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## **Coupling and scale effects: two main issues to begin to understand intergranular stress corrosion cracking in nickel bases alloy.**

J. Caballero, E. Chaumon, J. Nguejo, M. Whebi, T. Couvant, J. Crepin, I. de Curieres, C. Duhamel, F. Gaslain, C. Guerre, et al.

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J. Caballero, E. Chaumon, J. Nguejo, M. Whebi, T. Couvant, et al.. Coupling and scale effects: two main issues to begin to understand intergranular stress corrosion cracking in nickel bases alloy.. WORKSHOP MIST 2015 - Friction, Fracture, Failure - Microstructural Effects, Oct 2015, Montpellier, France. cea-02509691

**HAL Id: cea-02509691**

**<https://cea.hal.science/cea-02509691>**

Submitted on 17 Mar 2020

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**Coupling and scale effects:  
two main issues to begin to understand intergranular stress  
corrosion cracking in nickel bases alloy.**

**J. Caballero, E. Chaumon, J. Nguejo, M. Wehbi**

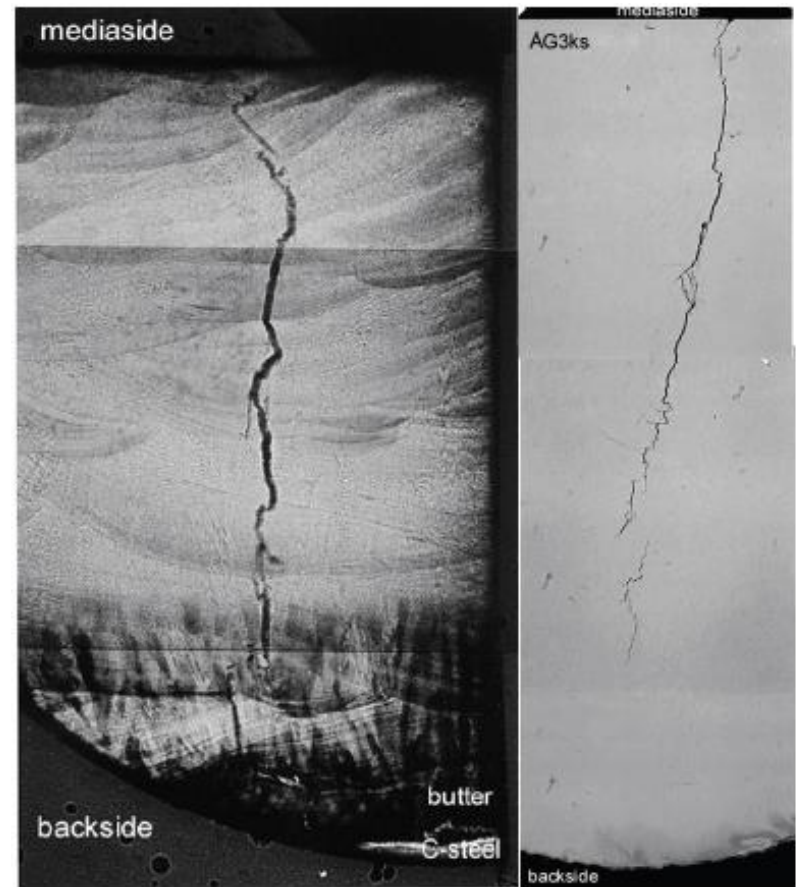
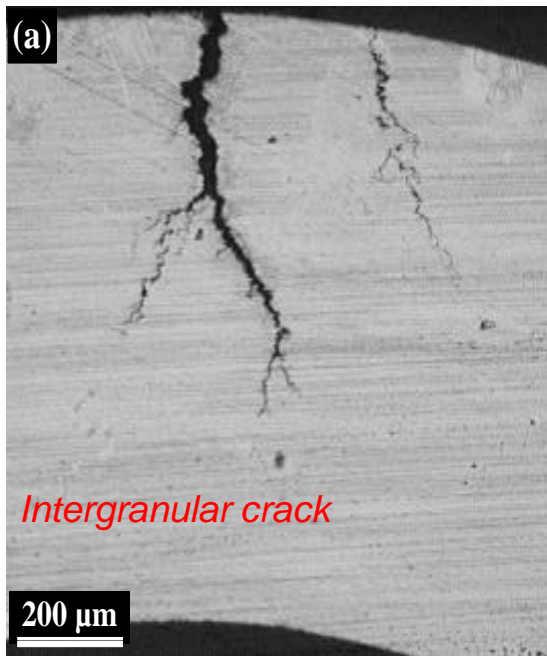
**T. Couvant, J. Crépin, I. de Curières, C. Duhamel, F. Gaslain, C. Guerre, E. Hérippe, M. Sennour**



Workshop MIST, 12-15 Octobre 2015

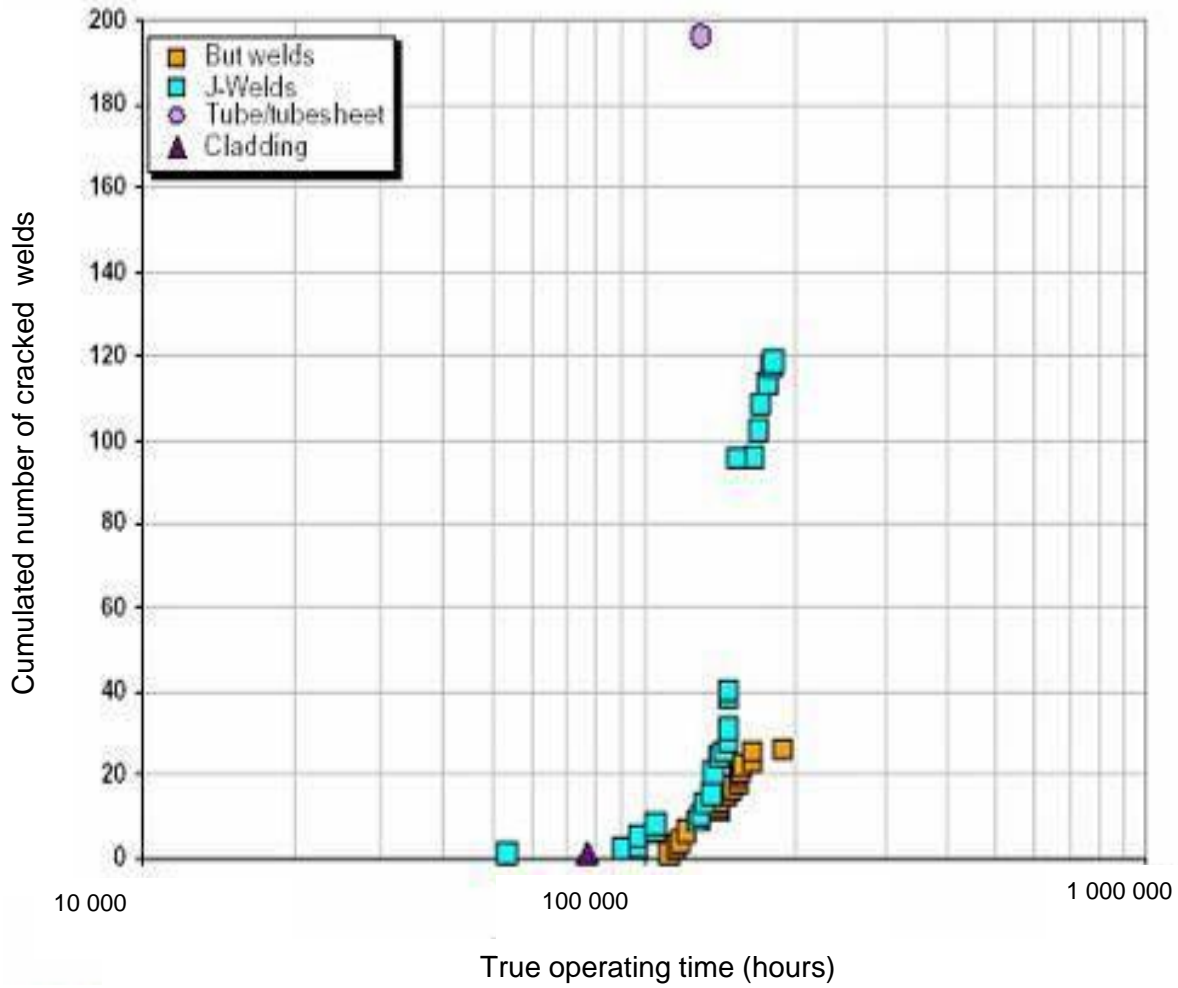
SCC cracks in Alloy 82 welds in J-Groove weld of Ringhals Steam Generator [2]

Stress corrosion cracking of Alloy 600 formed on U bend specimen at 325° C during 1200 hr [1]



[2] P. Efsing, B. Forssgren, R. Kilian, Proceedings of 12<sup>th</sup> International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors”, TMS 2005.

[1] M. Sennour, P. Laghoutaris, C. Guerre, R. Molins, Journal of Nuclear Materials, 393 (2009) 254-266

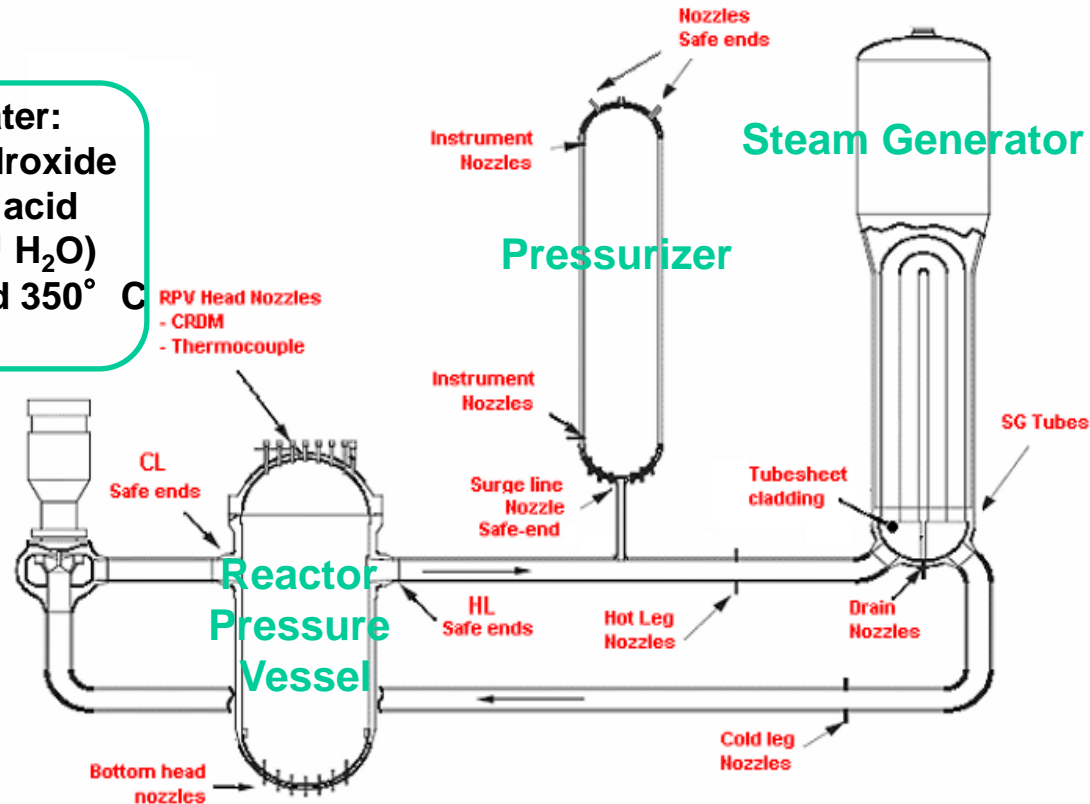


Life extension of PWR > 30 – 40 years

# Nickel-base welds used in PWRs

## Ni-base welds used in *primary circuit* of PWRs

Nominal primary water:  
2 ppm Li as lithium hydroxide  
1000 ppm B as boric acid  
Hydrogen ( $30 \text{ cm}^3 \cdot \text{kg}^{-1} \text{ H}_2\text{O}$ )  
Temperature:  $290^\circ \text{ C}$  and  $350^\circ \text{ C}$

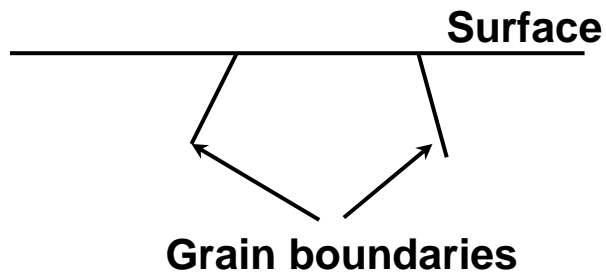


Scott, P., PWSCC of nickel base alloys & mitigation in PWRs, INL Seminar (2013)

# SCC initiation

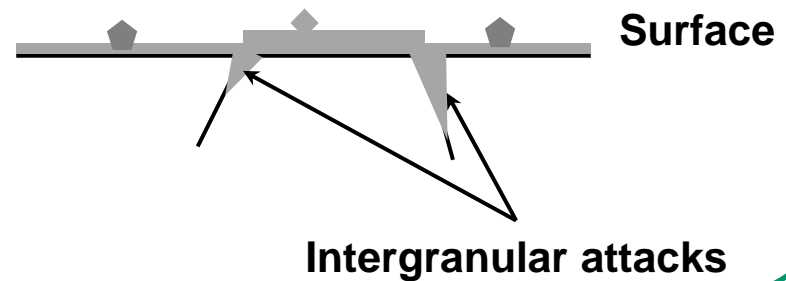
1

Environment  
Primary water



2

Environment  
Primary water



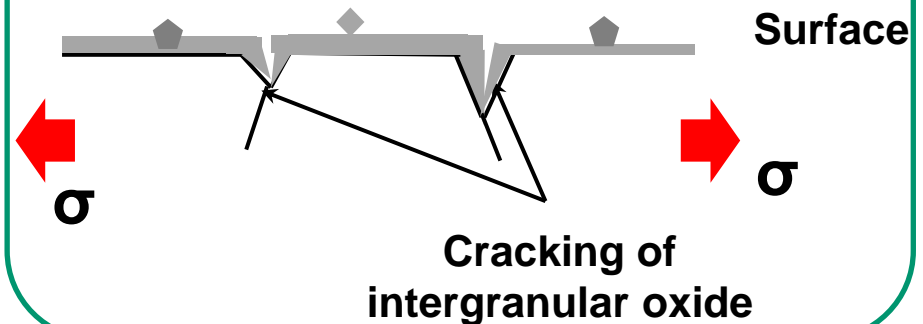
***Initiation = cracking of  
intergranular oxide***



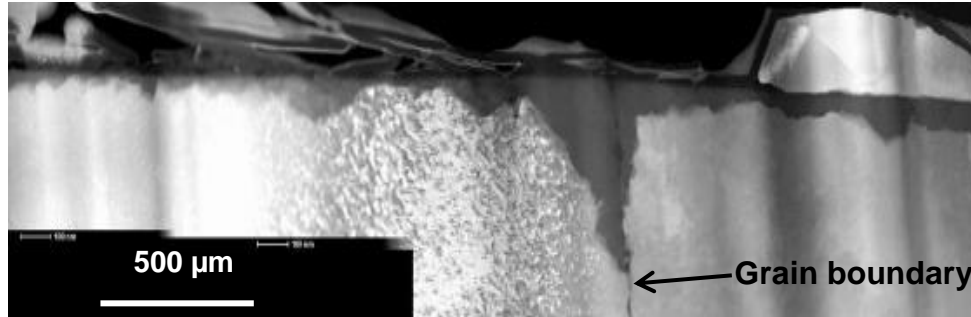
Critical oxide depth  
Critical stress

3

Environment  
Primary water

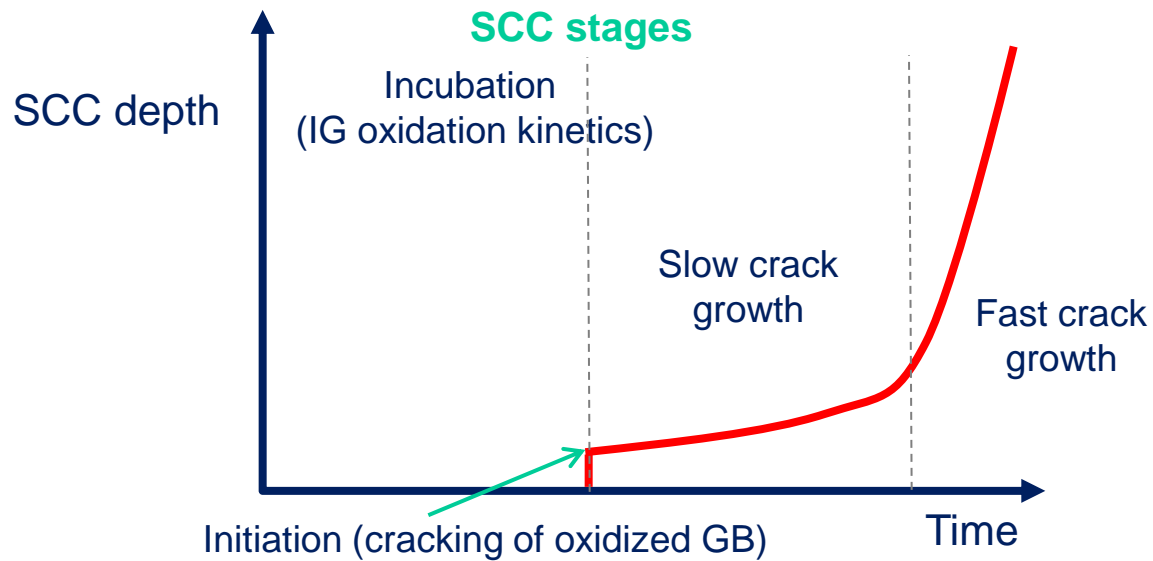


# Cracking scenario

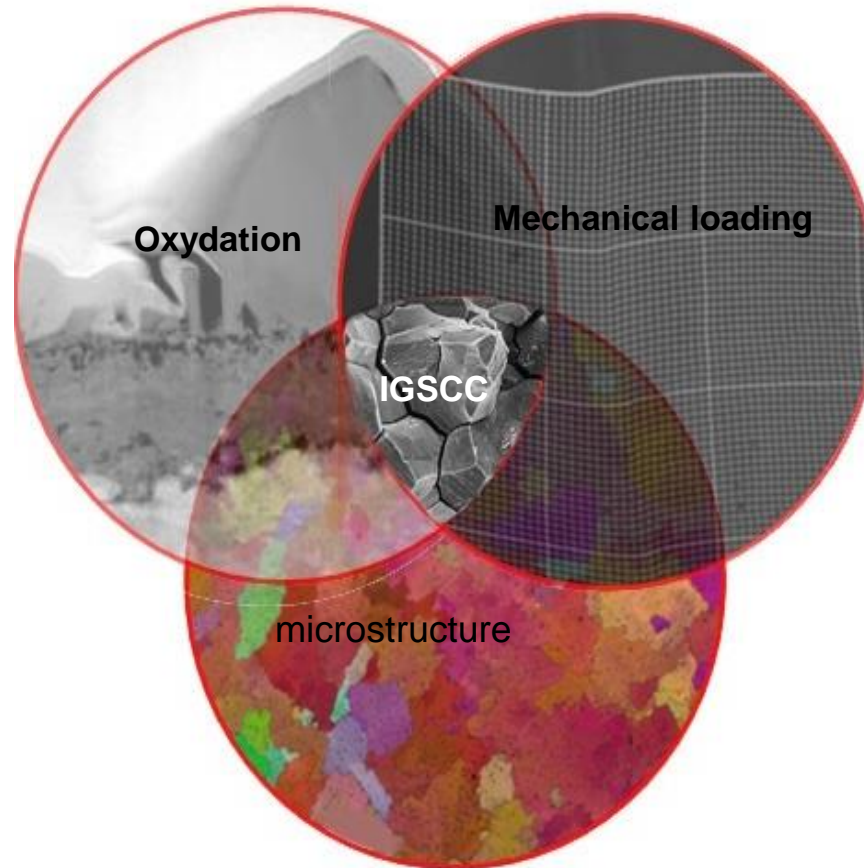


STEM HAADF image of the intergranular oxide penetration of Alloy 600

After 2000h in primary water at 360° C, DH= 30 mL H<sub>2</sub>/kg H<sub>2</sub>O



