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Poly-Si and SiC-based CVD coatings for high temperature structural applications

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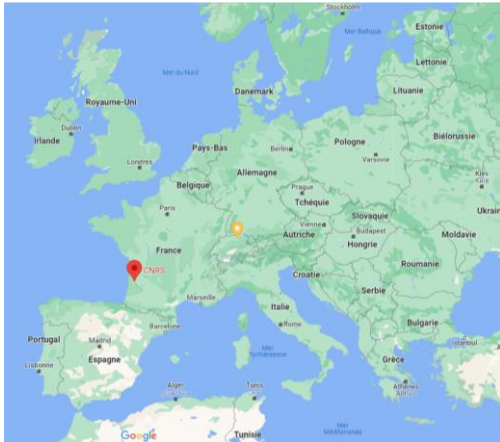
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Univ. Bordeaux, CNRS, Safran, CEA



université
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Fully dedicated to thermostructural ceramics and composites, especially CMCs & SiC/SiC



Poly-Si and SiC-based CVD Coatings for High Temperature Structural Applications

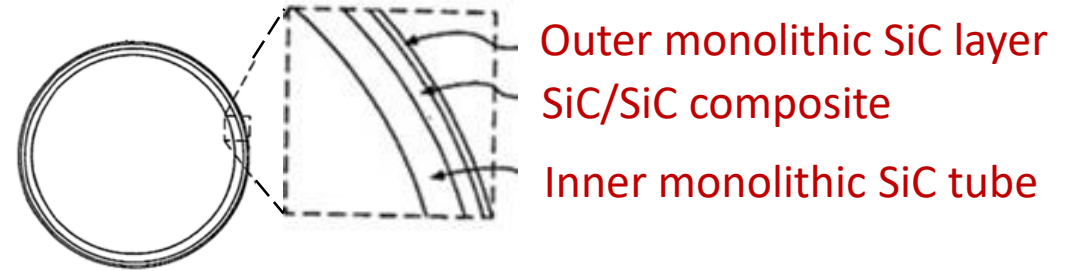
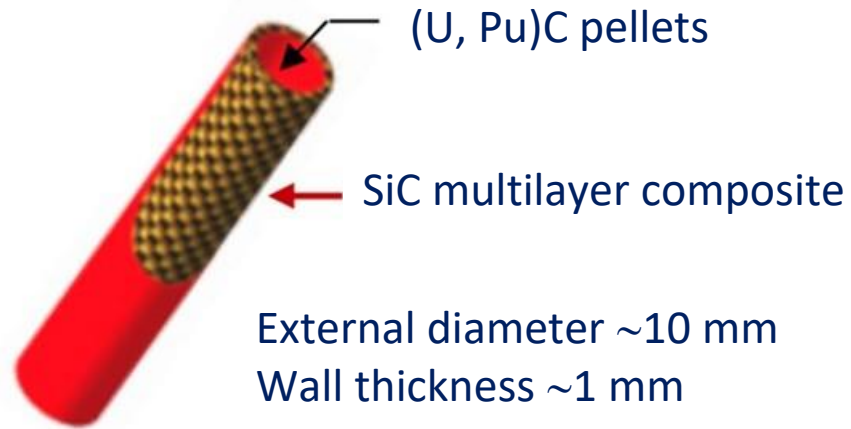
A. Le Doze, P. Drieux, S. Jacques, G. Couégnat, **G. Chollon**

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Applications of CVD Coatings : energy...

e.g., nuclear fuel claddings for future reactors



“Triplex” patent: 2006 (US)

High strength up to ~ 2000°C (accidental)
Corrosion resistance
Structural stability under neutrons
Neutron transparency, low activation

→ Pure & crystalline SiC coatings

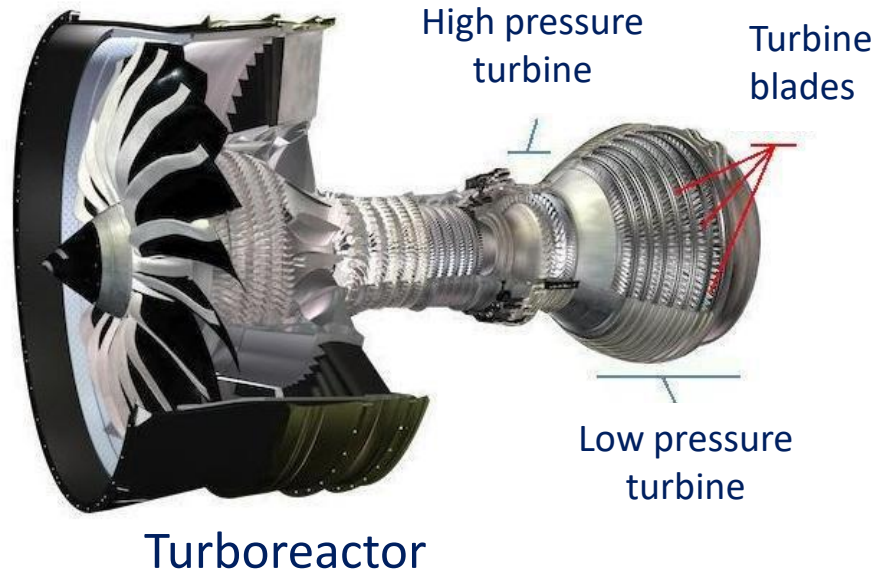
Tolerance to damage

→ Fiber composites



Applications of CVD Coatings : aeronautics...

e.g., SiC/SiC composite parts for civil aircraft engines



Substitute nickel superalloys for CMCs

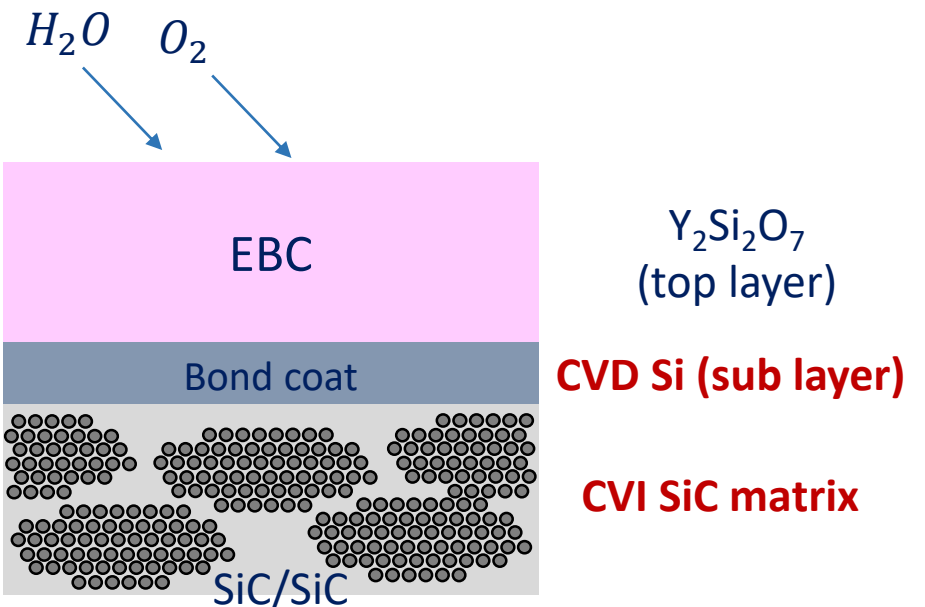
→ Increase operating temperature

→ Improve efficiency, reduce NOx and kerosene consumption

High strength up to ~ 1300°C
High creep resistance
High strength, low *CTE*
High thermal conductivity
Tolerance to damage
Corrosion resistance under high P_{H_2O}
Long service life

→ SiC/SiC composite

→ Environmental barrier coating

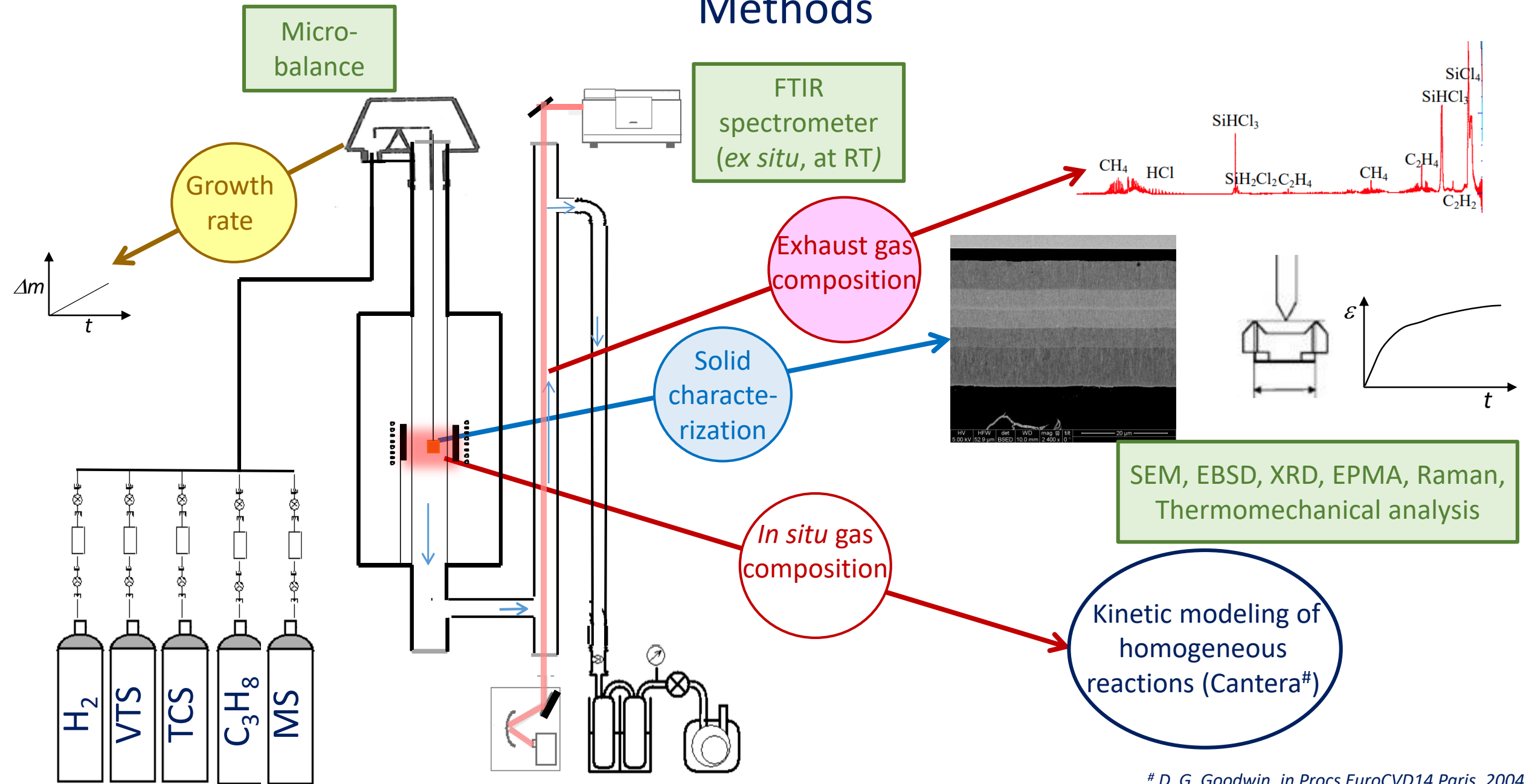


Objective: development of various HT structural CVD coatings

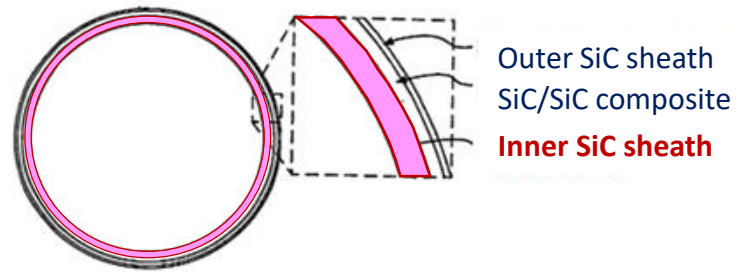
1- Monolithic CVD SiC tubes for nuclear fuel claddings

2- CVD poly-Si coating for an EBC bond coat

Methods



1- Monolithic CVD SiC tubes for nuclear fuel claddings



“Triplex” concept

Requirements

Geometry :

- Tubular, ~8 mm outer \varnothing
- Thickness > 100 μm
- Long lengths (~1m)

Properties :

- High density
- SiC stoichiometry
- High failure strain
(little S & V flaws)

Approach

Specific CVD reactor for

- high deposition rates
- continuous deposition

Investigate the CVD mechanism

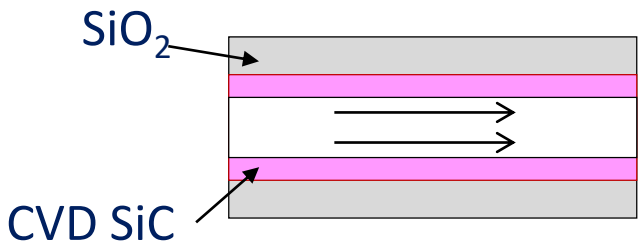
- Chemical analysis of the gas phase
- Deposition kinetics
- Chemical and structural analyses

Specific mechanical tests

- Suited to tubular geometry
- At room and HT

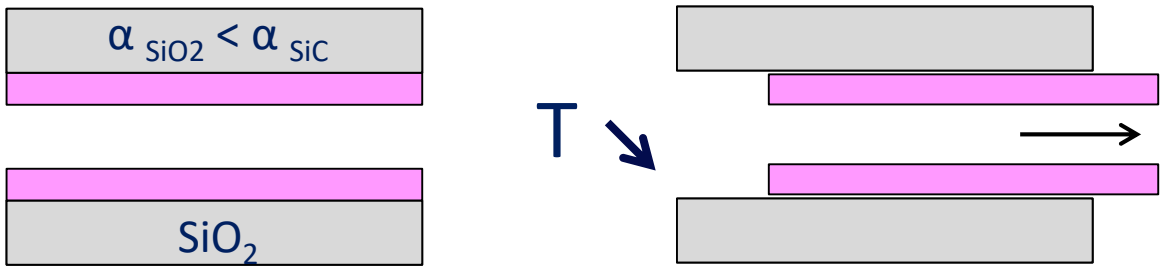
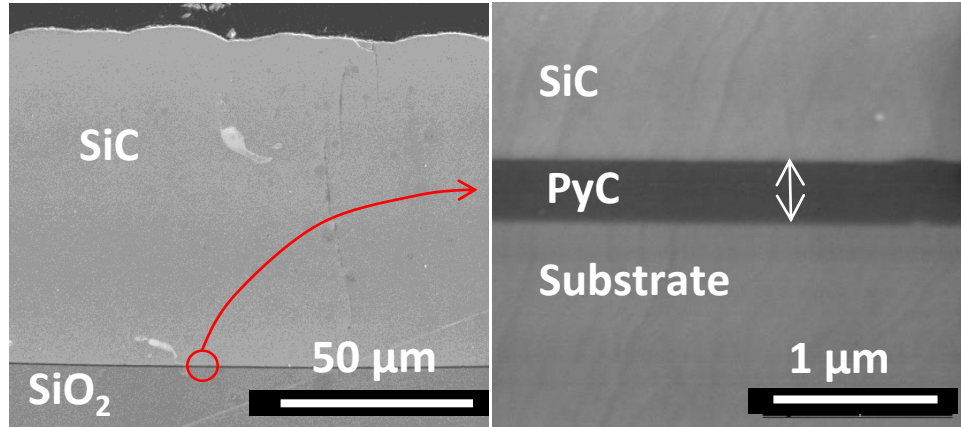
Choice of substrate

