



HAL
open science

Behaviour of ion irradiated chromium coatings on zircaloy-4 substrate

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

► **To cite this version:**

Alexia Wu, Joël Ribis, Jean-Christophe Brachet, E. Clouet. Behaviour of ion irradiated chromium coatings on zircaloy-4 substrate. The Nuclear Materials Conference 2016 - NUMAT 2016, Nov 2016, Montpellier, France. cea-02435085

HAL Id: cea-02435085

<https://cea.hal.science/cea-02435085>

Submitted on 10 Jan 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

DE LA RECHERCHE À L'INDUSTRIE



www.cea.fr

BEHAVIOUR OF ION IRRADIATED CHROMIUM COATINGS ON ZIRCALOY-4 SUBSTRATE

WU Alexia¹, RIBIS Joel¹, BRACHET Jean-Christophe¹,
CLOUET Emmanuel² et al.

¹ CEA Saclay DEN/ DMN/SRMA/LA2M

² CEA Saclay DEN/ DMN/SRMP

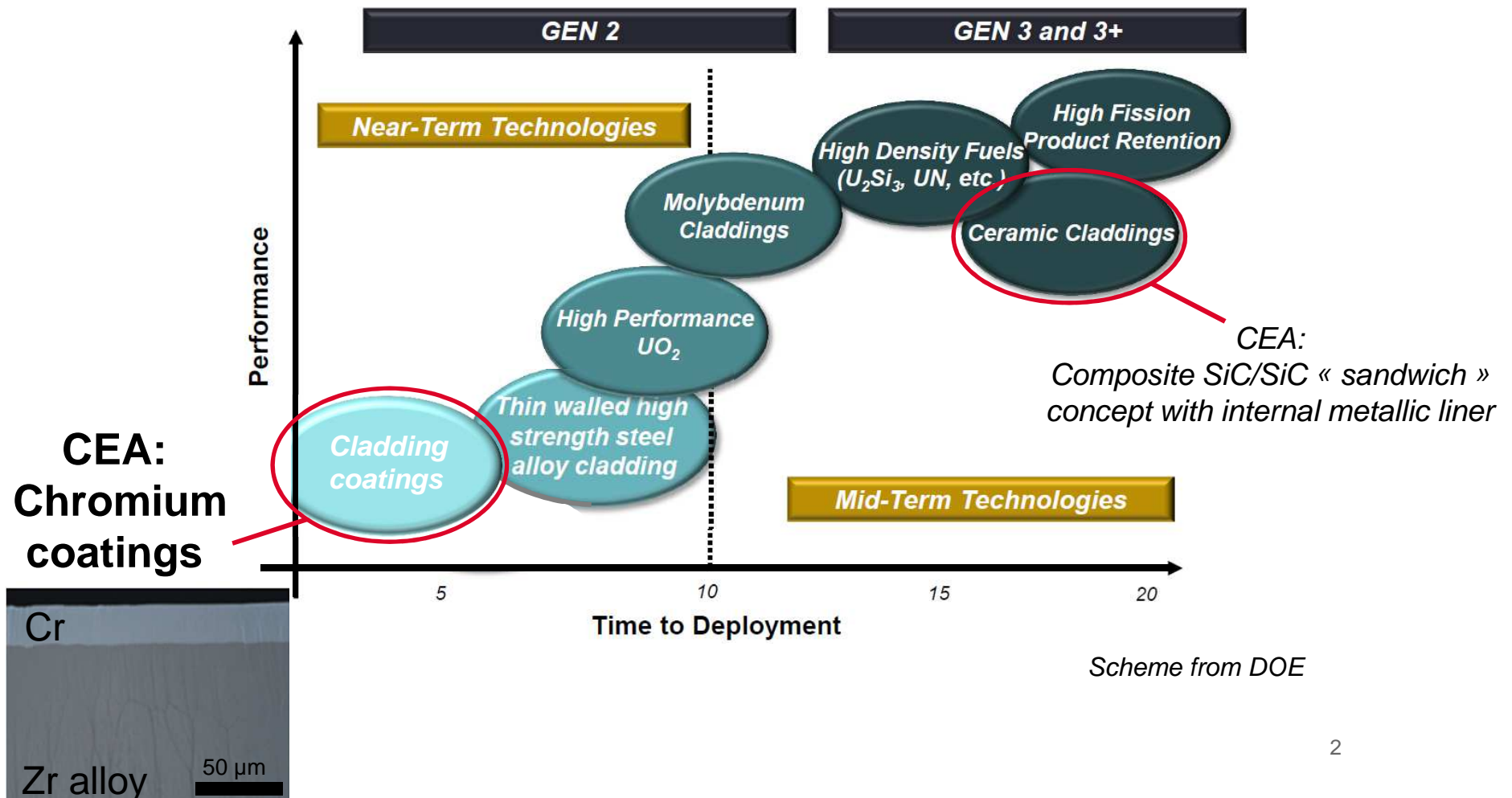
NuMat 2016

Montpellier, FRANCE

7-10 November, 2016

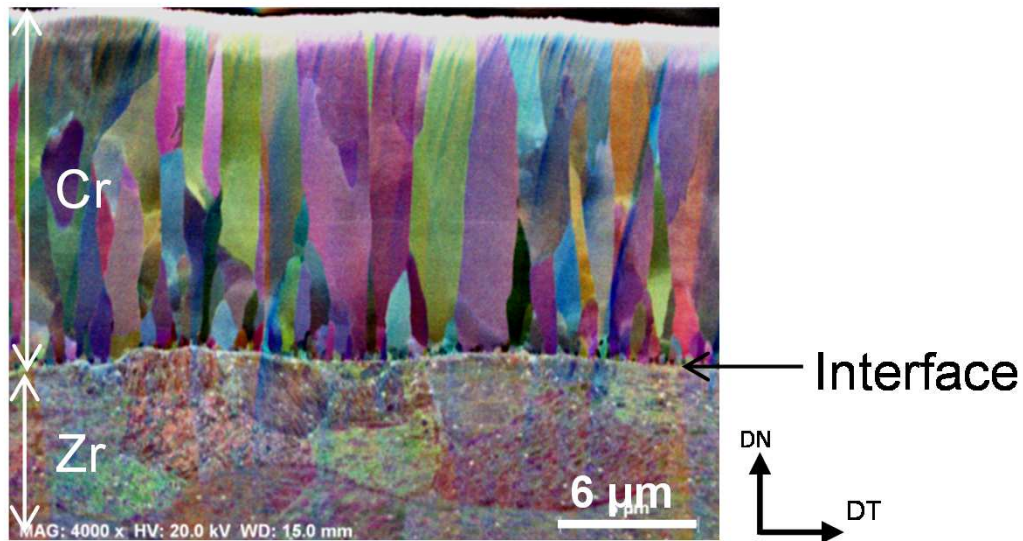


- Worldwide, several « Enhanced **Accidental Tolerant Fuels** » (EATF) concepts for LWRs are considered:



- **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 Cr₂O₃
 - 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 under irradiation?**



Irradiated chromium:

- Hardening / Embrittlement?

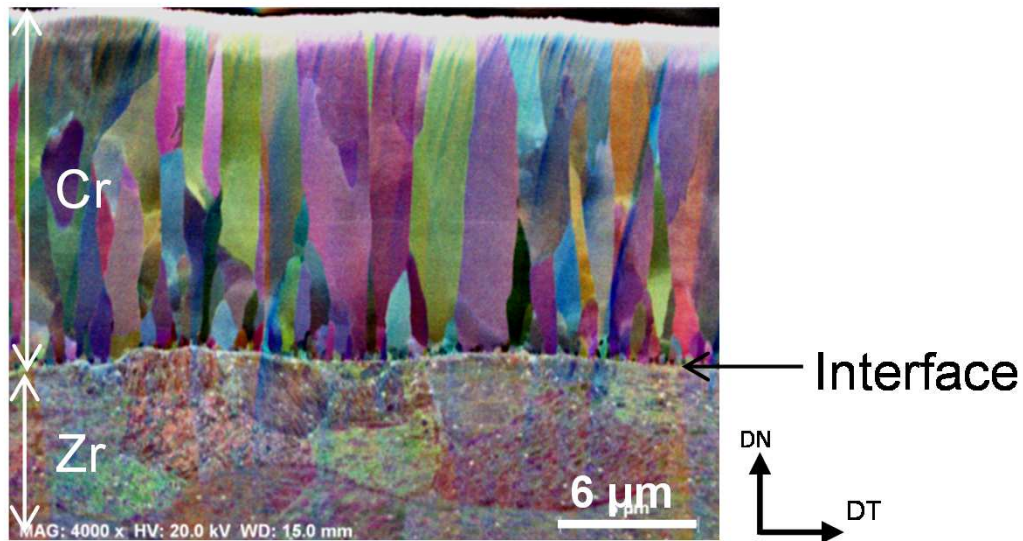
Zr/Cr irradiated interface:

- 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?

➤ Behaviour of Cr coated Zr base claddings under irradiation?



Irradiated chromium:

- Hardening / Embrittlement?

