Behaviour of ion irradiated chromium coatings on zircaloy-4 substrate

Alexia Wu, Joël Ribis, Jean-Christophe Brachet, E. Clouet

DE LA RECHERCHE À L'INDUSTRIE

BEHAVIOUR OF ION IRRADIATED CHROMIUM COATINGS ON ZIRCALOY-4 SUBSTRATE

WU Alexia[1], RIBIS Joel[1], BRACHET Jean-Christophe[1], CLOUET Emmanuel[2] et al.

1 CEA Saclay DEN/ DMN/SRMA/LA2M

2 CEA Saclay DEN/ DMN/SRMP

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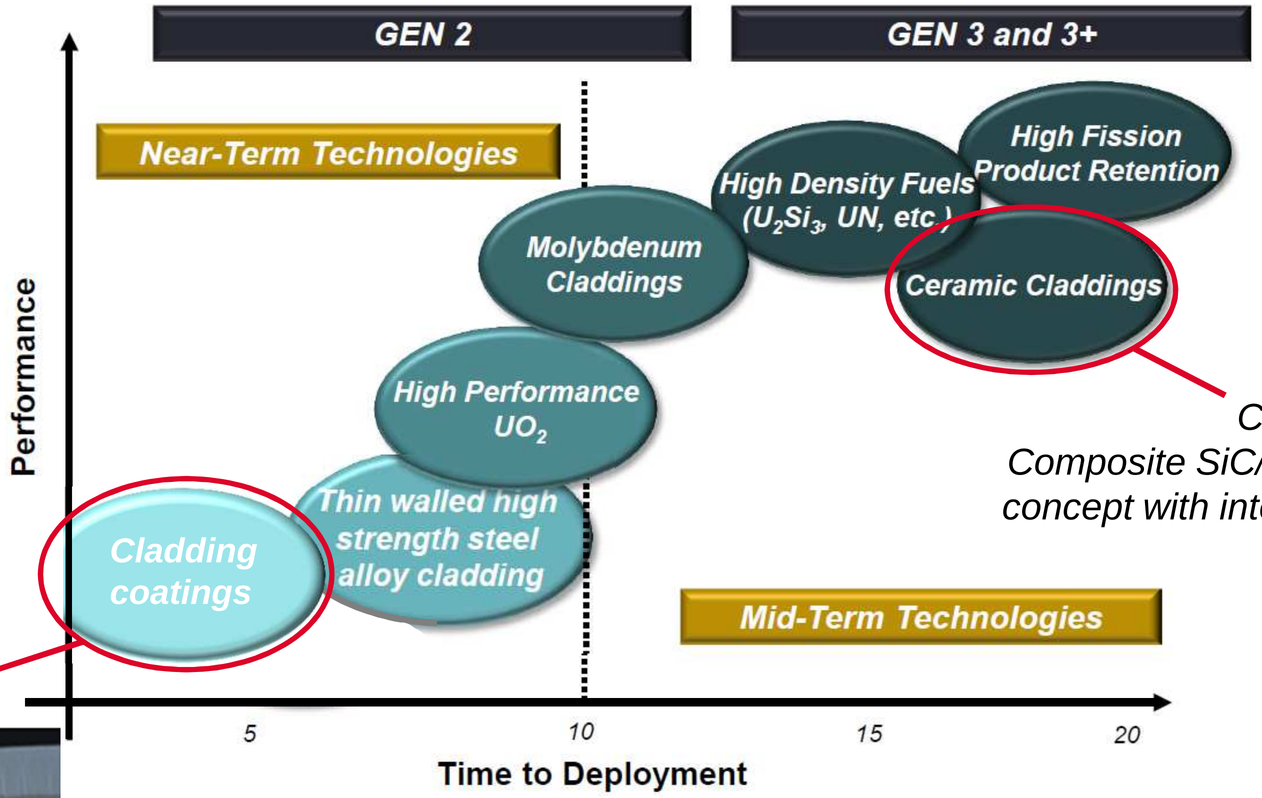
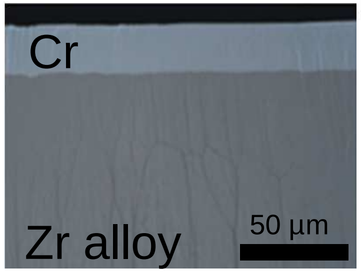
➤ Worldwide, several « Enhanced **Accidental Tolerant Fuels** » (EATF) concepts for LWRs are considered:



CEA: Chromium coatings



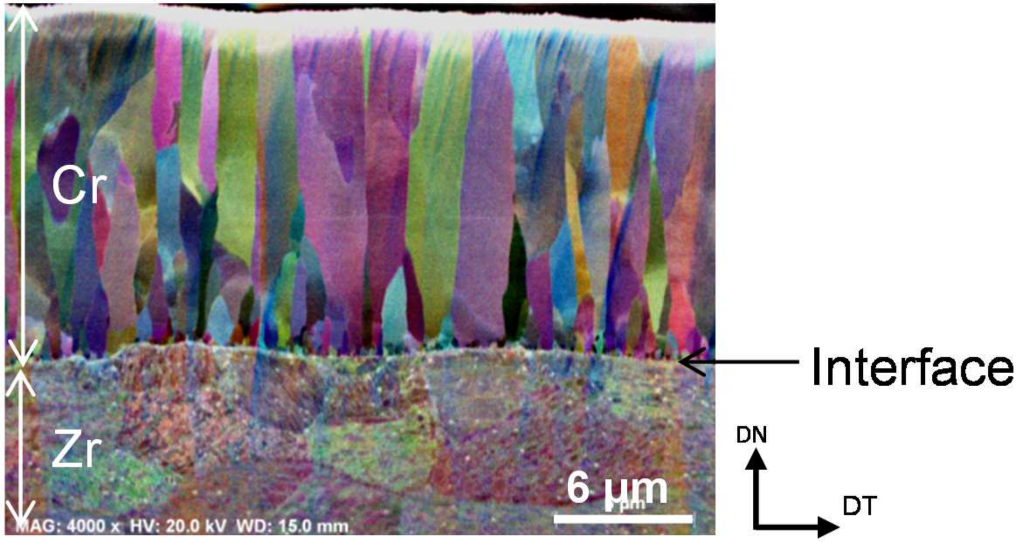
CEA: Composite SiC/SiC « sandwich » concept with internal metallic liner

Scheme from DOE

Nominal conditions:

- **Very good corrosion resistance** at 360°C in pressurized water with PWR chemistry and at 415°C in steam (100 bars) > 200 days
  => formation of less than 0,1µm thick Cr_2O_3
- As previously shown by *J. Bischoff et al previous talk,* **negligible impact of the Cr coating on the as-received mechanical behavior** of Cr coated Zirc-4 and M5® claddings

➢ Behaviour of Cr coated Zr base claddings <u>under irradiation</u>?



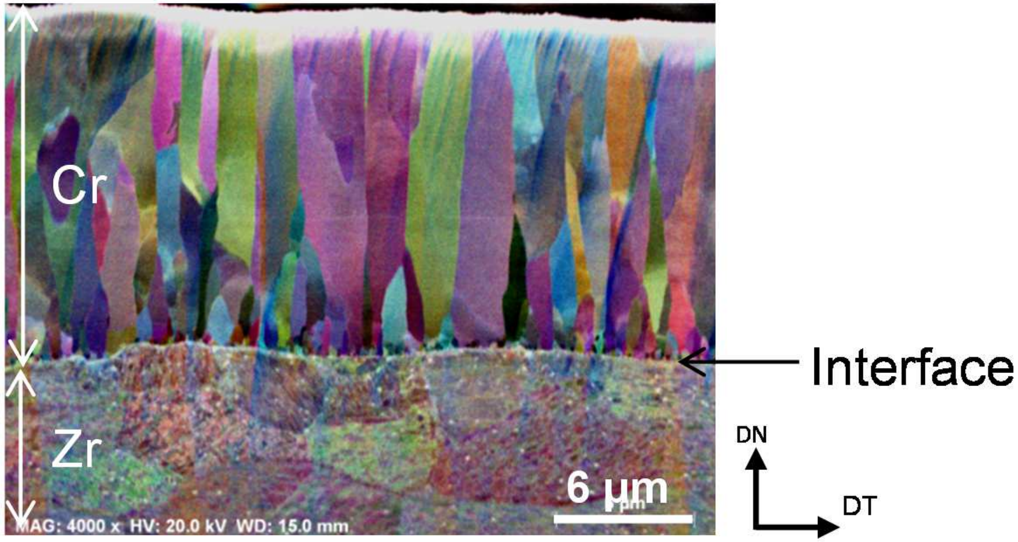
Irradiated chromium:
- Hardening / Embrittlement?

Zr/Cr irradiated interface:
- Chemical stability?
- Coherency? Crystallinity?
- Intermetallics ($ZrCr_2$) formation at the Zr-Cr interface? & their stability upon irradiation?

Irradiated zirconium substrate:
- Is there any coating consumption due to accelerated diffusion of chromium within Zr substrate?

PURPOSE OF THE PRESENT STUDY

- **Behaviour of Cr coated Zr base claddings under irradiation?**



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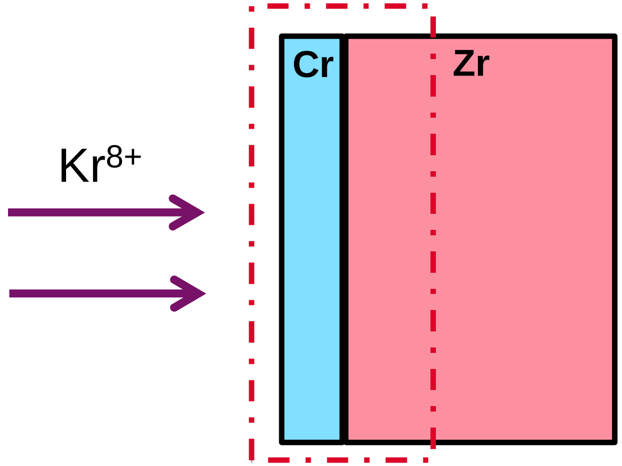
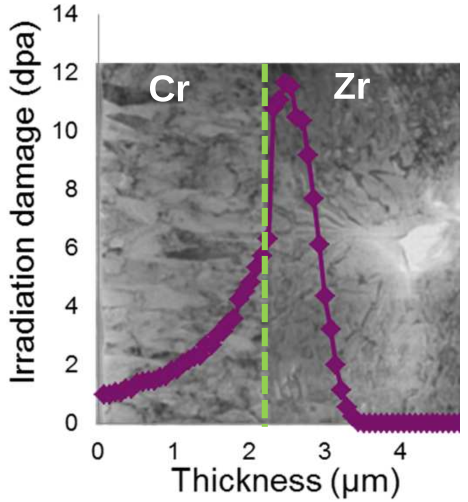
Irradiated zirconium substrate:
- Is there any coating consumption due to accelerated diffusion of chromium within Zr substrate?