Coatings inside vitreous silica tube



- Hot wall reactor
- + Very smooth surface
- + homogeneous coating
- Adhesion between SiC and SiO₂

⇒ Pyrocarbon coating to prevent SiC/SiO₂ interaction
+
CTE mismatch promotes delamination on cooling

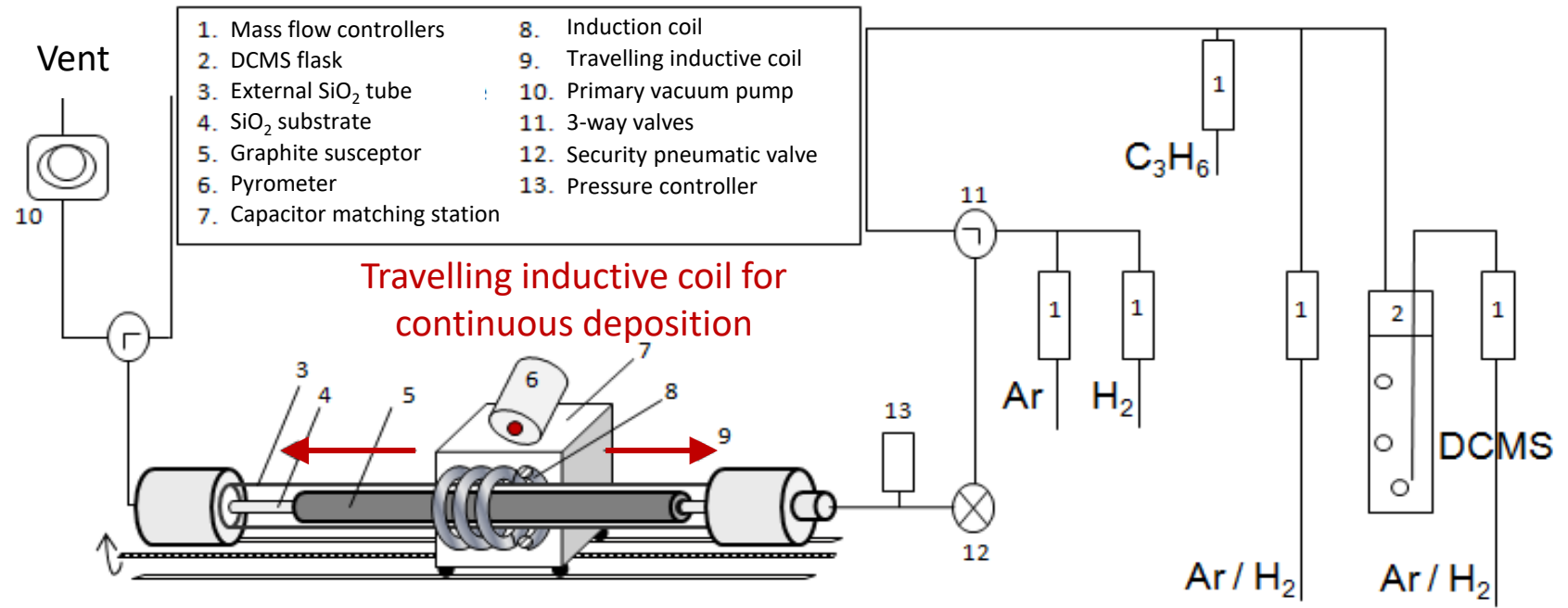


CVD reactor design

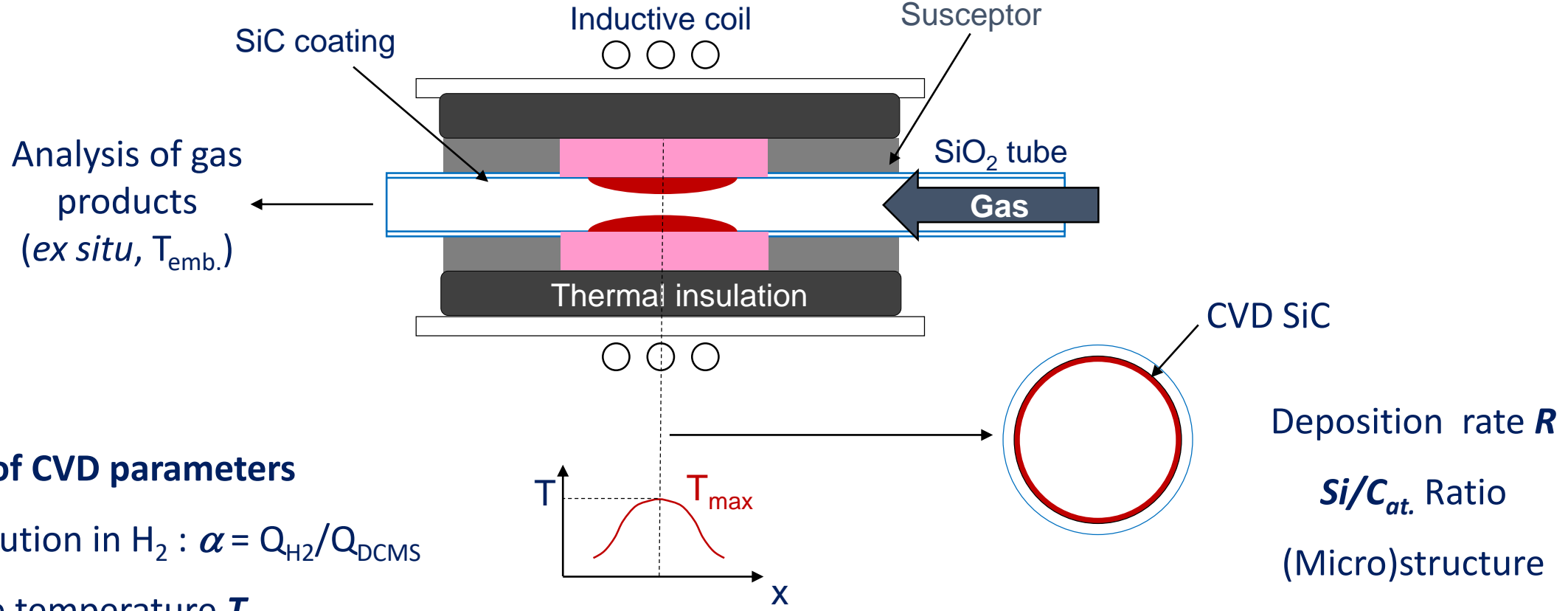
Precursor/conditions : $\text{CH}_3\text{SiHCl}_2$ (DCMS)/ H_2 at **atmospheric pressure**
→ high vapor pressure (48 kPa at 20 °C) : driven by H_2/Ar bubbling

Reactor design:

- External walls: horizontal silica tube L =1000 mm, $\varnothing = 50$ mm
- Heating: travelling RF induction coil, fixed graphite tube susceptor, T monitored by pyrometry
- Substrate : fixed SiO_2 tube inserted in the graphite susceptor
- Outlet: vent (APCVD) or rotary pump (vacuum testing, LPCVD of PyC)



Static configuration



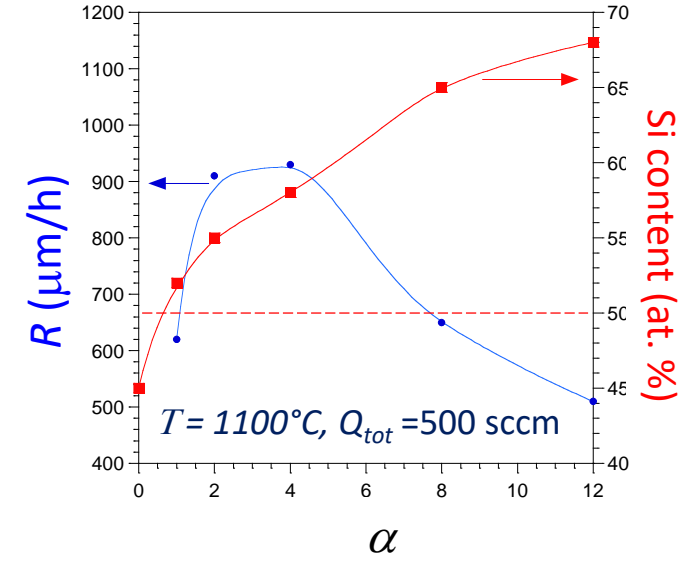
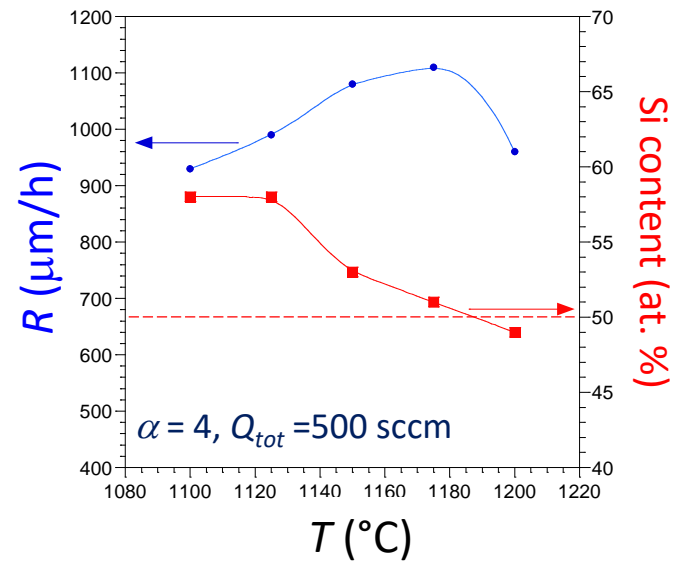
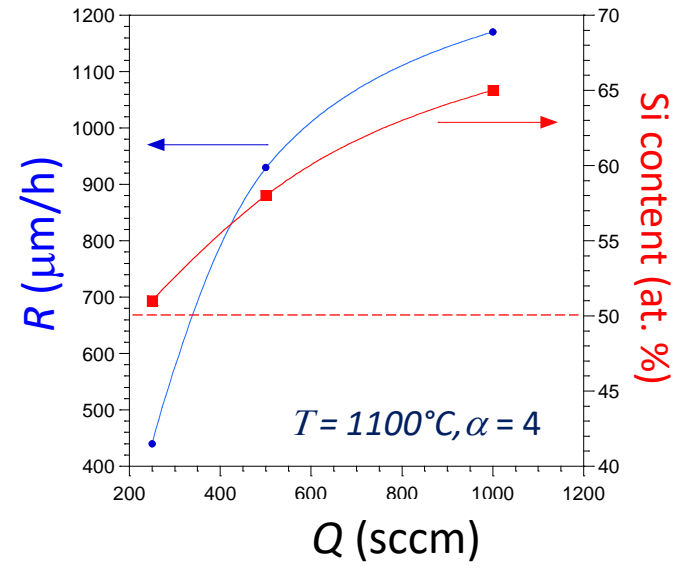
Influence of CVD parameters

DCMS dilution in H₂ : $\alpha = Q_{H_2}/Q_{DCMS}$

Substrate temperature T

Total flow rate Q (or residence time t_R)

Influence of CVD parameters



Strong increase of **R** with **Q**

Limited increase of **R** with **T**

→ mass transfer-limited regime

Composition varying from pure SiC to large Si excess

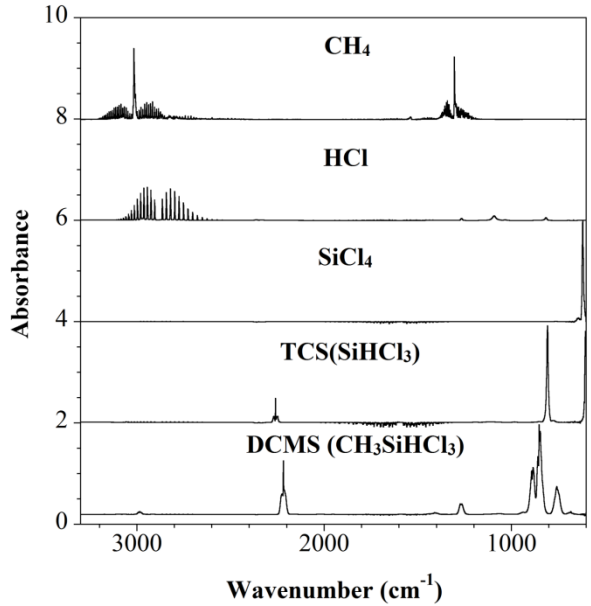
Si excess ↗ when **Q** ↗, **T** ↘ and **α** ↗

→ Influence of the DCMS decomposition rate (**T**, **t_r**)?

Influence of CVD parameters

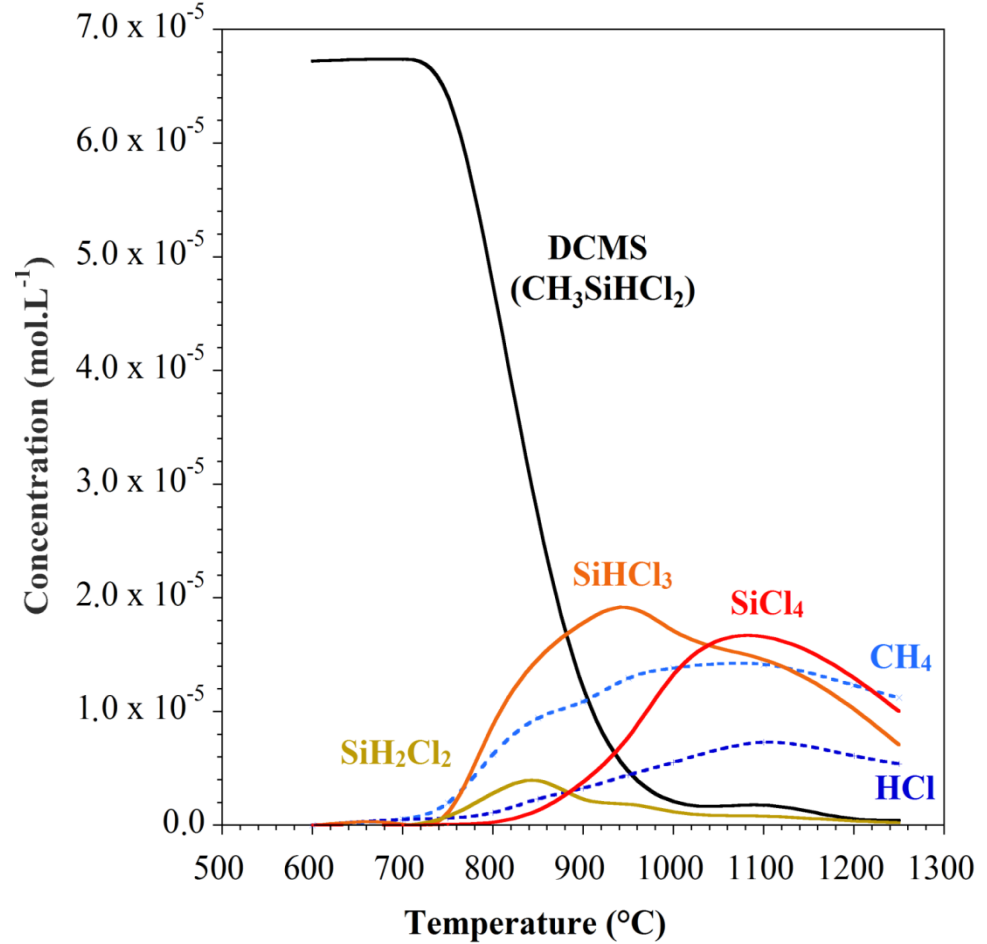
Influence of *T* on the gas phase (*ex situ*)

FTIR analysis of pure molecules
ab initio simulation of IR spectra



→ molar absorption coefficients ϵ of characteristic peaks

$\int A = \int \epsilon C L \rightarrow \text{Concentrations} = f(T)$



+ Thermo-kinetic calculations (CH₃•, HSiCl₂•, SiCl₂...)