Intergranular stress corrosion cracking (IGSCC) results from the local interaction between microstructure, oxidation and mechanical loading



Intergranular oxidation seems to be a limiting step in the initiation of IGSCC



## Environnemental conditions

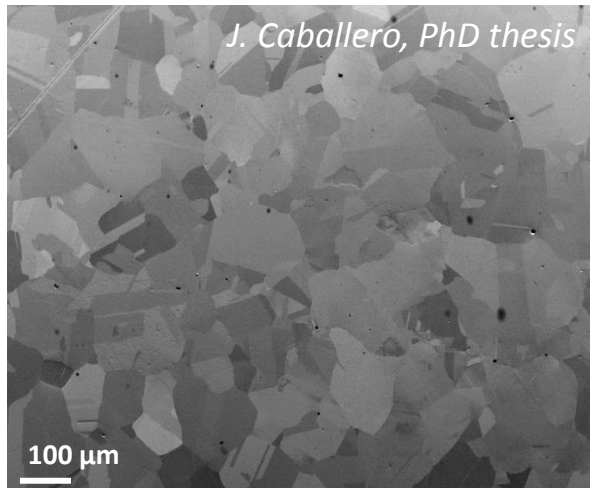
<b>Temperature</b>	<b>285 - 325 ° C</b>
<b>Pressure</b>	<b>155 bar</b>
<b>Boren (H<sub>3</sub>BO<sub>3</sub>)</b>	<b>10 -1200 ppm</b>
<b>Lithium (LiOH)</b>	<b>0,7 - 2,2 ppm</b>
<b>H<sub>2</sub></b>	<b>25 - 50 cm<sup>3</sup>.kg<sup>-1</sup>(TPN)</b>
<b>O<sub>2</sub></b>	<b>&lt; 5 ppb</b>
<b>pH<sub>300° C</sub></b>	<b>≈ 7</b>

## wt.% of the main elements

Name	Ni	Cr	Fe	
A182	> 59	13-17	6-10	weld metal
A600	> 72	14-17	6-10	base metal
A82	> 67	18-22	≤ 3	weld metal
A690	> 58	28-31	7-10	base metal
A152 / A52	bal.	28-31	8-12	weld metal

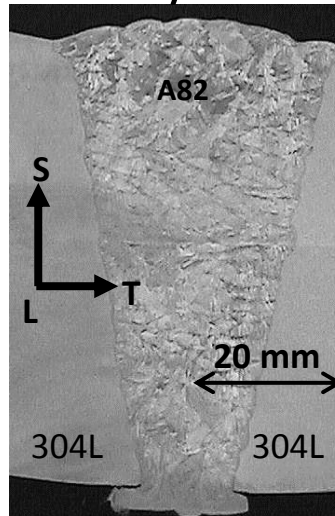
Cr content ↘

### A600

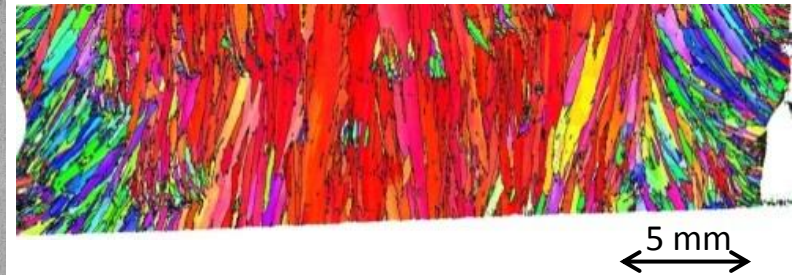


Possible IG chromium carbides

### A182 / A82



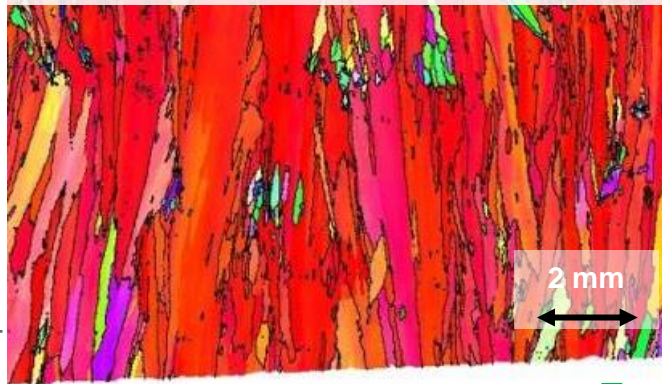
E. Chaumon, PhD thesis



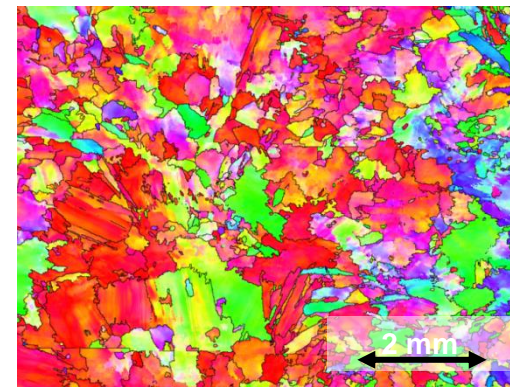
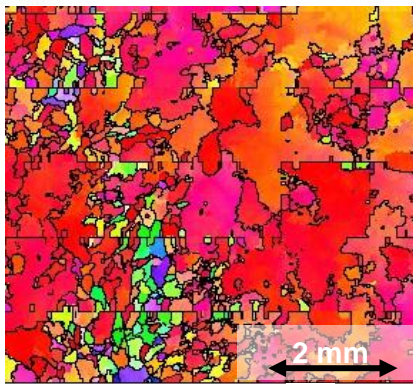
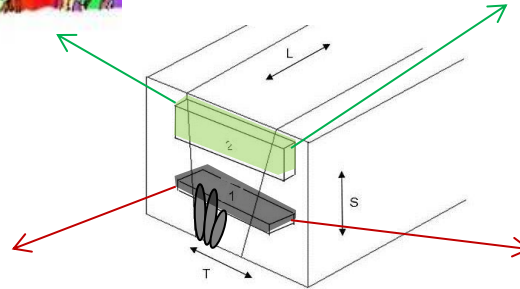
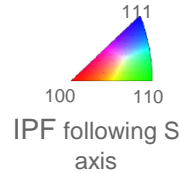
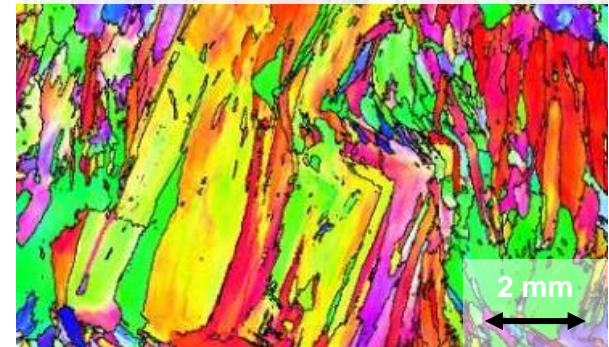
Possible IG niobium and chromium carbides

# Microstructure features (EBSD)

Weld B/AW : A82, 18%Cr, FCAW, as-welded

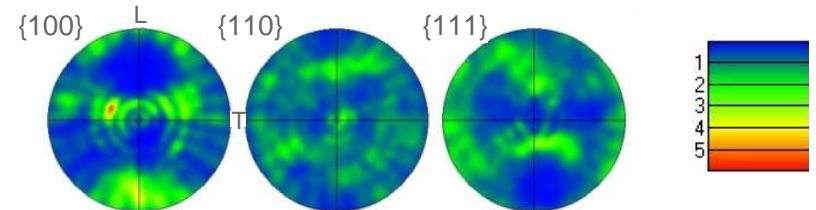
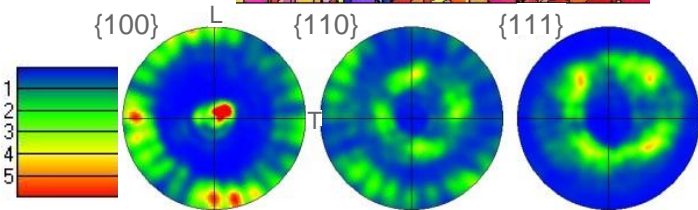


Weld A/AW : A82, 19%Cr GTAW, as-welded



Pole Figures

Pole Figures

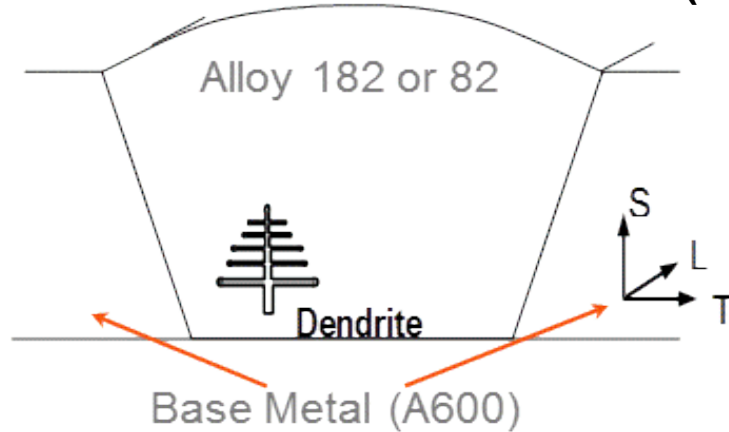


→ Crystallographic texture for **weld B/AW**, local texture for **weld A/AW** and no texture for **weld A/HT**

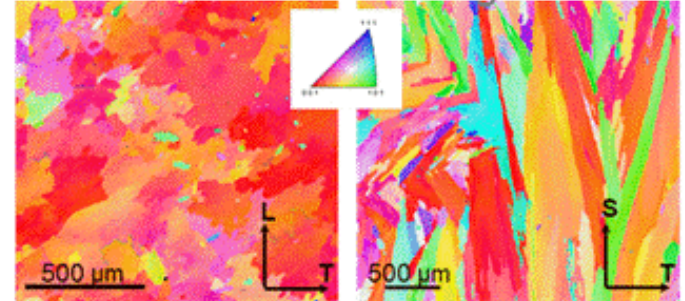
→ Morphology : Heterogeneous grain size and elongated grains along the S direction

# Materials

Cr content: **13 to 17 wt. % (Alloy 182)** and **18 to 22 wt. % (Alloy 82)**



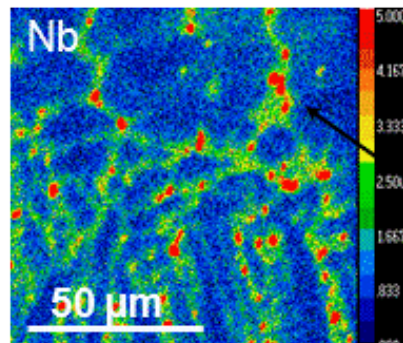
*Microstructural heterogeneities*



EBSD: Inverse Pole Figure (axis: S)

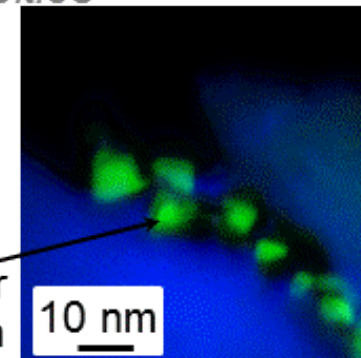
EBSD: Inverse Pole Figure (axis: L)

*Chemical heterogeneities*



Microprobe

Intergranular precipitation



EFTEM maps

■ Nickel  
■ Chromium

## Intragranular precipitation

Niobium carbides (NbC)  
Titanium carbonitrides (Ti(C, N))

## Intergranular precipitation

Niobium carbides (NbC)  
Chromium carbides



# SCC initiation TESTs

## ✓ Initiation tests

→ In an autoclave

→ Interrupted at 500 hours, 1500 hours, 2500 hours and 3500 hours

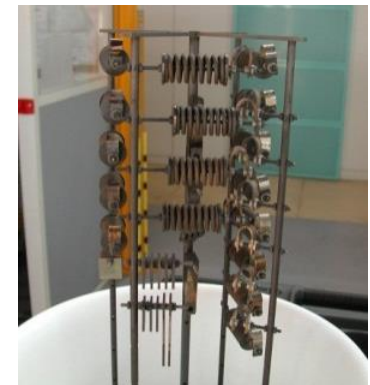
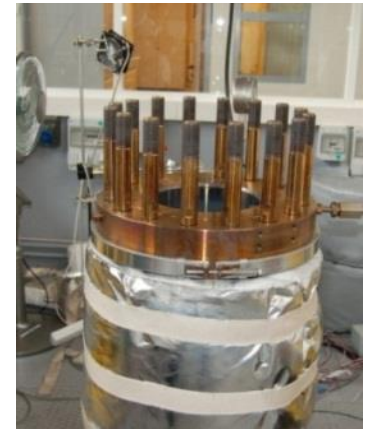


Samples dimensions :  
50mm x 9mm



→ Test environment: **hydrogenated steam**

	Conditions
Temperature	400° C
Total pressure	188 bar
Hydrogen partial pressure	0.7 bar