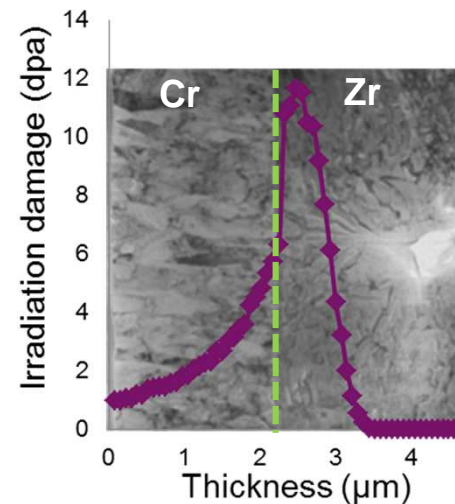
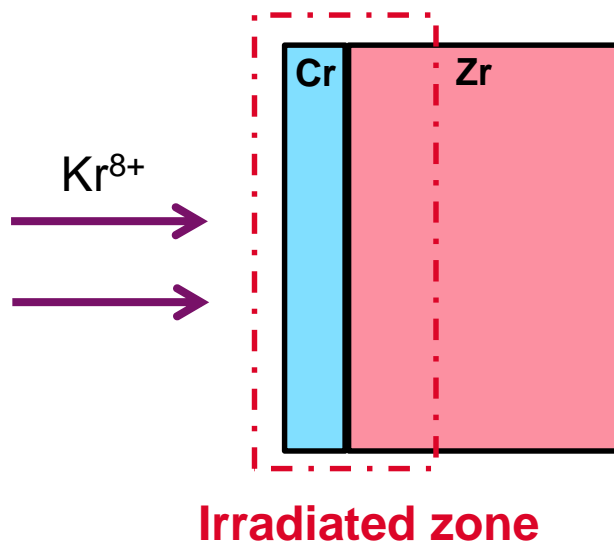
Zr/Cr irradiated interface:

- 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?

- 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 **$2,8 \cdot 10^{11} \text{ ion.cm}^{-2} \cdot \text{s}^{-1}$**
 - ~ **6 hours** irradiation
 - Dose **$5,97 \cdot 10^{15} \text{ ions.cm}^{-2}$**
 - Damage at the interface: **~10 dpa**

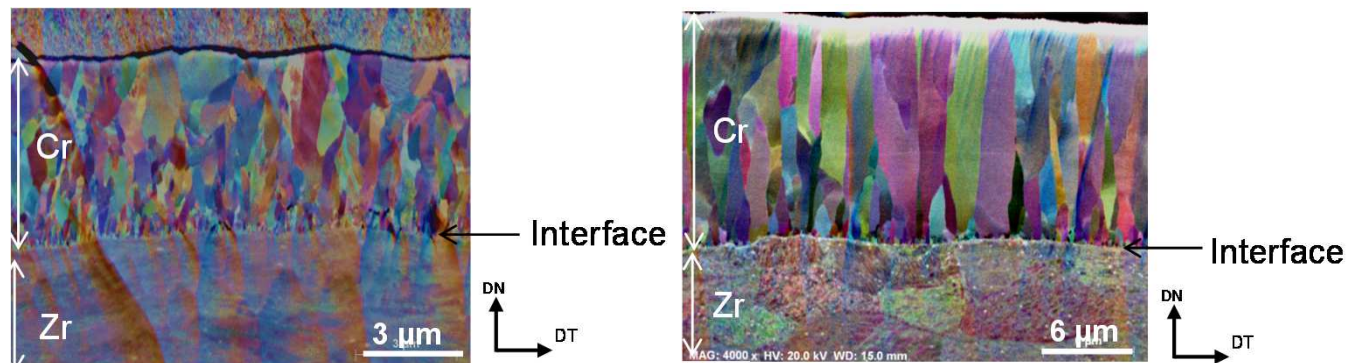


CHROMIUM COATING BEFORE IRRADIATION

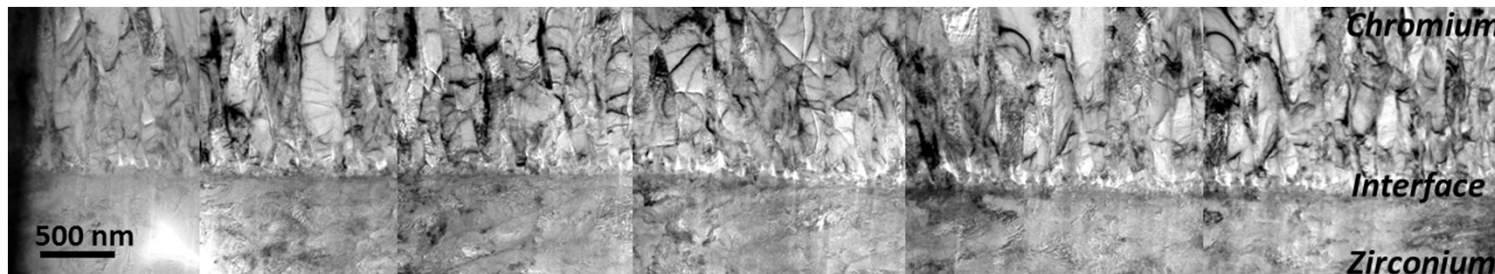
A. Wu, NuMat 2016 (7-10 November) – Montpellier

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

Typical chromium grains morphologies studied:

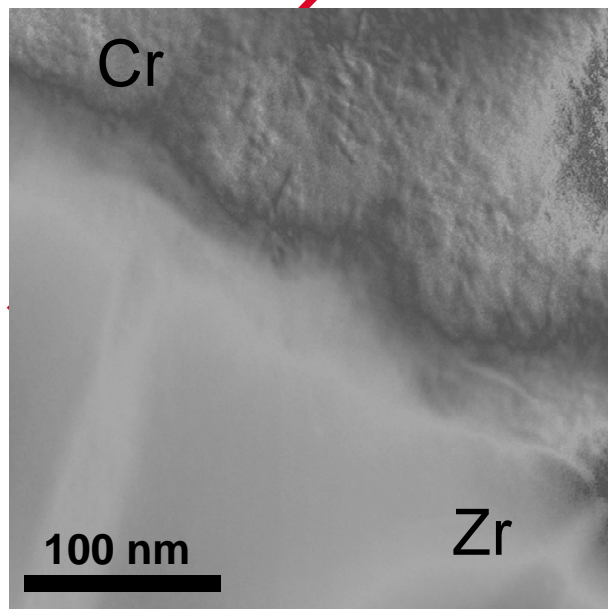
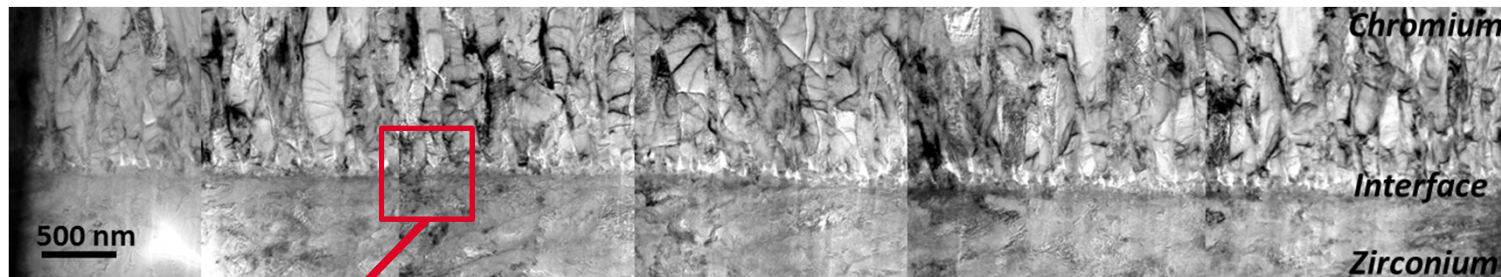


- Transmission Electron Microscopy characterisations:

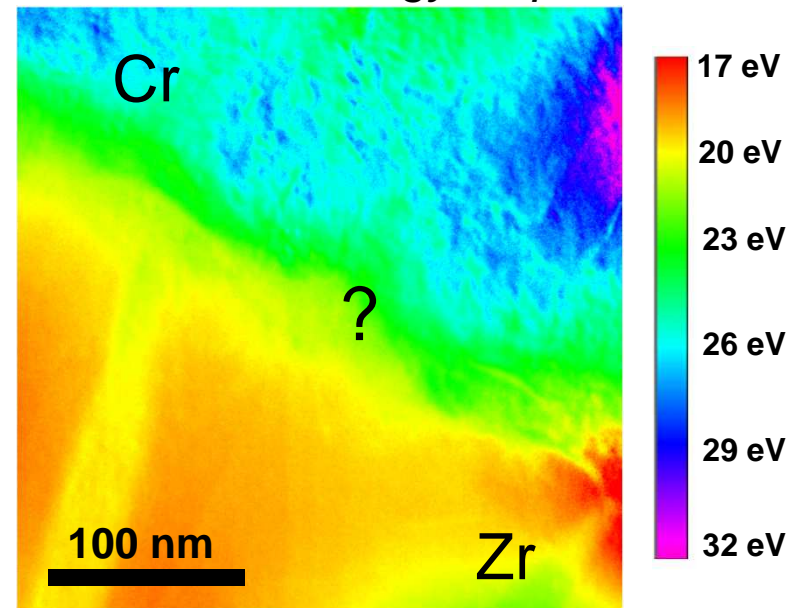


- No microcracks, no voids at the interface
- Fully dense coatings, very good chromium / zirconium bonding