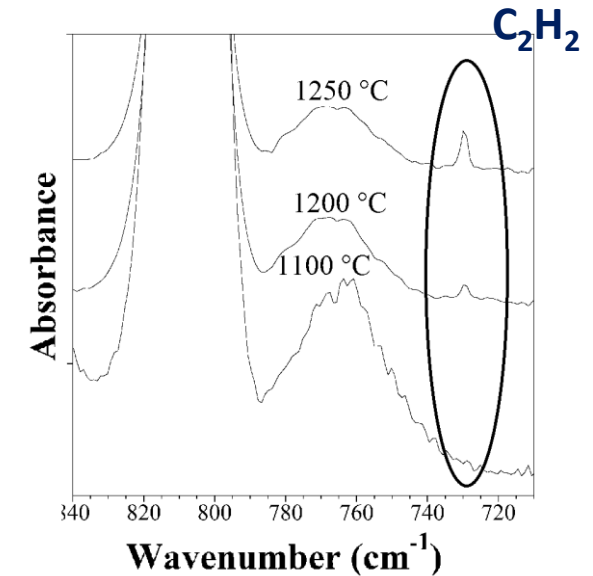
Influence of CVD parameters: discussion

Plausible homogeneous mechanism

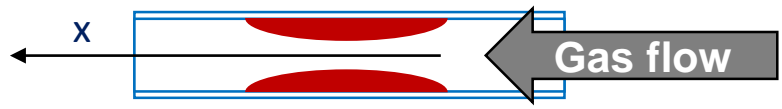
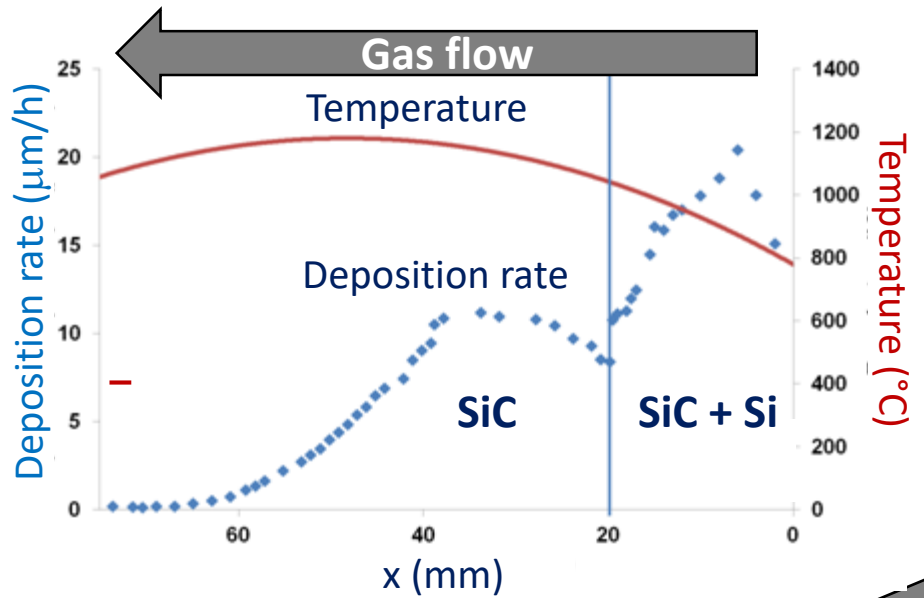
- DCMS dissociates into $\text{CH}_3^\bullet + \text{HSiCl}_2^\bullet$
- Cleavage of Si-H bonds (DCMS, HSiCl_2^\bullet) \rightarrow SiCl_2 (main Si silicon precursor)
- CH_3^\bullet recombines into CH_4 (stable)
- Formation of unsaturated hydrocarbons (e.g. C_2H_2) when T and $t_r \nearrow$

Consistent with changes of the coating composition

- SiCl_2 early formed and more reactive than CH_4
 - \rightarrow Si excess when $T \searrow$ and $Q_{tot} \nearrow$ ($t_r \searrow$)
- Reactive hydrocarbons appear when $T > 1100^\circ\text{C}$ and $t_r \nearrow$
 - \rightarrow Increase of C content
- Increase of H_2 concentration ($\alpha \nearrow$) \rightarrow reduction of SiCl_2 , stabilization of CH_4
 - \rightarrow Promotes the deposition of Si and prevents deposition of C



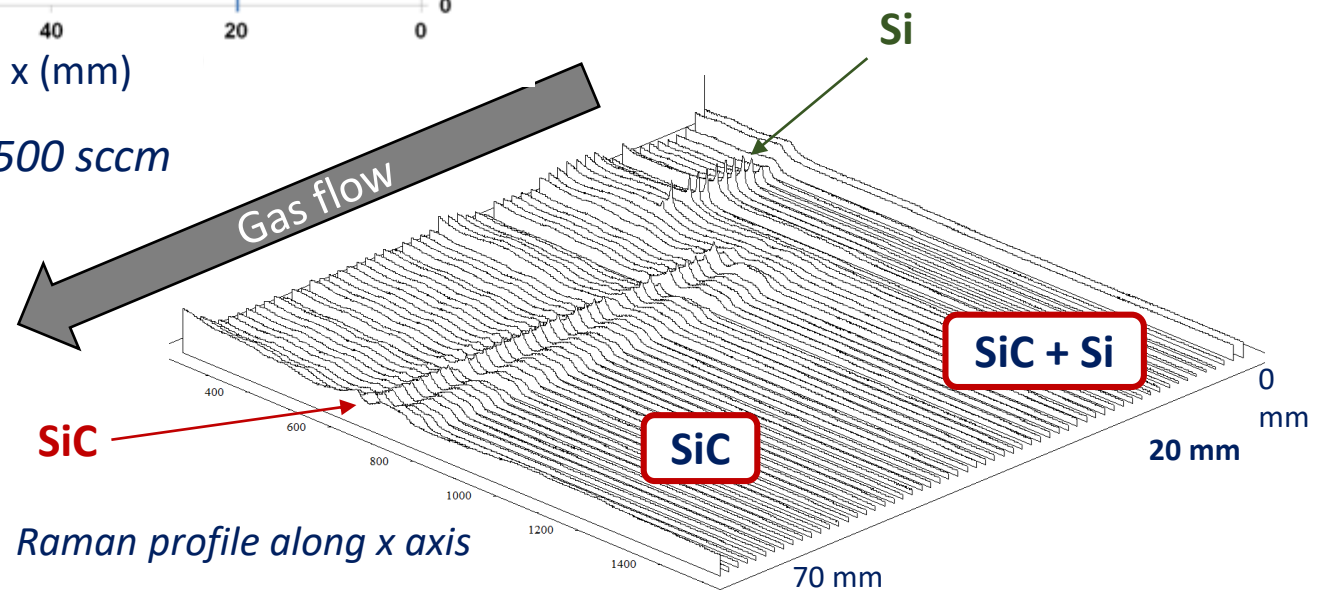
From static to continuous CVD: static



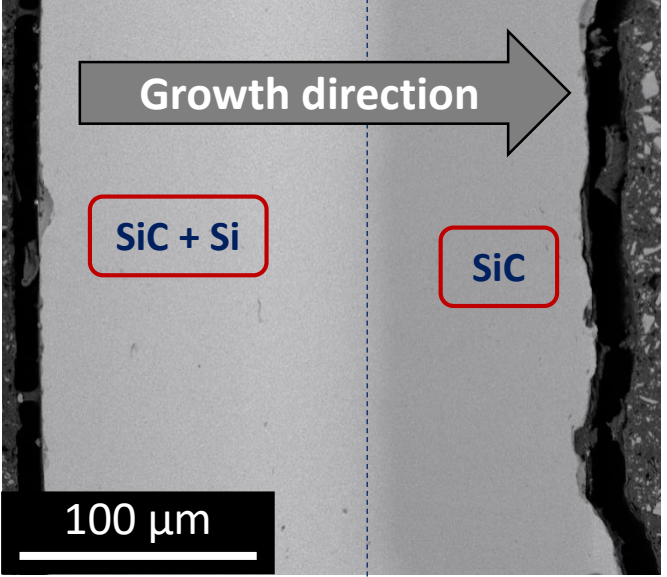
1st part of the coating :
 Deposition at low T / t_R
 → free Si
 → high deposition rate

2nd part of the coating:
 Deposition at high T / t_R
 → pure SiC
 → low deposition rate

$\alpha = 3, T = 1200 \text{ }^\circ\text{C}, Q_{tot} = 500 \text{ sccm}$

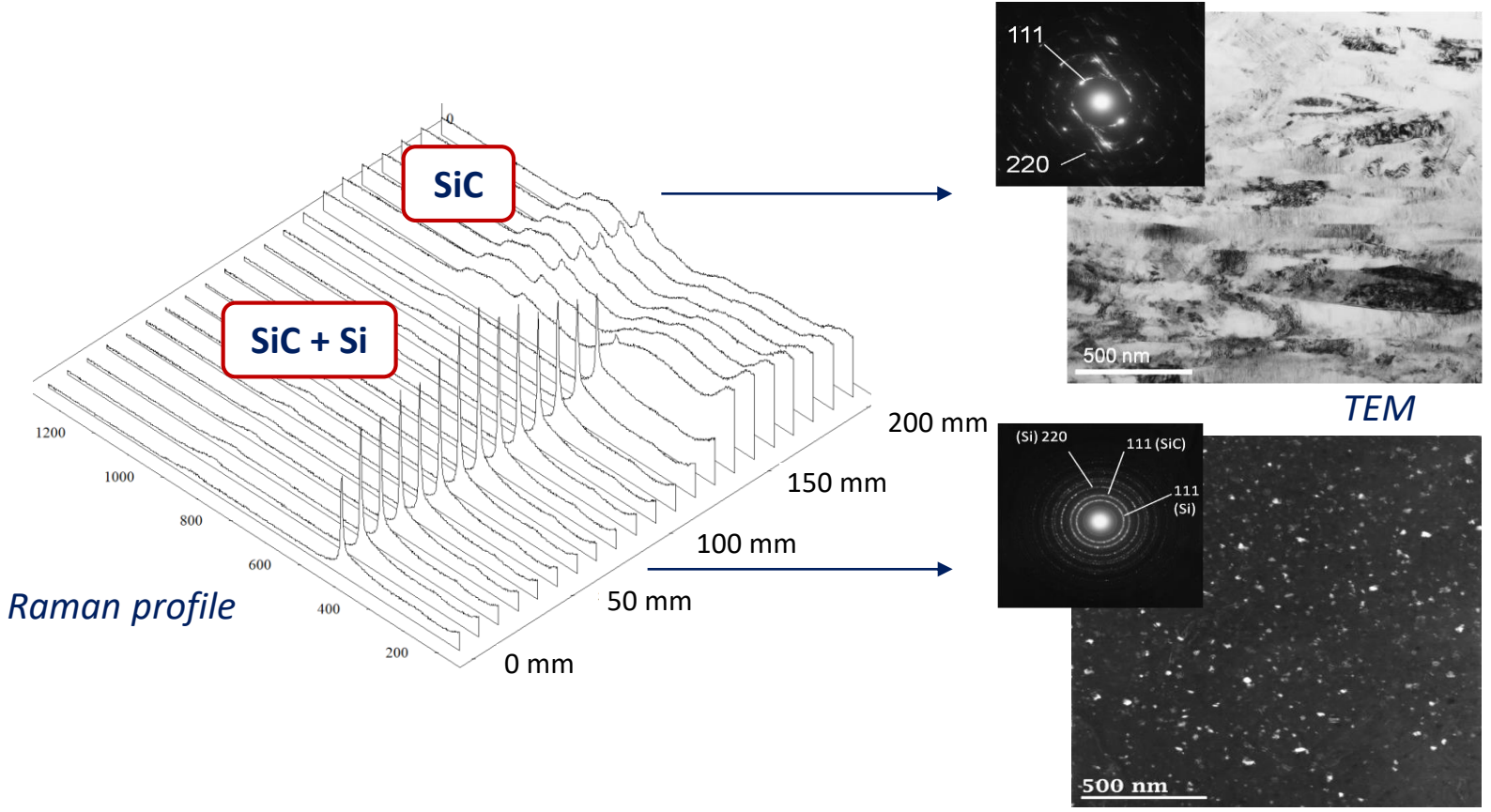
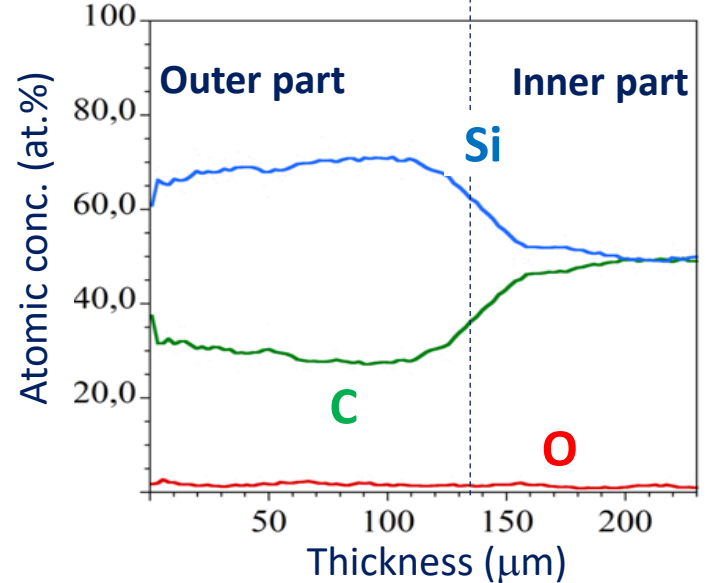


From static to continuous CVD: continuous



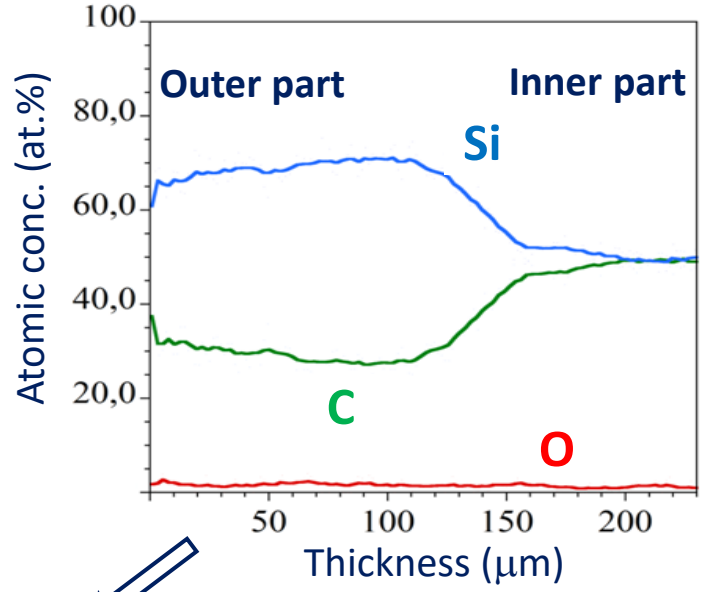
Longitudinal gradient in static → radial gradient in continuous

$$\alpha = 3, T = 1200 \text{ }^\circ\text{C}, Q_{tot} = 500 \text{ sccm}, v = 0.25 \text{ cm/min}$$

