



ETH Domain Strategic Focus Area in Advanced Manufacturing
Precision Free Form Manufacturing (PFFM) – TFA 1



Precision Additive Manufacturing of precious metal alloys (PREAMPA)

Academic Partners:

R. Logé (EPFL), C. Leinenbach (Empa), A. Neels (Empa), H. Van Swygenhoven (PSI), J. Löffler (ETHZ), R. Spolenak (ETHZ)

Industry partners :

PX Group, Heraeus Materials, Richemont-Varinor, Swatch-Asulab, Rolex SA, Patek Philippe, Audemars Piguet



Laser Powder Bed Fusion

Project idea and goals

Project idea

- Problems related to **Laser Powder Bed Fusion (LPBF) of precious metals**
 - High reflectivity and high thermal conductivity → **difficult to consolidate**
 - Residual **porosity**
 - Residual stresses in complex parts → **distortion**, cracking
- Optimization of LPBF process and materials and for the additive manufacture of **mm to cm sized precious metal** parts with high **accuracy** and improved **properties** in comparison to conventionally manufactured alloys

- Improvements on :
- **Materials** aspects
 - **Processing** aspects



Panerai ultra-lightweight titanium case, **3D printed**



jewelry

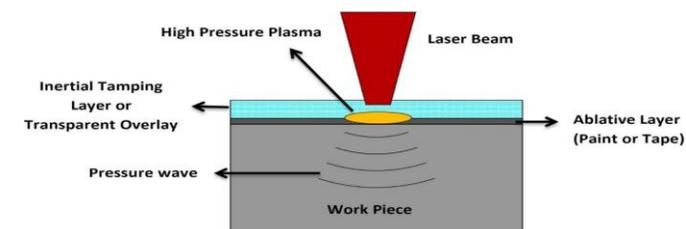
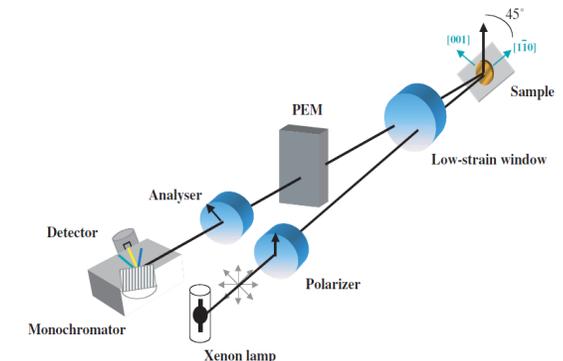
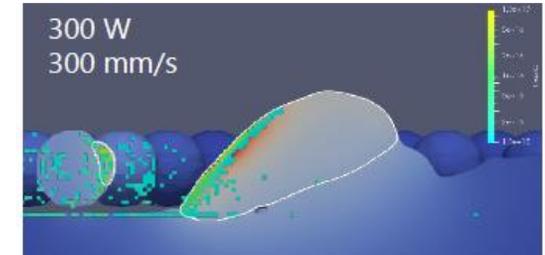
Optimization of **materials** for improved AM processing, and advanced characterization

- Novel **precious metal alloys** (Au, Pt based) with improved corrosion, wear resistance and strength.
 - Standard alloys : **316L steel, Cu and Cu-bronze, red gold (5N)**
 - High entropy alloy (**HEA**) : **Pt-Pd-Rh-Ir-Cu-Ni**
 - Bulk metallic glasses (**BMGs**) : **Zr-based AMZ4, Pd-based**

- Development of **sacrificial coatings** on powder particles for improved **absorptivity**

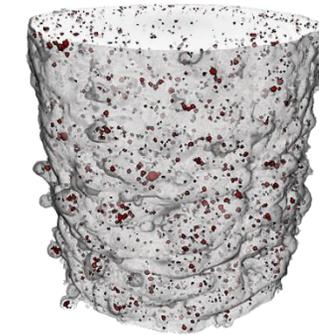
Optimization of AM **processing** for precious metal alloys

- Optimization of **conventional Laser Powder Bed Fusion (LPBF)** process
- Integration of lasers with **different wavelengths** (**green** and near-IR)
 - Better regulation of heating
 - Improvement of porosity content
- Integration of **monitoring** techniques
 - Residual stress measurement by Reflective Anisotropy Spectroscopy (RAS)
- Combination LPBF + **Laser Shock Peening (LSP)**
 - Control of residual stresses and cracking



Advanced *in situ* and *ex situ* characterization

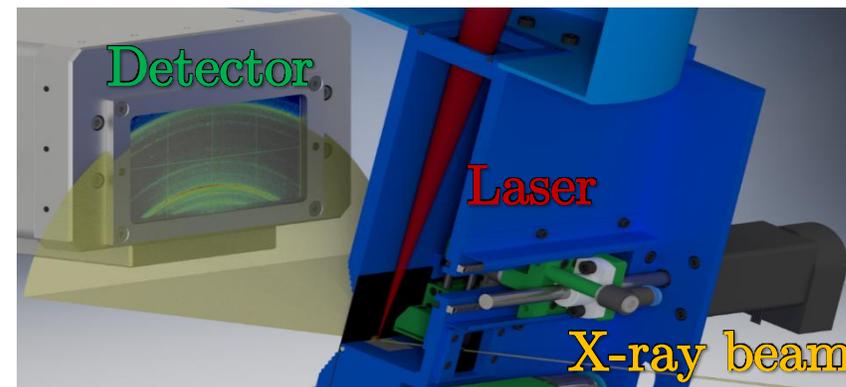
- 2D / 3D characterization (X-Rays & neutrons)
 - Porosity
 - Residual stresses
 - Phases in red gold or HEA, crystallites in BMGs



Porosity

- *Operando* LPBF (Synchrotron high energy X-Rays) at PSI

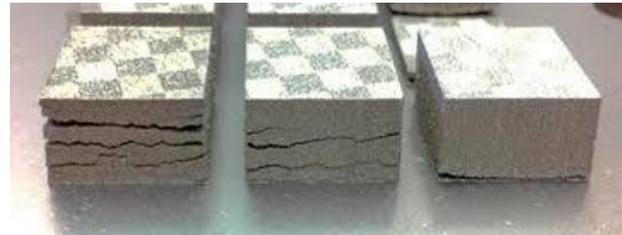
Probing material phases
and local temperature



48 months global objectives

Laboratory samples + parts representative of the challenges faced by the watch industry, with the following features :

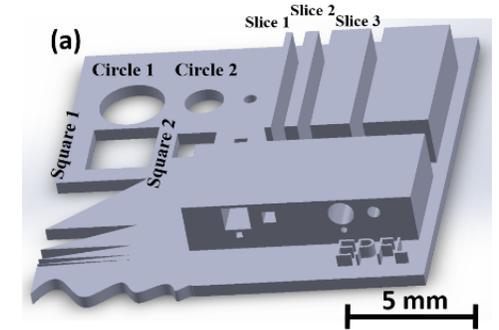
- **Hardness** > reported previously for standard PM alloys
- **Hardness** > 300 HV for **BMGs** and **HEAs**.
- Minimum **porosity** content, final target < 0.5%
- Absence of **cracks**
- **Strain to failure** > 1 to 2 %



Cracks



Simple geometries



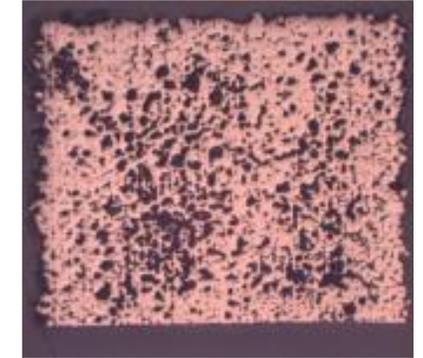
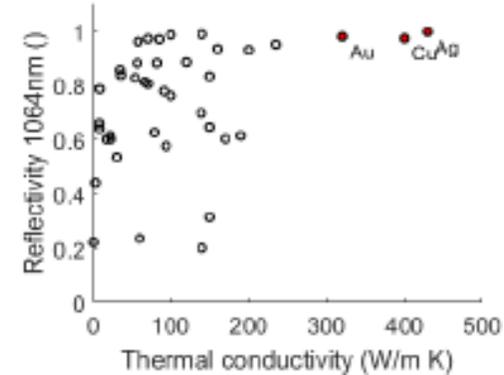
Watch industry benchmark

Achievements

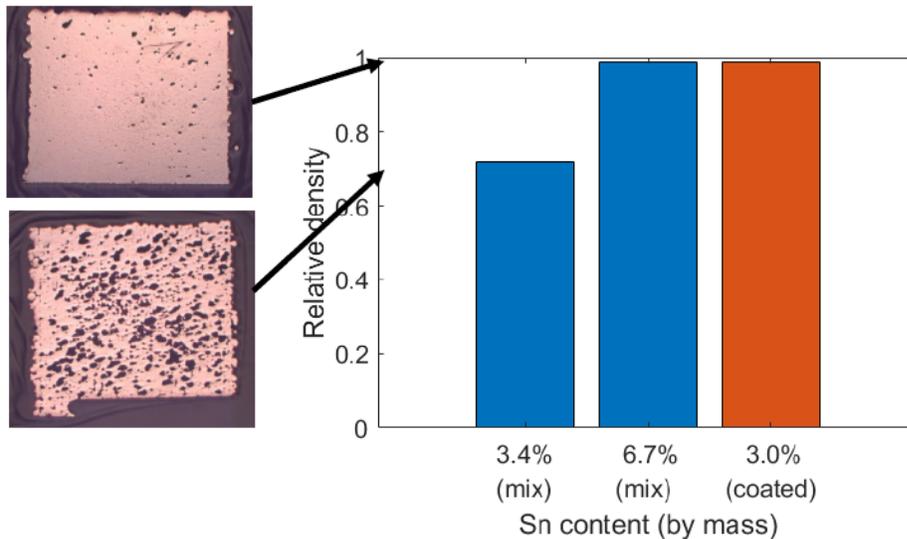
Standard alloys : understanding pore formation in Cu (model material) and development of defect mitigation strategies (PhD thesis V. Lindström, Empa)

- Reflectivity and thermal conductivity are very high
- This leads to **balling defects**, due to too low energy input
- Thermal conductivity needs to be kept high for most applications

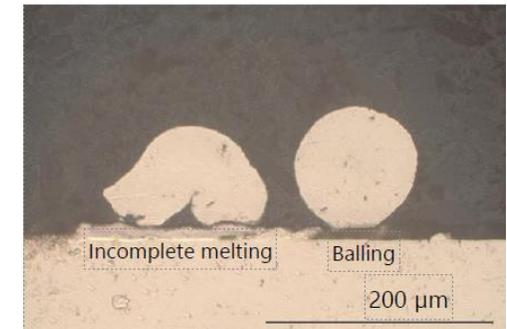
1. *Coating powders for lower reflectivity and lower thermal conductivity*



