# Amorphous chromium carbide coatings: low temperature DLI-MOCVD growth and characterization

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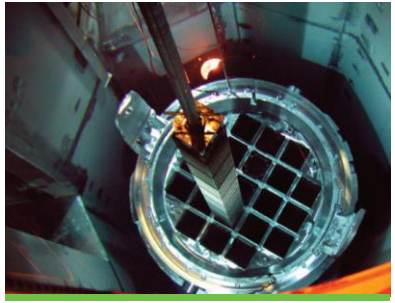
EuroCVD 22 Baltic ALD 16 | 2019
24-28.06.2019 | Luxembourg

## Nuclear fuel cladding

- Zirconium-based alloy tubes
  L = 4 m
  ID = 8 mm
  **Aspect ratio = 500**
- Maximum treatment temperature: **580°C**
- First containment barrier for the fission products

*Nuclear Fuel Assembly, Russia*
© Ria Novosti



*Nuclear assembly insertion*
© Foro Nuclear

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  L = 4 m
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- Maximum treatment temperature: **580°C**
- First containment barrier for the fission products

## Extreme environment

- Nominal: corrosion, irradiation…
- Accident: high-temperature oxidation, irradiation, hydrogen embrittlement

## → Need for protection

*Nuclear Fuel Assembly, Russia*
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*Burst cladding after oxidation*
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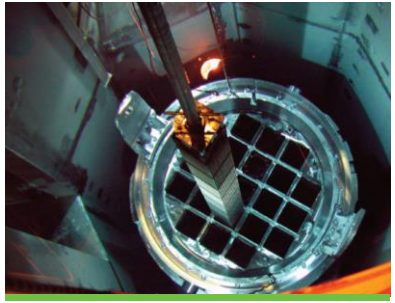

*Nuclear assembly insertion*
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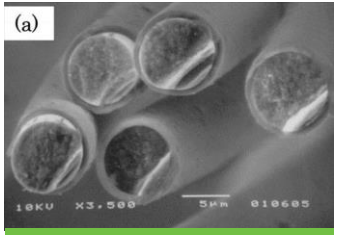
## 1. Great length

- **Continuous** deposition: fixed substrate & mobile source/activation or vice versa
- Functionalization of **fibers, filaments, flexibles substrates**

*Continuous deposition equipment on tapes*
*© CVD Equipment Corporation*




*SiC fibers with BN coating [1]*

[1] M. Suzuki et al., J. Ceram. Soc. Jpn. 111 (2003) 865-871

# DIFFICULTIES TO COAT INTERNALLY TUBES WITH A HIGH ASPECT RATIO (> 100)

## 1. Great length

- **Continuous** deposition: fixed substrate & mobile source/activation or vice versa
- Functionalization of **fibers, filaments, flexibles substrates**

## 2. Small internal diameter

- **"Not so"** small diameters → PVD, CVD, projection, electrodeposition…
- **"Really"** small diameters → CVD, ALD

*Continuous deposition equipment on tapes*
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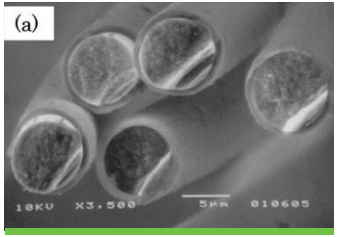


*SiC fibers with BN coating [1]*

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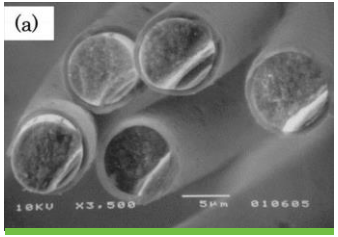


*SiC fibers with BN coating [1]*

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## 3. Both issues

- **Dynamic** configuration → high growth rate required, increased cost and complexity
- **Static** configuration → process optimization required, lower cost and complexity

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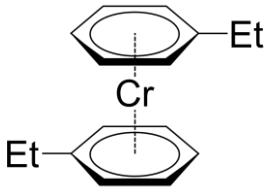
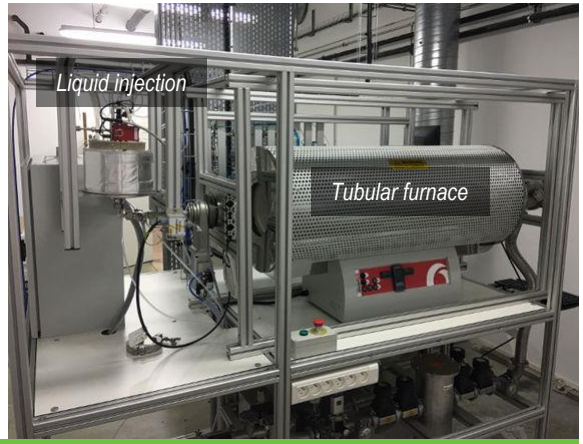
## DLI-MOCVD configuration