EXPERIMENTAL APPROACH

- Ion irradiations performed to get some fundamental insights on irradiation effects (*and thus to anticipate neutron irradiation behavior*)
- Ex-situ irradiation (Jannus Saclay)
    - **Bulk material**
    - **Ions Kr $^{8+}$**
    - Energy **20 MeV**
    - Irradiation temperature **400°C**
    - Average flux **$2,8.10^{11}$ ion.cm^{-2}.s^{-1}**
    - ~ **6 hours** irradiation
    - Dose **$5,97.10^{15}$ ions.cm^{-2}**
    - Damage at the interface: ~**10 dpa**

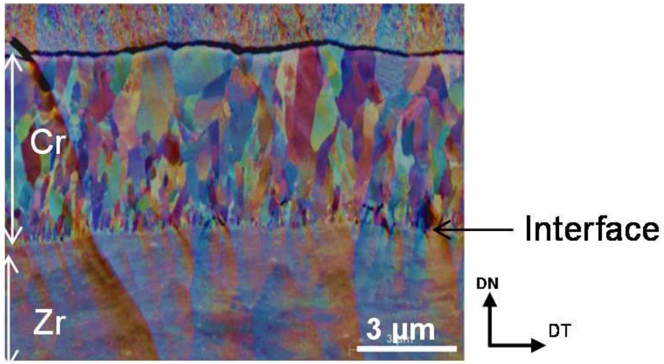


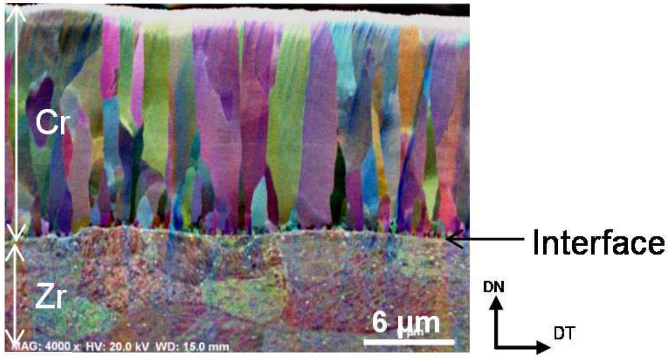
Irradiated zone



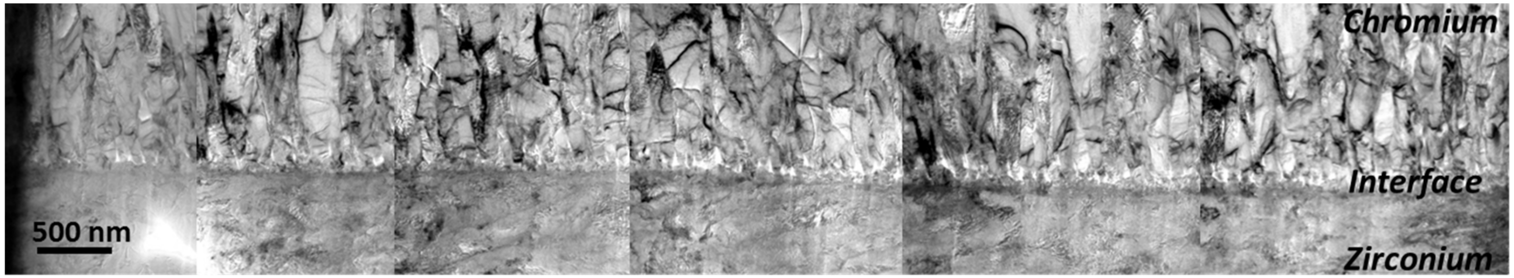
- For the purpose of this comprehensive study, different as-received coating microstructures produced/studied (different thicknesses, grain sizes...)

Typical chromium grains morphologies studied:



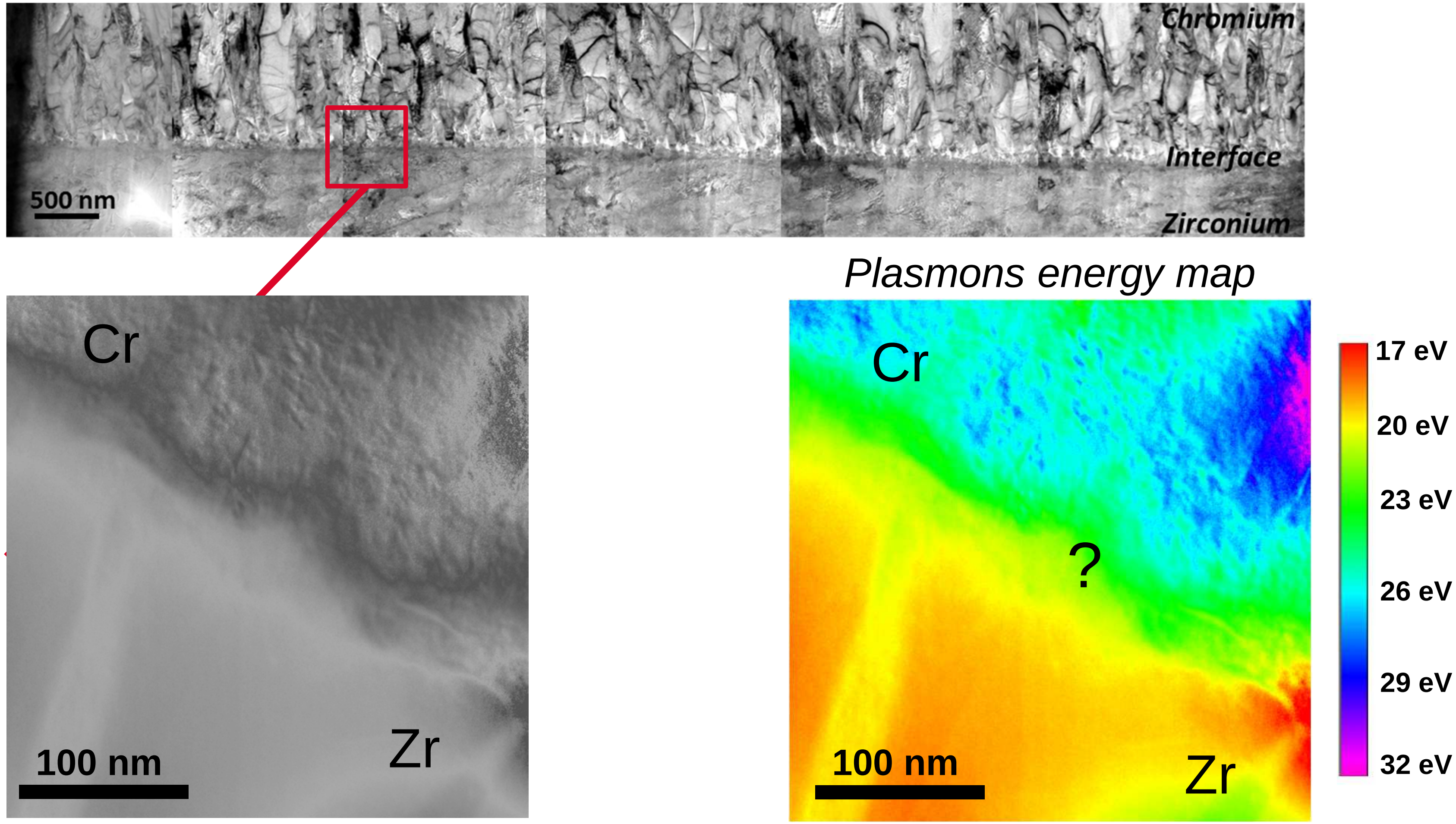


- Transmission Electron Microscopy characterisations:



- No microcracks, no voids at the interface
- Fully dense coatings, very good chromium / zirconium bonding

- TEM observation of a FIB thin foil sample



- Plasmons energy showing intermediate values at the interface?

CHROMIUM/ ZIRC-4 INTERFACE <u>BEFORE</u> IRRADIATION (2/4)

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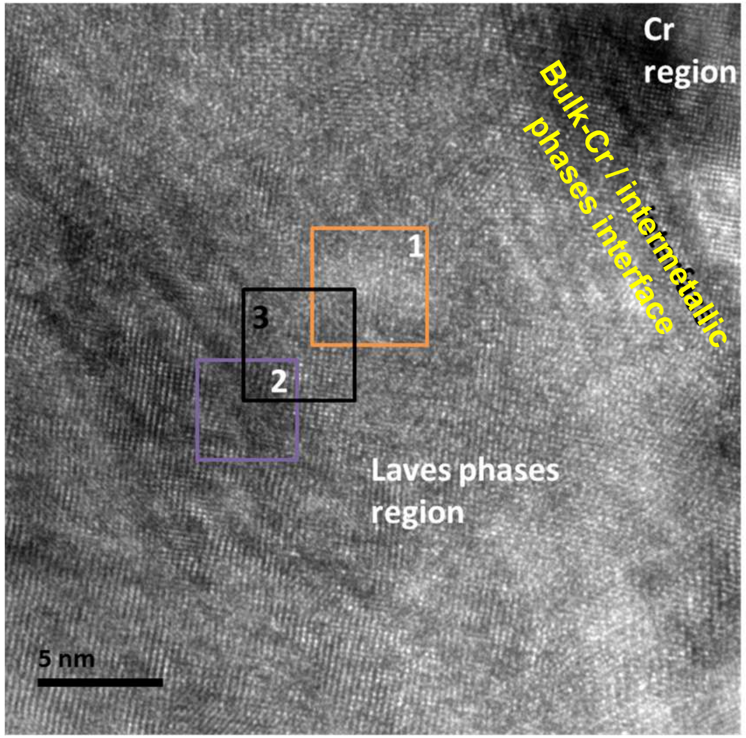
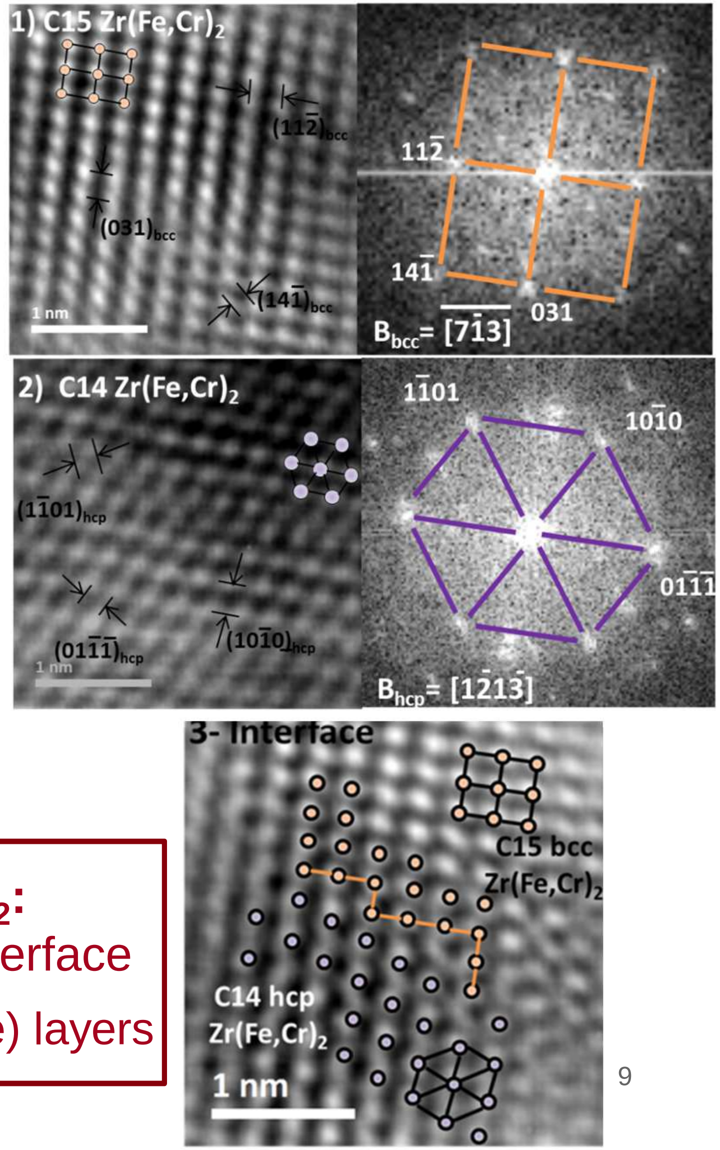
- High Resolution TEM (HRTEM) observation of a FIB thin foil sample



