

# **TEM *in situ* et applications**

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# Objectifs du cours et des TP

- ✓ Comprendre le fonctionnement d'un SEM
- ✓ Comprendre le fonctionnement d'un TEM
- ✓ Comprendre la formation du contraste d'une image
- ✓ Savoir extraire l'information d'une image
- ✓ Savoir choisir la bonne technique pour l'information souhaitée

Autres??

# Contenu

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- Pourquoi *in situ*?
- Traction en SEM
- TEM environnemental
- Effet de  $T$  et du faisceau
- Effet du courant sur une cellule solaire
- Tomographie par rayons X résolue en temps

# Pourquoi *in situ*?

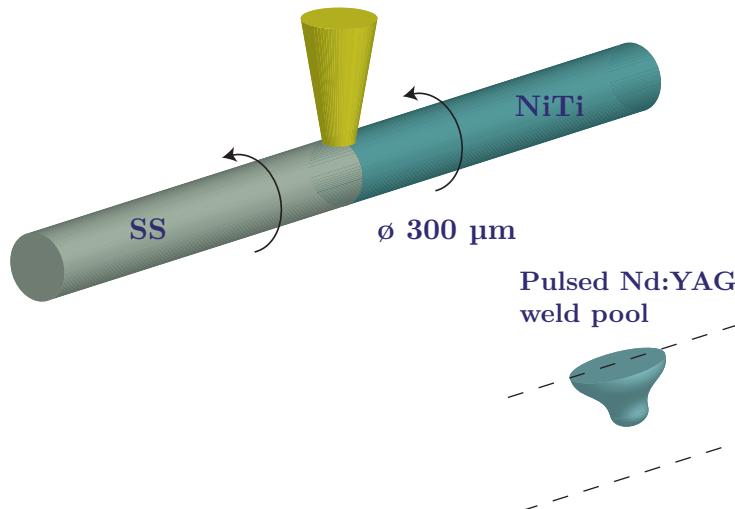
- Observations microscopie: *post mortem*
- L'échantillon est **arrêté dans son évolution temporelle**, préparé et observé
- Pour observer un échantillon en fonction d'un paramètre, il faut réaliser un échantillon par valeur du paramètre (traction, T, atmosphère, irradiation, etc.)
- En microscopie *in situ*, on essaye de suivre l'évolution d'un échantillon pour un ou plusieurs paramètres.

# Traction *in situ* en SEM

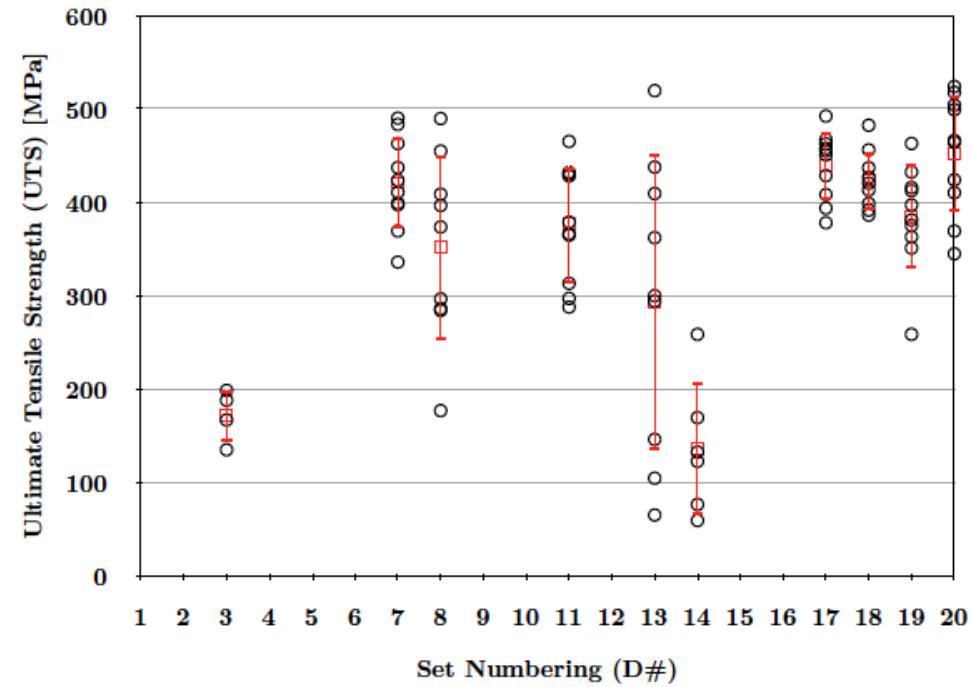
Soudures de fils NiTi avec des fils en acier inox

Observation des soudures avant et après tests de traction

Comment faire pour "voir" l'état de la soudure pendant la traction?

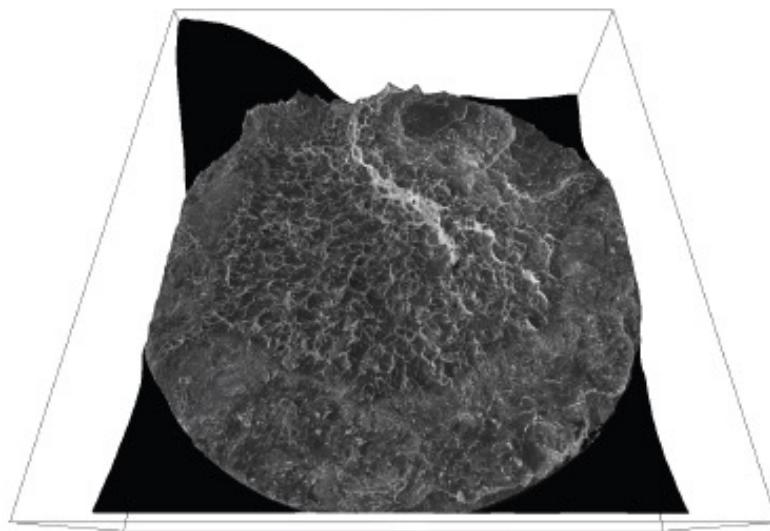


Résultats de tension de fracture pour 20 soudures, plusieurs échantillons répétés

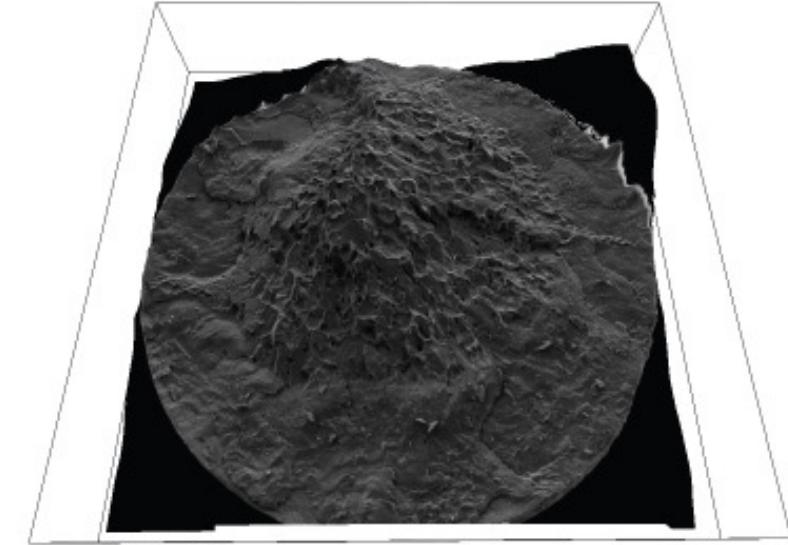


# Traction *in situ* en SEM

## Observations post mortem



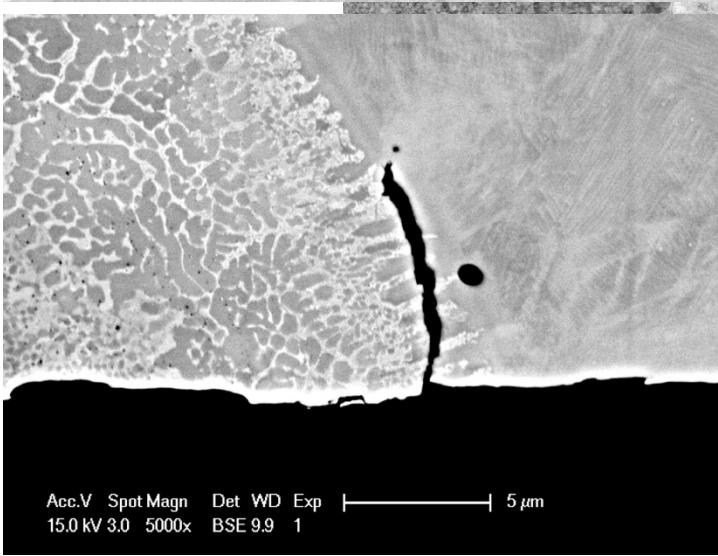
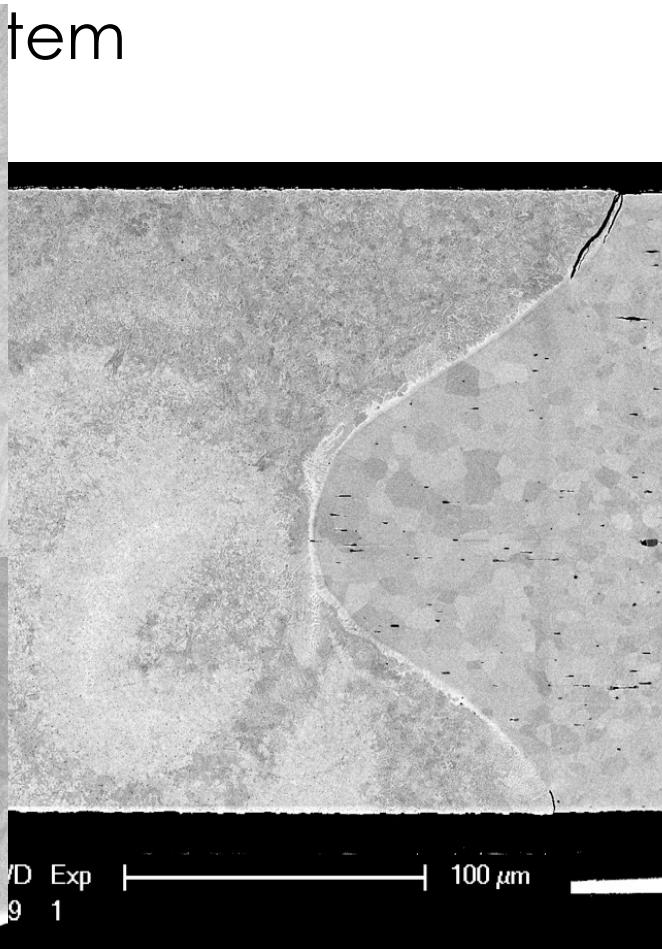
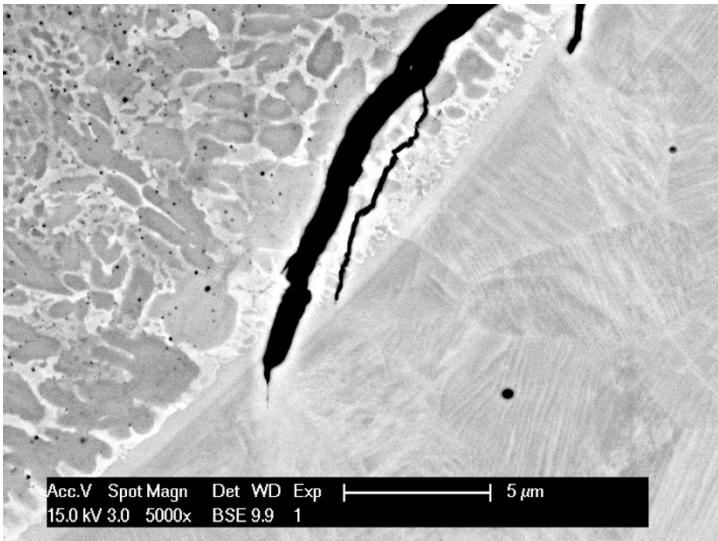
(a) Fracture surface viewed from the NiTi side  
(300 µm diameter wire).



(b) Fracture surface viewed from the SS side  
(300 µm diameter wire).

**Figure 6.2:** 3D reconstruction of both fracture surfaces showed a brittle rupture domain surrounding a ductile structure with characteristic microvoids in the center. The size of the box is 300 µm in the basic direction and around 60 µm in height.