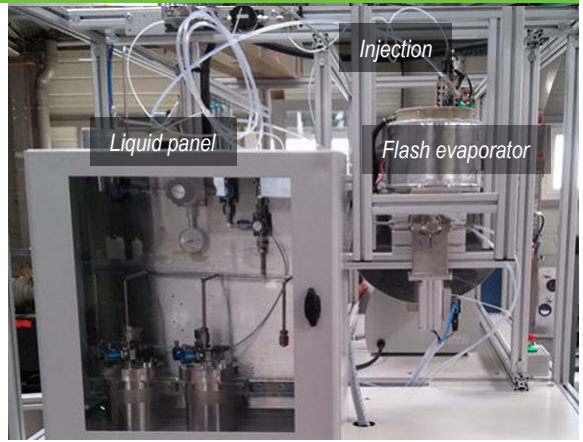
- **Static** hot-wall SS304L tubular reactor
  - One cylinder of L = 1 m by ID = 15 cm
  - A bundle of 1 m long nuclear claddings (1 to 16)
- **Direct liquid injection** of a **bis(arene)Cr$^{(0)}$** precursor
  - Liquid regulation
  - Stability of the precursor
  - **High stable flowrates**
- T = **300-500°C** → respect of **Zr metallurgy**
- P = **1-50 Torr**



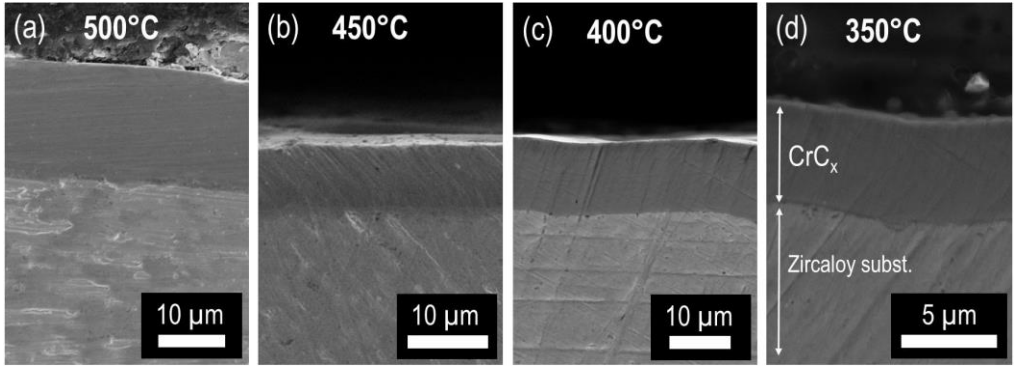

*Bis(ethylbenzene)chromium or BEBC*




*Pilot scale DLI-MOCVD reactor*



## Influence of the deposition temperature (500 to 325°C)




*SEM cross-sections of $CrC_x$ deposited on Zircaloy-4 substrates*

- From 500 to 350°C
  - **Homogeneous** and dense microstructure
  - No grain boundaries (glassy-like)

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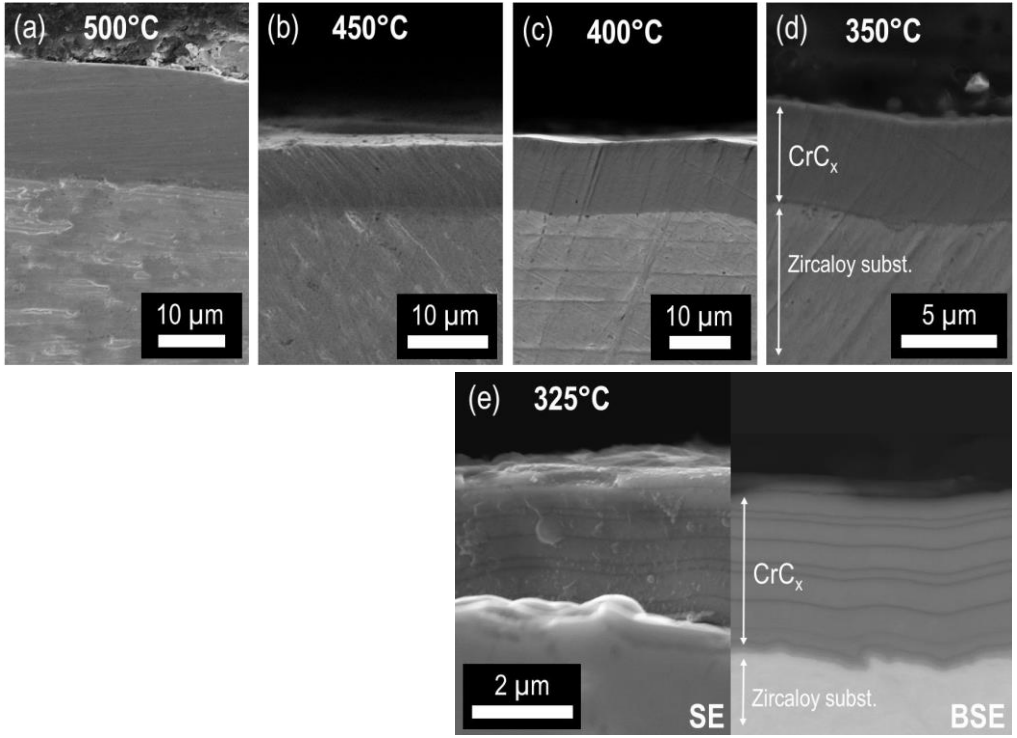