- TEM observation of a FIB thin foil sample



Plasmons energy map

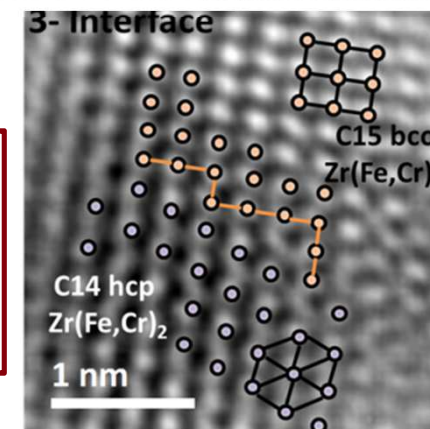
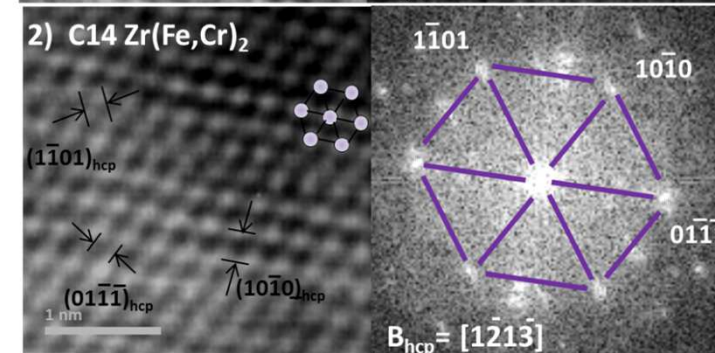
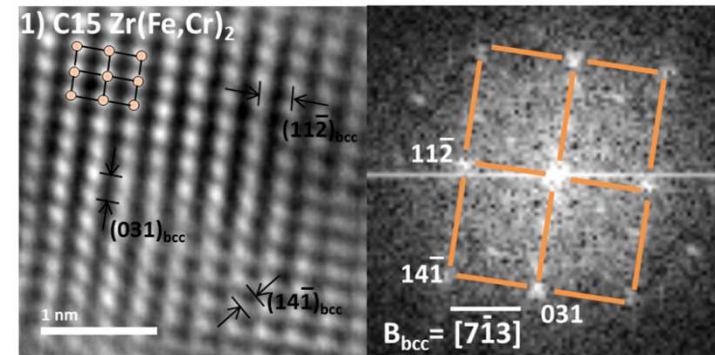
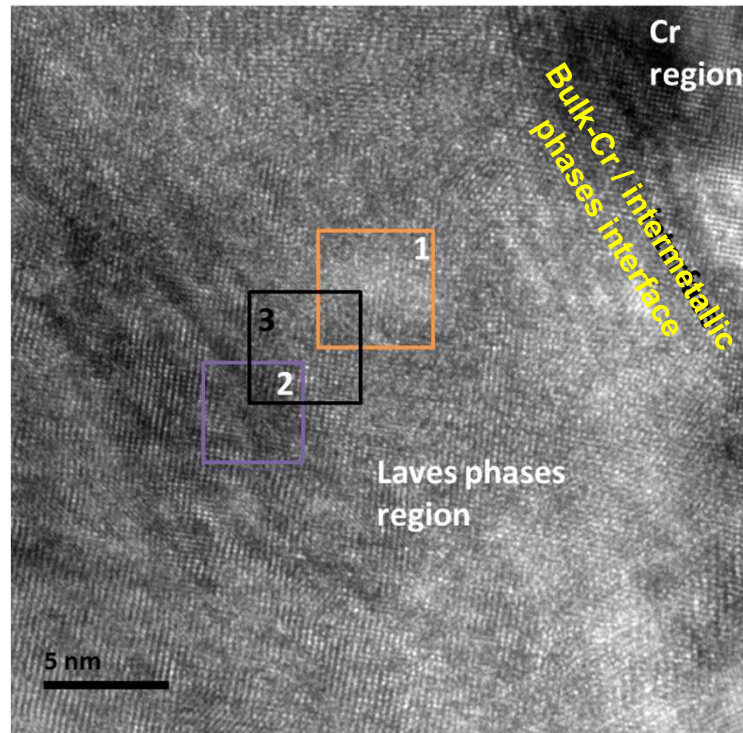


- Plasmons energy showing intermediate values at the interface?

CHROMIUM/ ZIRC-4 INTERFACE BEFORE IRRADIATION (2/4)

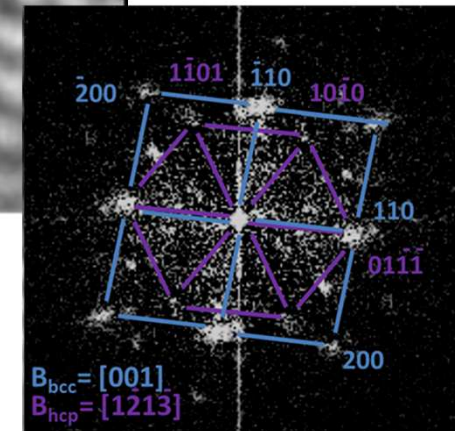
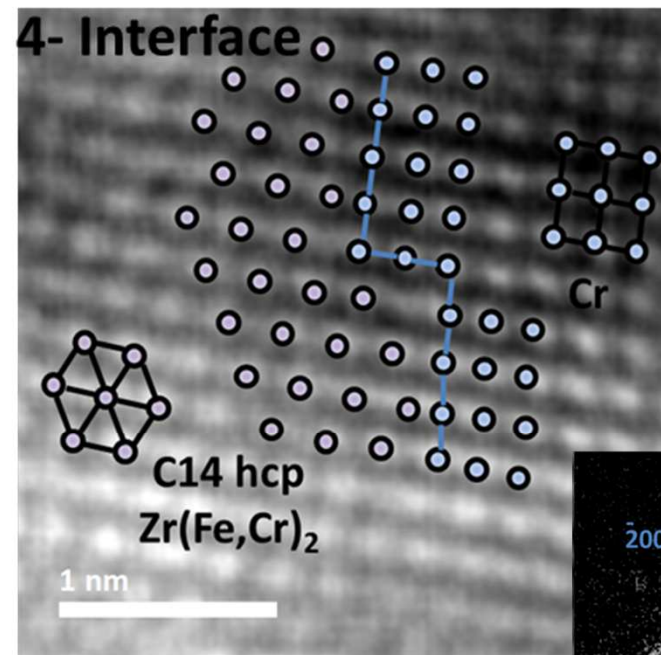
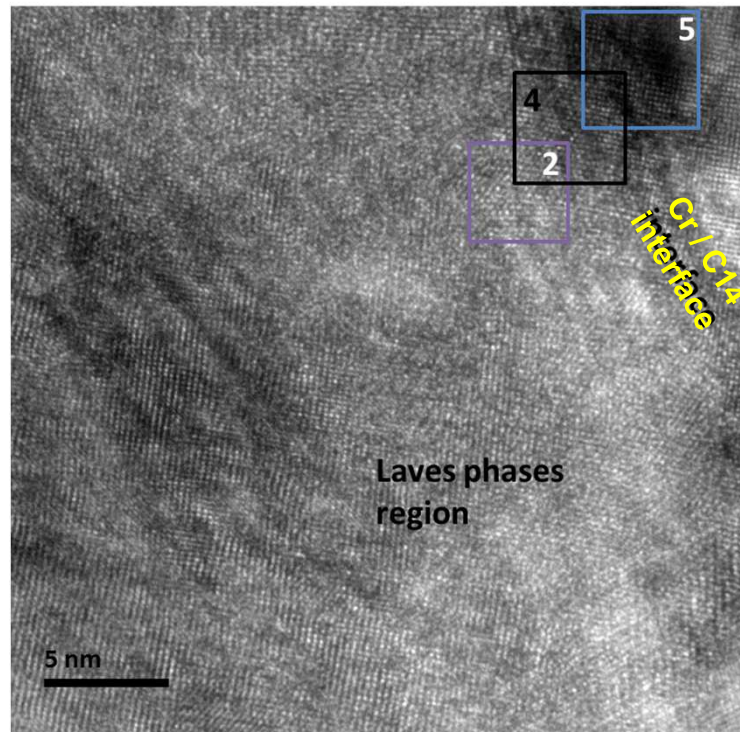
A. Wu, NuMat 2016 (7-10 November) – Montpellier