Ligne d'amarrage

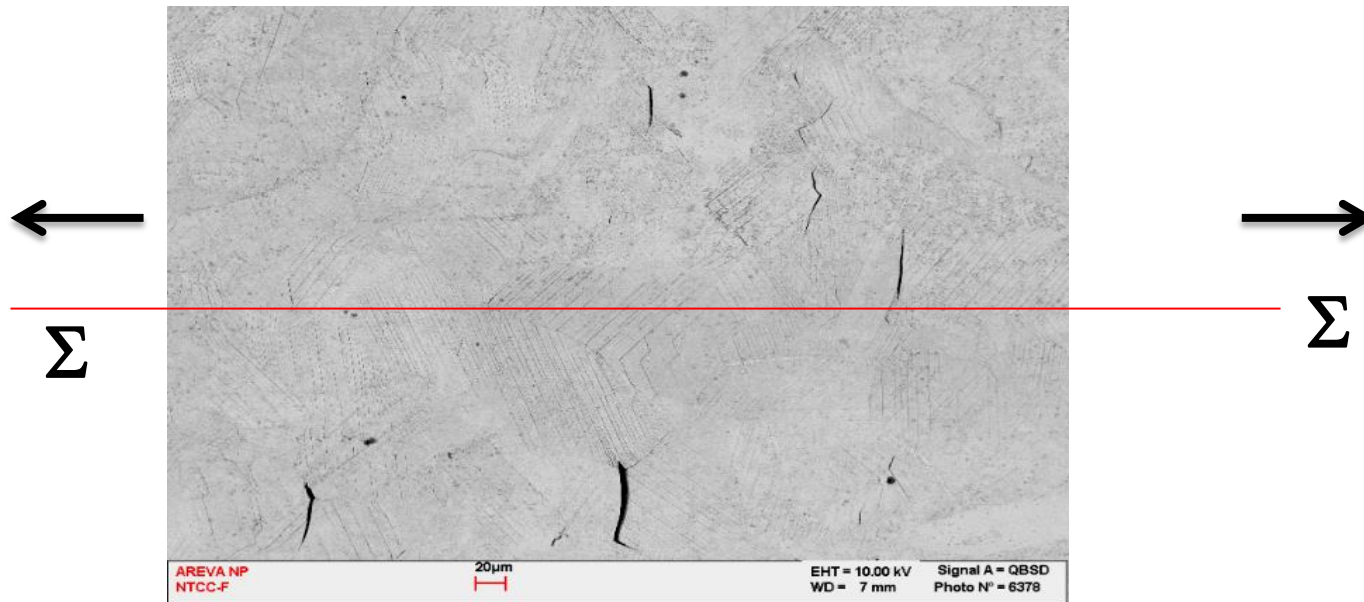


Autoclave



Machine de fluage

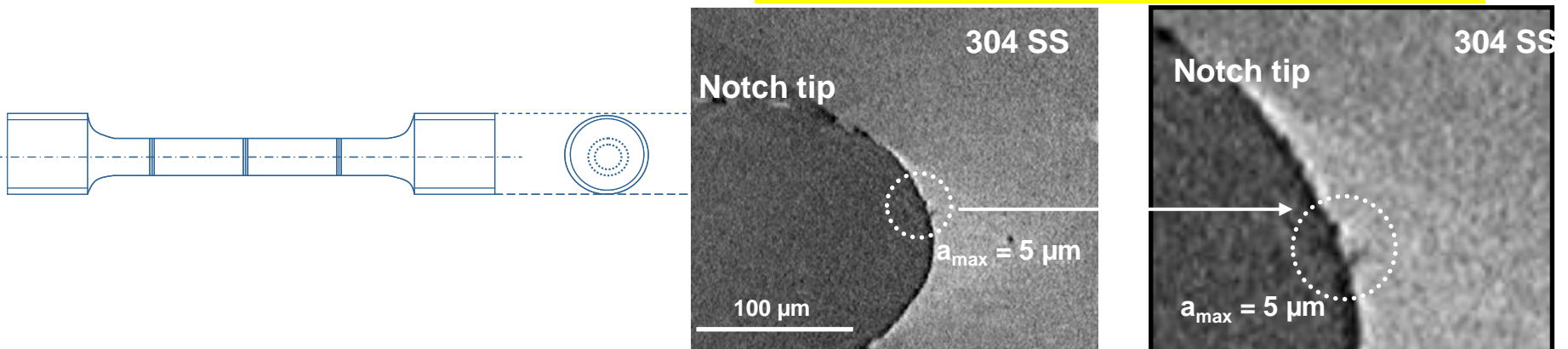




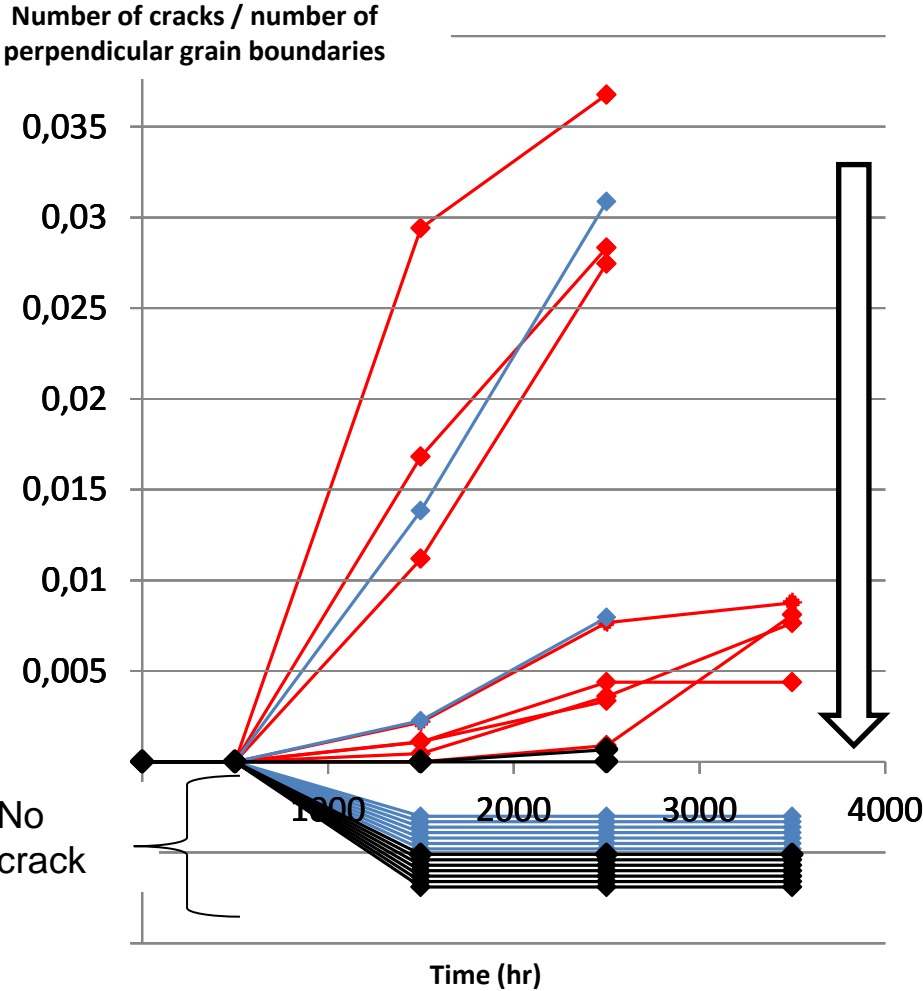
304 Stainless Steel, 5 dpa, 10%

Courtesy of M. Le Millier, chaire AREVA

Laminographie : résolution =  $0,77\mu\text{m}\cdot\text{pixel}^{-1}$



# INITIATION TEST : RESULTS



→ B/AW is more susceptible to SCC than A/AW

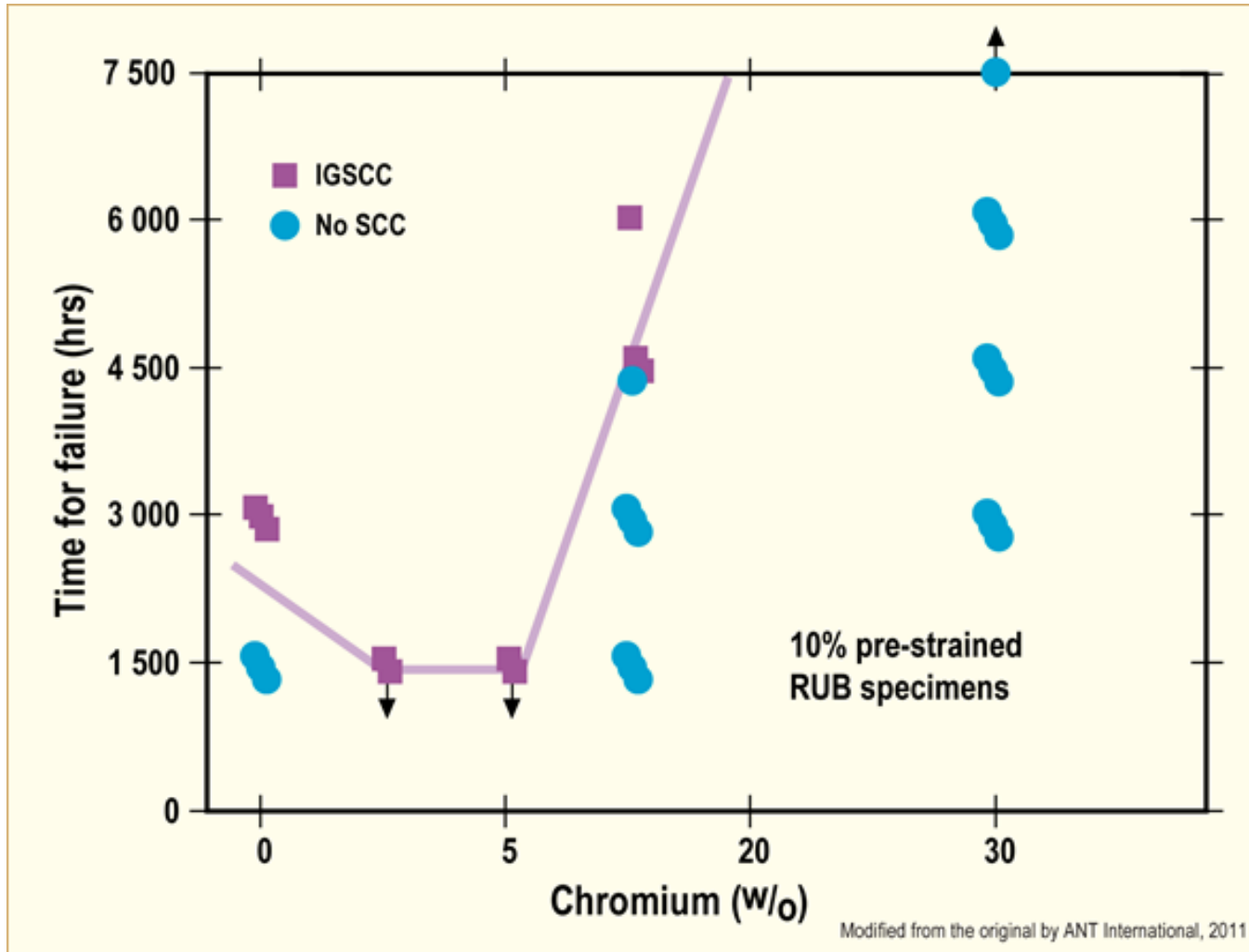
→ A/HT : less susceptible than A/AW  
 (benefic effect of the heat treatment : formation of intergranular chromium carbides [Sennour2013])

- Alloy B/AW : A82 18%Cr, FCAW, as-welded
- Alloy A/AW : A82 19%Cr, GTAW, as-welded
- Alloy A/HT : A82 19%Cr, GTAW, heat-treated

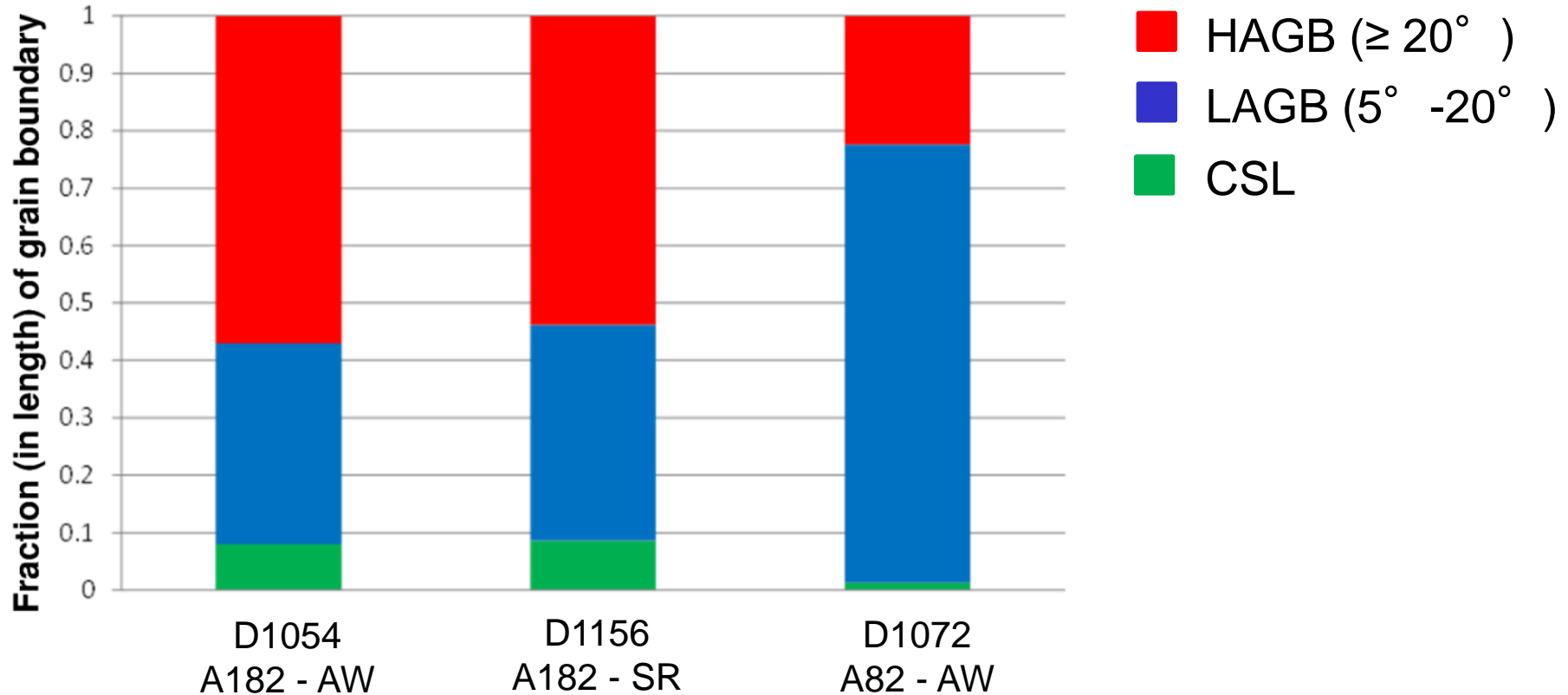


# Chromium content and SCC

- Increasing the chromium content decreases the SCC susceptibility



# Grain boundary character



SEM image

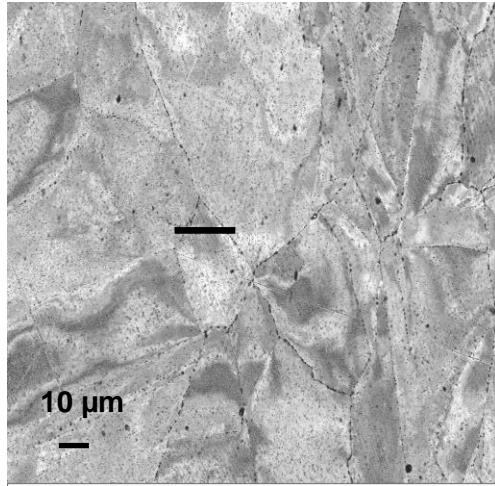
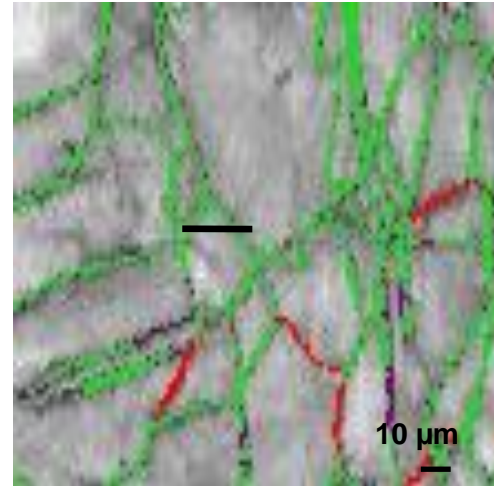
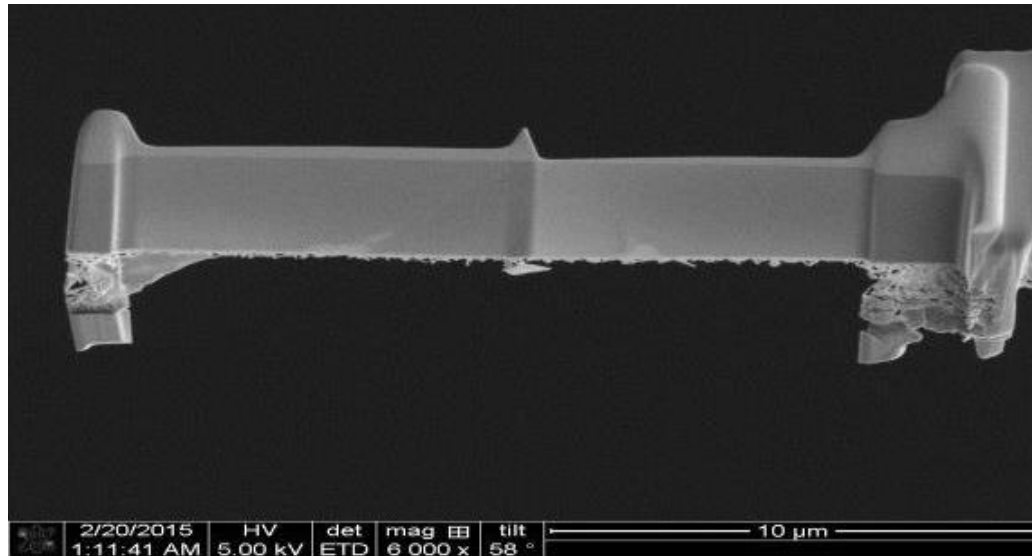


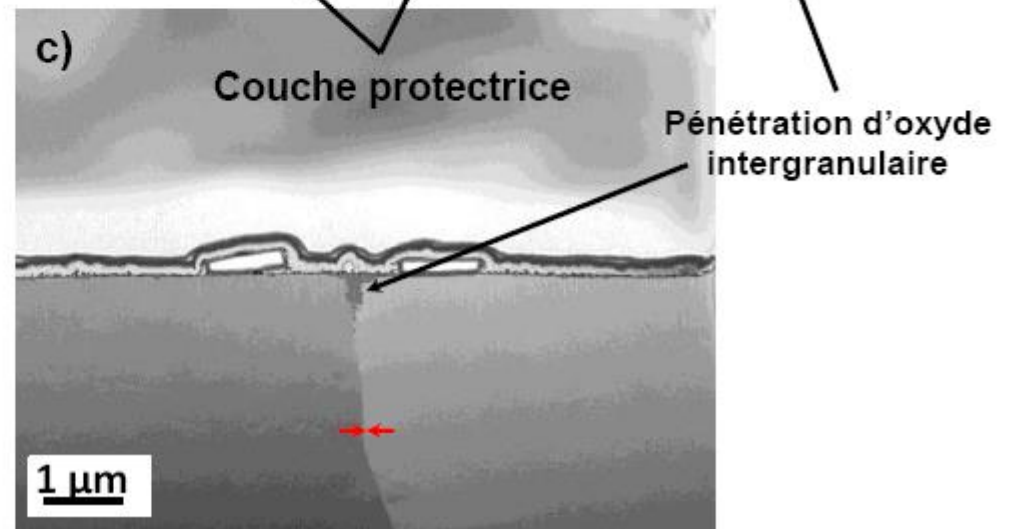
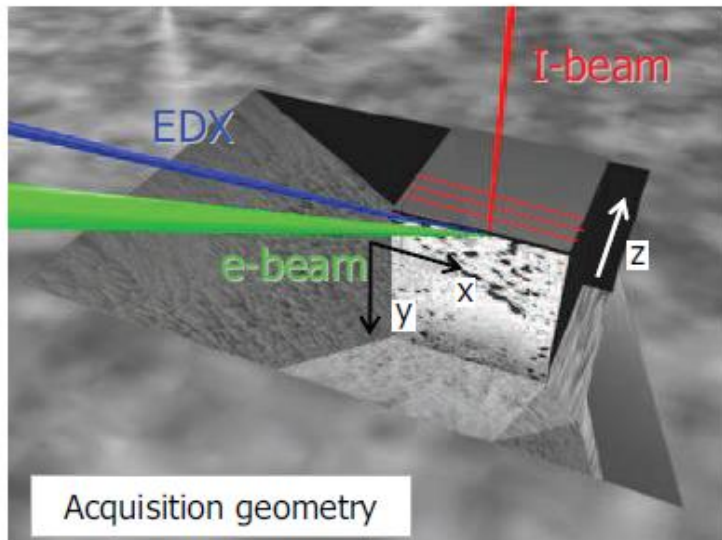
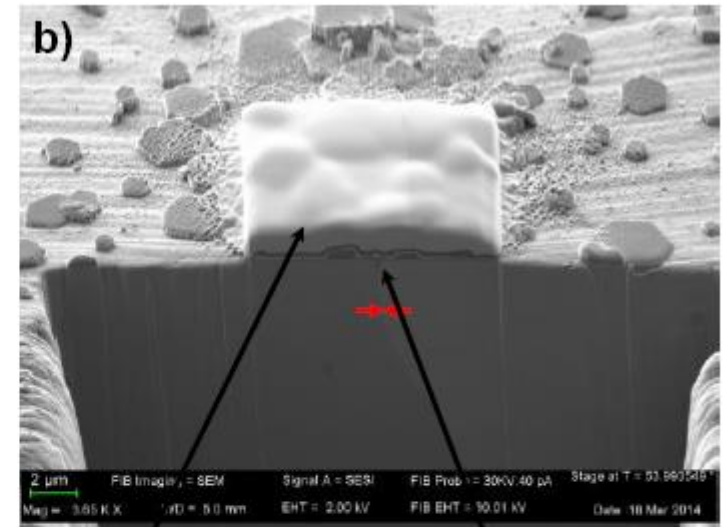
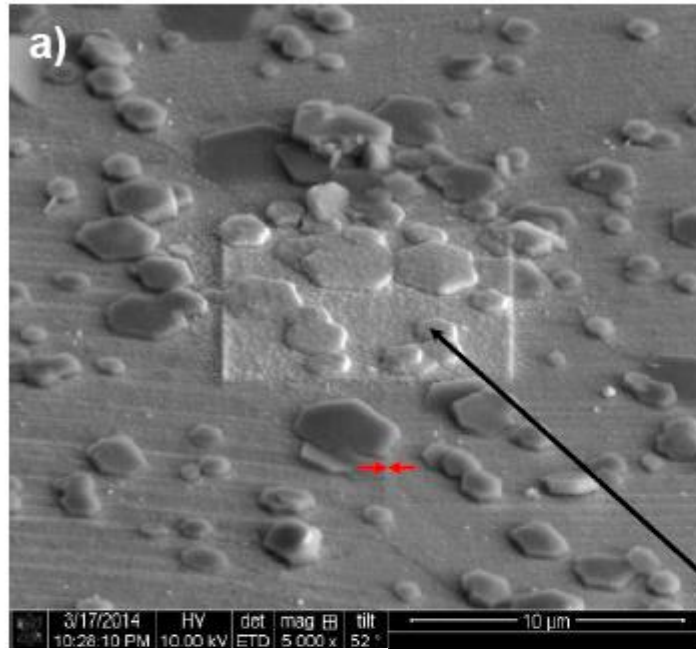
Image Quality map