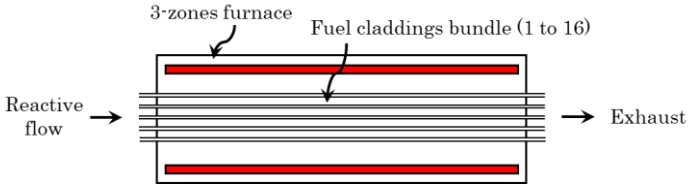

*SEM cross-sections of $CrC_x$ deposited on Zircaloy-4 substrates*

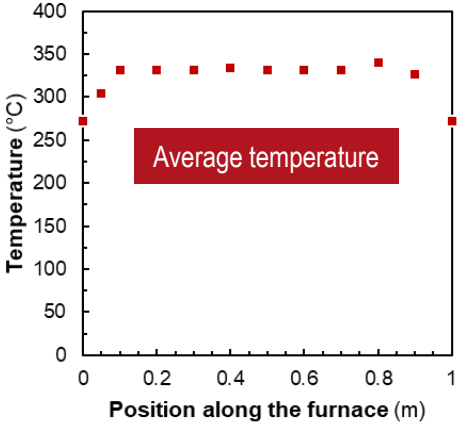
- From 500 to 350°C
  - **Homogeneous** and dense microstructure
  - No grain boundaries (glassy-like)
- Below 350°C
  - **Structuration** with a dense **multilayer** growth

## What happens ?

**Setpoint 325°C**

5 torr, 500 sccm $N_2$



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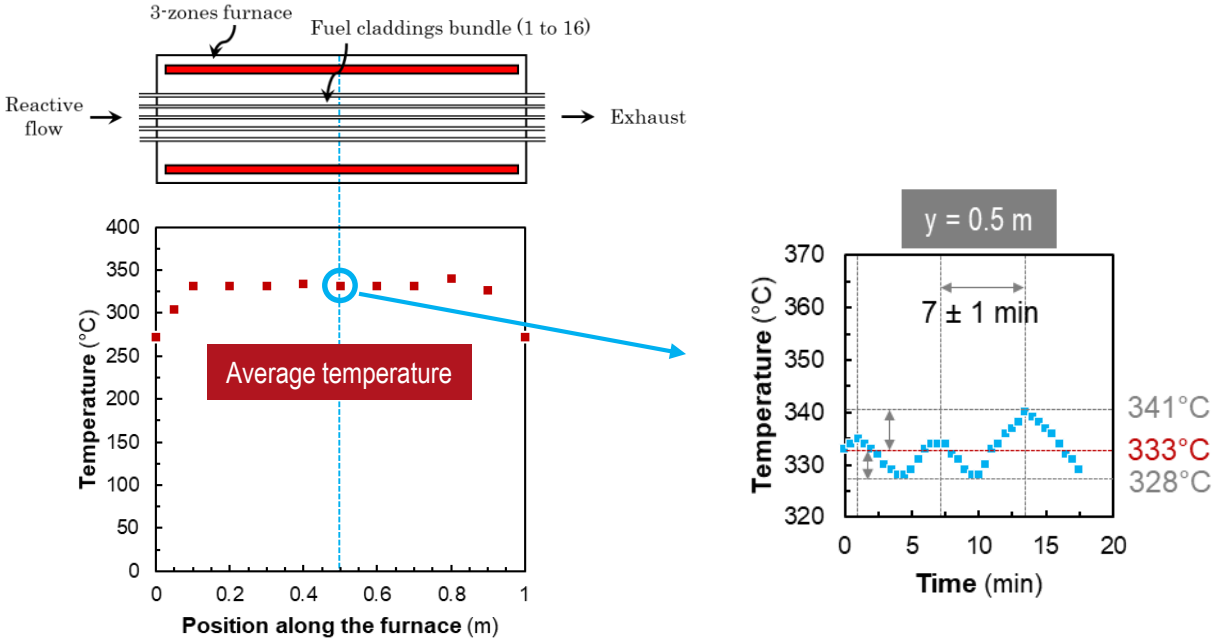