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



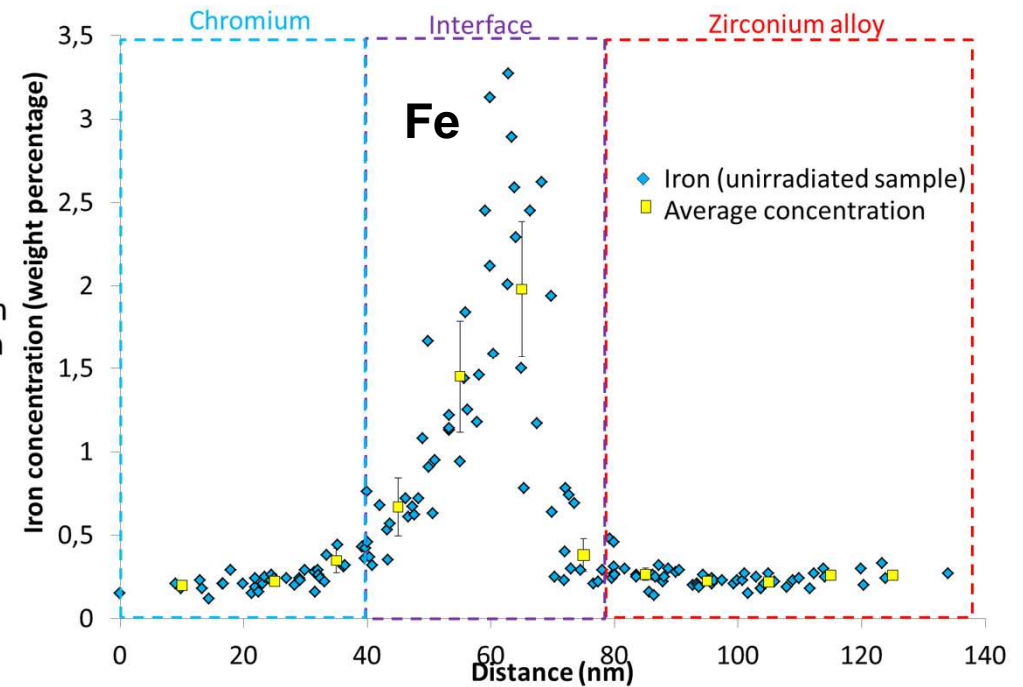
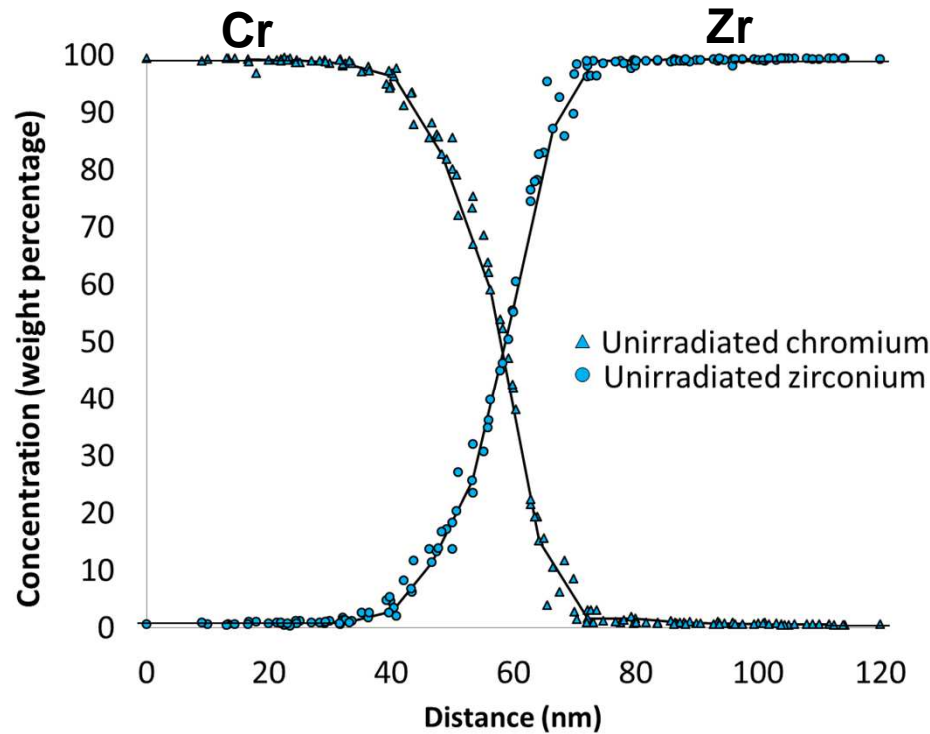
- Two intermetallic Laves phases $Zr(Cr,(Fe))_2$: C14 (hcp) & C15 (bcc) evidenced at Zr-Cr interface
=> polytype structure of the Laves phases (interface) layers

- HRTEM observation of a FIB thin foil sample



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

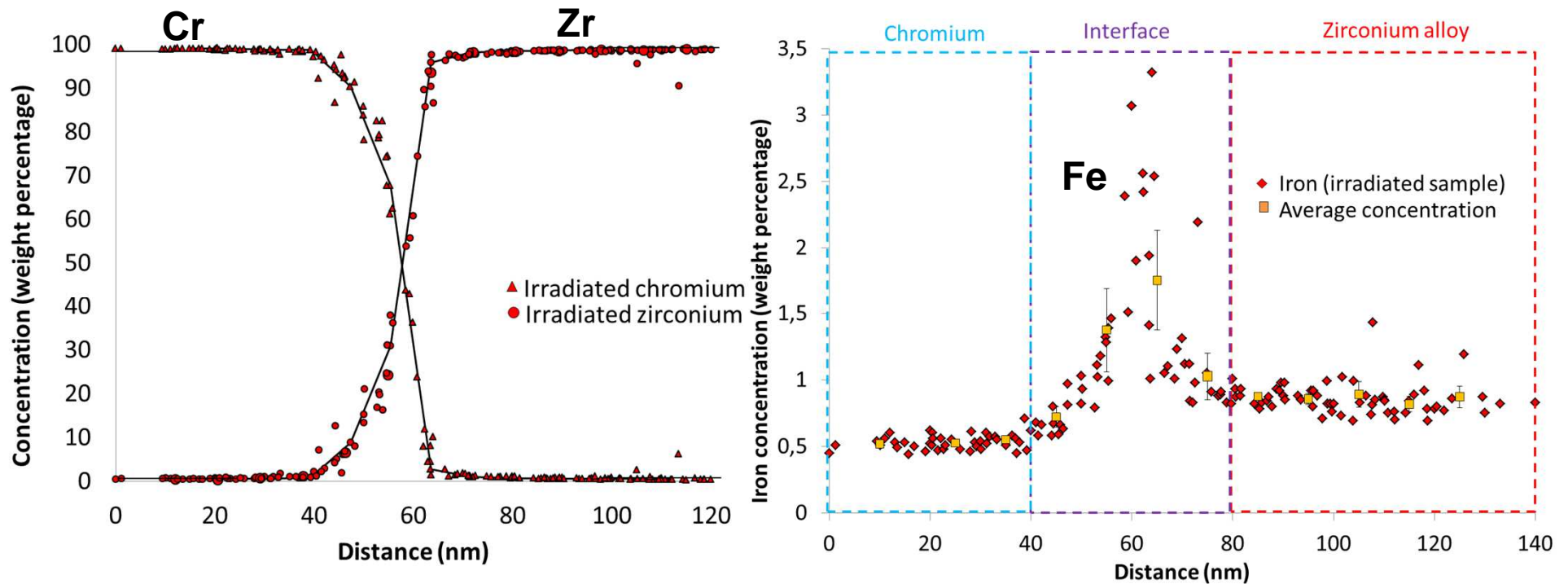
➤ Semi-quantitative chemical profiles (EDSX) at the interface



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

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

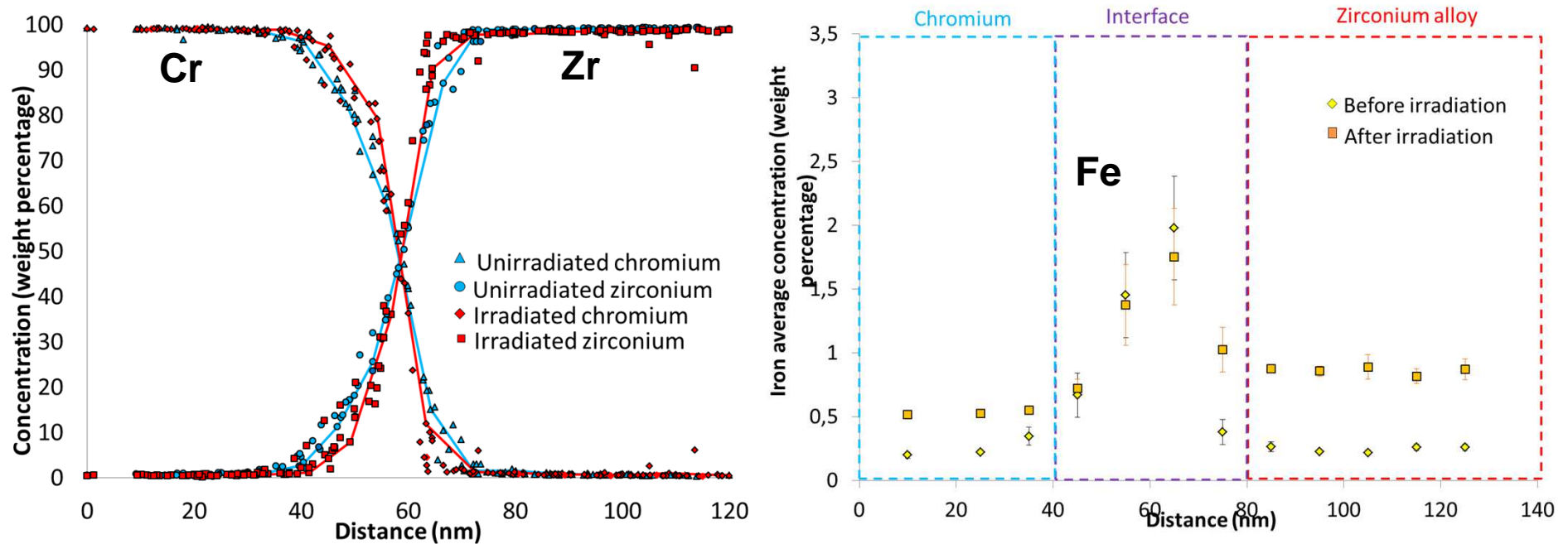
Ion irradiation up to ~10 dpa at the interface



