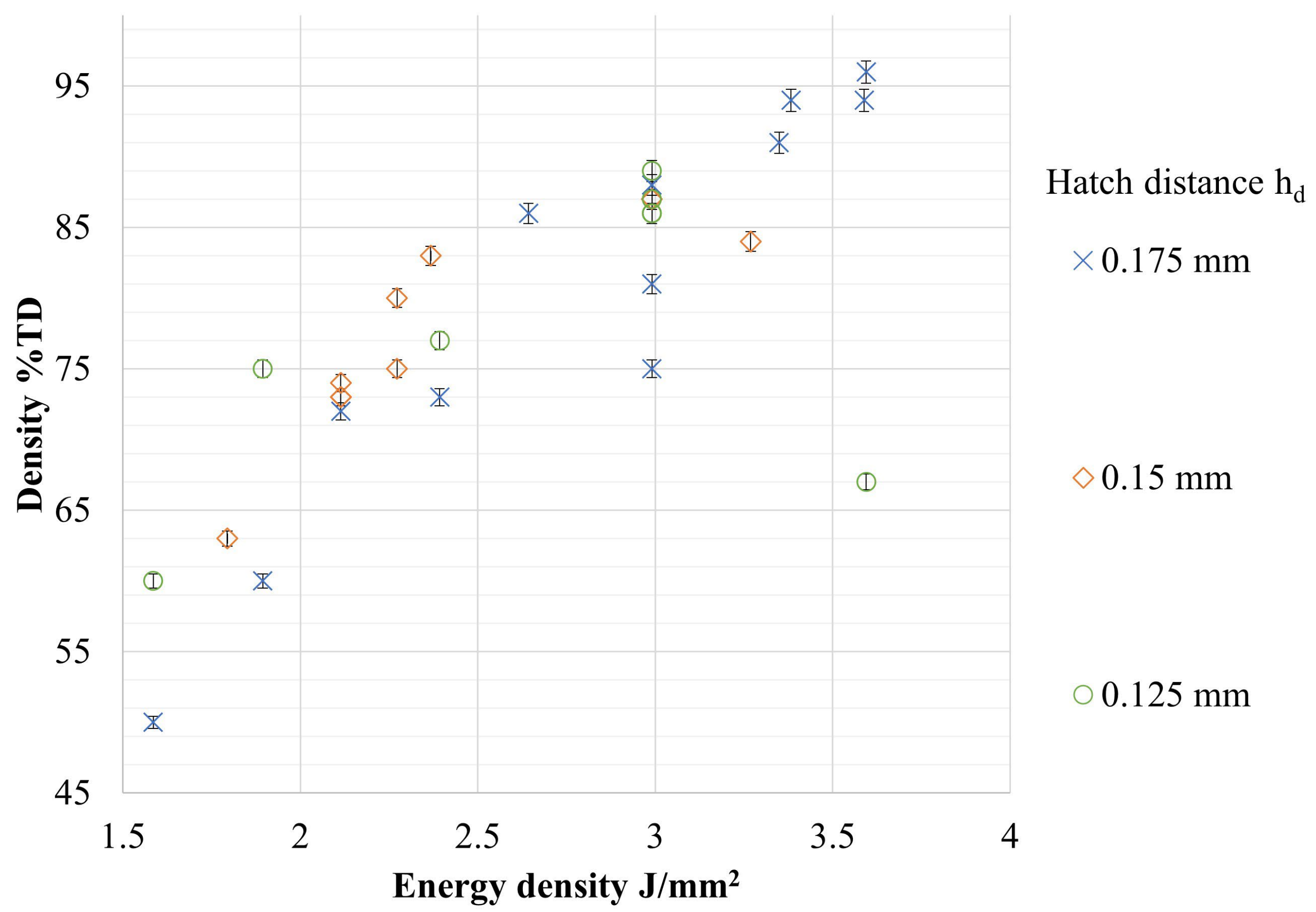
Laser processing

- Finding processing window for different lasers and material combinations
- Comparison of pulsed and continuous wave laser and different wavelengths for improving **laser absorption**

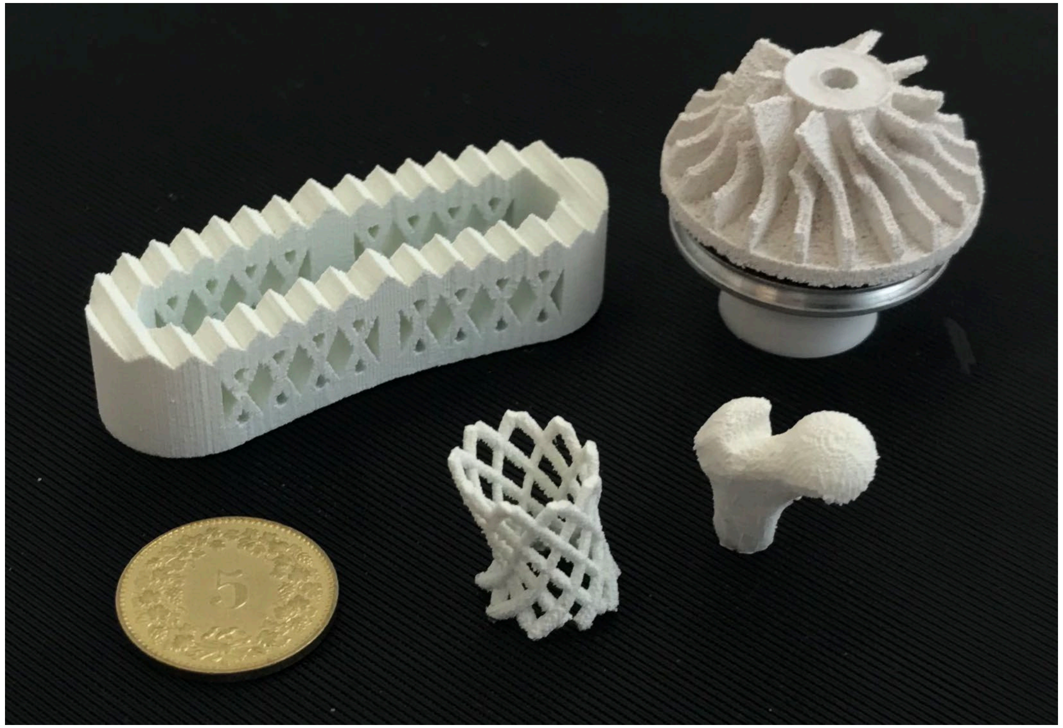
Optimize processing parameters for increasing density and **crack reduction**