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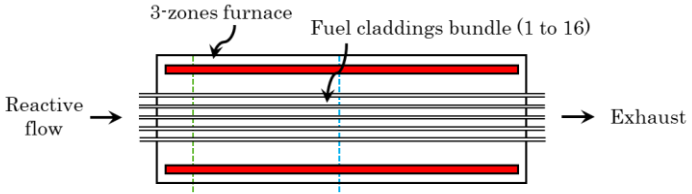
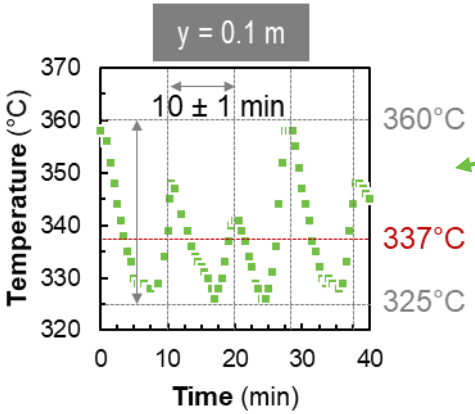
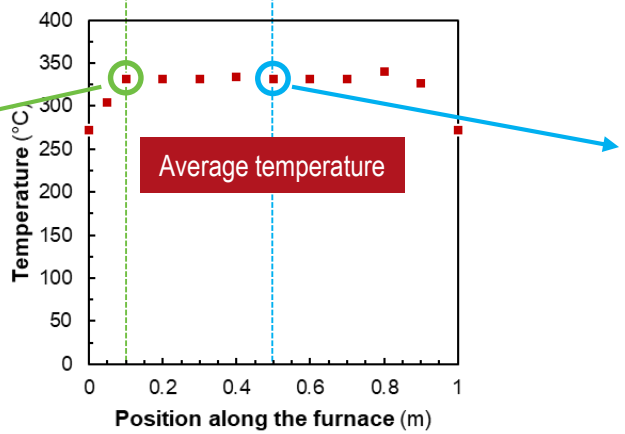
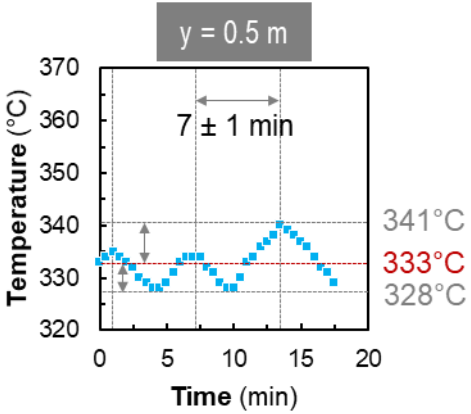