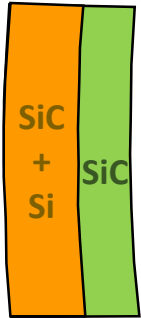
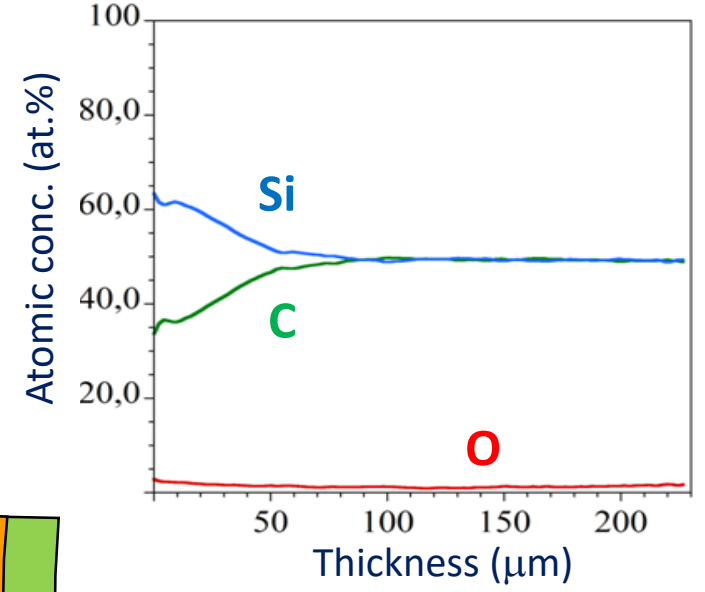


From static to continuous CVD: continuous

Improvement of the CVD process and the Si/C ratio



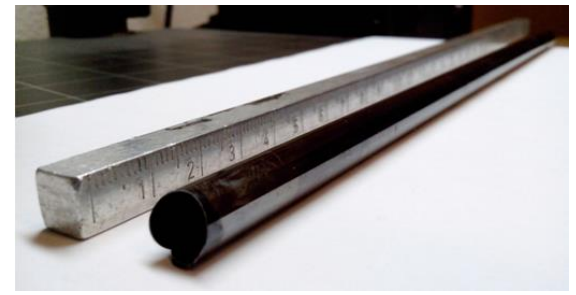
+ gas preheating
 (SiCl₂ ↘ C₂H₂ ↗)
 →
 + C₃H₆



20 cm-long and 220 μm-thick monolithic tube with 2 distinct zones in the thickness :

- External (first) part (150 μm): SiC + Si
- Internal (second) part (100 μm) : SiC

→ Thermomechanical behavior?



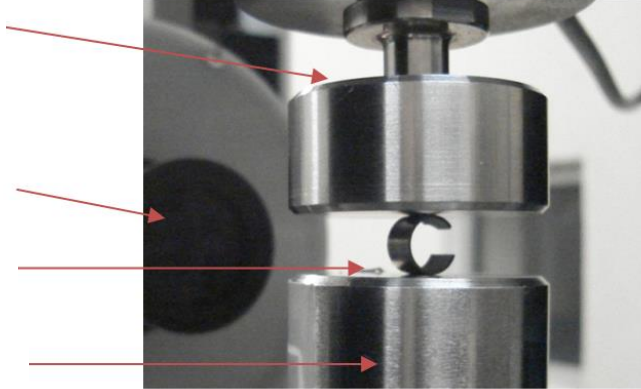
Mechanical properties at ambient

C-ring compression testing: suited to monolithic tubular ceramics (ASTM C1323-10)

- 1: Hard resin mounting,
- 2: cutting and polishing of both sides
- 3: cutting of the notch
- 4: resin removal and cleaning

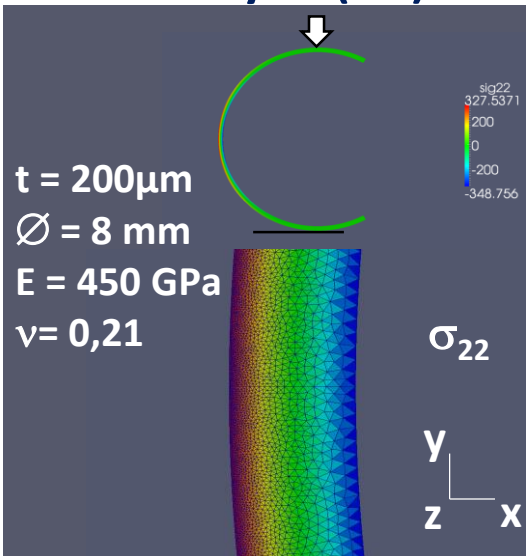


Load cell (max 20N)
 Camera
 Sample
 Plate

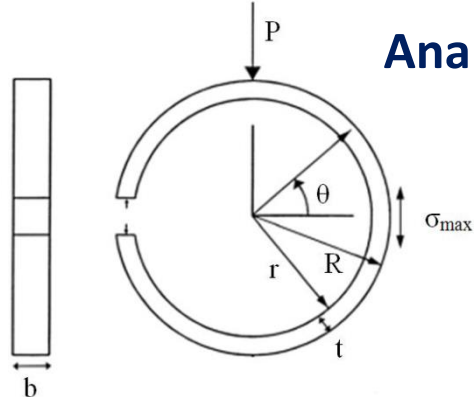


$\sigma^f \approx 400-600$ MPa
 $E \approx 350-400$ GPa
 $\epsilon^f \approx 0.15$ %
 (if homogeneous)

FE analysis (2D)



Analytical

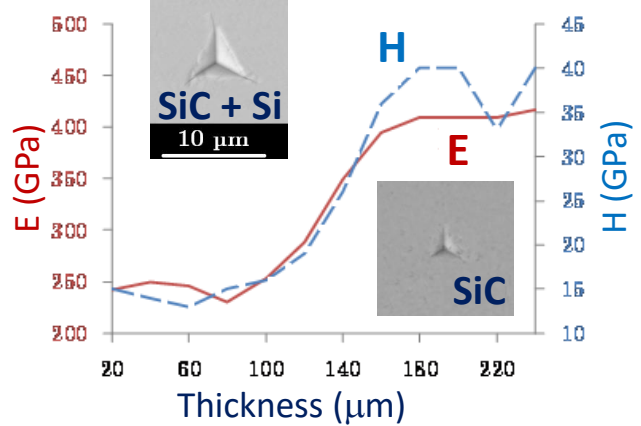


$$\sigma_{max} = \frac{PM(R - r_a)}{btR(r_a - M)}$$

$$M = \frac{R - r}{\ln\left(\frac{R}{r}\right)}$$

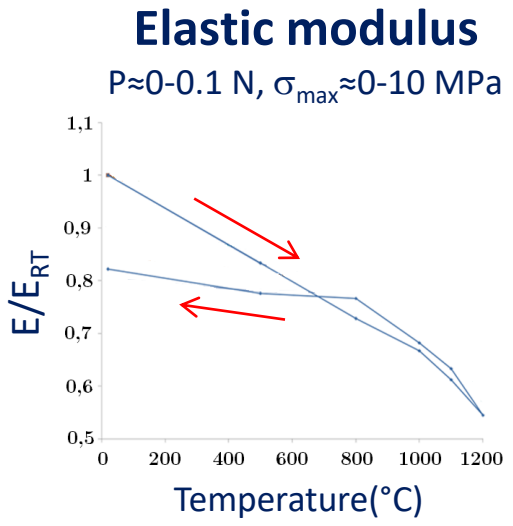
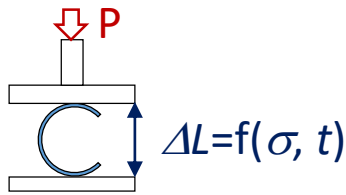
$$E = \frac{3\pi}{4000} \frac{(R + r)^3 \Delta\delta(mm)}{(R - r)^3 \Delta P(N)}$$

$$r_a = \frac{R + r}{2}$$

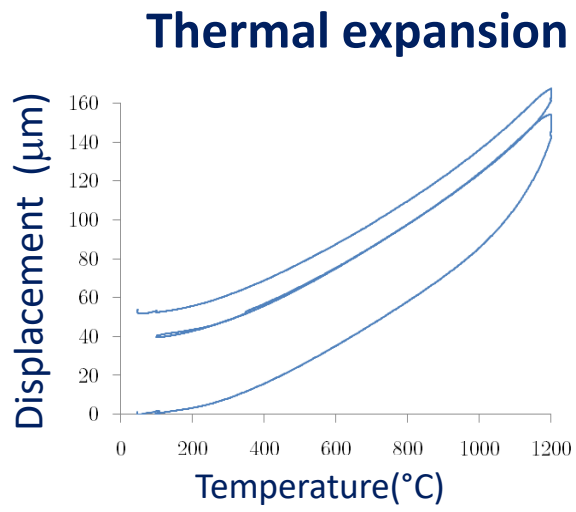


Mechanical properties at high temperature

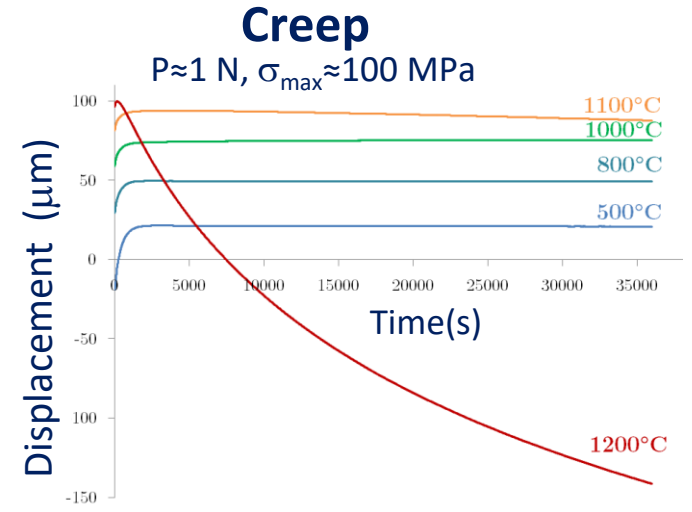
Thermomechanical analysis (TMA)



Strong decrease beyond 800 $^{\circ}\text{C}$
Residual drop of E after cooling at RT



Abnormal a value: $40 \cdot 10^{-6} \text{ K}^{-1}$!!!
Irreversible behavior for $T > 800 \text{ }^{\circ}\text{C}$
Residual displacement at RT



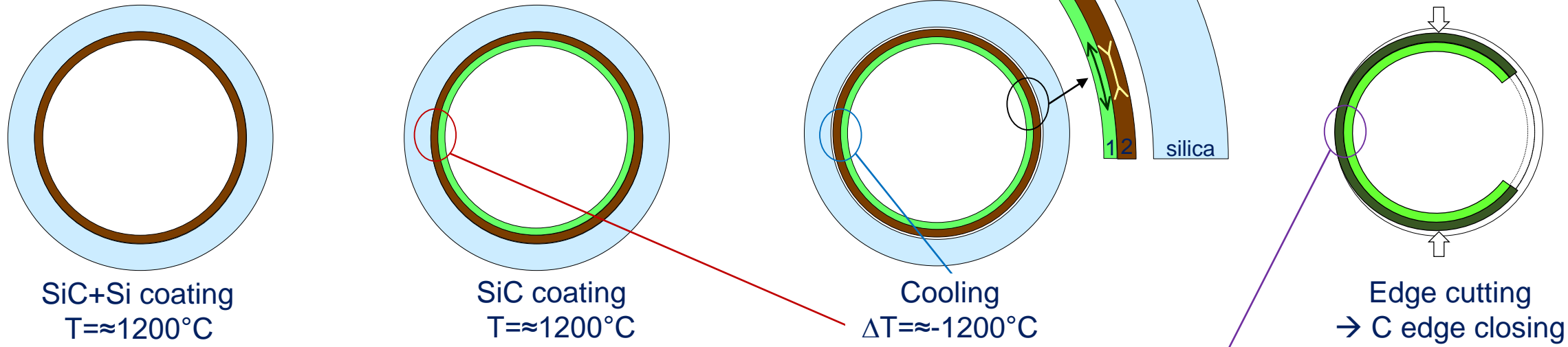
No creep below 1100 $^{\circ}\text{C}$
Gradual opening when $T \nearrow$!!!
Creep starts at 1100 $^{\circ}\text{C}$
Collapse for $T \geq 1200 \text{ }^{\circ}\text{C}$

- Decrease of E + creep at HT → **viscous flow** of free Si
- Irreversible behavior → **stress relaxation** of free Si
- Too high CTE + C opening → **bilayer structure ?**

Mechanical properties at high temperature: discussion

Existence of residual stresses related to HT deposition and bilayer structural effect

FE modeling of the bilayer coating, either entire-ring or C-ring

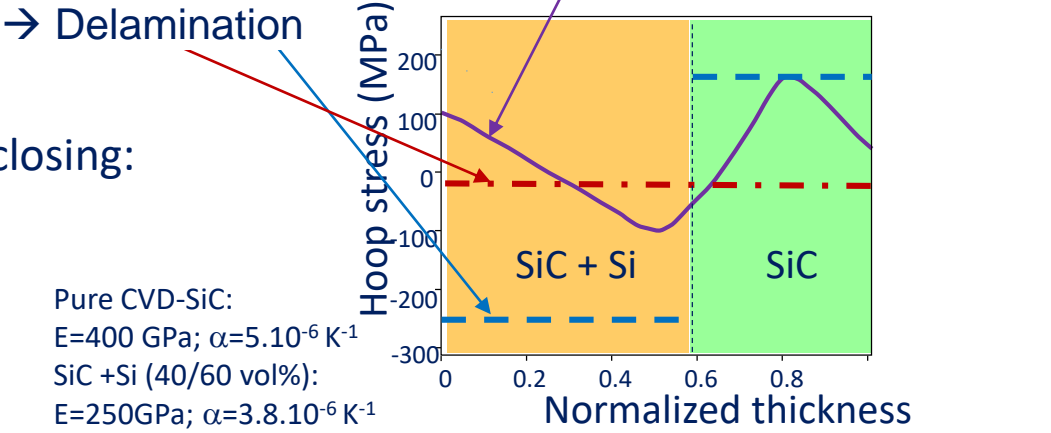


O-ring → 2 opposite residual stress levels in SiC+Si and SiC layers

C-ring → complex through-thickness residual stress field (C edge closing: residual stresses partly elastically relaxed)