2 PBF-LB of ATZ

- Part density up to 95%

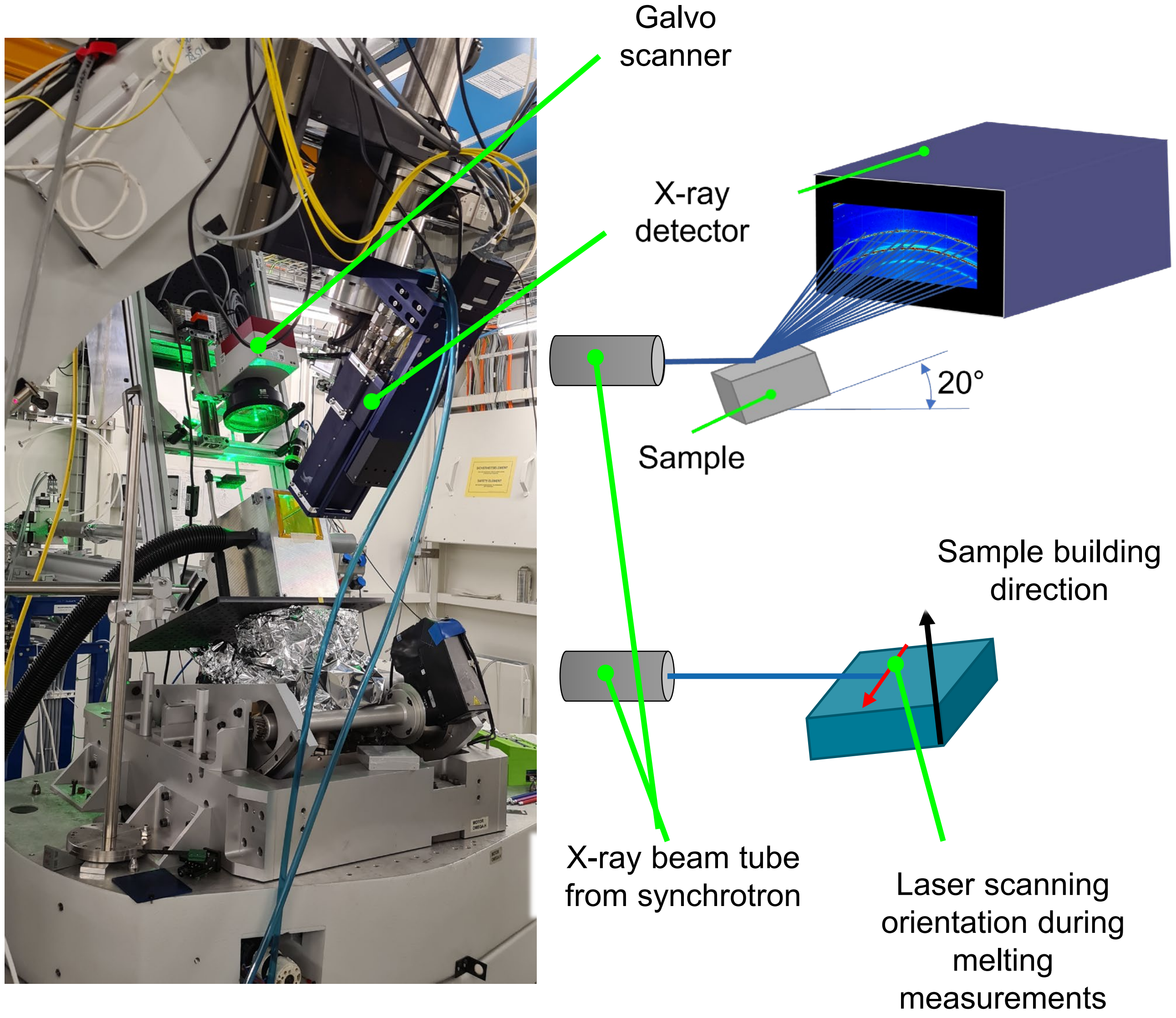


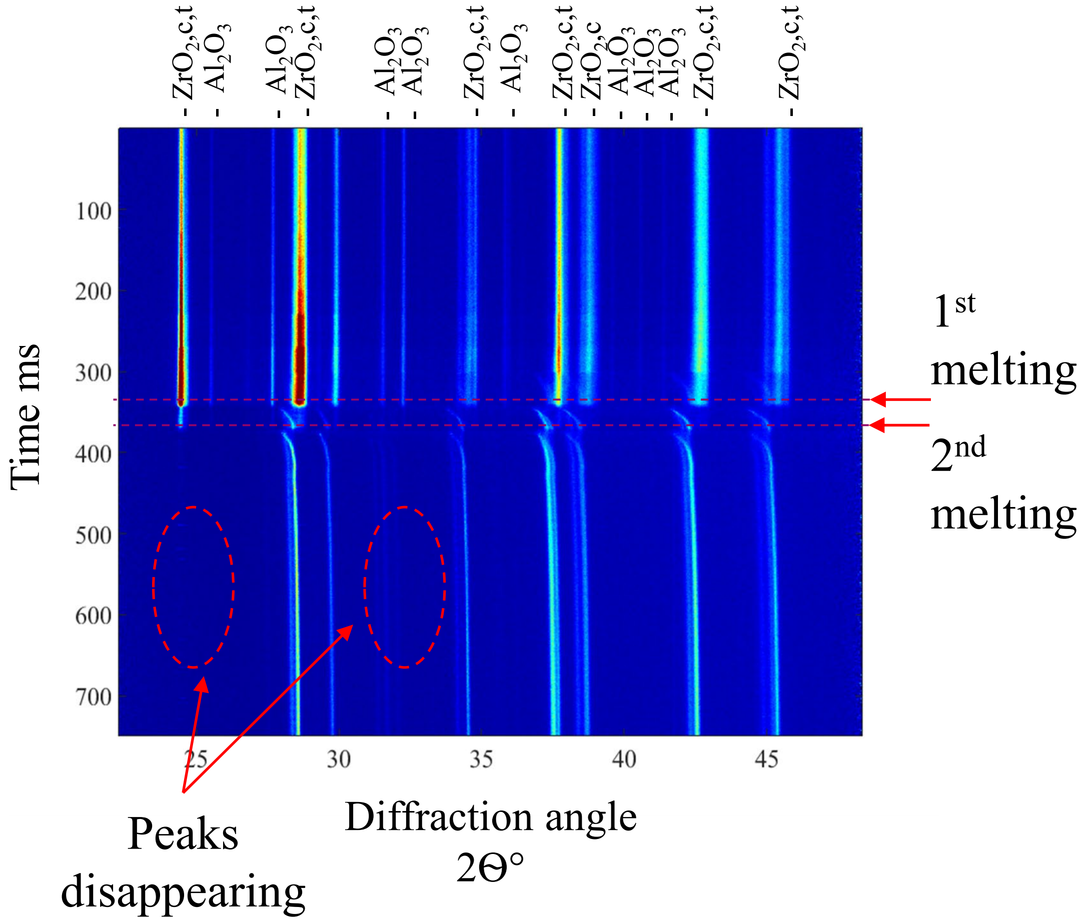
- Good geometrical freedom



Example of free form fabrication achieved during the project.
Material: ATZ (80 wg% ZrO_2 – 20 wg% Al_2O_3)
Laser source: Nd:YAG-laser

2 PBF-LB of ATZ



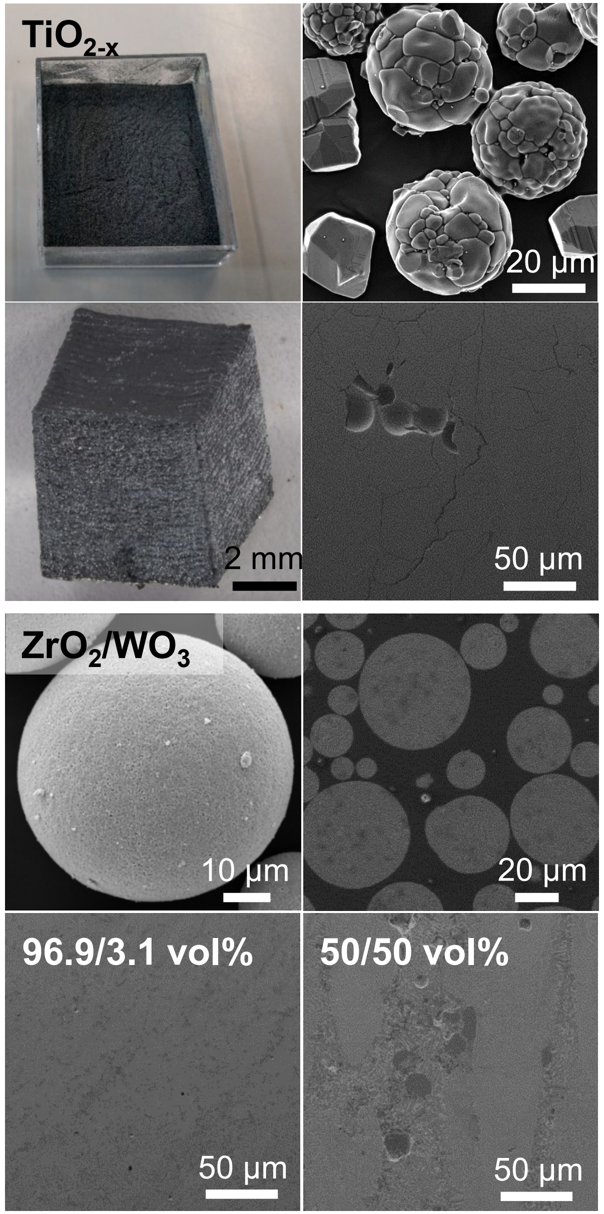


The ZrO_2 peaks disappear during melting indicating that **liquid phase sintering is not achieved.**

Reduction of CTE

- **Ammonium citrate dibasic is a suitable dispersant** for used powders (Al_2O_3, Fe_2O_3, MnO_2/Mn_2O_3, TiO_2, (WO_3) and ZrO_2)
- Production of **powders** with **high apparent, tapped density** and **good flowability** possible (spray-dried granules with bimodal distribution (McGeary), addition of coarse Al_2O_3 particles and thermal pre-treatment)
  → **Highest achieved part density of 98.6%**
- **Severe crack formation** by laser processing of **powders** with **0.7 vol%** and **10 vol% black TiO_{2-x}** due to **lack of** sufficient **in-situ formed Al_2TiO_5**
- **Crack reduction** with **50 mol% TiO_{2-x}** and **96.9 or 50 vol% ZrO_2/WO_3 granules** possible
- **Achieved part properties:**

	50 mol% TiO_{2-x}	96.9 vol% ZrO_2/WO_3 granules	50 vol% ZrO_2/WO_3 granules
Relative part density [%]	96.5	95.7	95.7
Compressive strength [MPa]	346.6 ± 47.9	327.9 ± 52.1	498.0 ± 89.3
Young‘s modulus [GPa]	90.2	51.3	99.7