— LAGB ( $\Delta\theta \leq 15^\circ$ ) — HAGB ( $\Delta\theta > 15^\circ$ )



# FIB/SEM tomography

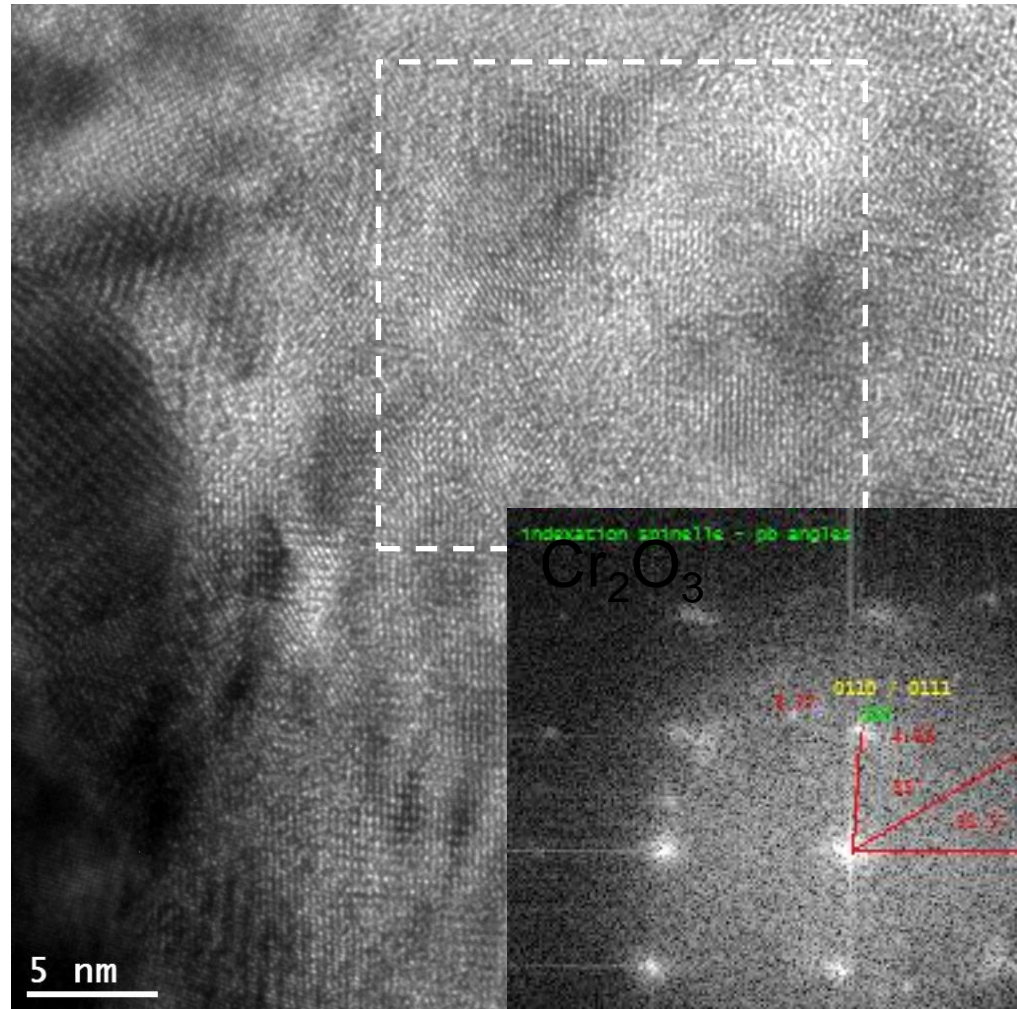
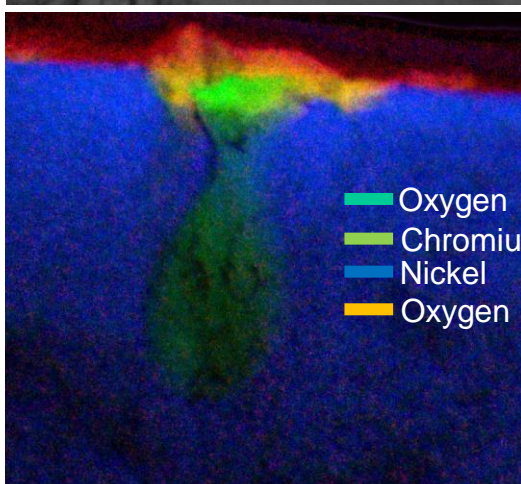
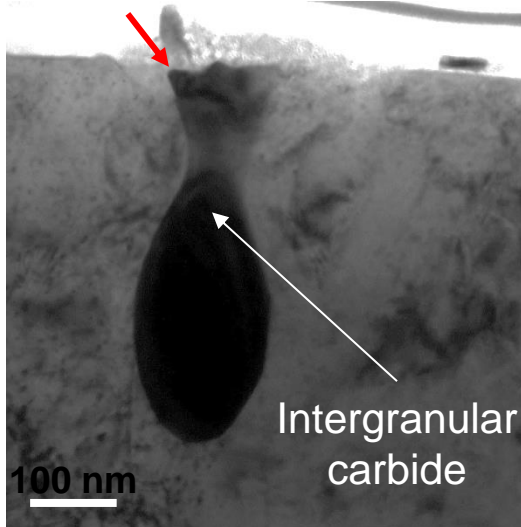


# Oxidation and chromium carbides

Alloy 600  
325° C – 100h  
30 mL H<sub>2</sub>/kg H<sub>2</sub>O

- Formation of Cr<sub>2</sub>O<sub>3</sub> around the carbide

Emerging carbide



J. Caballero, PhD thesis

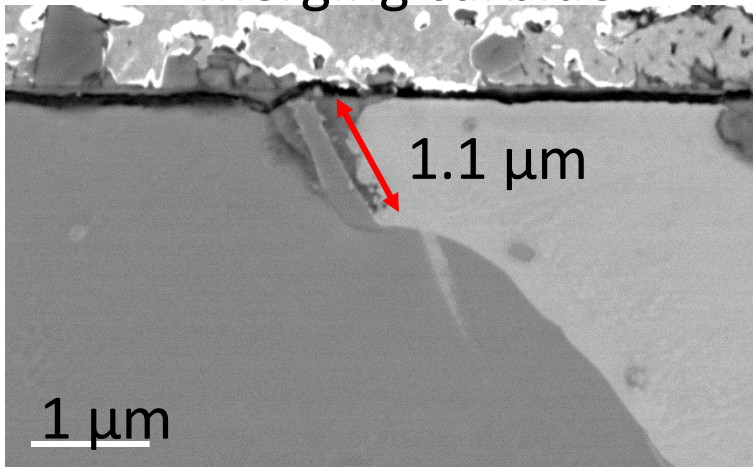
# Emerging vs. non emerging carbides

Alloy 600  
360° C – 1000h  
20 mL H<sub>2</sub>/kg H<sub>2</sub>O

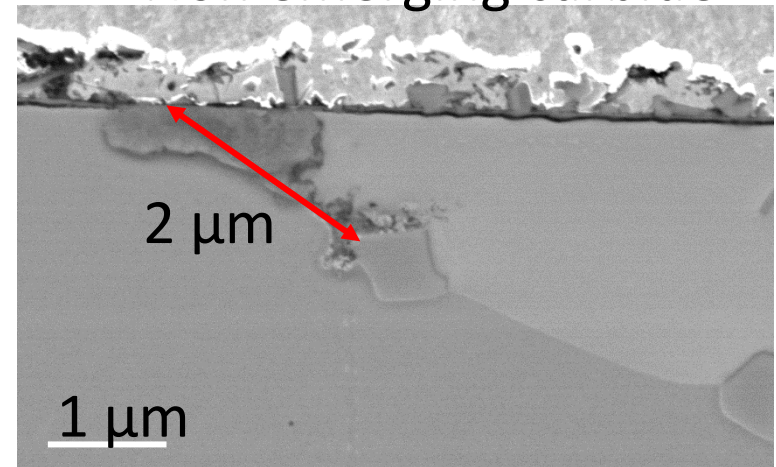
- Enhanced reactivity at the interfaces between carbide and matrix
- For long oxidation times , intergranular oxidation depth seems shorter in case of emerging carbides.