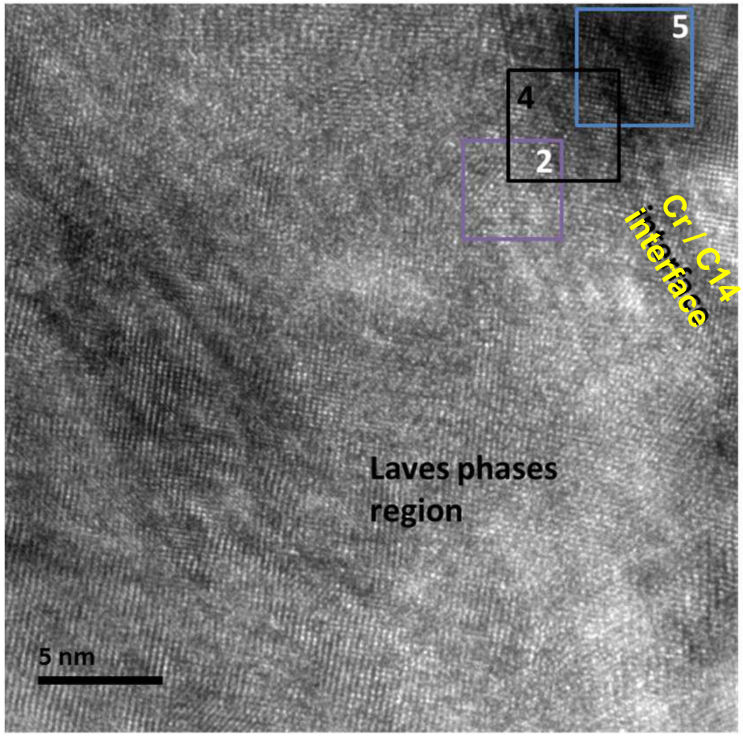


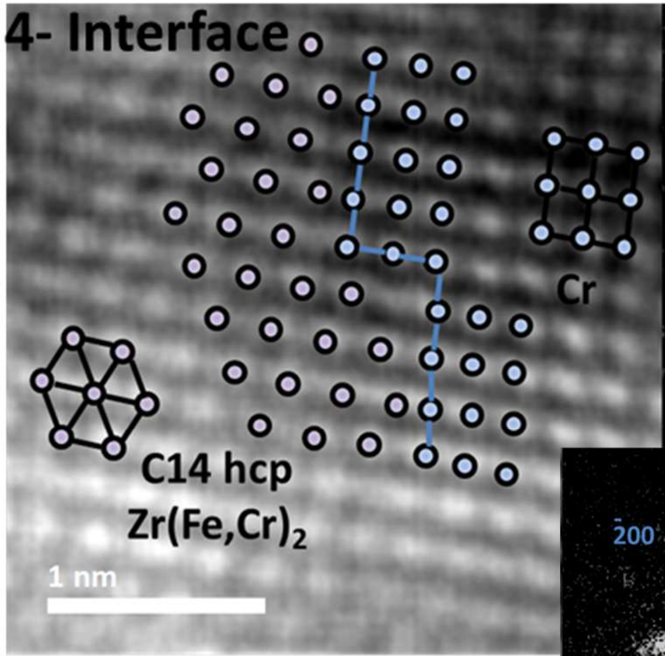
- **Two intermetallic Laves phases $Zr(Cr,(Fe))_2$:**
  C14 (hcp) & **C15 (bcc)** evidenced at Zr-Cr interface

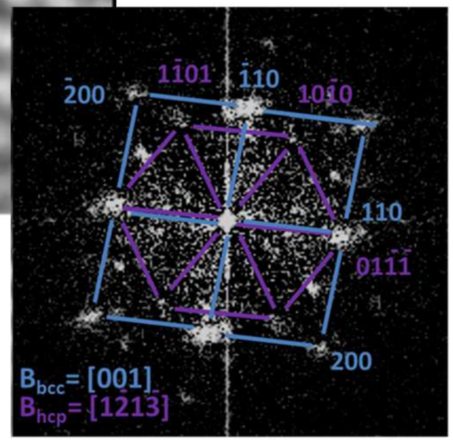
=> polytype stucture of the Laves phases (interface) layers

CHROMIUM/ ZIRC-4 INTERFACE BEFORE IRRADIATION (3/4)

- HRTEM observation of a FIB thin foil sample

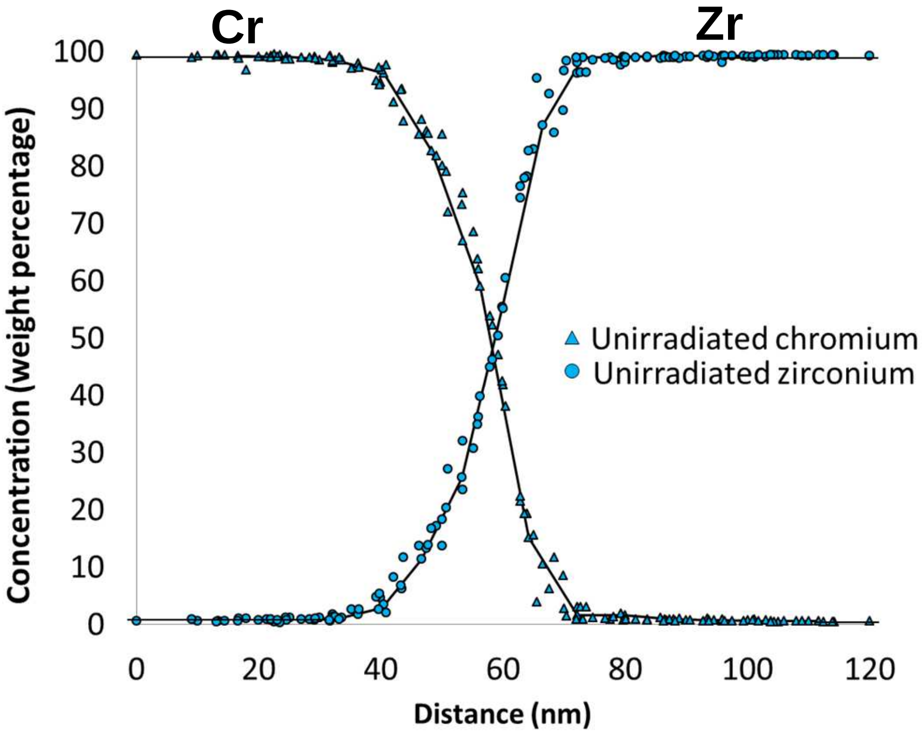


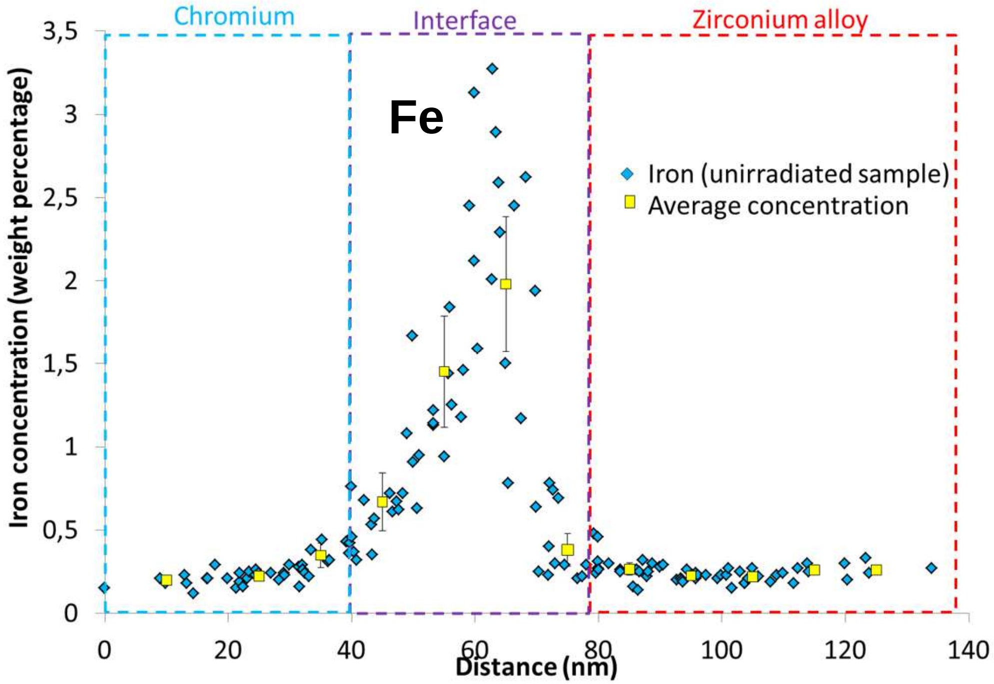




- Ledged interface **between C14 - $Zr(Cr,(Fe))_2$ and Cr => cristallographic continuity**
- Coherency along $[110]_{Cr}$ // $[01\bar{1}\bar{1}]_{C14}$