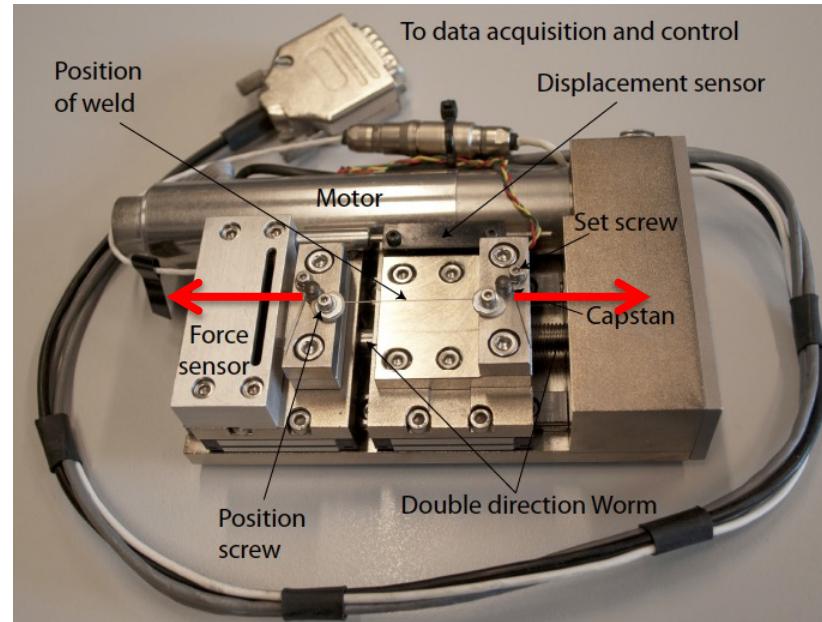
# Traction *in situ* en SEM



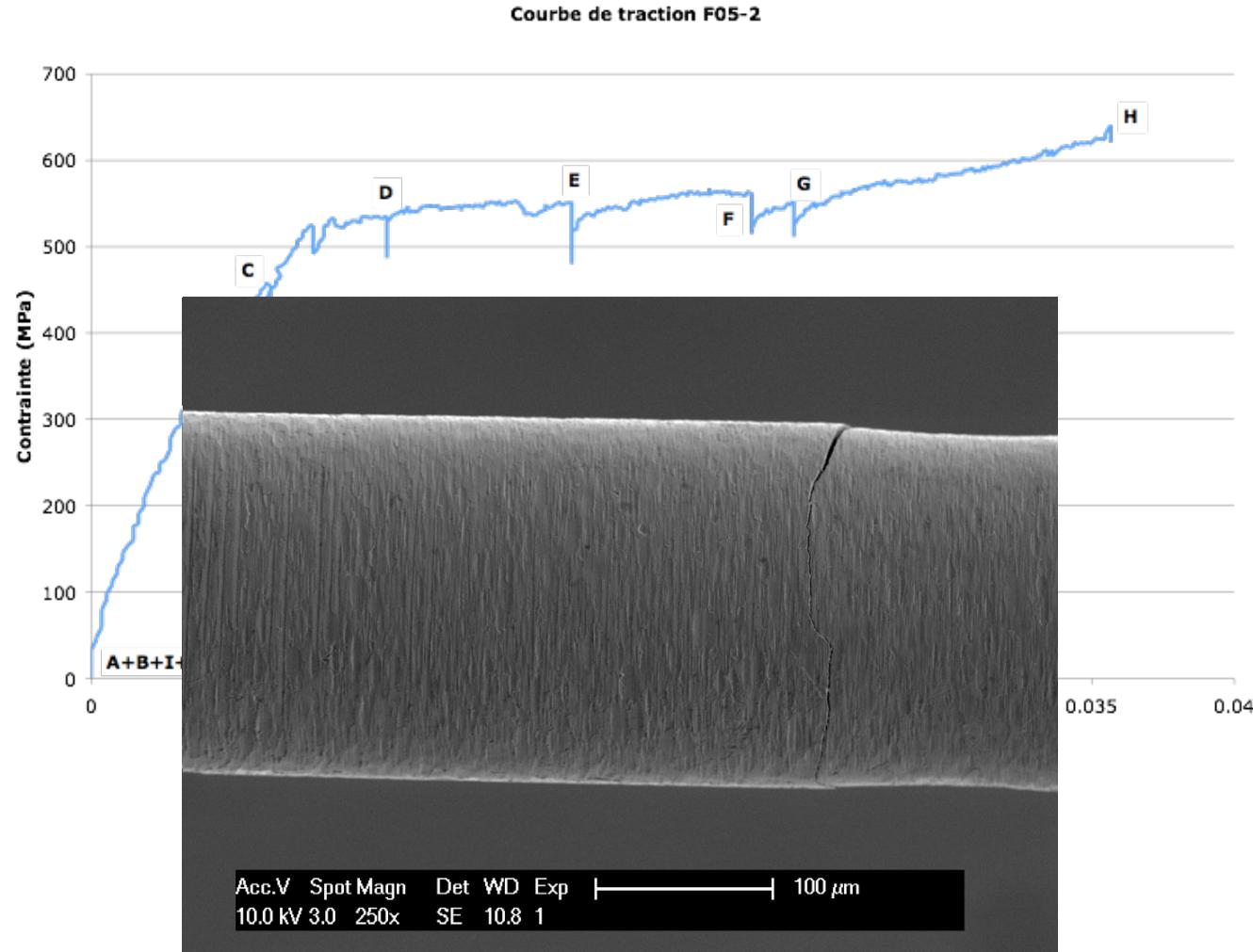
# Traction *in situ* en SEM

Platine de traction: mesure de la contrainte  
en fonction de la déformation

Observation simultanée de l'échantillon

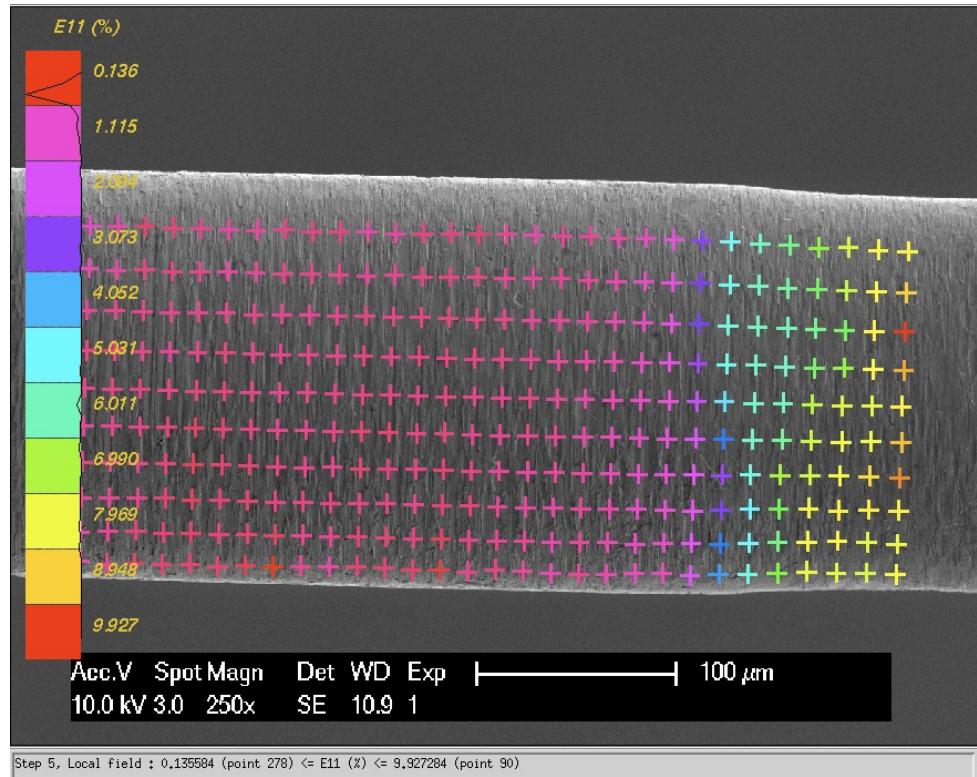


# Traction *in situ* en SEM



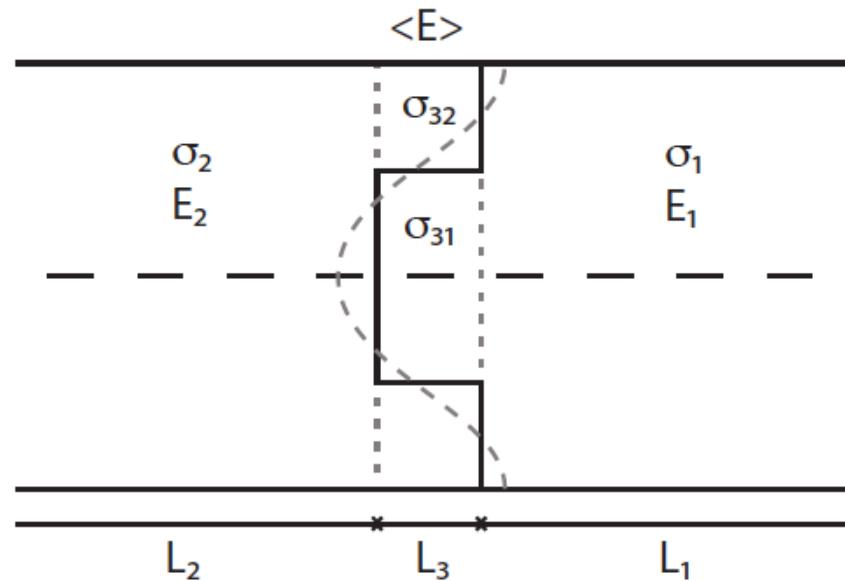
# Traction *in situ* en SEM

- Maillage de déplacements
- Calcul des déformations



# Traction *in situ* en SEM

## Modèle de déformation



**Figure 6.13:** Composite model used for a simple stress distribution analysis between NiTi (domain 1) and (SS + weld) (domain 2).

# TEM environnemental: SOFC

- Réaction électrochimique d'un fuel avec un gaz oxydant
- Une pile est la répétition d'éléments unitaires
- Une cellule + interconnection = un **repeat element**:
  - Cellules à support anode

- NiO-YSZ
- Ni-YSZ pendant l'opération

**Electrolyte fin YSZ**

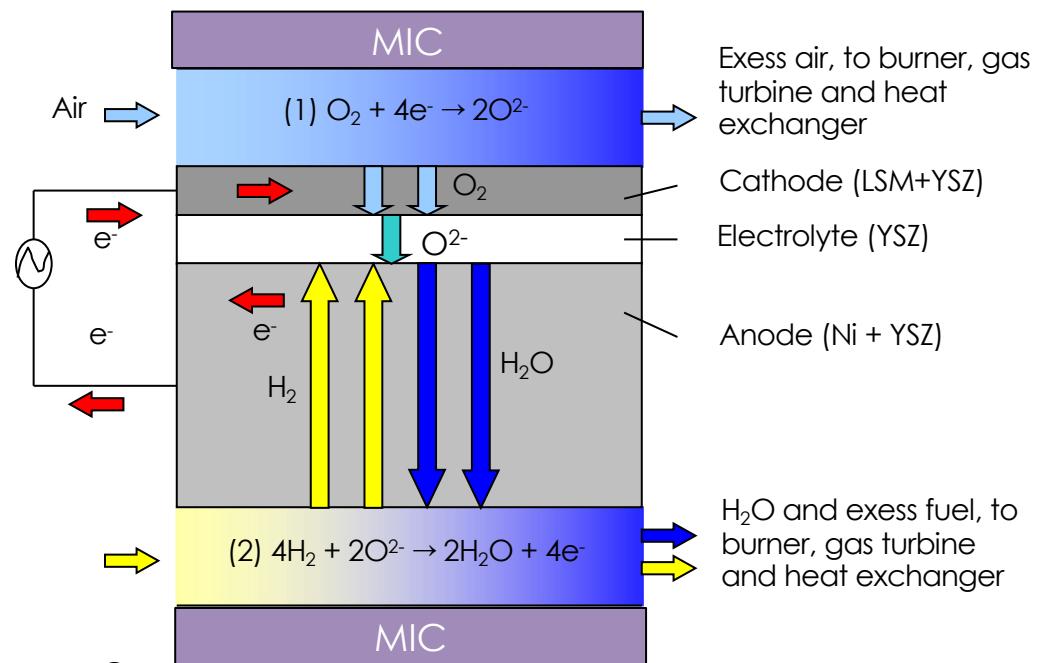
**Cathode** YSZ + LSM

– Couche de collection de courant  
LSM ou LSC

– Couche de **diffusion** de gaz (GDL)

– Interconnection métallique (MIC)

Fuel  
Air  
Excess air, to burner, gas turbine and heat exchanger



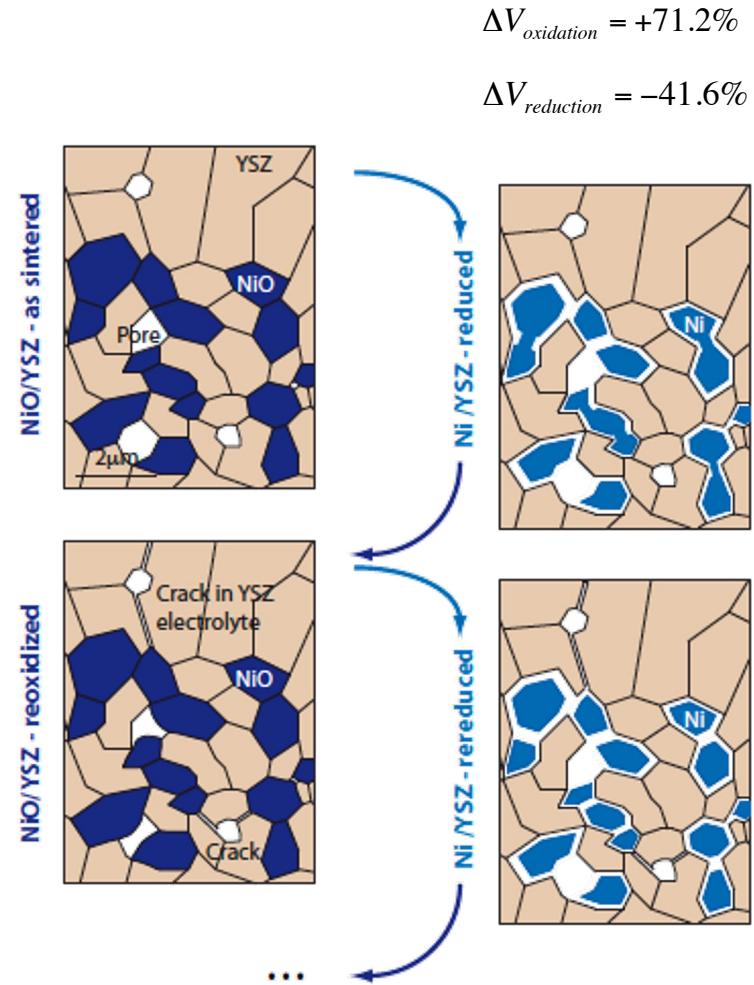
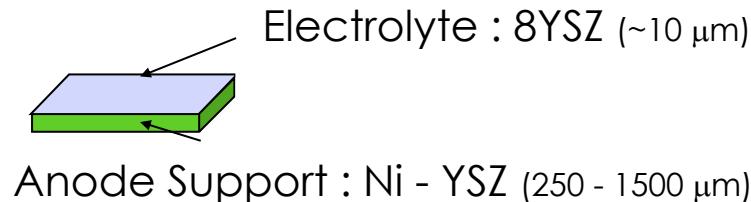
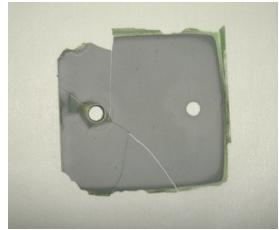
**Mécanismes derrière les dégradation de performance?**



# TEM environnemental: SOFC

Les anodes NiO-YSZ sont instables lors d'un cycle réduction-réoxydation

- Fissures dans l'électrolyte
- Perte de performance
- Porosité lors de la réoxydation
- Frittage et coalescence du Ni pendant la réduction