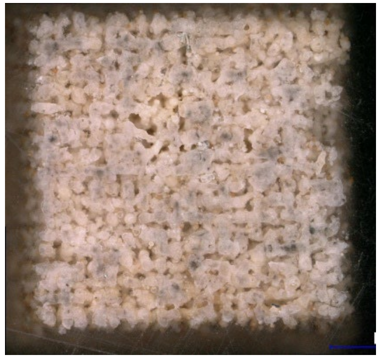


Porosity control by laser parameters

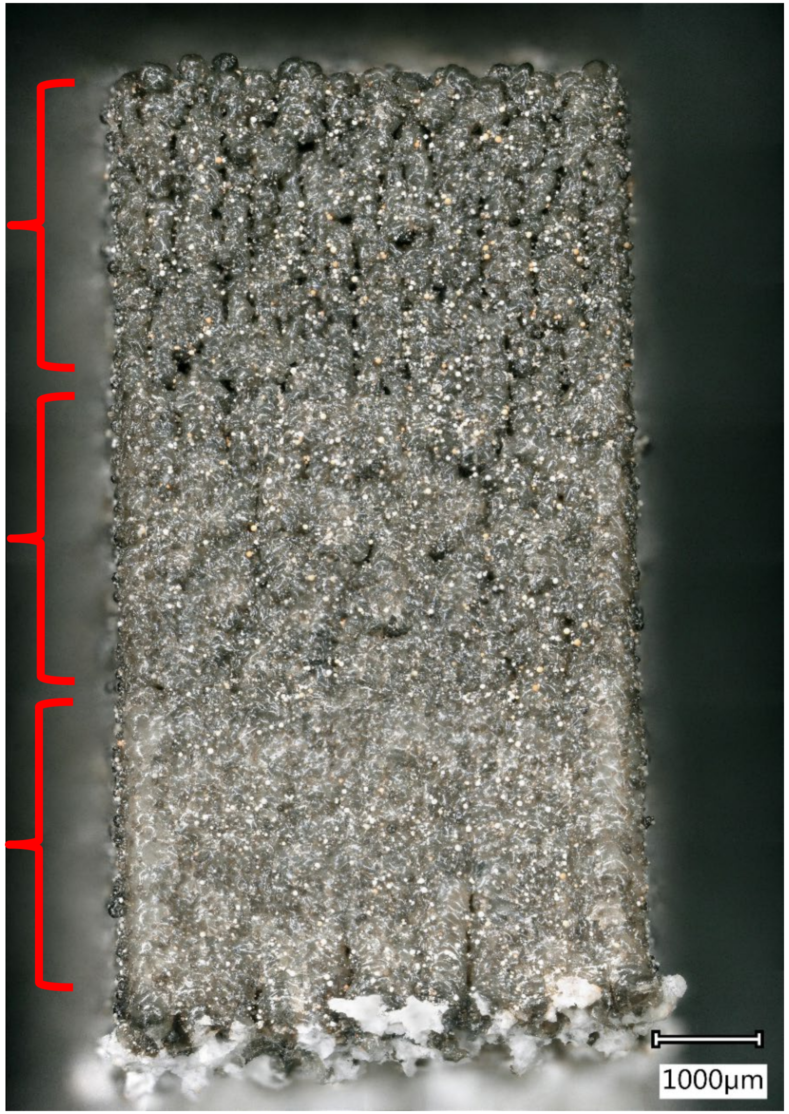
Gradient structure

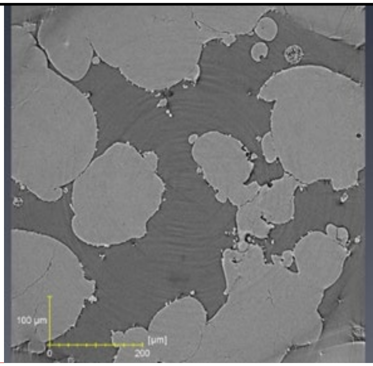
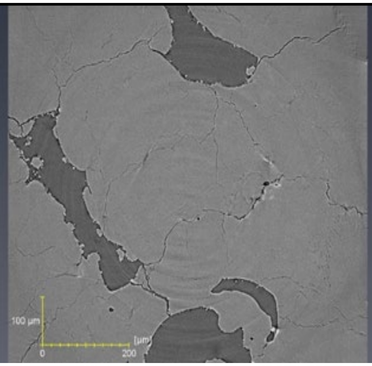
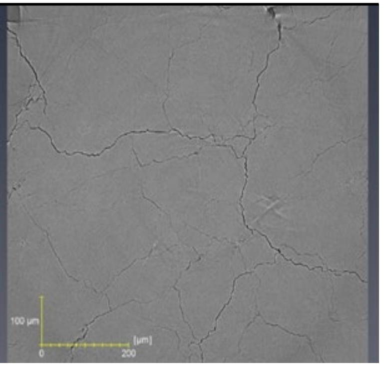
- Example of porosity, controlled by varying laser scan speed and hatch distance
- High flexibility on gradient porosity direction