- Semi-quantitative chemical profiles (EDSX) at the interface



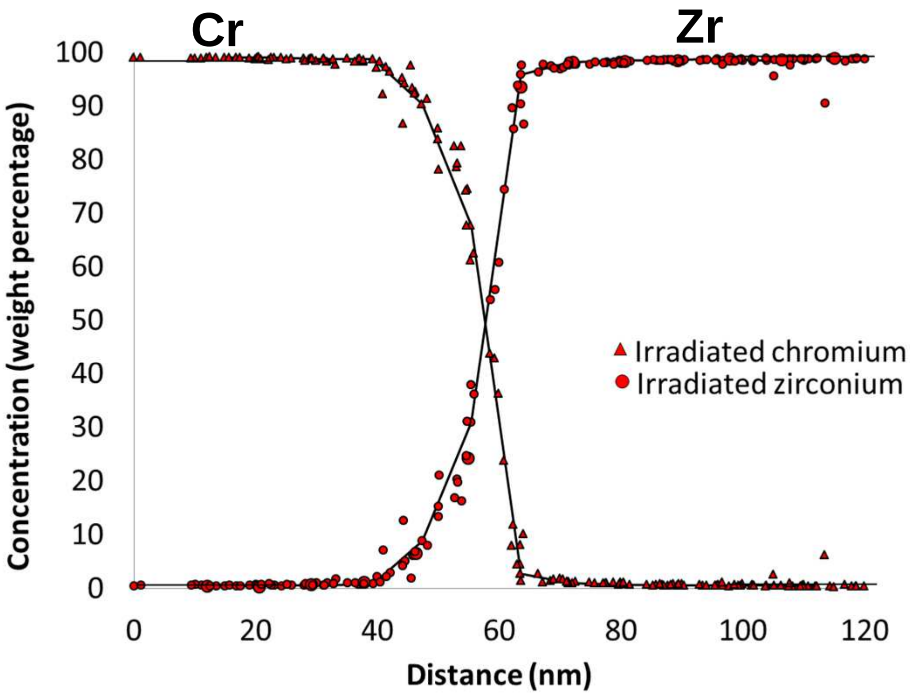


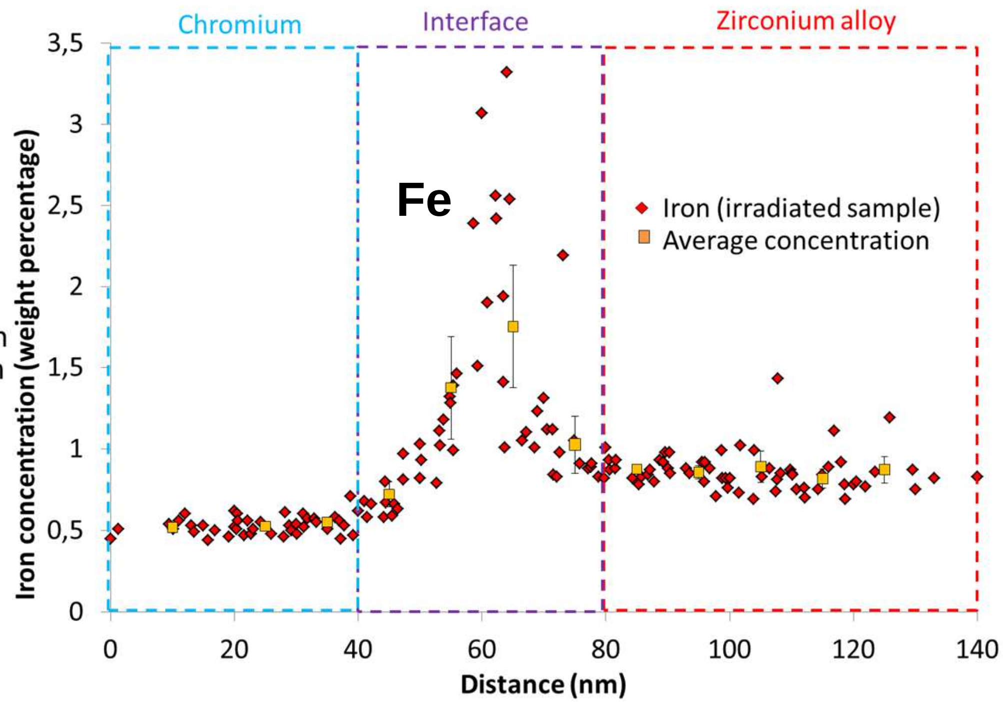
- *Some Fe enrichment at the interface prior to irradiation*
- *Evolution after irradiation?*

CHROMIUM/ ZIRC-4 INTERFACE AFTER IRRADIATION (1/8)

➢ **Semi-quantitative chemical profiles (EDSX) at the interface**

Ion irradiation up to ~**10 dpa** at the interface



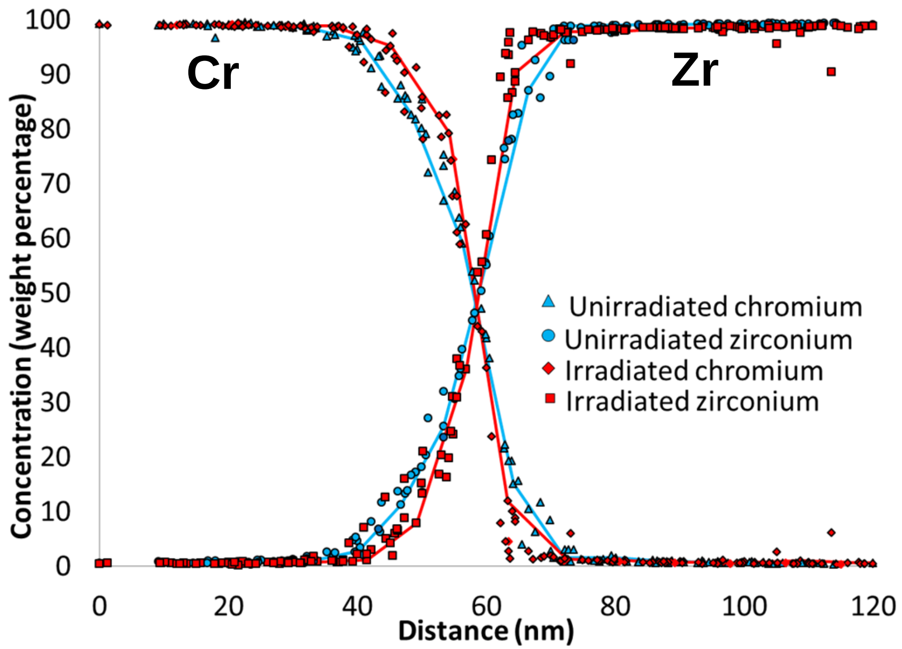


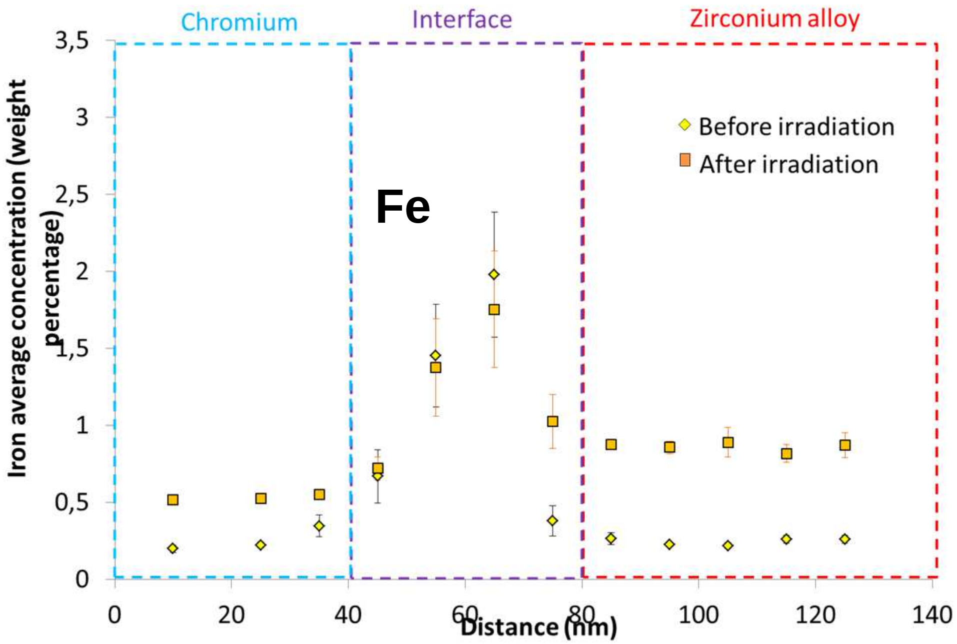
➢ *Fe enrichment still present at the interface after irradiation*

CHROMIUM/ ZIRC-4 INTERFACE AFTER IRRADIATION (2/8)

➢ **Semi-quantitative chemical profiles (EDSX) at the interface**
=> Comparison before/after irradiation

Ion irradiation up to ~**10 dpa** at the interface





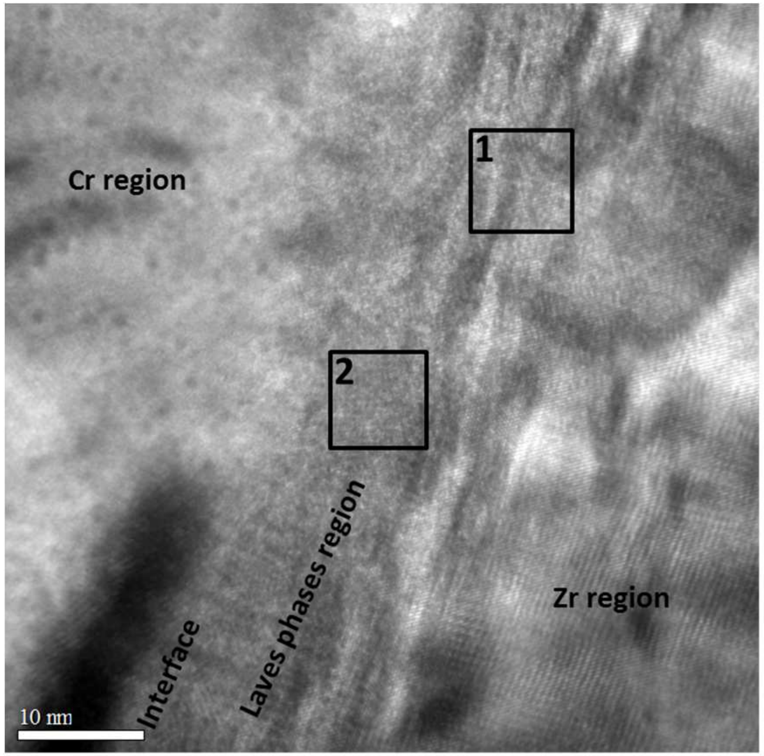
➢ No significant additional interdiffusion between Cr and Zr after irradiation:
=> **Overall chemical stability of the interface**