➤ Fe enrichment still present at the interface after irradiation

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

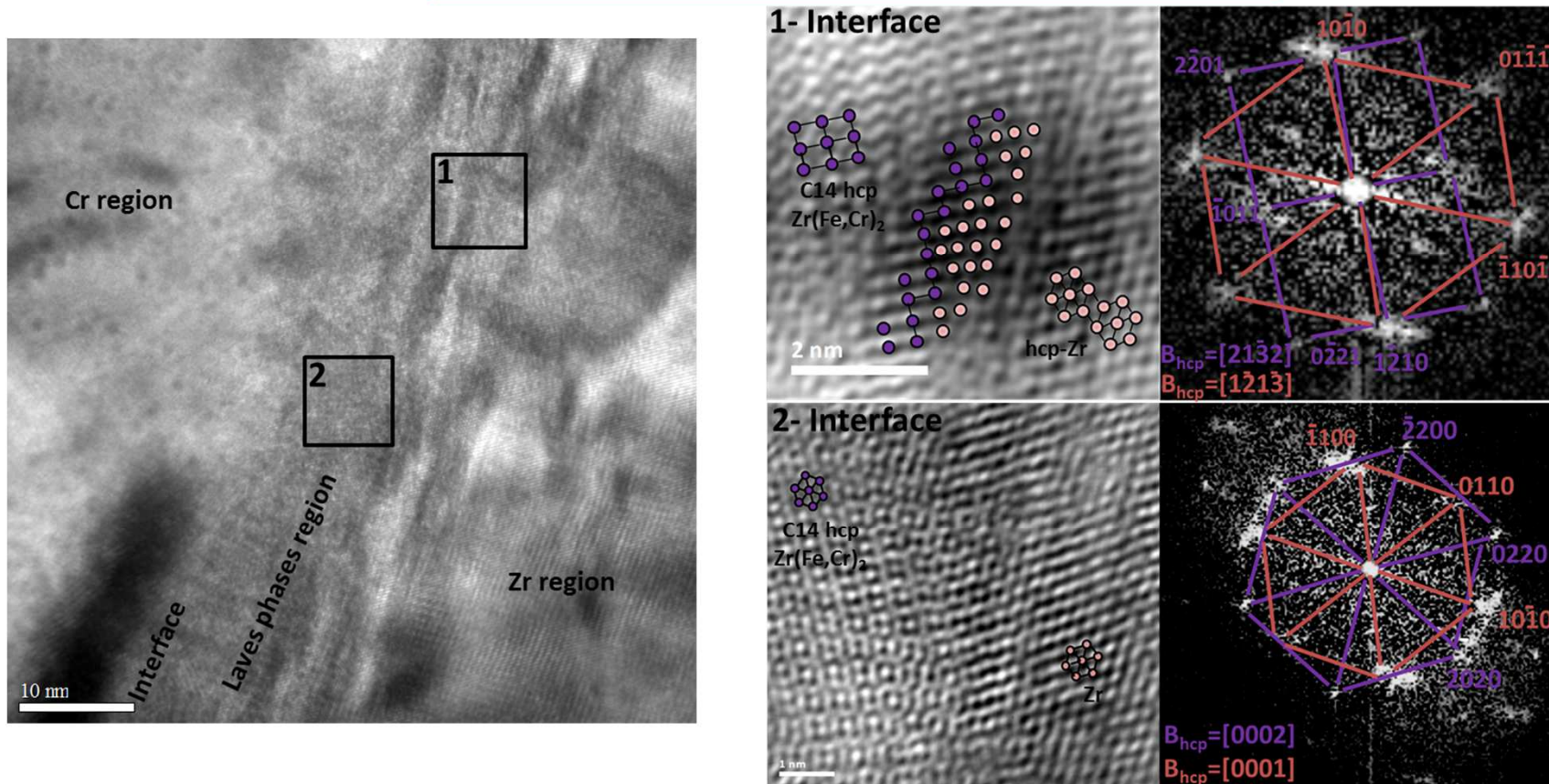
Ion irradiation up to ~10 dpa at the interface



- 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*

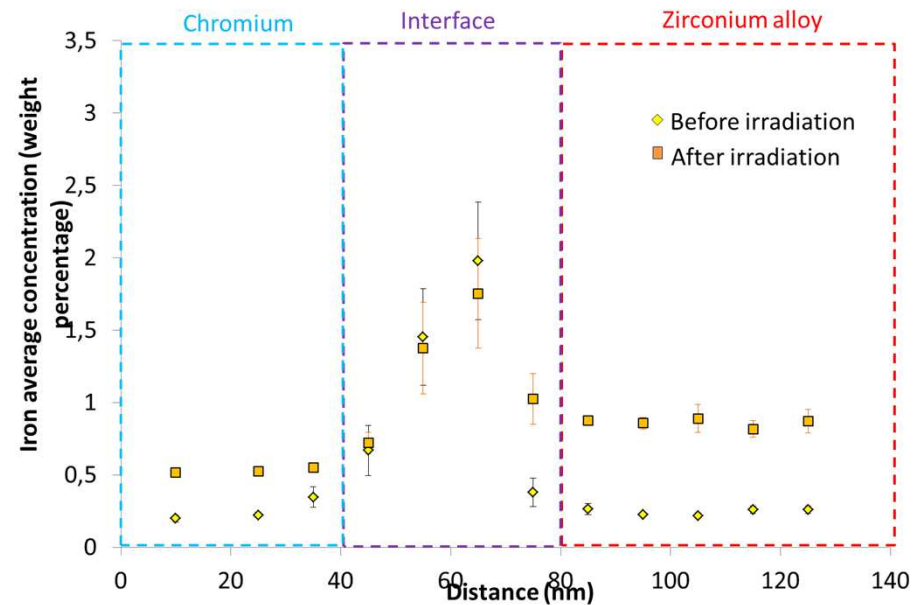
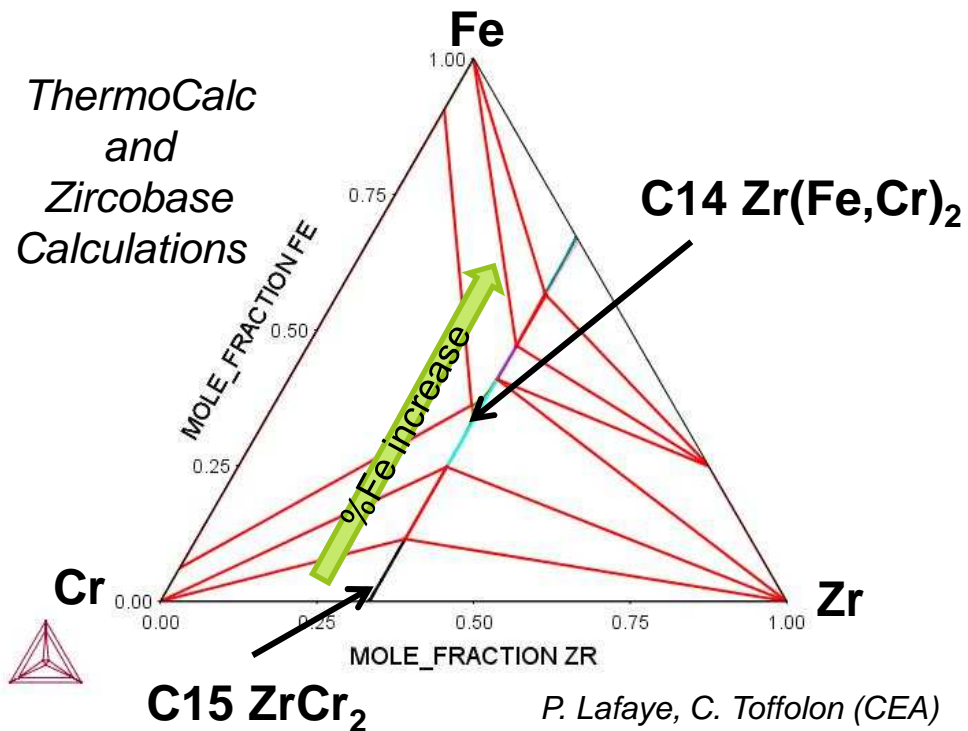
- HRTEM observation of a FIB thin foil sample **after irradiation**