1000h

Emerging carbide



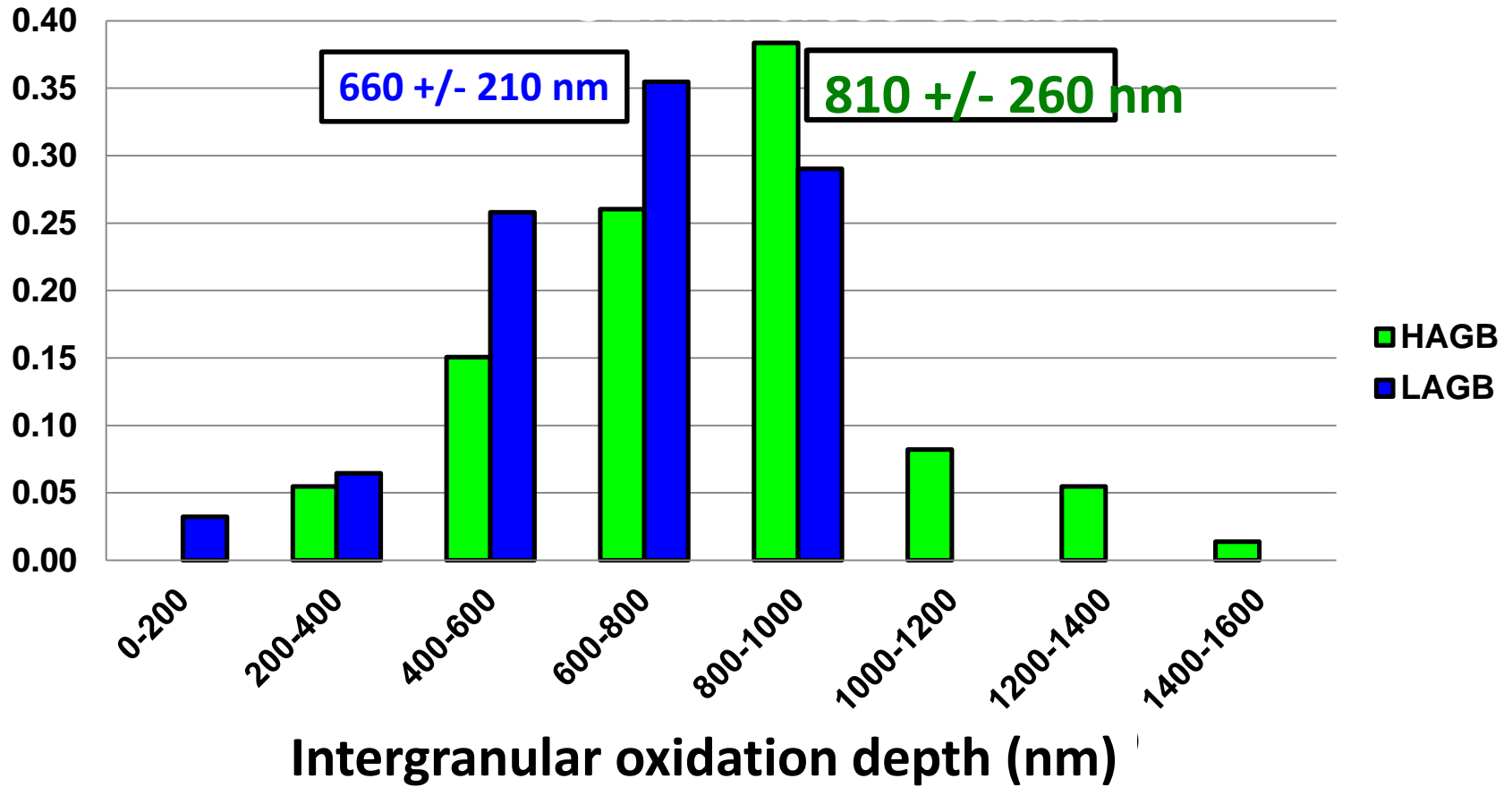
Non emerging carbide



# Grain boundary character and oxidation

Alloy 182  
360° C – 1000h  
30 mL H<sub>2</sub>/kg H<sub>2</sub>O

- Higher intergranular oxidation depth along HAGB than along LAGB

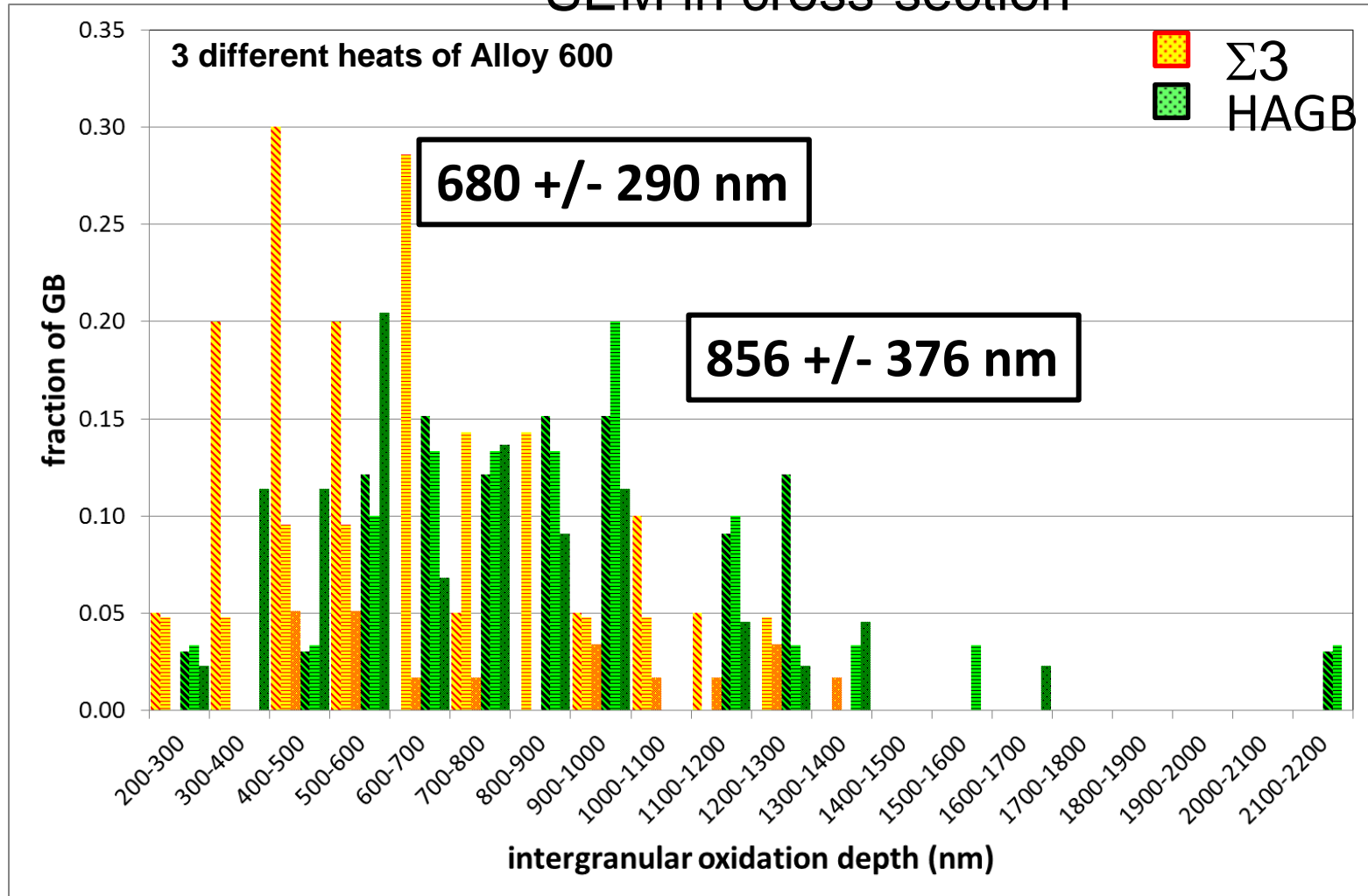


# Grain boundary character and oxidation

Alloy 600  
360° C – 1000h  
20 mL H<sub>2</sub>/kg H<sub>2</sub>O

- Higher intergranular oxidation depth along HAGB than along  $\Sigma 3$

## SEM in cross-section



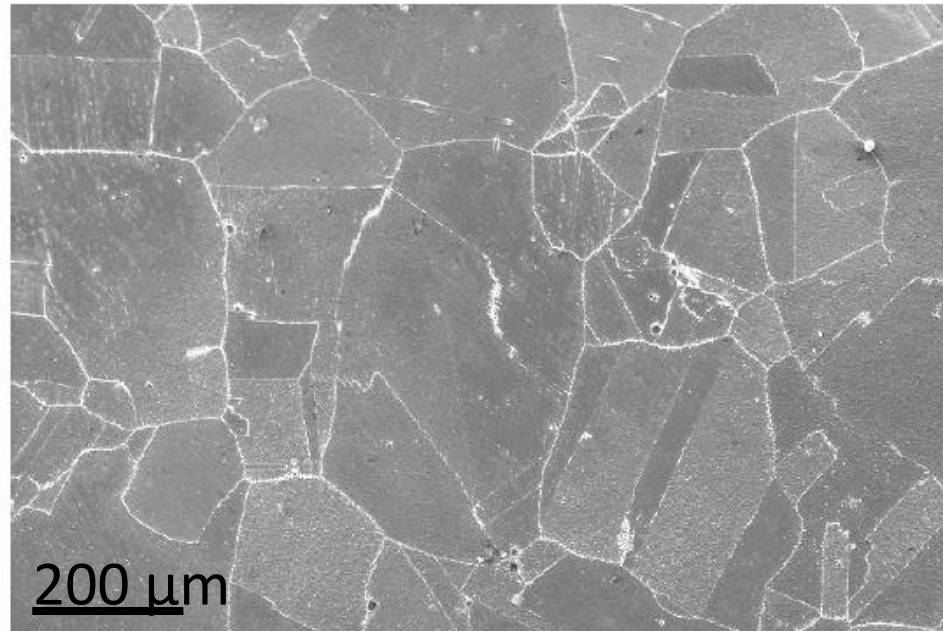
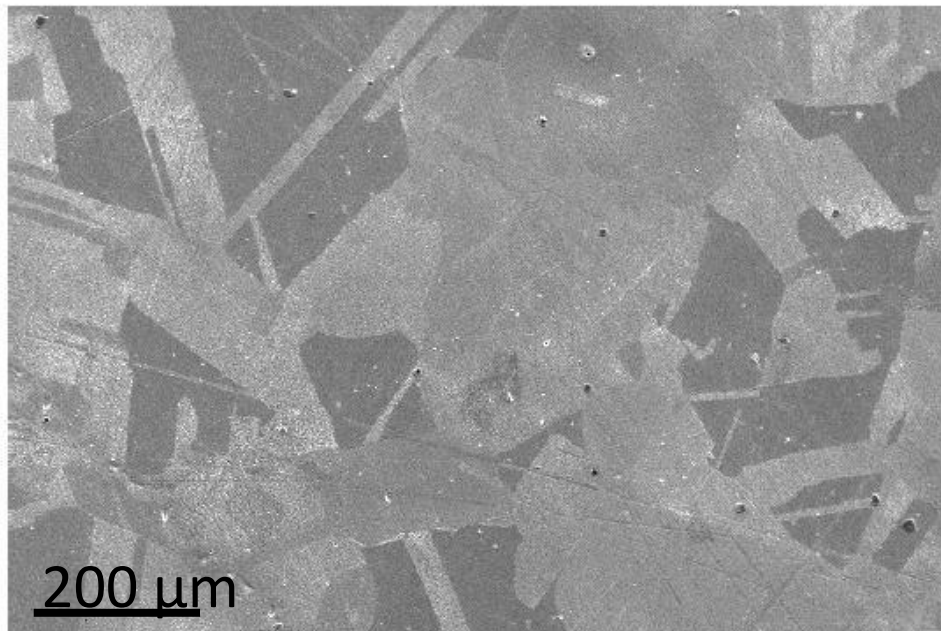


# What about GB with no carbides?

- Need for **model microstructures**
- Model microstructures prepared from a commercial heat of Alloy 600

SOLUTION-ANNEALED

SOLUTION-ANNEALED + THERMALLY TREATED

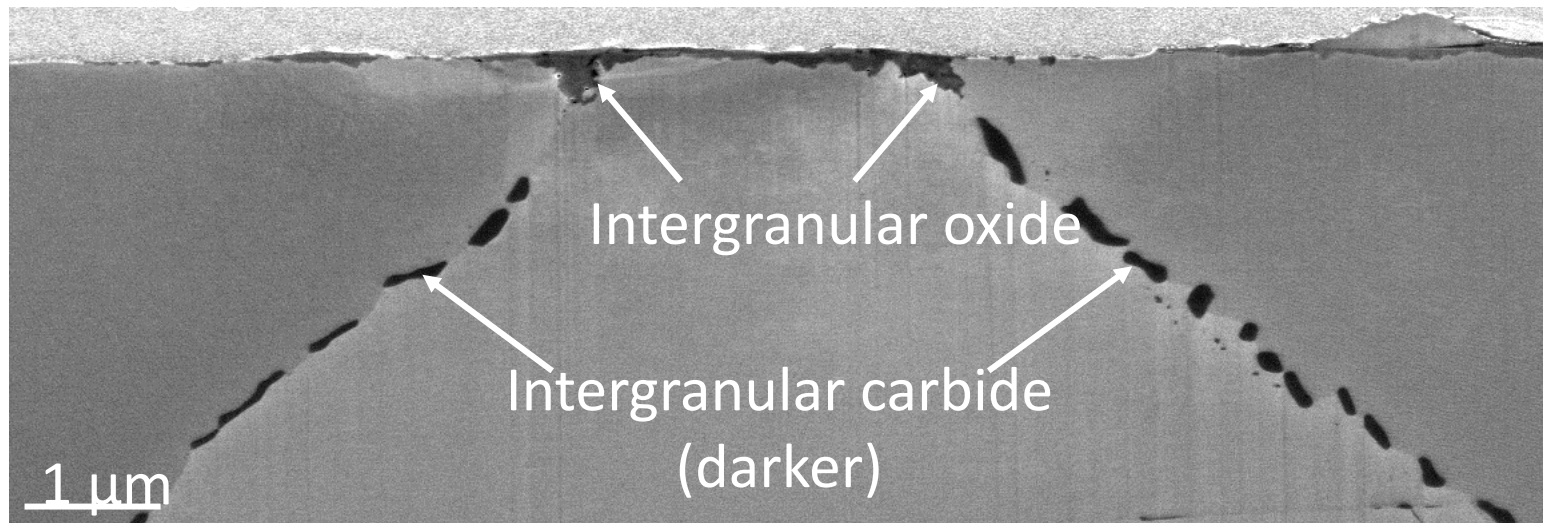
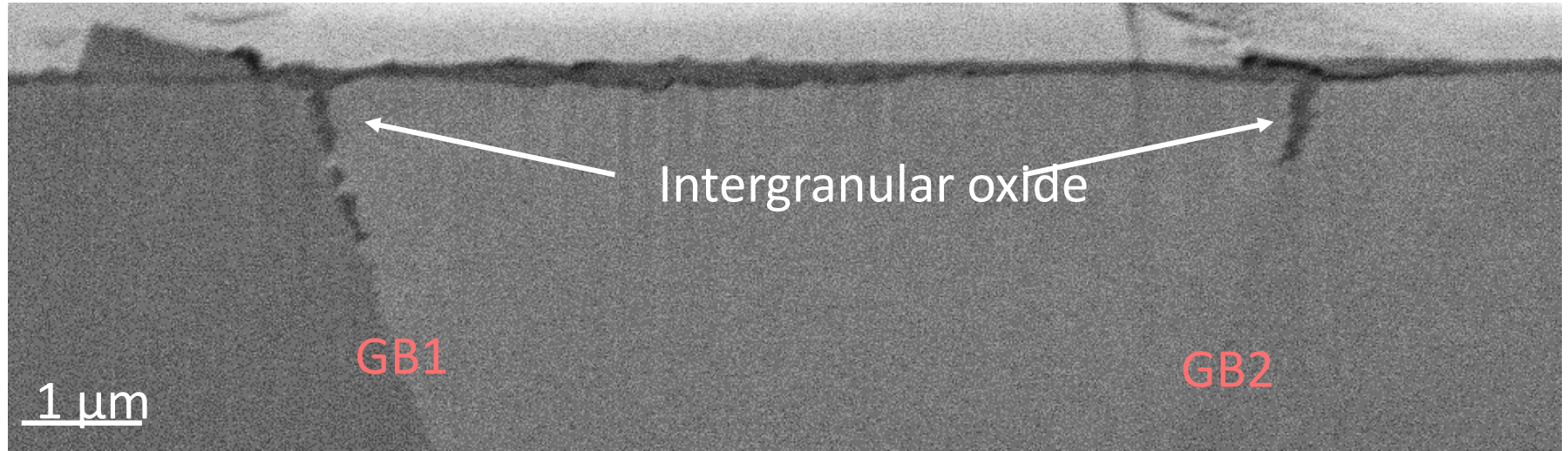


Dissolution of chromium  
carbides

Quasi-continuous  
precipitation of intergranular  
chromium carbide

# Alloys with model microstructures

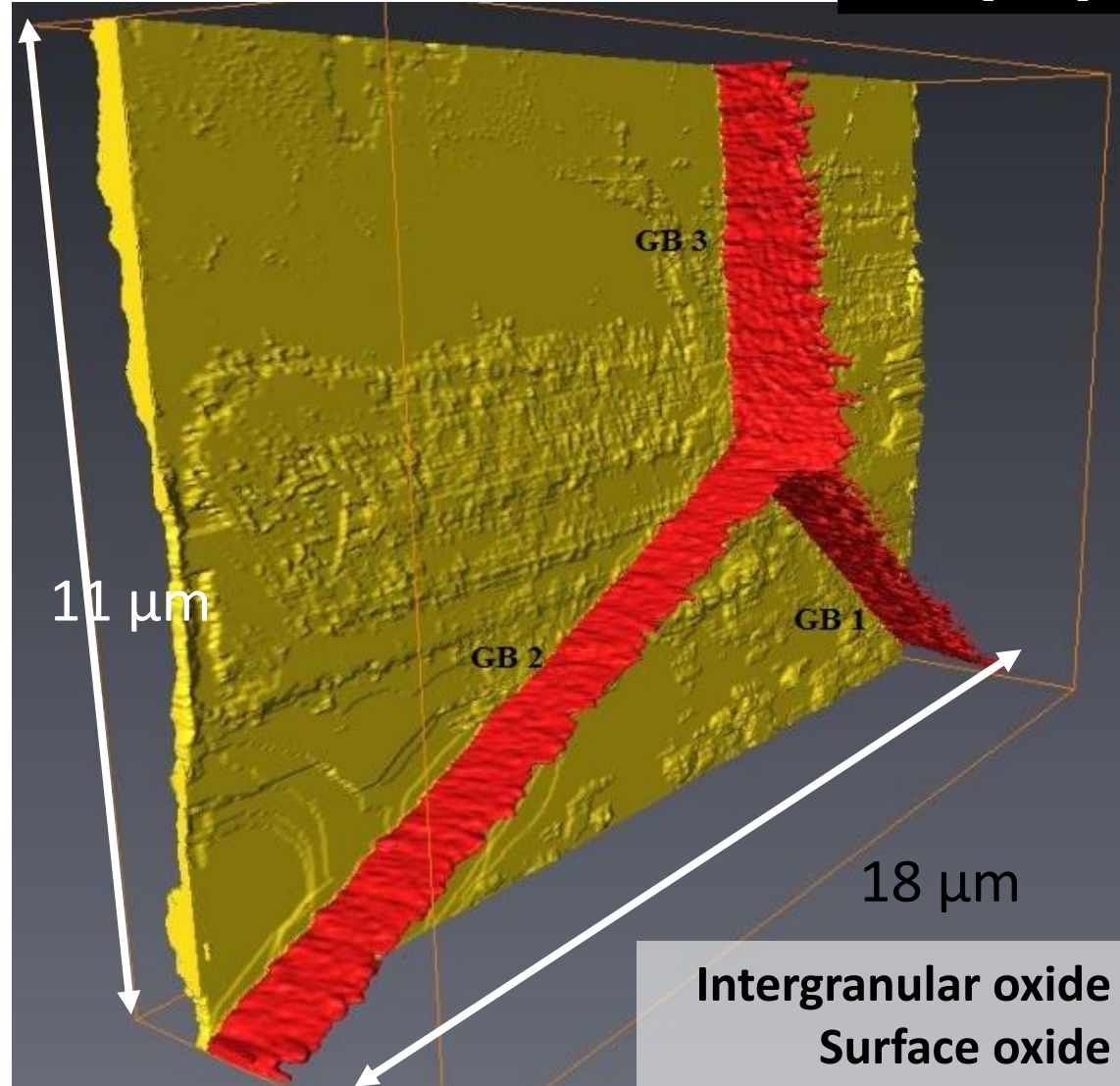
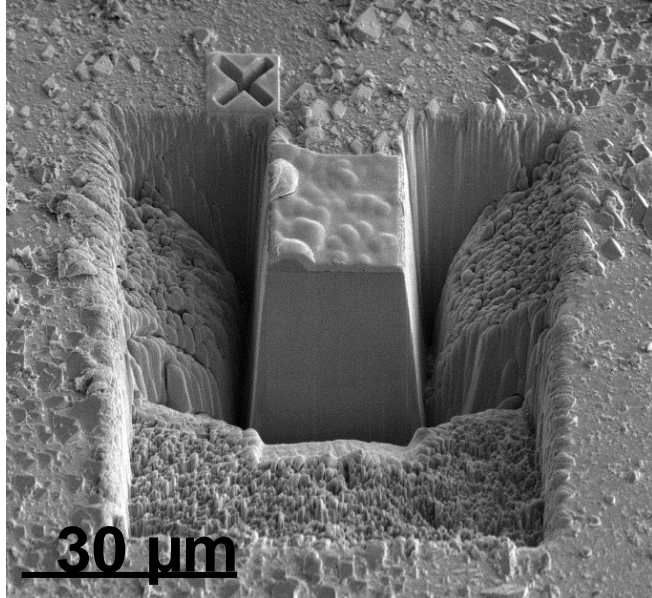
Alloy 600  
325° C – 1400h  
30 mL H<sub>2</sub>/kg H<sub>2</sub>O



# Alloy 600 without carbides

Alloy 600  
325° C – 1400h  
30 mL H<sub>2</sub>/kg H<sub>2</sub>O

## FIB 3D Slicing



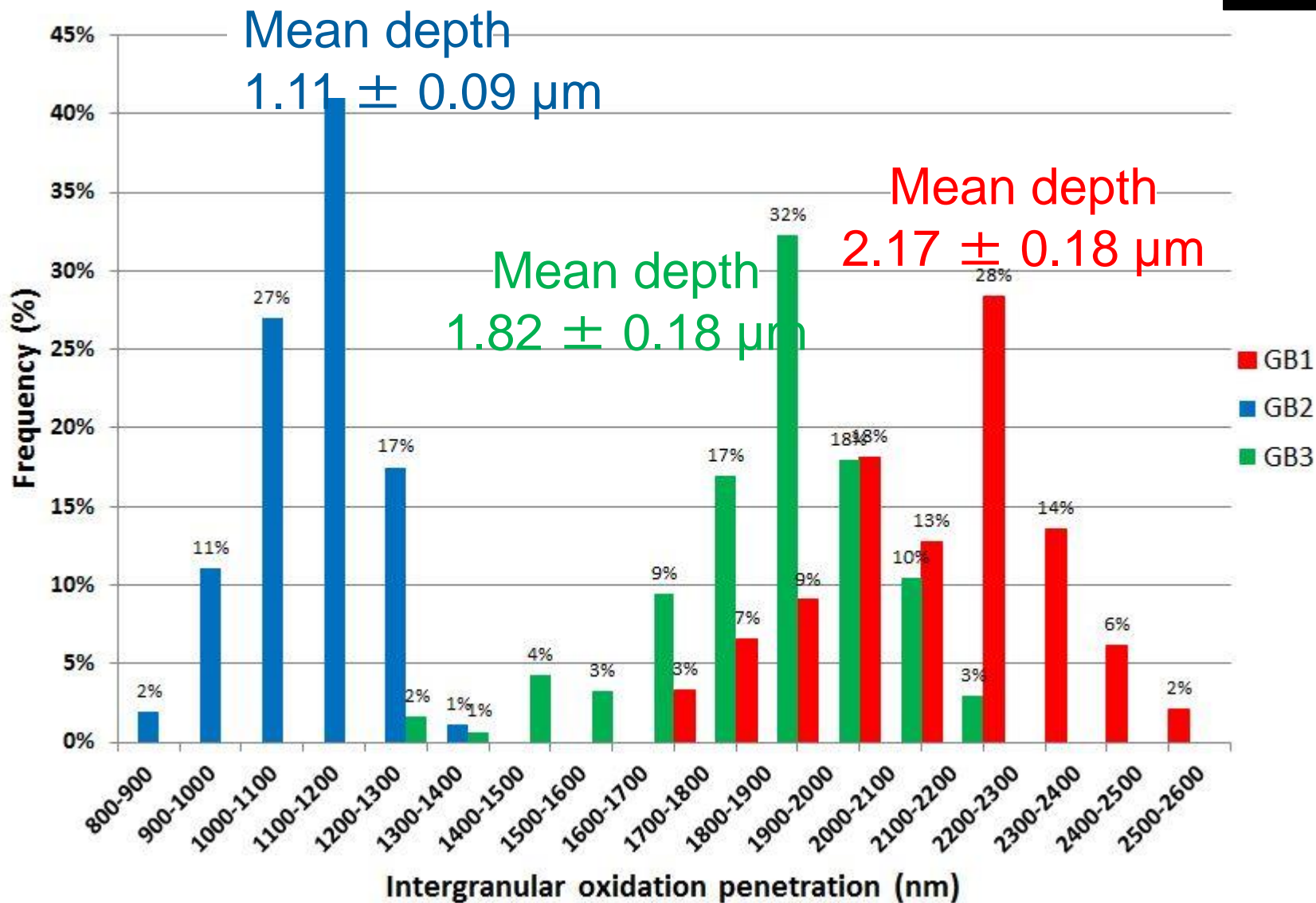
FIB/SEM facility  
Equipex MATMECA

H.T. Le, internship (2015)