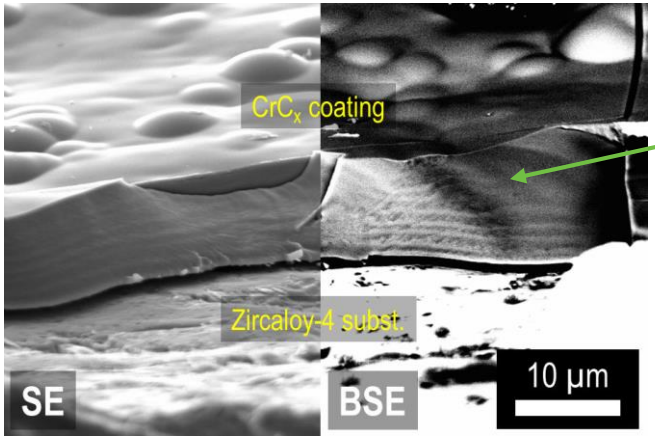



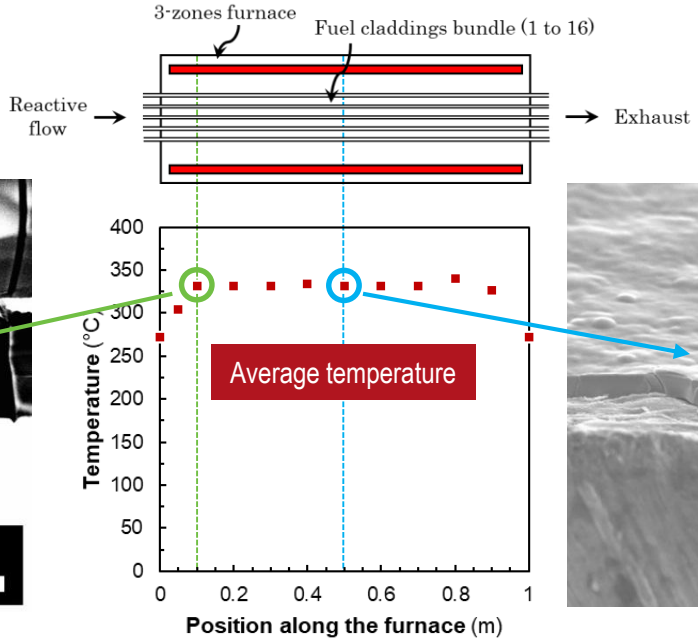



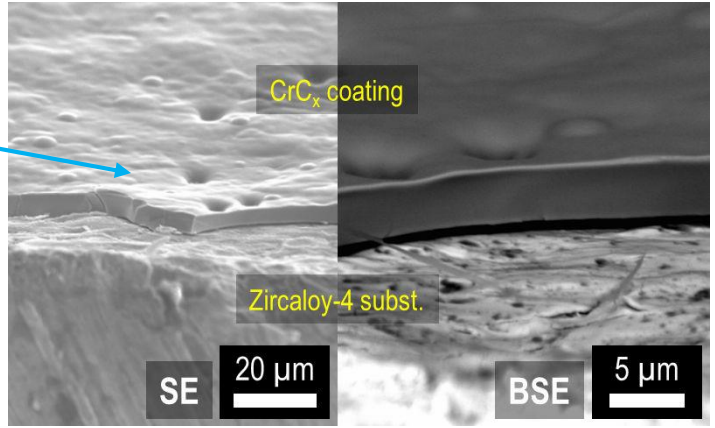

+ ΔT enhanced by the colder reactive vapor injected at the reactor entrance

## What happens ?

**Setpoint 325°C**



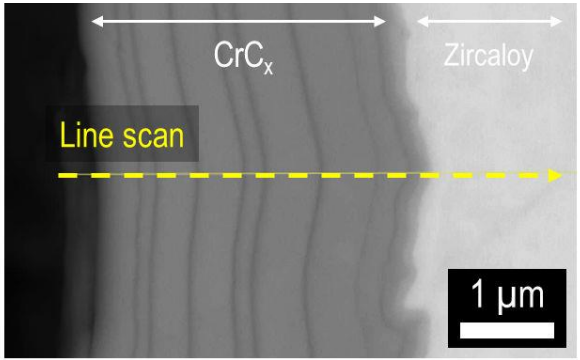



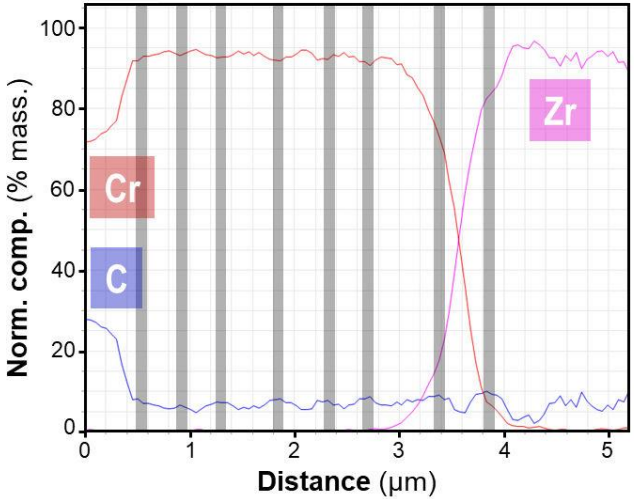
## What happens ?

**Setpoint 325°C**

- Multilayer growth correlated with temperature changes
  - Thermal variation with a **10 ± 1 min period**
  - Deposition **time ~ 88 min**
  - **8 ± 1** dark and **8 ± 1** light **layers**
- Multilayer structure
  - Change of heterogeneous kinetic mechanism at low T
  - A certain **ΔT** with a **low T** is required
  - **Periodic** activation and extinction of **elementary heterogeneous reactions**
  - **Alternating** layers with **different C content** (dark layers are C enriched)

*SEM cross-section of $CrC_x$ deposited on Zircaloy-4 at 325°C and associated EDS line scan*

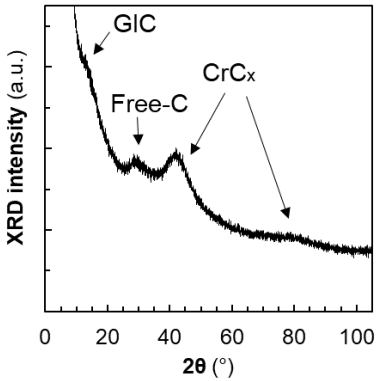


## XRD structure

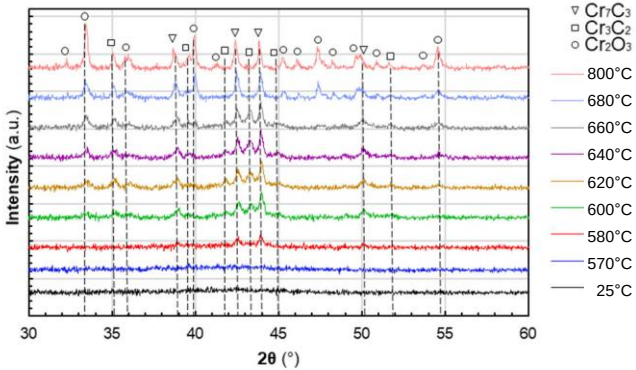
- From 500 to 350°C
  - **Amorphous** nano-composite $CrC_x$
  - **Crystallization** of $Cr_7C_3$, $Cr_3C_2$ and $Cr_2O_3$ during annealing