Balling



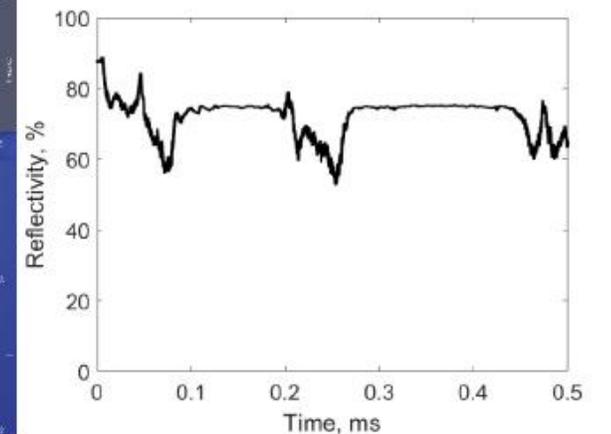
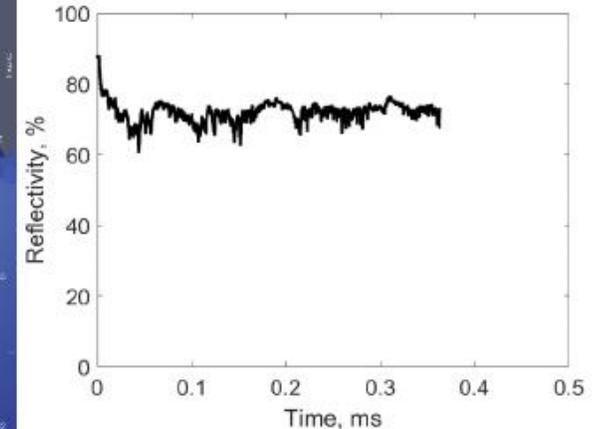
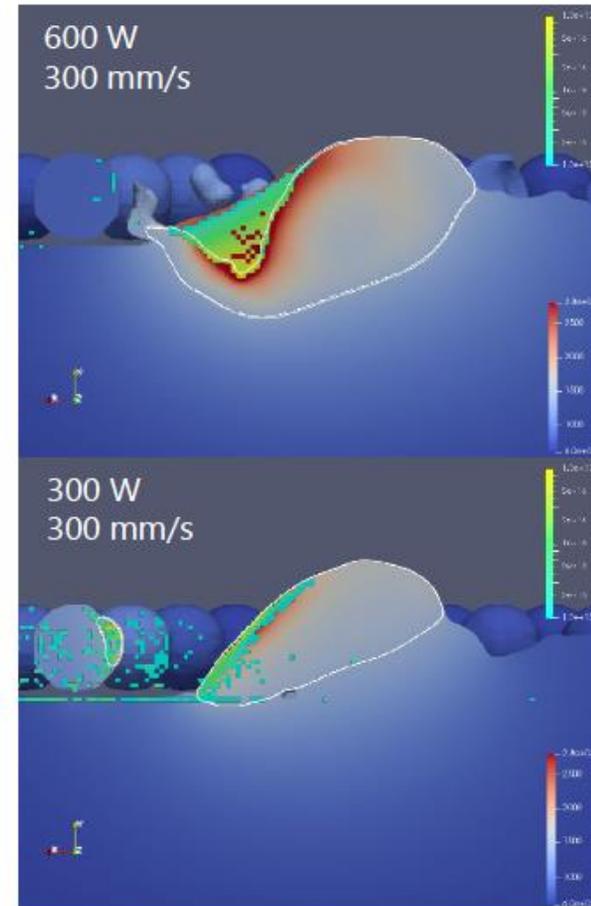
Coated powders
→ less porosity
compared to powder
mixtures of similar
composition



Standard alloys : understanding pore formation in Cu (model material) and development of defect mitigation strategies (PhD thesis V. Lindström, Empa)

1. Coating powders for lower reflectivity and lower thermal conductivity

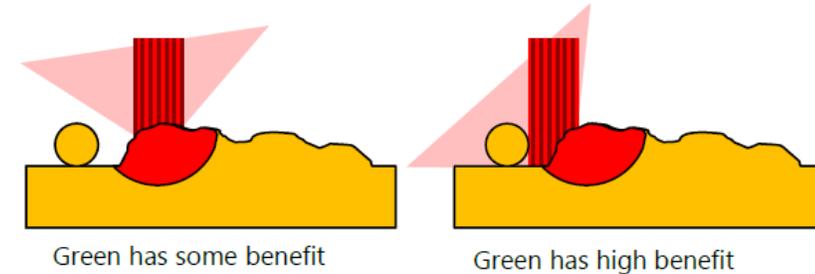
- Melt pool CFD simulations (OpenFoam)
 - High power : laser mainly on melt pool
 - Lower power : laser reflected on the powder bed
- Pre-heating of powders, enhanced with coating



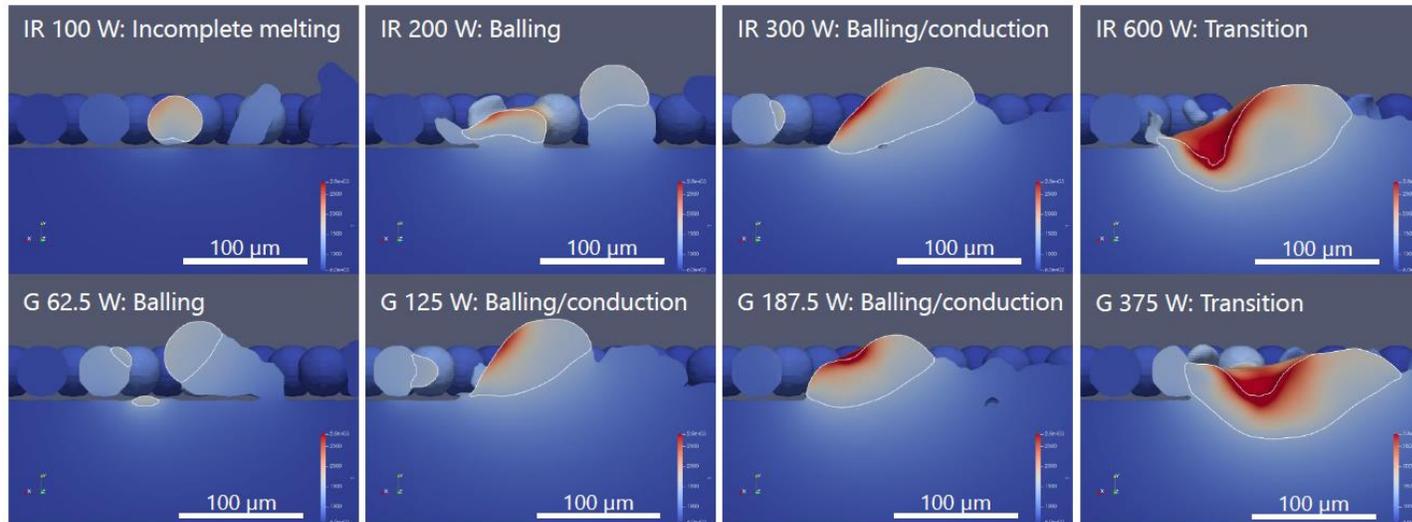
Standard alloys : understanding pore formation in Cu (model material) and development of defect mitigation strategies (PhD thesis V. Lindström, Empa)

2. Green laser - another path for balling reduction

- Lower reflectivity
- Lasers and optics more expensive
- Benefit of green laser is determined by if laser shines on liquid or on powder



IR
green

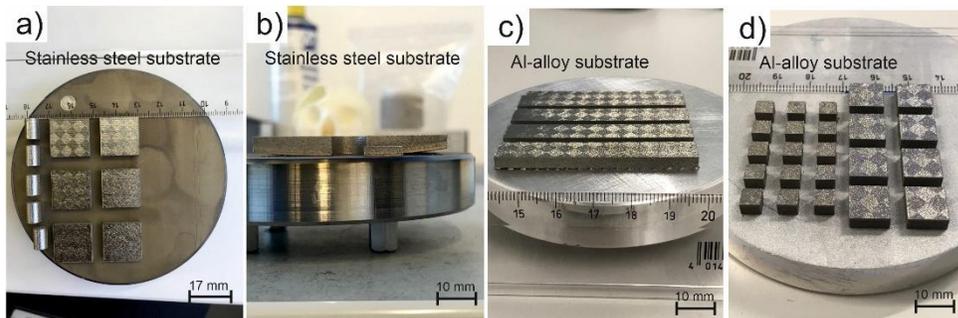


~40% lower power needed with green laser at high power

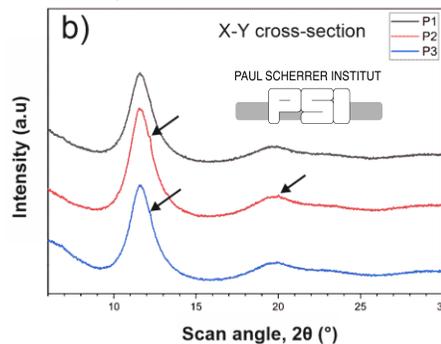
LPBF of Zr-based Bulk Metallic Glass (Zr-BMG)

PhD N. Sohrabi, EPFL & Postdoc G. Kurtuldu, ETHZ

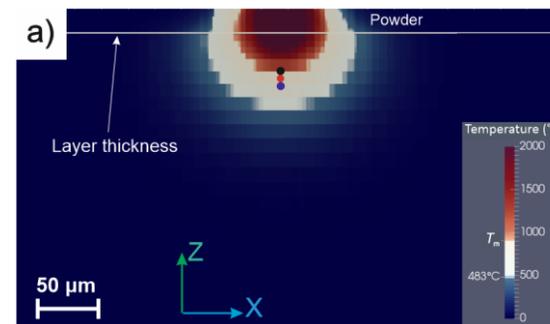
Printed parts (substrate !)