F. Gaslain et al., 14th European Workshop on modern developments and applications in microbeam analysis (2015)

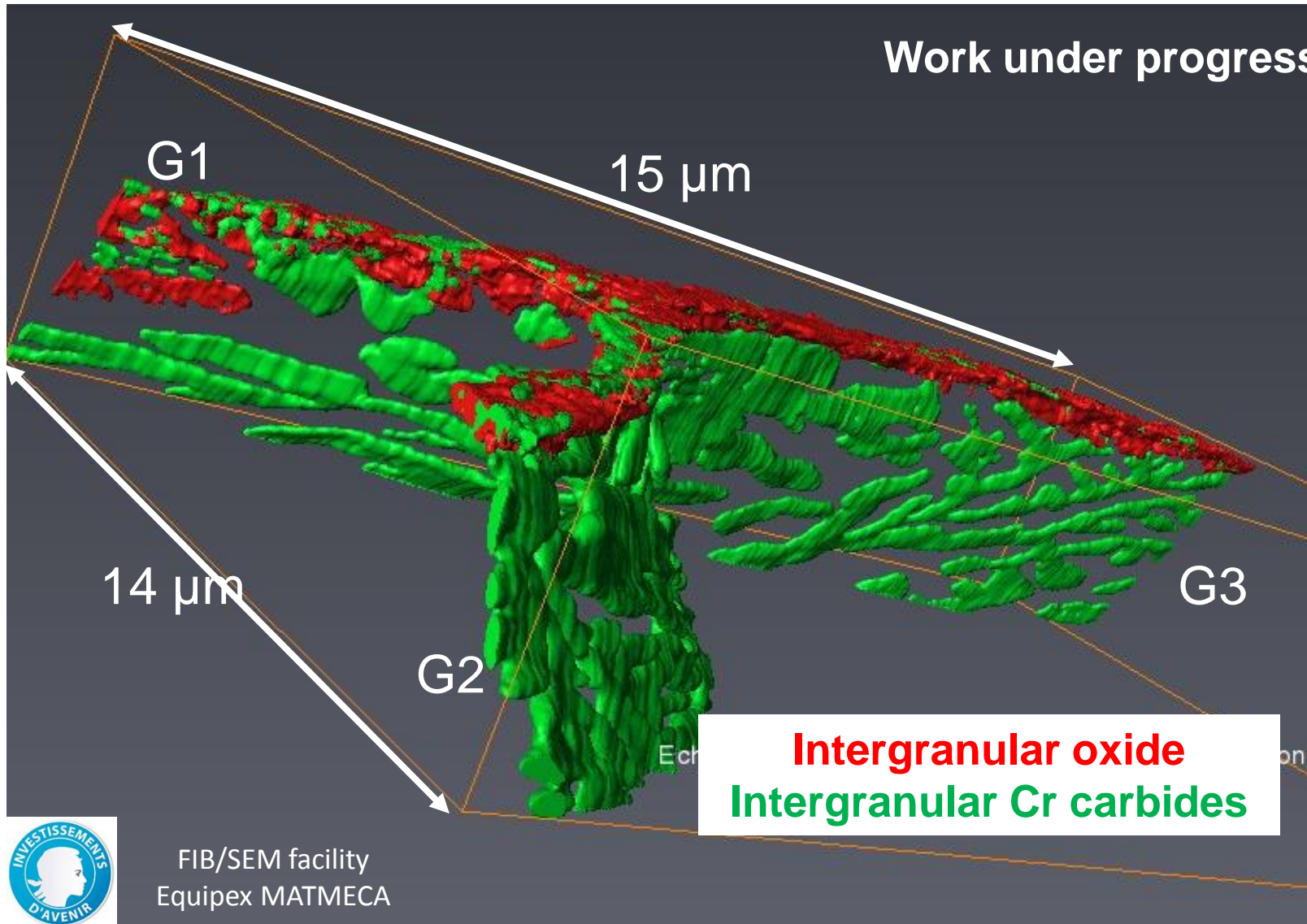
# Alloy 600 without carbides

Alloy 600  
325° C – 1400h  
30 mL H<sub>2</sub>/kg H<sub>2</sub>O



# Alloy 600 with carbide precipitation

Alloy 600  
325° C – 1400h  
30 mL H<sub>2</sub>/kg H<sub>2</sub>O

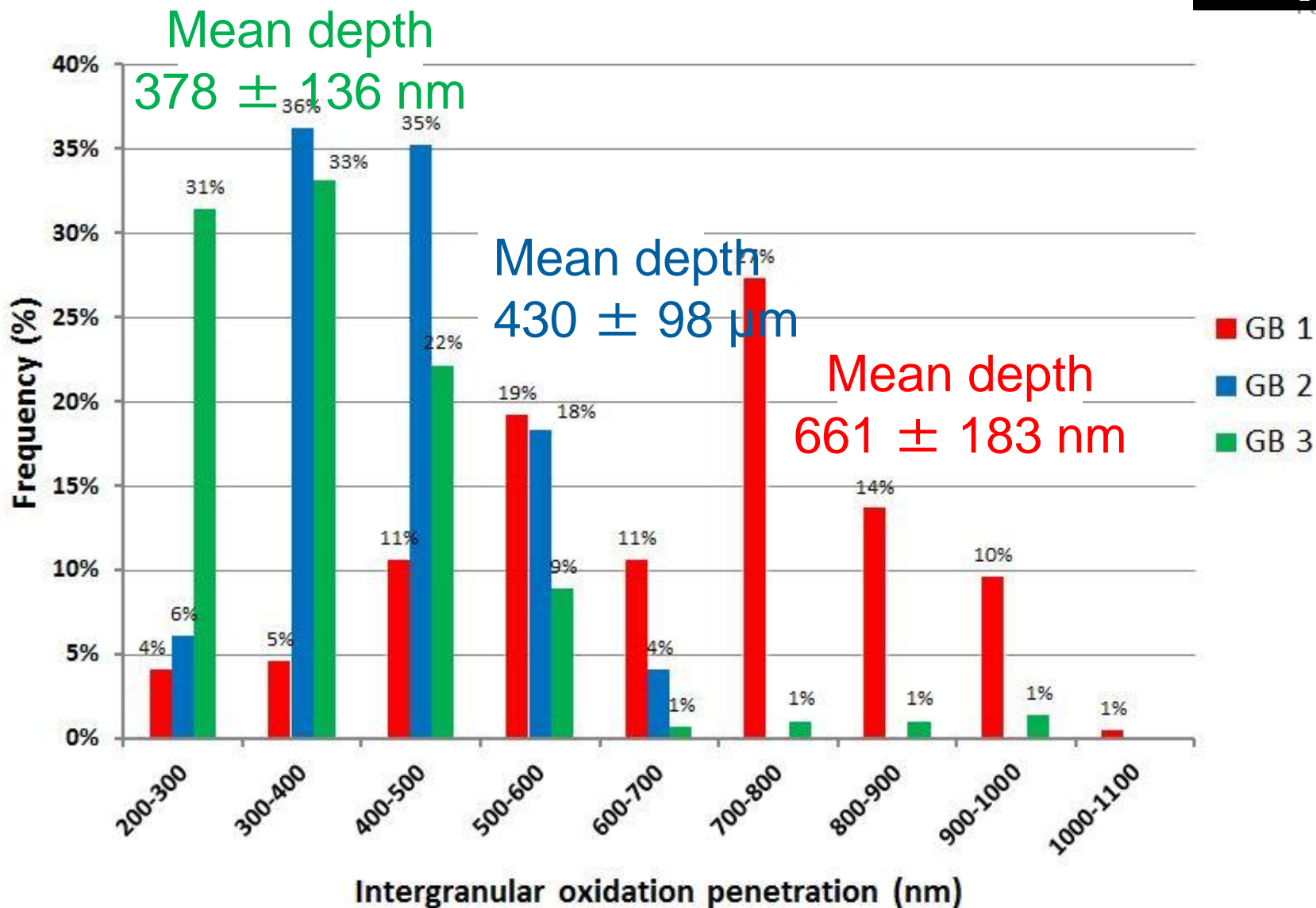


H.T. Le, internship (2015)

F. Gaslain et al., 14th European Workshop on modern developments and applications in microbeam analysis (2015)

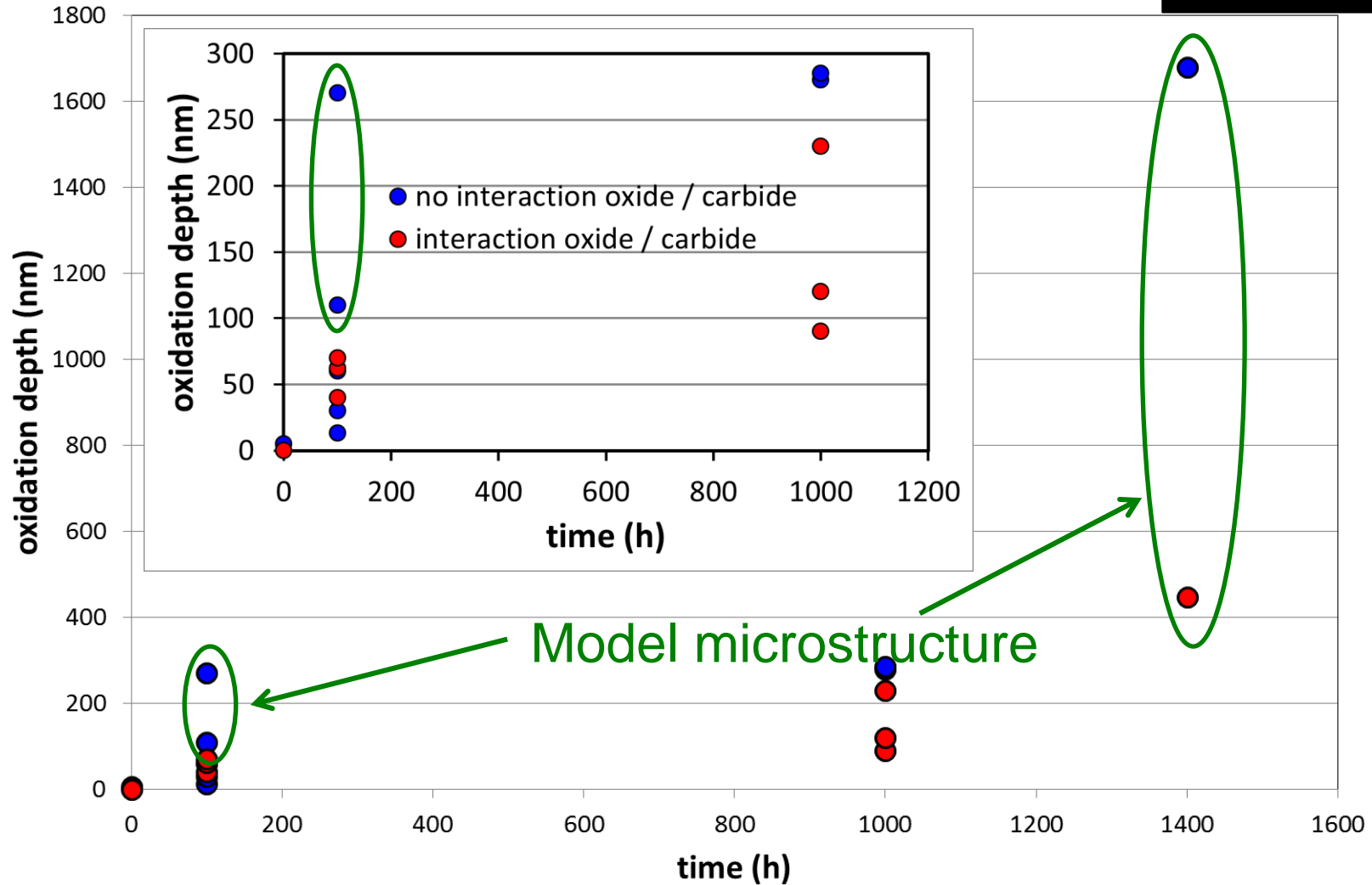
# Alloy 600 with IG chromium carbides

Alloy 600  
325° C – 1400h  
30 mL H<sub>2</sub>/kg H<sub>2</sub>O



# Oxidation kinetics at 325° C

Alloy 600 – Alloy 182  
325° C  
30 mL H<sub>2</sub>/kg H<sub>2</sub>O



- **Beneficial effect of intergranular Cr carbides on IG oxidation significant:**
  - for long oxidation times ( $t \geq 1000\text{h}$ )
  - when compared to solution-annealed specimens ( $t = 100\text{h}$ )

- IG oxidation deeper along:
  - HAGB than LAGB
  - HAGB than  $\Sigma 3$
- Beneficial effect of intergranular chromium carbides on IG oxidation
- What is the effects of carbide type ( $\text{Cr}_7\text{C}_3$ ,  $\text{Cr}_{23}\text{C}_6$ ), carbide distribution, carbide size on IG oxidation?
- Coupled effect grain boundary character / IG carbide precipitation?
- What is the nature of the oxide / carbide interaction?
  - Change in the nature of the oxide:  $\text{Cr}_2\text{O}_3$  rather than spinel-type oxide?
  - Change in the oxidation kinetics: slower at the oxide / carbide interface rather than at the alloy GB?



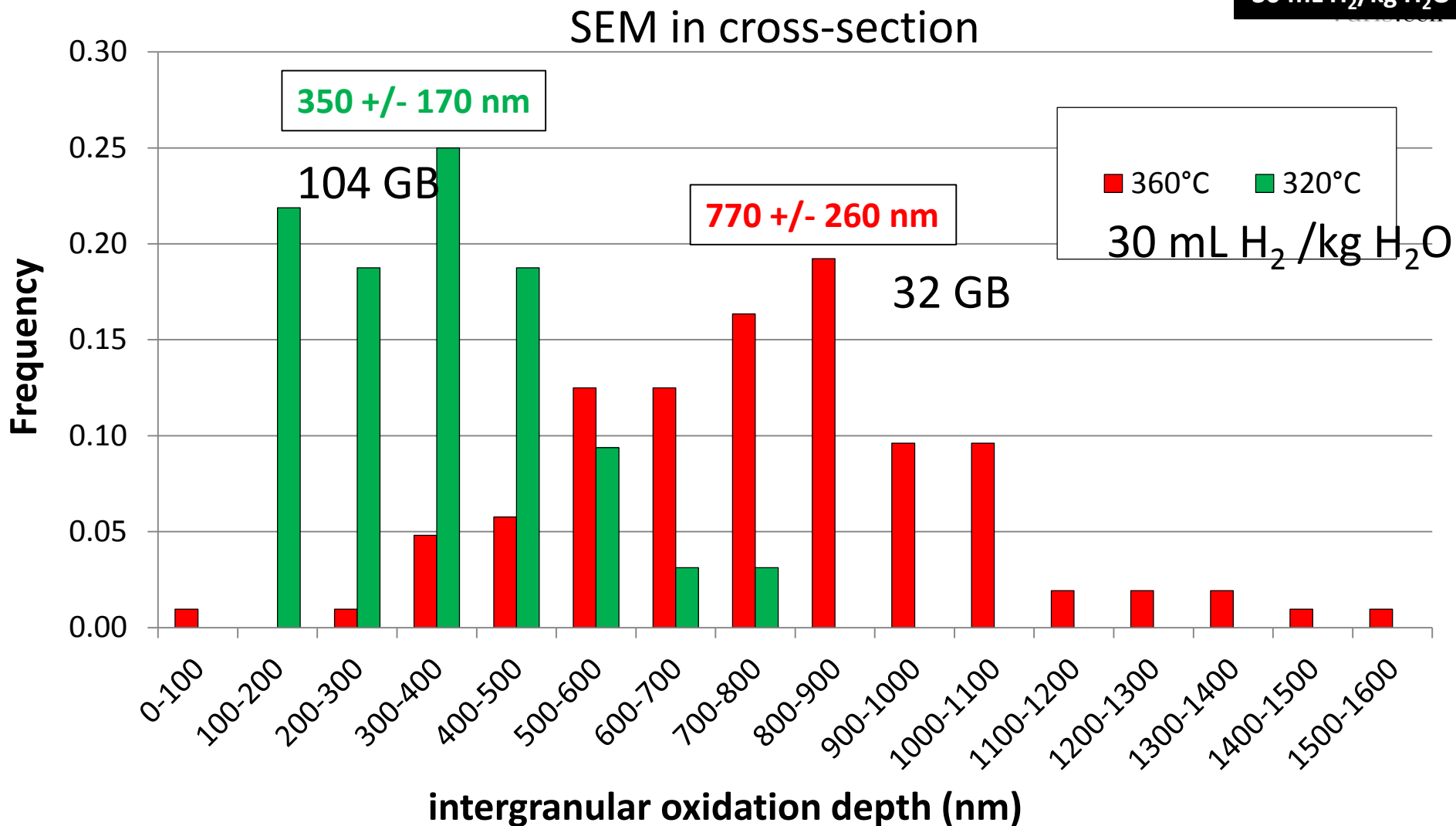
Need for more statistical data and model microstructures



- Metallurgical factors
  - Grain boundary character
  - Intergranular chromium carbides
  
- Environment
  - Temperature
  - Dissolved hydrogen content
  
- Mechanical factors
  - Pre-straining
  - Oxidation under stress

# Temperature

Alloy 182  
1000h  
30 mL H<sub>2</sub>/kg H<sub>2</sub>O



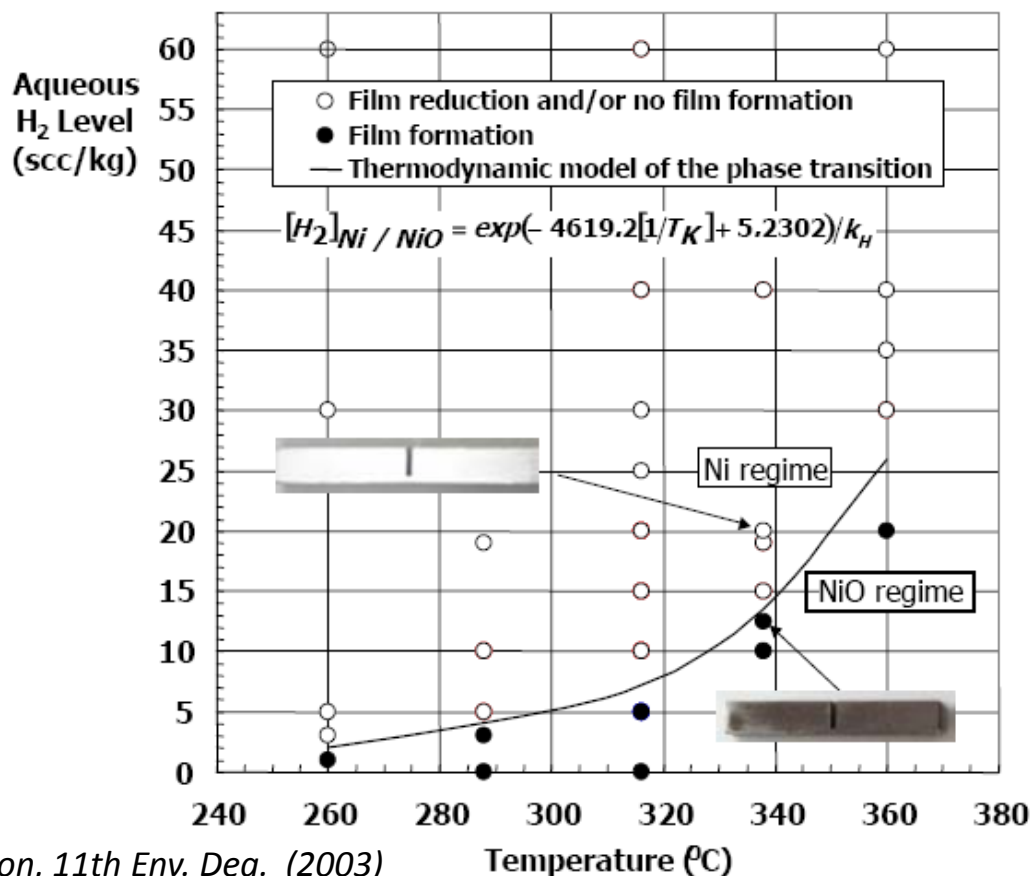
Estimated activation energy for intergranular oxidation:  $Q \approx 57 \text{ kJ.mol}^{-1}$