Porosity induced by hatch distance, MnO_2 dopant

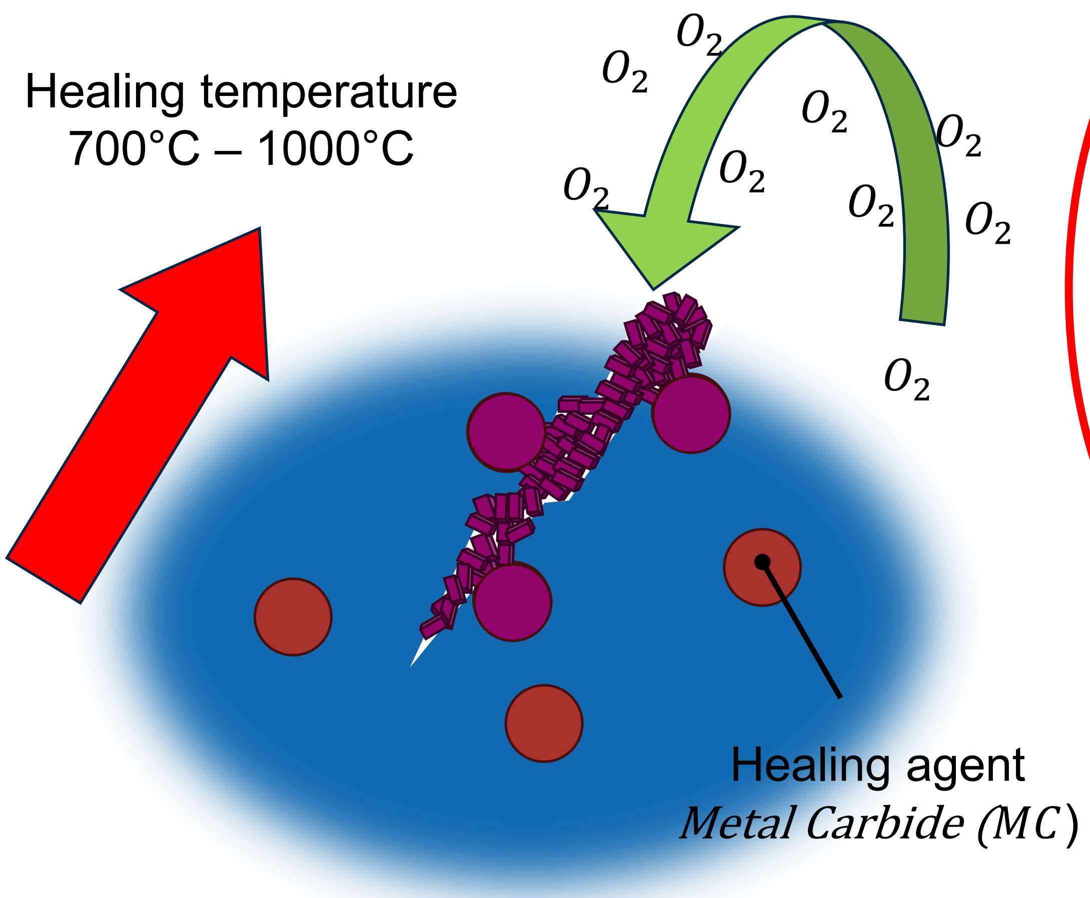


Porosity induced by scan speed, Fe_2O_3 dopant



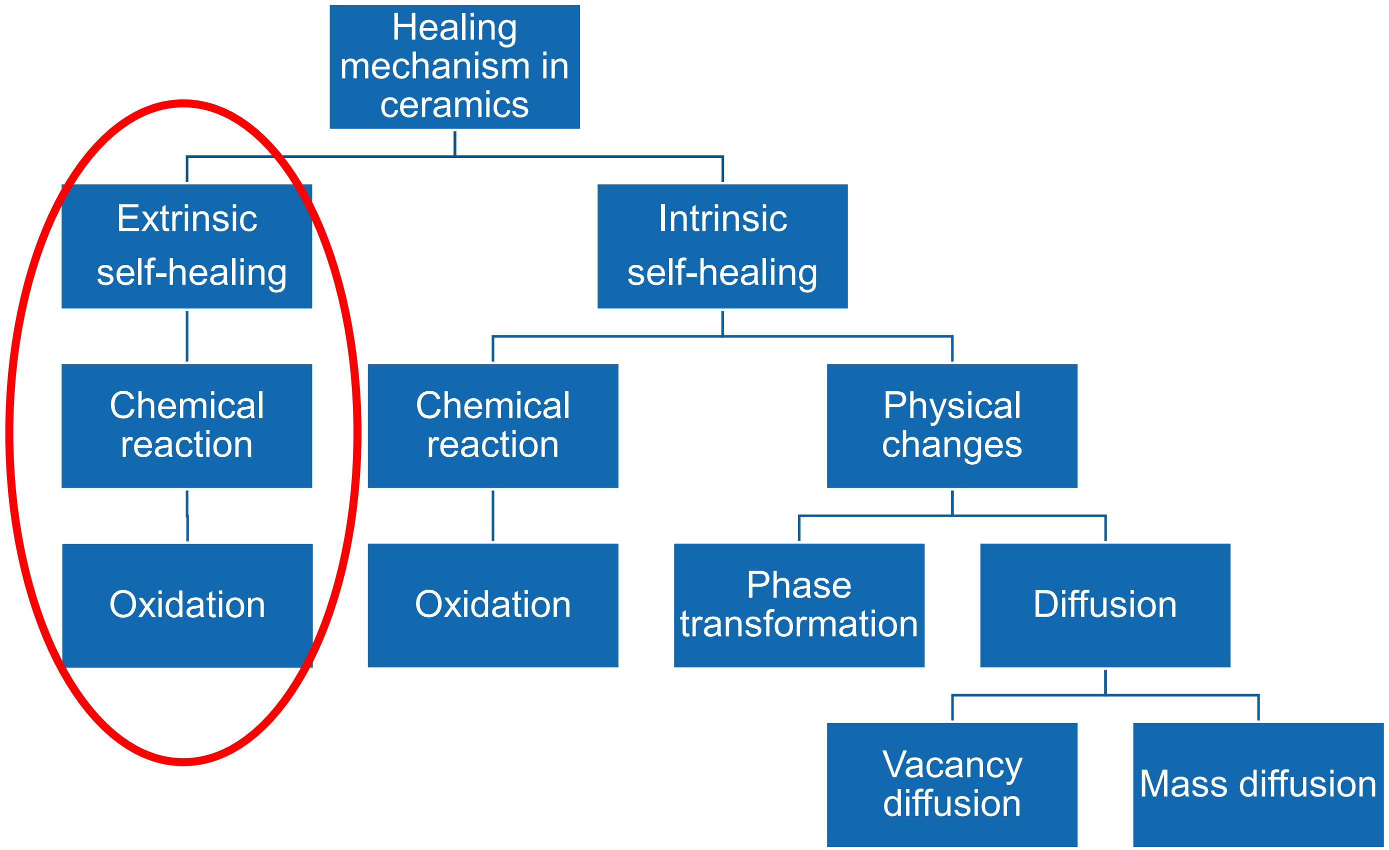
Scan speed	10 mm/s	5 mm/s	2 mm/s
Density	68 %	86 %	96 %
Tomography at synchrotron			

1 Self-healing ceramics



The healing occurs if $V_{MOx} > V_{MC}$

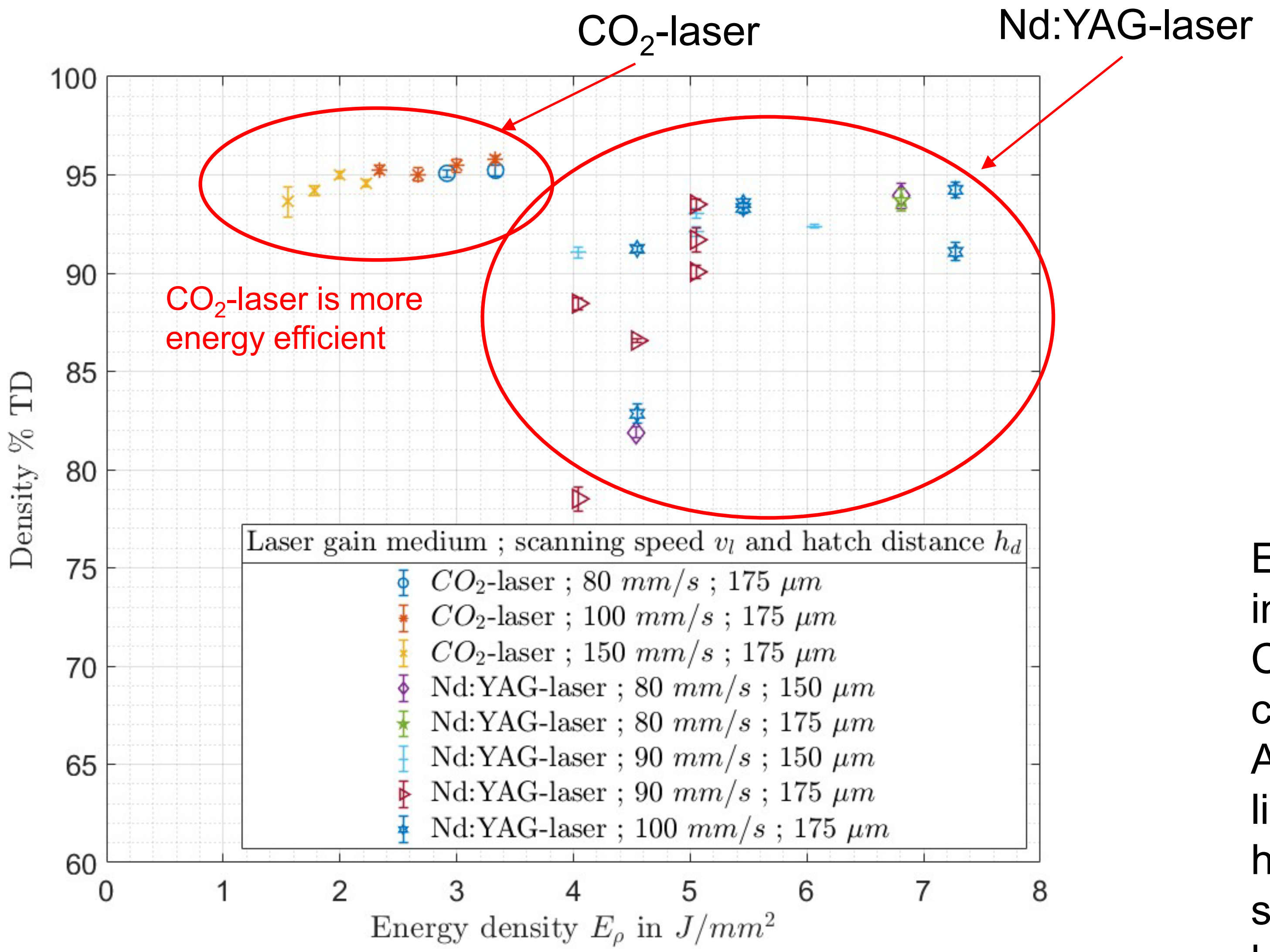
V_{MC}: *volume of the healing agent*
V_{MOx}: volume of the healing product

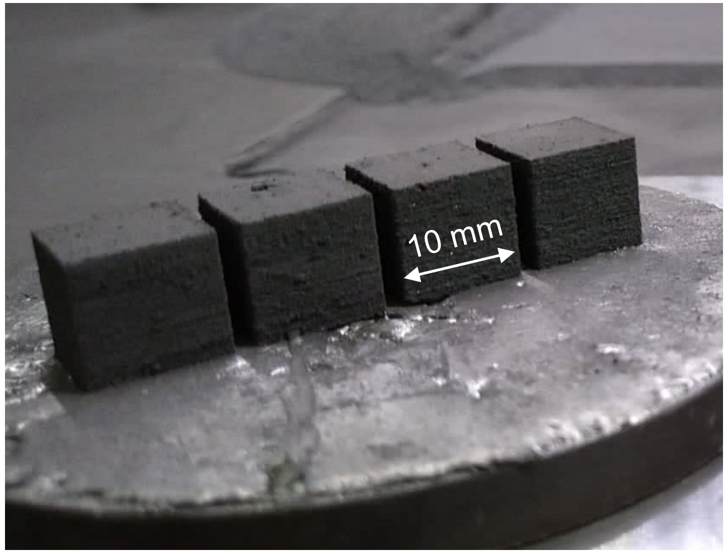


The most effective self-healing mechanism is the oxidation rection

- Extrinsic self healing: active healing particles in an inert matrix.
  Healing particles: SiC, TiC, Ti …
- Intrinsic self healing: the matrix can actively heal by oxidation reaction.
  Intrinsic healing ceramic: Ti_2AlC, Cr_2AlC