Ion irradiation up to ~10 dpa at the interface



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

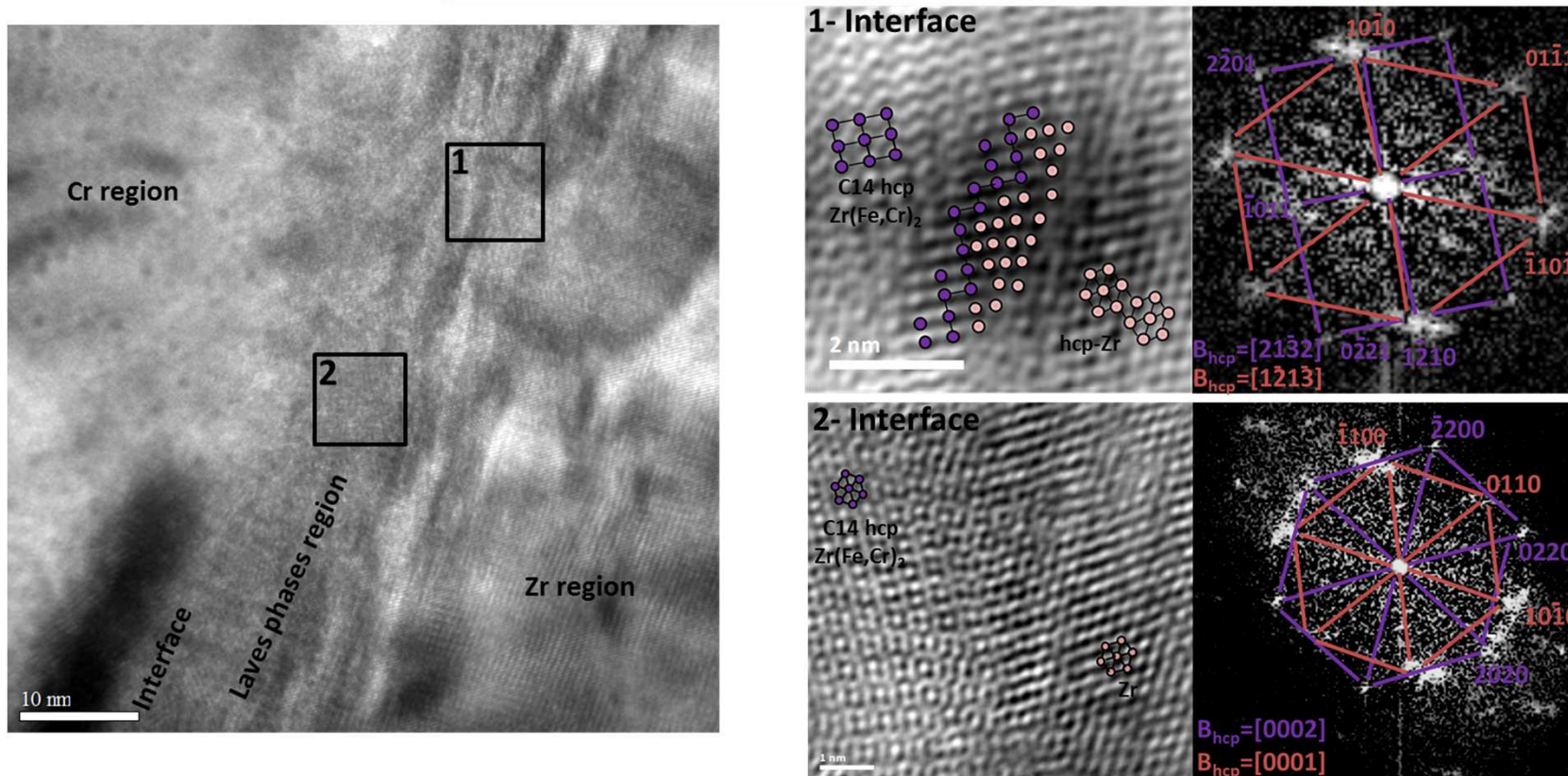
Ternary phase diagram Zr,Cr,Fe
(400°C)



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

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

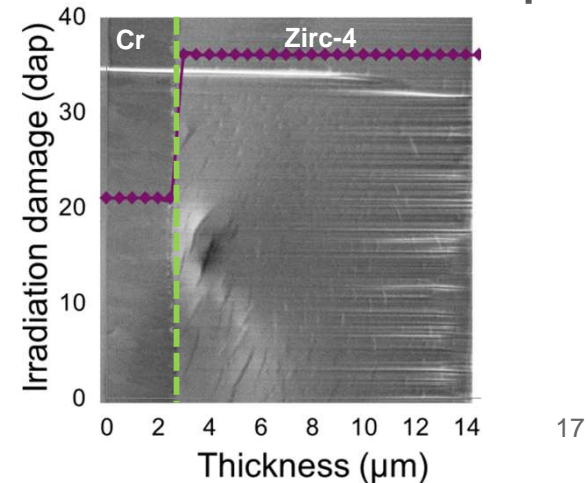
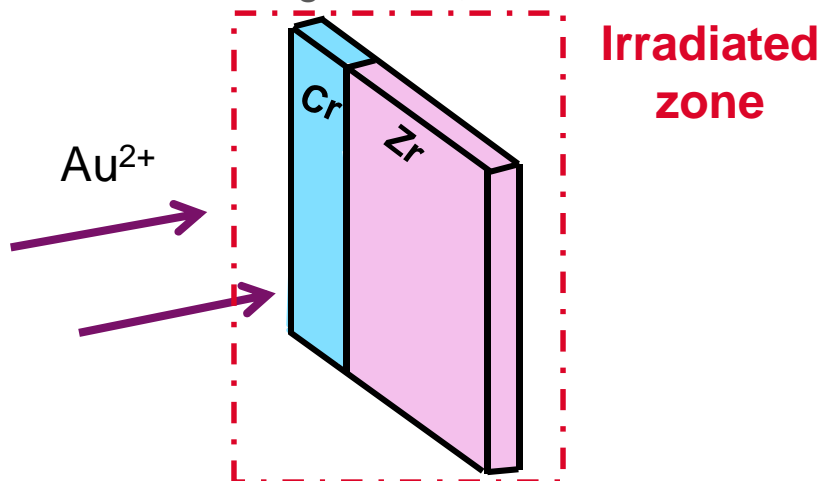
Ion irradiation up to **~10 dpa** at the interface



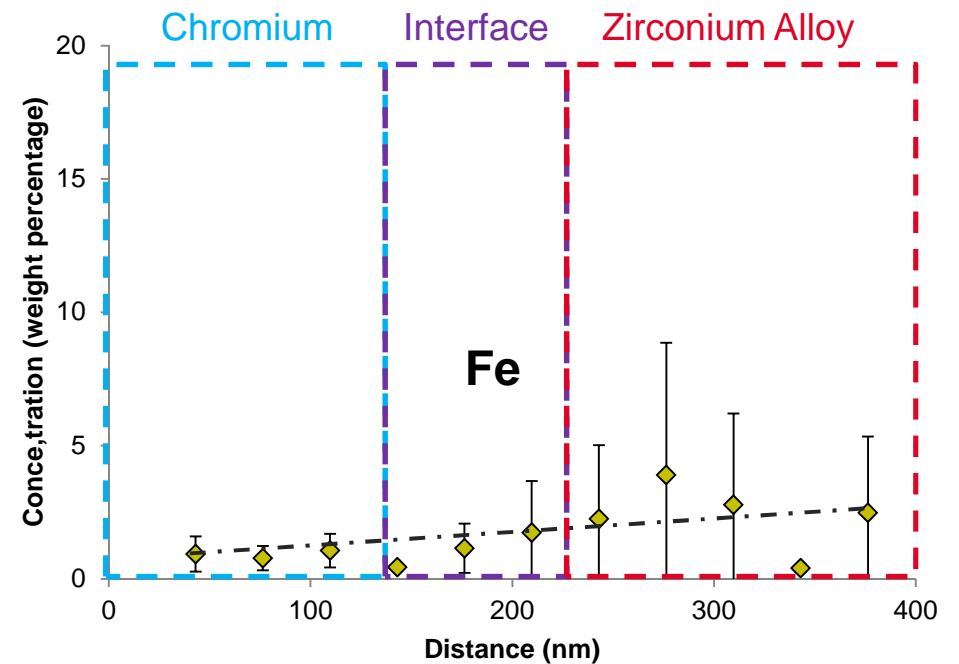
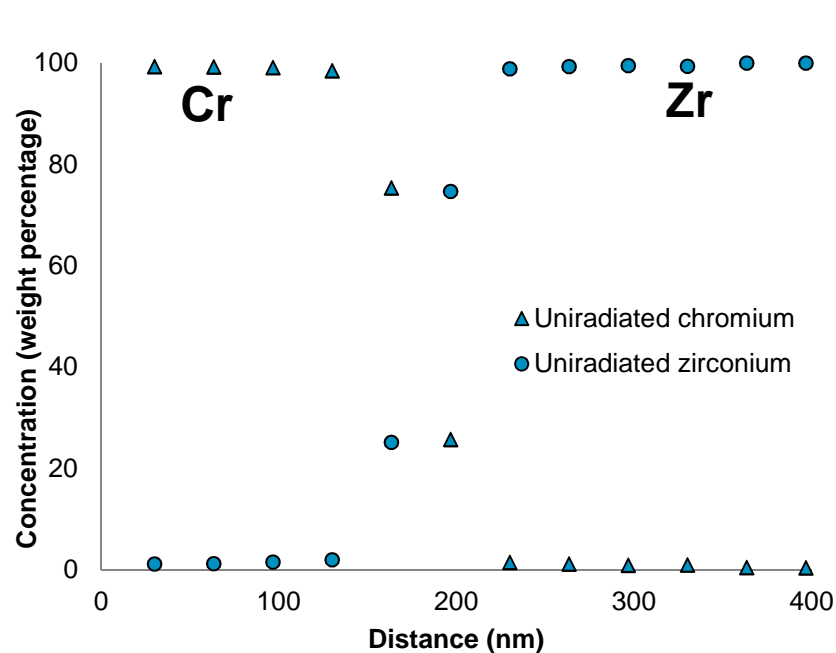
- Only C14 Laves phase observed (disappearance of the C15?)
- **Crystalline interfaces maintained after irradiation**
- Coherency along some crystallographic directions $[10\bar{1}0]_{Zr} // [1\bar{2}10]_{C14}$

