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Development of an austenitic/martensitic gradient steel connection by additive manufacturing

Dr. Flore Villaret
EDF/CEA, France

15 December 2021

NEA Nuclear Energy Agency

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Meet the Presenter

Dr Flore Villaret recently completed her PhD at the French Atomic Energy Commission (CEA) in the field of materials sciences (metallurgy). She is now a research engineer at the R&D Department of Electricité de France (EDF). She works on developing additive manufacturing of metal components for energy applications such as nuclear reactors and hydraulic power generation. She is also vice president of the French metallurgy and material society young division.

She won the 2021 “Pitch your Gen IV Research” competition with a very creative and original video presenting her PhD work in additive manufacturing metallurgy for Gen IV reactors (available at https://www.youtube.com/watch?v=v2IiEHMVyGc). She was also awarded by the French metallurgy and material society with the Bodycote best PhD thesis award.

Email: flore.villaret@edf.fr

Examples of materials for nuclear reactors

Austenitic steels

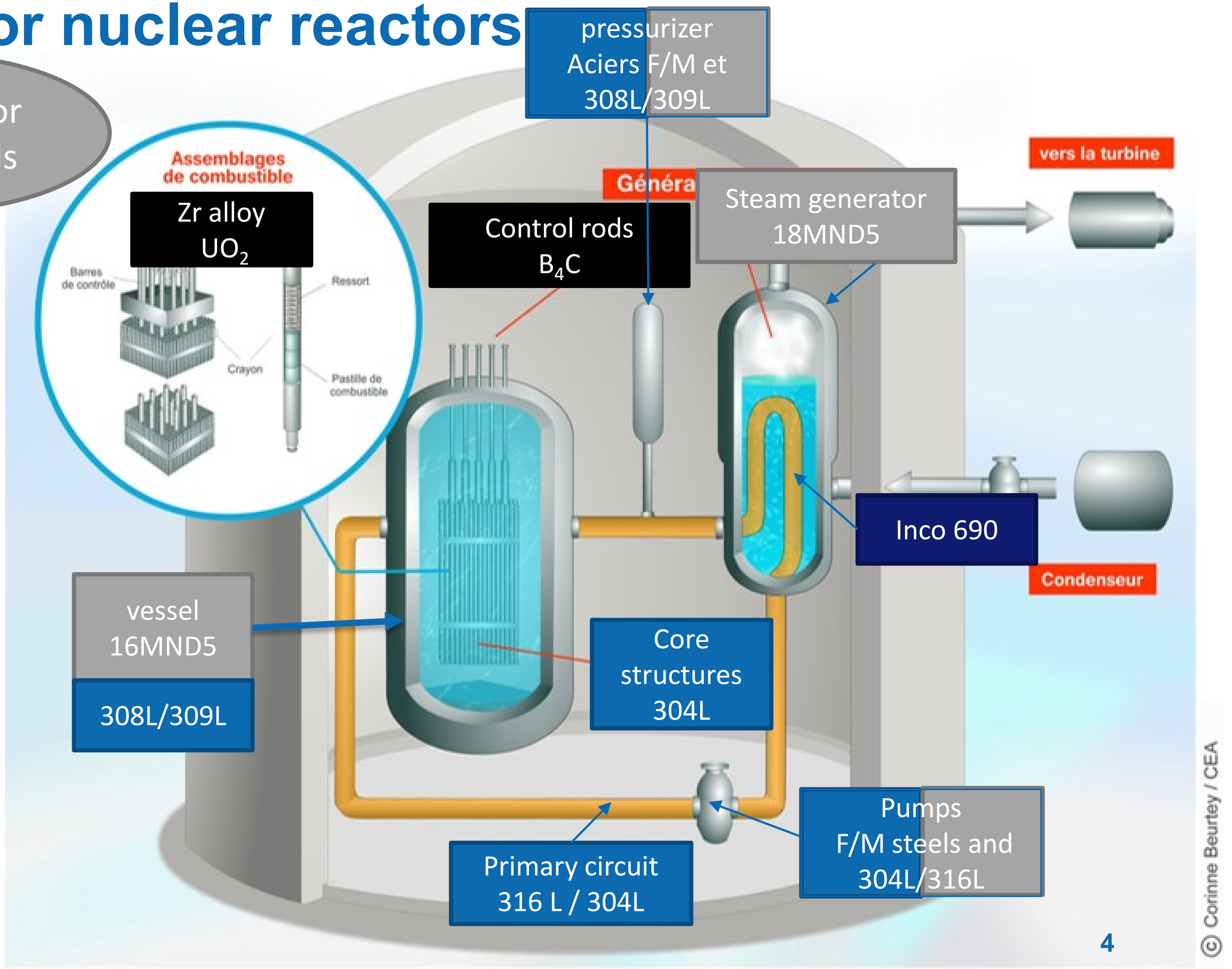
Martensitic or bainitic steels

Ni base alloys

other

- **Diverse operating conditions depending on the location in the reactor :**
  - Different temperatures

    (for ex. water from primary circuit : ~300°C, fuel rods : ~ 650 °C)
  - Corrosion
  - Irradiation
  - …
- **Different metallic materials required**
- **Need to join them together, mainly by welding**
- **Possibility to use metallic additive manufacturing**



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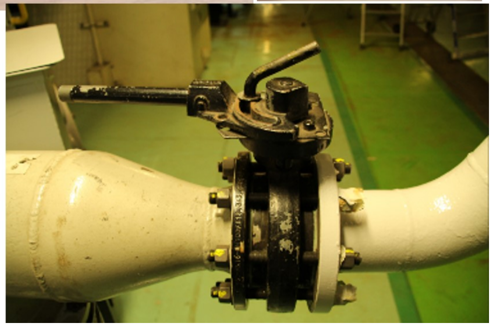
Additive manufacturing for present and future nuclear reactors

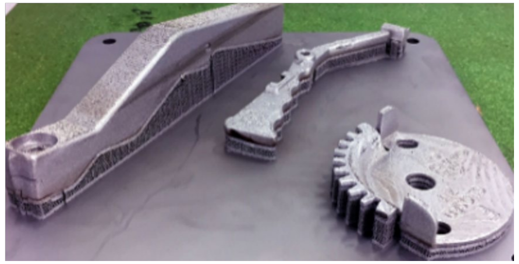
Already in use

PBF

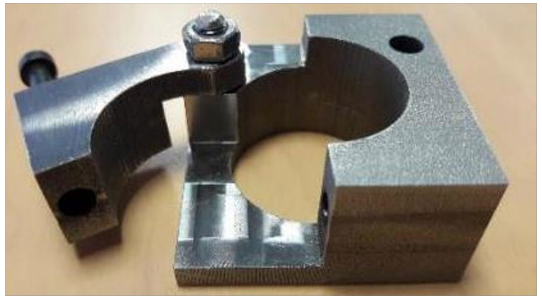


Valve stopper

Obsolete manual control



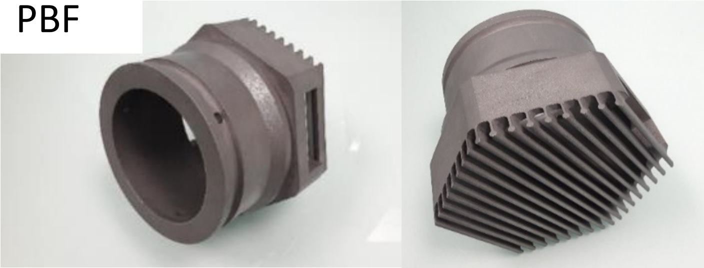
Tools for fuel handling (316L)



Future

PBF

SFR sodium flow grid



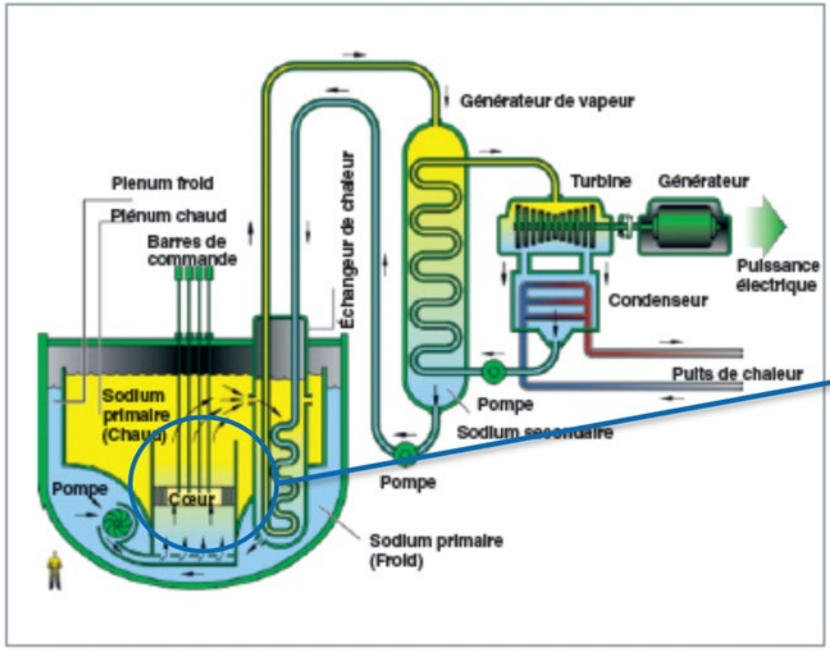
SFR fuel rod stowage device

DED

Adding a pipe connection

Example studied here : spike/HT welds in SFR

Sodium Fast Reactor



Fuel assemblies

Fuel rods, grouped and maintained in the core by the Hexagonal Tube in Fe-9Cr-1Mo steel (EM10 grade) (good mechanical strength at high temperatures and resistance to swelling under irradiation)

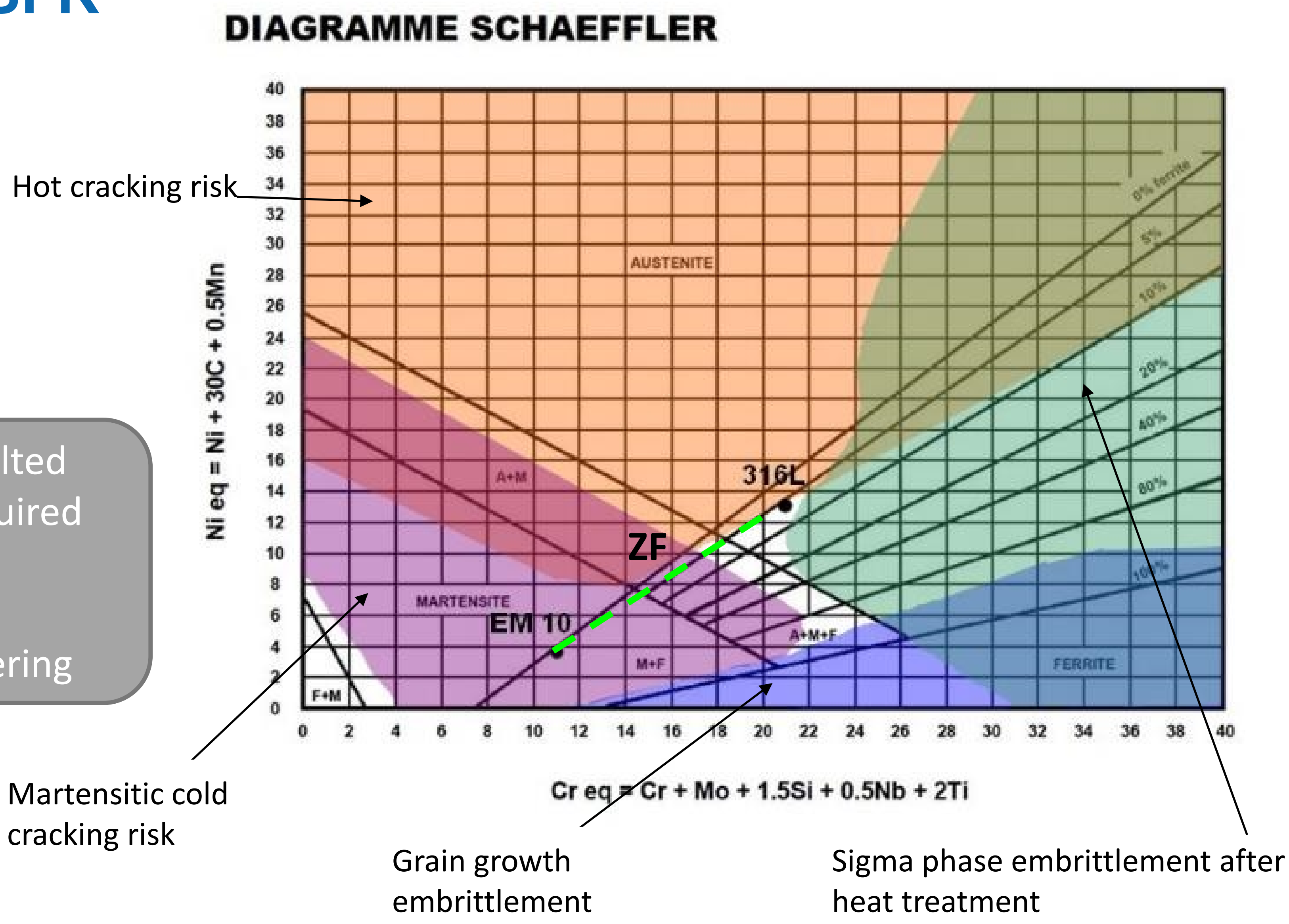
Spike/HT weld

Assembly spike, 316L steel (17Cr – 12Ni – 3 Mo) (interlocked in the austenitic steel base)

spike/HT welds in SFR

Without filling metal

- Risk of cold cracking in the melted area →pre-heating part is required
- Post welding heat treatment required for martensite tempering



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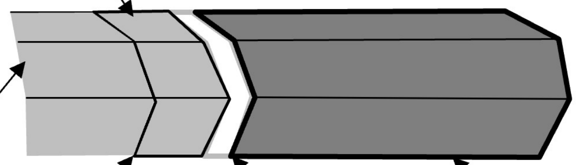
Industrial solution : TIG welding with inconel 82 filling metal

With filling metal

Joining by TIG welding

Joining part (316L) (French SFR Phenix assemblies only)



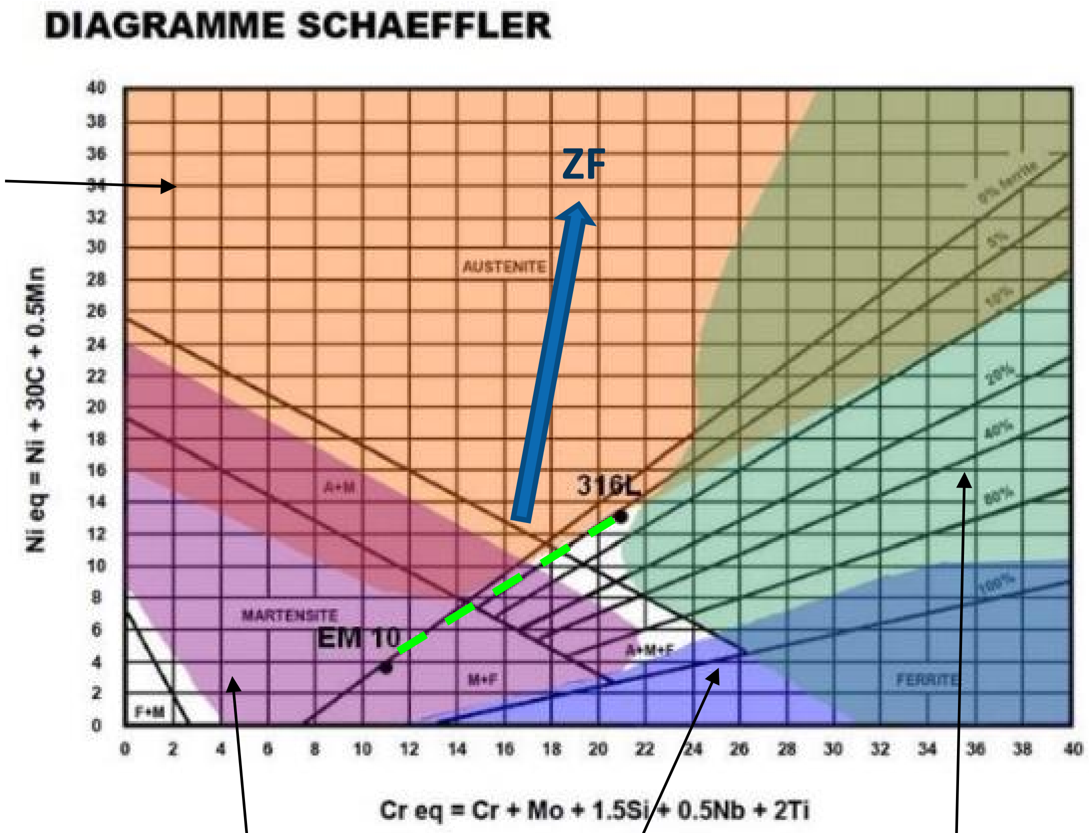
Assembly spike (316L austenitic steel)

Homogeneous weld 316L/316L

Bimetallic weld, filling metal Inconel 82

Hexagonal tube (Fe-9Cr-1Mo martensitic steel)

Hot cracking risk



Martensitic cold cracking risk

Grain growth embrittlement

Sigma phase embrittlement after heat treatment

Hot cracking risk
-> good process control required

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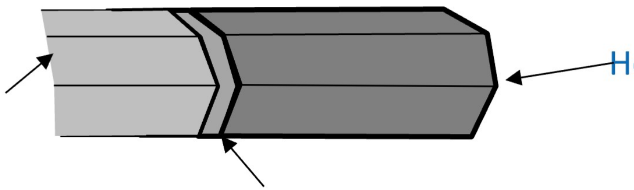
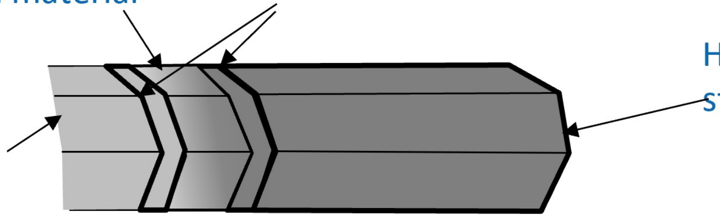
Generic development of alternative solutions to TIG welding

- Dissimilar Electron Beam welding



- Alternatives solutions : « traditional » powder metallurgy
  – Graded part made by SPS (Spark Plasma Sintering) or HIP (Hot Isostatic Pressing)