3.1 Laser processing

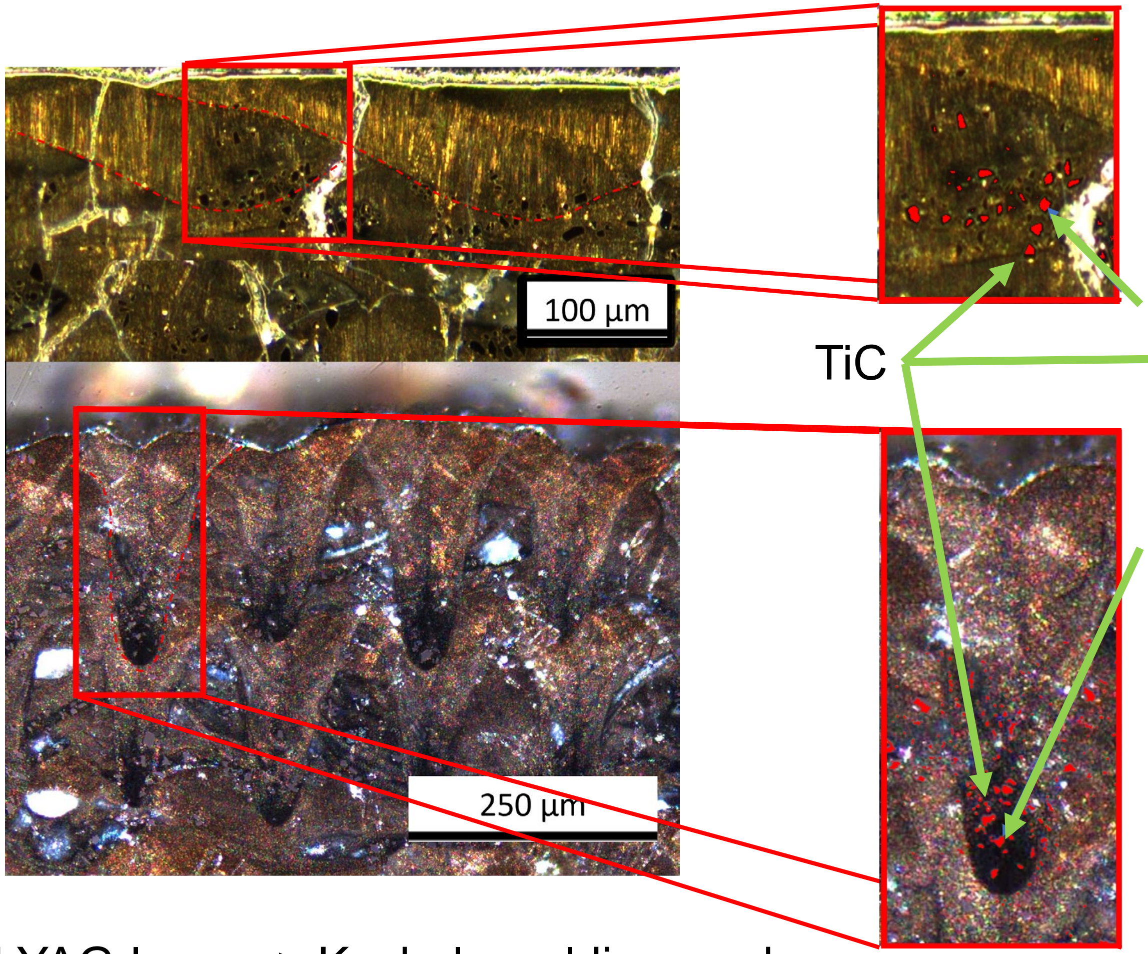




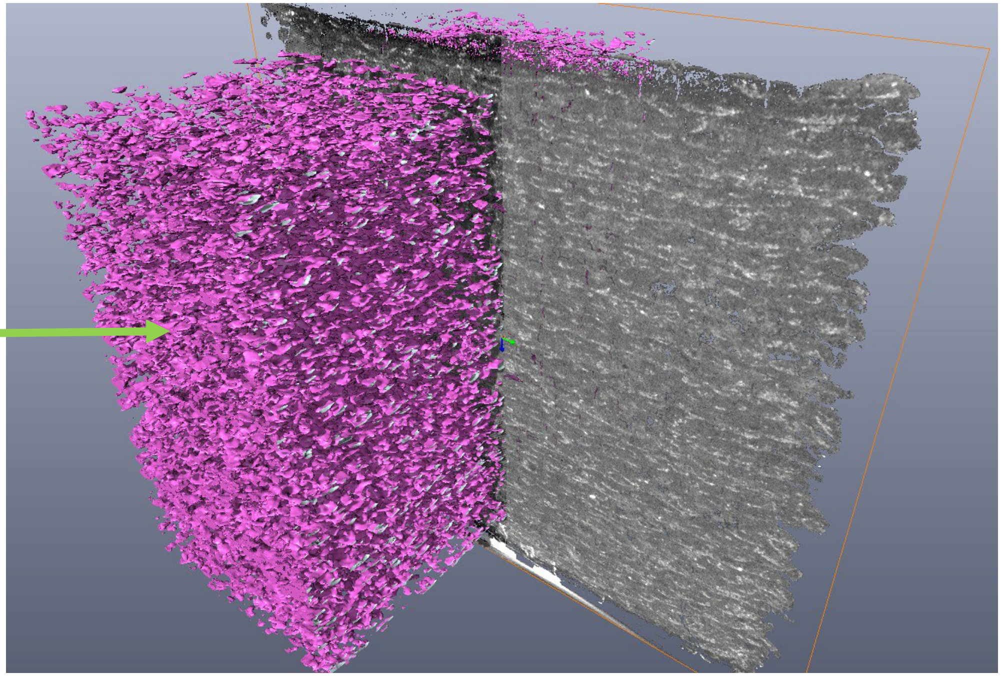
Example of cubes used for the parameter investigation.
CO_2-laser and Nd:YAG-laser are compared.
A set for parameters exists for both laser lights enabling densities of ≈ 95% TD, however the CO_2-laser achieves more steady results consistently achieving higher part densities for different parameter sets.