# Environmental factors and SCC

Two main factors:

- Temperature
  - Dissolved hydrogen content
- } Electrochemical potential (EcP)

$$\Delta EcP = EcP_{Ni / NiO} - EcP_{metal} = 1000 (RT / 2F) \ln ([H_2]_{test} / [H_2]_{Ni / NiO})$$



# Environmental factors and SCC

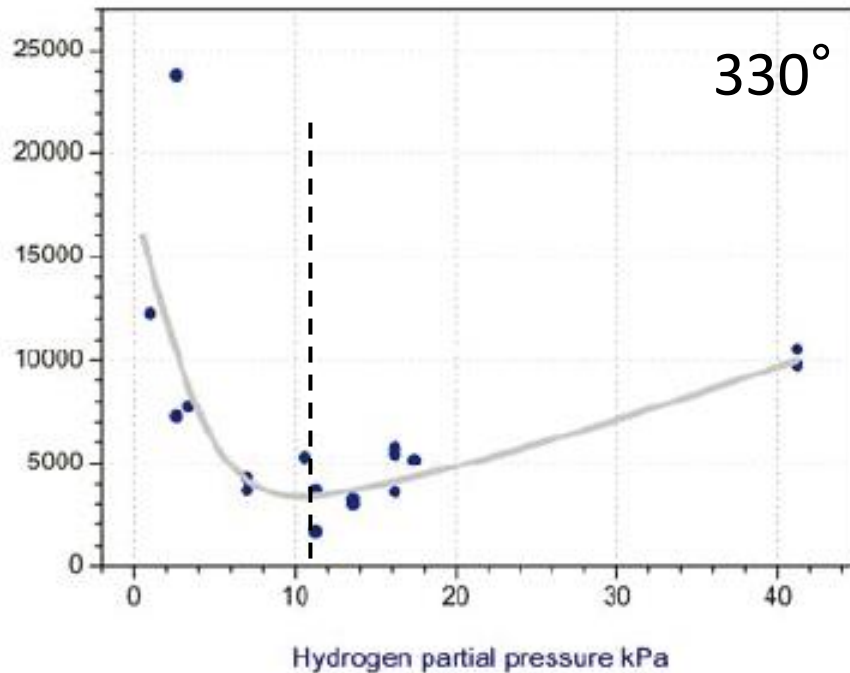
- Activation energy for crack initiation: 30 – 220 kJ.mol<sup>-1</sup>

Activation energy measured for a constant EcP: 140 ± 33 kJ.mol<sup>-1</sup>

*Richey et al., 12th Env. Deg. (2005)*

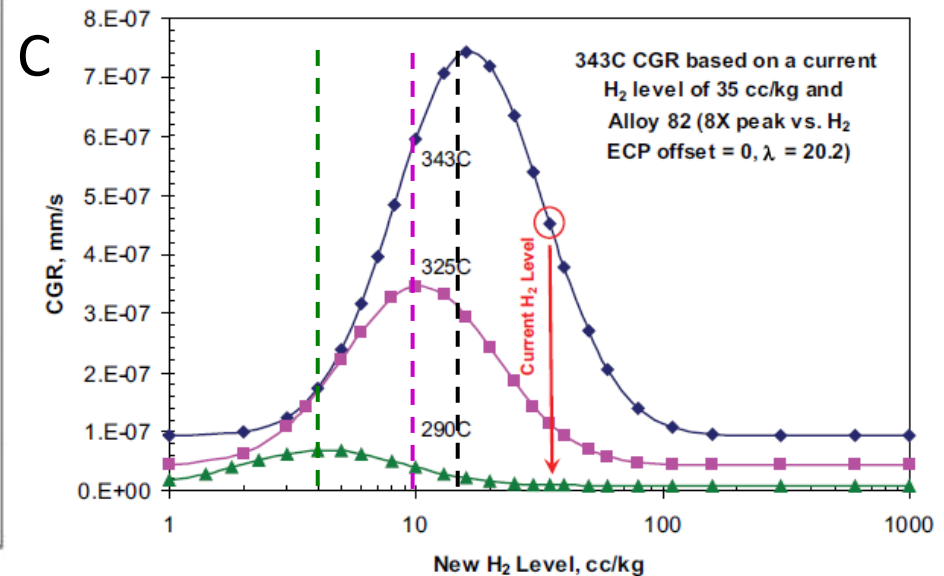
- Effect of H<sub>2</sub> content  
INITIATION

*P. Andresen (2007)*



*A. Molander et al., 15<sup>th</sup> Env. Deg. (2011)*

## PROPAGATION

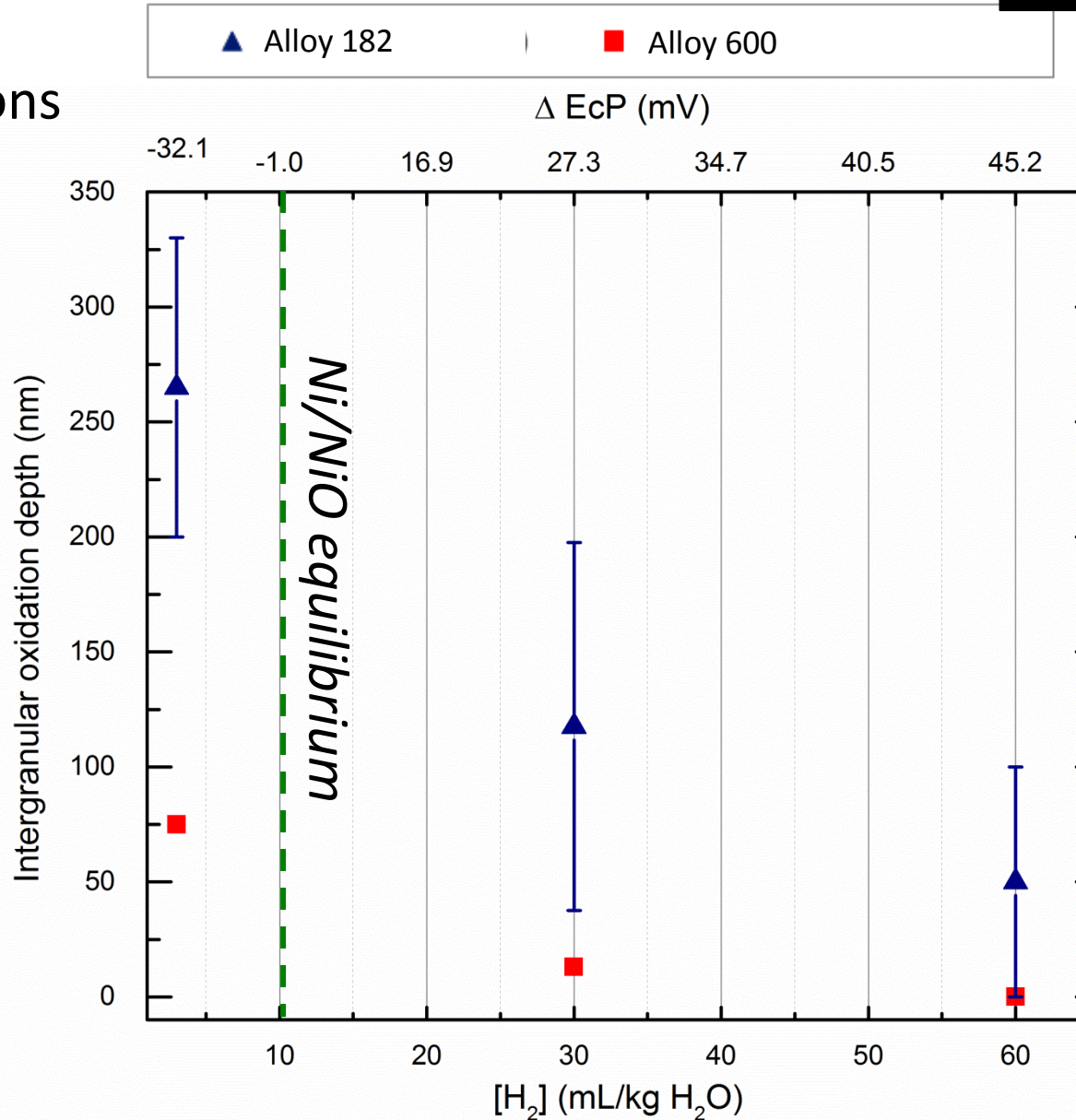


Maximum crack growth rate at the Ni/NiO equilibrium

# Dissolved hydrogen content

Alloy 182 – Alloy 600  
325° C  
100h

325° C - 100h  
TEM observations

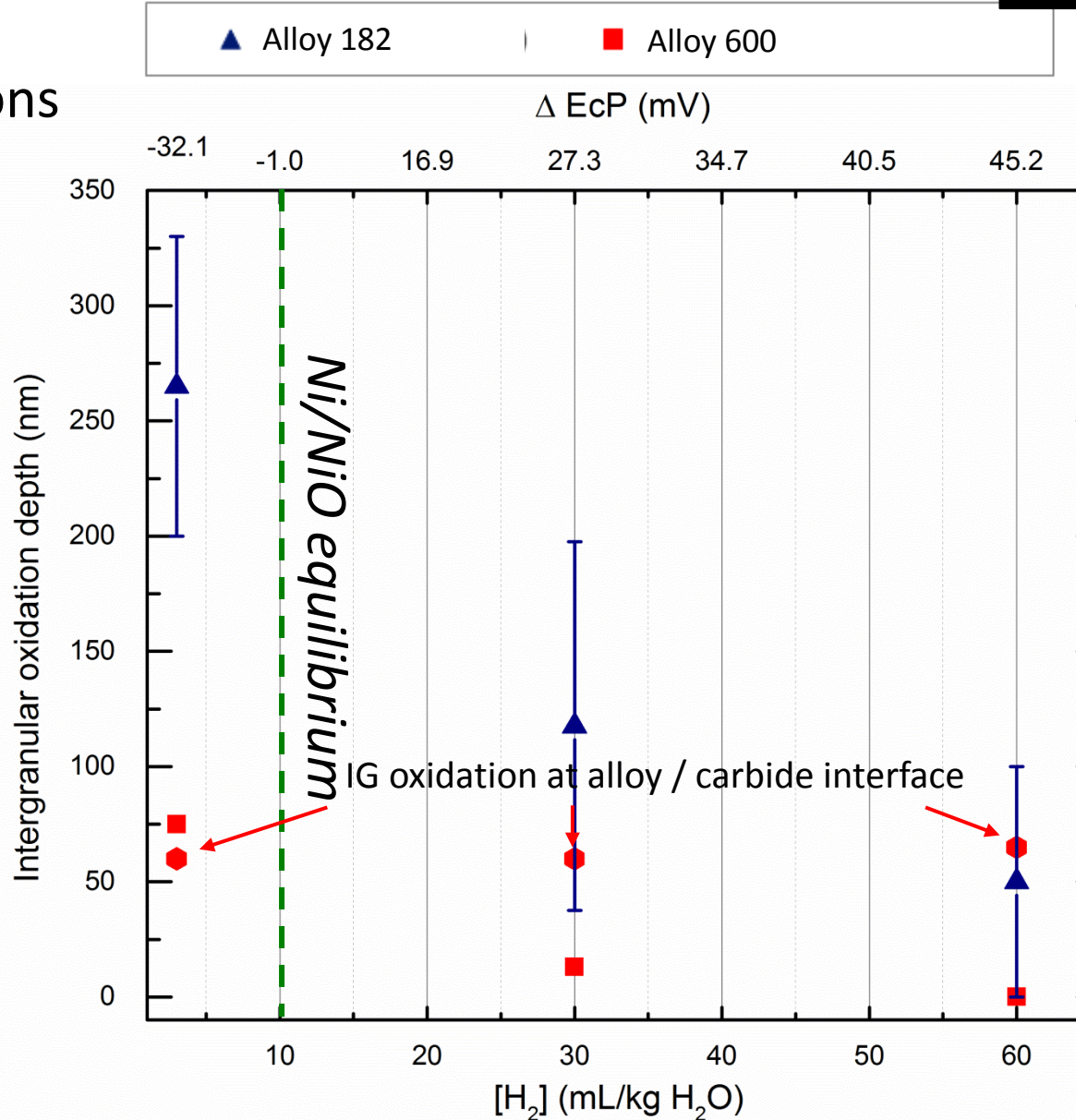


M. Wehbi, PhD thesis (2014)  
J. Caballero, PhD thesis

# Dissolved hydrogen content

Alloy 182 – Alloy 600  
325° C  
100h

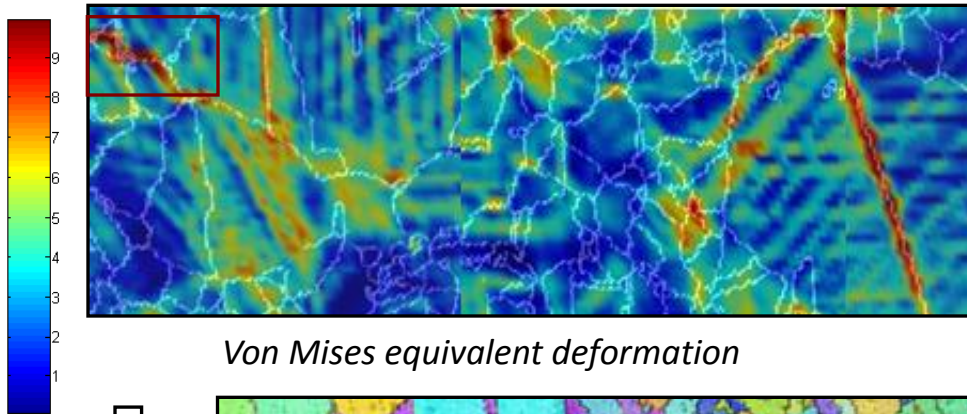
325° C - 100h  
TEM observations



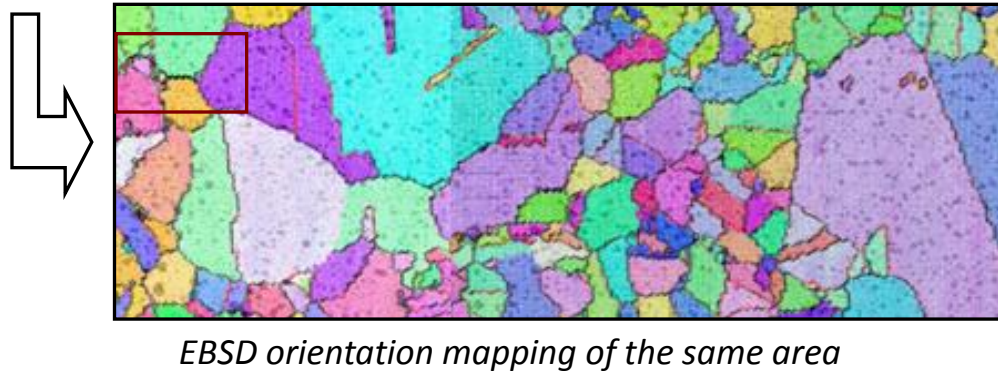
M. Wehbi, PhD thesis (2014)  
J. Caballero, PhD thesis

- Metallurgical factors
  - Grain boundary character
  - Intergranular chromium carbides
  
- Environment
  - Temperature
  - Dissolved hydrogen content
  
- Mechanical factors
  - Pre-straining
  - Oxidation under stress

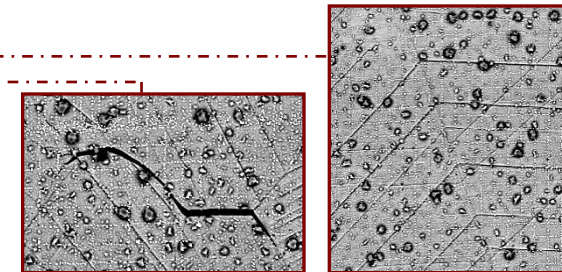
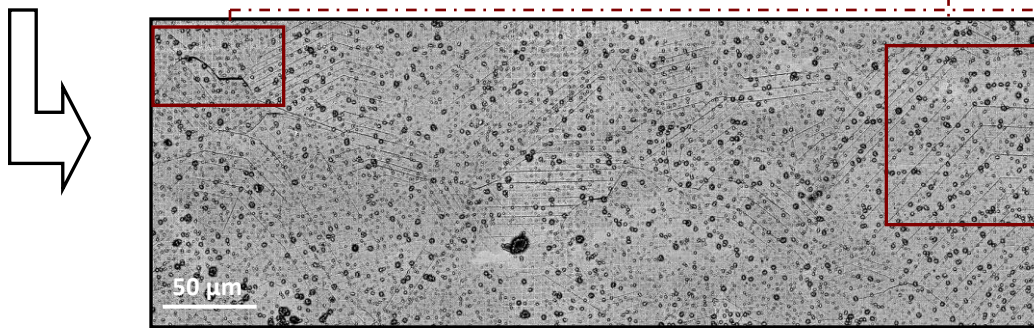
# Coupling between microstructure and strain fields



Strain field measurements  
(Von Mises equivalent deformation)



- Microstructure,
- Crystallographic orientations,
- Grain boundary character,
- Schmid factor,...