- 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 Au²⁺
 - Energy 4 MeV
 - Irradiation temperature 400°C
 - Average flux $2,8 \cdot 10^{11}$ ion.cm⁻².s⁻¹
 - Total dose $6 \times 8 \cdot 10^{14}$ ion.cm⁻²
 - Dose totale
 - In Cr: ~ 21 dpa
 - In Zr: ~ 36 dpa
 - At the interface: ~ 30 dpa



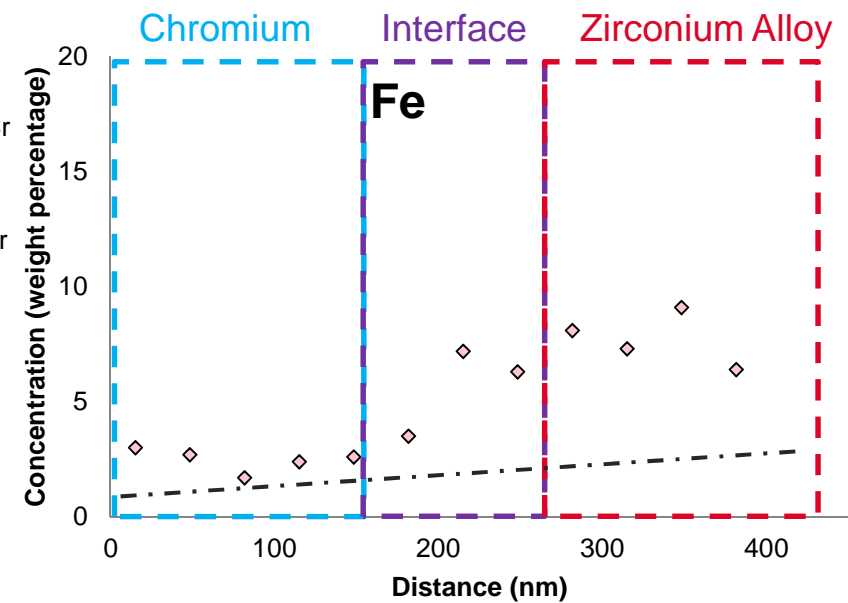
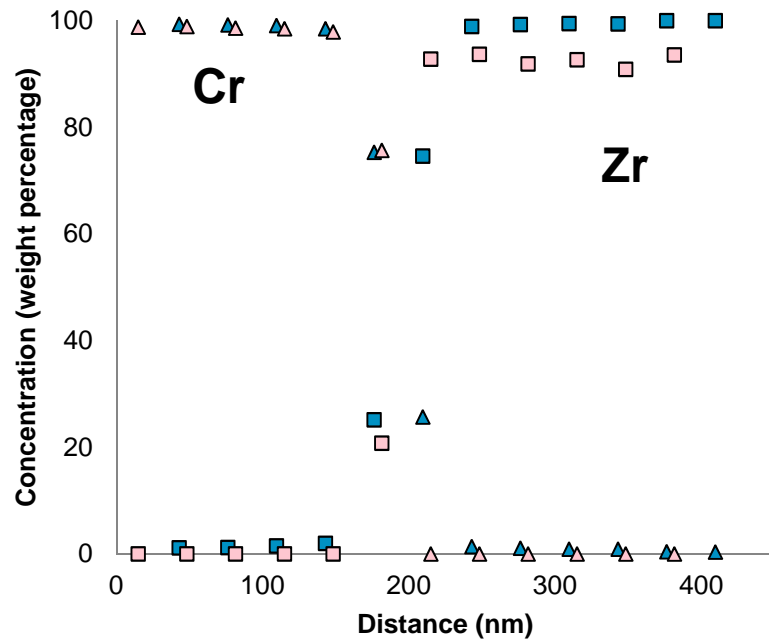
➤ In-situ characterisations: EDS before irradiation



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

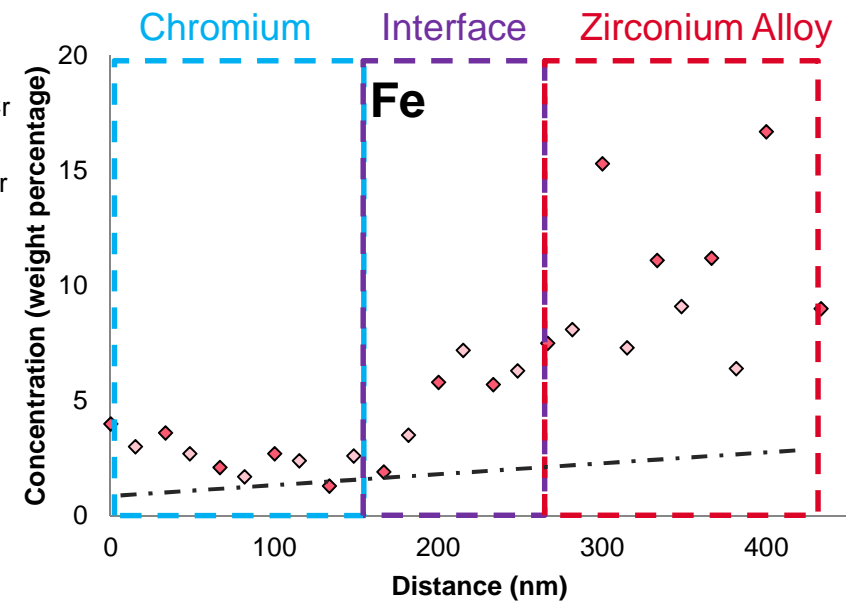
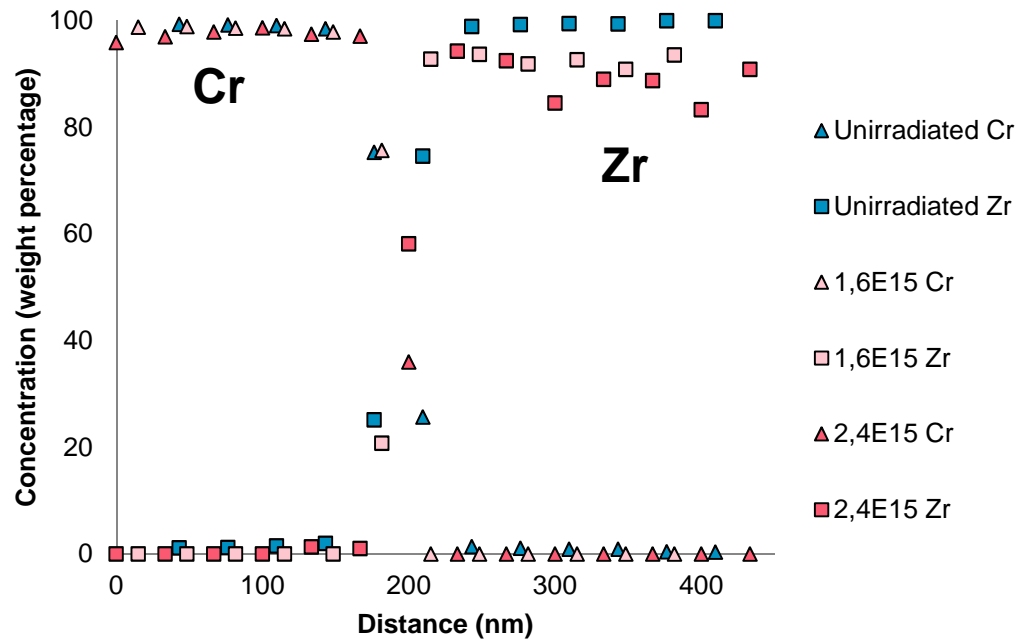
➤ In-situ characterisations: EDS during ion irradiation