3.1 Laser processing

CO_2-laser => Conduction welding mode



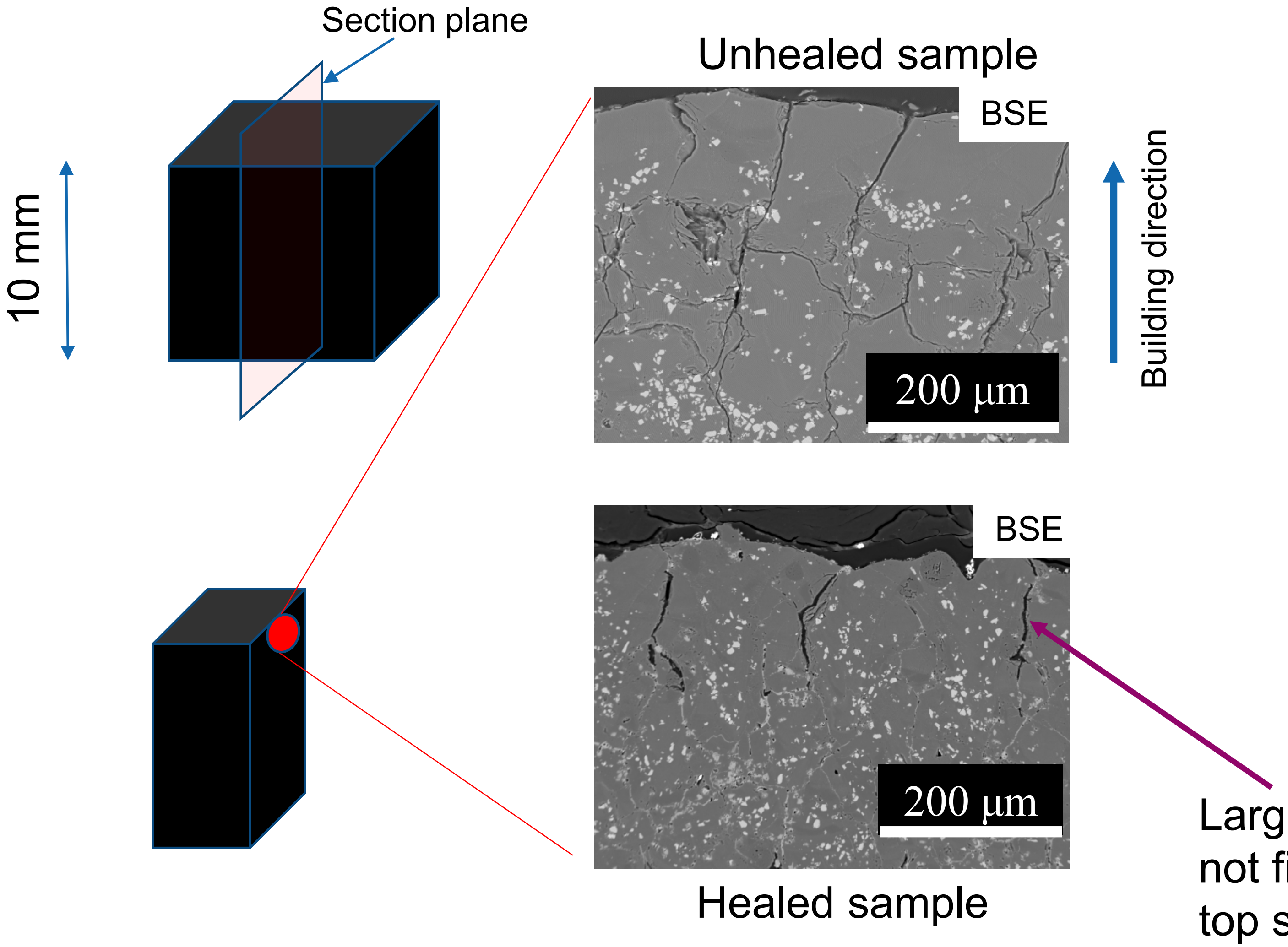
Nd:YAG-laser => Keyhole welding mode



Micro CT-scan, the TiC is visible in purple.
The TiC segregates in within the melt pool.
This phenomena decreases the homogeneity of healing particles dispersion.

3.2 Healing of AM components

- Heat treatment in air at 900°C for 3h

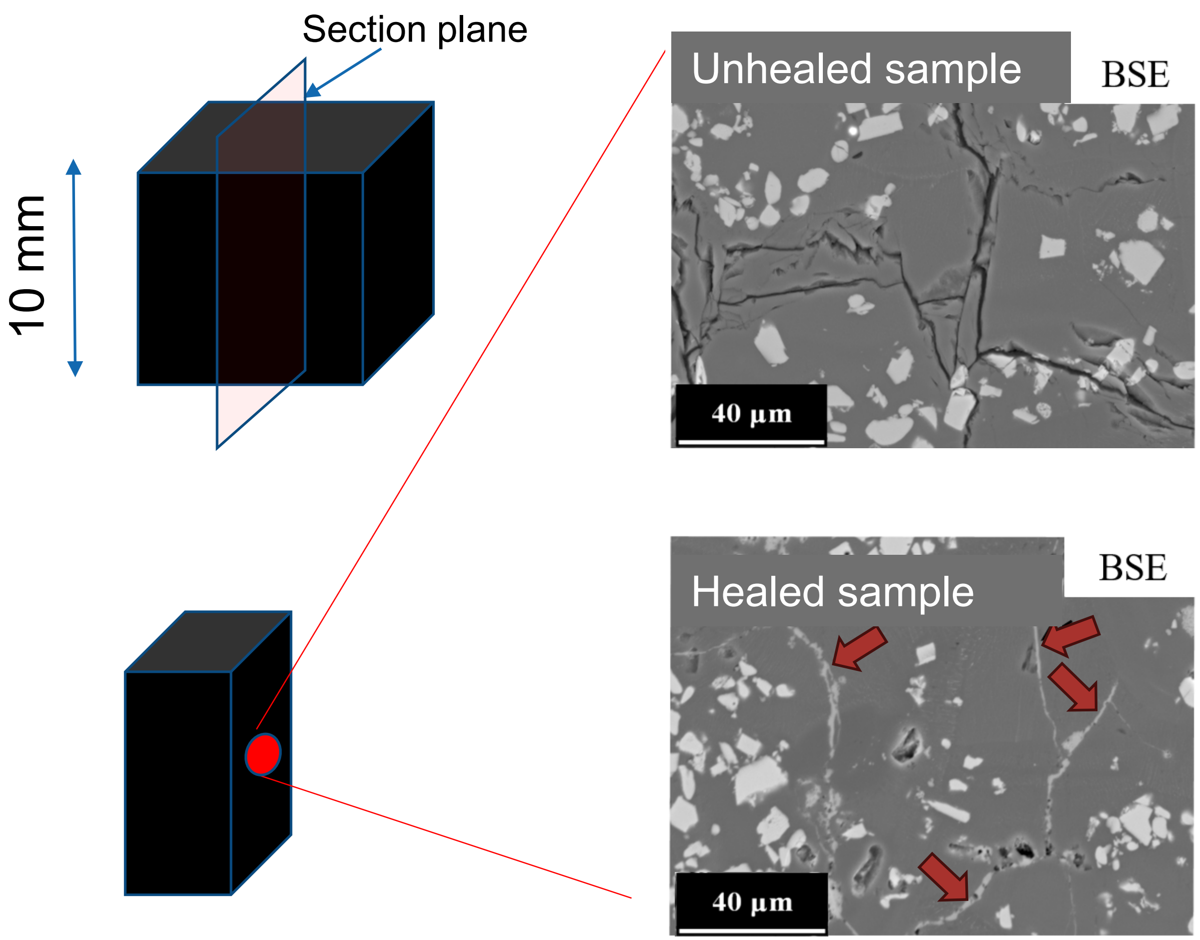


Large cracks not filled on the top surface.

- Within 200 µm from the surface cracks a phase fills the cracks.
- On the upper surface, the surface scanned by the laser, present larger not healed crack.
- Towards the surface the TiC concertation is lower because of the segregation.

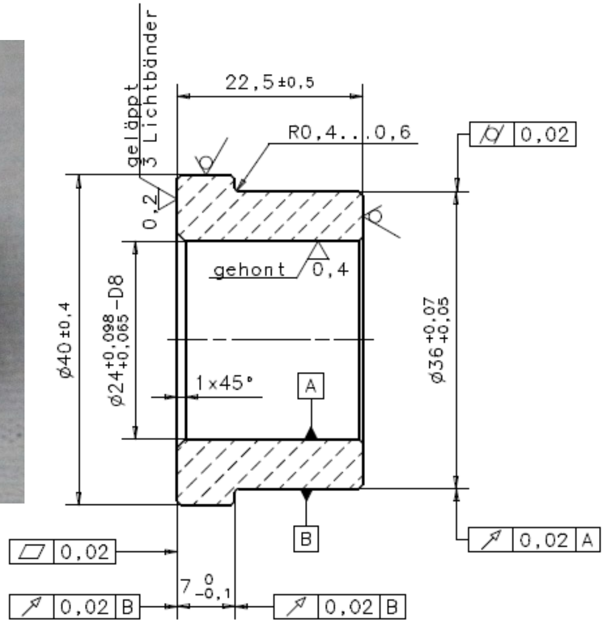
3.2 Healing of AM components

- Heat treatment in air at 900°C for 3h



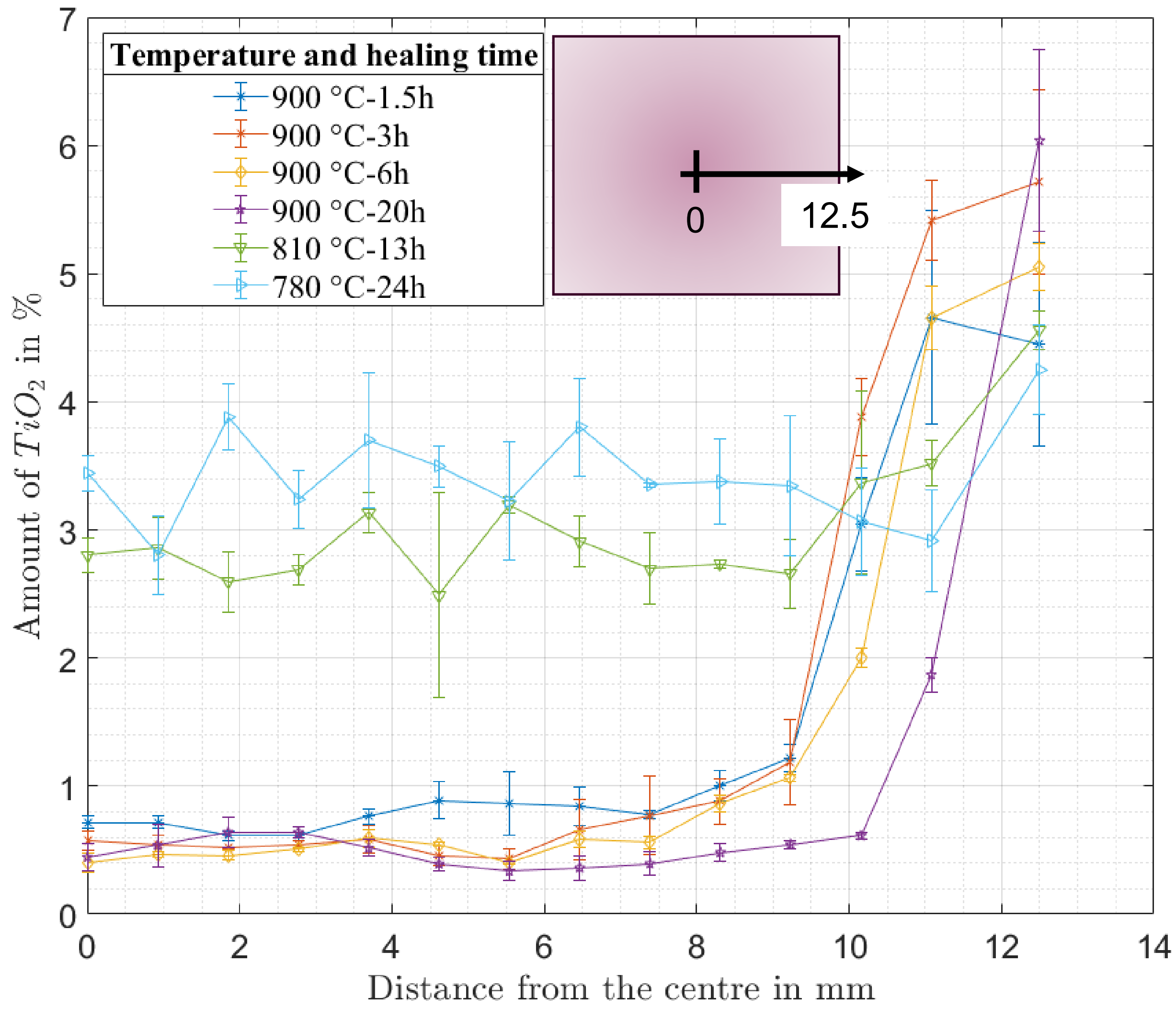
- The healing was effective in the depth of a cube of 10 mm × 10 mm × 10 mm.