*Typical XRD pattern of $CrC_x$ deposited on Zircaloy-4 substrates from 500 to 325°C*




- Below 350°C
  - **Amorphous** nano-lamellar $CrC_x$
  - **Crystallization** of $Cr_7C_3$, $Cr_3C_2$ and $Cr_2O_3$ during annealing **at similar temperatures**

*In situ HT-XRD pattern of $CrC_x$ deposited on nitrided Si substrate at 500°C*



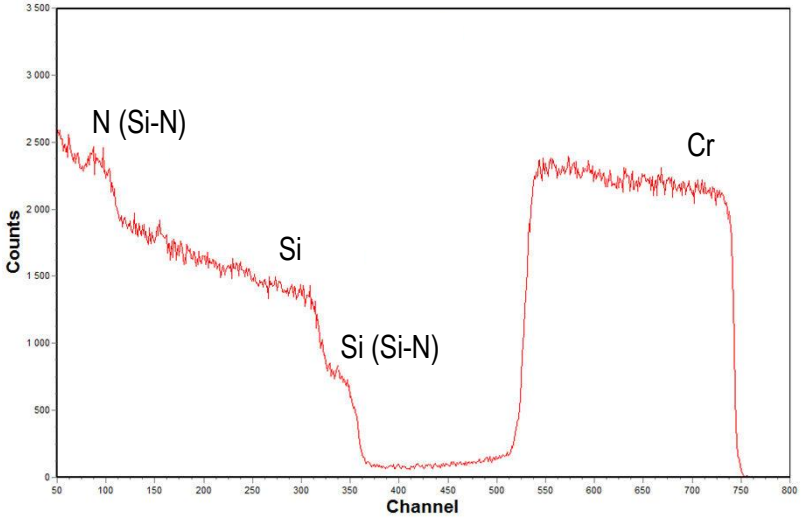

**→ No influence between 325 and 500°C**

**(Deposition of crystallized chromium carbides coatings above 500°C)**

## Atomic composition and density

- From 500 to 350°C
  - EPMA composition: **Cr:C = 2:1** with max. 5 at.% O
  - RBS density : **5.6 ± 0.4** g.cm$^{-3}$
- Below 350°C
  - EPMA composition: **Cr:C = 2:1** with max. 5 at.% O
  - RBS density : **6.1 ± 0.2** g.cm$^{-3}$

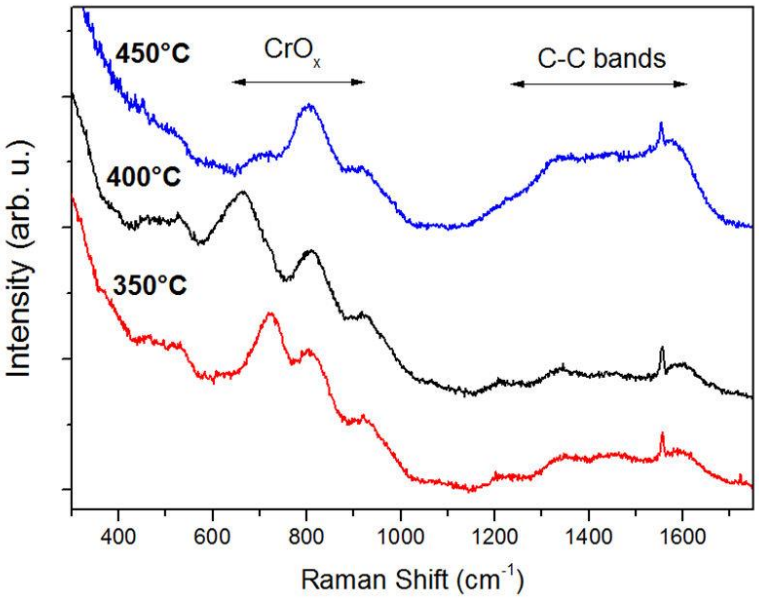
**→ No influence between 325 and 500°C**




*Typical Rutherford Backscattering Spectrometry of $CrC_x$ deposited on nitrided Si substrates*

## Raman spectroscopy

- Two domains of bands
  - **Oxides**
  - **Carbon**
- Oxides consist **exclusively of Cr oxides**
- No significant evolution of carbon bands with T
- **Oxides/Carbon** intensity ratio **decreases with an increasing T**




*Raman analyses of $CrC_x$ coatings deposited on Zircaloy at various temperatures*