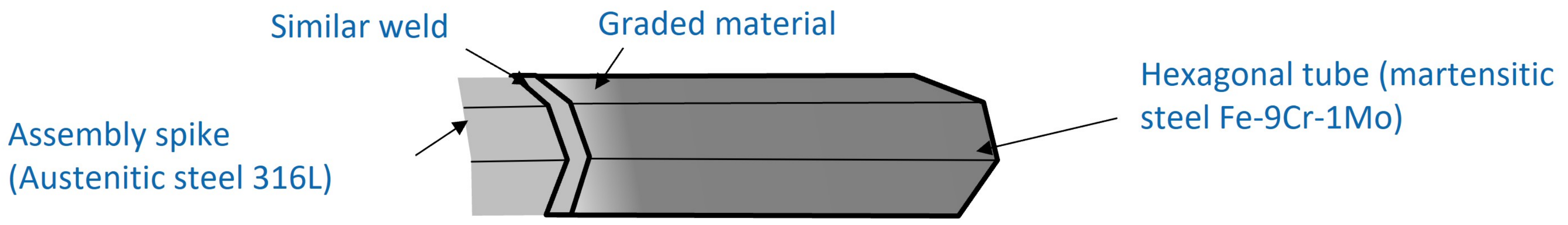
    - For each process SPS or HIP :
    - Homogeneous materials
    - Direct assembly
    - Mix
    - Mix assembly



Generic development of alternative solutions to TIG welding

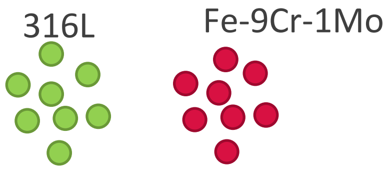
- Alternative solutions : additive manufacturing
  - Assembly with a graded connexion obtained by additive manufacturing or directly built on part by DED (Direct Energy Deposition) or PBF (Powder Bed Fusion)

    - For each processes PBF or DED :
    - Homogeneous materials
    - « direct » graded part
    - Progressive graded part



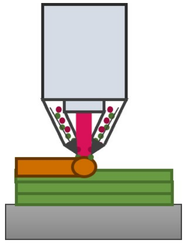
Outlines

I. Materials : powder used for the study



II. Additive manufacturing

1) 316L and Fe-9Cr-1Mo homogeneous materials
2) Graded materials



III. Conclusions and perspectives

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Outlines

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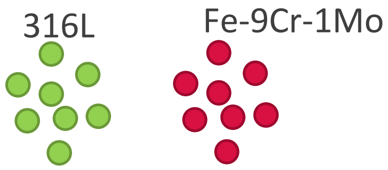

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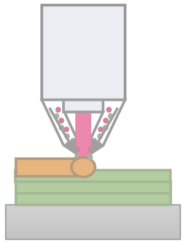


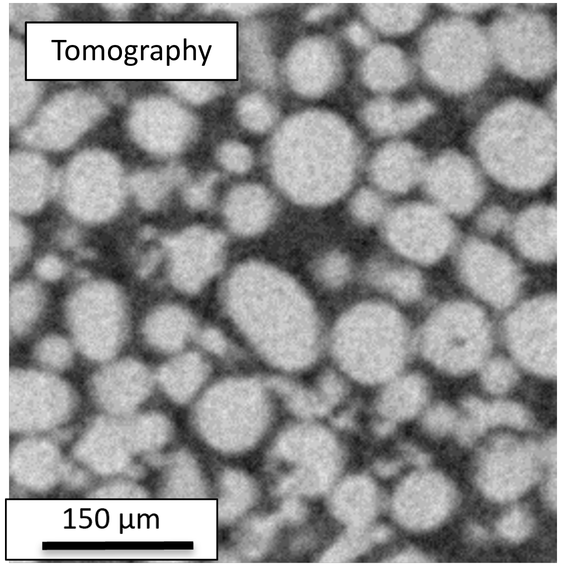
III. Conclusions and perspectives

Austenitic steel 316L

C	Cr	Mo	Ni	Mn	Si	N	O
0,016	17,7	2,33	12,6	0,29	0,58	0,08	0,015

% mass, supplied by Erasteel powder

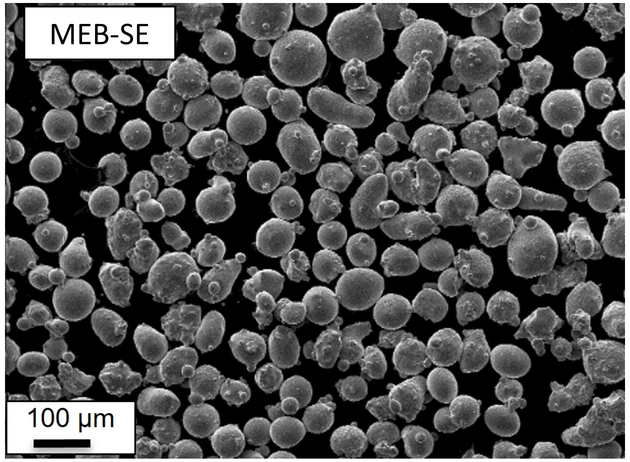
- Between 16 and 19 % Cr (stainless)
- Between 10 and 13 % Ni (austenitic, CFC)
- L for « low carbon » -> maximum 0,03 %C

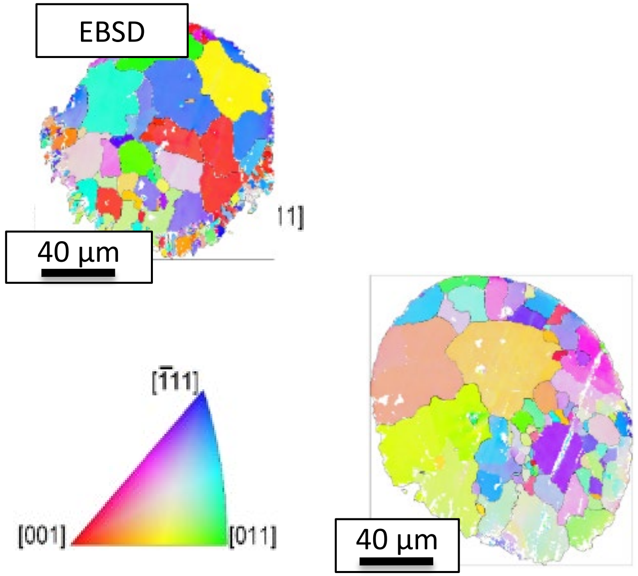


Aspect ratio: 1,3

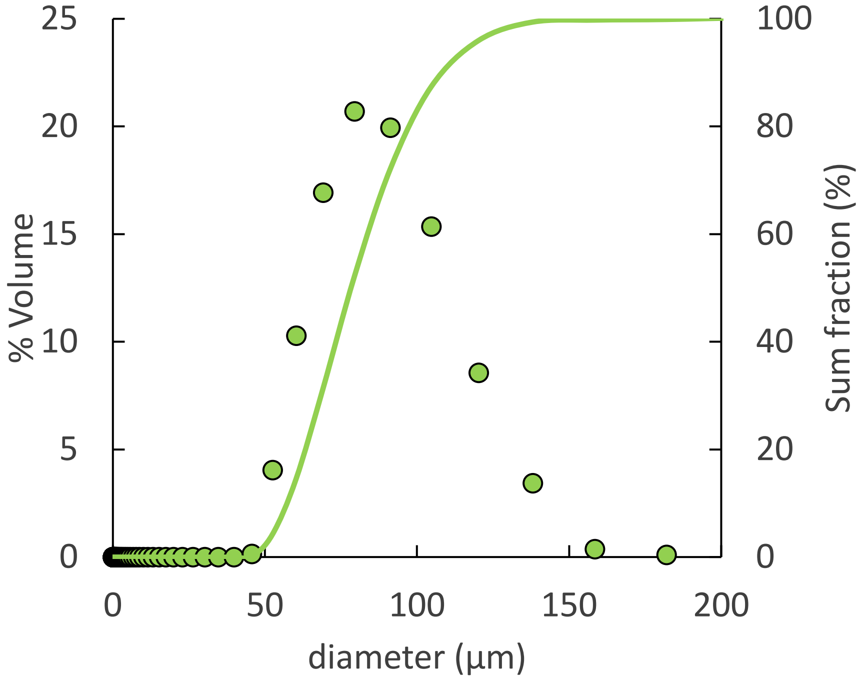
Porosity : 1 %

1 voxel = 2 µm





D_{10} (µm)	D_{50} (µm)	D_{90} (µm)
57	78	108



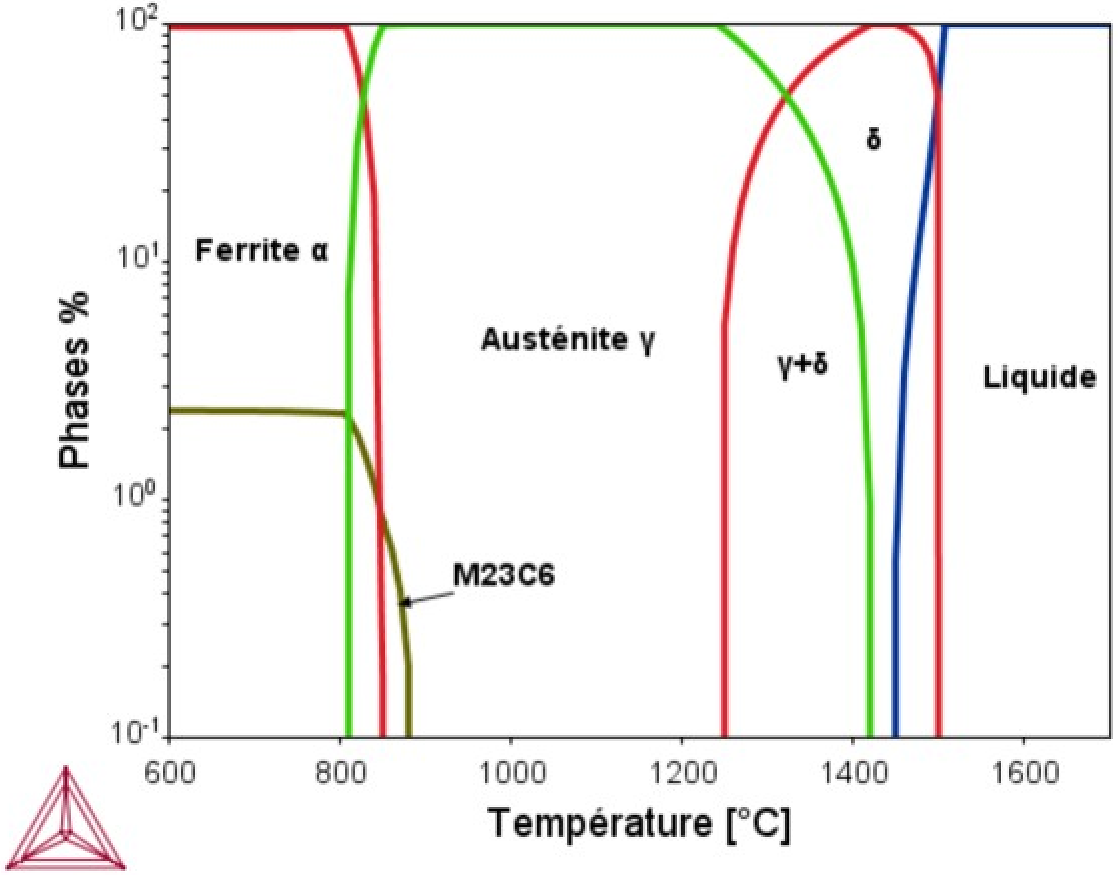
Martensitic steel Fe-9Cr-1Mo

C	Cr	Mo	Ni	Mn	Si	N	O
0,10	9,3	1,04	0,22	0,48	0,28	0,004	0,047

% mass, supplied by Nanoval

- Around 9 %Cr et 1 %Mo
- Around 0,1 %C
- Martensitic (CC) -> resistant to irradiation swelling and satisfying mechanical properties under service temperature

Different phases depending on temperature



Fe-9Cr-1Mo martensitic steel

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Fe-9Cr-1Mo	0,10	9,3	1,04	0,22	0,48	0,28	0,004	0,047

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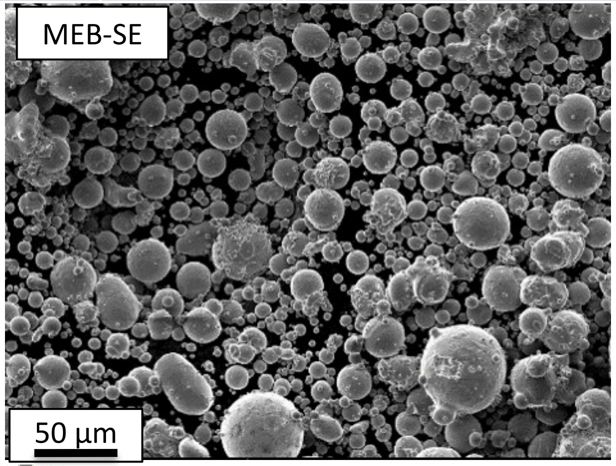
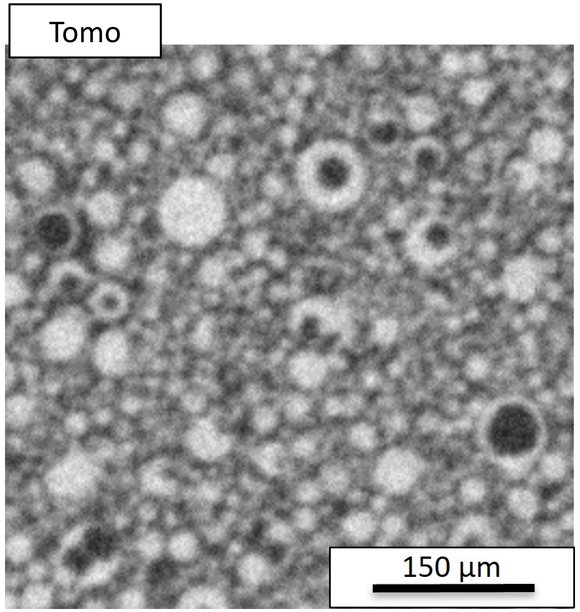
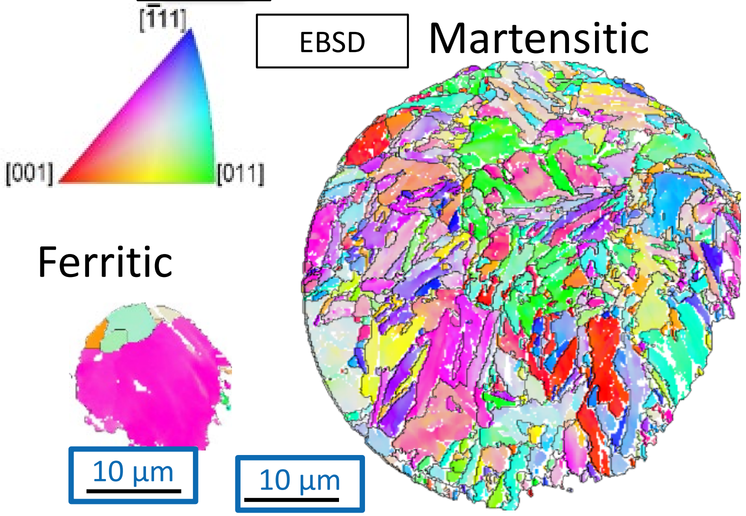


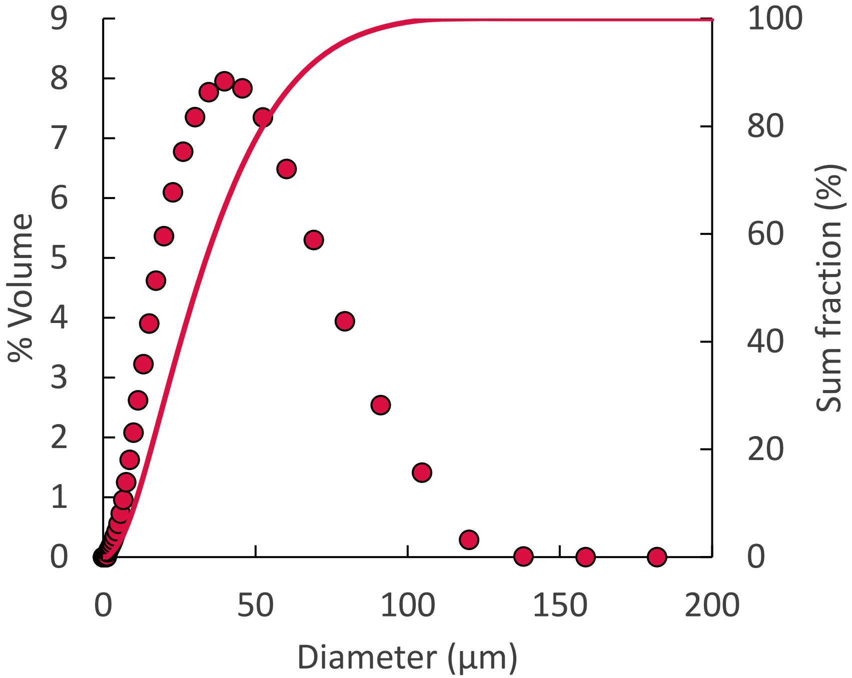
D_{10} (µm)	D_{50} (µm)	D_{90} (µm)
10	30	65



1 voxel = 2 µm

Aspect ratio : 1,3
Porosity : 4 %





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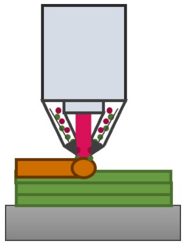
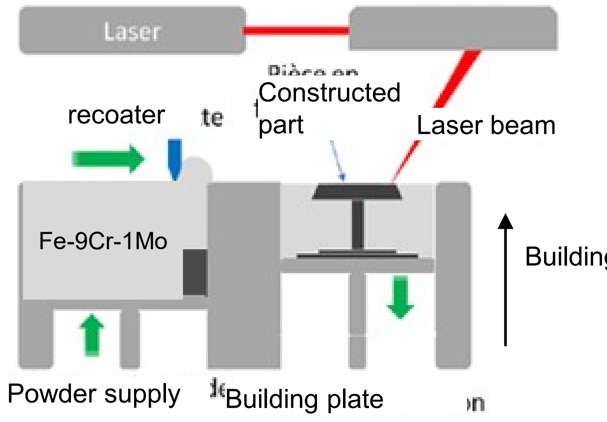