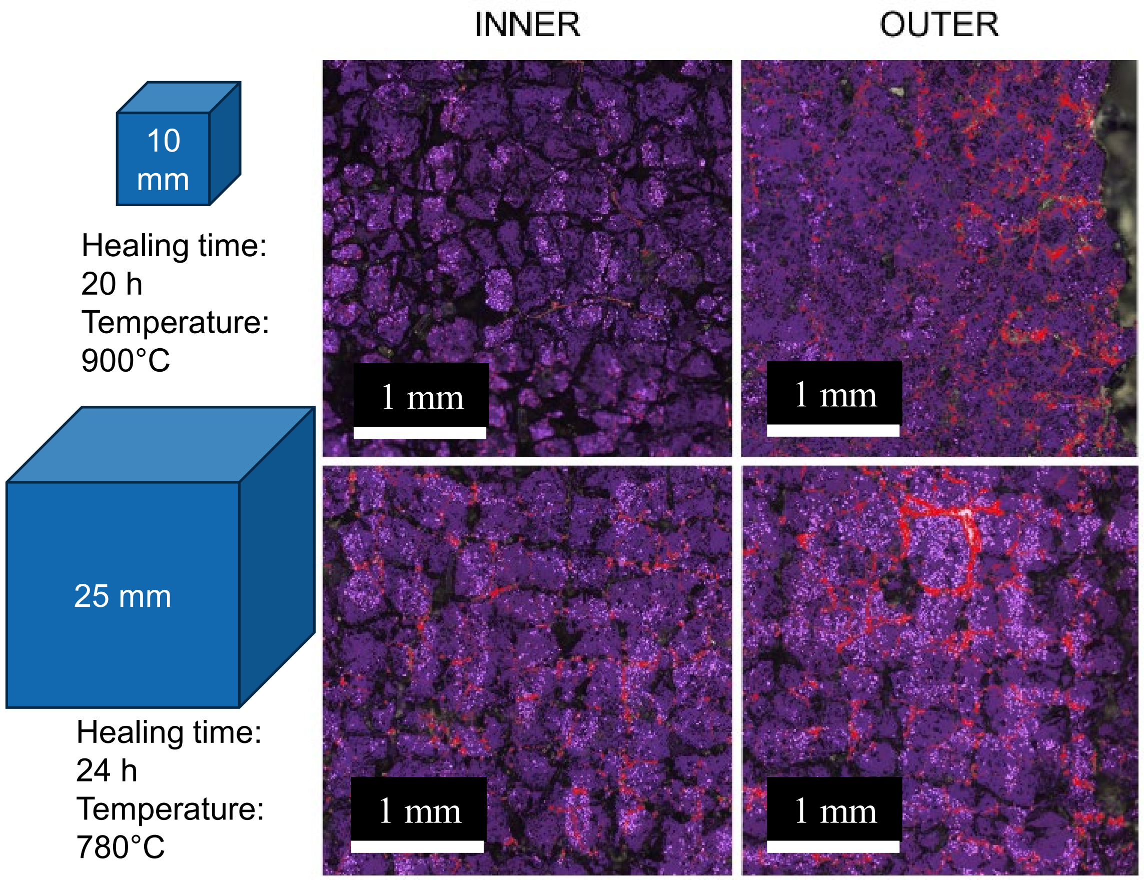
- The self-healing effect is present also within the most inner part of the samples tested.



3.2 Healing of AM components

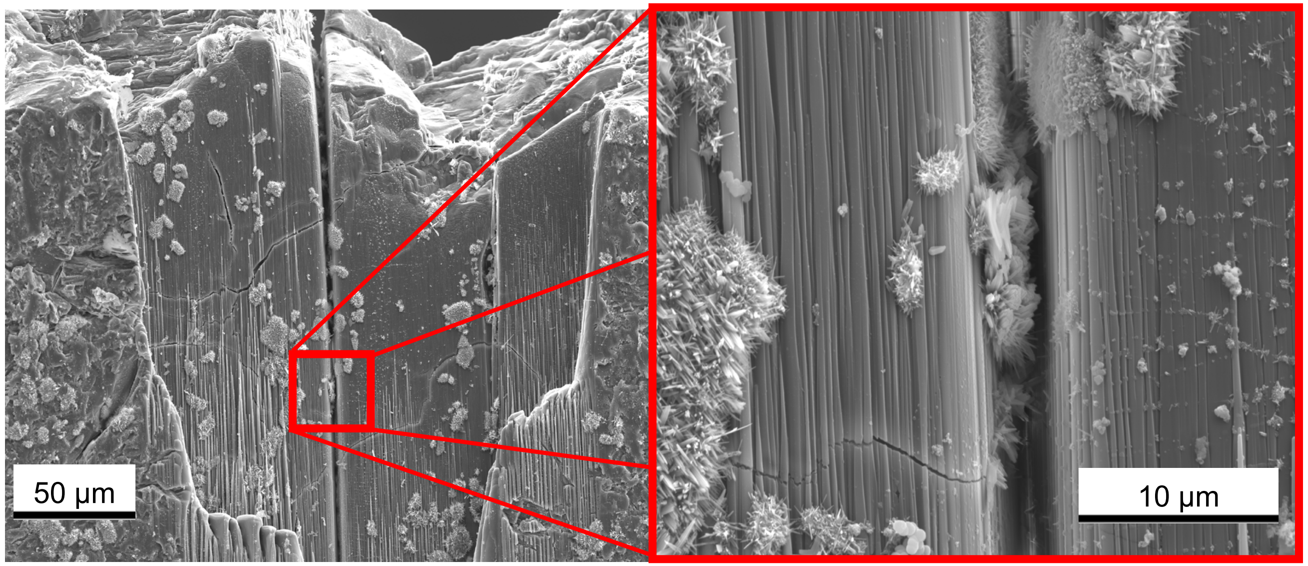
Measured amount of TiO_2 within the section of the cube