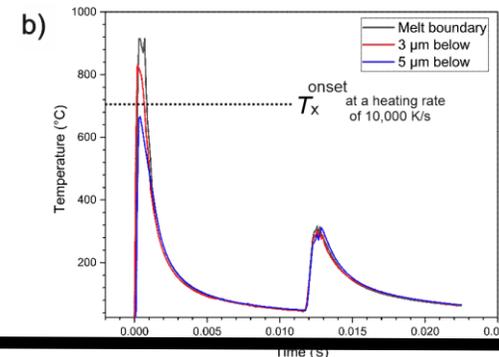
Synchrotron



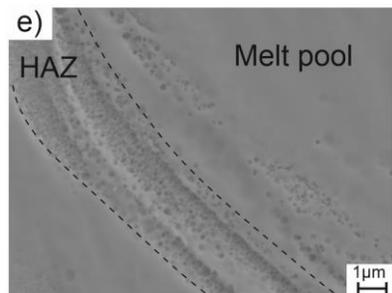
FE simulation



FE simulation



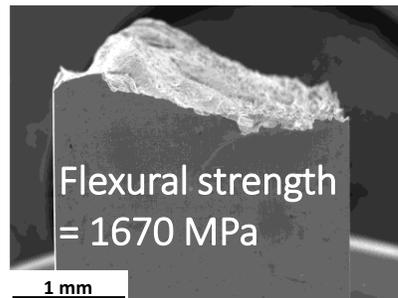
FESEM



The width of the crystallized region is around 3 μm

N. Sohrabi, J. Jhabvala, R. Logé
EPFL-LMTM

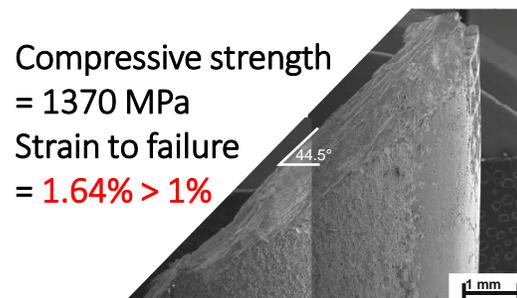
3-point bending



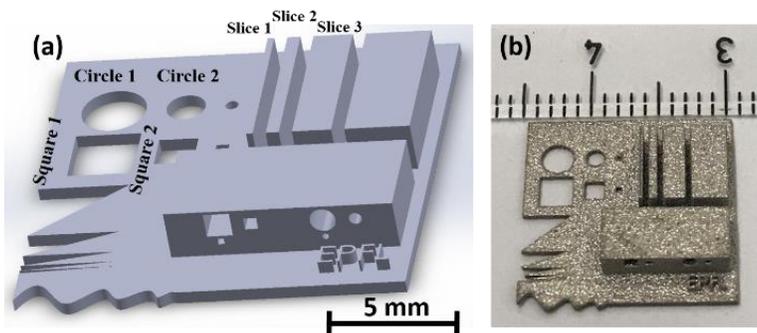
Hardness (HV2) = 455 > 300

The accuracy was at least 40 μm.

Compression



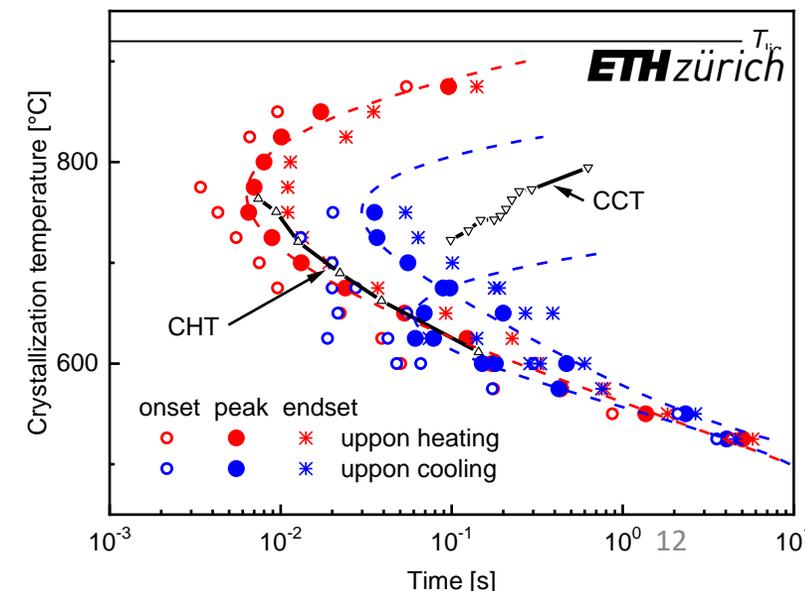
Benchmark



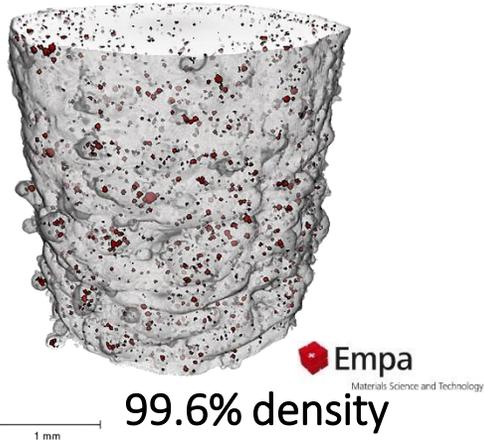
Time-Temperature-Transformation (TTT) diagrams

Using fast differential scanning calorimetry (FDSC)

J. Schawe, G. Kurtuldu, J. Löffler (ETHZ-LMPT)

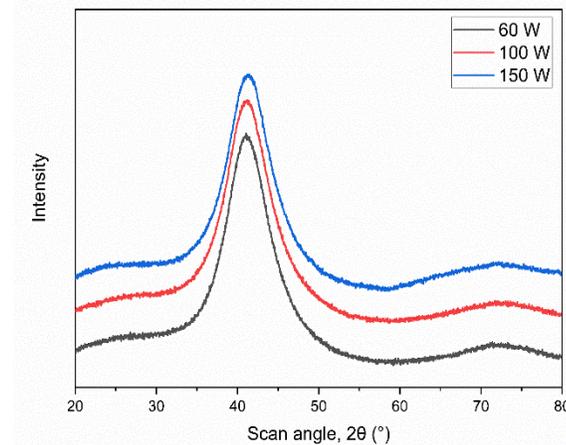


X-ray tomography

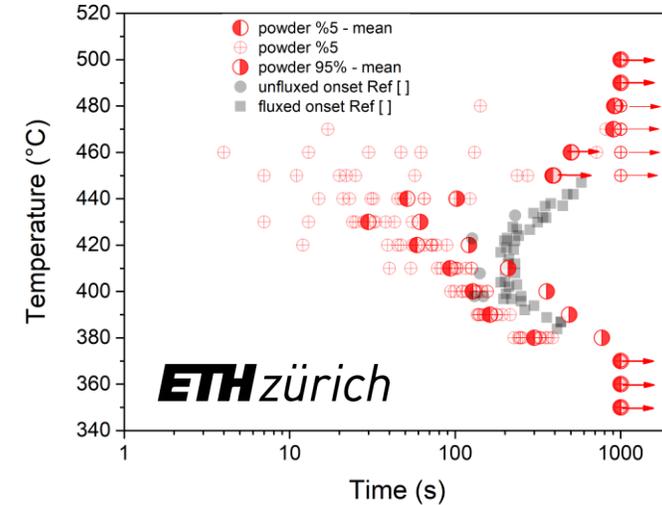


Annapaola Parrilli (Empa-CXA)

XRD



FDSC



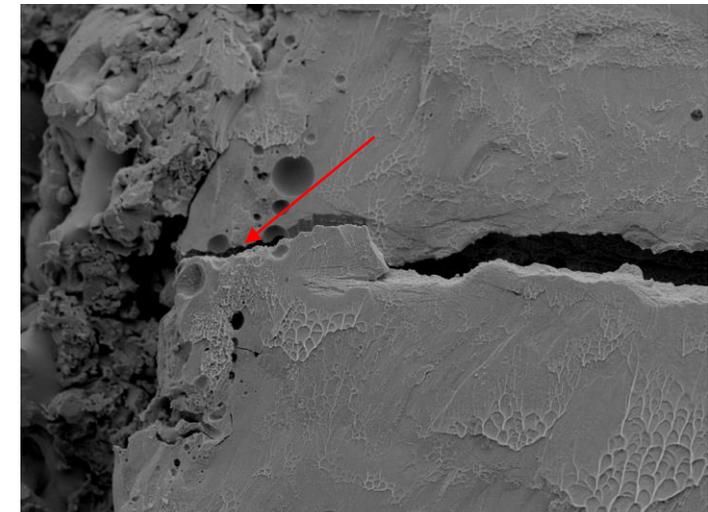
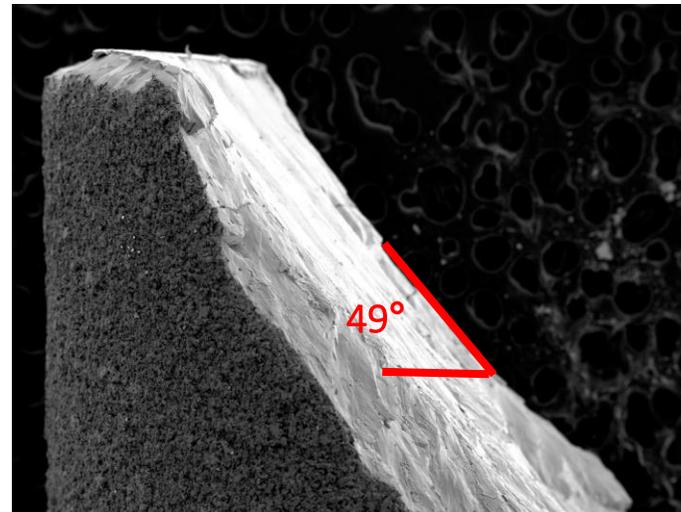
G. Kurtuldu,
J. Löffler
(ETHZ-LMPT)

Hardness (HV1)= 498 > 300

Compressive strength= 1140 MPa

Strain to failure= 1.17% > 1%

N. Sohrabi et al., Applied Materials Today, 2021

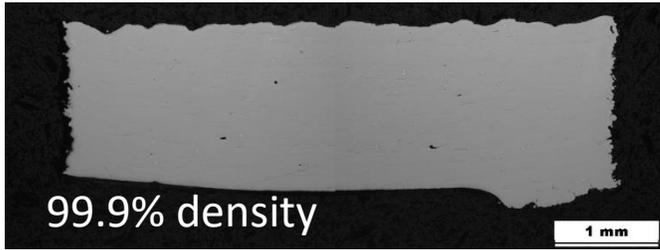


Lower than expected, due to the presence of porosities

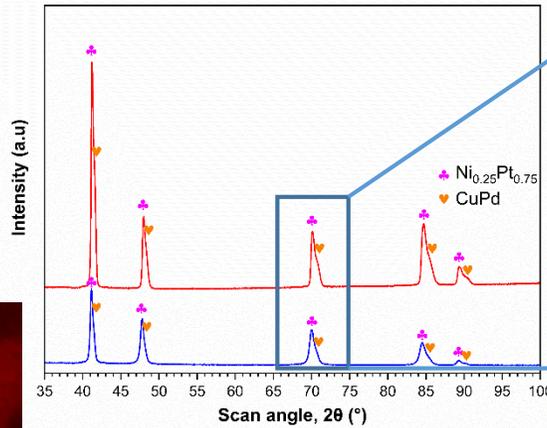
LPBF of a precious (Pt-Pd-Rh-Ir-Cu-Ni) High Entropy Alloy