$T \nearrow$ → C edge opening : residual stresses relaxed

$T > 1100^\circ\text{C}$ → creep or stress relaxation through viscous flow of Si

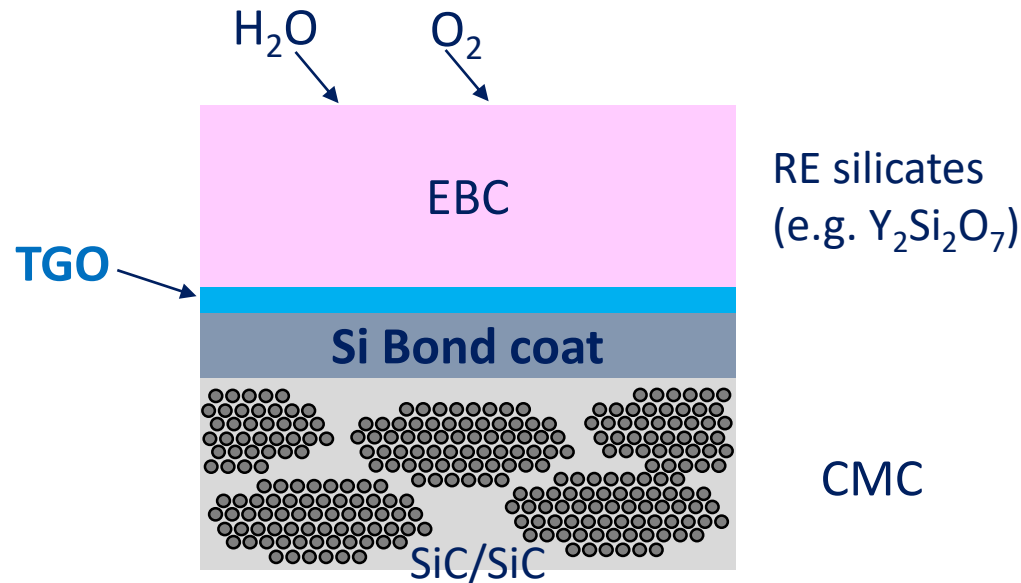


2- CVD poly-Si coating for an EBC bond coat

Issue, solution and objective

Environmental Barrier Coating (EBC) [Spitsberg2005][Zhu2018][Xu2017]

→ Limit diffusion of oxidizing species (O_2 and H_2O) and SiC volatilization ($Si(OH)_4$)



Si bond coat (currently deposited by plasma spraying) ensures **chemical** and **thermomechanical compatibility** with EBC/CMC

Degradation of EBC/CMC system :

- Foreign objects [Bhatt2008]
 - Volatilization [Richards2016]
 - Reaction with CMAS [Poerschke2018]
 - Formation of **thermally grown oxide (TGO)**
- **residual stresses, cracks, delamination**

[Richards2015a, b] [Richards2016]

Lifetime of the EBC system determined by thermomechanical properties of its constituents



Need to **better modulate properties** of the Si BC
→ accurate control of **microstructure** (→ **CVD**)

Synthesis

Requirements

Approach

Characterize ~100 μ m-thick coatings

Substrate

- C single filament ($\varnothing=10\mu\text{m}$, $E=60\text{GPa}$)

Characterization

- Microstructure \rightarrow SEM, EBSD, TEM
- Properties \rightarrow TMA (3-point bending)

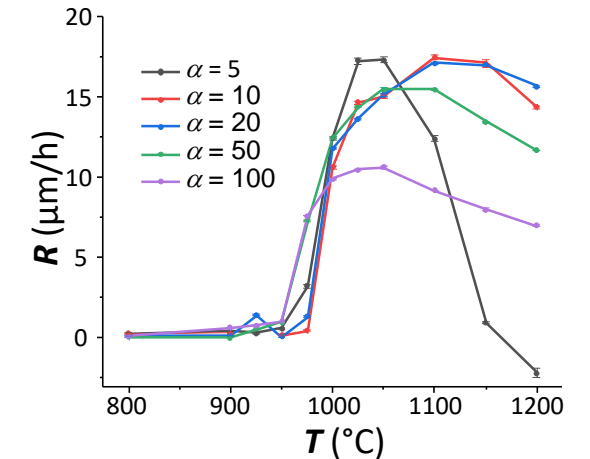
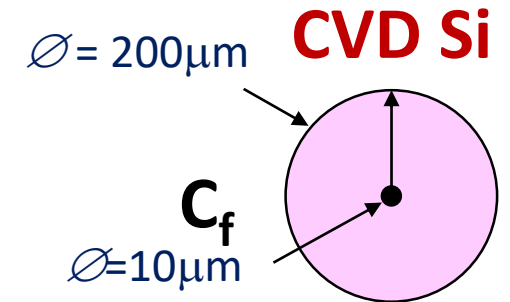
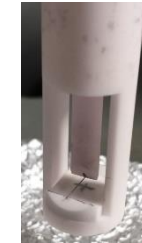
Adjust R

Tune the Si CVD microstructure
[Bloem1973], [Teyssandier1999], [Hammond2001]

Adjust CVD parameters

- T
- $\alpha = Q_{\text{H}_2}/Q_{\text{SiHCl}_3}$

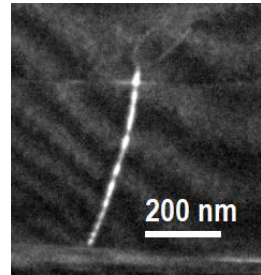
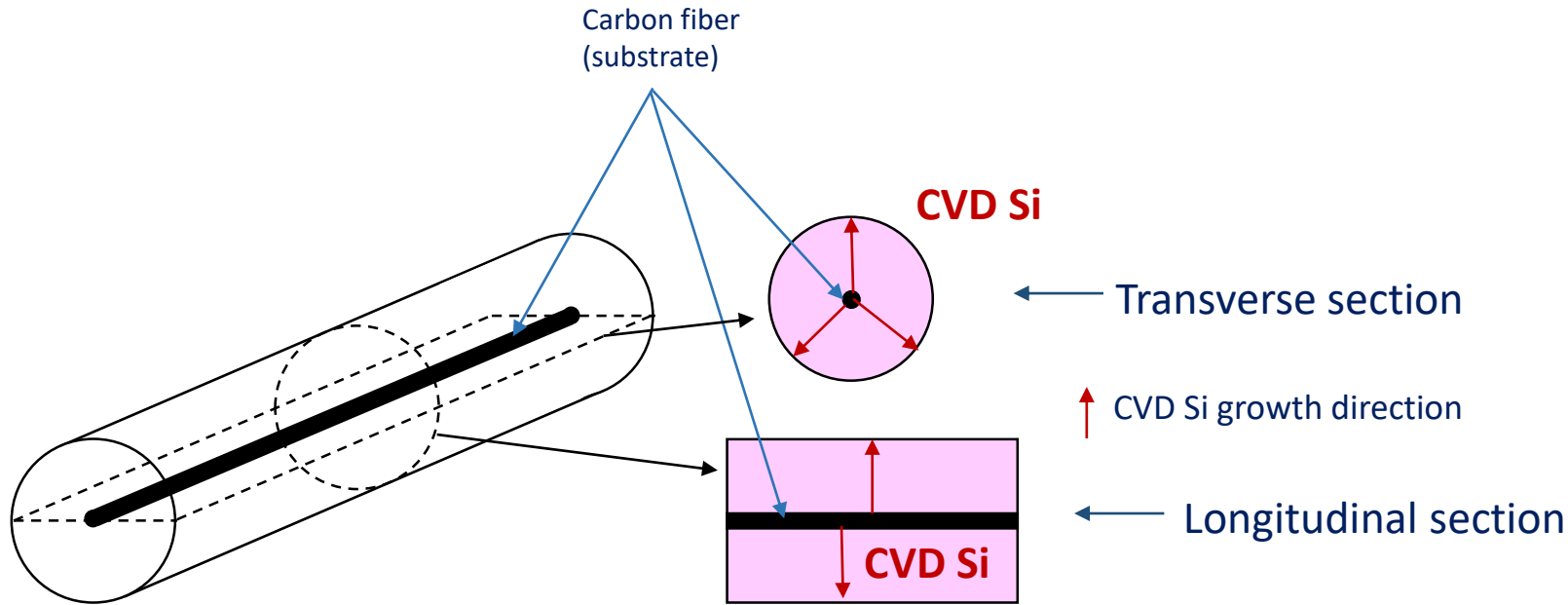
Thermal annealing (HT) 1350 $^{\circ}\text{C}$



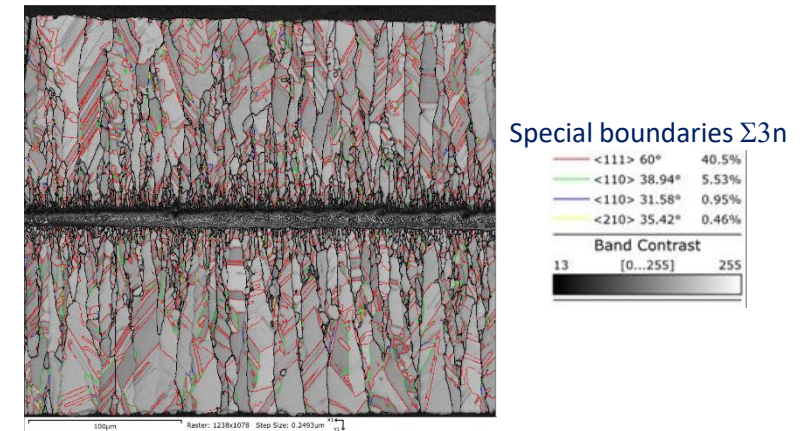
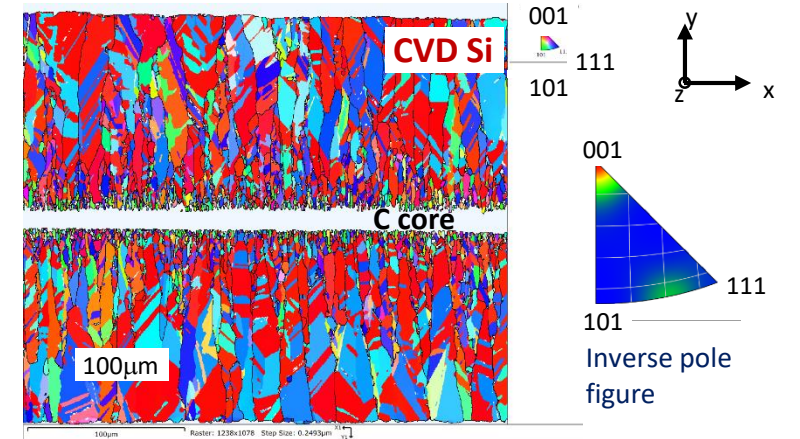
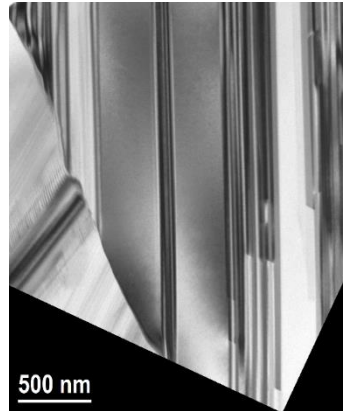
	M4	M3	M2	M1
T ($^{\circ}\text{C}$)	1000		1100	
α	5	20	20	75

$P = 5 \text{ kPa}$, $Q_{\text{tot}} = 400 \text{ sccm}$

Specimen preparation and microstructure analysis



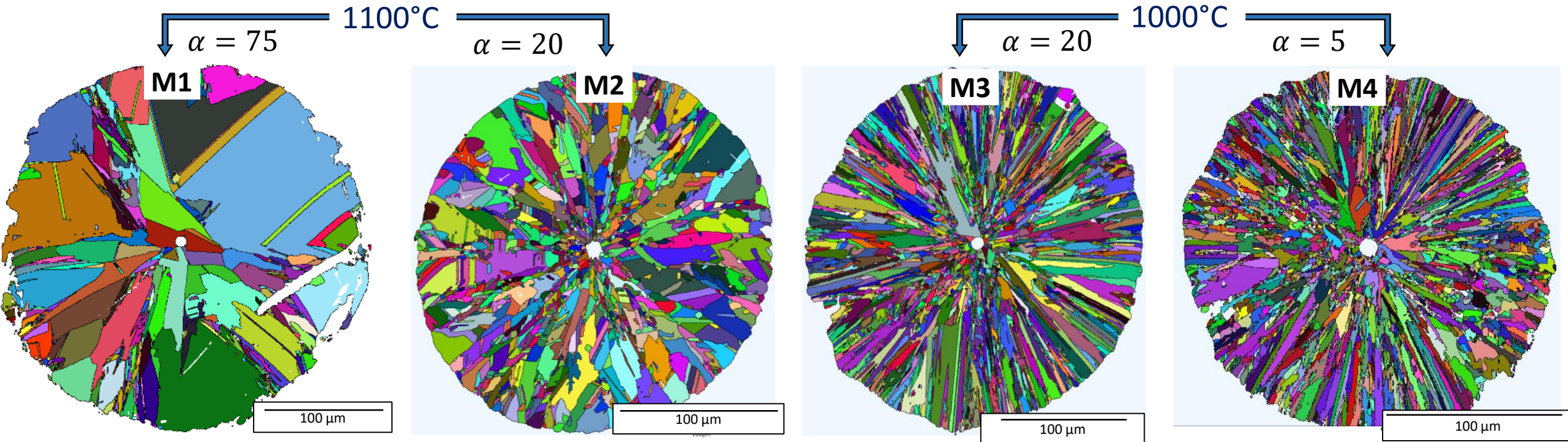
TEM: GB, microtwins, dislocations



- EBSD:
- Texture analysis
 - Grain surface area
 - GB type (Special ($\Sigma 3n$)/Random); density)

Microstructure (EBSD)

Influence of **CVD conditions** on **grain size**



Supersaturation \nearrow \rightarrow nucleation density \nearrow \rightarrow grain size \searrow

Microstructure (EBSD)