# TEM environnemental: SOFC

FEI TITAN E-CELL™ au Center for Electron Nanoscopy, DTU

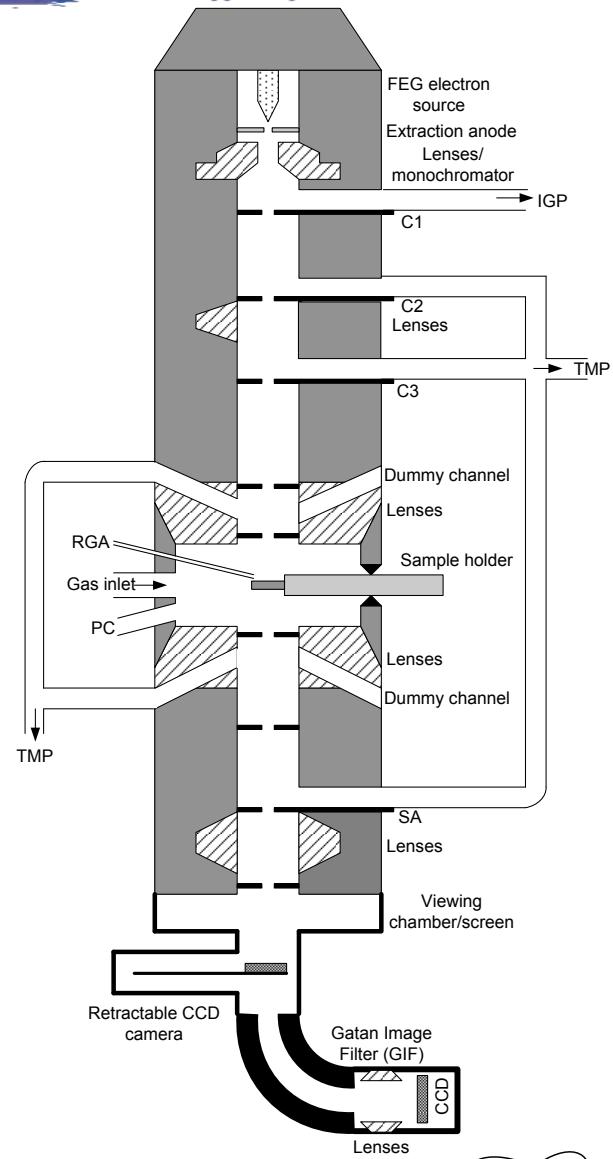
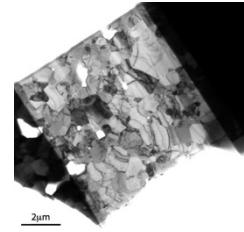
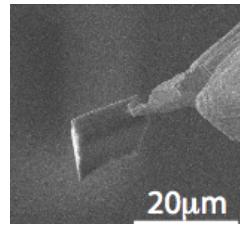
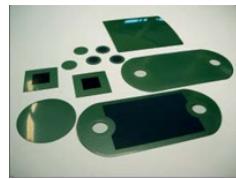
- Differential pumping apertures allow S/TEM gas experiments

- *In situ* reduction
- *In situ* reoxidation

- Tantalum sample holder (reduction only)

- Inconel sample holder (reduction and oxidation)

Apertures, turbomolecular pumps (TMPs) and ion getter pump (IGP) allow a gas pressure of up to ~ 15 mbar to be achieved at the position of the sample, while retaining an ultra-high vacuum ( $<10^{-10}$  mbar) at the field emission gun (FEG) electron source. Other additional components of the ETEM include a plasma cleaner (PC) and a residual gas analyzer (RGA).



# TEM environnemental: SOFC

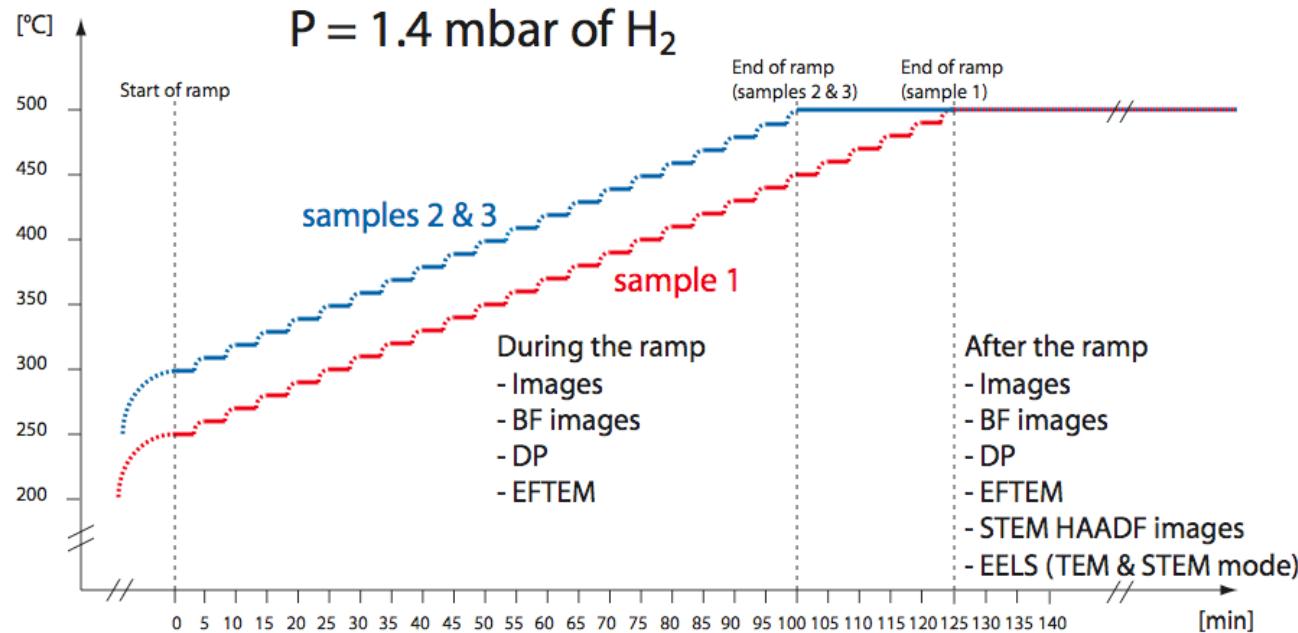
3 expériences sous 1.4 mbar d'H<sub>2</sub>

–Rampe de température

- La température augmente de 10° C par 5 minutes
- De 250° /300° C à 500° C

–Images bright field, clichés de diffraction, EFTEM, STEM HAADF, EELS

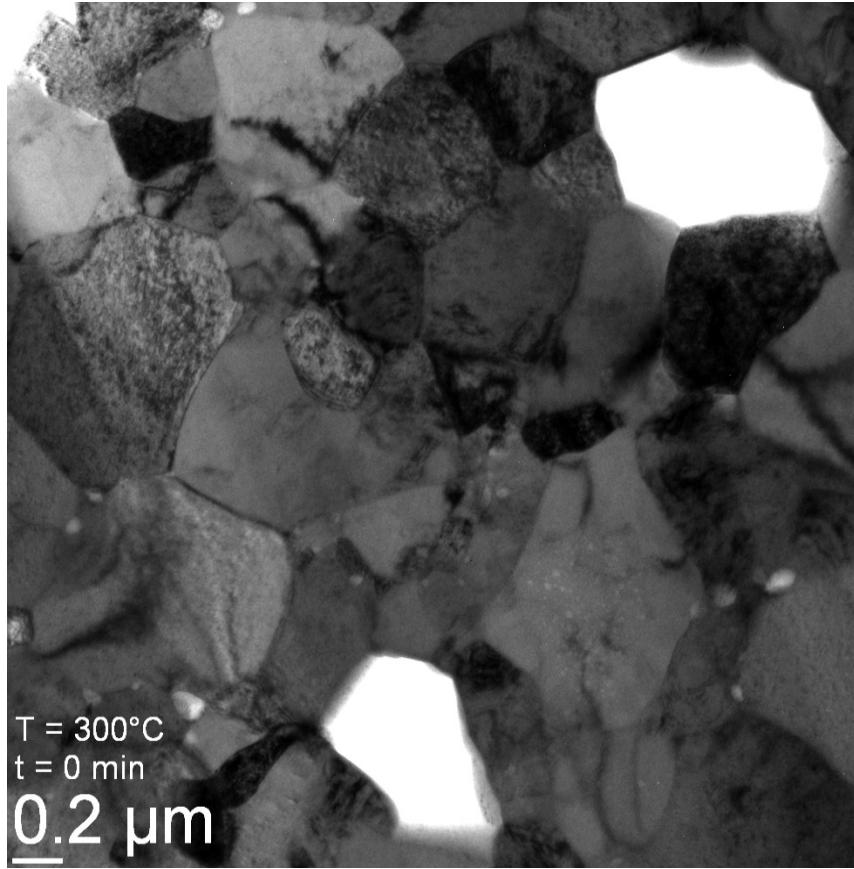
In situ reduction



# TEM environnemental: SOFC

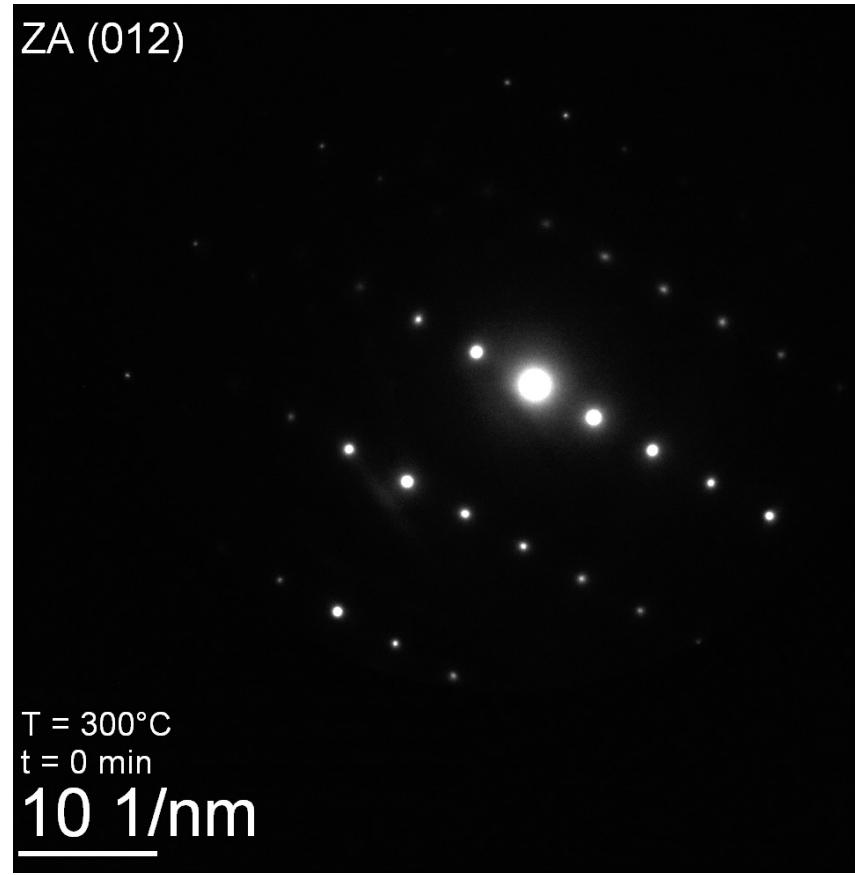
Images BF à 6300x

-Cartographie nickel EFTEM



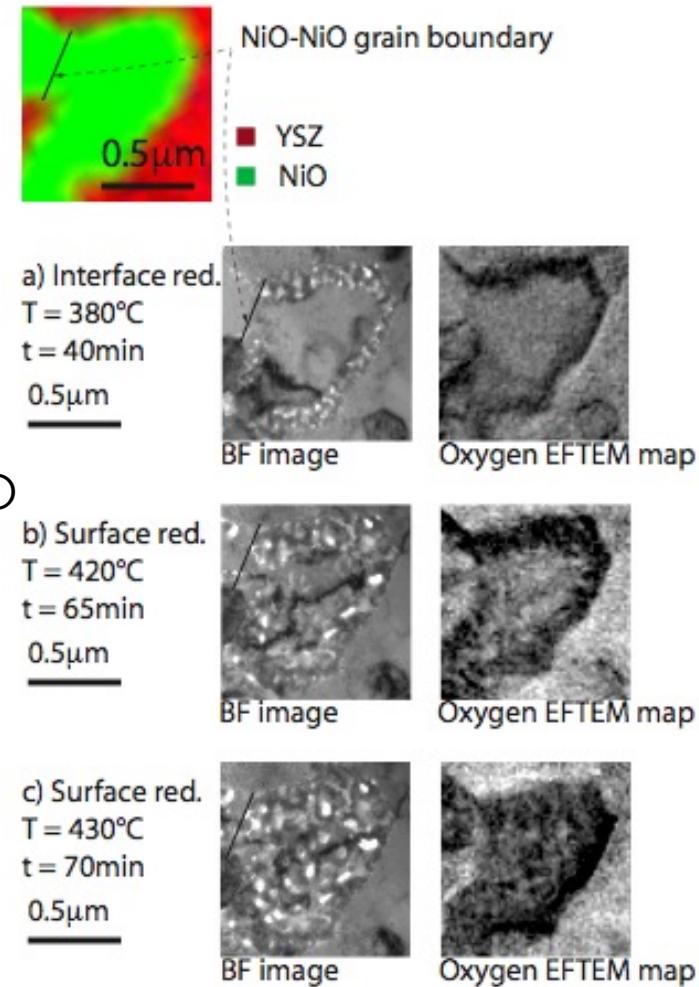
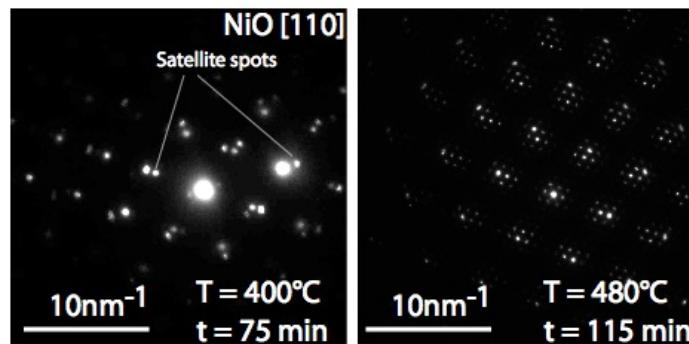
- Cliché de diffraction d'un grain NiO

ZA (012)