PhD N. Sohrabi, EPFL

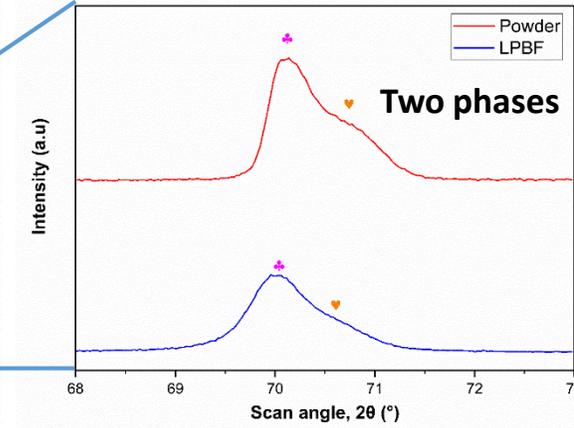
OM



XRD

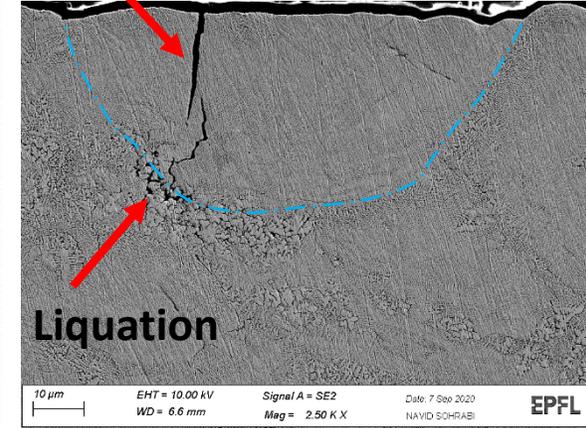


XRD

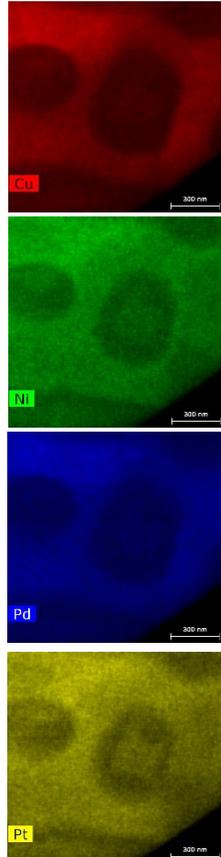
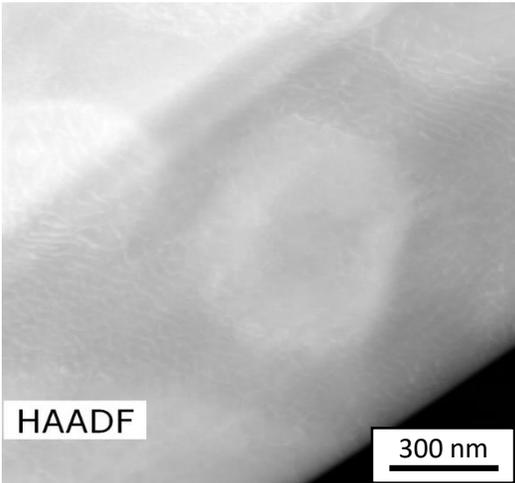


Solidification

FESEM

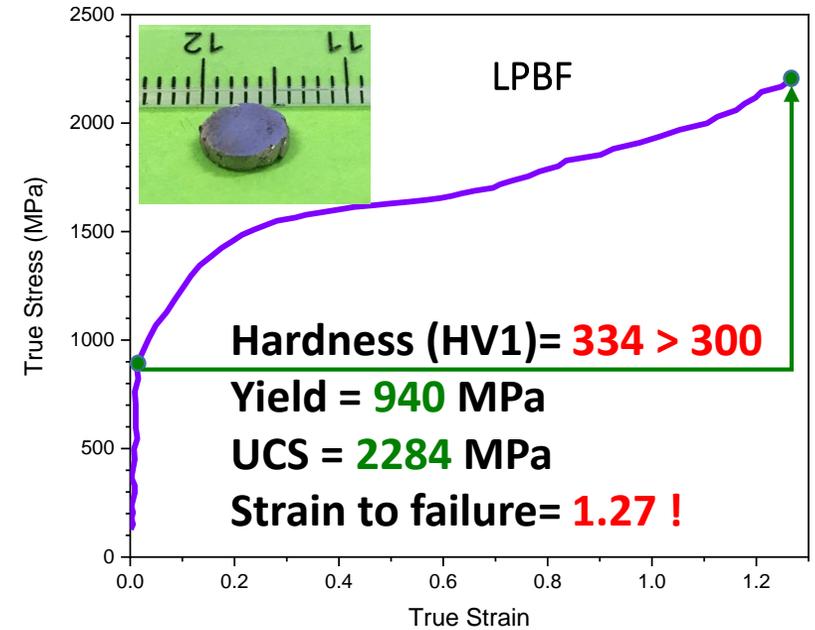
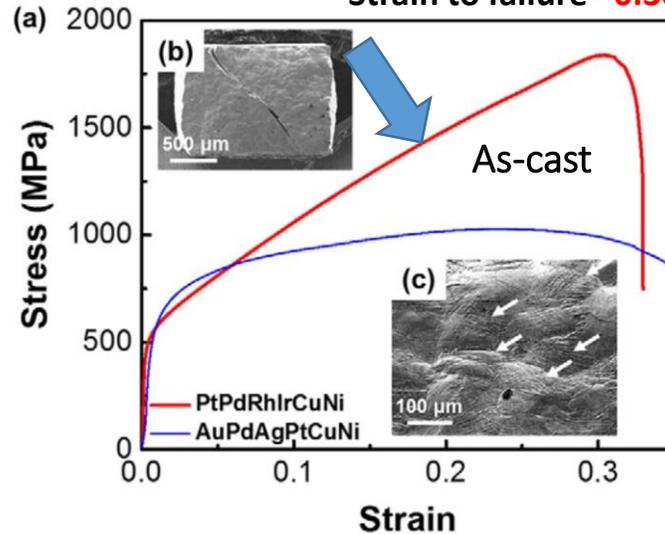


STEM



Compression test

Yield= 527 MPa
Ultimate= 1839 MPa
Strain to failure= 0.30

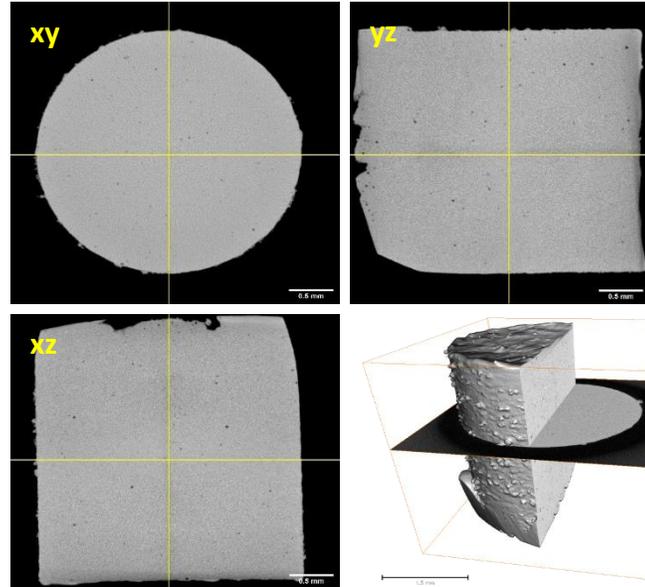


Advanced *in situ* and *ex situ* characterization

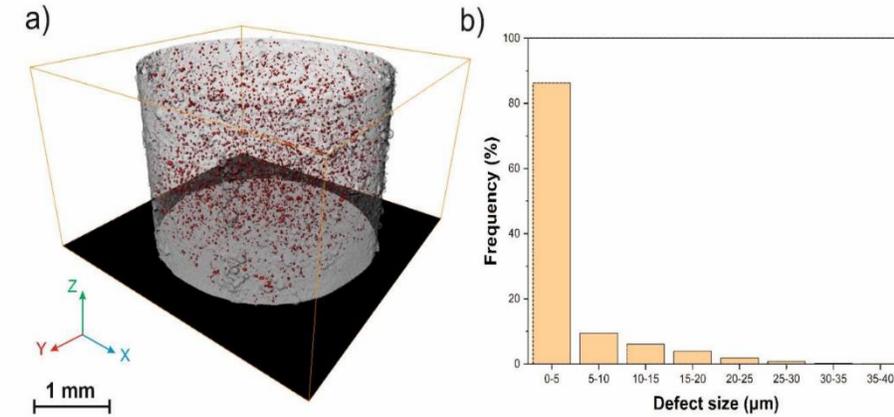
X-ray diffraction and micro-CT analysis - Empa CXA (A. Neels, A. Parrilli)

Analysis on:

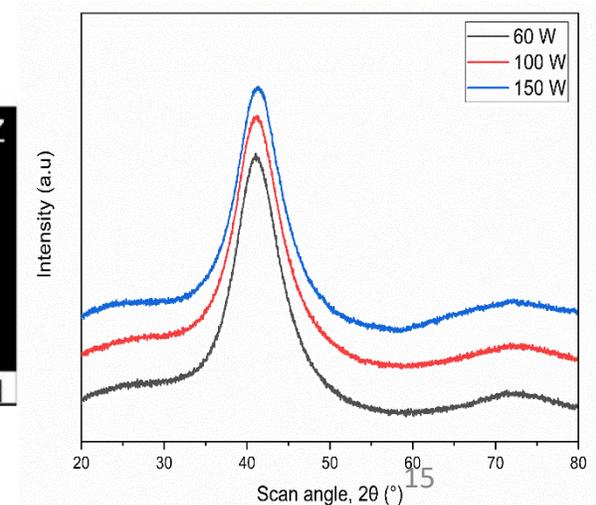
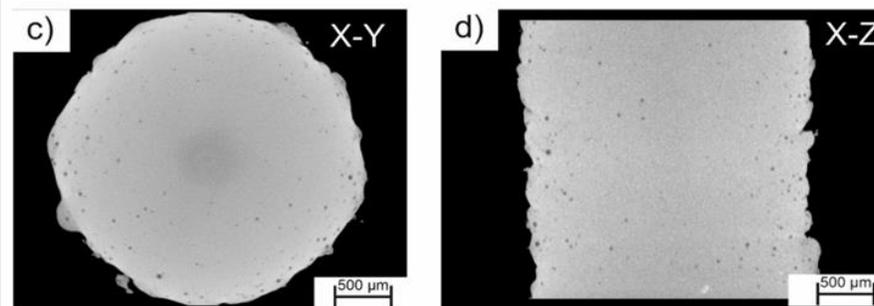
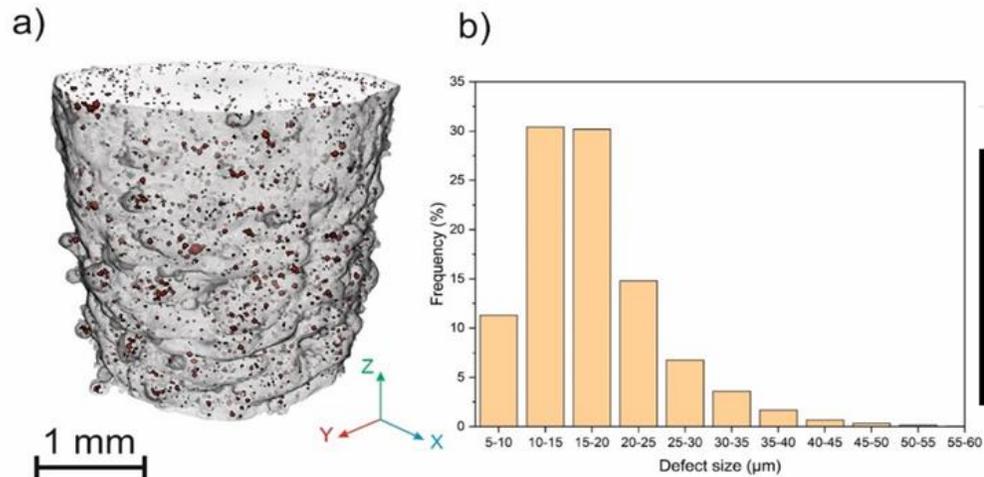
- Porosity
- Cracks
- Pore size distribution
- Pores localization
- Crystallinity



Zr-based BMG



Pd-based BMG

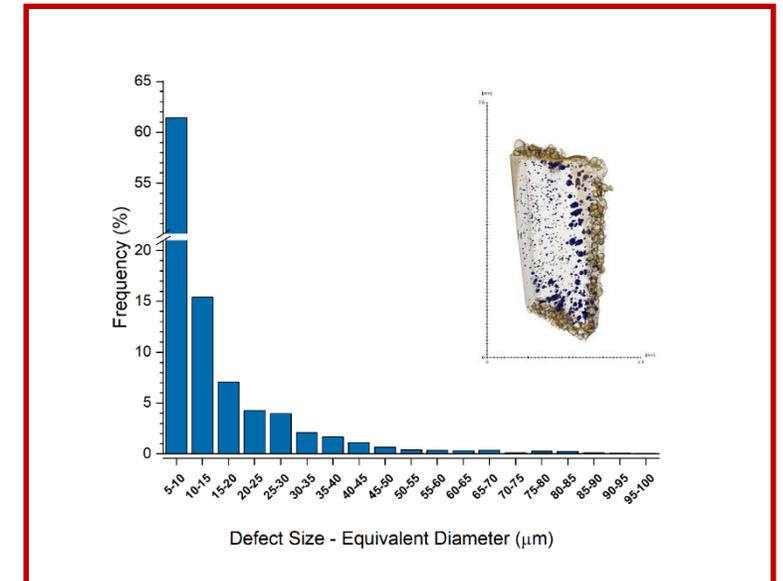
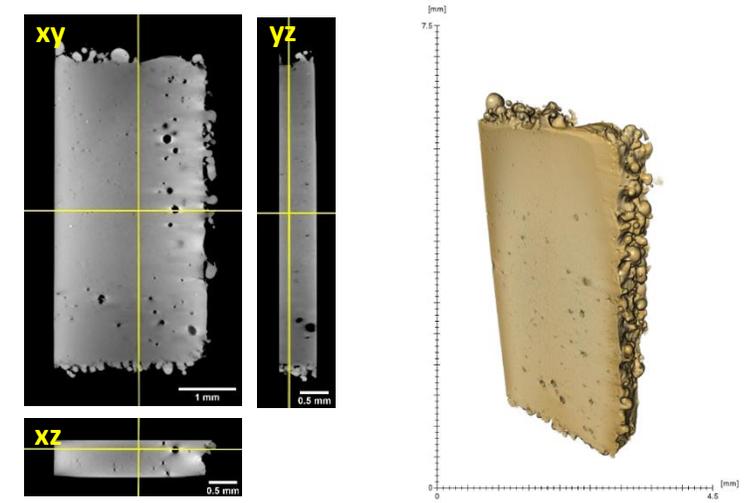
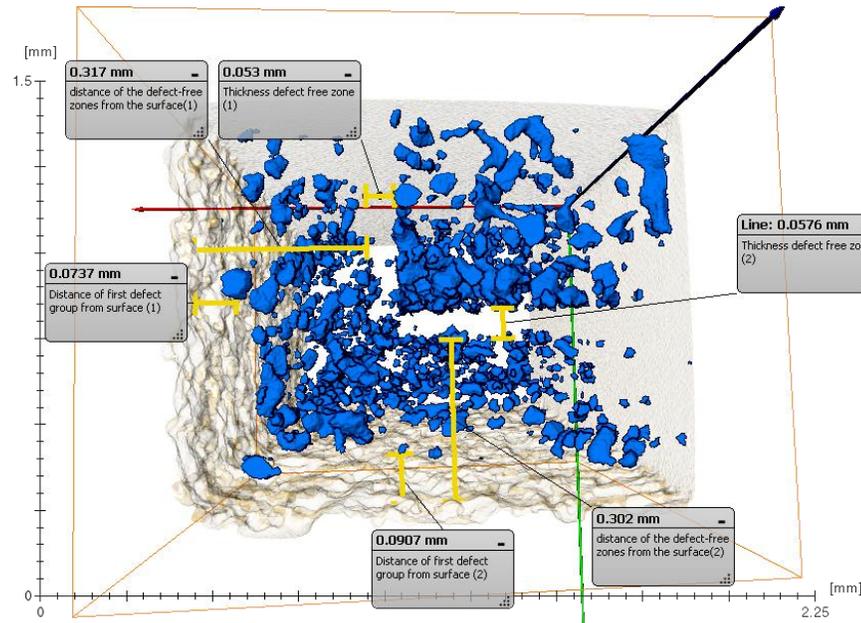
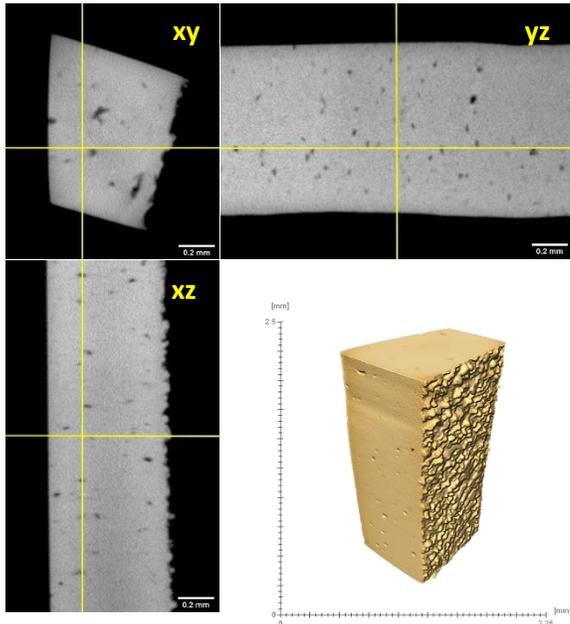


Advanced *in situ* and *ex situ* characterization

X-ray micro-CT analysis - Empa CXA (A. Neels, A. Parrilli)

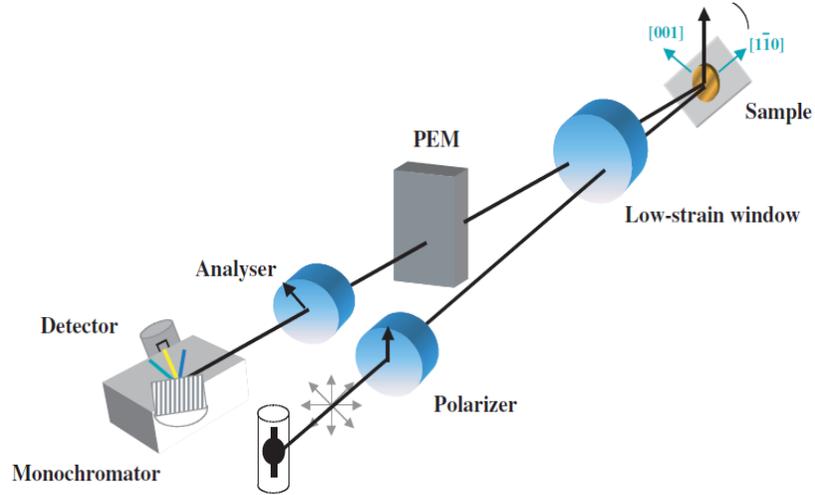
Gold Alloys

Image x-ray CT analysis and image processing protocols setup development for the porosity quantification and localization



Optimization of processes - Reflectance Anisotropy Spectroscopy (RAS)