Ion irradiation up to ~10 dpa at the interface



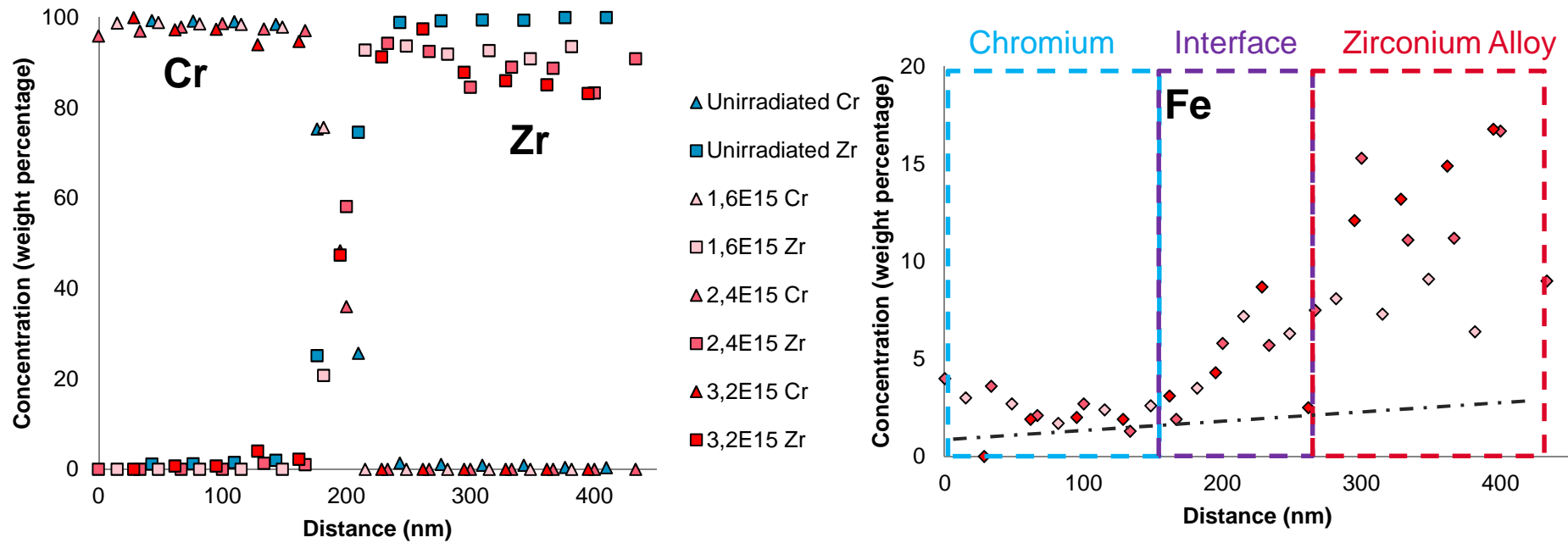
➤ In-situ characterisations: EDS during ion irradiation

Ion irradiation up to ~15 dpa at the interface



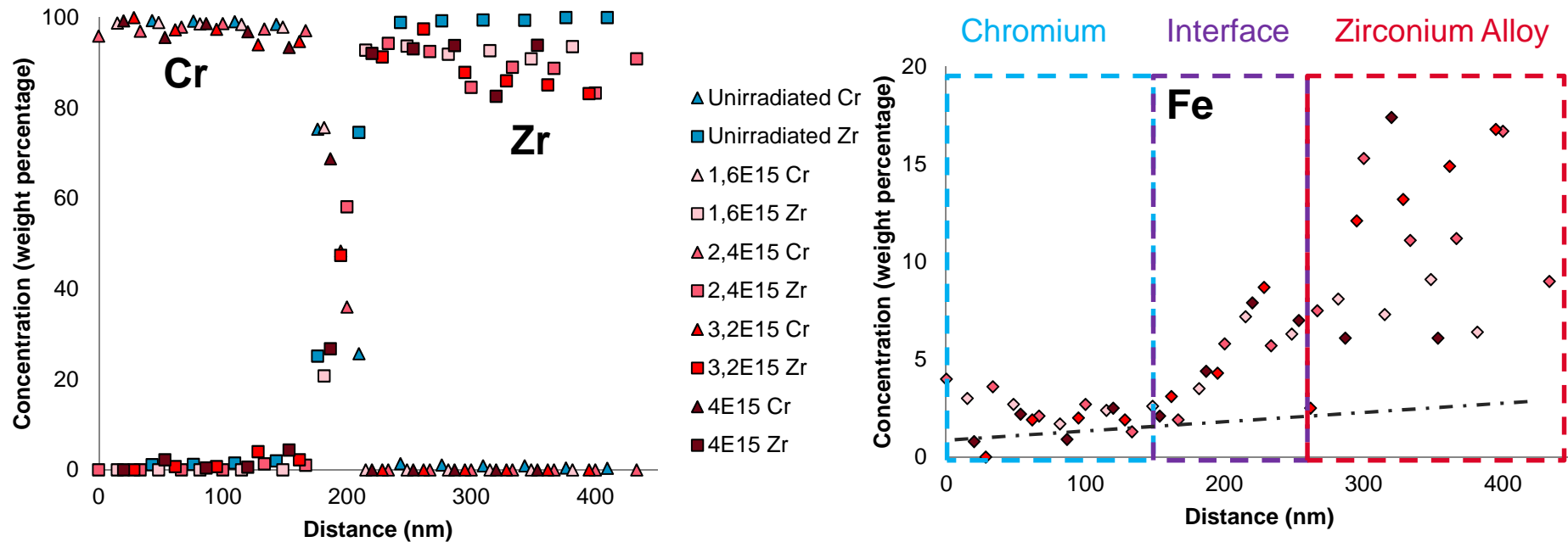
➤ In-situ characterisations: EDS during ion irradiation

Ion irradiation up to ~20 dpa at the interface



➤ 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)*

- 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?*

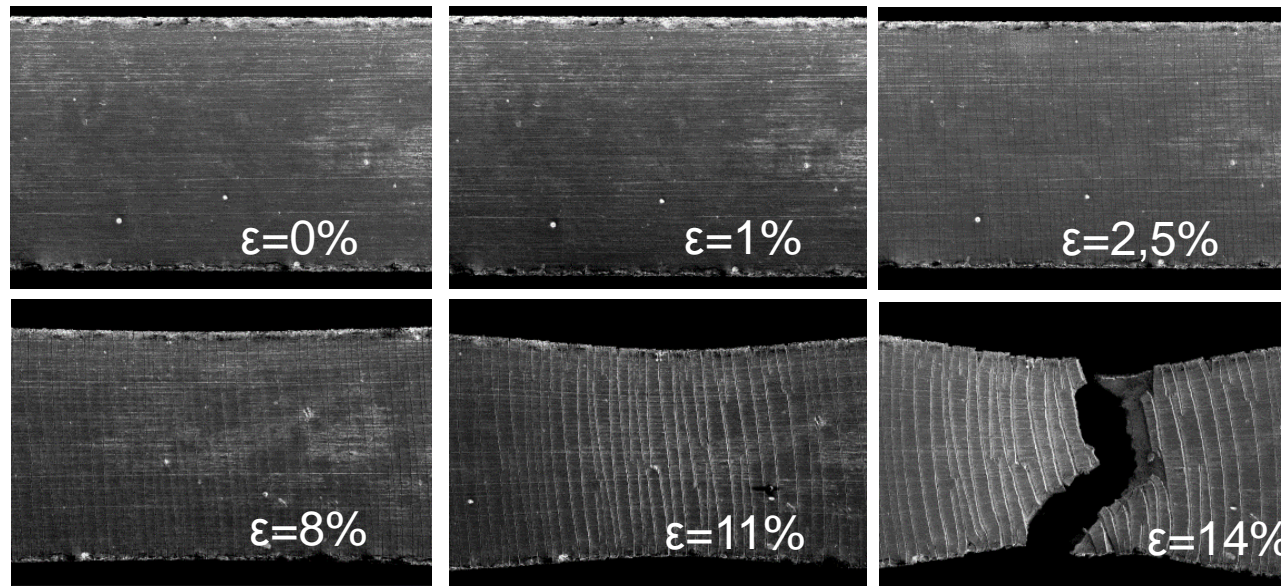
Irradiated zirconium substrate:

- *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**

➤ **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...*)

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

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

THANK YOU FOR YOUR ATTENTION

ACKNOWLEDGEMENTS:

B. Arnal, S. Urvoy, E. Rouesne, J. Roubaud, D. Hamon,
F. Barcelo, T. Guilbert, C. Toffolon, P. Lafaye T. Vandenberghe,
M. Le Saux, C. Cobac, J. Rousselot, C. Cabet, Y. Serruys,
F. Leprêtre, E. Bordas, S. Pellegrino, H. Martin, P. Trocellier,
A. Gentils, C. Baumier, S. Picard, C. Bachelet, A. Billard,
E. Monsifrot, F. Schuster, F. Lomello, I. Idarraga, M. Le Flem...

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

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

⇒ Potential physical mechanisms:

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



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



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

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 and 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...