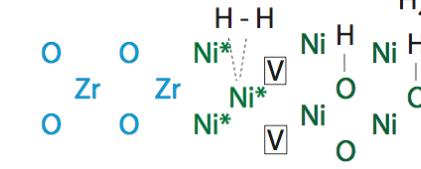
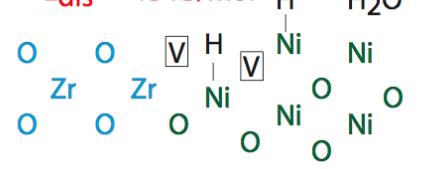
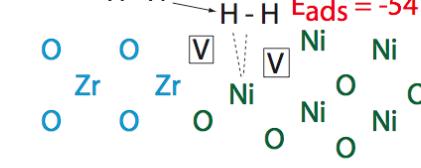
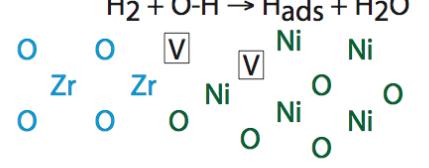
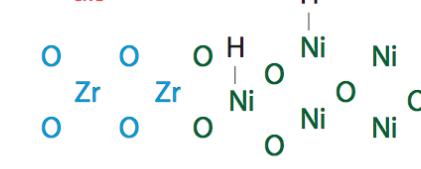
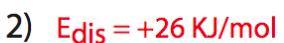
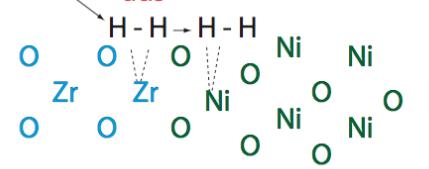
# TEM environnemental: SOFC

- Réduction  $NiO + H_2 \rightarrow Ni + H_2O$ 
  - Compression de volume de 40%
- Création de nanoporosité intergranulaire
- La réaction commence aux interfaces NiO-YSZ à 330° C
- Réduction aux surfaces libres à 420° C
- Croissance épitaxiale du Ni métallique sur NiO
  - Spots satellite - double diffraction
  - $a_{NiO} = 0.418 \text{ nm}$  et  $a_{Ni} = 0.368 \text{ nm}$
  - Pas de spots satellites pour le Ni pur



# TEM environnemental: SOFC

Réduction initiés aux interfaces NiO-YSZ à 330° C



**YSZ transmet les espèces actives (H<sub>2</sub>)**  
**Initiation de la réduction**

Désorption d'eau

Création de lacunes

Nouveaux sites d'adsorption: Ni adjacent aux lacunes d'oxygène

Création d'amats de Ni clusters à l'interface

Réaction autocatalytique

Les lacunes coalescent en cavités en direction du centre des grains de NiO

Réduction du NiO par les surfaces libres à 420° C

$$n_s = N e^{-\Delta H / 2RT}$$

-Assez de génération thermique des lacunes d'oxygène à la surface

- Nombre d'équilibre  $n_s$ , N nombre total de site cations & anions, différence d'enthalpie  $\Delta H$

-Energie d'activation de réduction du NiO  $E_a = 96.4 \text{ kJ mol}^{-1}$ , Jankovic et al.

# TEM environnemental: SOFC

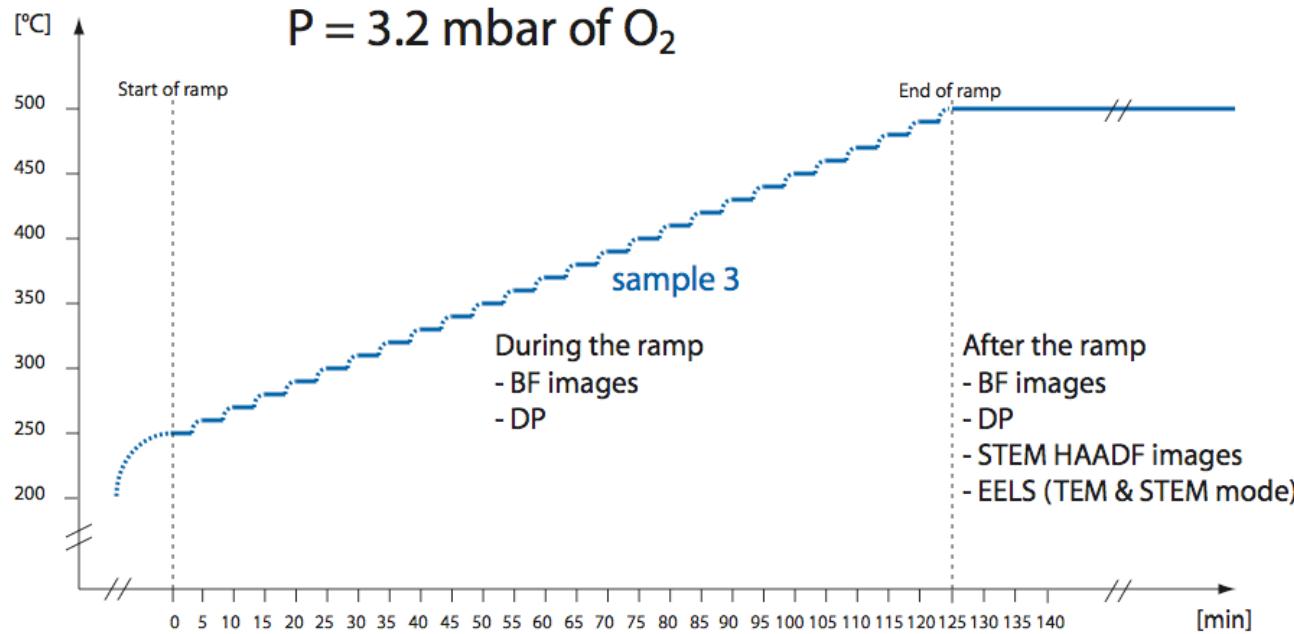
Réoxydation: 1 expérience sous 3.2 mbar d' $O_2$

–Rampe de température

- Temperature augmente de 10° C par 5 minutes
- De 250° C à 500° C

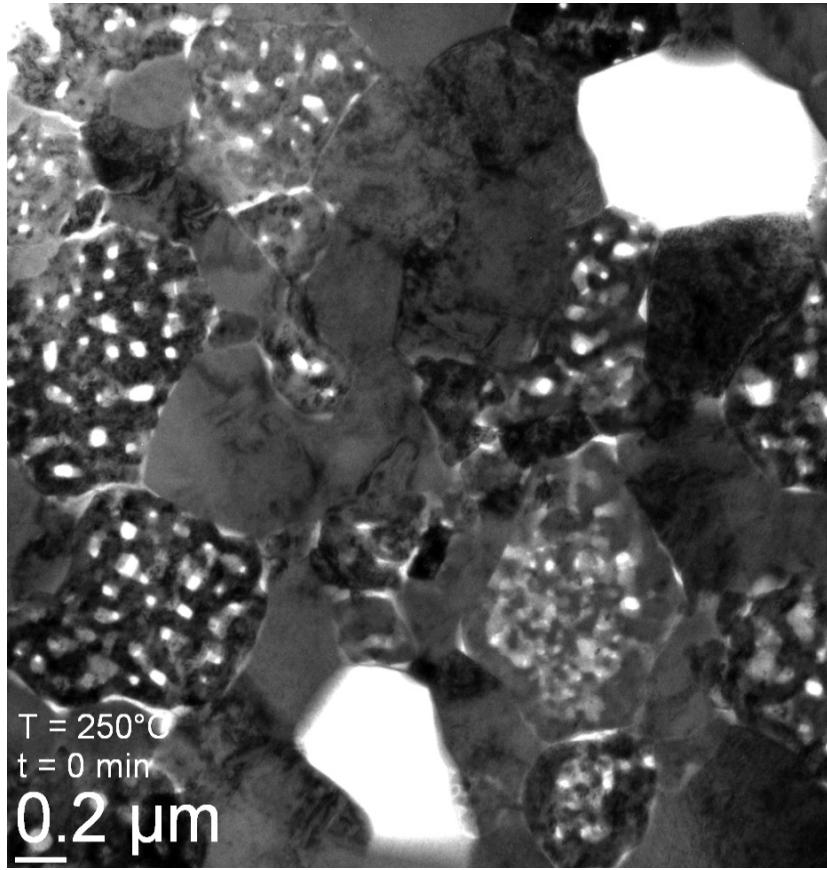
–Images bright field, clichés de diffraction, STEM HAADF, EELS

In situ reoxidation

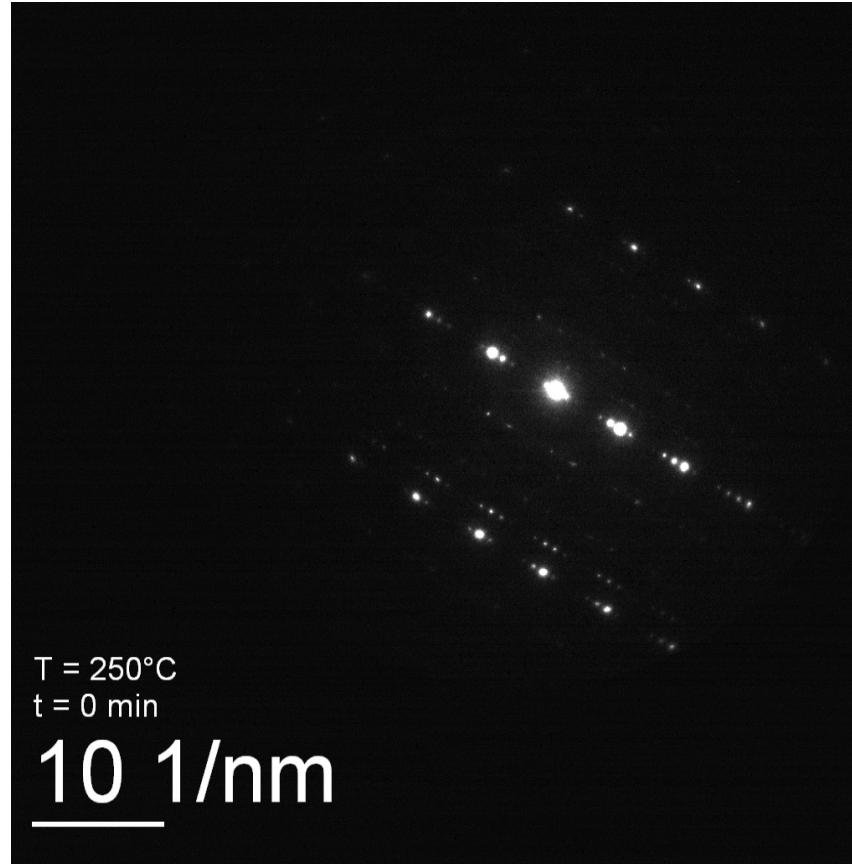


# TEM environnemental: SOFC

Images BF à 6300x

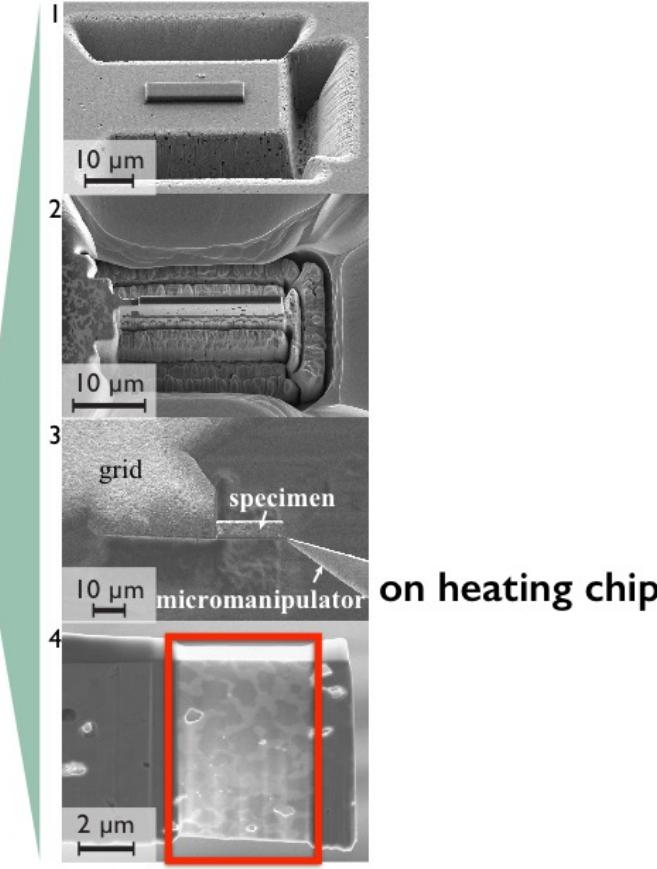
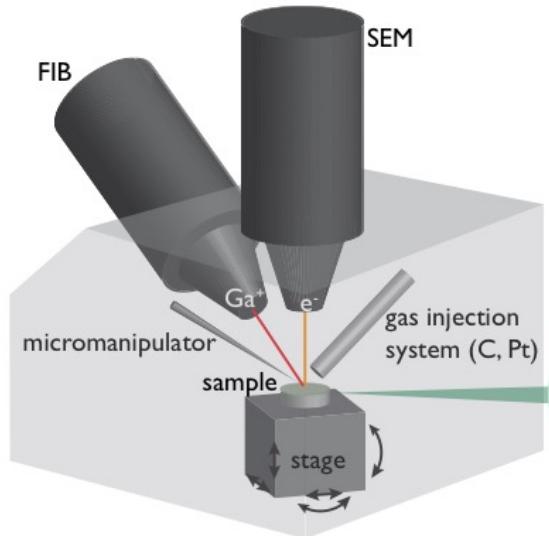