Stresses and phase sensitivity – PhD M. Volpi, ETHZ

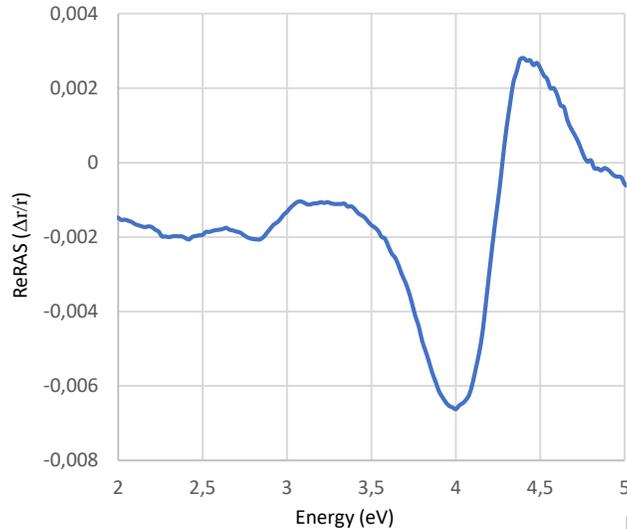


$$\frac{\Delta r}{r} = \frac{2(r_s - r_p)}{r_s + r_p}$$

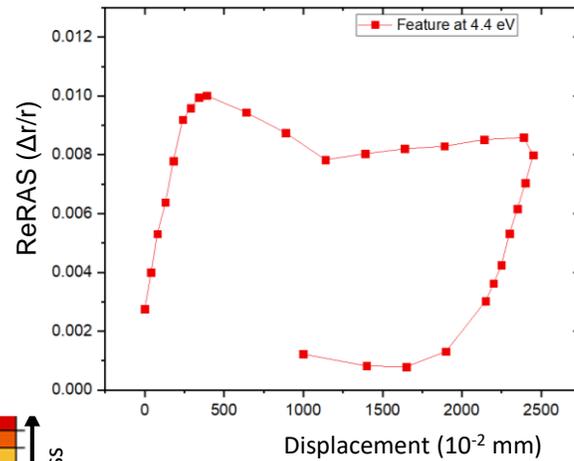
$$= \frac{\Delta \epsilon}{\sqrt{\epsilon}(\epsilon - 1)}$$

$$\delta \epsilon_{ij} = W_{ijkl} * \epsilon_{kl}$$

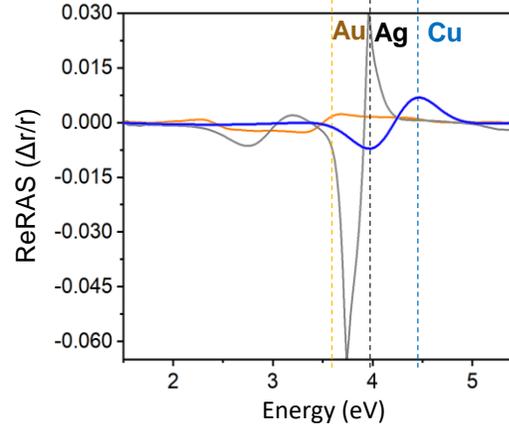
Pure Cu - RAS



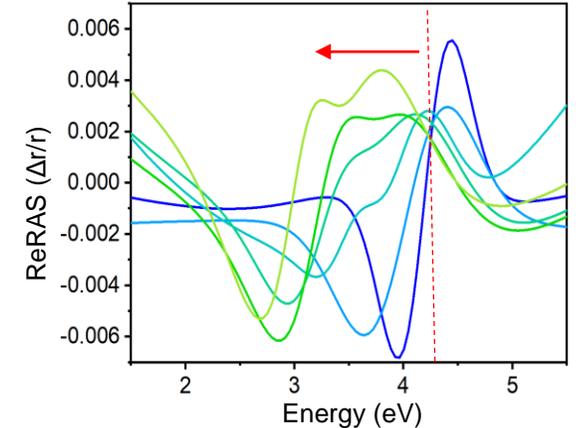
Mechanical sensitivity



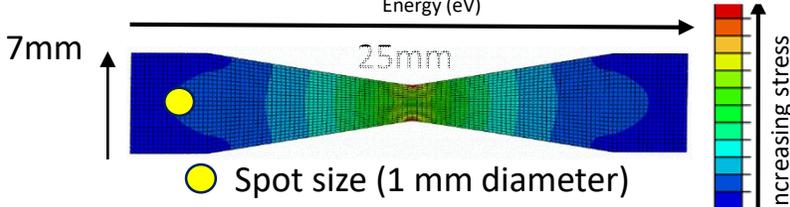
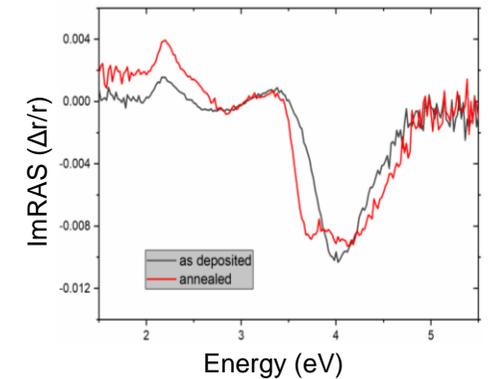
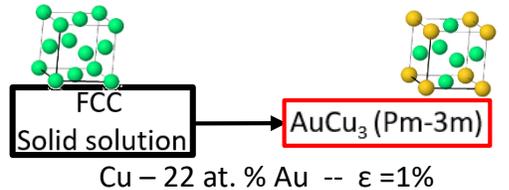
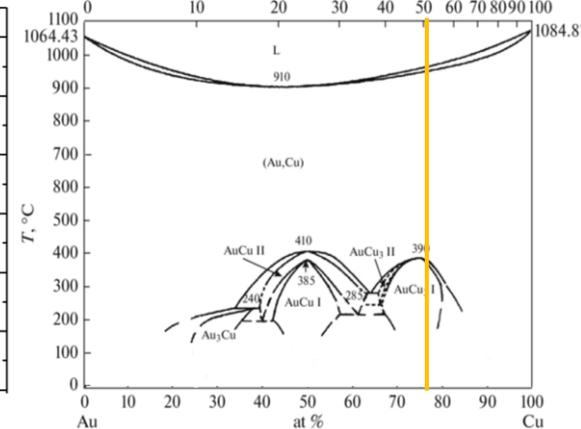
Element sensitivity



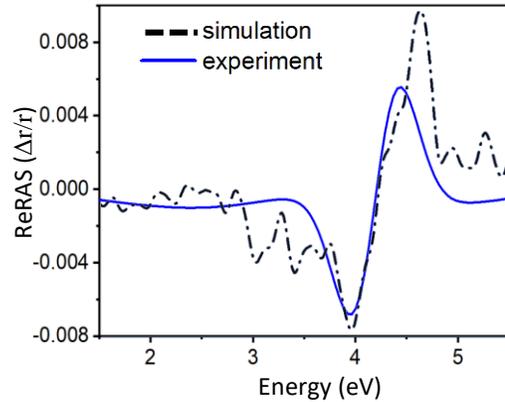
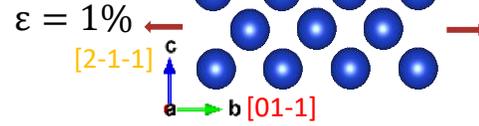
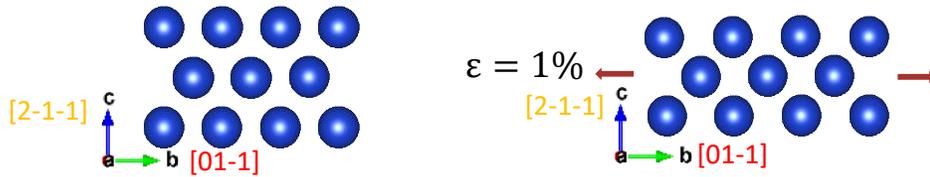
Composition sensitivity: Cu-Zn alloy



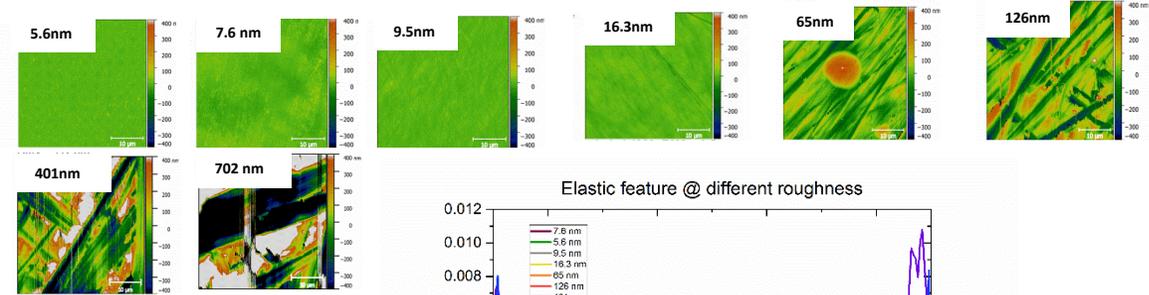
Chemical order sensitivity



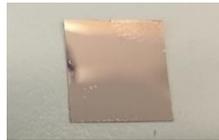
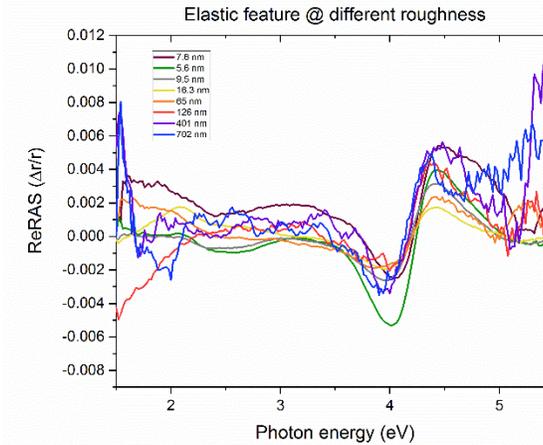
Reflectance Anisotropy Spectroscopy (RAS) and ab-initio simulations - PhD M. Volpi, ETHZ



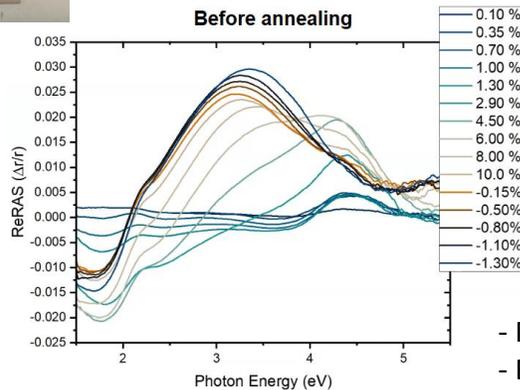
- **Strain sensitive feature is a bulk related effect!**



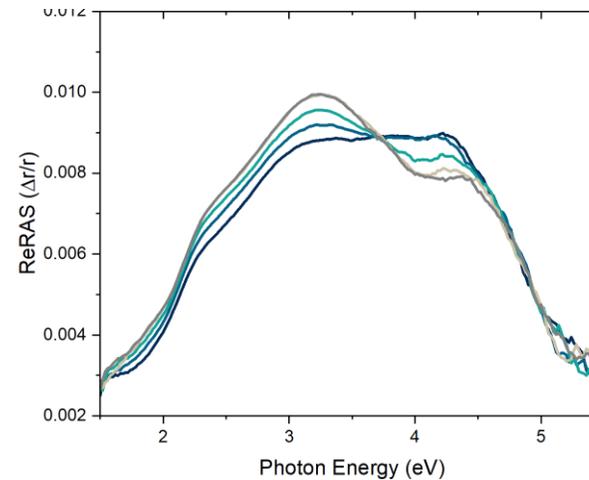
- **Roughness does not hinder the feature**
- **Higher roughness -> signal-to-noise ratio drops**