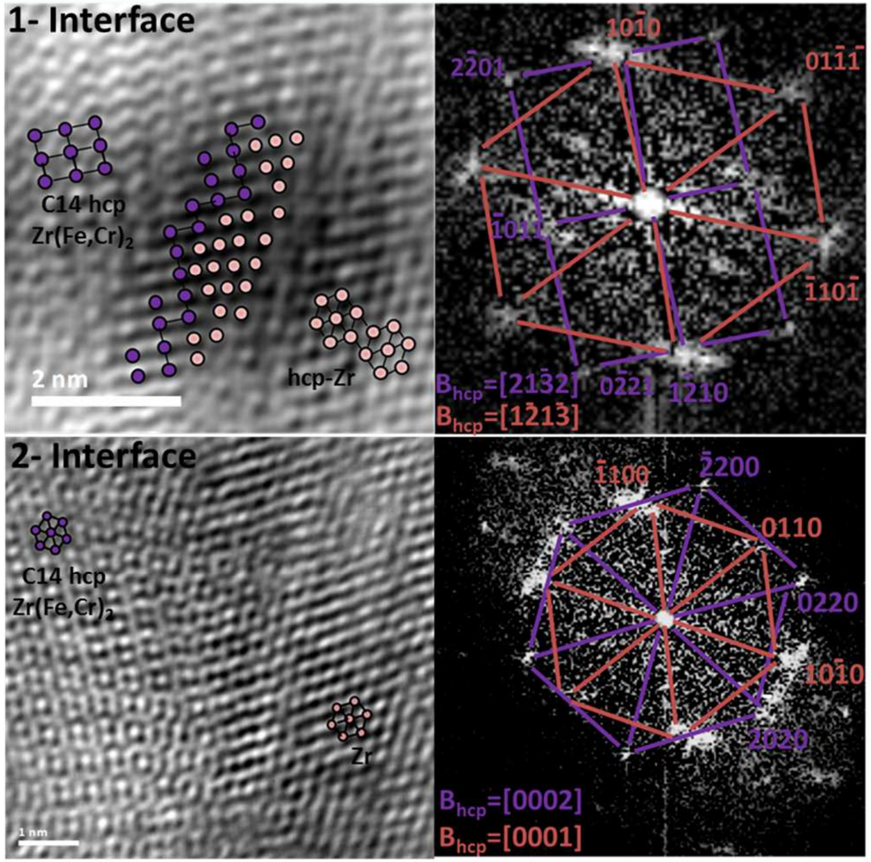
➢ *No significant additional Fe enrichment at the interface*
but apparent %Fe increase in neighbouring Zr and Cr after irradiation

CHROMIUM/ ZIRC-4 INTERFACE AFTER IRRADIATION (3/8)

- HRTEM observation of a FIB thin foil sample **after irradiation**

Ion irradiation up to ~**10 dpa** at the interface

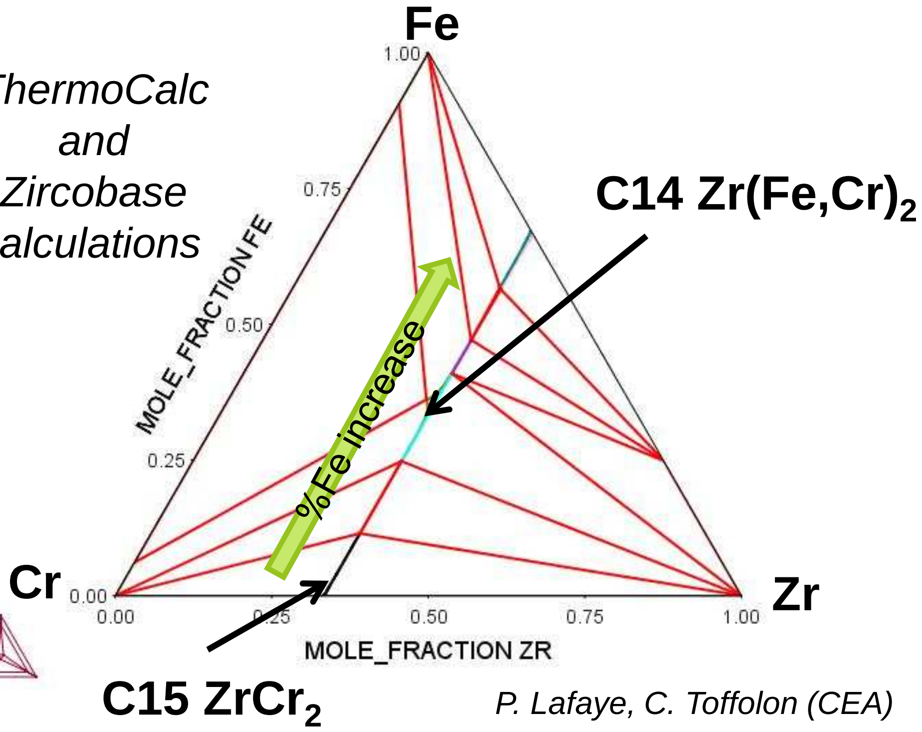




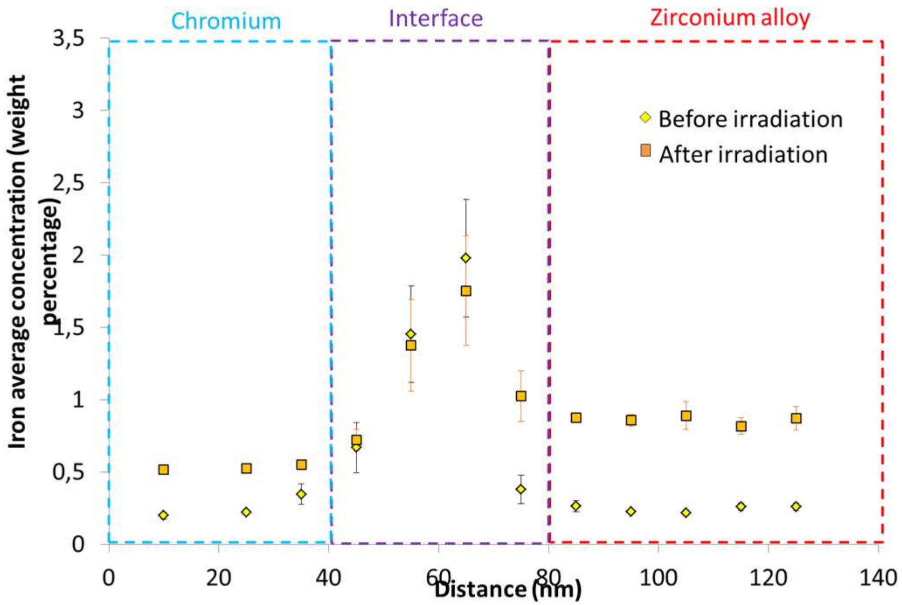
- *Only C14 Laves phase observed (disappearance of the C15?)*

Ternary phase diagram Zr,Cr,Fe (400°C)

ThermoCalc and Zircobase Calculations



P. Lafaye, C. Toffolon (CEA)



➢ *Possible explanation: Transformation of C15 Laves phase to C14 due to thermodynamic stabilizing effect of Fe*

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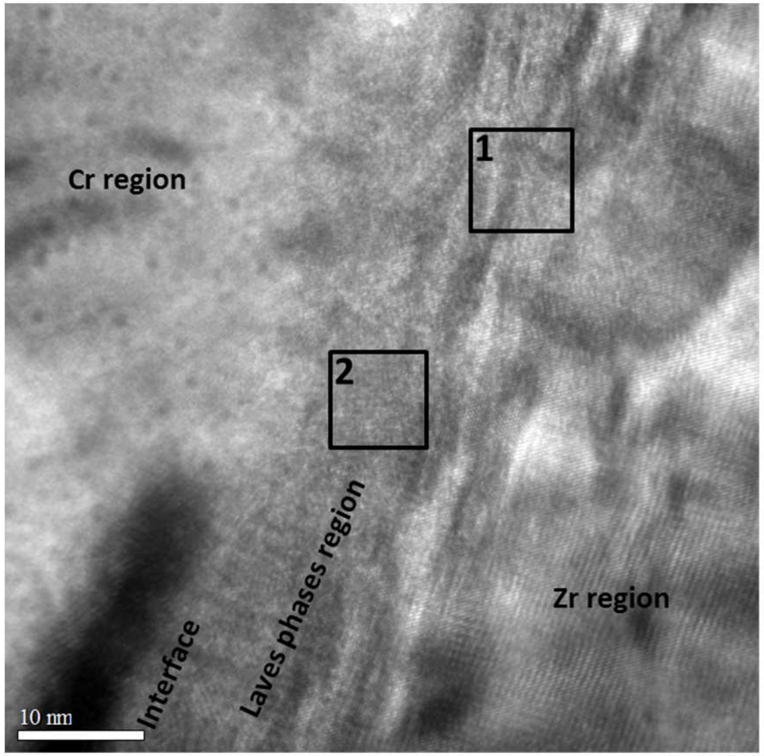
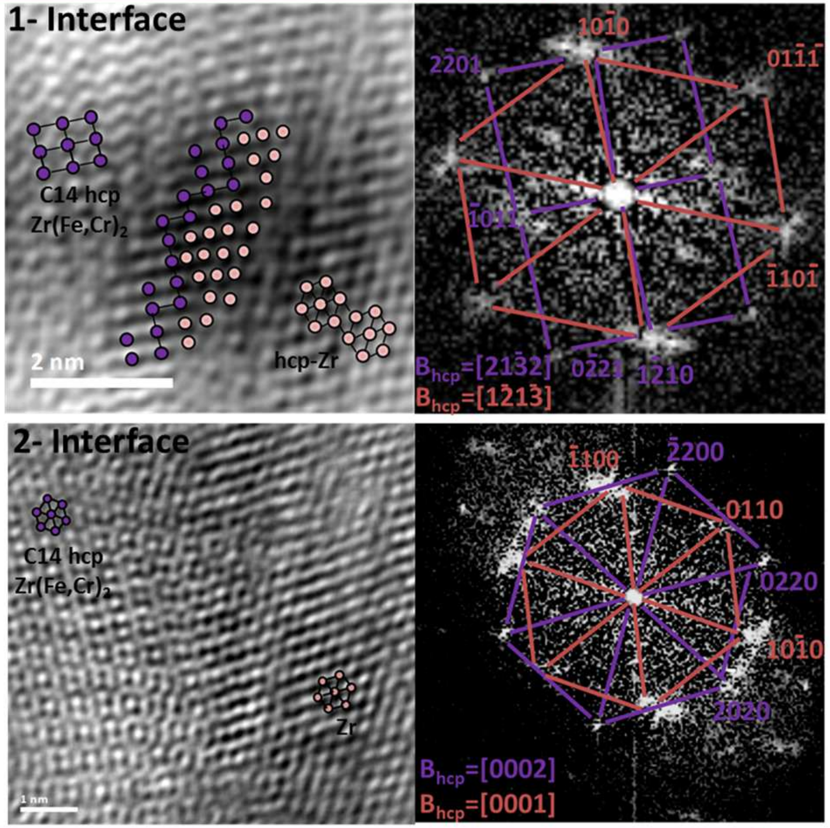
- HRTEM observation of a FIB thin foil sample **after irradiation**