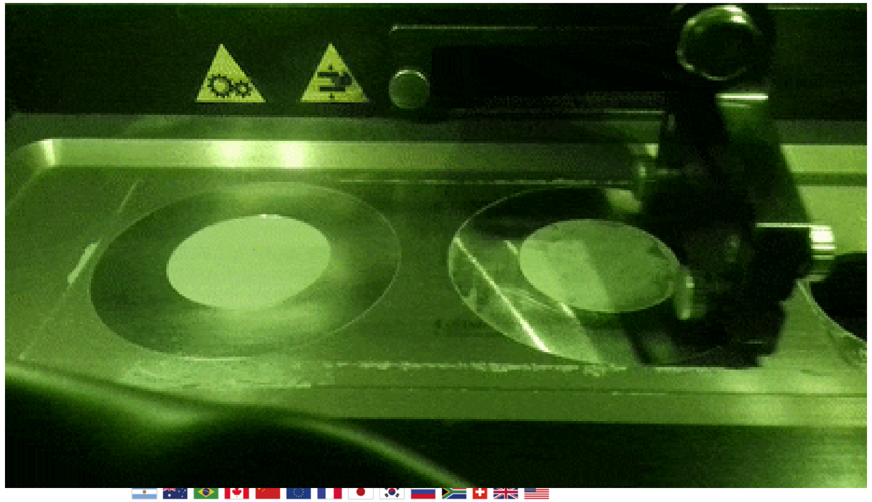
III. Conclusions and perspectives

Two processes compared

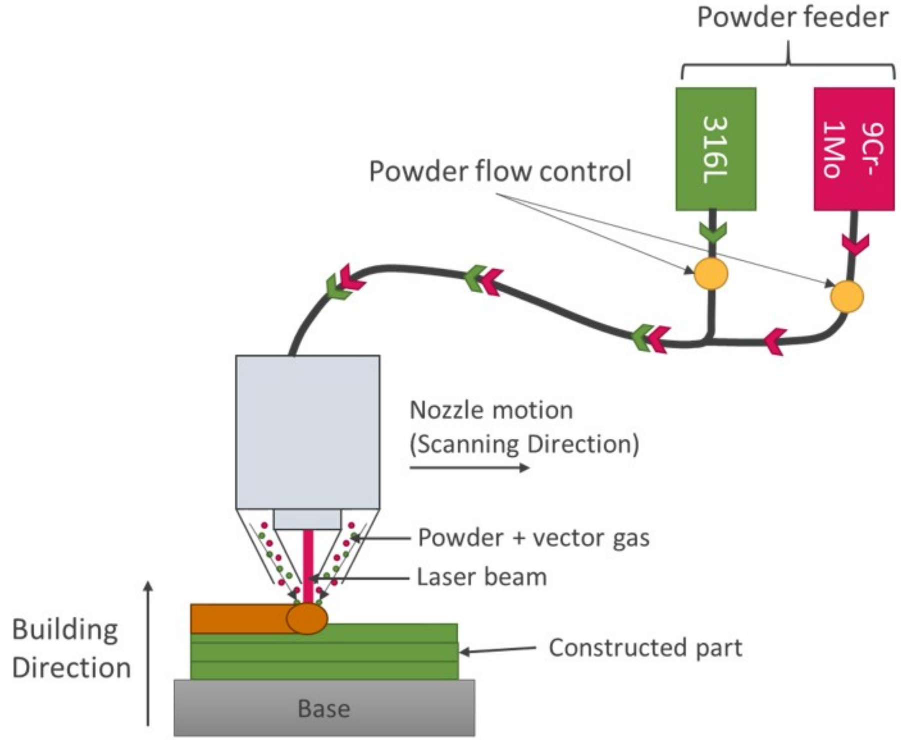
PBF-LB

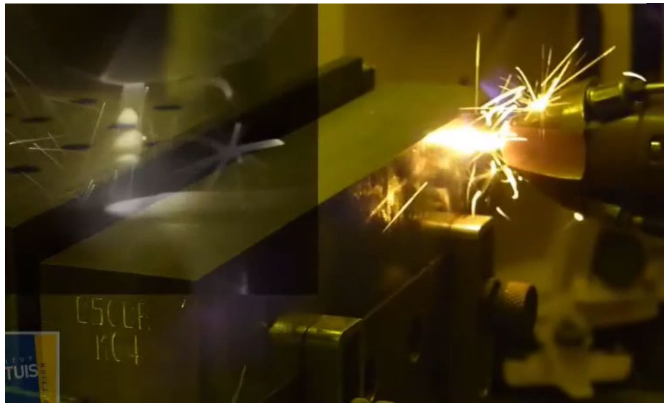


Adapted from Vasquez E., 2019;



DED-LB



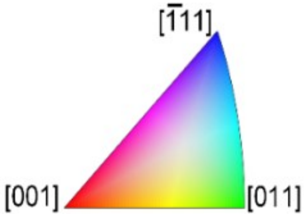


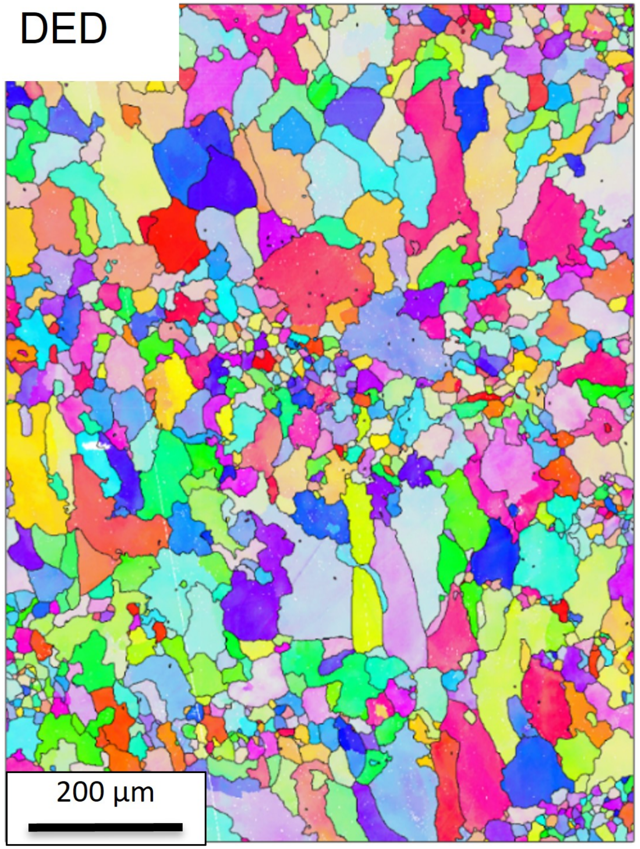
	PBF	DED
Surface Energy density ($P/v.D_{spot}$) (J/mm^2)	10	57
Volume energy density ($P/v.D_{spot}.h$)(J/mm^3)	500	285

316L – additive manufacturing

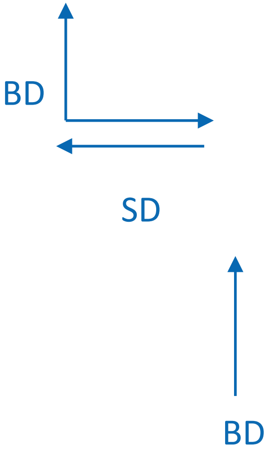
316L

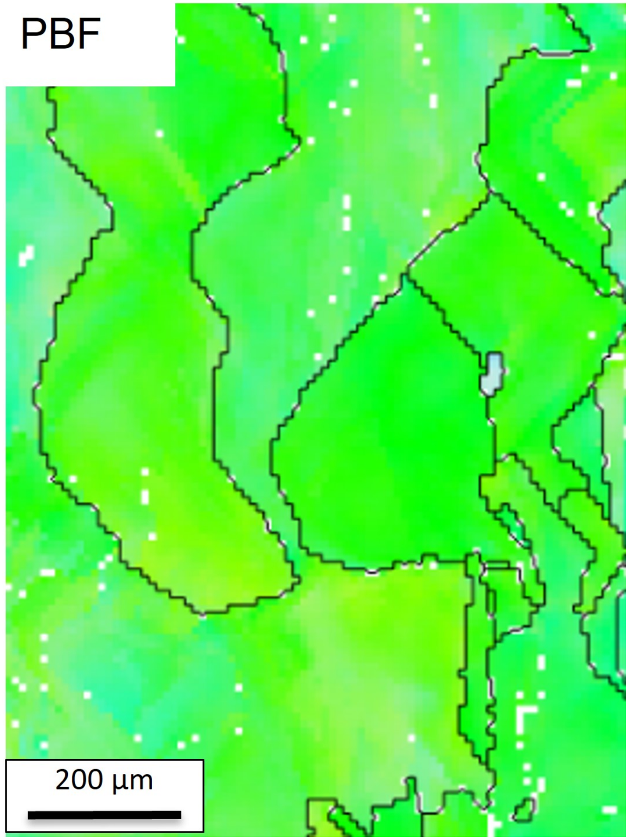
- austenitic
- Typical microstructure for AM 316L





Austenite





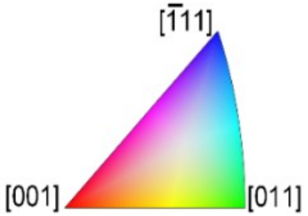
Austenite

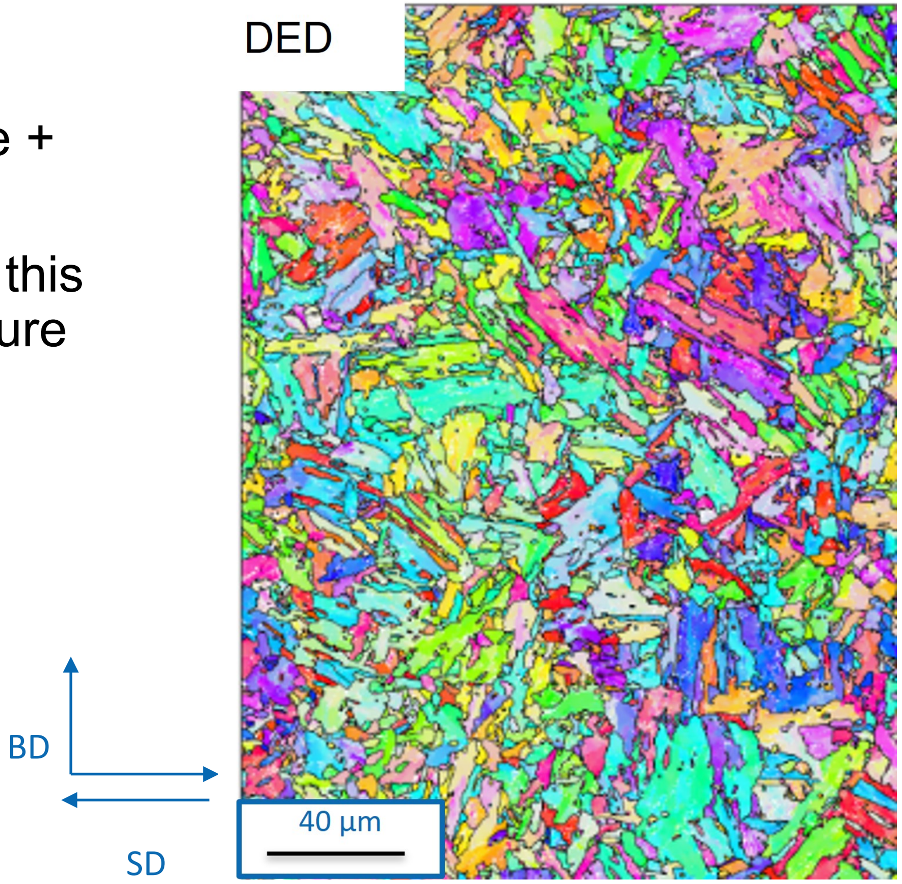
Fe-9Cr-1Mo – additive manufacturing

Fe-9Cr-1Mo

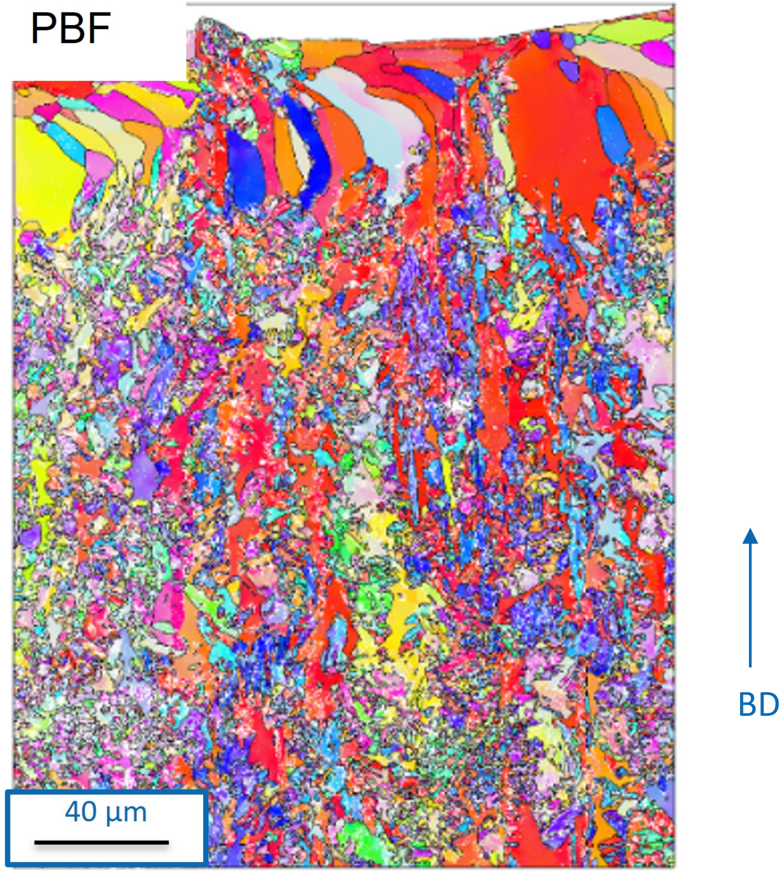
- DED = martensitic
- PBF more surprising: ferrite + martensite

→ In depth study required for this ferritic/martensitic microstructure





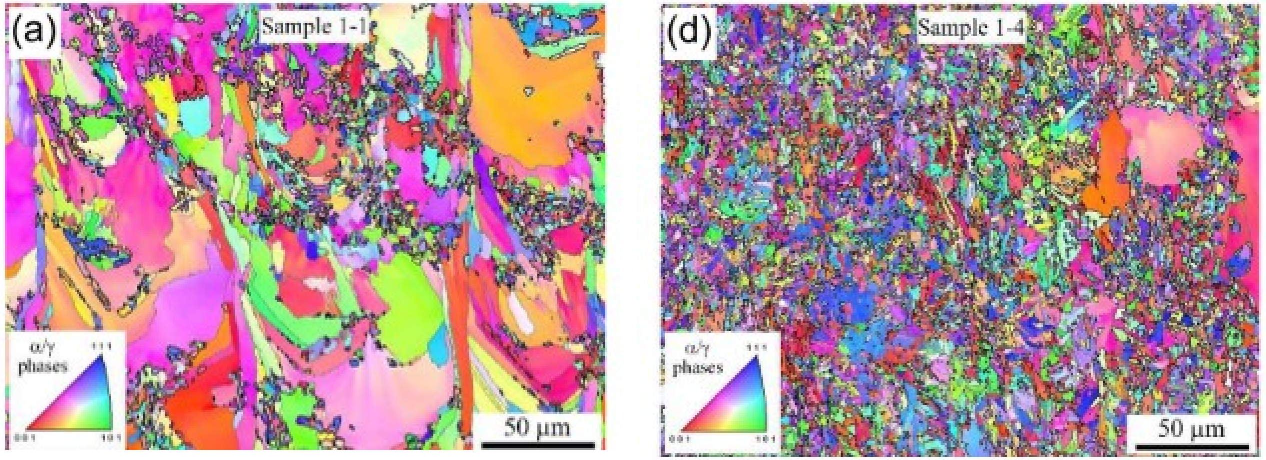
Martensite



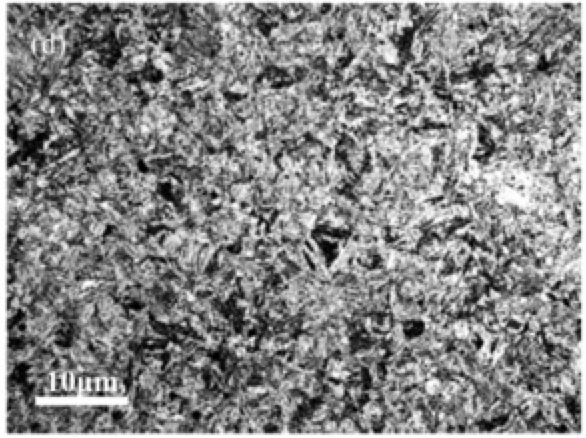
Ferrite + martensite

Additive manufacturing of ~~martensitic~~ ferritic steels ?

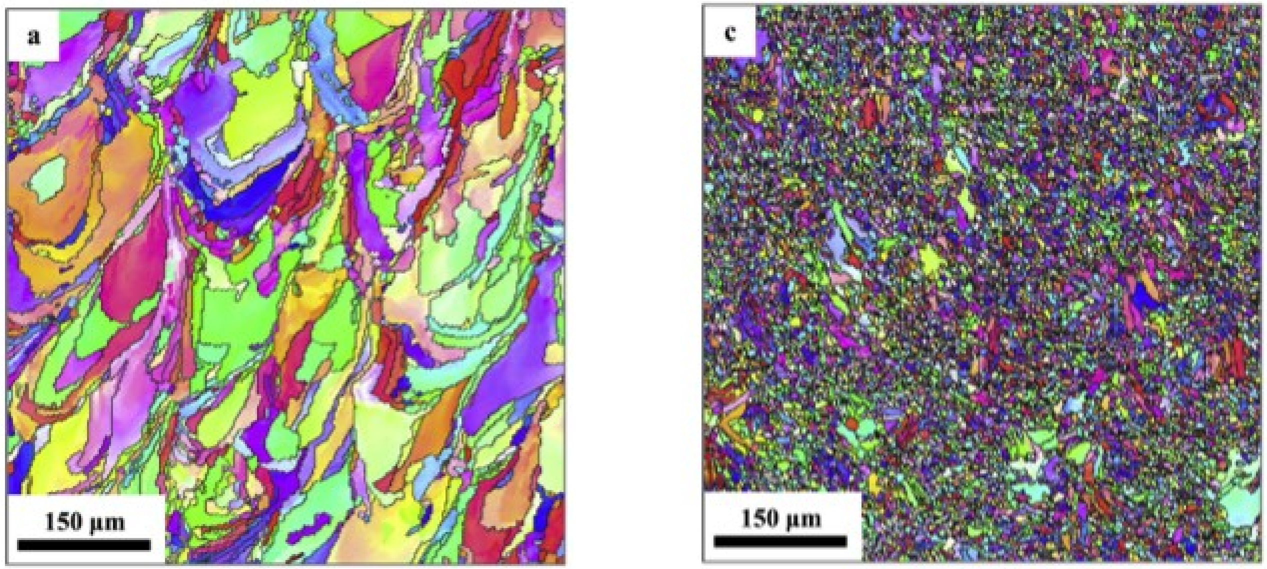
Y. Sun et al. 2020: 17-4PH by PBF same powder, same parameters, different wall thicknesses