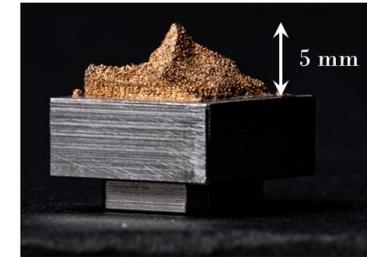
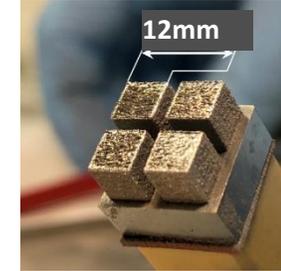
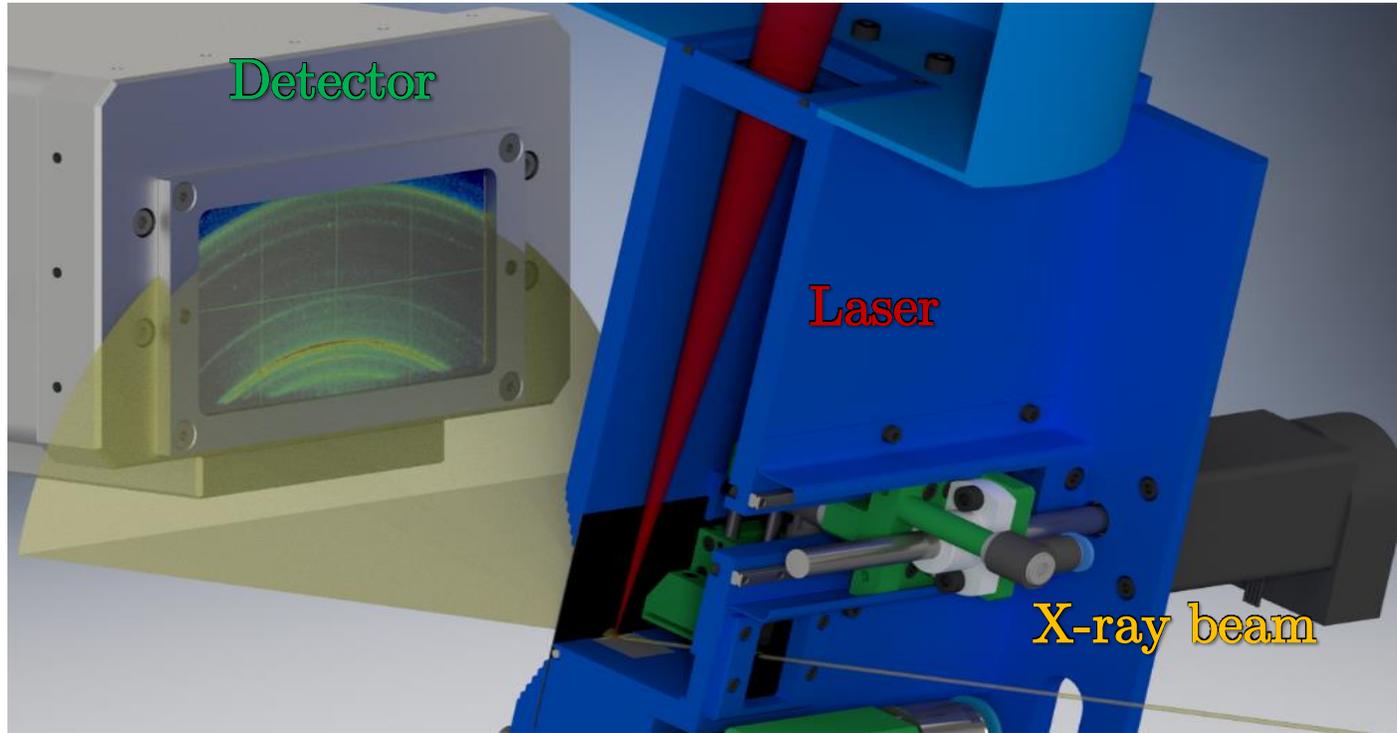
Thin Film Cu – 8 wt% Sn



- Mechanically polished
- BIB



- **Fast residual stress mapping**
- **Cannot be extended to a 3D printer yet due to sample roughness**



Matterhorn from STL file

PREAMPA

Samy Hocine (PhD EPFL), Steven Van Petegem, Charlotte de Formanoir, Cynthia Chang, T. Maimaityli, Helena Van Swygenhoven

Beamline scientists:

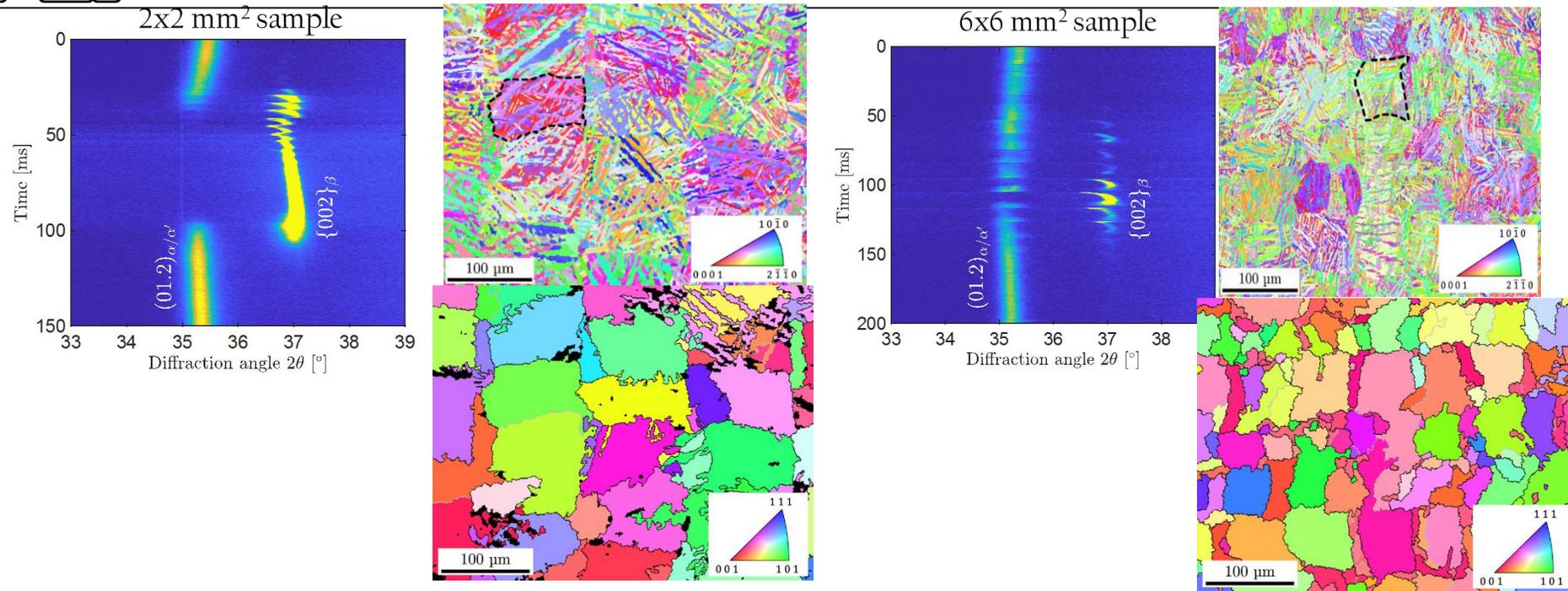
MicroXAS: Daniel Grolimund, Dario. Ferreira Sanchez

MS Nicola Casati

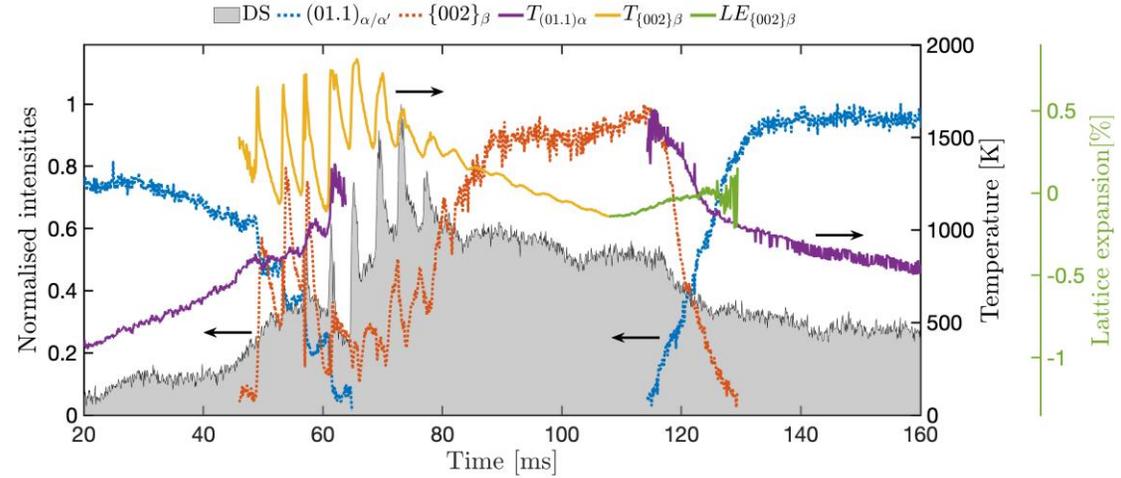
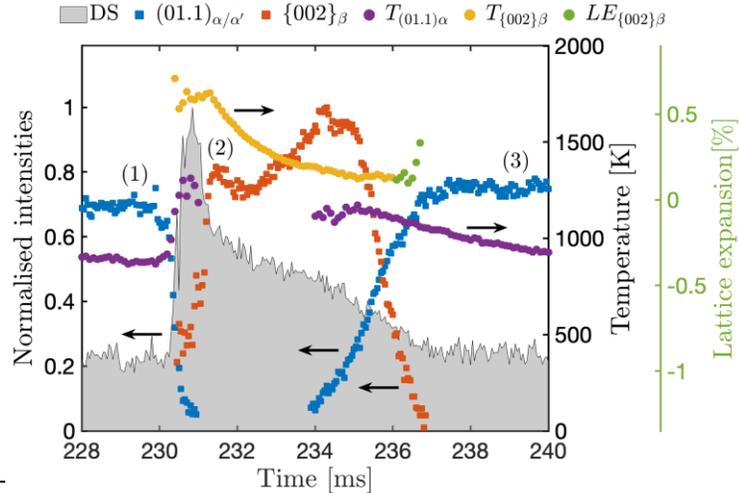
Detector group