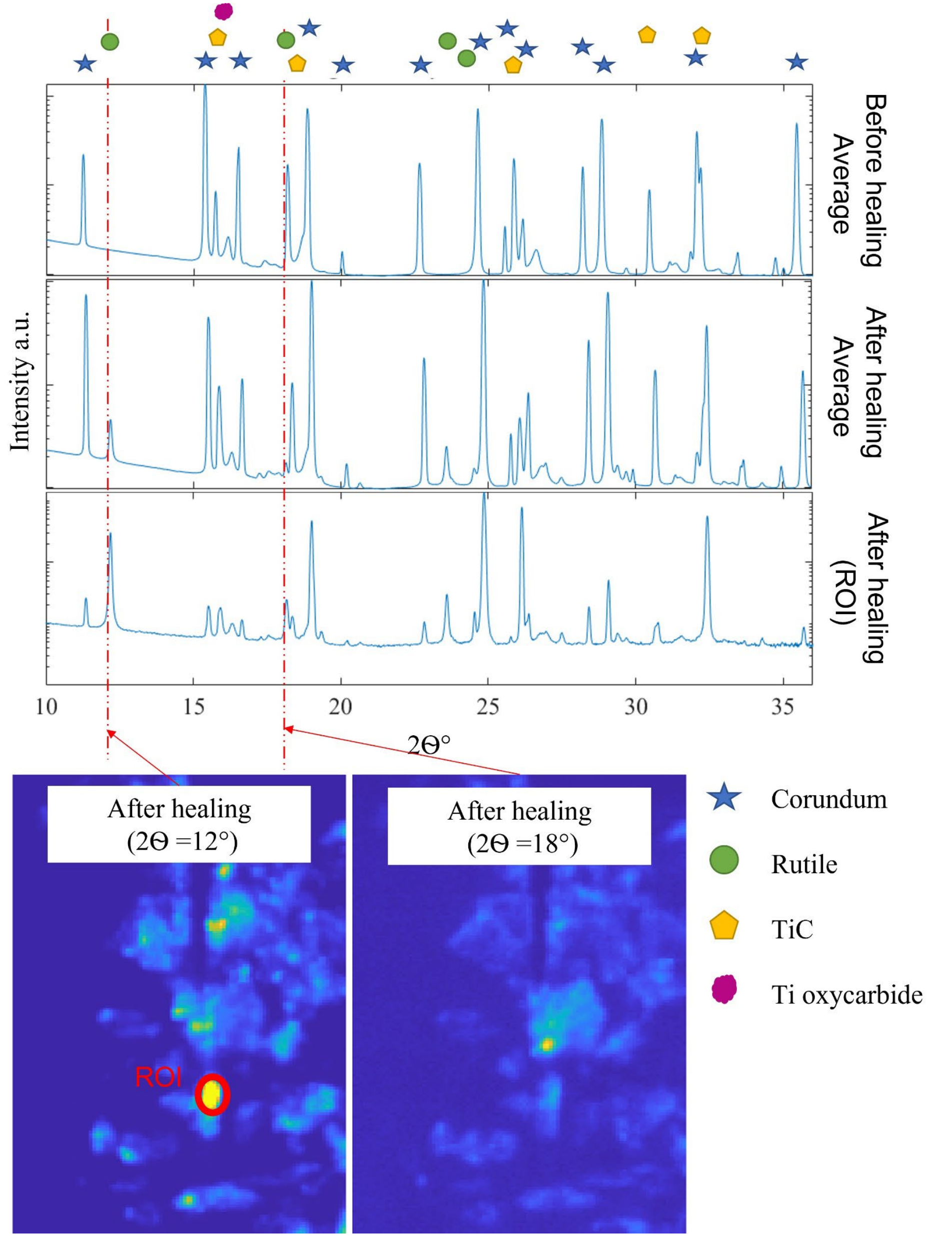




Healing process diffusion and reaction dependent➔ follows Arrhenius equation
Healing seals off oxygen contact
Slow enough healing at low temperatures enables deep penetration of oxygen into the sample

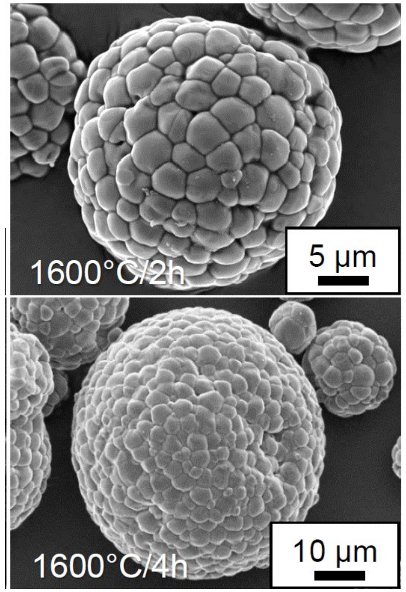
3.2 Healing of AM components

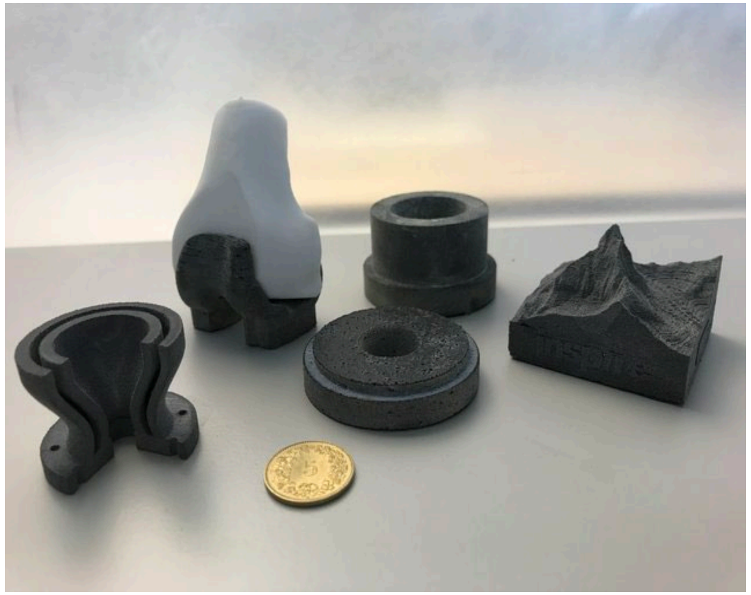




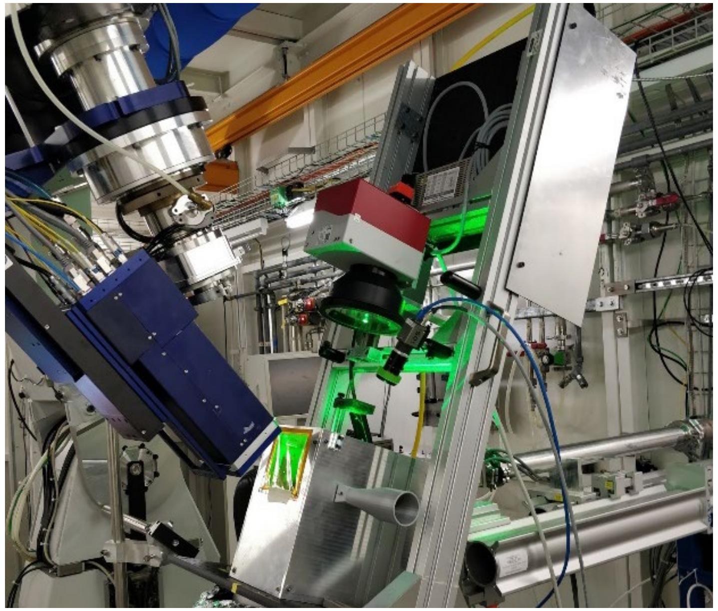
- Crystal are growing within the artificial crack
- Oxide grows as a needle like structure from TiC
- TiC oxidises into rutile

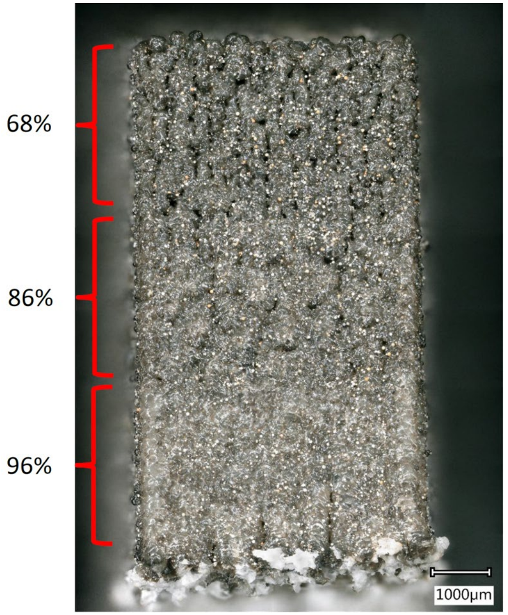
Results of Fuorclam





- 3 PhD theses:
  Stefan Pfeiffer, Kevin Florio, Fabrizio Verga
- 3 directions of Exploration into direct LPBF of Ceramics
  - bimodal particle size distribution with nanoparticles for partial melting
  - ceramic alloying with reduced CTE: addition of
    ZrO2/WO3 → ZrW2O8
    TiO2/Al2O3 → Al2TiO5
  - self healing ceramics: addition of TiC
    TiC + 2O2 → TiO2 + CO2 + volume expansion
- Enabler for creating thick-walled parts in LPBF
- ➔ powder preprocessing is crucial
- ➔ beam wavelength, absorption enabling dopants
- Scientific methodology to observe phase change in situ in LPBF
- Generating a novel methodology to create materials with graded density and strength





- Industrial collaboration are already in place for a successful implementation of the Al_2O_3 – TiC ceramic

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Thank you for your kind attention!
Vielen Dank für Ihre Aufmerksamkeit!
Merci pour votre attention!