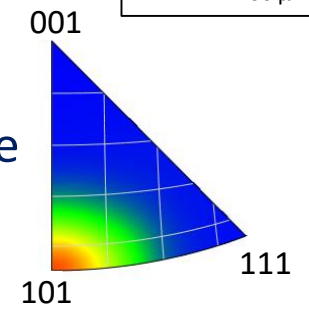
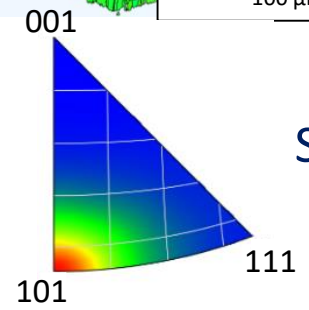
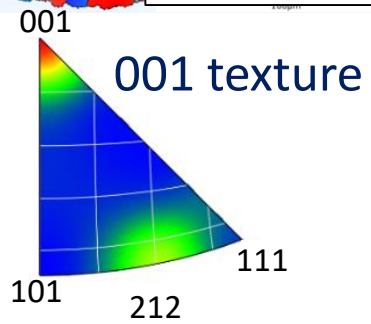
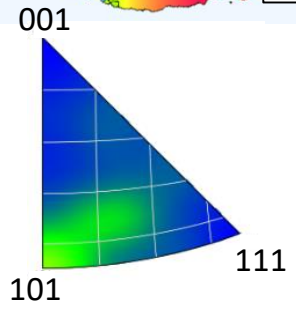
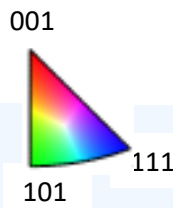
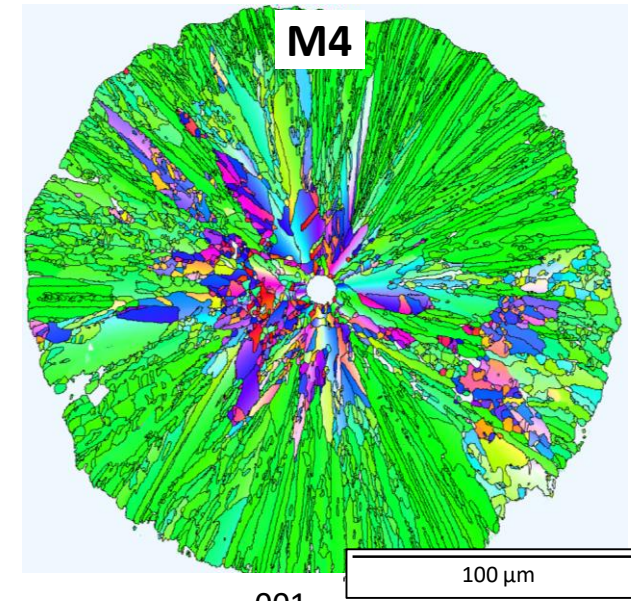
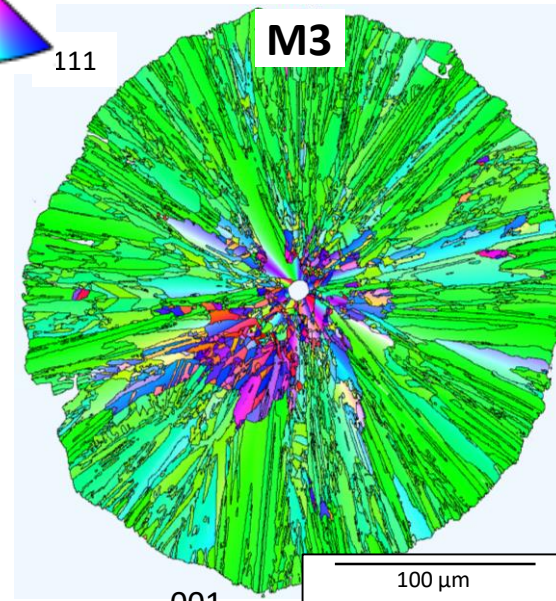
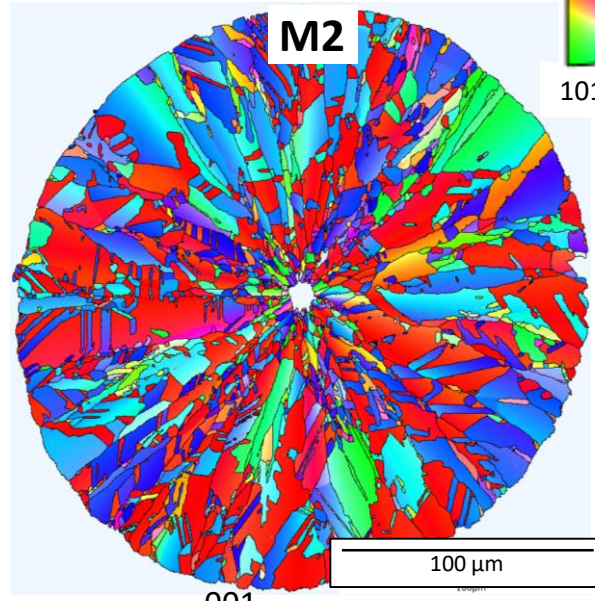
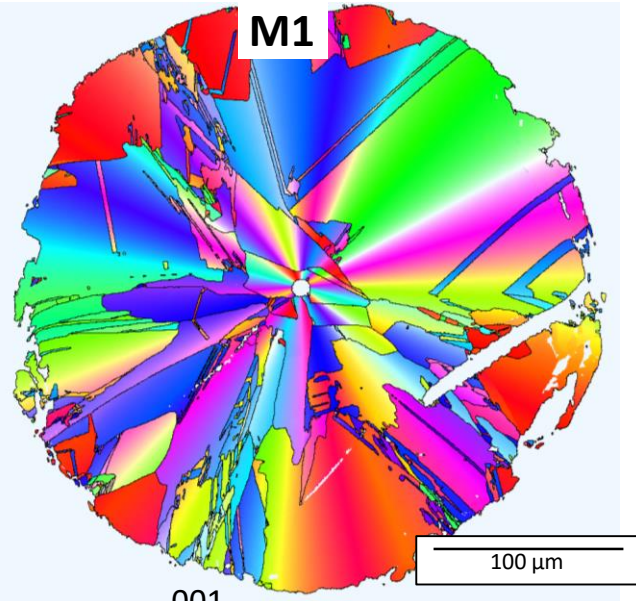
Influence of **CVD conditions** on texture

1100°C $\alpha = 75$

$\alpha = 20$

$\alpha = 20$ 1000°C

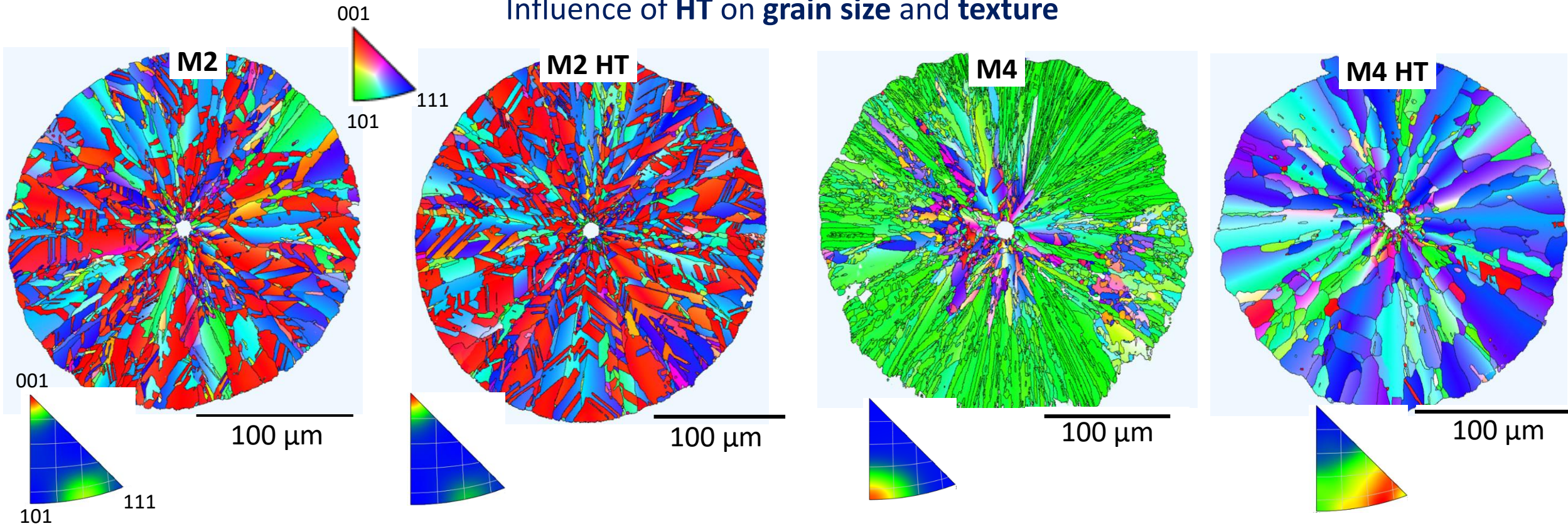
$\alpha = 5$



Evolutionary selection growth mechanism [Van der Drift 1967]

Microstructure (EBSD & TEM)

Influence of HT on grain size and texture



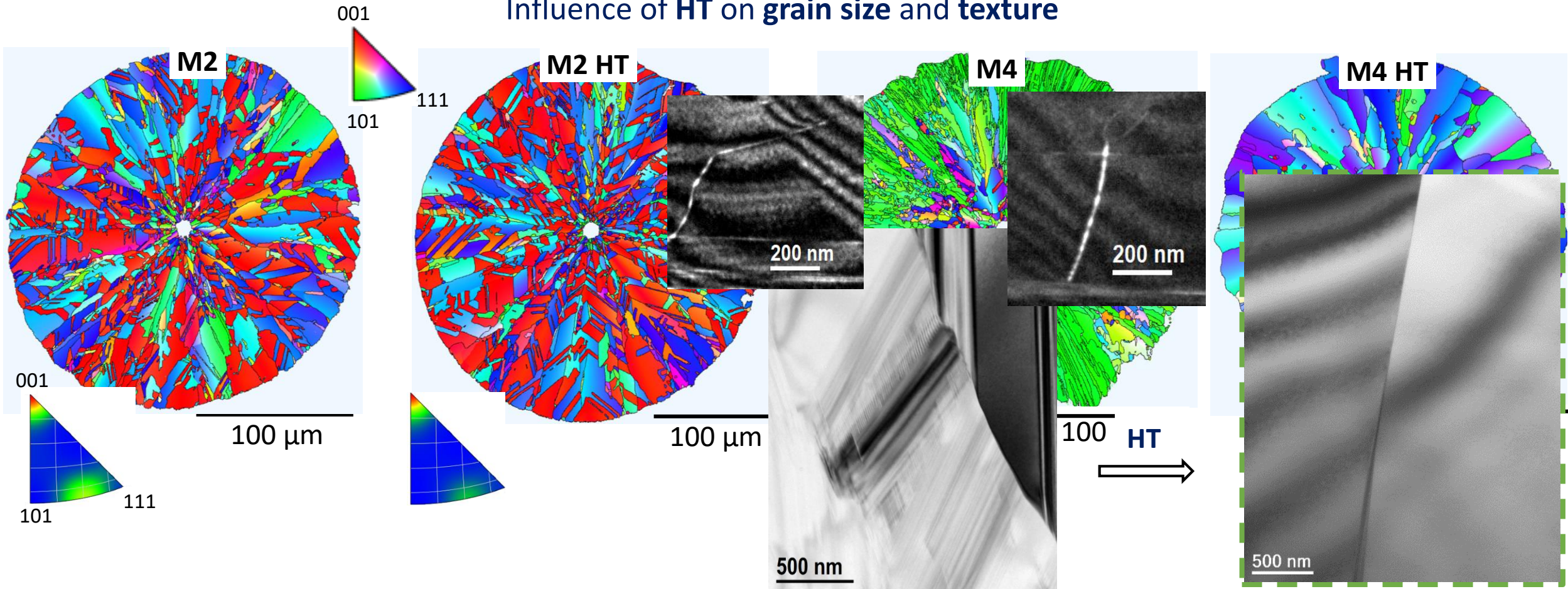
M2 ($T=1100^{\circ}\text{C}$, $\alpha=20$): no effect of HT

M4 ($T=1000^{\circ}\text{C}$, $\alpha=5$): Grain growth, texture change, removal of twins & dislocations

Supersaturation $\nearrow \rightarrow$ dislocation & twin density $\nearrow \rightarrow$ driving forces of recrystallization \nearrow [Schins 1967]

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Influence of HT on grain size and texture



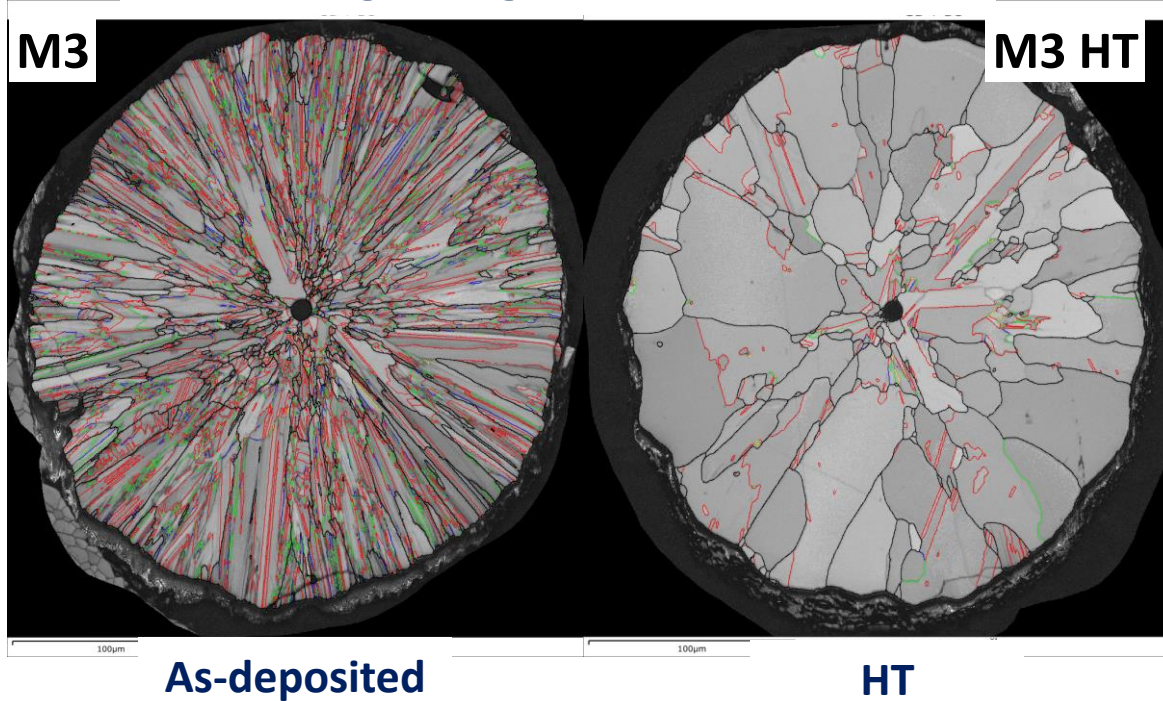
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Supersaturation ↗ → dislocation & twin density ↗ → driving forces of recrystallization ↗ [Schins 1967]

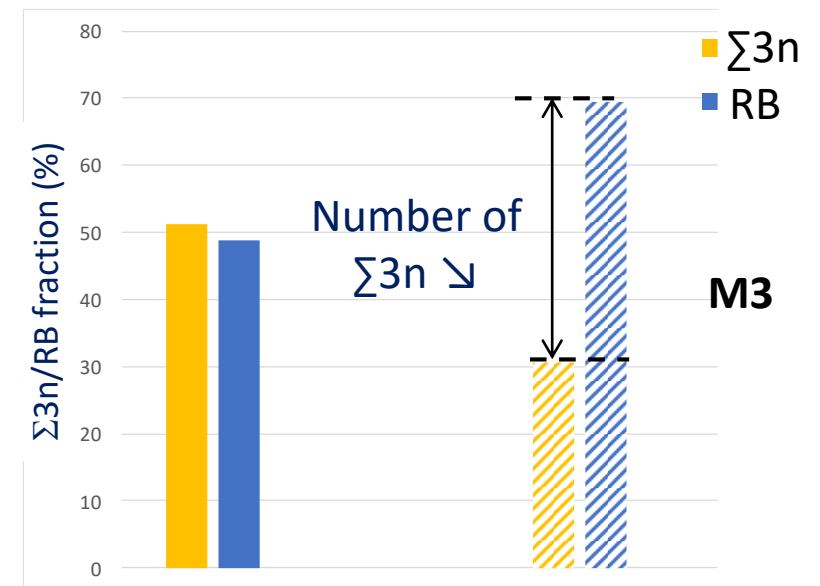
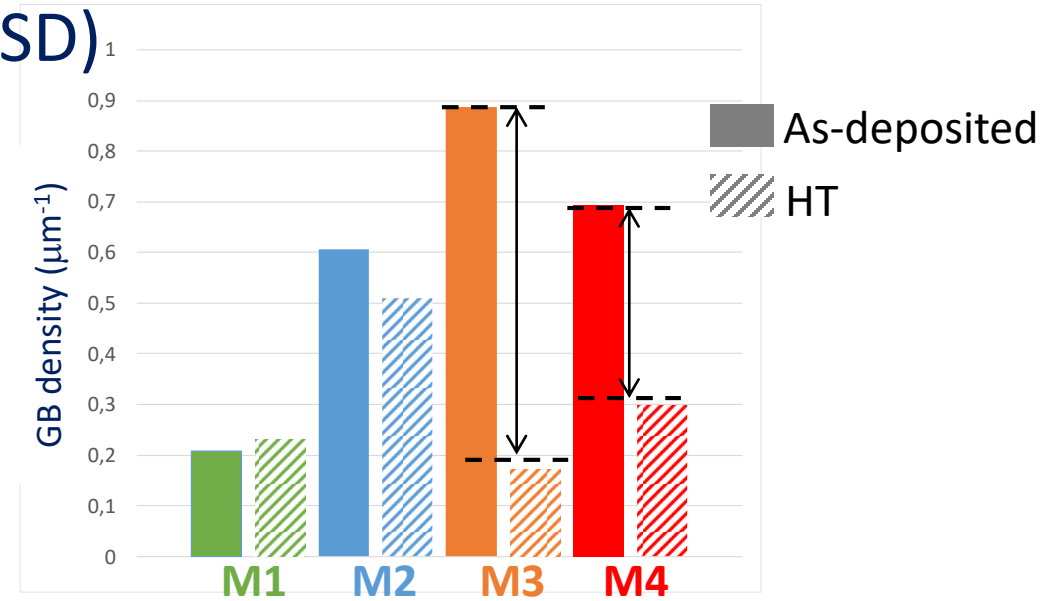
Microstructure (EBSD)