Z. Xia et al. 2020: Reduced activation martensitic steel (9Cr-1W) by DED

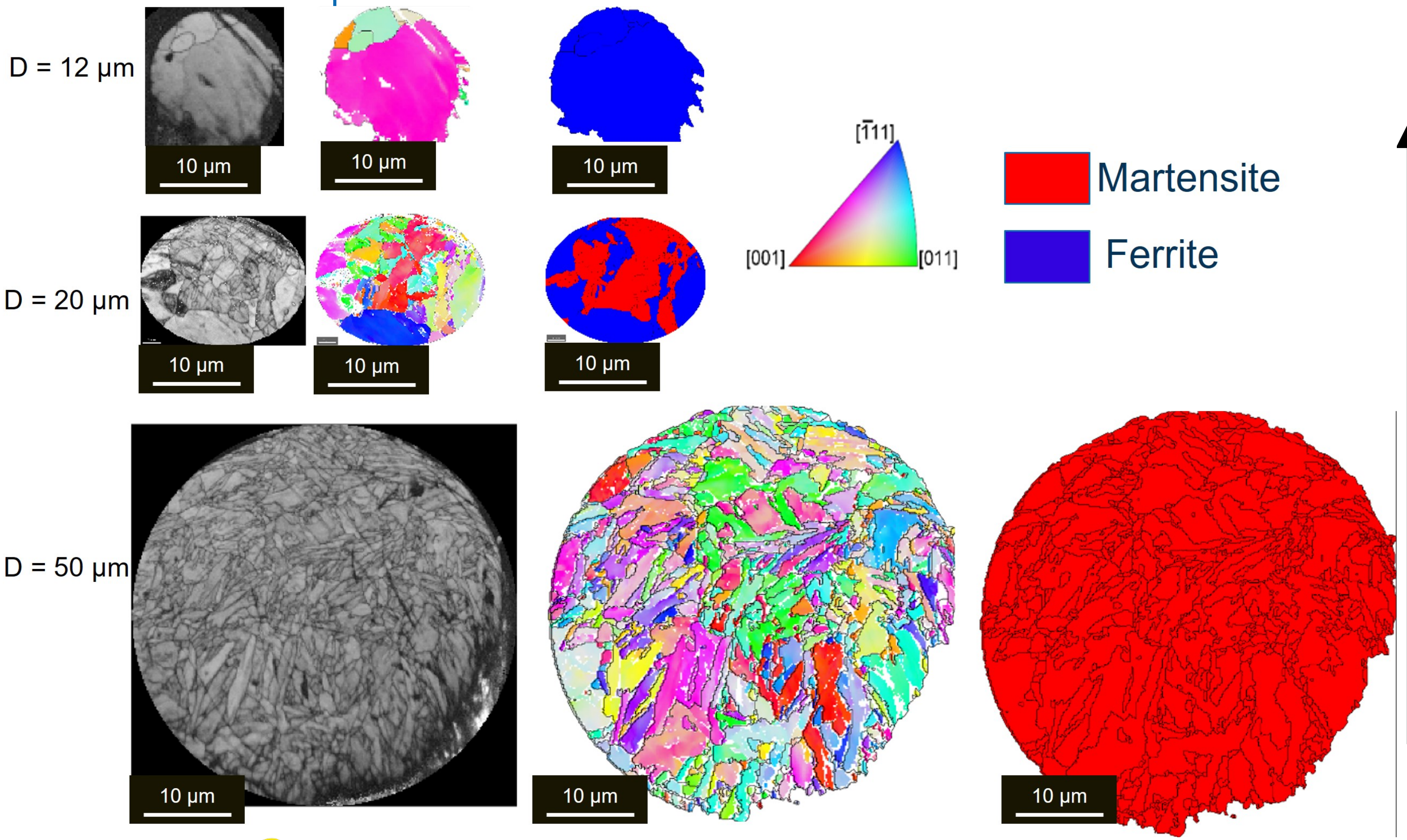


S. Vunnam et al. 2019: 17-4PH by PBF same processing parameters different powders



Let’s study something simpler: powder microstructure

Fe-9Cr-1Mo powder

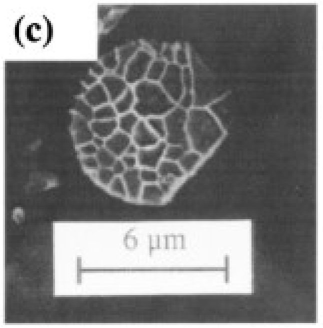


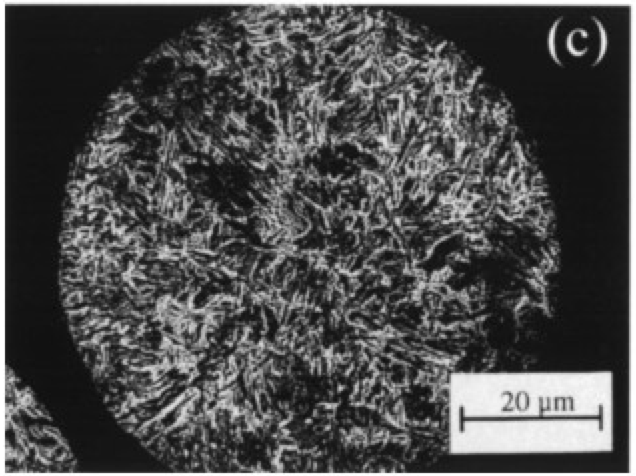
Pryds and Pedersen 2002:
12Cr-1Mo-0.2C martensitic (?) steel powder

~4.10^5 °C/s

Faster cooling

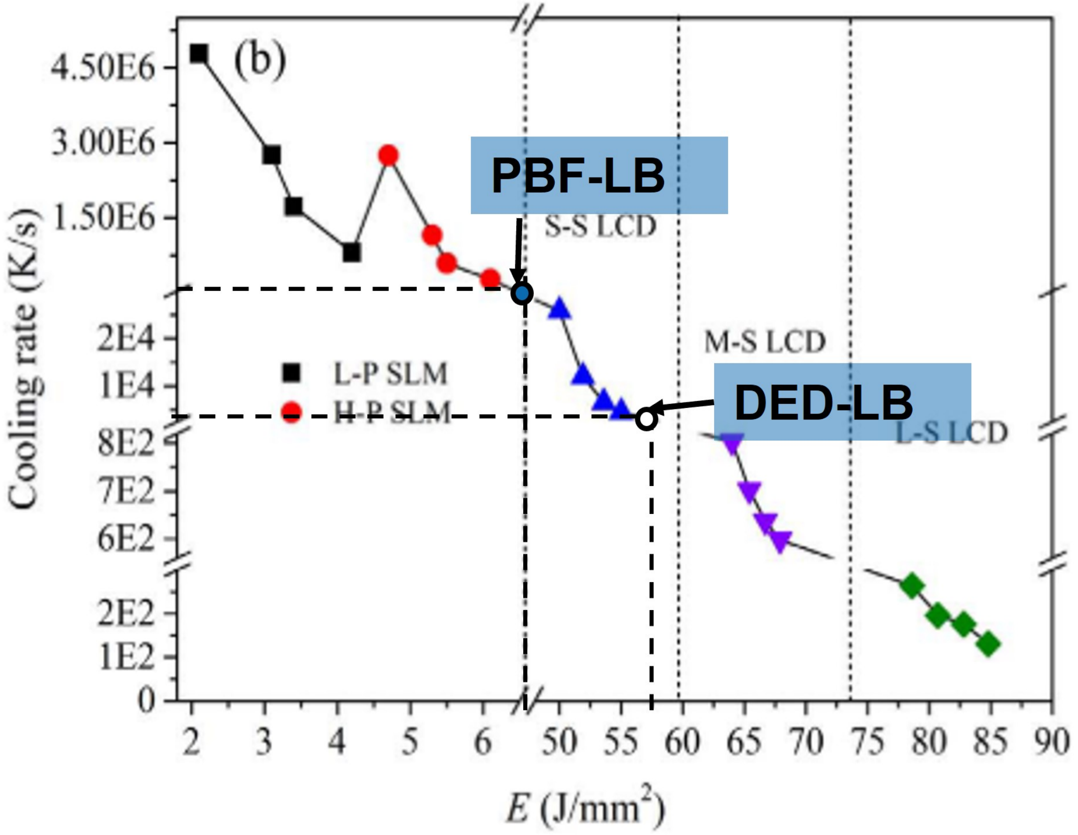
~2.10^4 °C/s





faster cooling → more ferrite !
Contradiction with the usual CCT diagram

Link with additive manufacturing



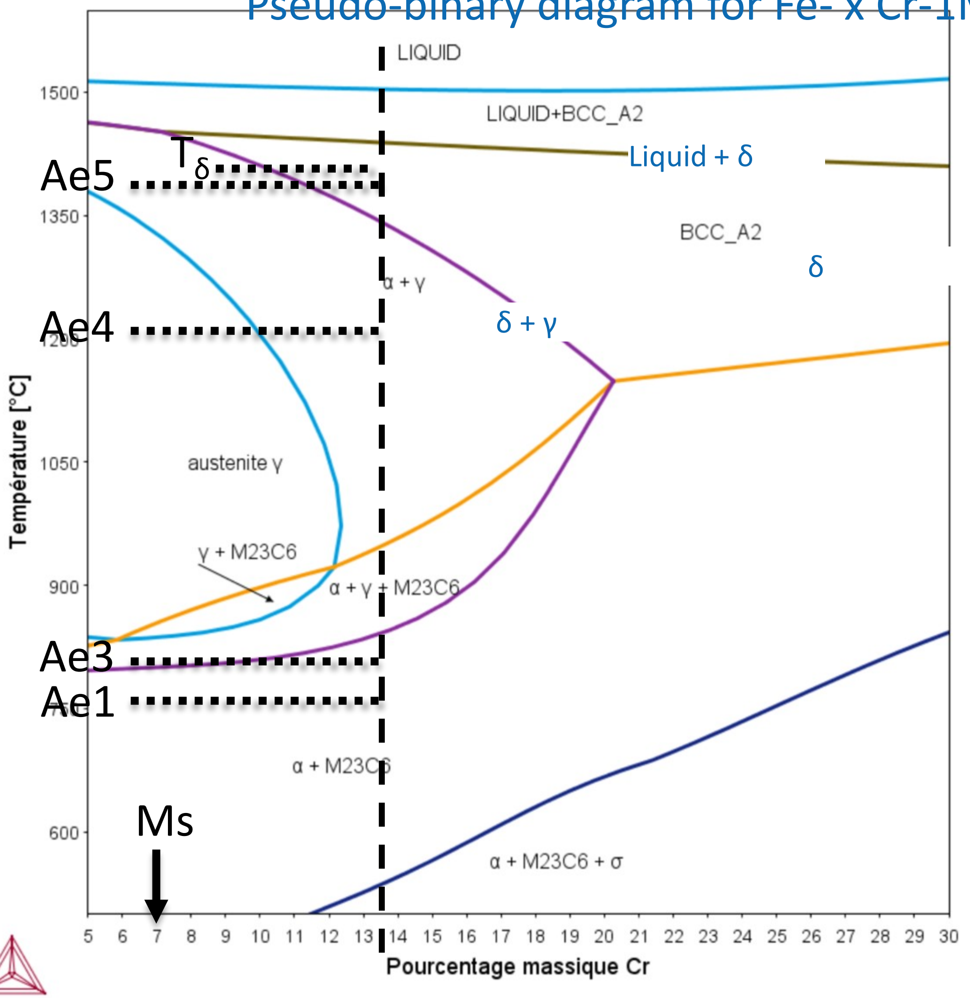
PBF cooling ~ 100 x faster than DED

Increasing cooling rate is decreasing the martensite fraction in powder and in additive manufacturing (very fast cooling rates)

M. Ma, Z. Wang, et X. Zeng, « A comparison on metallurgical behaviors of 316L stainless steel by selective laser melting and laser cladding deposition », *Mater. Sci. Eng. A*, vol. 685, p. 265-273, 2017

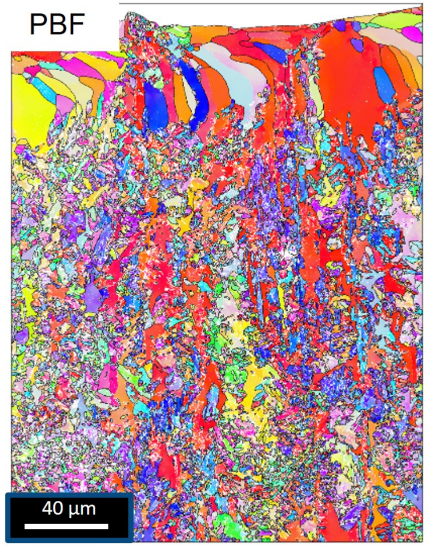
Fe-9Cr-1Mo equilibrium phase diagram

Pseudo-binary diagram for Fe- x Cr-1Mo



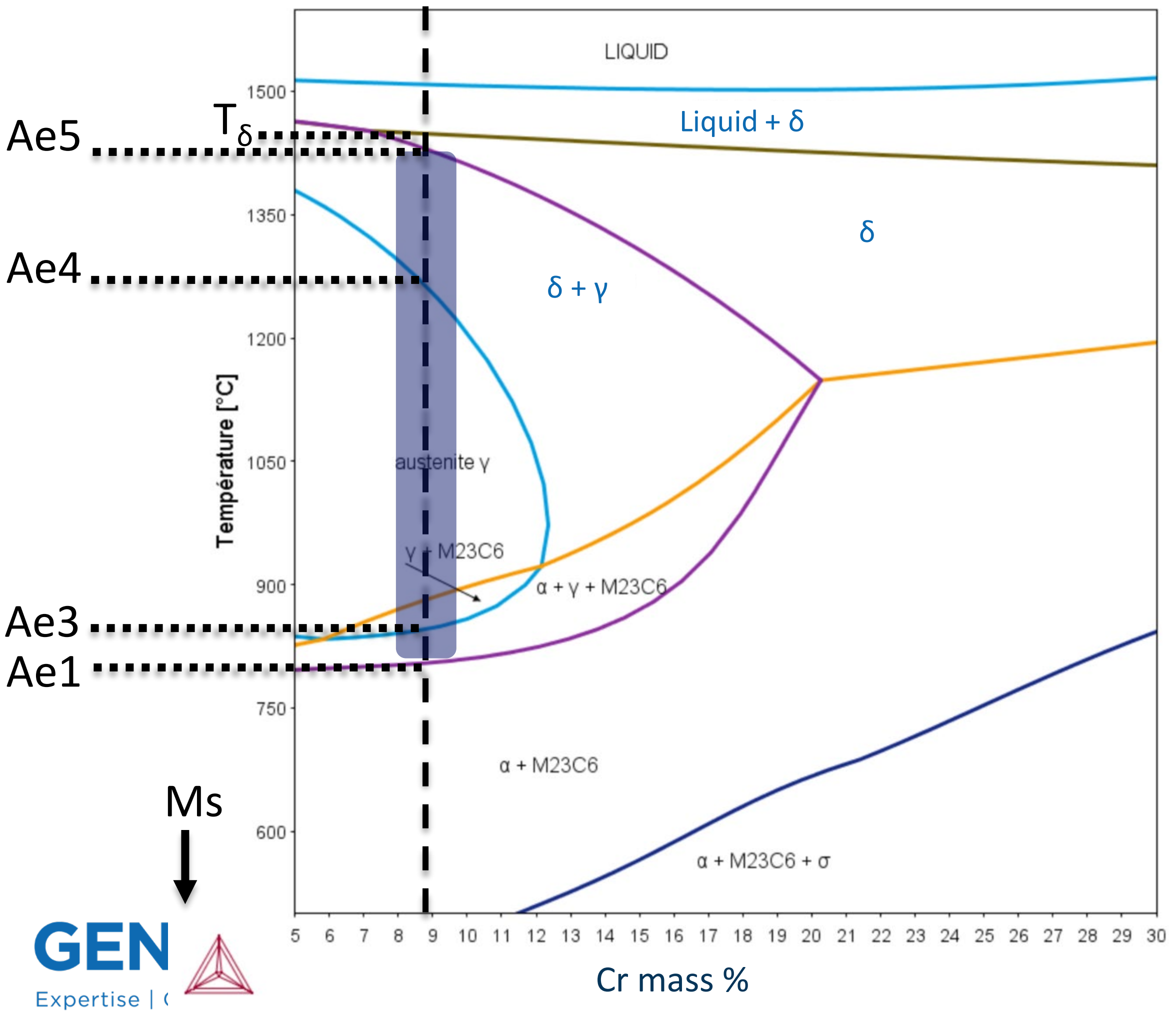
Cr mass %

- At equilibrium:
  - Delta ferrite solidification
  - δ -> γ transformation
  - $M_{23}C_6$ precipitation
  - γ -> α transformation (usually replaced by martensite)

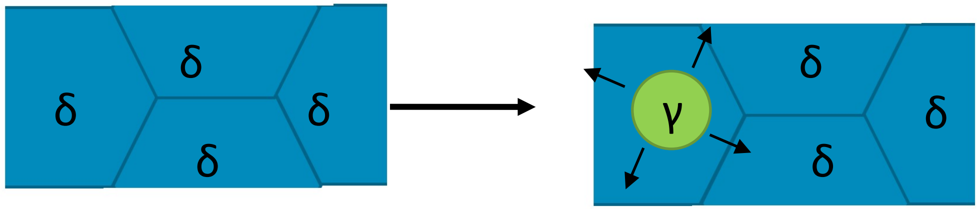


Can we by-pass austenite ?