- Clichés de diffraction



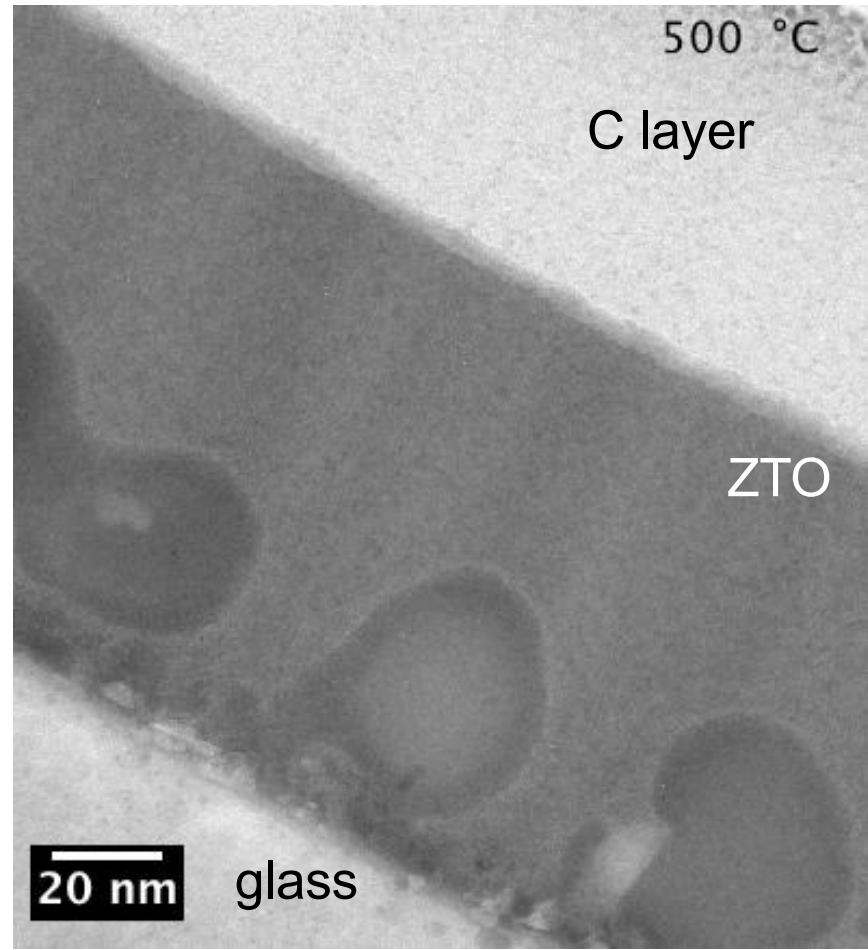
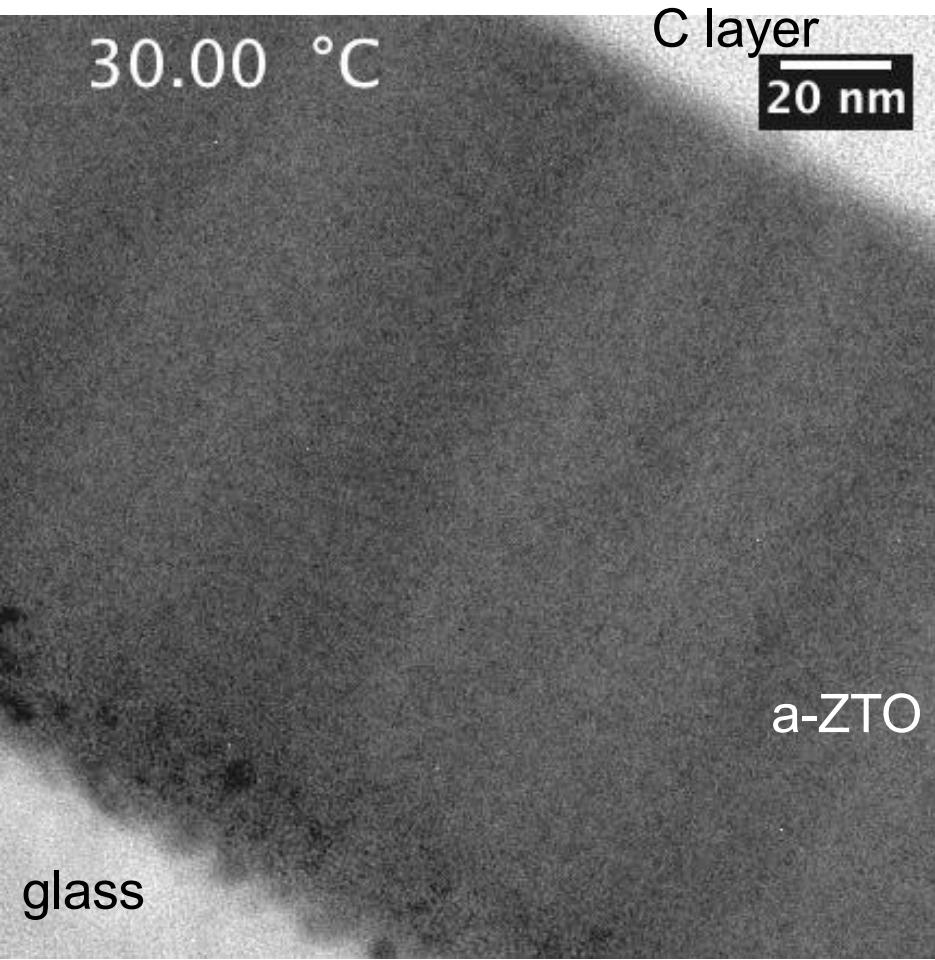
# Chauffage in situ de Zn-Sn-O (ZTO)

## Préparation de l'échantillon par FIB

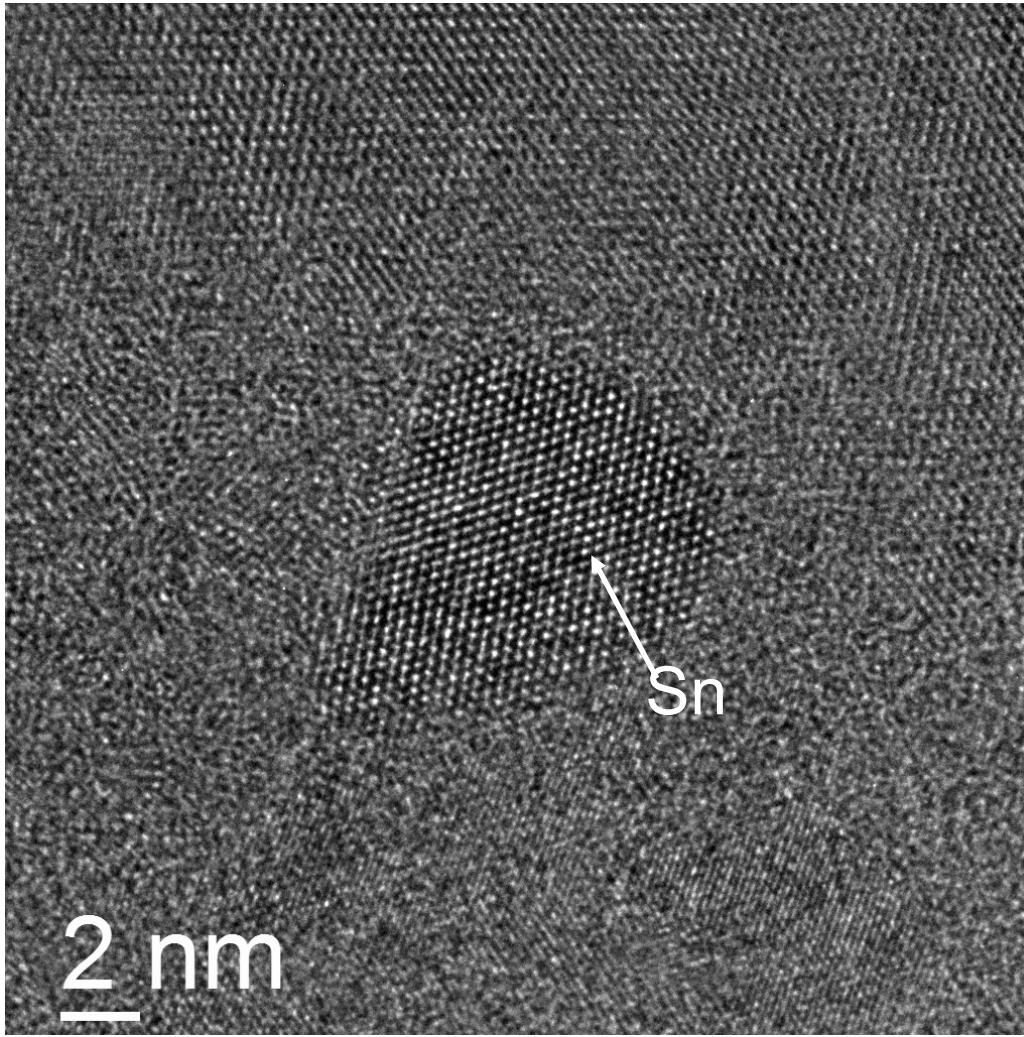


Q. Jeangros, PVlab

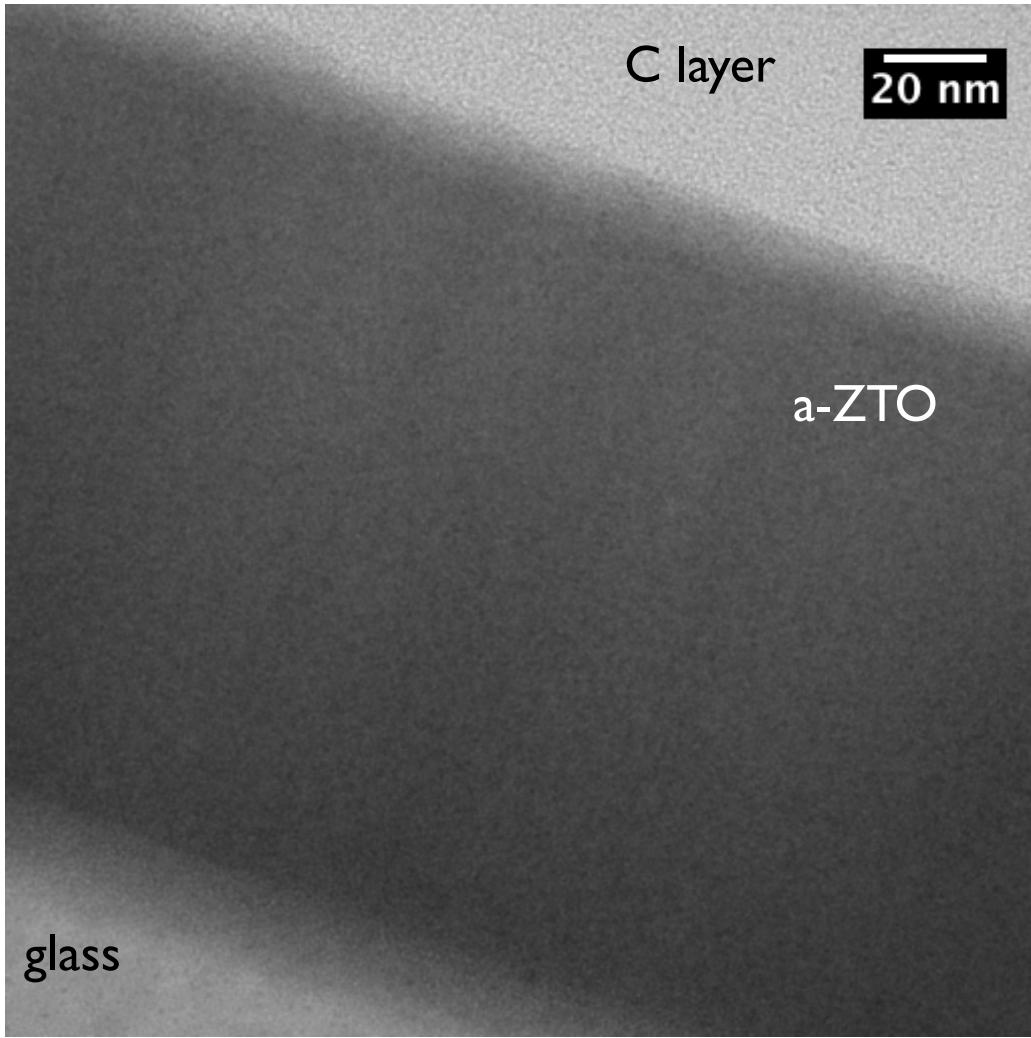
# In situ heating of FIB-prepared ZTO up to 500 °C



# Post-heating HRTEM



# Post-heating TEM



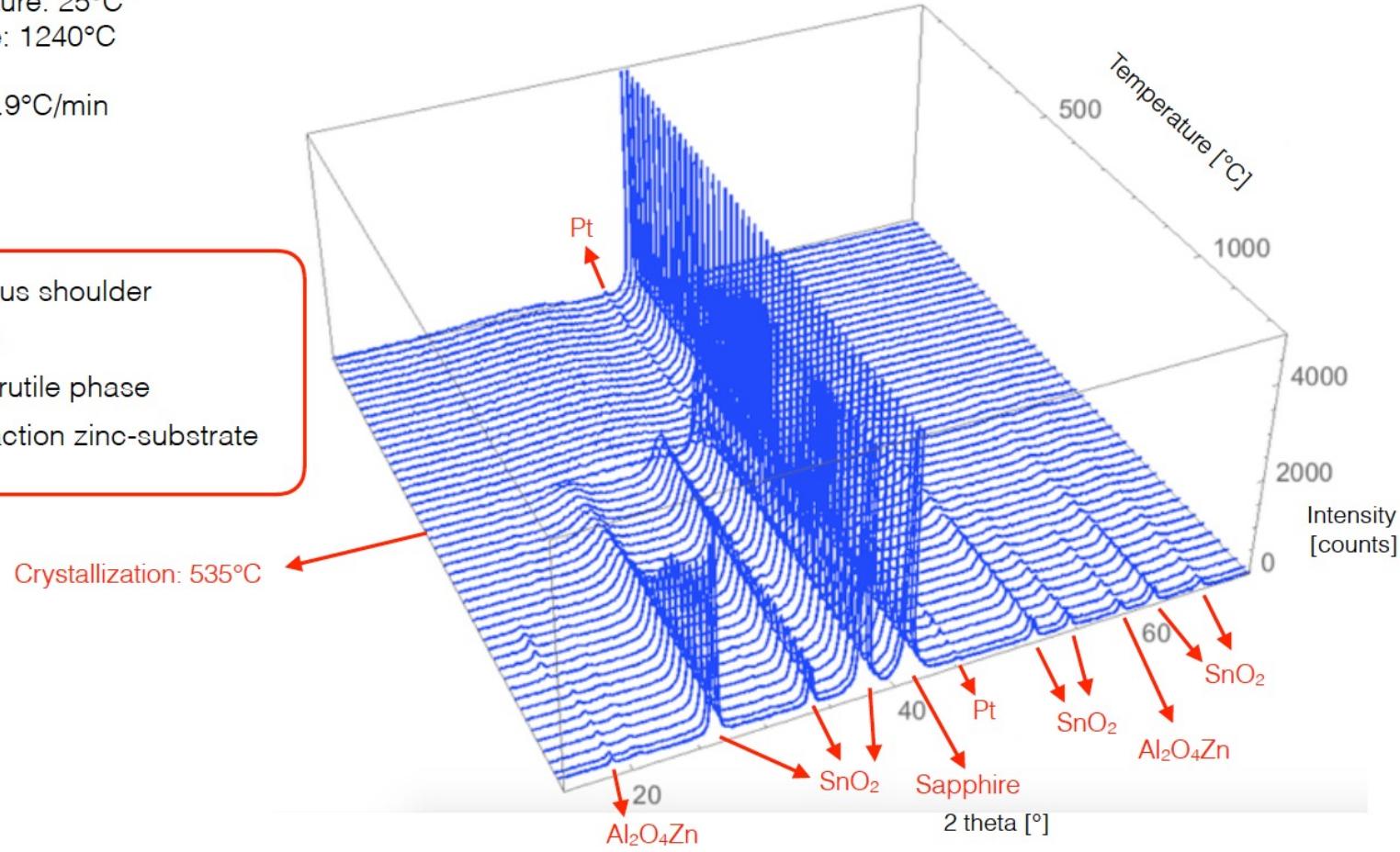
- **still amorphous where not illuminated**
- **electron beam induced phase change due to substrate...**
- **sample preparation!!!**