Gemma Tinti

Role of scanning vector length in Ti6Al4V



β phase lasts **7 ms** for the **6 mm** scanning vector
 β phase lasts **84 ms** for the **2 mm** scanning vector

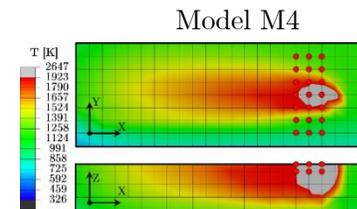
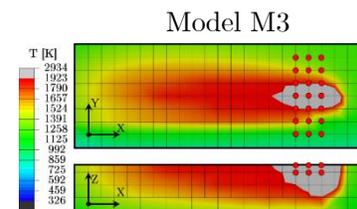
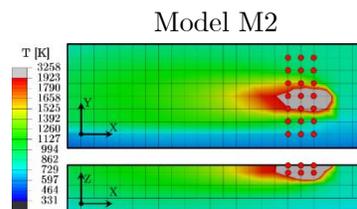
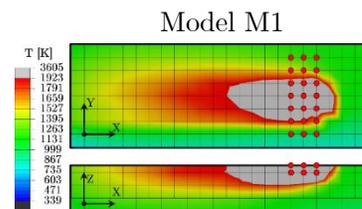
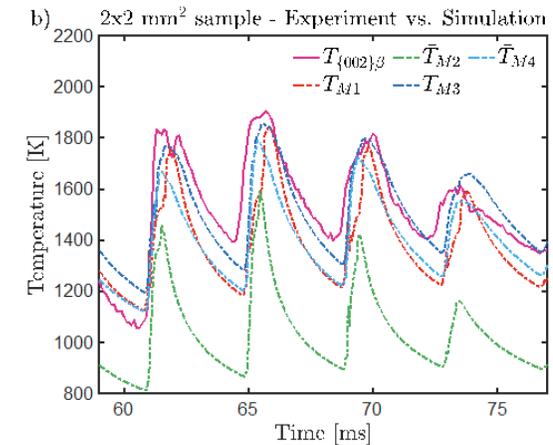
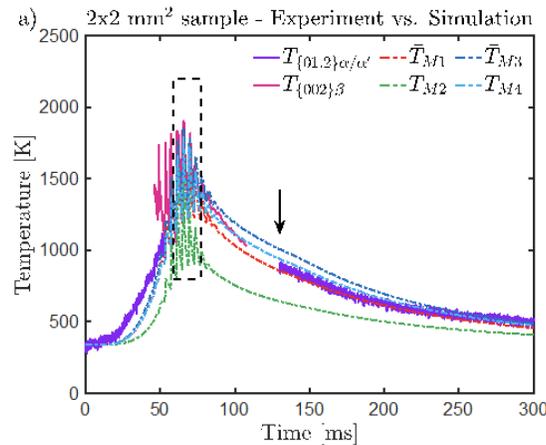
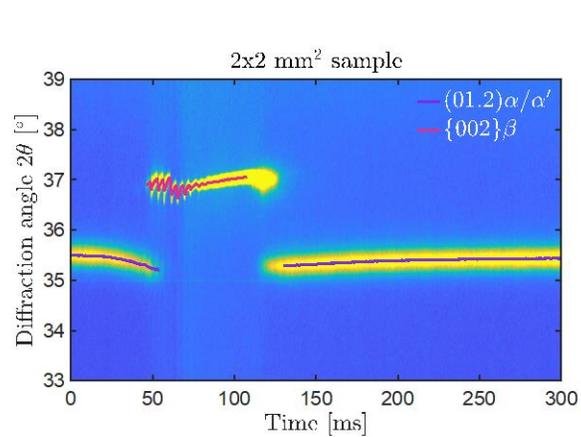


Parameters	M1 [Zhang et al. 2019]	M2 [Mirkoohi et al. 2019]	M3 [Ali et al. 2018]	M4 [Ali et al. 2018]
Laser heat flux	Ellipsoid	Double ellipsoid	Cylindrical + Parabolic	Cylindrical + Parabolic
Absorption	55%	55%	60%	60%
Convection losses	20 W/m ² .K	20 W/m ² .K	20 W/m ² .K	20 W/m ² .K
Radiation losses	Accounted	Accounted	Ignored	Accounted
Material properties	[Mills 2002]	[Mills 2002]	[Mills 2002] Enhanced k	[Mills 2002] Enhanced k

M3 and M4 enhanced k

$$k^*(T) = \lambda * k(T) \text{ with } \lambda = \begin{cases} 1 & \text{if } T < T_{melt} \\ 4 & \text{if } T > T_{melt} \end{cases}$$

to account for Marangoni convection inside melt pool



Achieved project objectives

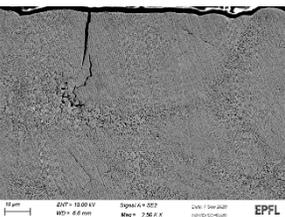
Laboratory samples + parts representative of the challenges faced by the watch industry, with the following features :

- **Hardness** of PM alloys > **300 HV**
- Minimum **porosity** content, final target < **0.5%**
- Absence of **cracks**
- **Strain to failure ϵ_f** > **0.01 to 0.02**

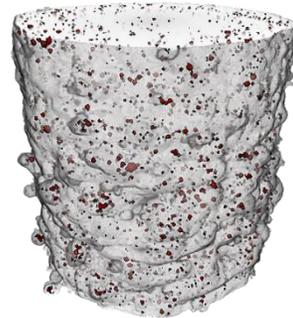


**Pt-Pd-Rh-Ir-Cu-Ni
High Entropy Alloy**

0.1 % porosity
334 HV
UCS 2.28 GPa
 $\epsilon_f = 1.27 !!$

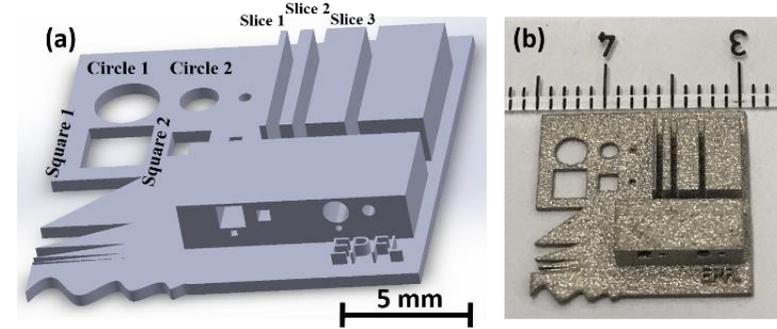


Cracks :
improved by
LSP

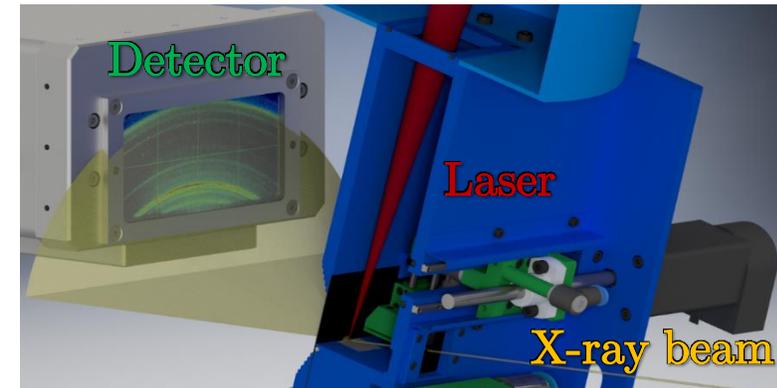


Pd-BMG

0.4 % porosity
498 HV
 $\epsilon_f = 0.012$



Watch industry benchmark
Zr-BMG : 455 HV
Geometrical accuracy at least 40 μm



Operando LPBF printing at Synchrotron

Publications (peer reviewed journals)

1. G. Kurtuldu et al., Proceedings of the National Academy of Sciences, 115 (2018), 6123-6128.
2. S. Hocine et al., Materials Today 34 (2020), 30-40.
3. S. Hocine et al., Additive Manufacturing 34 (2020) 101194.
4. V. Lindström et al., Materials 13.16 (2020): 3493.
5. N Sohrabi et al., Surface and Coatings Technology 400 (2020), 126223.
6. W. Yan et al., Nature Nanotechnol. 15 (2020) 875 – 882.
7. G. Kurtuldu, J. F. Löffler, Adv. Sci. 7, 1903544 (2020) 1 – 7.
8. S. Hocine, H. Van Swygenhoven, S. Van Petegem, Additive Manufacturing 37 (2021) 101747
9. M. Chen et al., Operando quantification of thermal cycles along the build direction during laser powder bed fusion of Ti-6Al-4V. Additive Manufacturing, in review
10. N Sohrabi et al., Materials, 2021, 14(19), 5627
11. N Sohrabi et al., Applied Materials Today, 2021, 24, 101080
12. N. Sohrabi, J. E. K. Schawe, J. Jhabvala, J. F. Löffler, R. E. Logé (2021), Scr. Mater. 199, 113861
13. N Sohrabi et al. (2021), Metals, 11(7), 1064
14. N. Sohrabi, J. Jhabvala, G. Kurtuldu, M. Stoica, A. Parrilli, S. Berns, E. Polatidis, S. Van Petegem, S. Hugon, A. Neels, J. F. Löffler, R. E. Logé (2021), Materials and Design, 199, 109400
15. N. Sohrabi, J. Jhabvala, R.E. Logé (2021), Metals 11, 8, 1279.
16. M Volpi, S Beck, A Hampel, H Galinski, A Sologubenko, R Spolenak, Sensing strain-induced symmetry breaking by reflectance anisotropy spectroscopy, Applied Physics Letters 119 (15), 151602
17. M. Volpi, R. Spolenak, A. Sologubenko, Structural ordering in Cu-Au thin films by Reflectance Anisotropy Spectroscopy and Transmission Electron Microscopy, to be submitted to JMR.

PhD theses

1. S. Hocine (2020), **Operando X-ray diffraction during laser 3D printing: from machine design to experiments and computer simulations**, PhD thesis EPFL TH8326.
2. M. Volpi (2021), **Reflectance Anisotropy Spectroscopy as a tool for characterization of additively manufactured precious alloys**, PhD thesis ETHZ, <https://doi.org/10.3929/ethz-b-000510774>
3. N. Sohrabi (2021), **Laser powder bed fusion of Metallic Alloys with Enhanced Microstructures and Properties**, PhD thesis EPFL 9034.
4. V. Lindström (2021), **Defect formation and mitigation during laser powder bed fusion of copper**, PhD thesis EPFL 9050,