Pseudo-binary diagram for Fe- x Cr-1Mo



- **It is mainly the time spent between Ae5 and Ae1 which controls the austenite formation**
  - Let's assume an austenite nucleus is immediately formed at Ae5 and study how it will grow
  - Austenite growth is manly controlled by diffusion
  - Very fast cooling rates → only interstitial elements (C, N) have time to diffuse
  - In our Fe-9Cr-1Mo : 4 ppm of N vs 1000 ppm of C → only C diffusion is considered

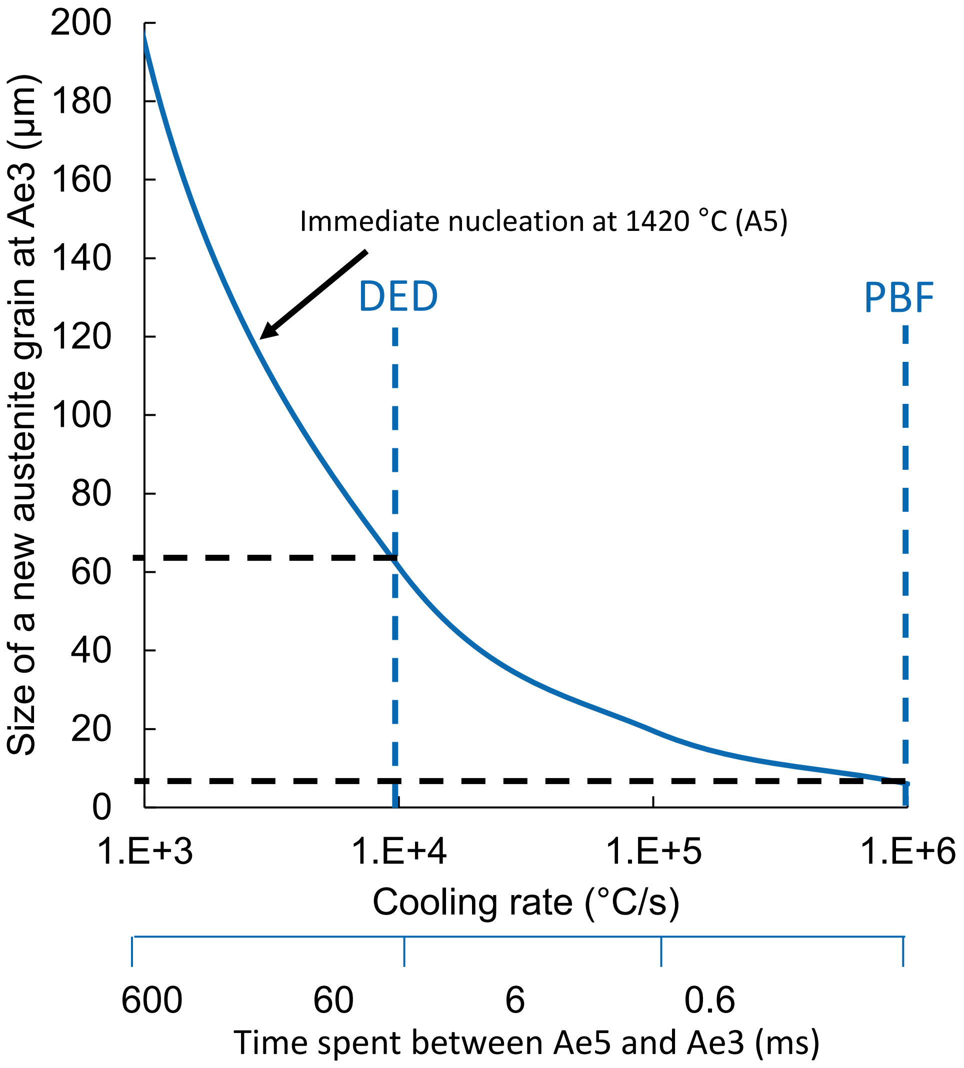


Can we by-pass austenite ?

$$r_f = f(T) = r_{\delta+\gamma} + \int_{Ae3}^{Ae4} 2\left(D(T).\frac{dT}{v}\right)^{0.5}$$

Austenite new grain size at Ae3	PBF	DED
Immediate nucleation	6 µm	60 µm

- Strong effect of the cooling rate on the growth on an austenite nucleus
- In DED : time spent between Ae5 and Ae3 (60 ms) is sufficient to allow austenite to grow until δ ferrite disappear
- In PBF : time spent between Ae5 and Ae3 is too short (6 ms), only small austenite grains are formed and δ ferrite remains



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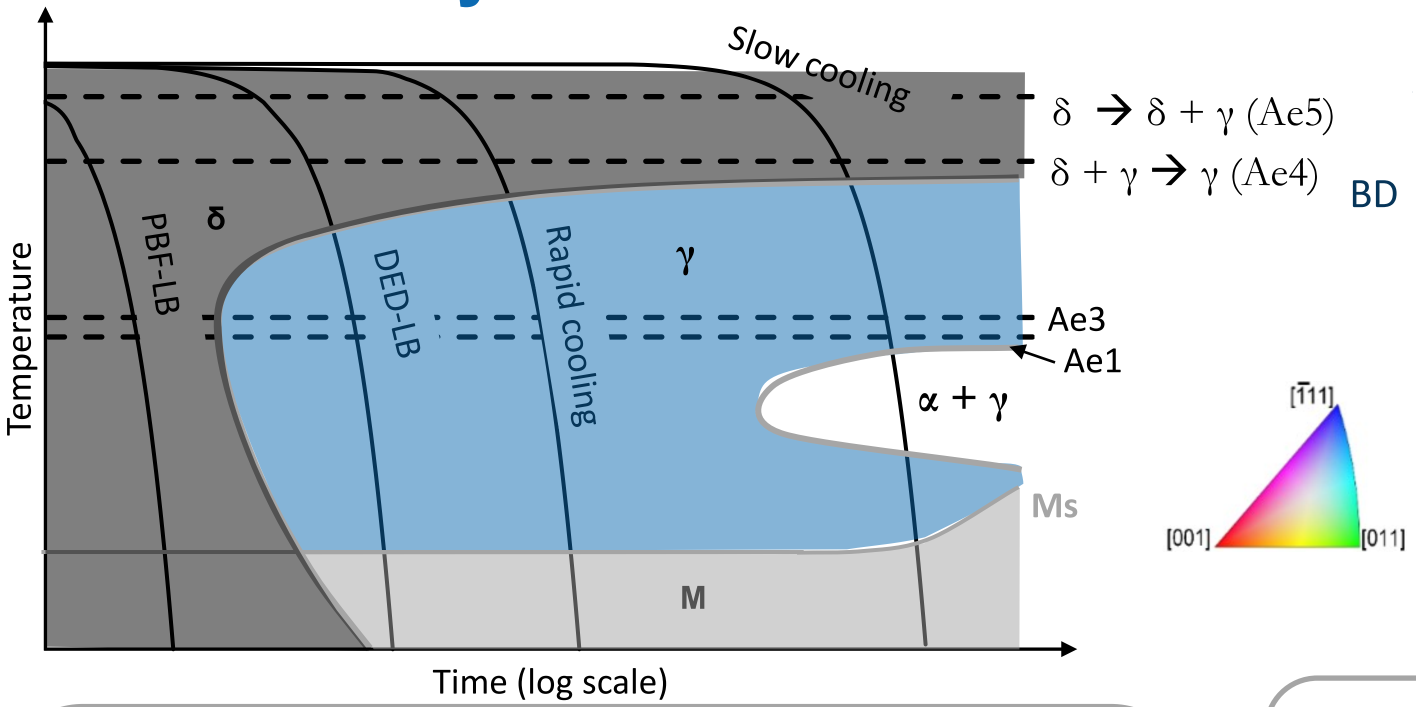
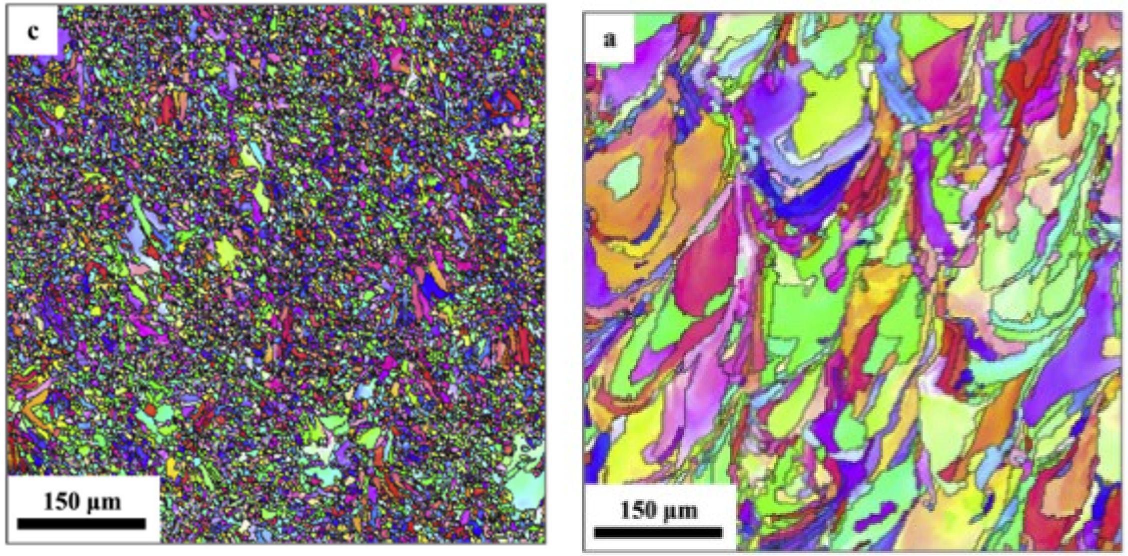
Summary and link with microstructures





S. Vunnam et al. 2019: 17-4PH, PBF

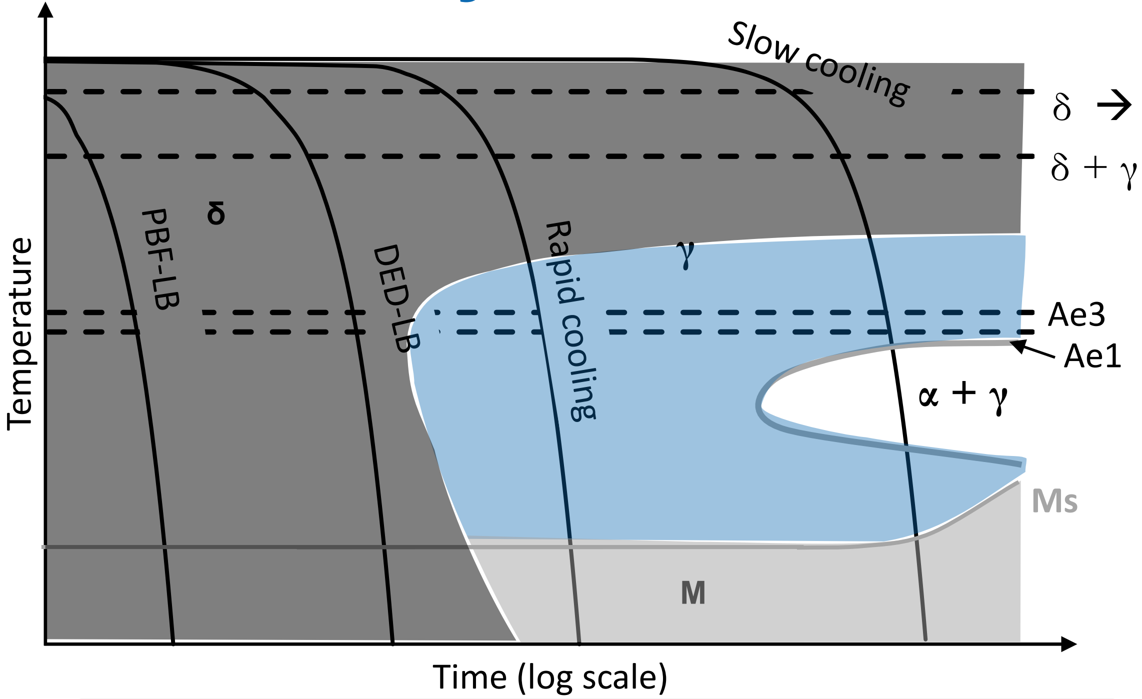
- **A very precise control of the chemical composition and the building parameters is required to control the as built microstructure of martensitic steels in AM**
- **This model could be used to set a relation between composition and cooling speed to control the microstructure**

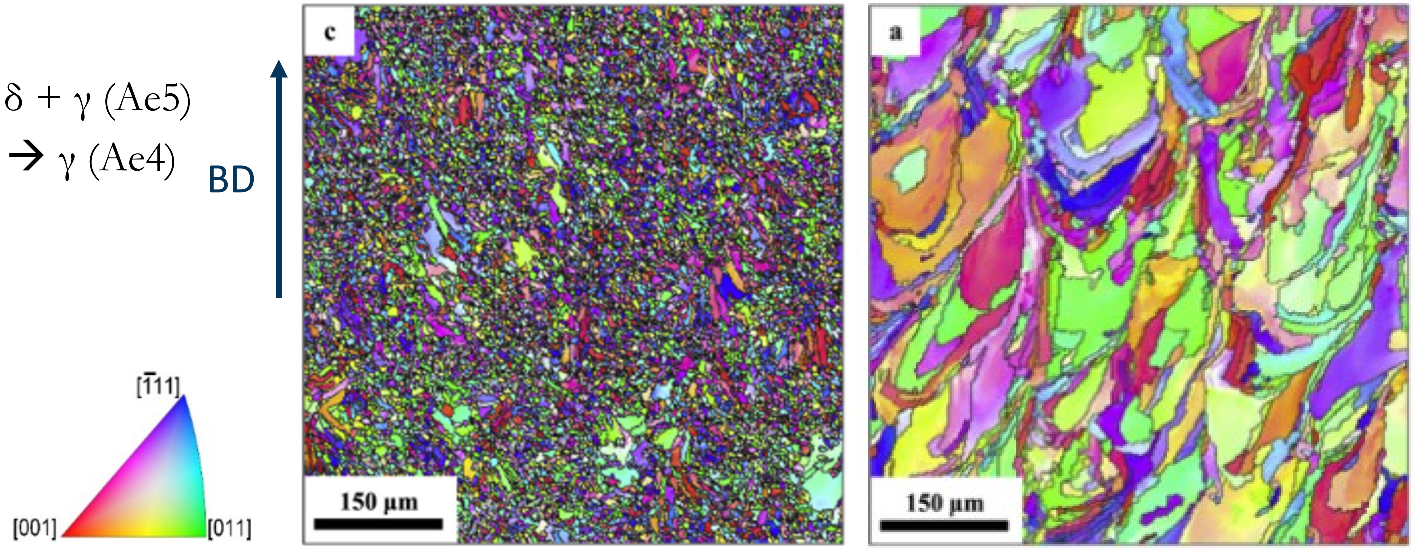
- **Delta ferrite usually avoided in welds (decrease impact strength and lower mechanical properties after ageing)**
- **Better resistance under irradiation of martensitic structures**

Results published in

F. Villaret, X. Boulnat, P. Aubry, J. Zollinger, D. Fabrègue, et Y. de Carlan, « Modelling of delta ferrite to austenite phase transformation kinetics in martensitic steels: Application to rapid cooling in additive manufacturing », *Materialia*, vol. 18, p. 101157, août 2021, doi: 10.1016/j.mtla.2021.101157.

Summary and link with microstructures





S. Vunnam et al. 2019: 17-4PH, PBF

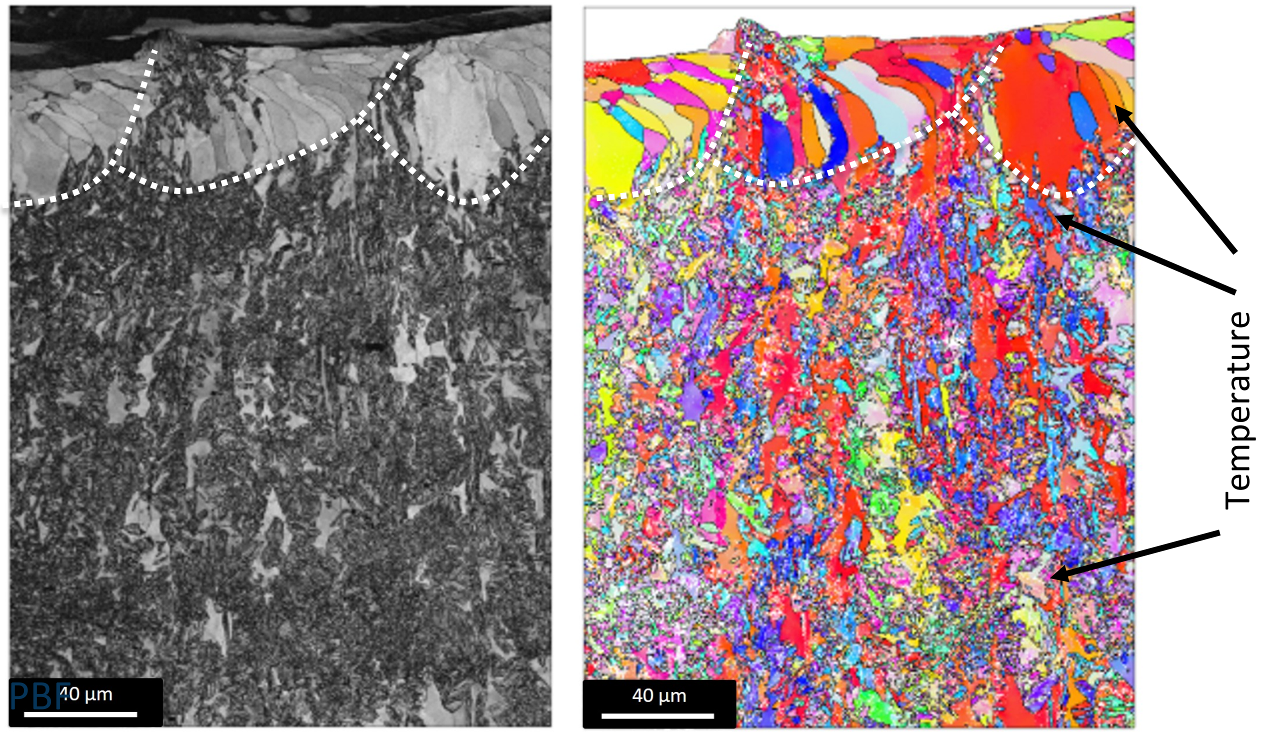
- **A very precise control of the chemical composition and the building parameters is required to control the as built microstructure of martensitic steels in AM**
- **This model could be used to set a relation between composition and cooling speed to control the microstructure**

- **Delta ferrite usually avoided in welds (decrease impact strength and lower mechanical properties after ageing)**
- **Better resistance under irradiation of martensitic structures**

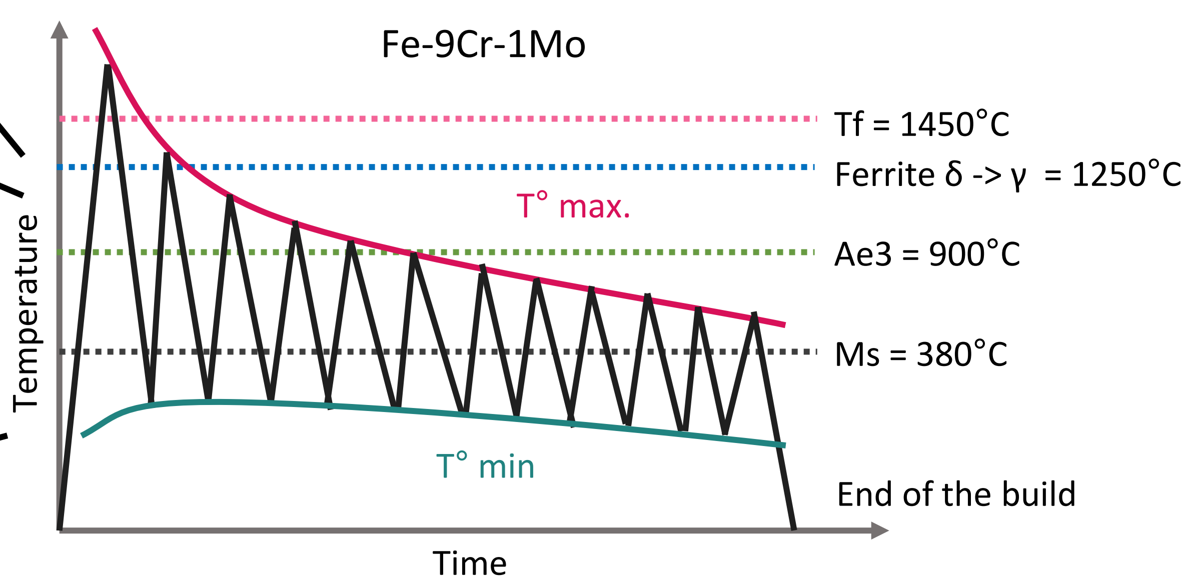
Results published in

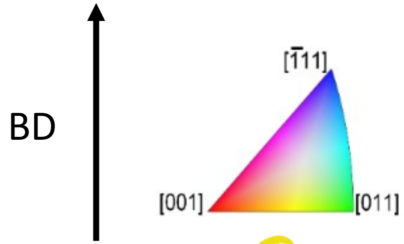
F. Villaret, X. Boulnat, P. Aubry, J. Zollinger, D. Fabrègue, et Y. de Carlan, « Modelling of delta ferrite to austenite phase transformation kinetics in martensitic steels: Application to rapid cooling in additive manufacturing », *Materialia*, vol. 18, p. 101157, août 2021, doi: 10.1016/j.mtla.2021.101157.