Changes of grain boundaries



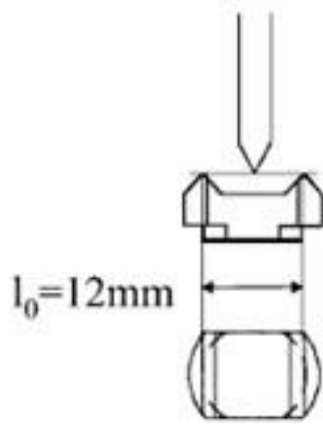
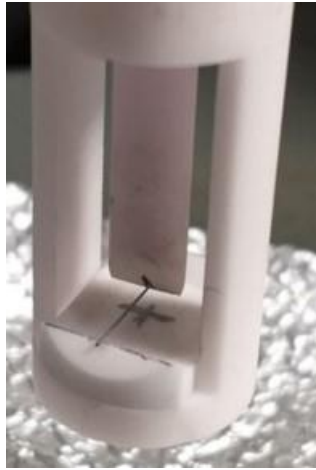
M1 and **M2**: low effect of HT

M3 and **M4** : Removal of initial boundaries and twins (especially $\Sigma 3n$) during recrystallization



Thermomechanical analysis

Creep tests at increasing loads



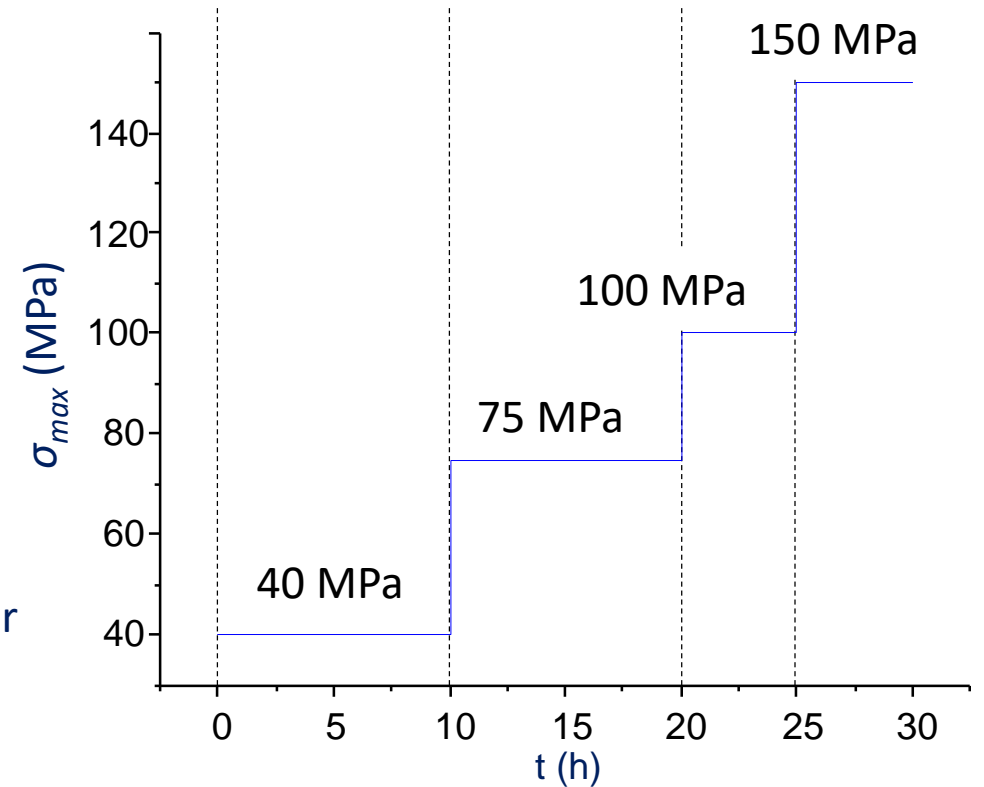
$$\sigma_{max} = \frac{8 l_0}{\pi d_0^3} F$$

$$\varepsilon_{max} = 6 \frac{d_0}{l_0^2} y$$

l_0 : Filament length
 d_0 : Filament diameter
 F : load
 y : deflection



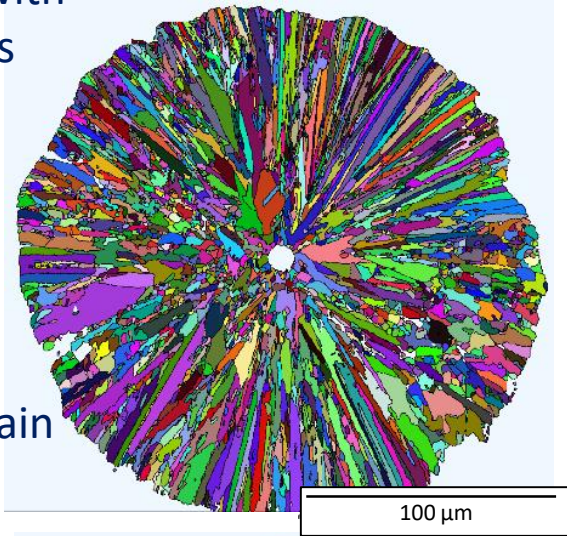
3-point bending device and tested sample



- Assuming:
- homogeneous material (elastic strain)
 - similar creep strain in compression & tension
 - no redistribution of radial stresses (stress exponent ~ 1)