Ion irradiation up to ~**10 dpa** at the interface





- *Only C14 Laves phase observed (disappearance of the C15?)*
- **Crystalline interfaces maintained after irradiation**
- Coherency along some crystallographic directions $[10\bar{1}0]_{Zr}$ // $[1\bar{2}10]_{C14}$

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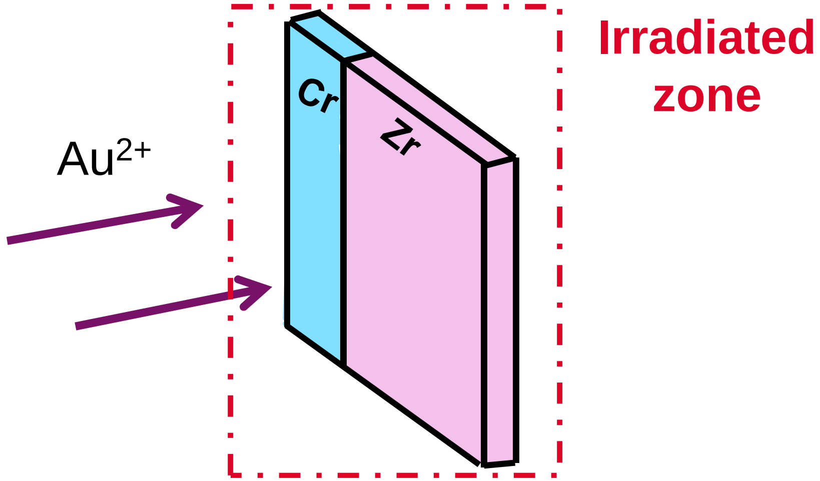
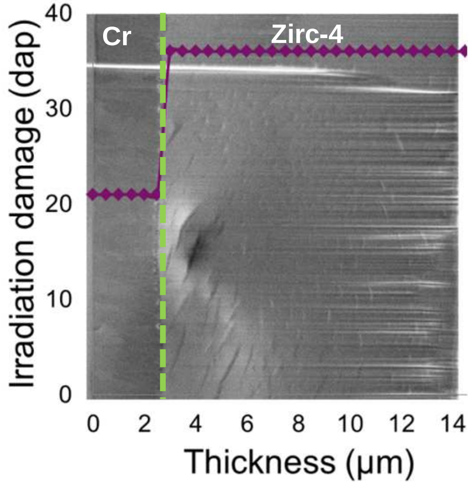
- Up to 10 dpa at the interface:
  - **Chemical stability of the overall Zr/Cr profil**
  - **Crystalline interfaces maintained after irradiation**
  - *Some Fe enrichment at the Zr-Cr interface before and after irradiation*
  - *Potential stabilisation of the intermetallic phases C14 at the interface?*

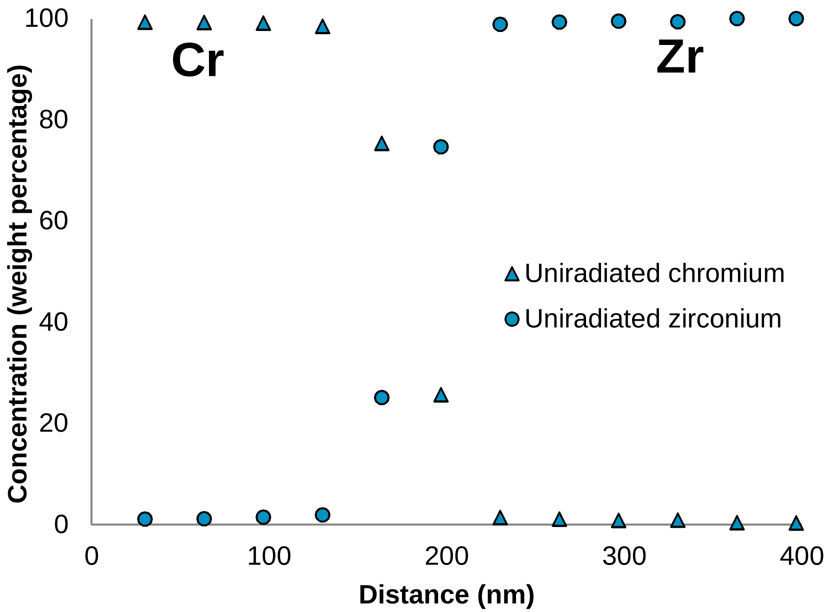
- What happens if we increase the damage?
  - **In-situ irradiation** (Jannus Orsay) up to **30 dpa** at the interface
    - **FIB thin foil sample**
    - **Ions Au $^{2+}$**
    - Energy**4 MeV**
    - Irradiation temperature**400°C**
    - Average flux **$2{,}8.10^{11}$ ion.cm^{-2}.s^{-1}**
    - Total dose 6 x 8.10^{14} **ion.cm^{-2}**
    - Dose totale
      - **In Cr: ~ 21 dpa**
      - **In Zr:~ 36 dpa**
      - **At the interface: ~ 30 dpa**

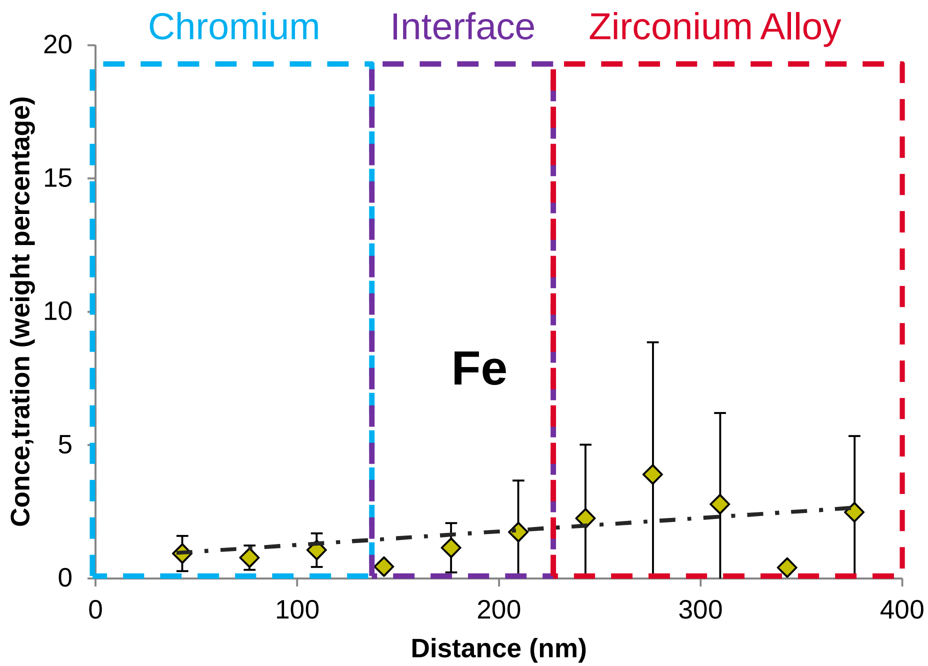




CHROMIUM/ ZIRC-4 INTERFACE AFTER IRRADIATION (7/8)

➢ **In-situ characterisations:** EDS **before irradiation**



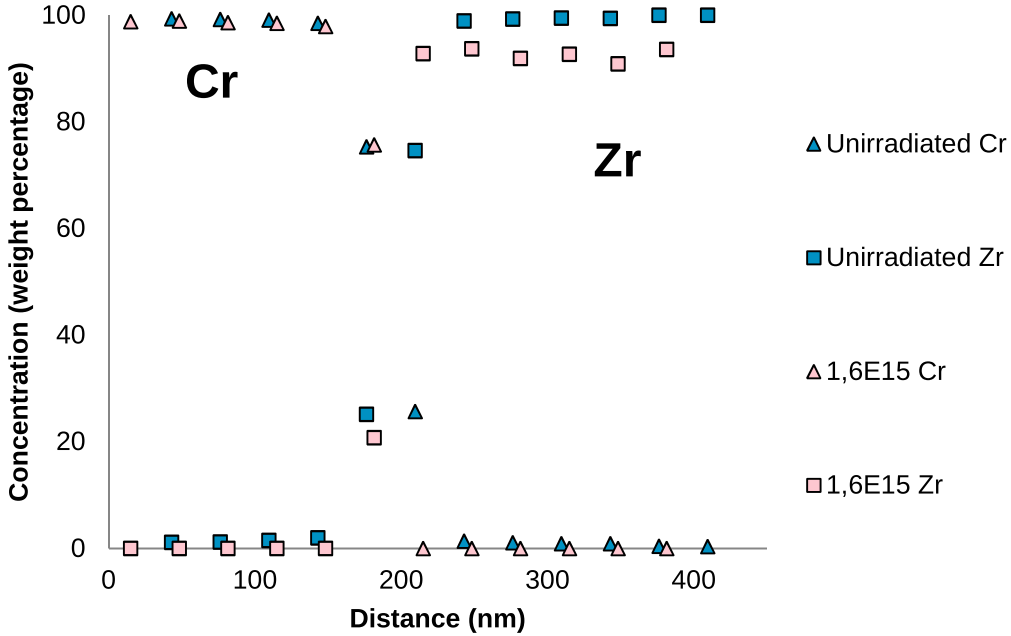


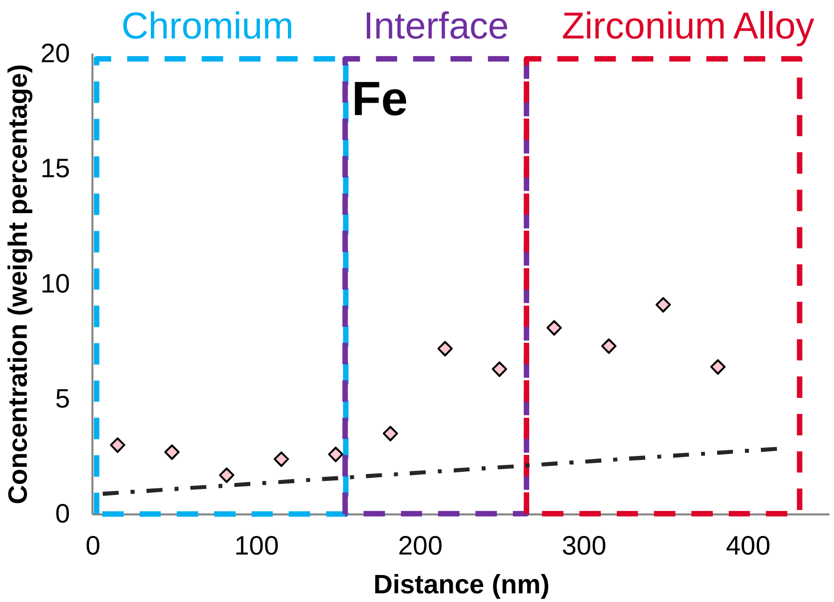
➢ *On some very localized zone, apparent Fe enrichment into the Zircaloy-4 substrate just close to the Zr-Cr interface*