Let’s go back to PBF microstructure



Scheme of the thermal cycle on a given layer





- Last layer ferritic
- Previous layers austenitized several times → martensite

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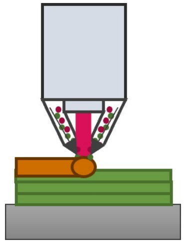
Outlines

I. Materials : powder used for the study

II. Additive manufacturing

1) 316L and Fe-9Cr-1Mo homogeneous materials

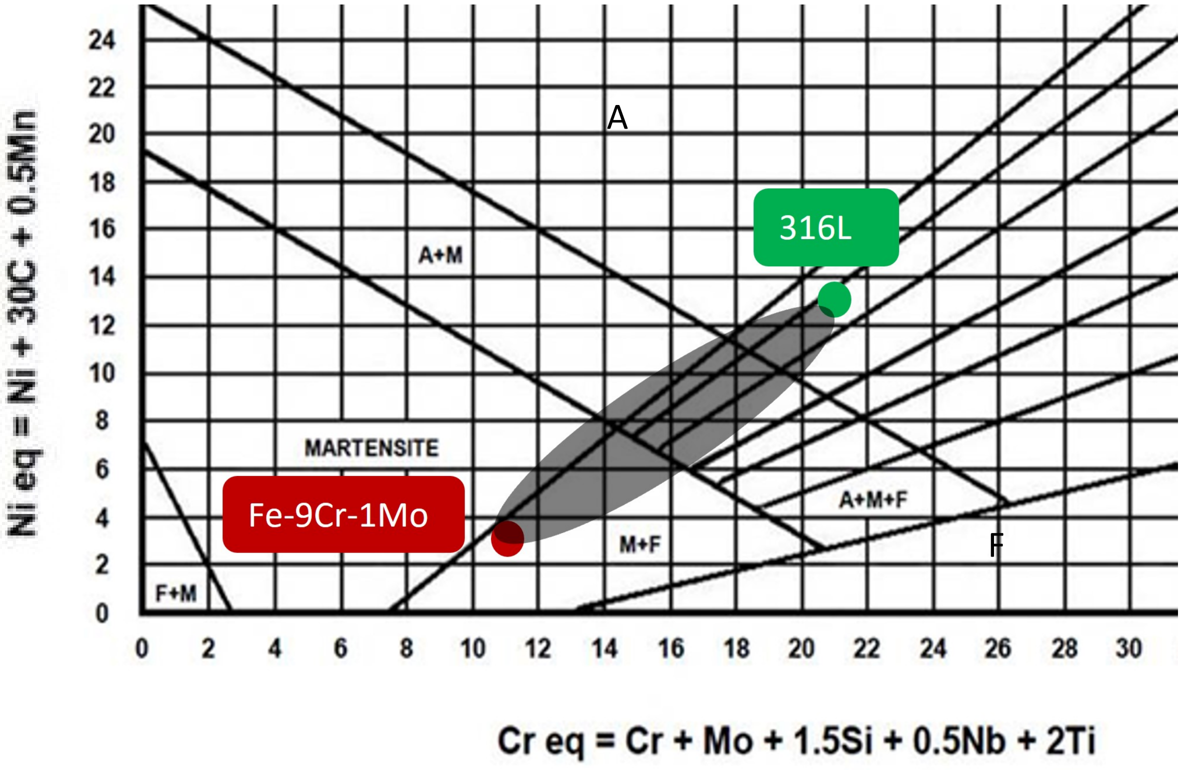
2) Graded materials



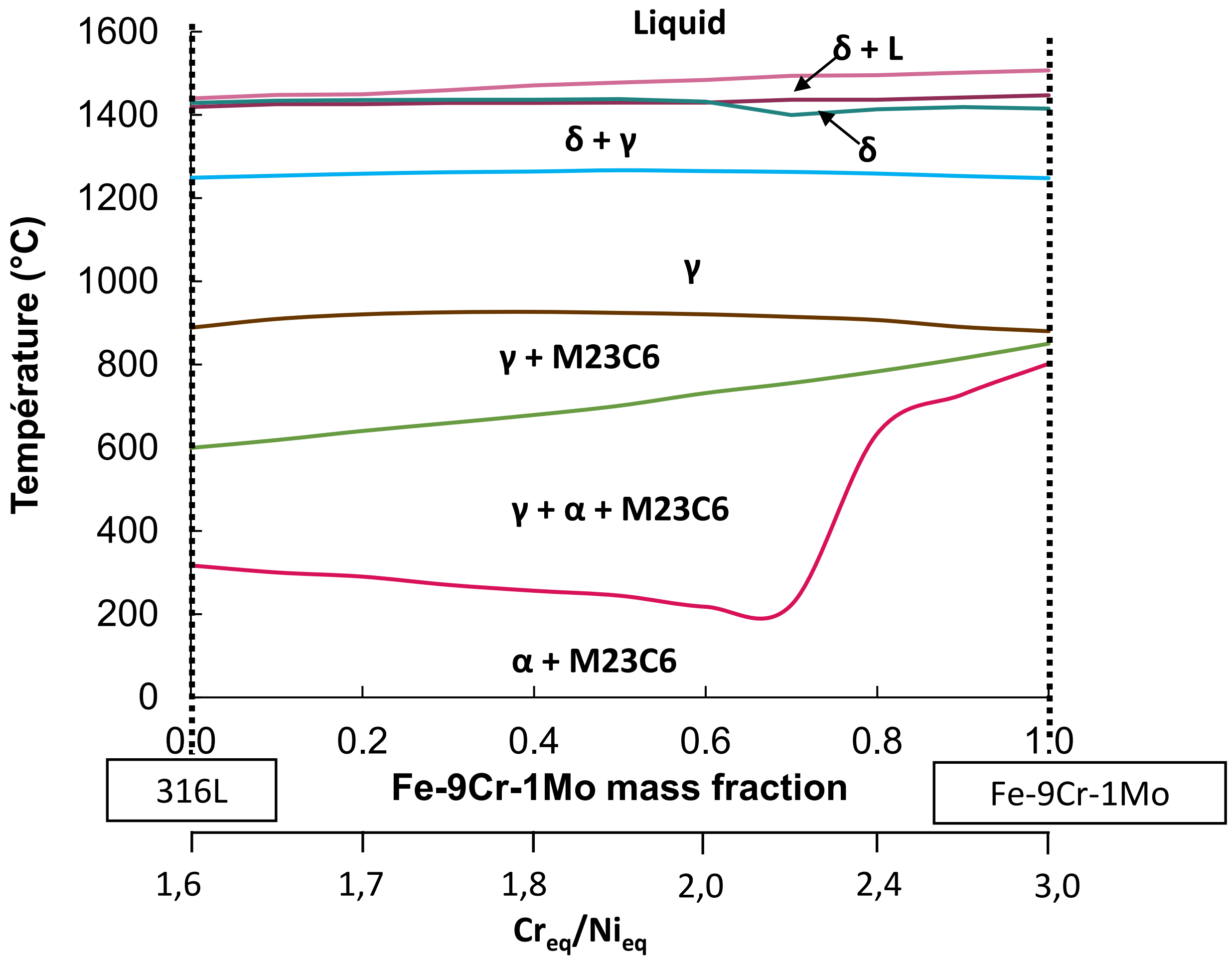
III. Conclusions and perspectives

Link between compositions and microstructures

Schaeffler diagram

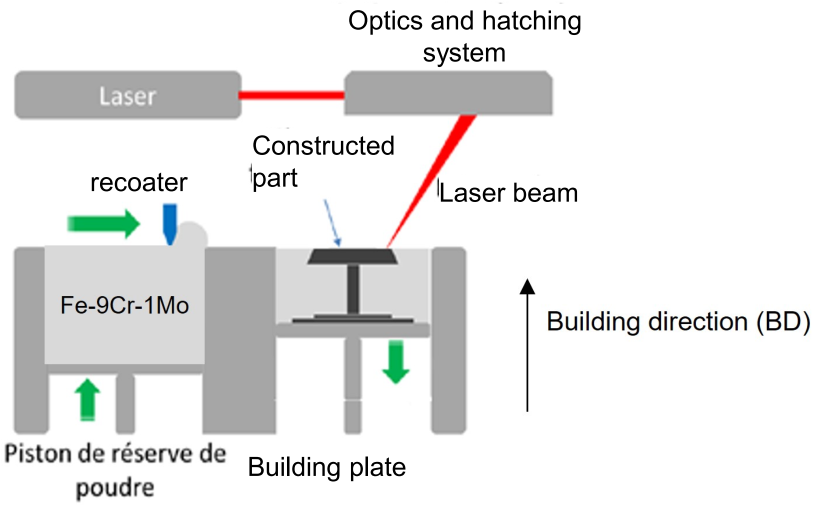


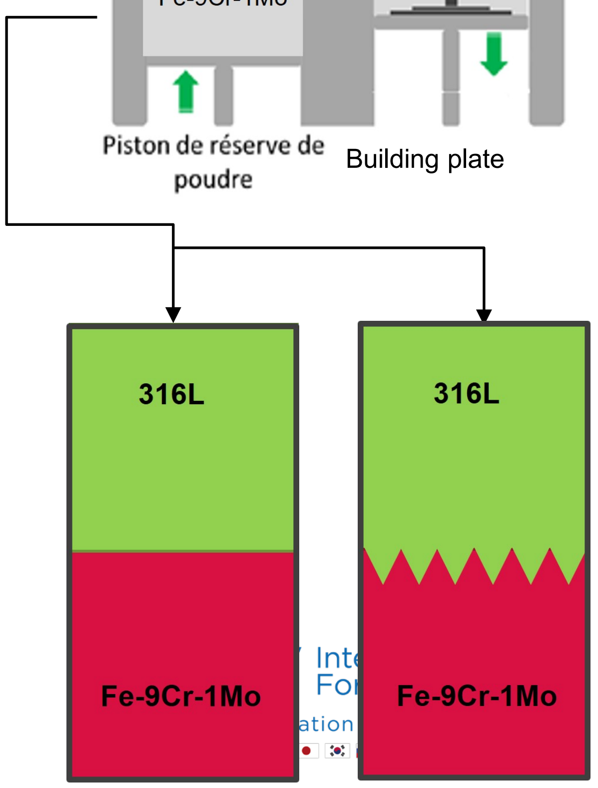
Pseudo binary diagram at equilibrium 316L/ Fe-9Cr-1Mo



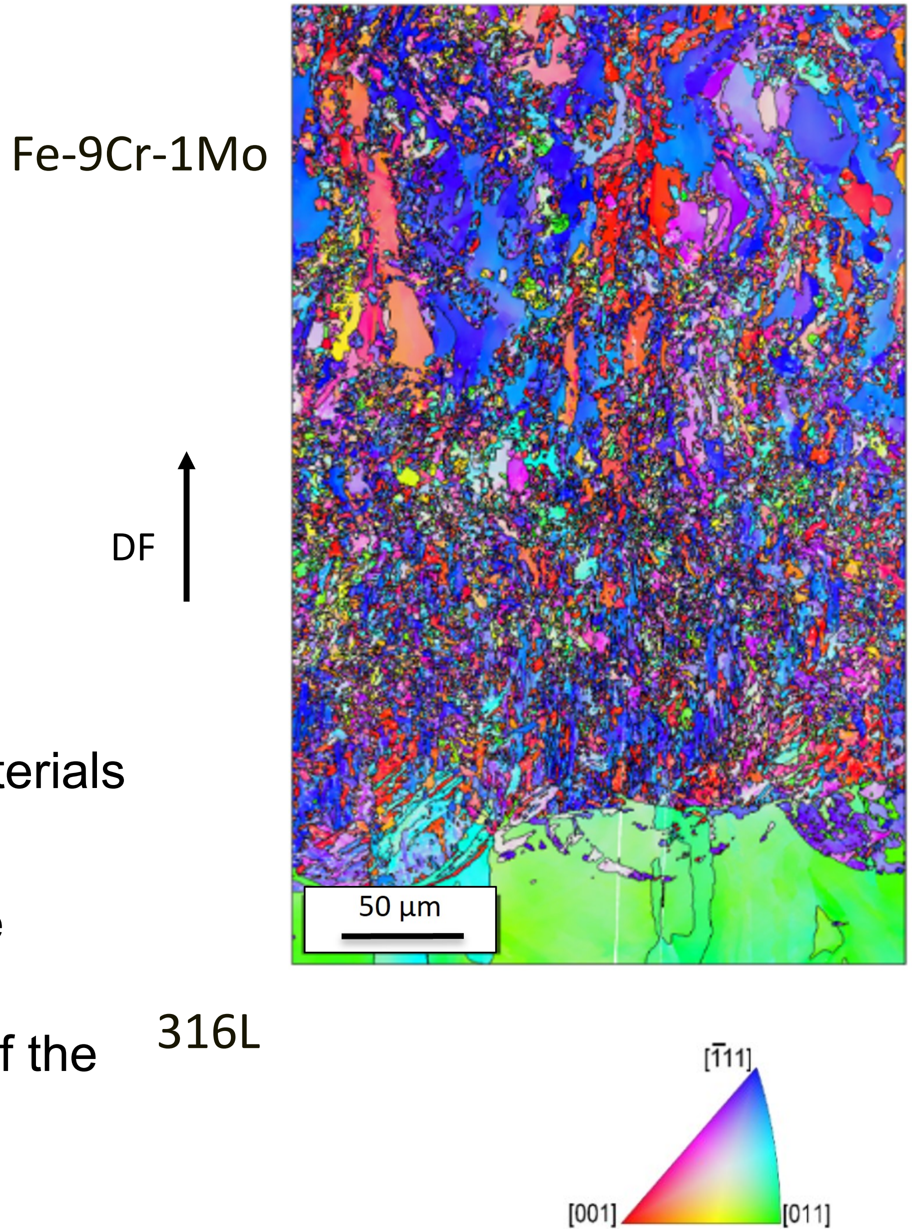
- Change from austenite to martensite
- Many different microstructures in few millimeters
- Possible to form A+M+F mix

PBF gradient material ?



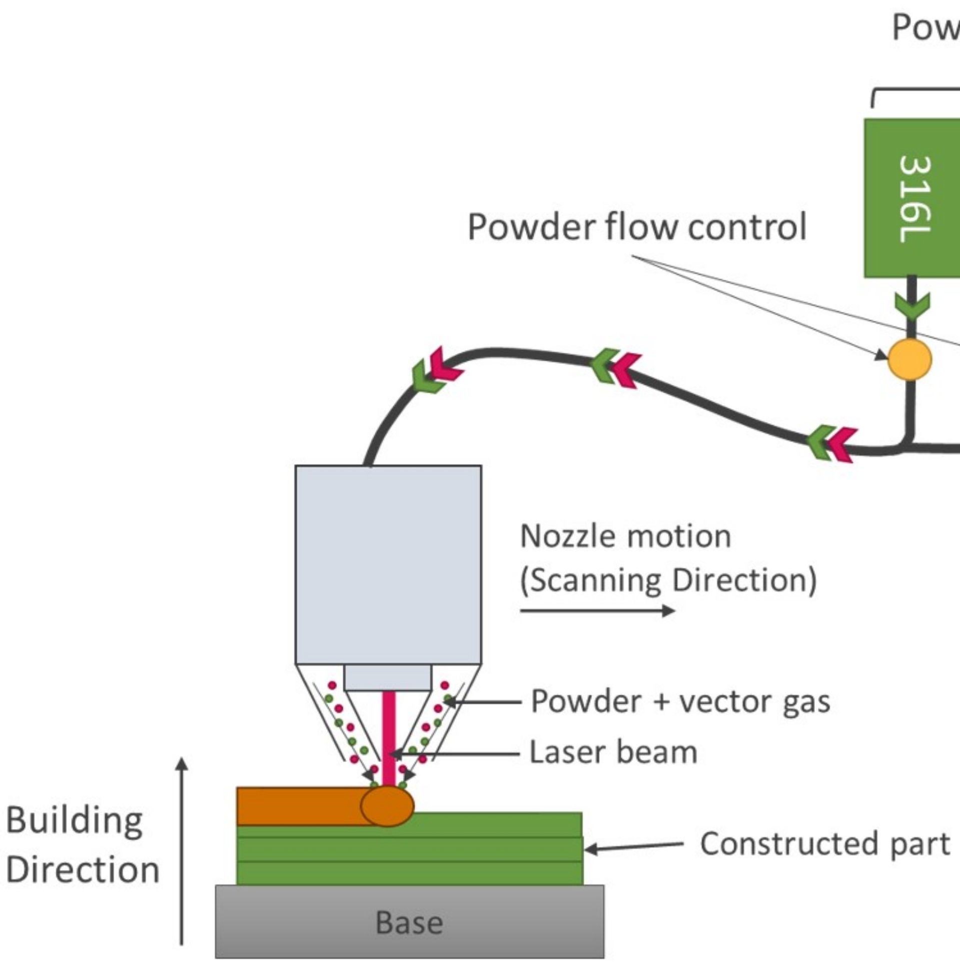


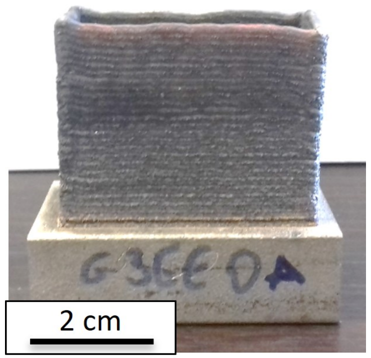
CEA Saclay



- Filling the powder reserve with 2 materials
- Junctions without defects
- Possibility to control the extent of the gradient by the filling method
- Microstructure change at the place of the chemical gradient : A -> M -> M+F

Matériaux à gradient par DED-LB





PIMM, Arts et Métiers Paris

- Building parameters optimized for 316L
- P and v kept constant for 316L and Fe-9Cr-1Mo
- D varies from a sample to another to control the layer height
- Composition is controlled at each layer by the powder flow