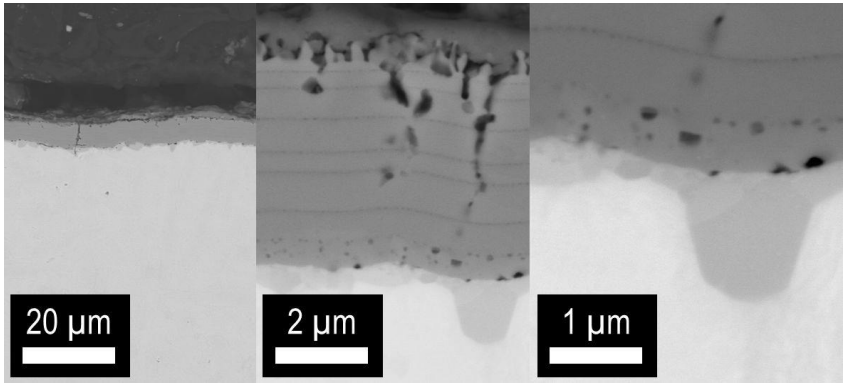
**→ Lower surface oxidation for higher deposition temperatures**

## Conclusions

- MOCVD is viable at a pilot-scale ~ 1 m
  - **Protection** of **metallic parts** for **extreme environments**
  - **Temperatures low** enough for Zr and other materials
  - DLI delivers high and stable MO precursor flows
- Joint experimental-numerical approach
  - Kinetics experimental studies coupled with numerical modeling
  - Assistance for **process optimization** and **scale-up**
- Flexible deposition of amorphous $CrC_x$ over a wide thermal range (500 to 350°C)
  - **Similar properties**, hard coatings (26 GPa, not presented here) and resistant to high-temperature oxidation in air and steam (not presented here)
- Different mechanism below 350°C
  - Multilayer growth triggered by periodic adequate temperature variations
  - **Participation of different** heterogeneous **reactions**

## Perspectives

- Benchmarking of $CrC_x$ performance as a function of their deposition temperature
  - **Influence of the multilayer** structure
  - Resistance to **high-temperature oxidation**
  - Selection of an **optimized temperature** for the deposition
- Development of DLI-MOCVD at a pilot scale
  - **Continuation of** the protection of nuclear fuel cladding application and other **tubular applications**
  - **Extension** of the pilot scale **to other chemical systems**
  - **Extension to 3D** model **components** of several cm




*SEM cross-section of $CrC_x$ coating deposited on Zircaloy at 325°C, annealed for 4 h at 550°C under Ar, oxidized at 1100°C for 15 min under ambient air and finally quenched in water at room temperature*

*Example of a 3D model component elaborated by additive manufacturing that will be functionalized (diameter ~10 cm)*

# Thank you for your attention

# Any questions?

**Other contributions :** The authors would like to thank Michaël OUGIER, Cédric CHARVILLAT for HT-XRD, Olivier MARSAN for Raman spectroscopy, Philippe DE PARSEVAL and Sophie GOUY for EPMA, Hervé GUEGAN and Benoît RIDARD for RBS.

**Funding:** This research was funded by the "Investments for the Future" Program (No. ANR-10-LABEX-44-01) and by the Cross-Cutting program on Materials and Processes Skills of the Commissariat à l'Energie Atomique (CEA).

**Acknowledgments:** This research work was performed within the framework of the Centre of Excellence of Multifunctional Architectured Materials "CEMAM".

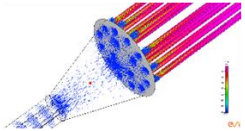
# Solutions

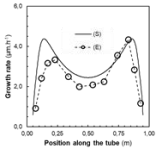
## Issues to overcome

- Sophisticated implementation
  - Cost and time consuming
  - Complex processes
- Use of harmful and expensive chemicals
  - Low conversion yields
  - Manipulation of big reactants quantities
  - Manipulation of big effluents quantities
  - Lost costs (mainly precursor)

- Numerical and experimental coupling
  - Assistance for process optimization
  - Assistance for process scale-up
  - Saves money and time

[ A. Michau et al., Coatings 8 (2018) ]
[ T. Duguet, B2-2-FrM5, ICMCTF 2019]

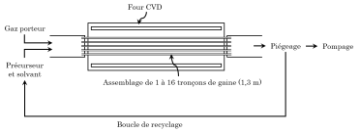





| Reactions | |
|---|---|
| (1) | $Cr(C_9H_6)_{2\,(g)} \rightarrow CrC_9H_{6\,(g)} + C_9H_{6\,(g)}$ |
| (2) | $CrC_9H_{6\,(g)} + Cr_{(s)} \rightarrow Cr_{(b)} + C_9H_{6\,(s)} + Cr_{(s)}$ |
| (3) | $C_9H_{6\,(s)} \rightarrow 6\,C_{(b)} + 3H_{2\,(g)}$ |
| (4) | $C_9H_{6\,(s)} \rightarrow C_9H_{6\,(g)}$ |
| (5) | $Cr(C_9H_6)_{2\,(g)} + Cr_{(s)} \rightarrow Cr_{(b)} + CrC_9H_{6\,(s)} + C_9H_{6\,(s)}$ |
| (6) | $Cr(C_9H_6)_{(s)} + Cr_{(s)} \rightarrow Cr_{(b)} + C_9H_{6\,(s)} + Cr_{(s)}$ |