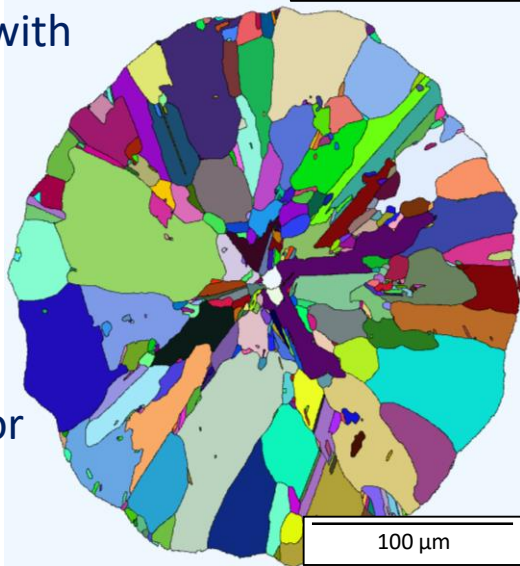
Thermomechanical analysis

Fine grains with many defects
M4

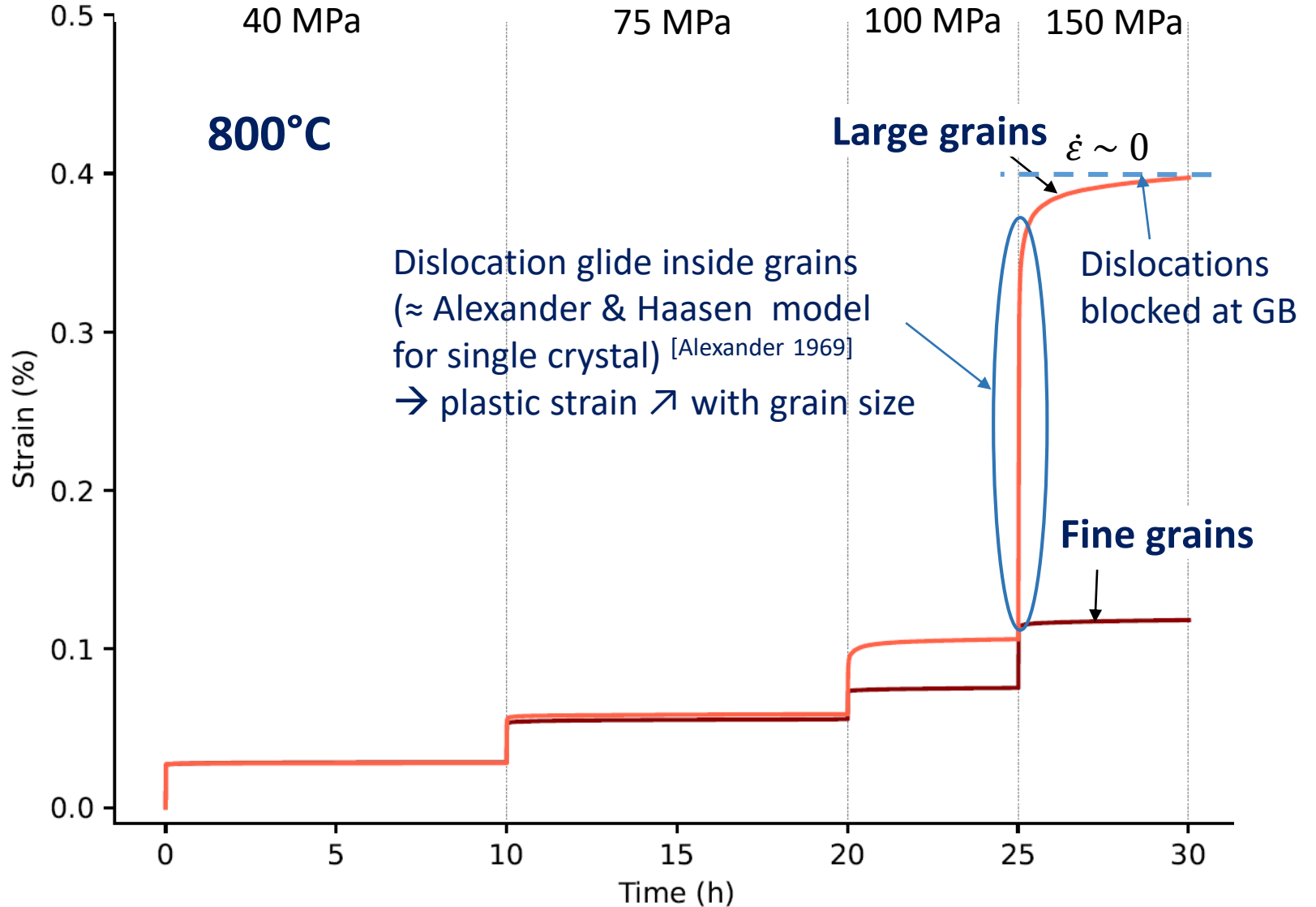


800°C
~no plastic strain

Large grains with few defects
M3 HT

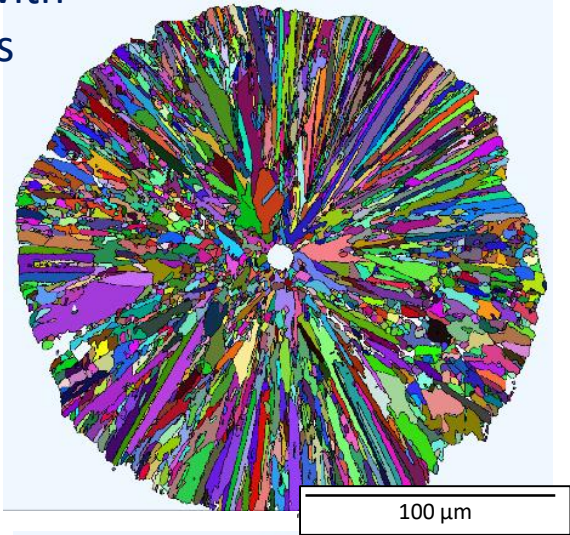


800°C
Plastic strain for $\sigma > 150\text{MPa}$



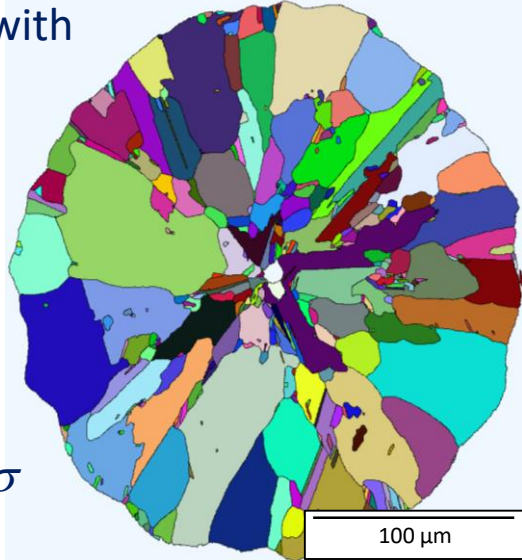
Thermomechanical analysis

Fine grains with many defects
M4

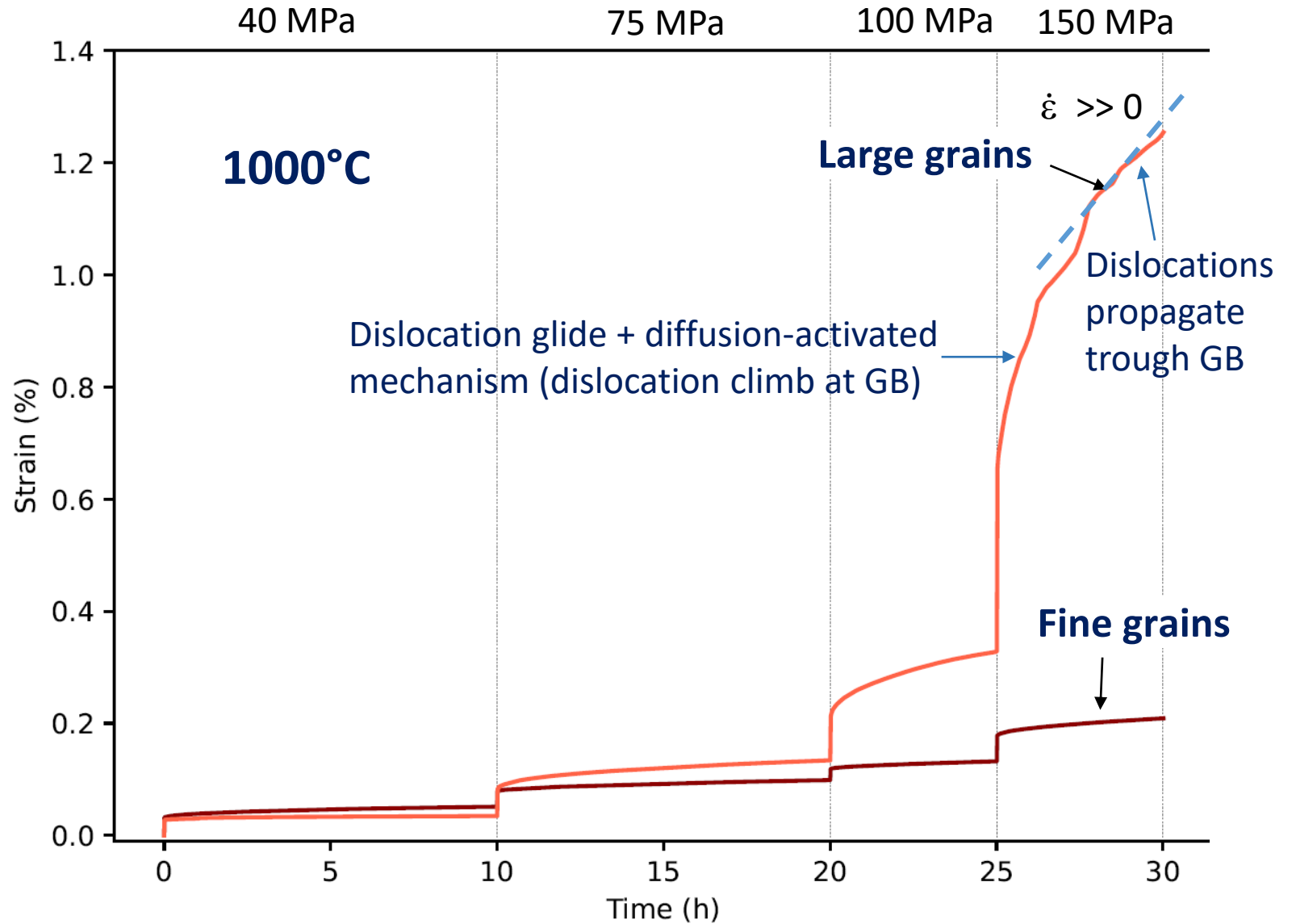


1000°C
Limited plastic strain

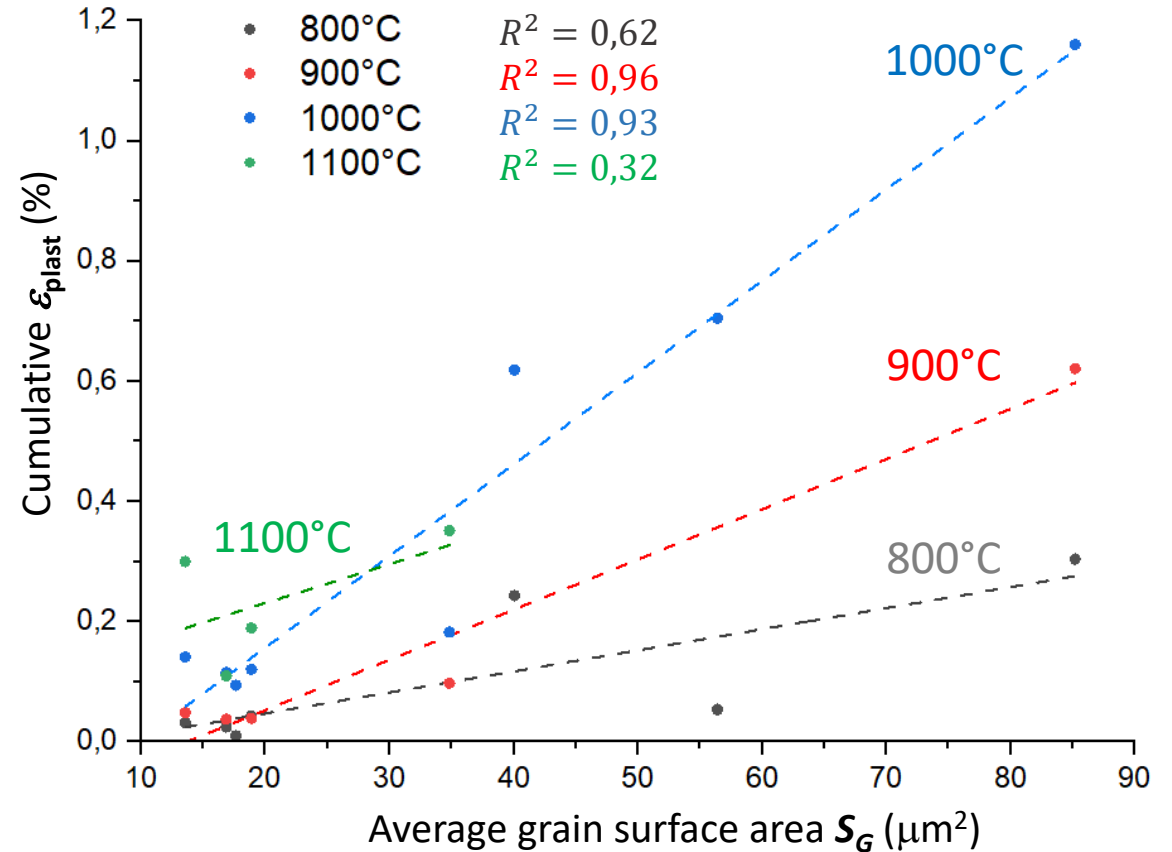
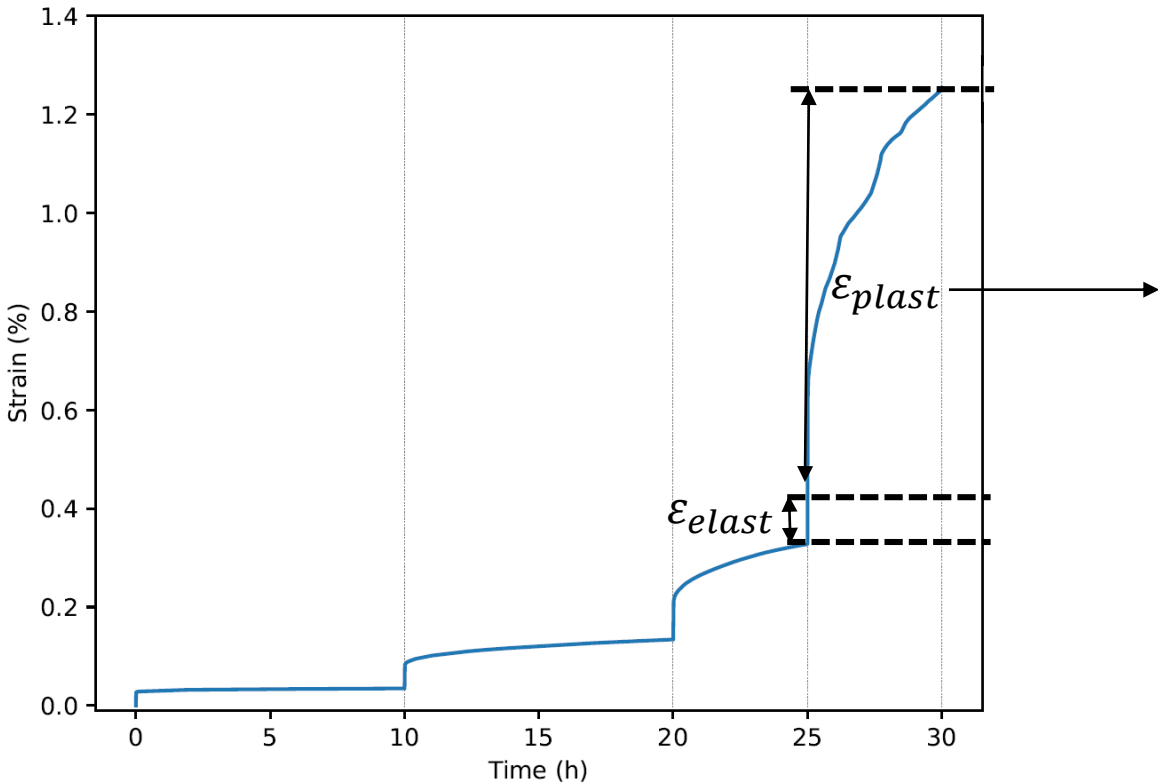
Large grains with few defects
M3 HT



1000°C
High plastic strain for all σ



Thermomechanical analysis

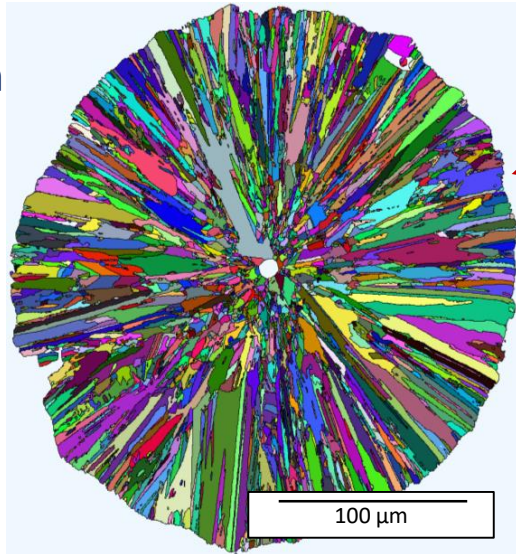


800, 900, 1000°C: clear correlation between ϵ_{plast} and S_G
 → Dislocation formation, sliding and blocking
 (at GB or interaction inside grain) [Alexander & Haasen1969]

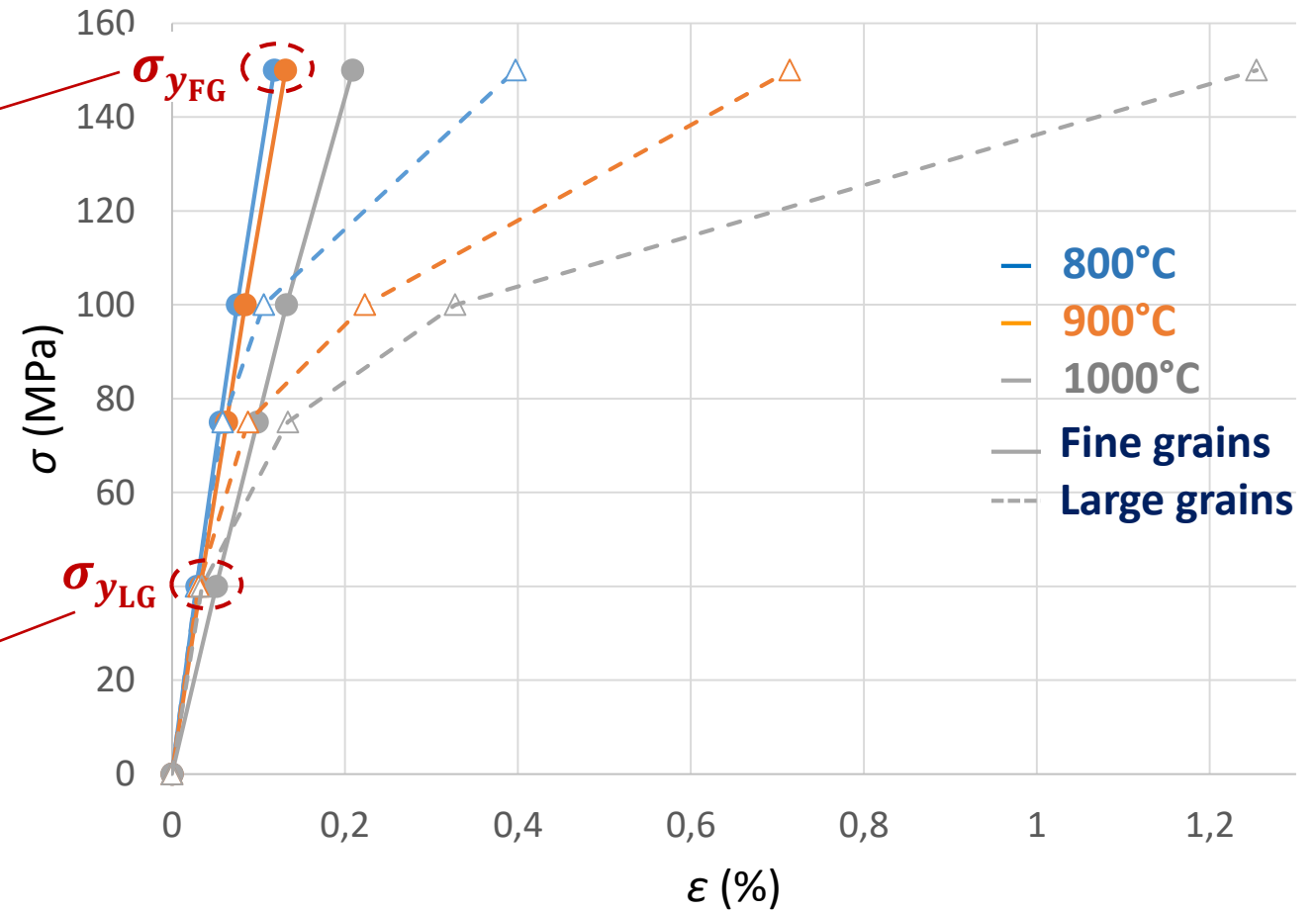
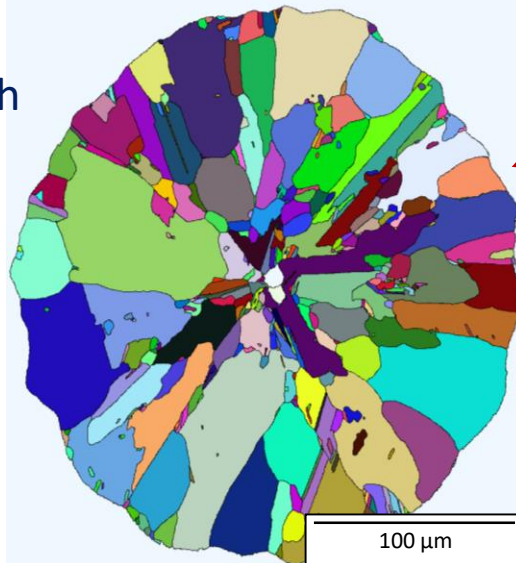
1100°C: no correlation between ϵ_{plast} and S_G
 → Diffusion activated inside grain and at GB

Thermomechanical analysis

Fine grains with many defects
M4



Large grains with few defects
M3 HT



Yield stress (σ_y) decreases when grain size increases: Hall-Petch [Hall 1951, Petch 1953]

CONCLUSIONS

Reactor design (adaptation to substrate, heat and gas flow management...)

Multiple experimental approach (R , gas and solid analyses) for better understanding of the process

→ *missing real in situ investigations (hot gases, heterogeneous reactions) ?*

Multiple numerical approach (heat/mass transfer, thermodynamic, thermokinetic, ...) complementary

→ *often far from equilibrium...*

→ *lack of thermodynamic/kinetic data (precursor decomposition, P dependance...)*

CVD SiC: control of homogeneous phase crucial for R and Si/C ratio. Heterogeneous reactions hard to identify. The link with the (micro)structure still to be established.

Excess silicon enhances creep strain & thermal stresses → C_3H_6 addition + preheating.

CVD poly-Si : nucleation critical (thickness uniformity, surface defects), supersaturation determine dislocation/twin density, grain size and recrystallization at HT (in use or after HT).

Creep controlled by grain size & boundaries → Compromise to be found for use as a BC...

TMA : no ideal geometry (depends on T uniformity, substrate, thickness, texture, strain/stress field...)