CHROMIUM/ ZIRC-4 INTERFACE AFTER IRRADIATION (8/8)

➢ **In-situ characterisations:** EDS **during ion irradiation**

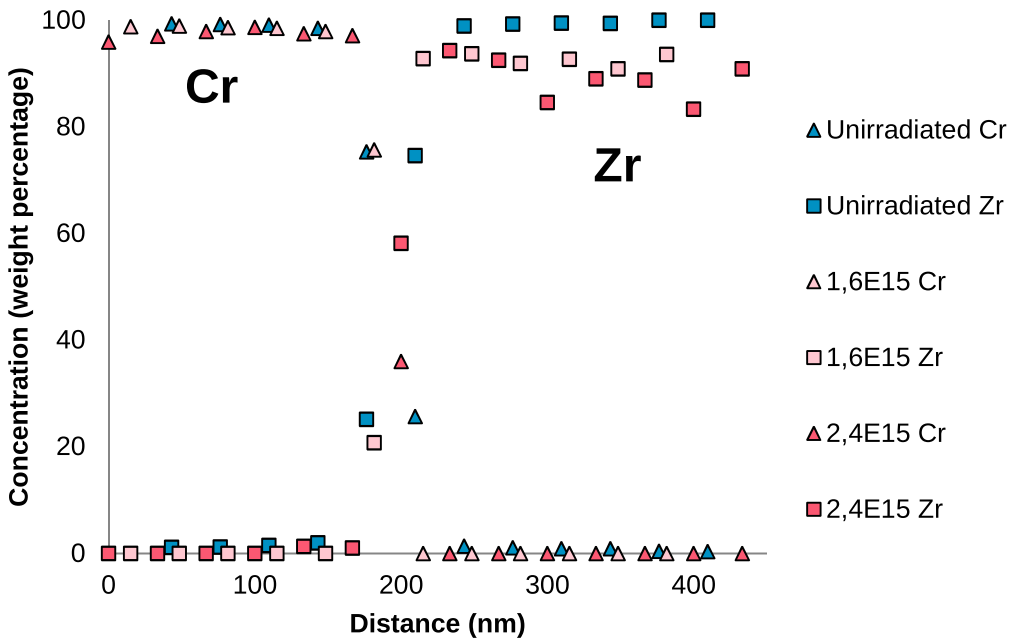
Ion irradiation up **to ~10 dpa** at the interface

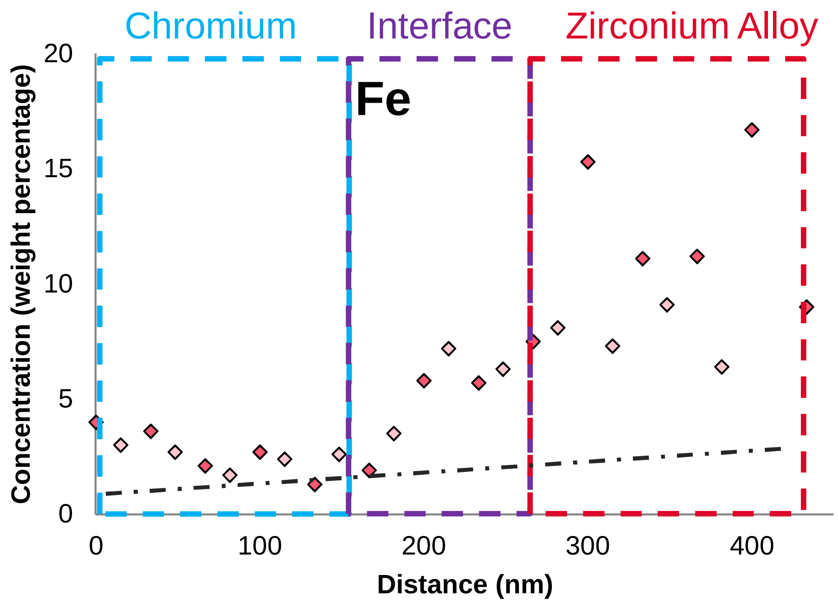




➢ **In-situ characterisations:** EDS **during ion irradiation**

Ion irradiation up **to ~15 dpa** at the interface





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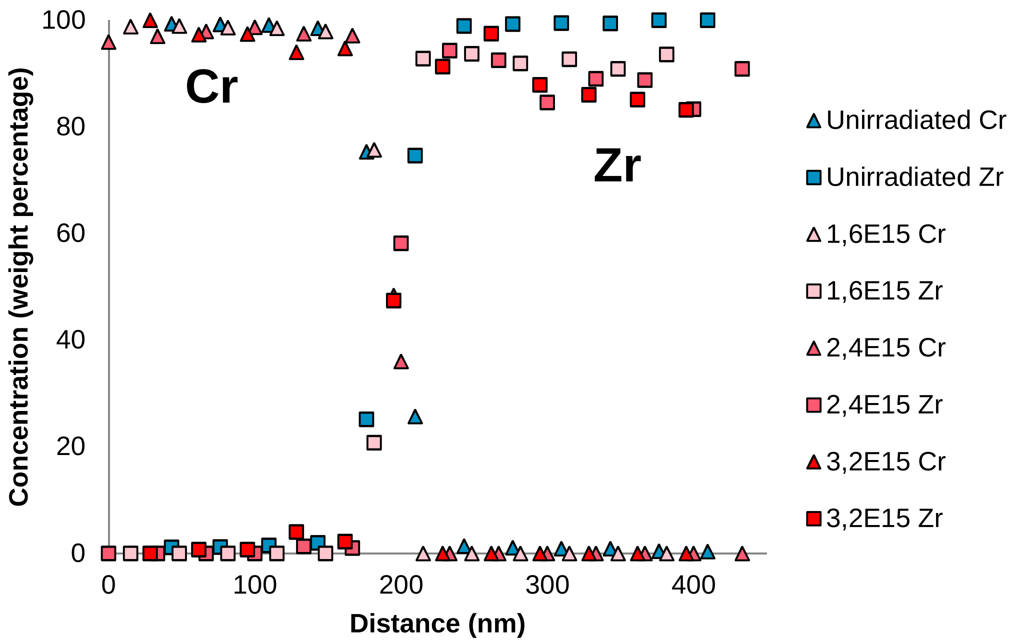
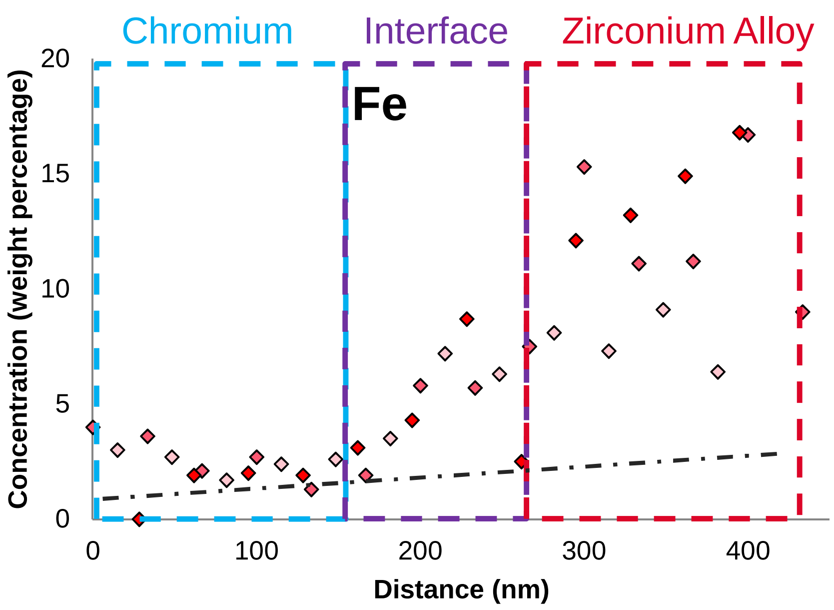
➢ **In-situ characterisations:** EDS **during ion irradiation**

Ion irradiation up **to ~20 dpa** at the interface





CHROMIUM/ ZIRC-4 INTERFACE AFTER IRRADIATION (8/8)

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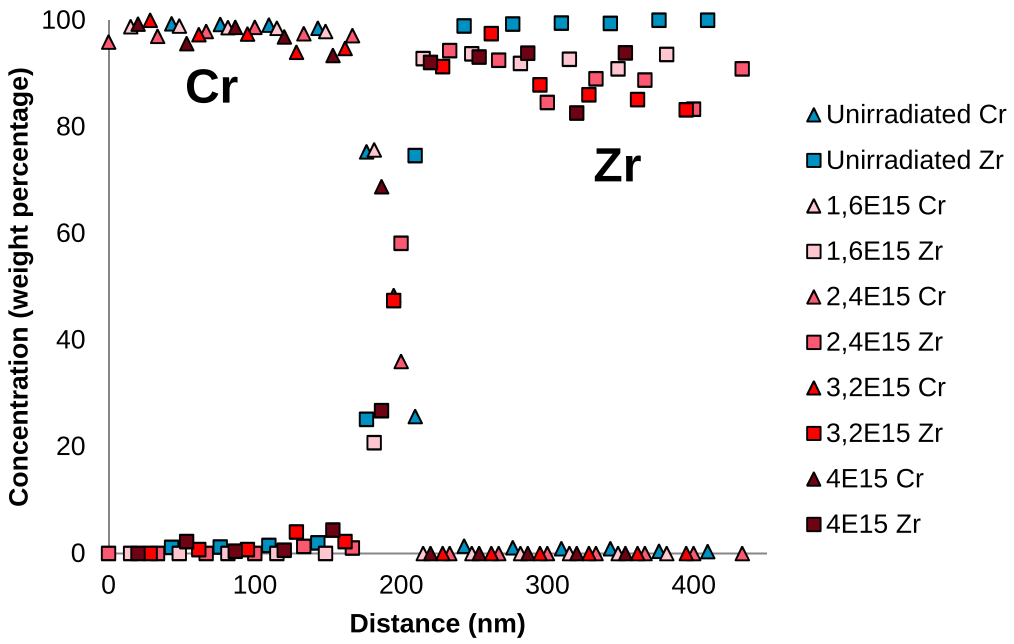
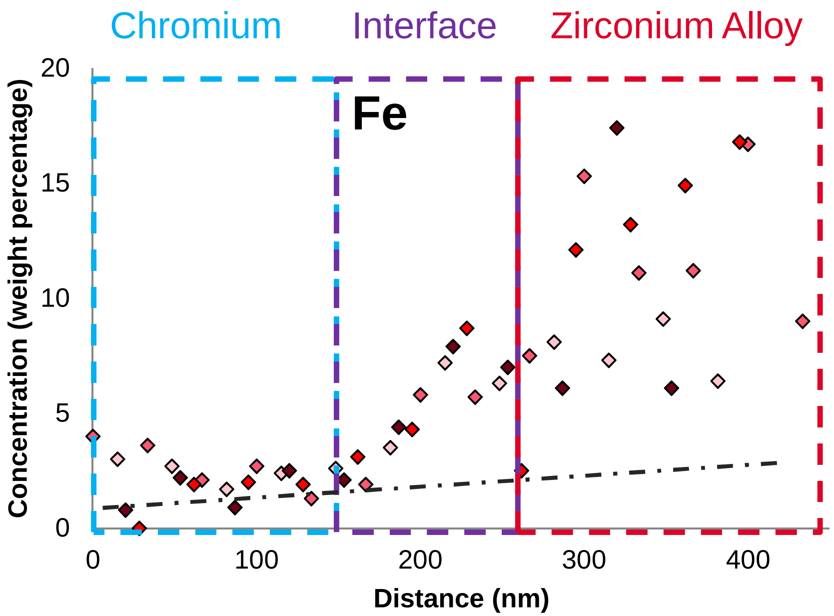
- **In-situ characterisations:** EDS **during ion irradiation**