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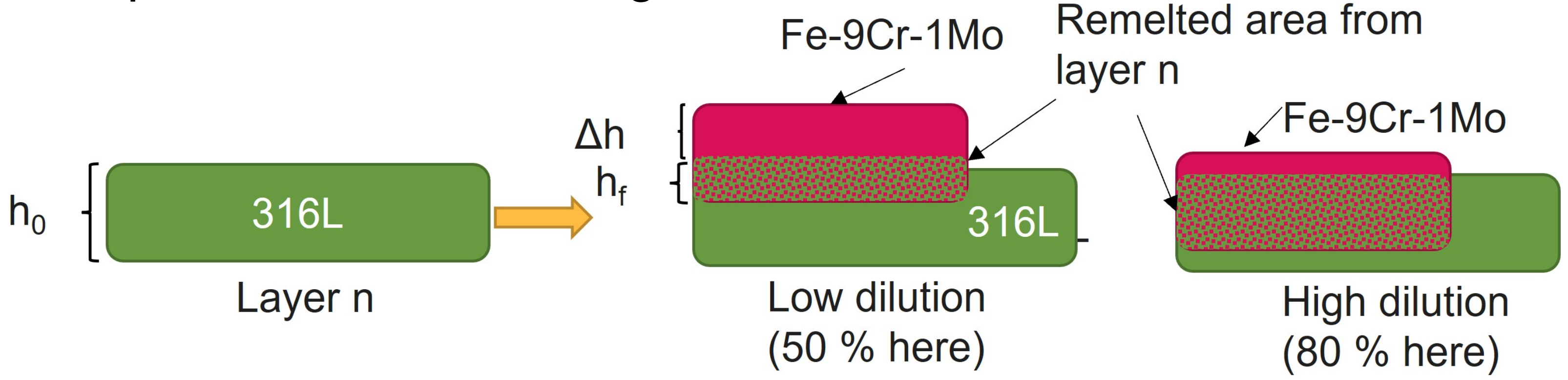
Dilution in additive manufacturing

- In AM, dilution = overlap rate between two beads (remelting rate)

→ Concept used a lot in welding



layer n+1 (Fe-9Cr-1Mo)

$$\text{Dilution: } D = \frac{h_0 - \Delta h}{h_0}$$

Composition of layer n+1, C_{n+1} :

$$C_{n+1} = C_n \times D + C_{proj} \times (1 - D)$$

With P = 400 W and v = 300 mm/min kept constant, D is function of powder flow (g/min)

Power (W)	Scanning speed (mm/s)	316L flow (g/min)	Fe-9Cr-1Mo flow (g/min)	Layer height (µm)	Dilution	Volume energy density
400	5	4	2	200	80 %	285
		12	10	600	50 %	95

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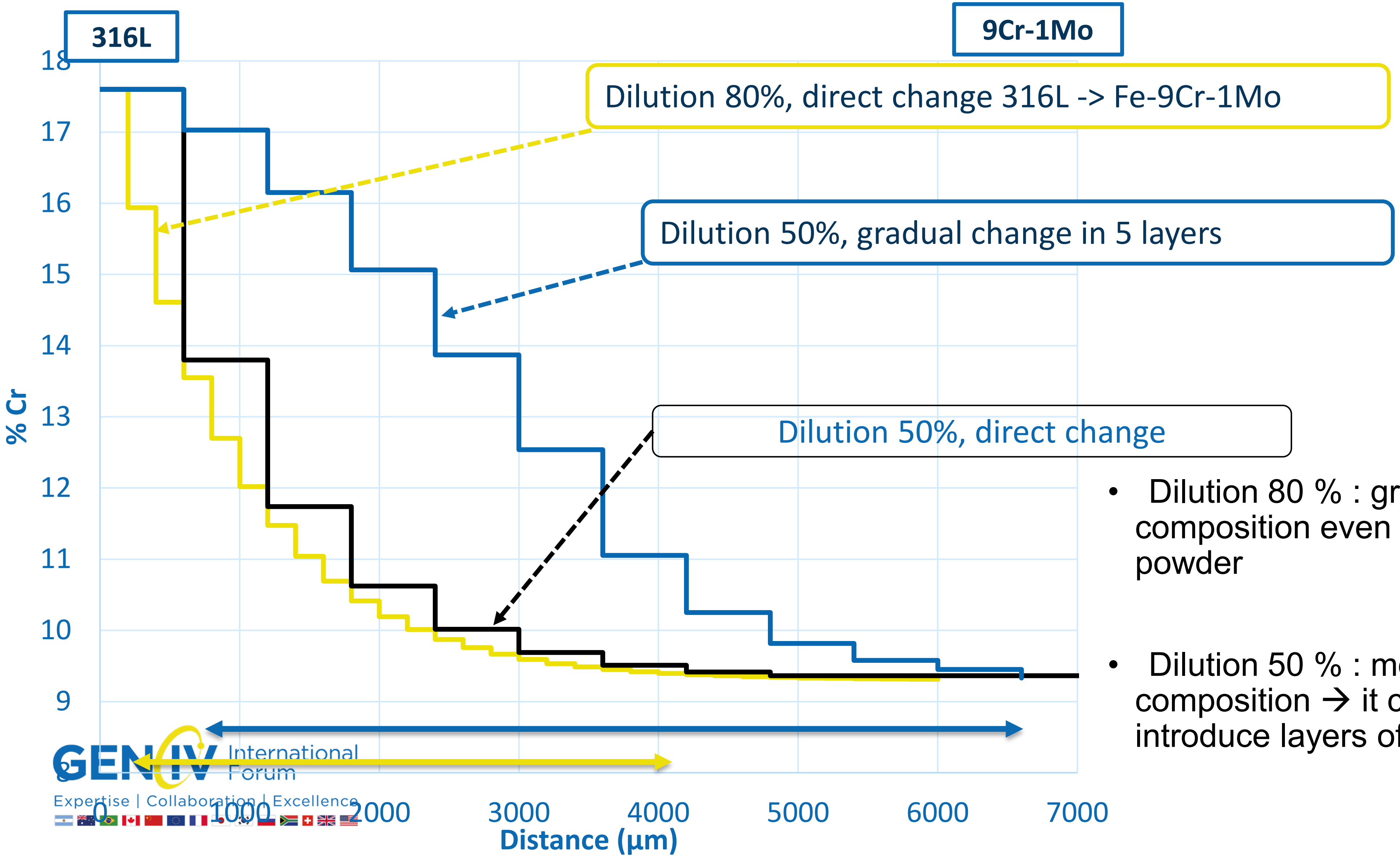
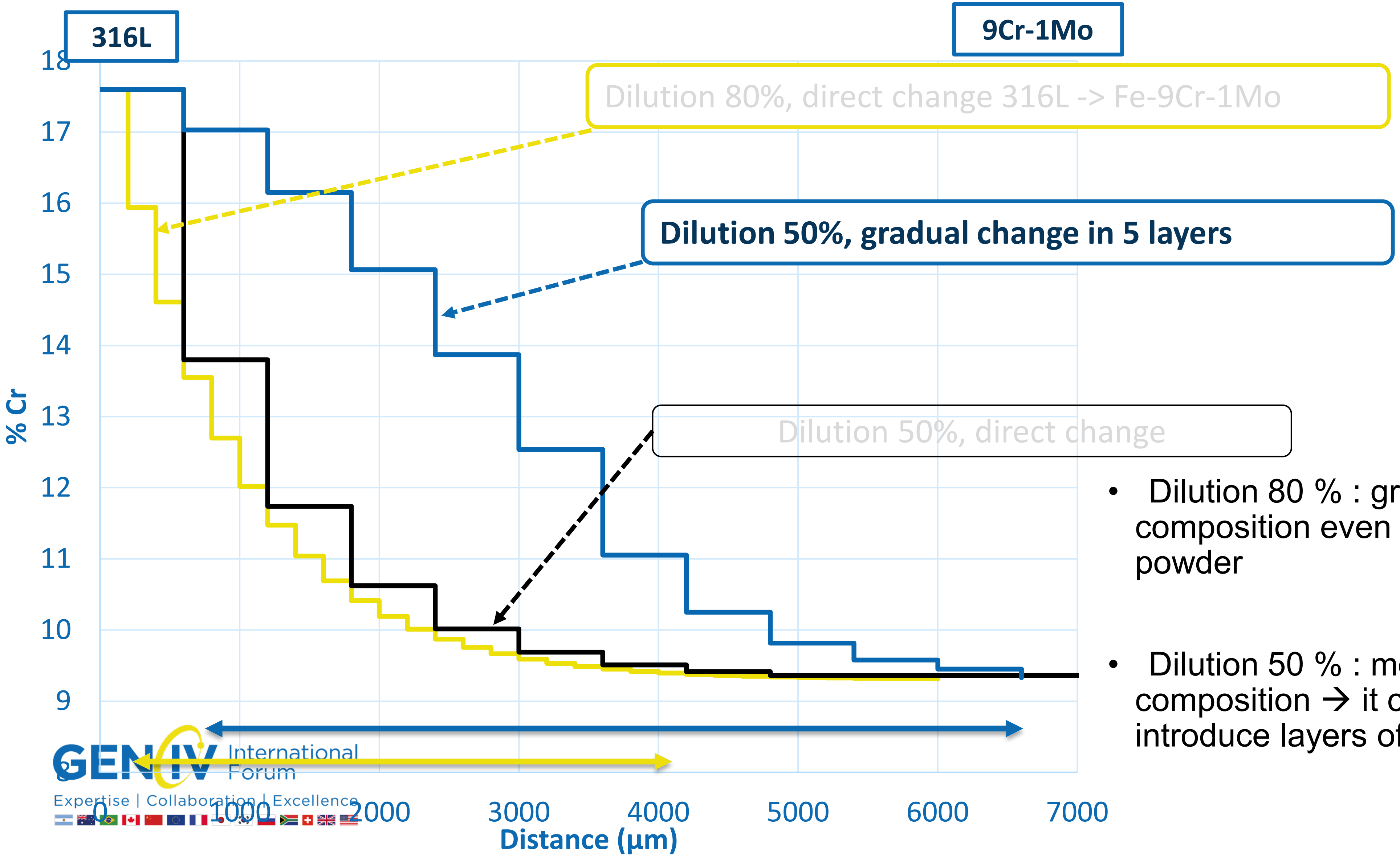
Theoretical composition in the gradient calculated with the dilution



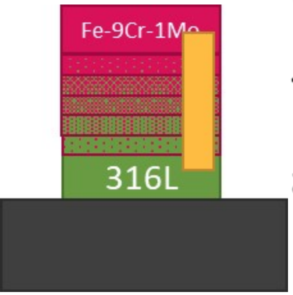
- Dilution 80 % : gradual change of the composition even with a direct change of powder
- Dilution 50 % : more abrupt change of composition → it could be useful to introduce layers of intermediate composition

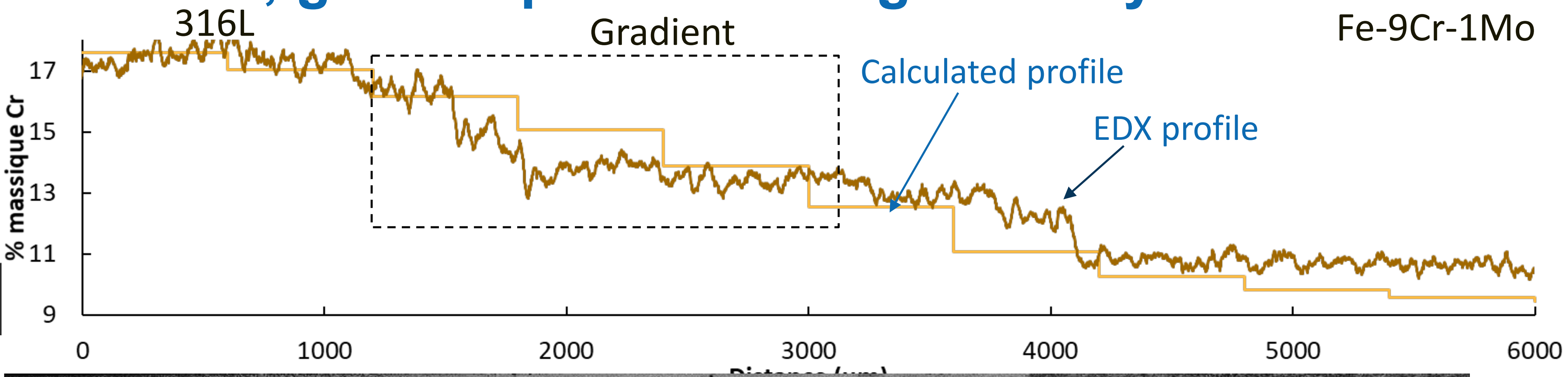
Theoretical composition in the gradient calculated with the dilution

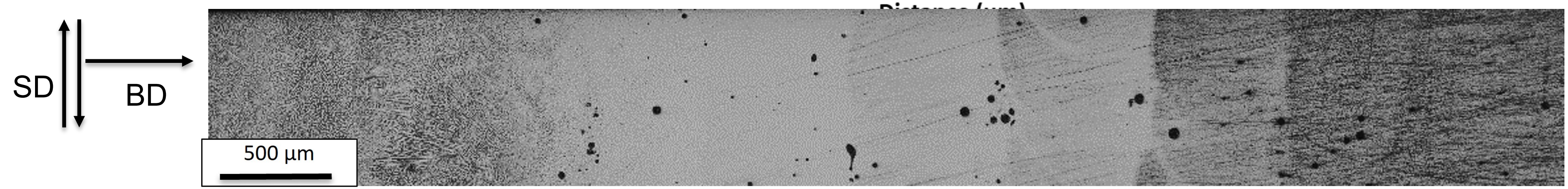


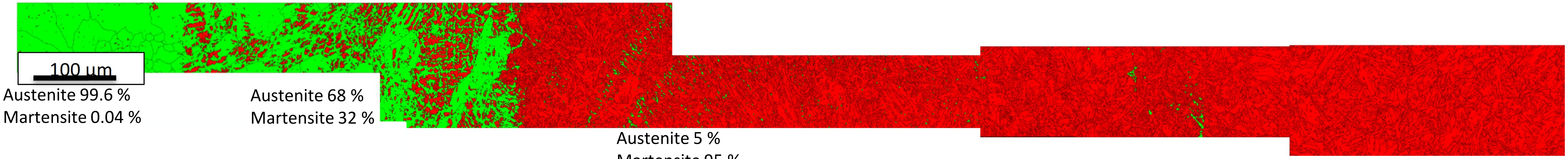
- Dilution 80 % : gradual change of the composition even with a direct change of powder
- Dilution 50 % : more abrupt change of composition → it could be useful to introduce layers of intermediate composition

Dilution 50 %, gradual powder change in 5 layers









Austenite 99.6 %
Martensite 0.04 %

Austenite 68 %
Martensite 32 %

Austenite 5 %
Martensite 95 %

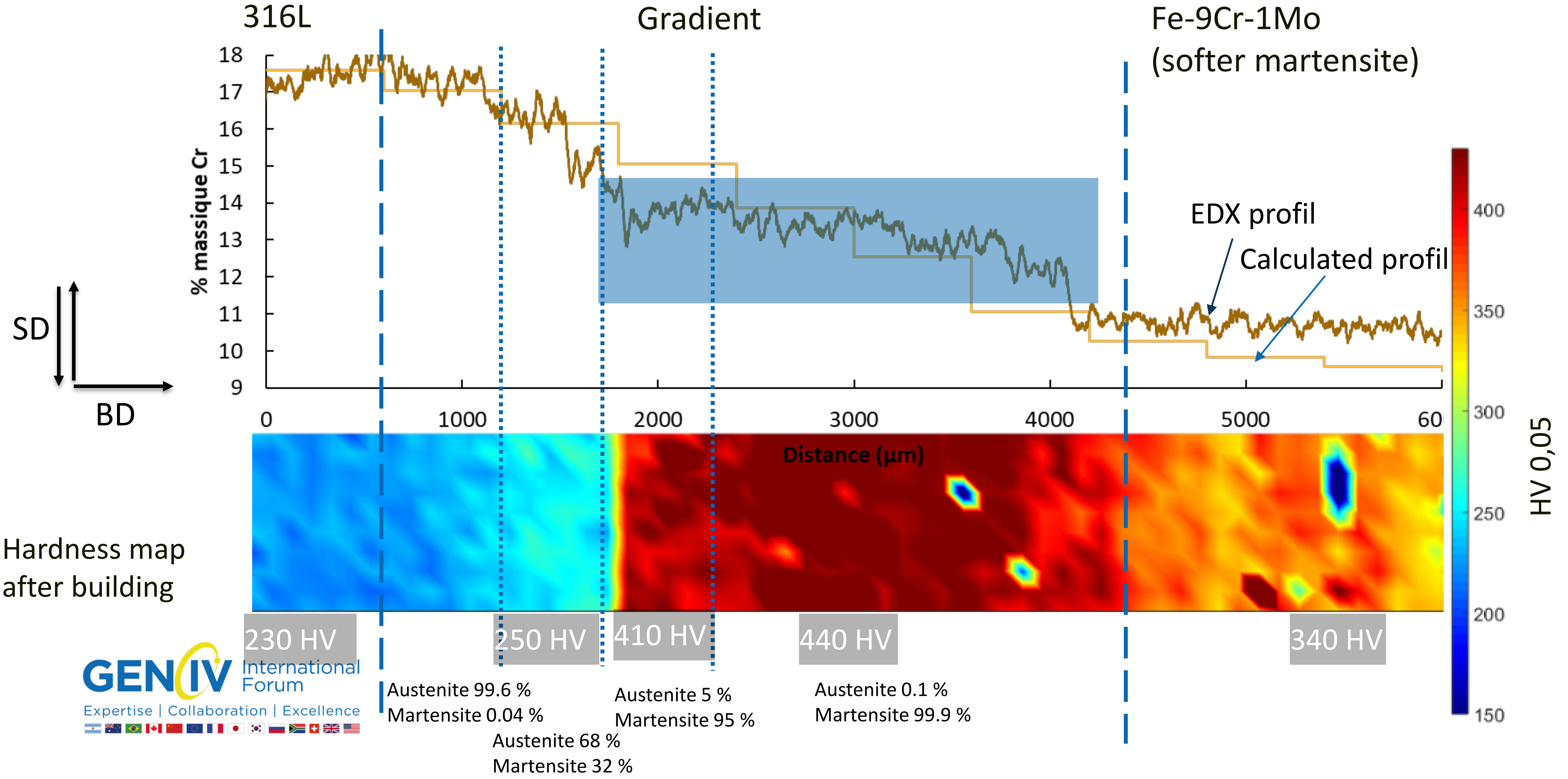
Austenite 0.1 %
Martensite 99.9 %

Austenite (FCC)