# In situ XRD

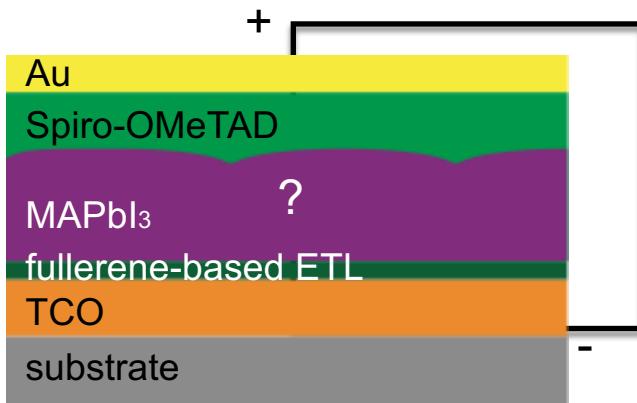
## In situ X-ray Diffraction

Substrate: Sapphire  
 Starting temperature: 25°C  
 Final temperature: 1240°C  
 Atmosphere: air  
 Annealing rate: 4.9°C/min

Presence of amorphous shoulder  
 Crystallization: 535°C  
 Appearance of  $\text{SnO}_2$  rutile phase  
 $\text{Al}_2\text{O}_4\text{Zn}$  phase: interaction zinc-substrate

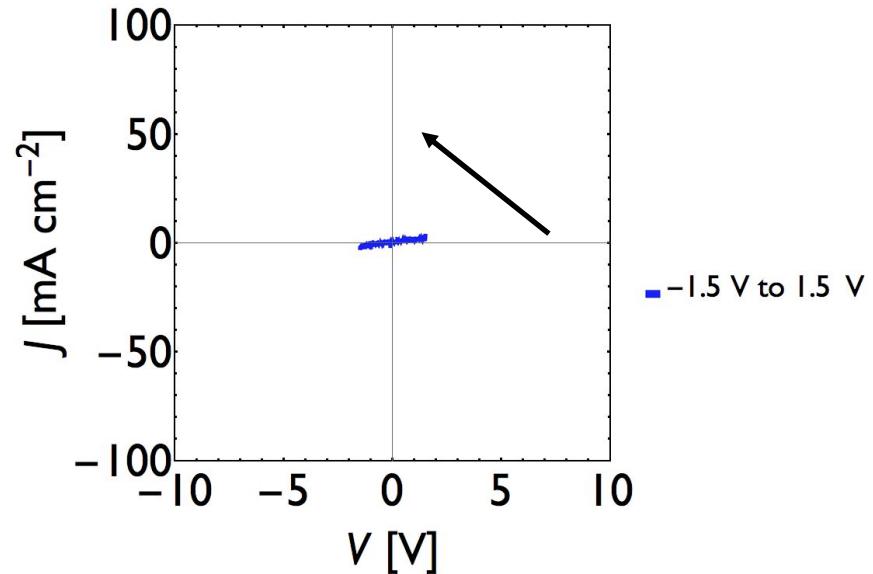
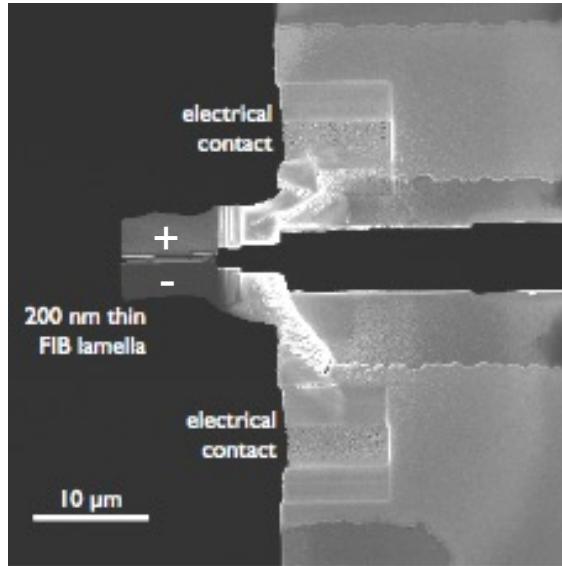


# Perovskite solar cell under electrical bias



FIB lamellae  
contacted to MEMS  
biasing chips

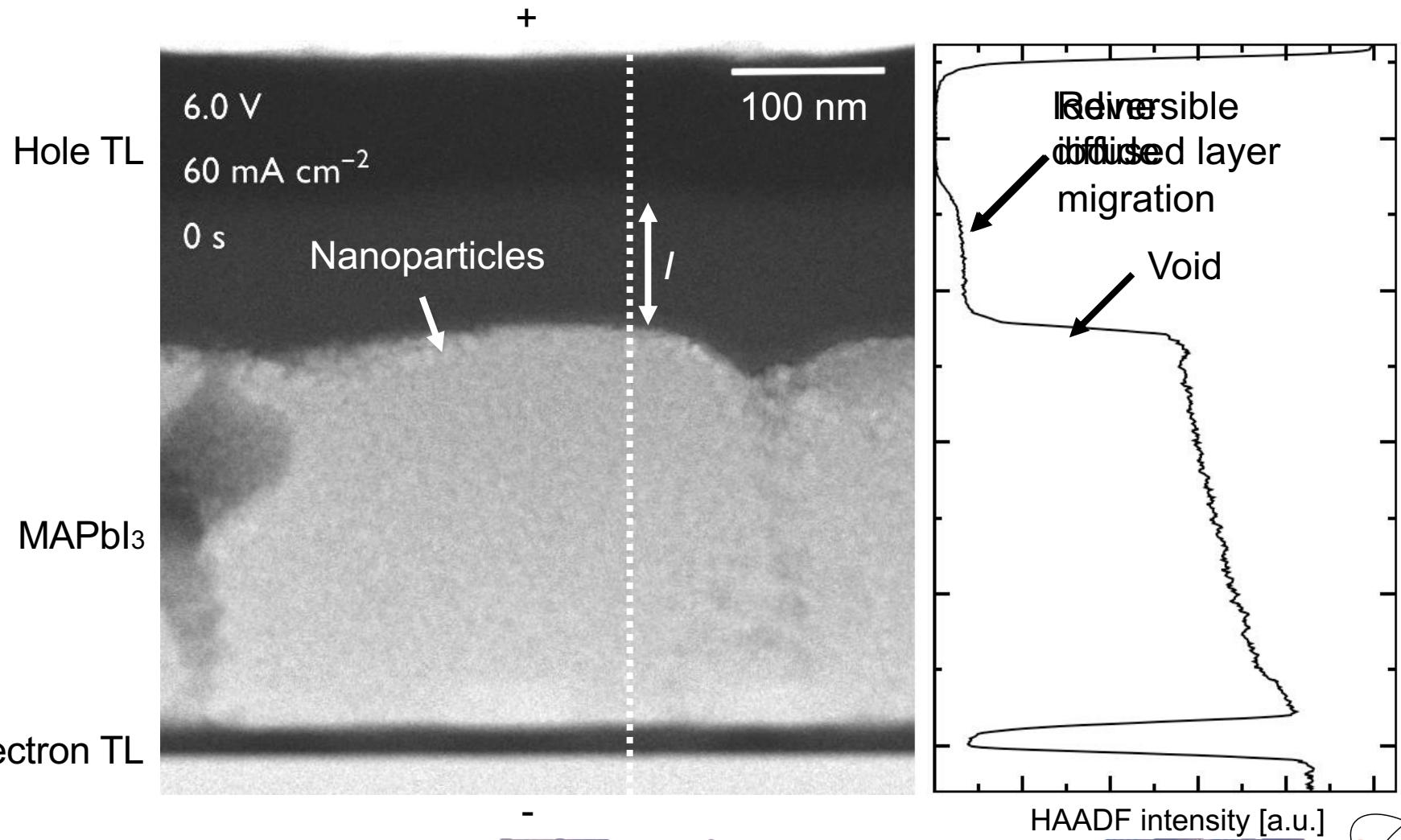
Changes in electrical properties  
► Cell microstructure?



Q. Jeangros, et al. Nano Letters 2016, 16, 7013-7018

# Perovskite solar cell under electrical bias

Positive bias on HTL



# TomoX: résolution en temps

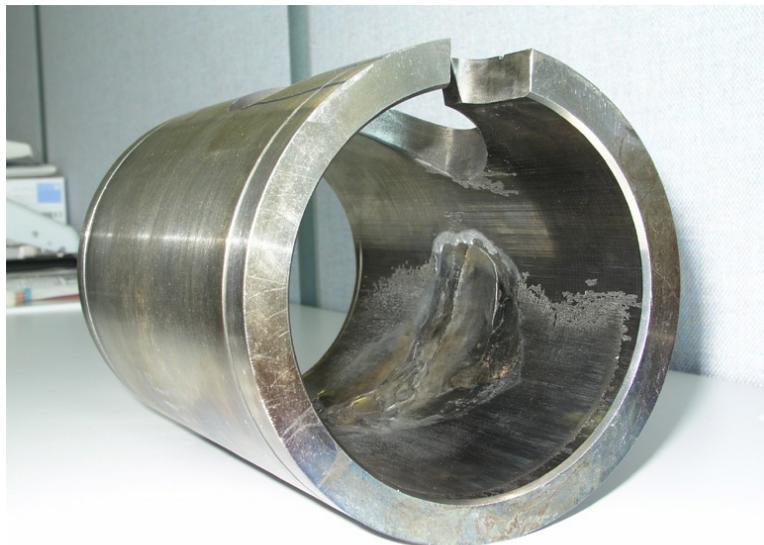
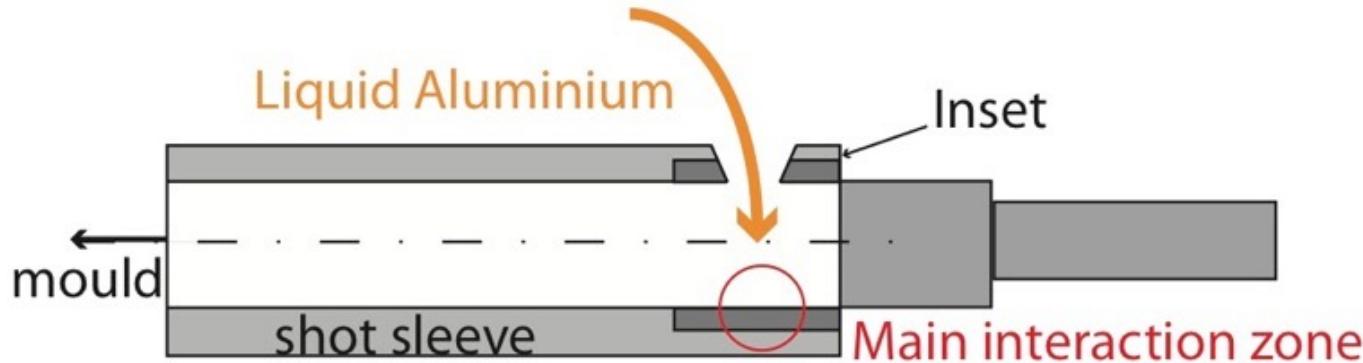
Besoin de connaître l'évolution temporelle,  
pour des temps courts.

Observations post-mortem permettent d'avoir  
des "photos" à des temps donnés =>  
beaucoup d'échantillons!!

Tomographie par rayons X permet  
Etude de phénomènes transitoires dans les  
matériaux