- Gaseous effluents recycling
  - Conversion yields close to 100 %
  - Minimization of chemical manipulations
  - Drastic reduction of harmful effluents
  - Increased viability

[ A. Michau et al., SCT 332 (2017) 96 ]



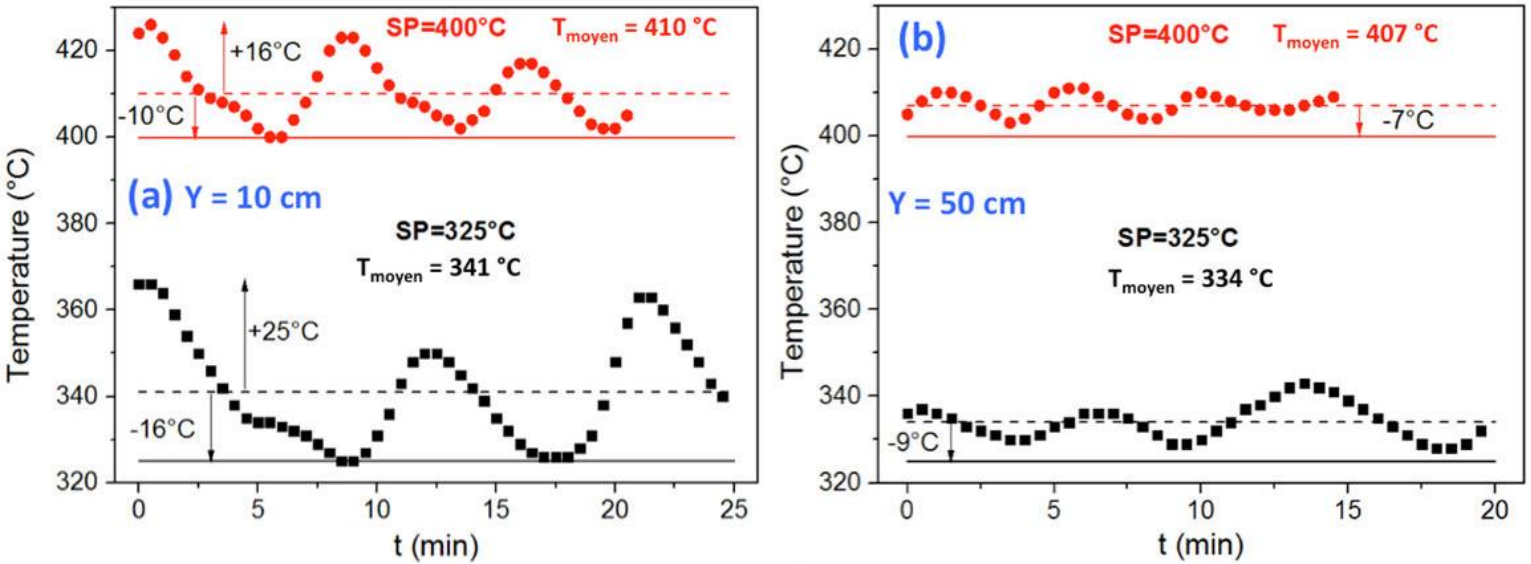



**Figure 19** : variation temporelle de la température expérimentale mesurée à l'intérieur d'une gaine à deux abscisses différentes : (a) en zone d'entrée (y = 10 cm) et (b) en zone centrale (y = 50 cm). Conditions : montage mono-gaine (axisymétrique), 5 torr, 500 sccm $N_2$. Traits en pointillé = valeur moyenne ; traits continus = consigne (SP). Dans tous les cas, **on observe une valeur moyenne supérieure à la consigne de plusieurs degrés** (au minimum 7°C de plus).

$$\text{BEBC} \rightarrow a\text{-}Cr_7C_3 + a\text{-}C$$
$$\text{BEBC} \rightarrow a\text{-}Cr_7C_3 + a\text{-}Cr_3C_2$$

| | Reactions |
|---|---|
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| (3) | $C_6H_{6\ (s)} \rightarrow 6\ C_{\ (b)} + 3H_{2\ (g)}$ |
| (4) | $C_6H_{6\ (s)} \rightarrow C_6H_{6\ (g)}$ |
| (5) | $Cr(C_6H_6)_{2\ (g)} + Cr_{\ (s)} \rightarrow Cr_{\ (b)} + CrC_6H_{6\ (s)} + C_6H_{6\ (s)}$ |
| (6) | $Cr(C_6H_6)_{\ (s)} + Cr_{\ (s)} \rightarrow Cr_{\ (b)} + C_6H_{6\ (s)} + Cr_{\ (s)}$ |