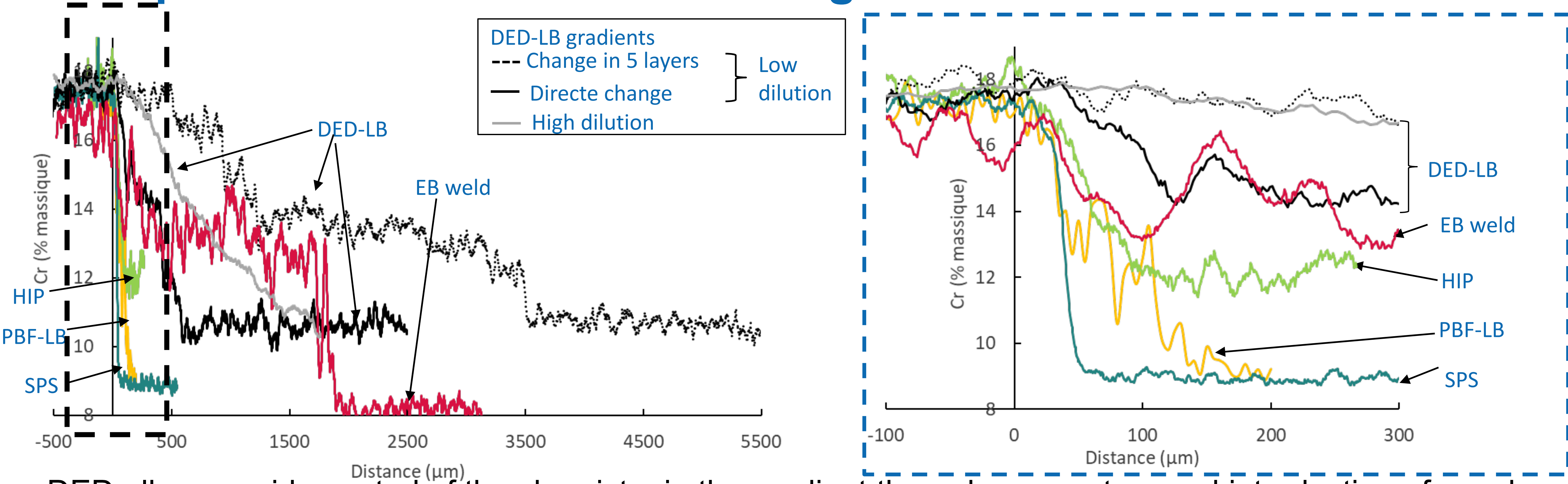
Martensite (BCC)

- Gradient over several mm
- Good correlation between measured/calculated gradient
- Evolution of the austenite fraction with the composition

Dilution 50 %, gradual powder change in 5 layers



Comparison between the different gradients



- DED allows a wide control of the chemistry in the gradient through parameters and introduction of powder mix
- Short gradients can be obtained in PBF (low layer height)
- SPS and HIP sintering processes allow to obtain short gradients (diffusion)
- Possibility to control and anticipate the chemistry and the length of the gradient in DED by :
  - The blown composition (chemistry)
  - The dilution rate used (manufacturing parameters)

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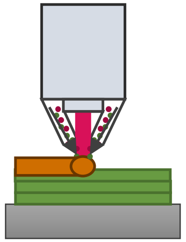
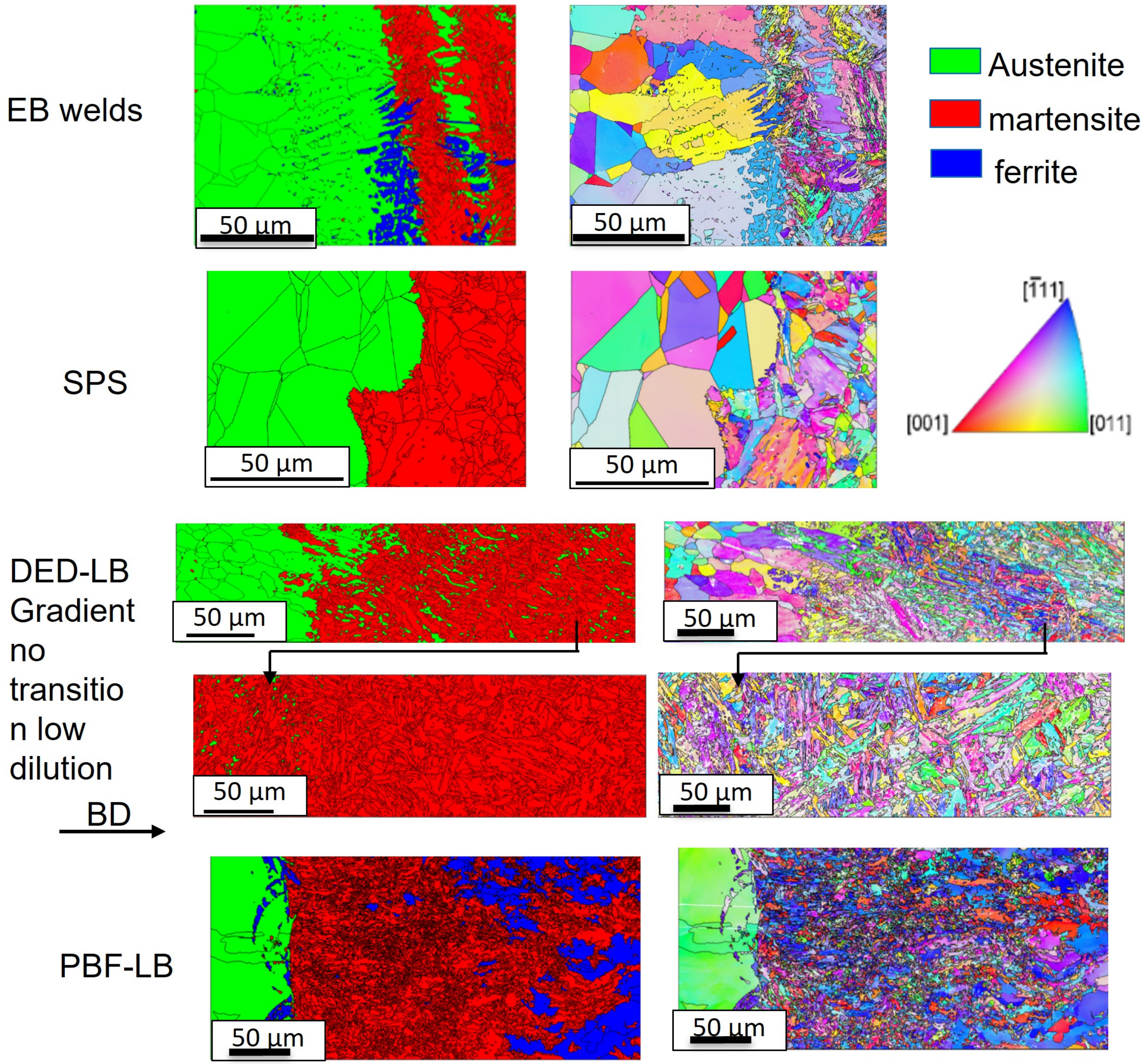


III. Conclusions and perspectives

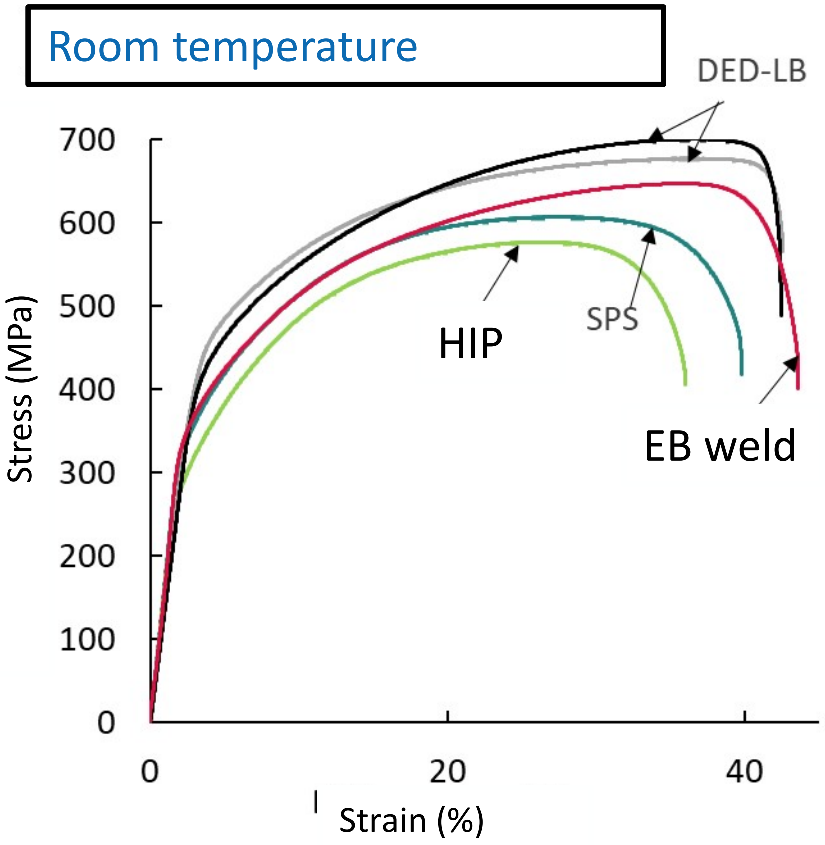
Conclusions : microstructure

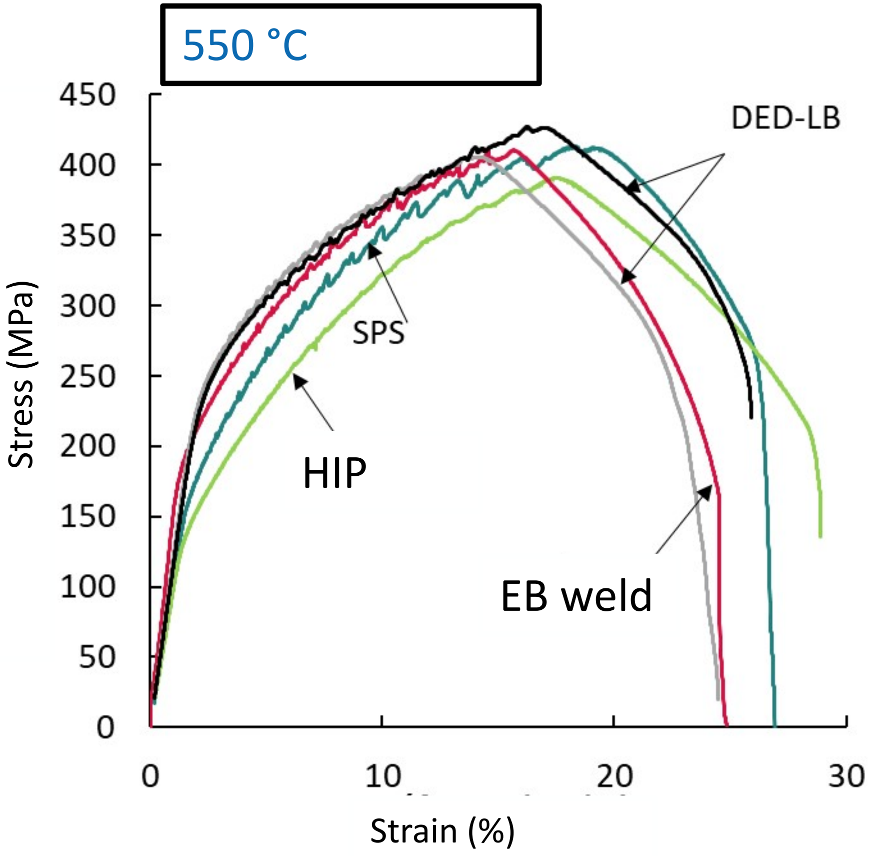


- Relationships between composition and cooling rate : microstructure control in martensitic steels
- Metallurgical continuity assured between the two materials
- Diverse microstructures depending on the process used
  - Local melting with welding
  - Transformation of the whole material without melting with SPS/HIP
  - Transformation of the whole material with melting in AM
- Links between chemistry – microstructure – microhardness
- Prediction and control of chemistry in DED

Conclusions : tensile tests

- After heat treatment 630 °C/8 h





- Similar macroscopic behavior
- Failure on the 316L side at 20°C and 400°C, on the Fe-9Cr-1Mo side at 550°C
- Encouraging results for the use of these materials in an industrial context
- Need for a more complete evaluation of these junctions

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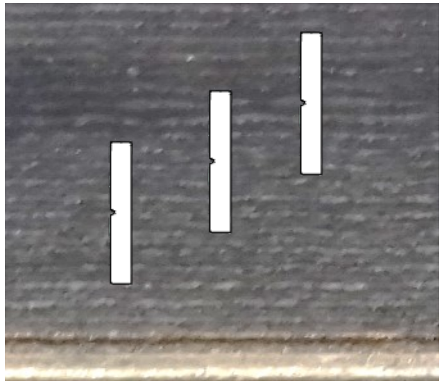
Proposals for further studies

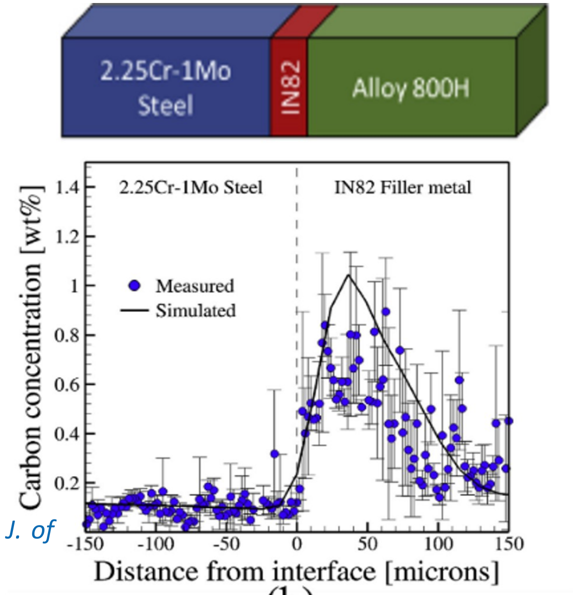
- Toughness



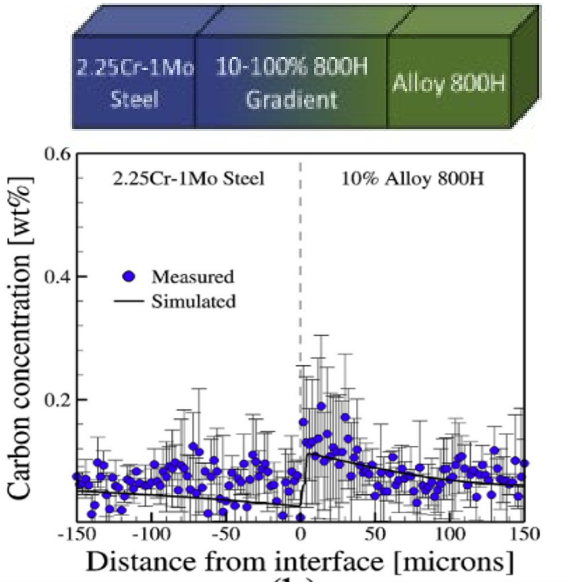
- Aging (carbon diffusion, introduction of a barrier material)

235 h at 725 °C

Zuback, J. S et al. (2019), *J. of Alloys and Compounds*.



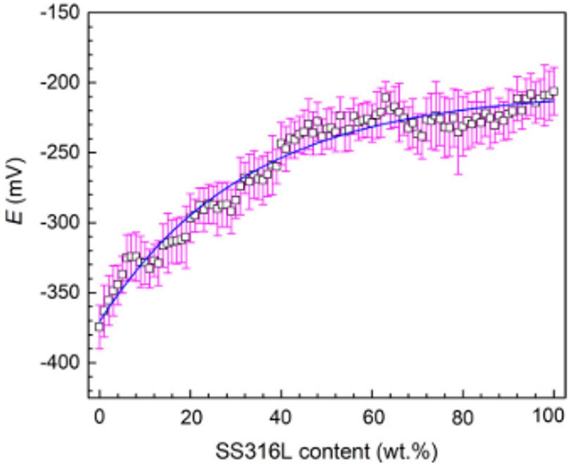
(b)



(b)

Alloy 800H = 21 %Cr et 34 % Ni (γ)

- Corrosion



Gradient 316L/SS431 (martensitic at 18 %Cr)

J. Nie et al, Addit. Manuf. 35 (2020)

- Irradiation

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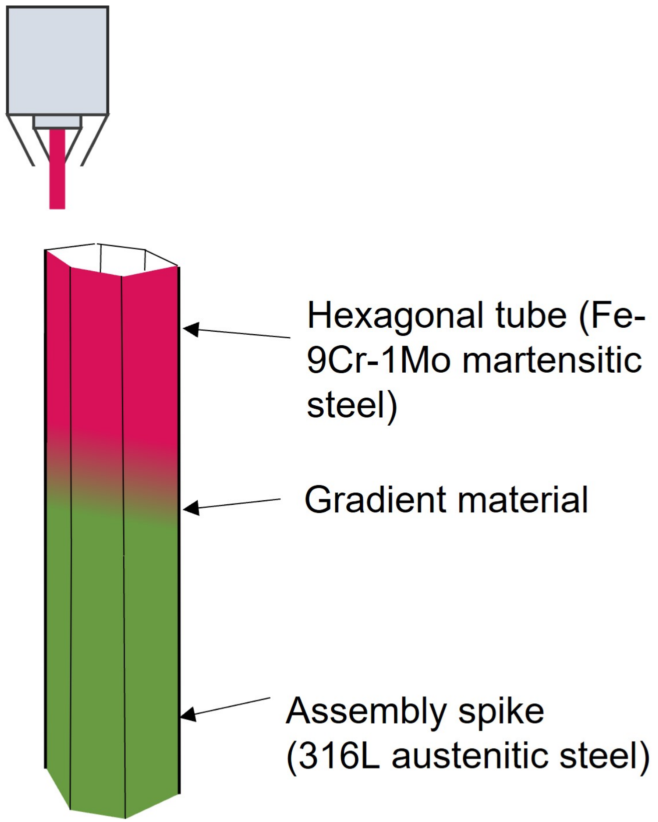
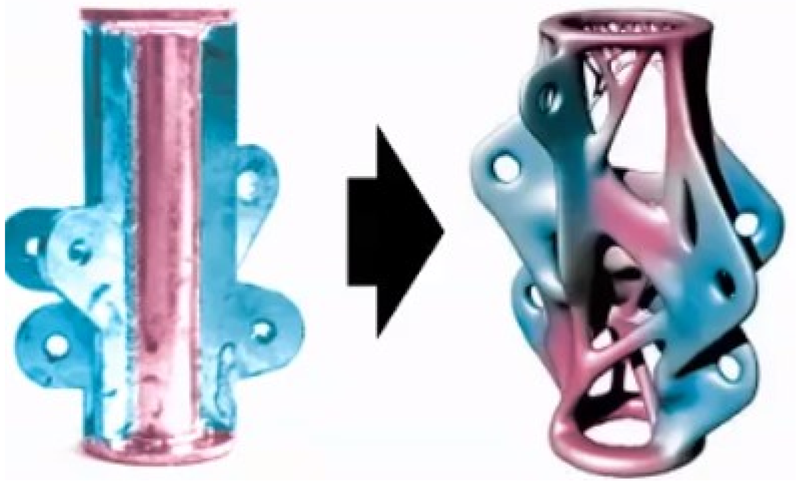
Toward the fourth dimension…

Toward the fourth dimension…





P. Hosemann, NUMAT 2020

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Thank you

Flore Villaret
Flore.villaret@edf.fr
EDF R&D
MMC – C24
Avenue des Renardières
77250 – Moret sur Loing
FRANCE

Upcoming Webinars

Date24	Title	Presenter
27 January 2022	ESFR SMART a European Sodium Fast Reactor concept including the European feedback experience and the new safety commitments following Fukushima accident	Mr. Joel Guidez, CEA, France
24 February 2022	AI in support of NE Sector	Prof. Nawal Prinja, Jacobs, UK
23 March 2022	Scale Effects and Thermal-Hydraulics: Application to French SFR	Mr. Benjamin Jourdy, CEA, France