Ion irradiation up **to ~25 dpa** at the interface





- **Stability of the Zr / Cr profiles after irradiation up to 25 dpa**
- *Apparent additional Fe enrichment into the Zirc-4 substrate close to the interface when the irradiation dose increases (needs more statistics)*

CONCLUSIONS

- **Cr coated Zr-alloys** are considered as **potential EATF claddings for LWRs**
- **As received coatings** show **no cracking/voids at the interface**
- **First ion irradiation experiments performed (at 400°C)**
- **HRTEM and microchemical** analyses focused on the **Zr/Cr interface**:

Zr/Cr irradiated interface:
- *Chemical stability?*
- *Coherency? Crystallinity?*
- *Intermetallics ($ZrCr_2$) formation at the Zr-Cr interface? & their stability upon irradiation?*

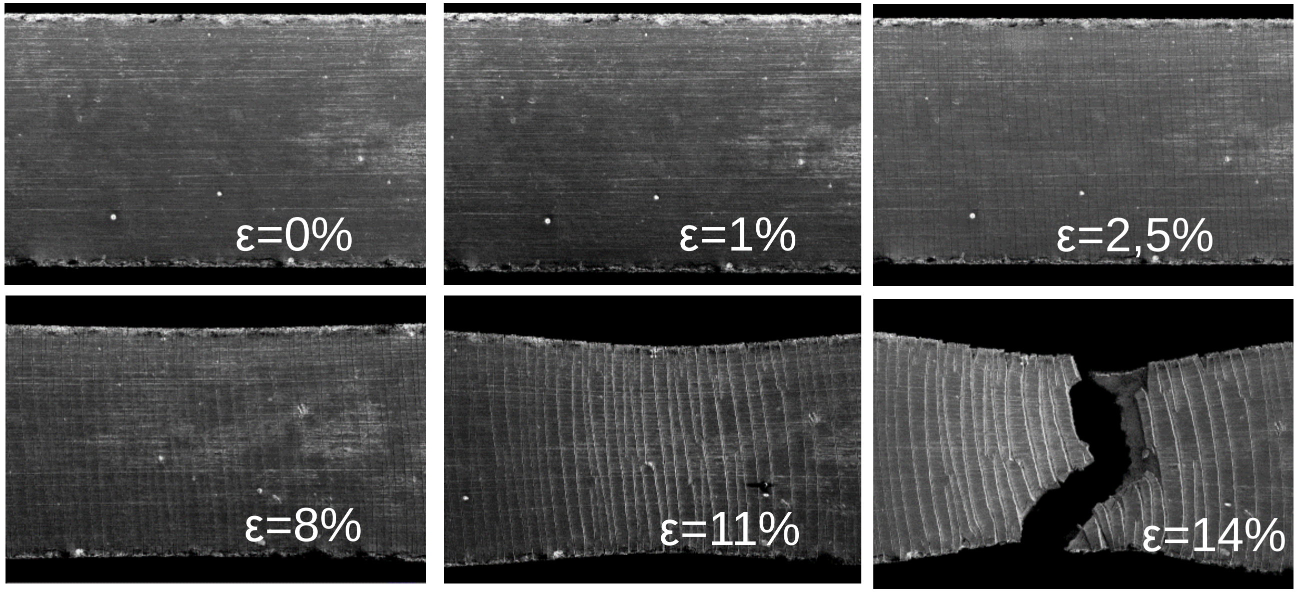
Irradiated zirconium substrate:
- Is there any coating consumption due to accelerated diffusion of chromium within Zr substrate?

- **No evolution of the Cr/Zr profile** → **no accelerated interdiffusion** of Cr⇔Zr under ion irradiation at 400°C
- **Cristallographic continuity a the interface maintained after irradiation** (~**10 dpa)**
- ***C15 and C14 Zr(Fe,Cr)$_2$ intermetallic Laves phases*** *and some Fe enrichment* **highlighted before/after irradiation**

> **No irradiation accelerated Cr coating consumption and Cr coating adhesion preserved after ion irradiation**

ON-GOING WORK

- **In-situ (SEM) mechanical testing** of unirradiated and irradiated coatings



No Cr coating delamination up to rupture

- Study of the **chromium hardening under irradiation**
  (*nanohardness measurements and scratch tests planned...*)

<u>Further (Longer Term) CEA-AREVA-EDF R&D on Cr coated Zr base claddings</u>:

- *Study of **last generation Cr coated cladding tubes**, including **M5®** substrate*
- ***Neutron irradiation on-going or planned** (Halden...)*

THANK YOU
FOR YOUR ATTENTION

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Fe ENRICHMENT AT THE Zr/Cr INTERFACE
=> WHERE DOES THE IRON COME FROM?

⇒ **Likely from the Zircaloy-4 substrate (0,2 wt% Fe)**

⇒ **<u>Potential physical mechanisms:</u>**

➢ **1) Fe is a fast interstitial-like diffusing elements in Zr**

IF: Local depletion of Fe in Zirc-4 close to Zr/Cr interface → Chemical Fe gradient in Zirc-4 → Net diffusion flux of Fe atoms

➢ **2) Limited content of residual Fe in the Zirc-4 matrix solid-solution**

SPPs C14-$Zr(Fe,Cr)_2$ precipitates in the Zirc-4 partially dissolve and/or loose some Fe → Diffusion of Fe at the interafce

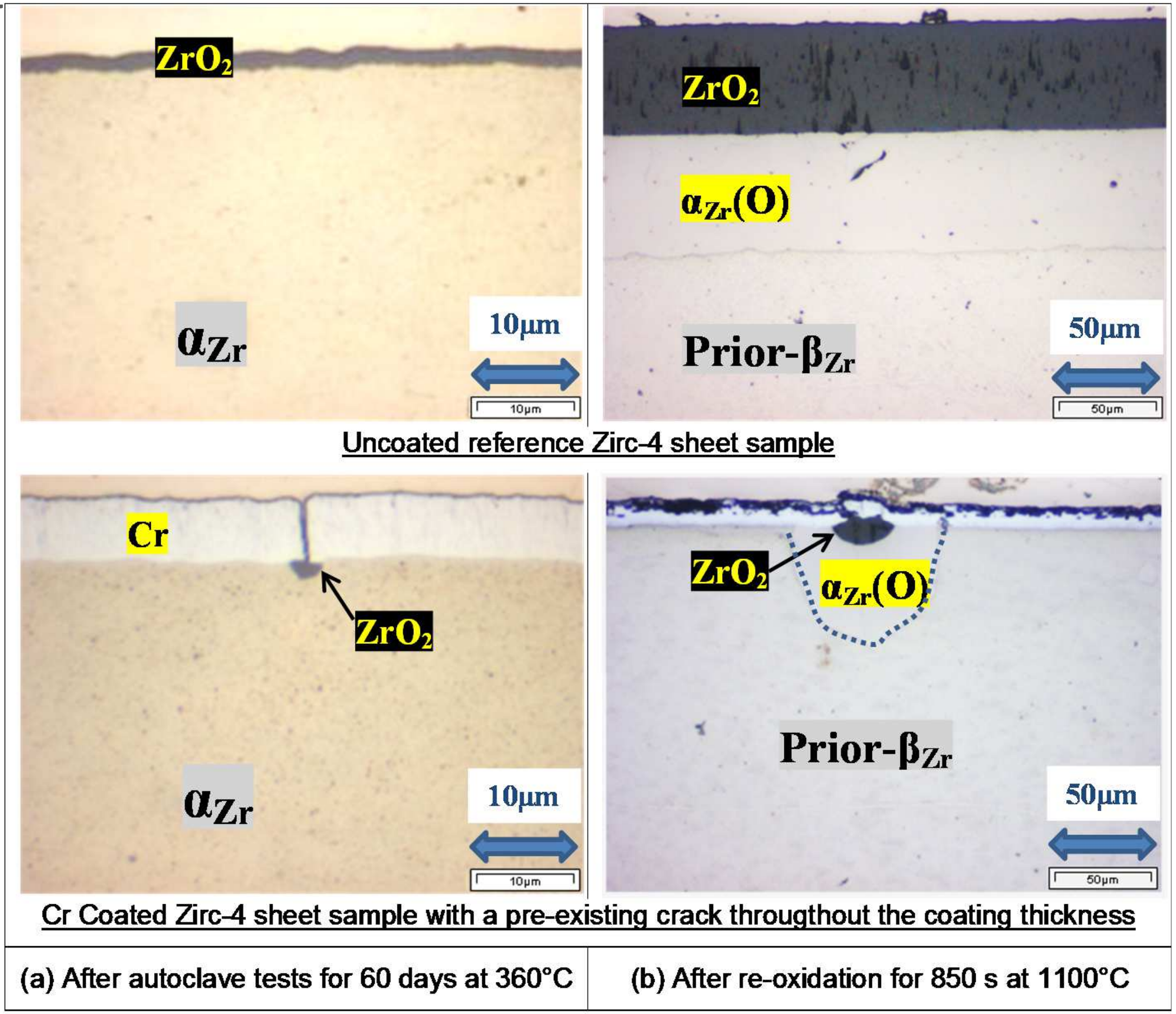
➢ **Needs complementary experiments** to confirm and get a better understanding of this phenomena.

Impact of pre-existing Cr coating defects

The potential negative impact of a pre-existing defect (i.e., as-received crack) within the Cr coating on the subsequent coated clad oxidation is an important issue:

⇒ Results obtained so far show only a limited an very localized impact of a pre-existing thru-wall Cr layer crack on the subsequent oxidation behavior for both nominal and accidental (LOCA) conditions (i.e., neither local accelerated corrosion, nor coating spallation)

⇒ However, further work is necessary: longer oxidation times…



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