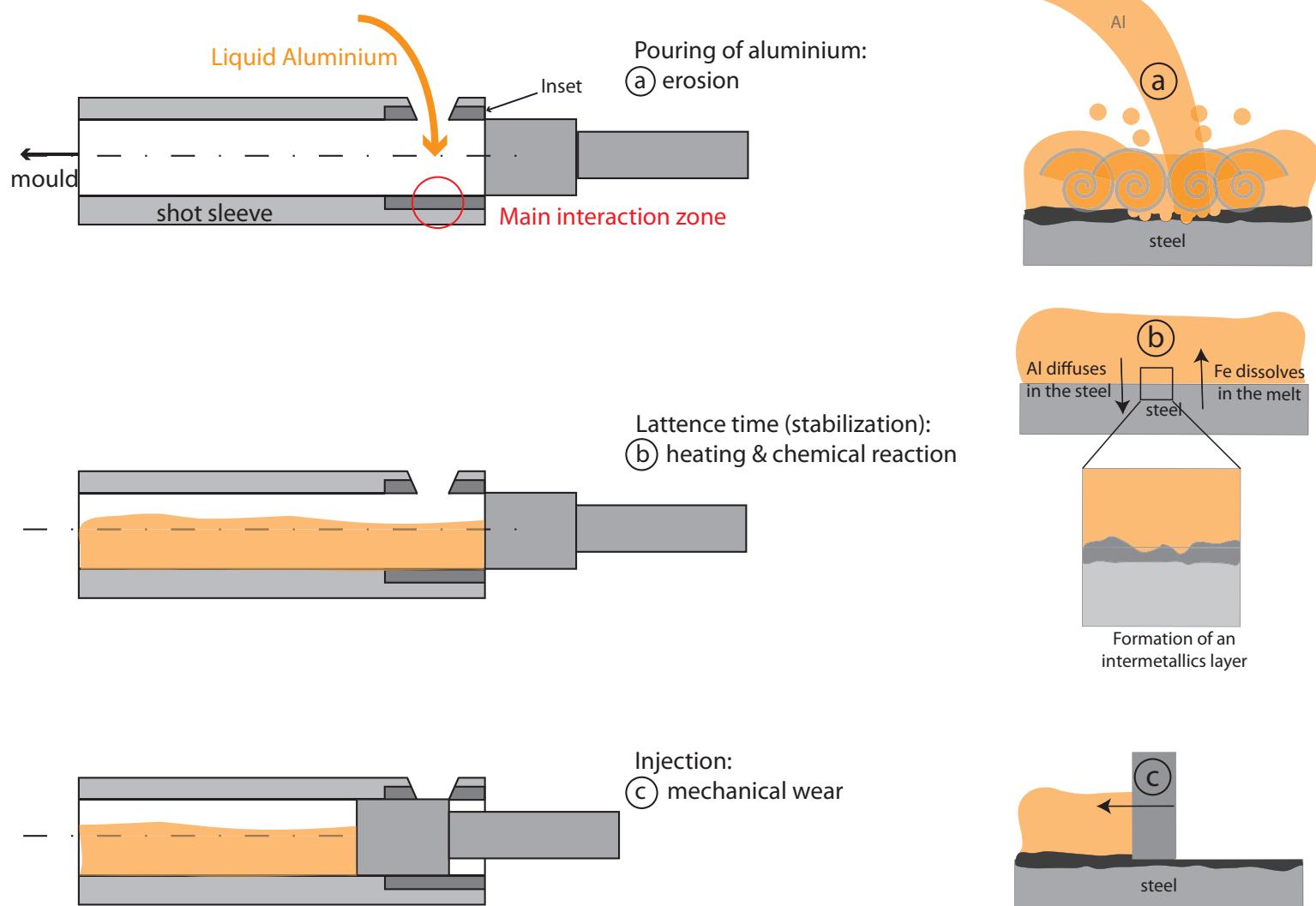
# TomoX: résolution en temps

Cylindres d'injection d'Al liquide: corrosion



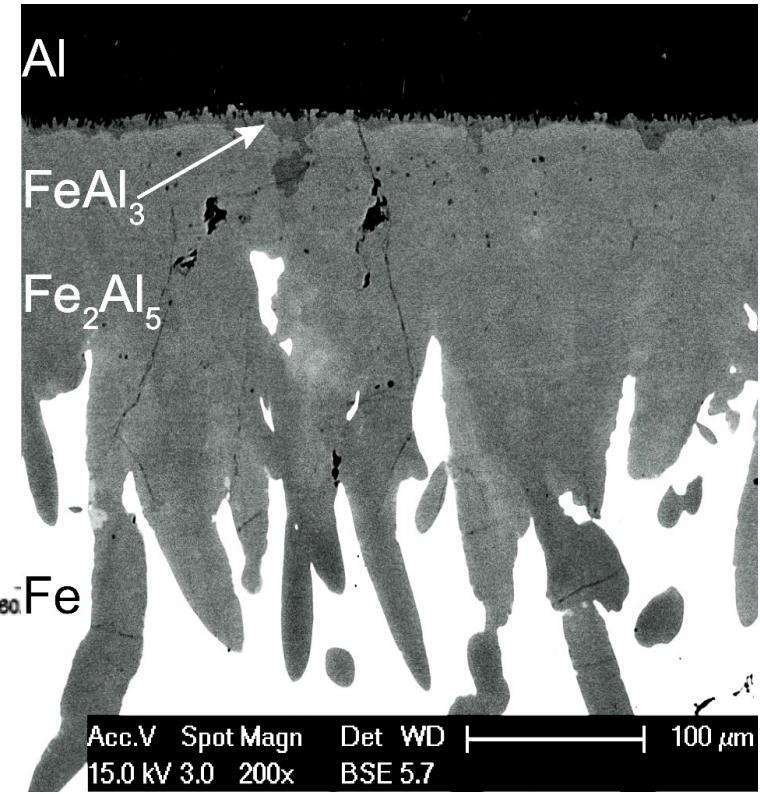
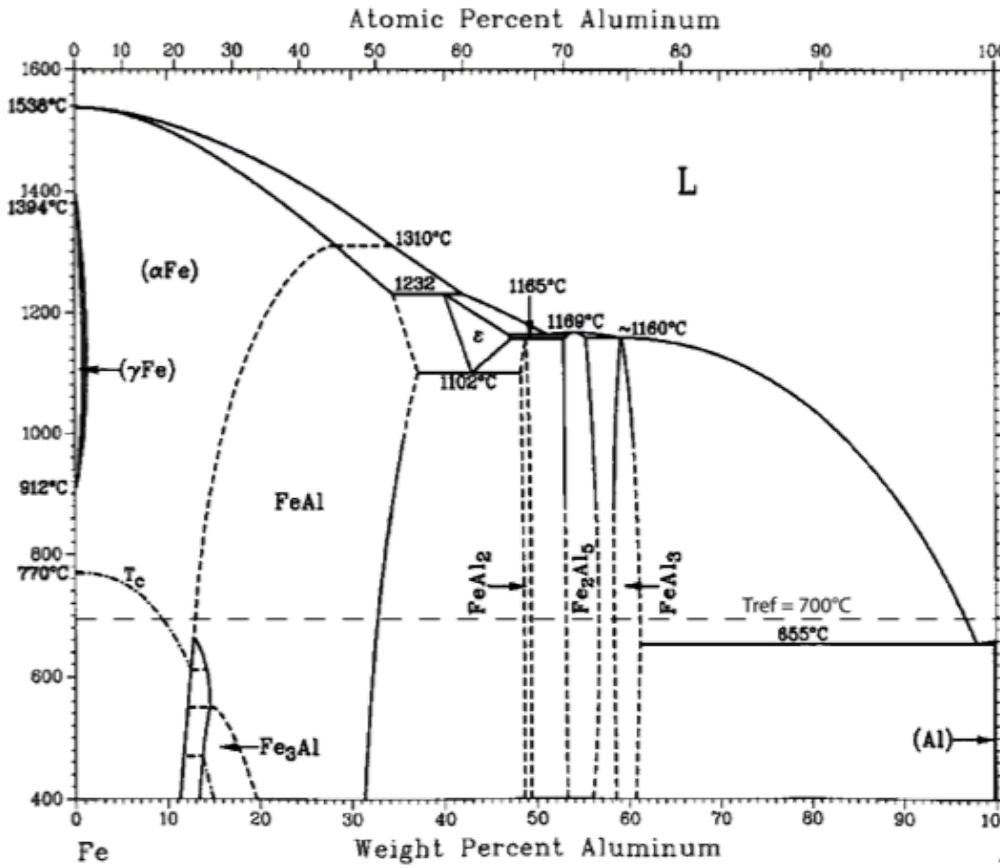
Worn inset after few thousand cycles

# TomoX: résolution en temps



# TomoX: résolution en temps

## Couples de diffusion Al-Fe

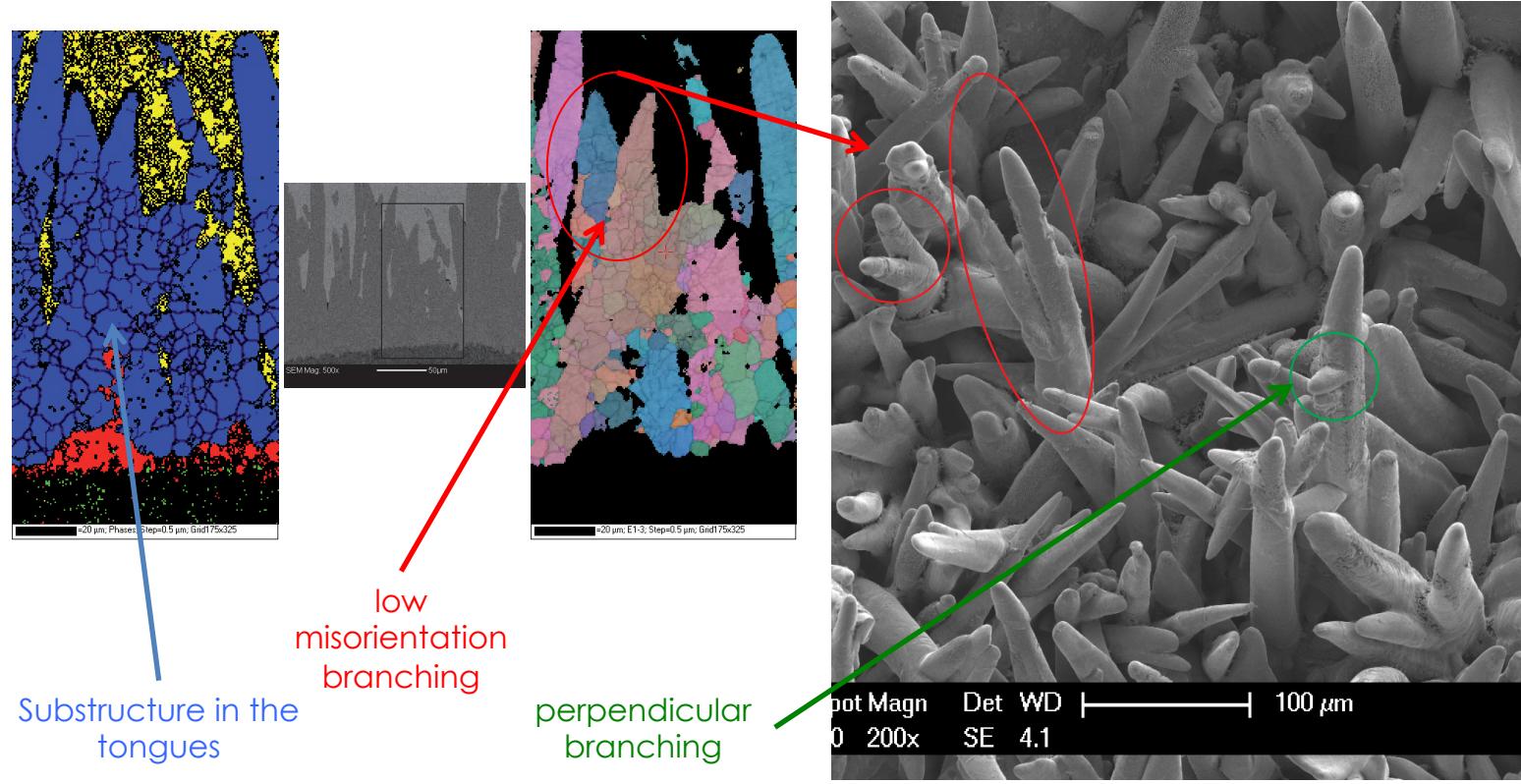


T.B. Massalski and U.R. Kattner. *Binary alloy phase diagrams*.  
ASM International, Materials Park, OH, 1990.

G. Pasche, A. Hessler-Wyser, and R. Schaeublin, poster,  
MSE conference Darmstadt, Germany, 2010.

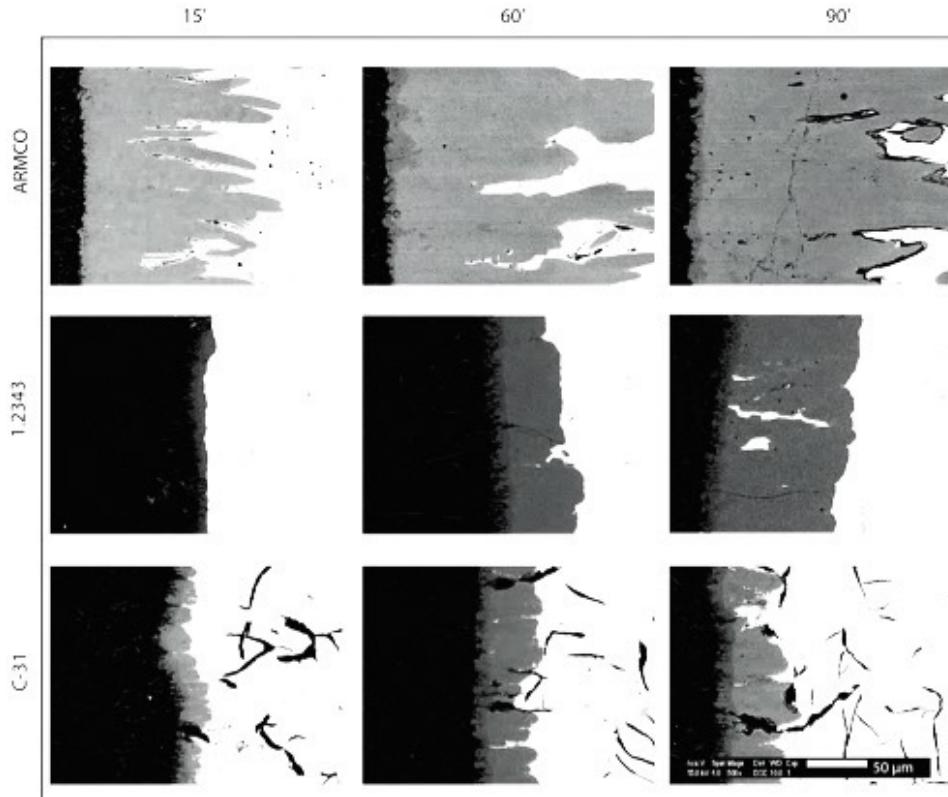
# TomoX: résolution en temps

## Morphologie: structure et embranchements

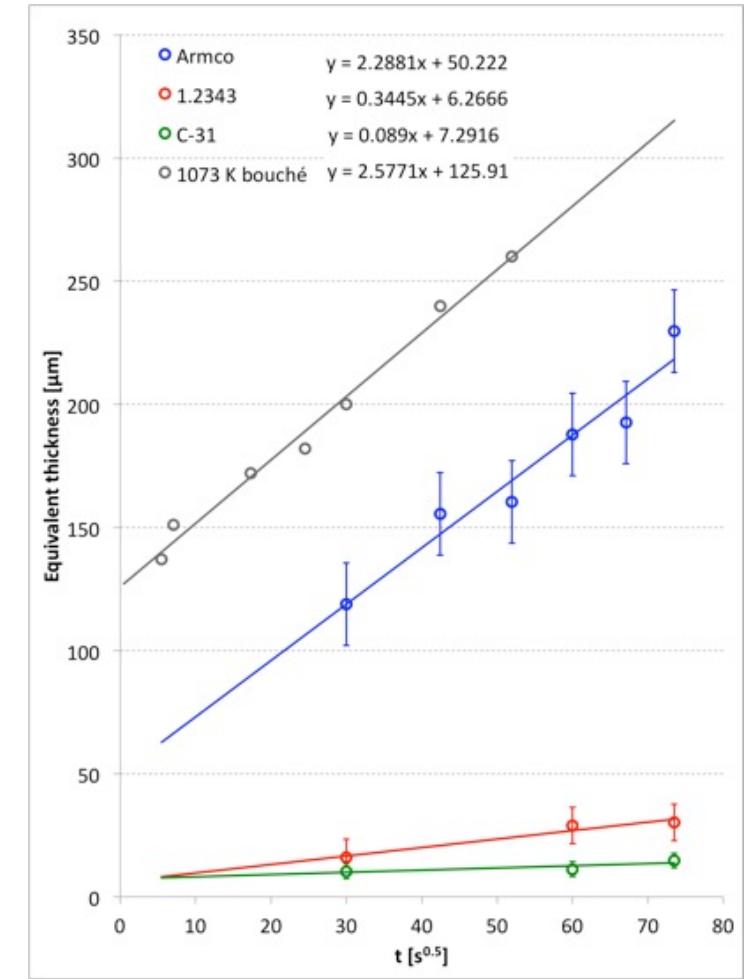


# TomoX: résolution en temps

## Cinétique de la couche $\text{Fe}_2\text{Al}_5$

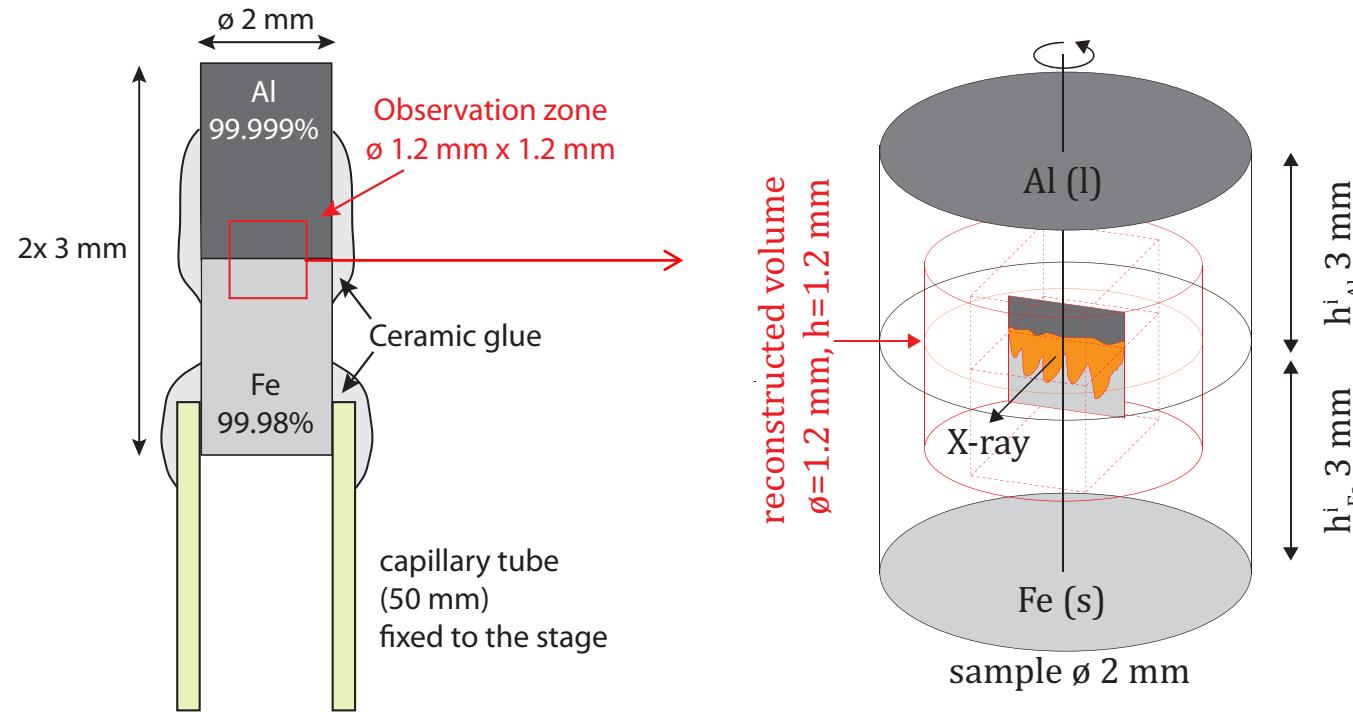


Il manque l'information en t!!



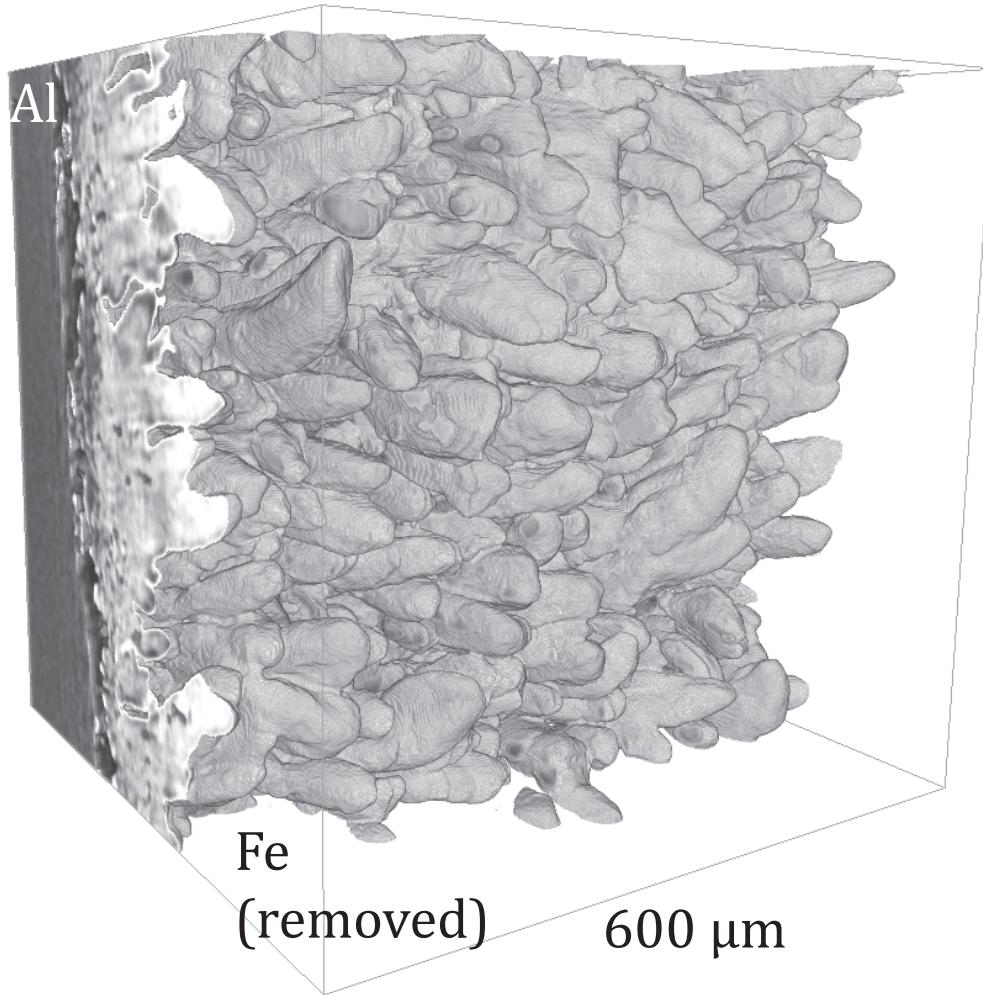
# TomoX: résolution en temps

## Principe tomographie



One acquisition every 2 minutes  
voxel size  $1.2 \times 1.2 \times 1.2 \mu\text{m}^3$

# TomoX: résolution en temps

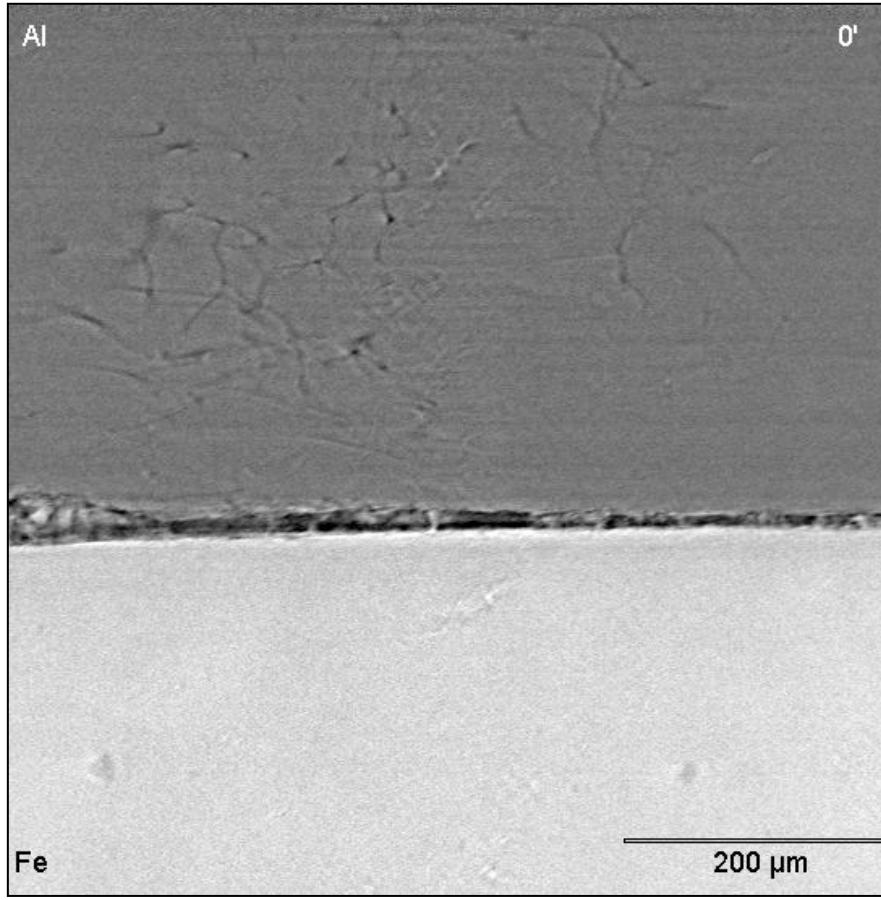


Reconstruction 3D  
après 1 heure, Fe  
non représenté

Structure en  
langues de l'inter-  
métallique

# TomoX: résolution en temps

Observation 2D résolue en temps

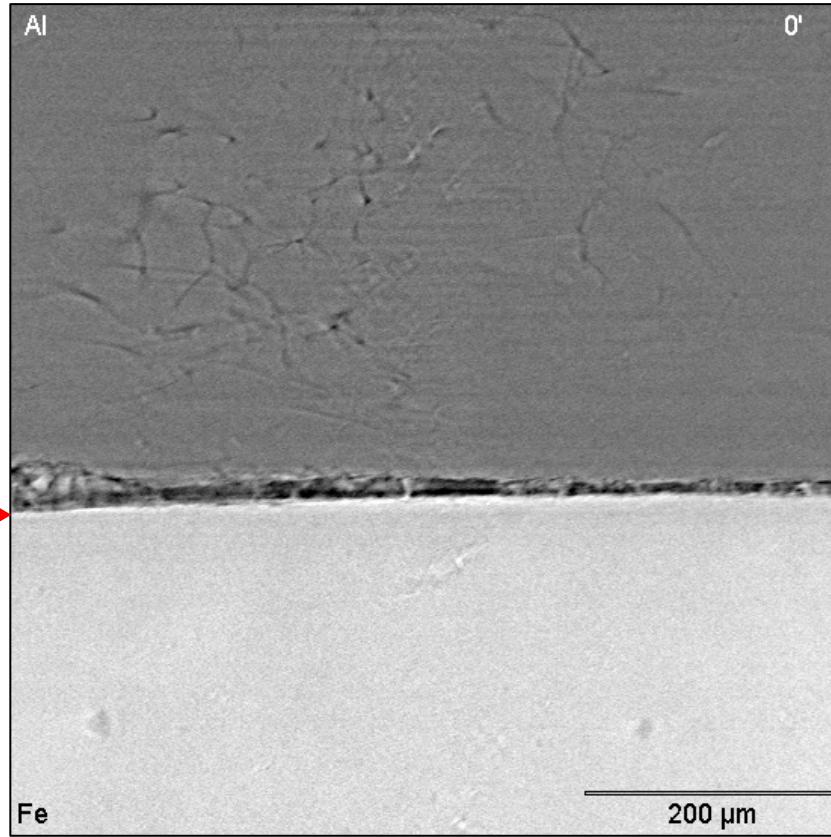


Durée totale de l'expérience  $\approx 10\text{h}$

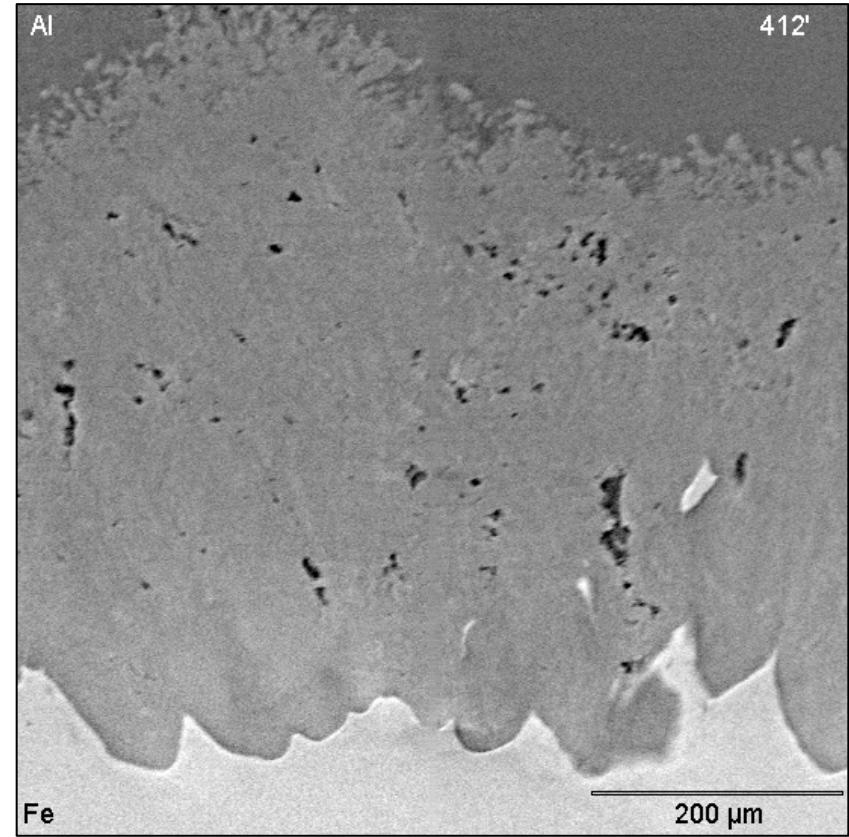
Résolution en t:  
2 min

# TomoX: résolution en temps

Début de la réaction



Saturation du bain



# Growth rate for B & D

Deux modes de croissance des intermétalliques