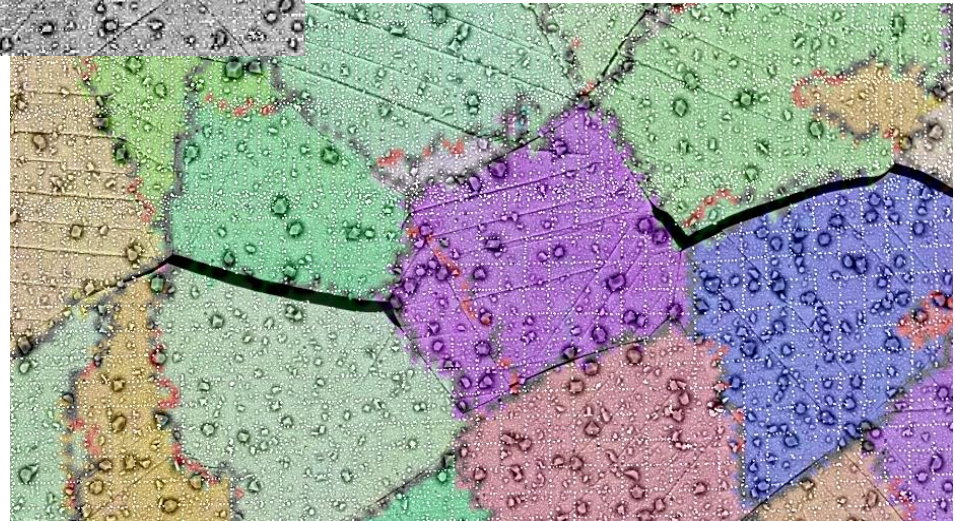
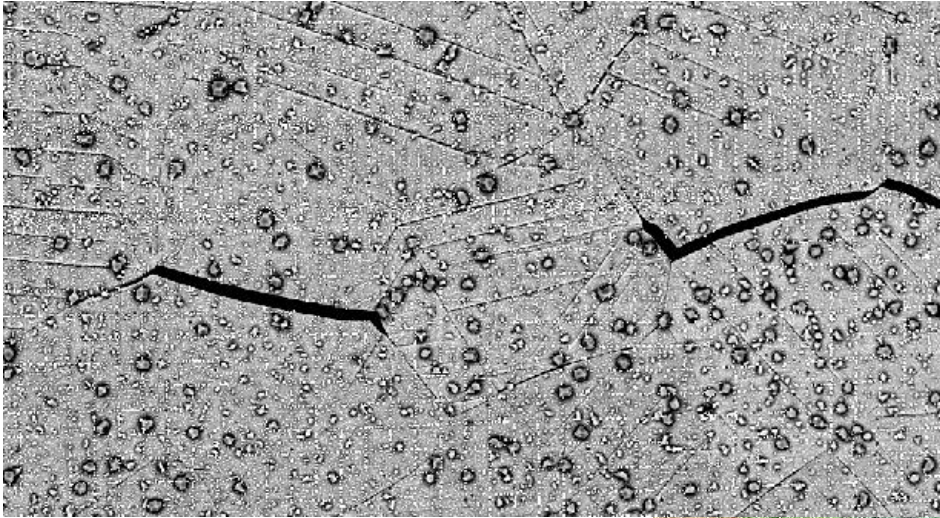


- Cracking features
- Oxidation
- Slip bands

→ Application to IASCC of austenitic stainless steels

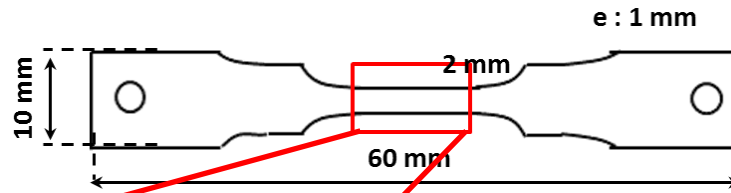


5 dpa, 2% macroscopic strain

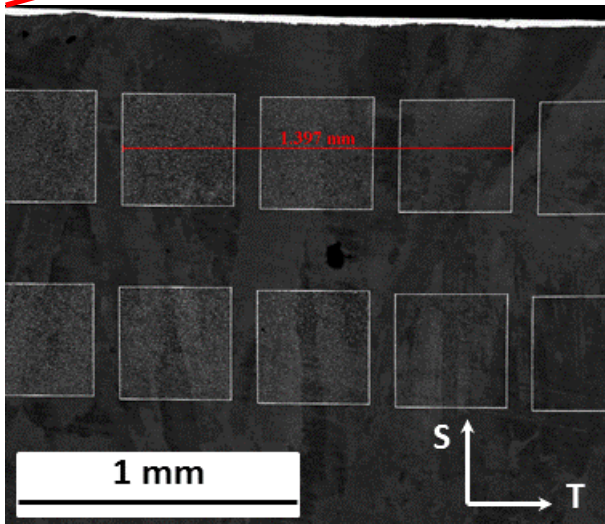


# Effect of pre-straining

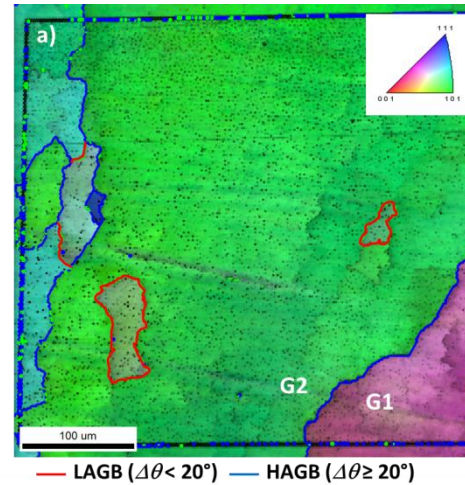
Alloy 82  
360° C - 1000h  
30 mL H<sub>2</sub> / kg H<sub>2</sub>O



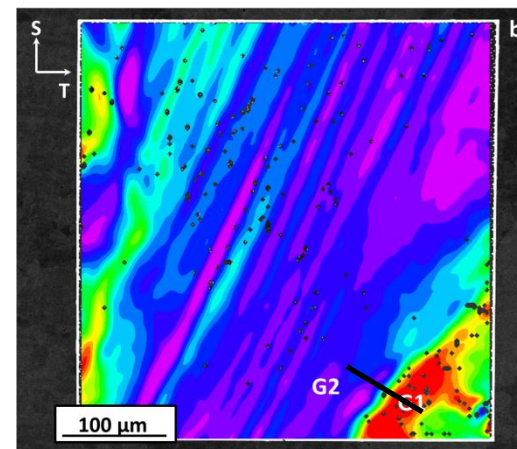
Tensile specimens – mirror finish  
Macroscopic deformation: 0, 7, 20%



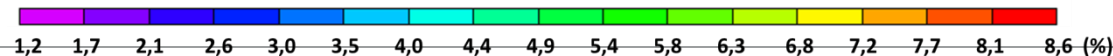
8 fields (400 μm x 400 μm)  
gold speckle (diameter : 1 μm)



EBSD orientation maps



Strain field measurement

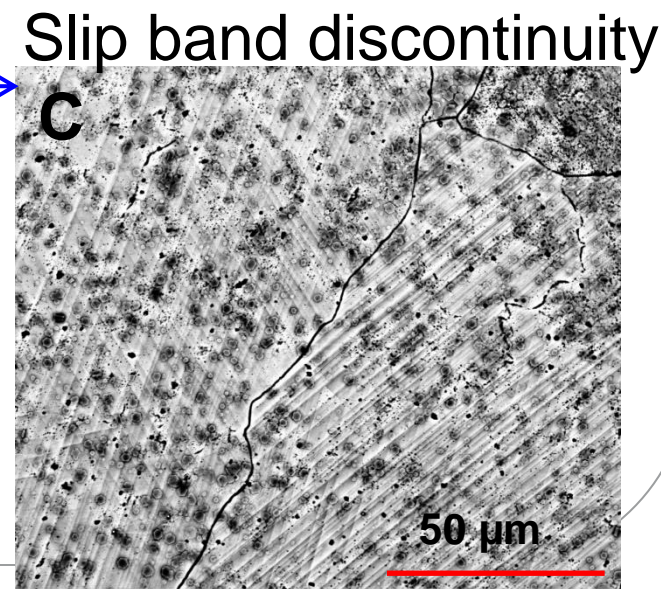
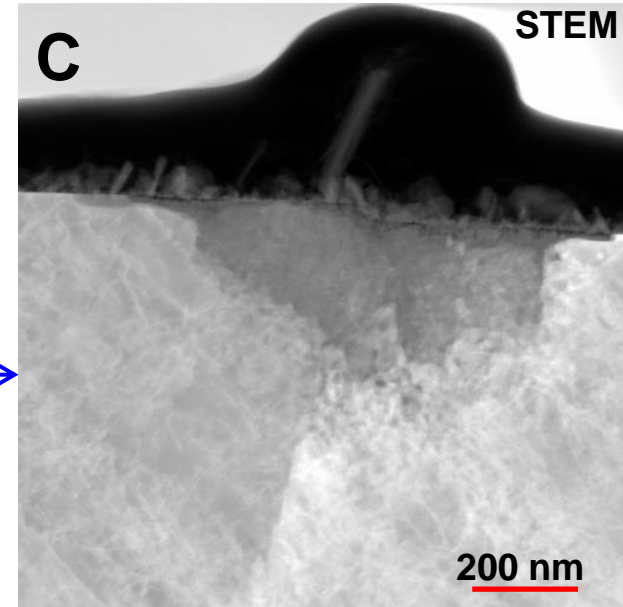


# Effect of pre-straining

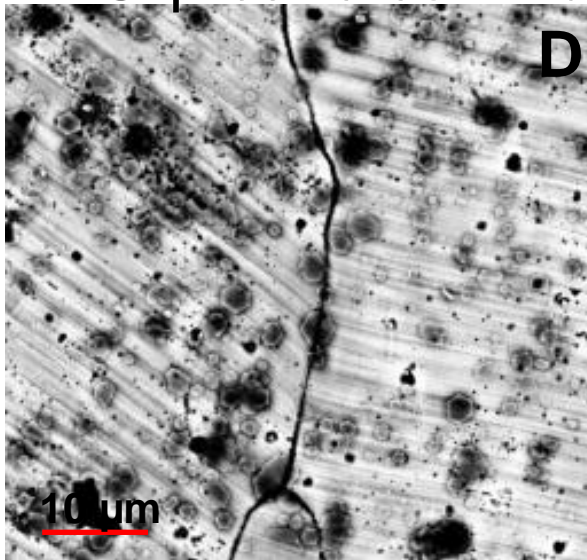
Alloy 82  
360° C - 1000h  
30 mL H<sub>2</sub> / kg H<sub>2</sub>O

## Grain boundaries studied after oxidation

GB	GB misorientation (°)	Mean local strain (%)	Local strain gradient (%)
A	40	0	-
B	5	7	0
C	40	6	6
D	30	13	0



Slip band continuity



Slip band discontinuity

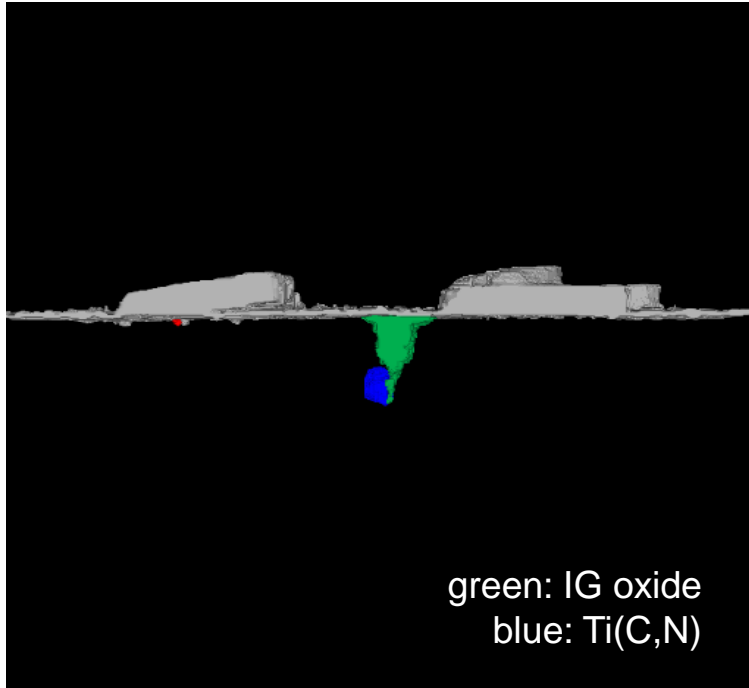
# Effect of pre-straining

Alloy 82  
360° C - 1000h  
30 mL H<sub>2</sub> / kg H<sub>2</sub>O

Grain boundary D

Grain boundary length: 6  $\mu\text{m}$

$\epsilon_{\text{von Mises}}$  : 0,13 – strain discrepancy: 0 %

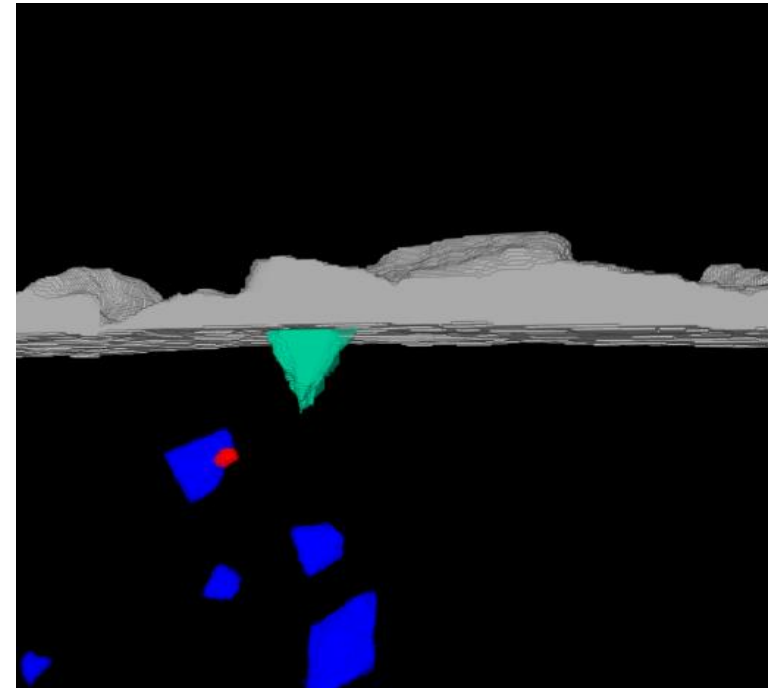


Mean oxidation depth:  
550 +/- 50 nm

Grain boundary C

Grain boundary length : 3  $\mu\text{m}$

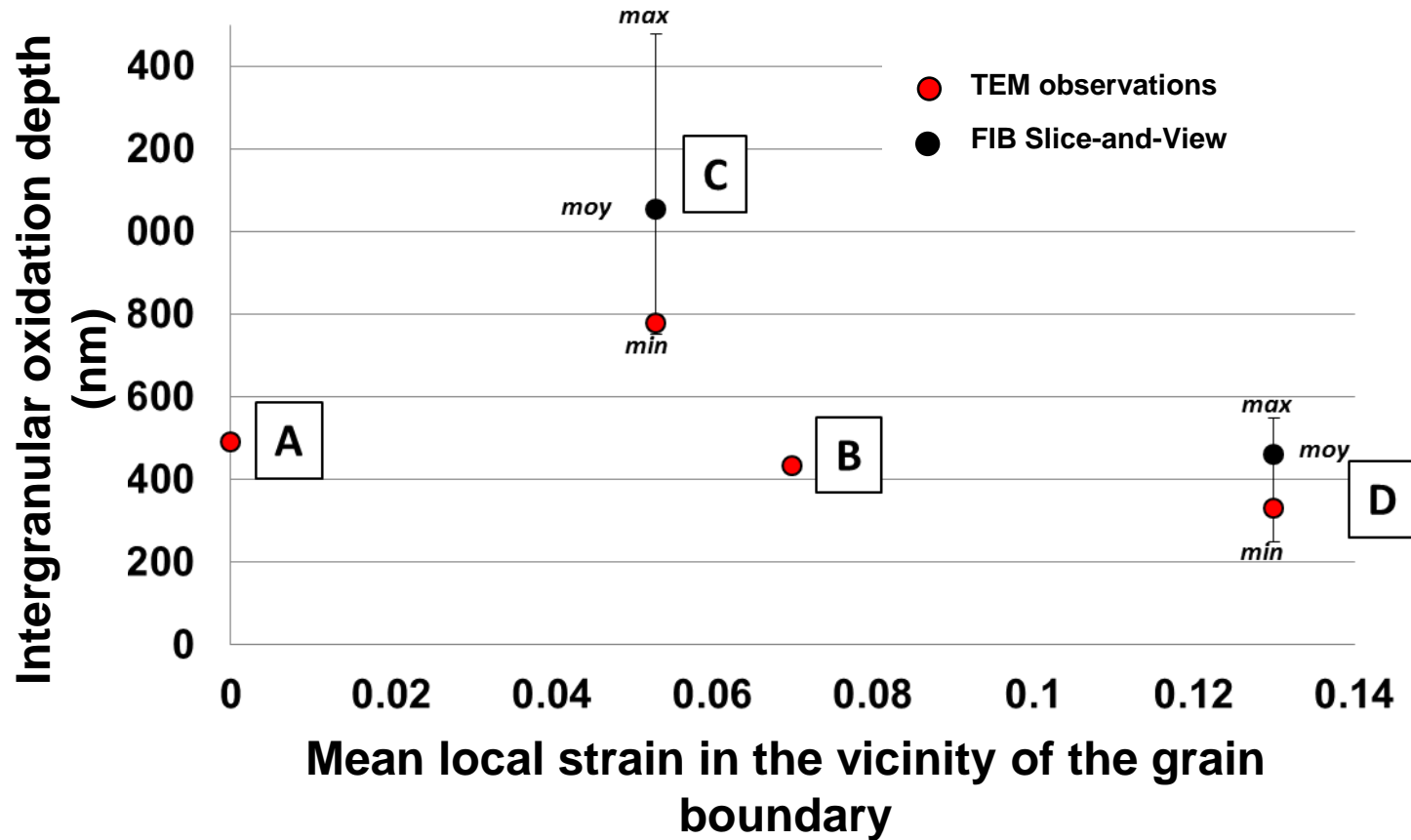
$\epsilon_{\text{von Mises}}$  : 0,06 – strain discrepancy: 6 %



Mean oxidation depth:  
1050 +/- 180 nm

A strain gradient between neighbouring grains seems to promote:

- Intergranular oxidation
- Oxide depth scattering along the GB



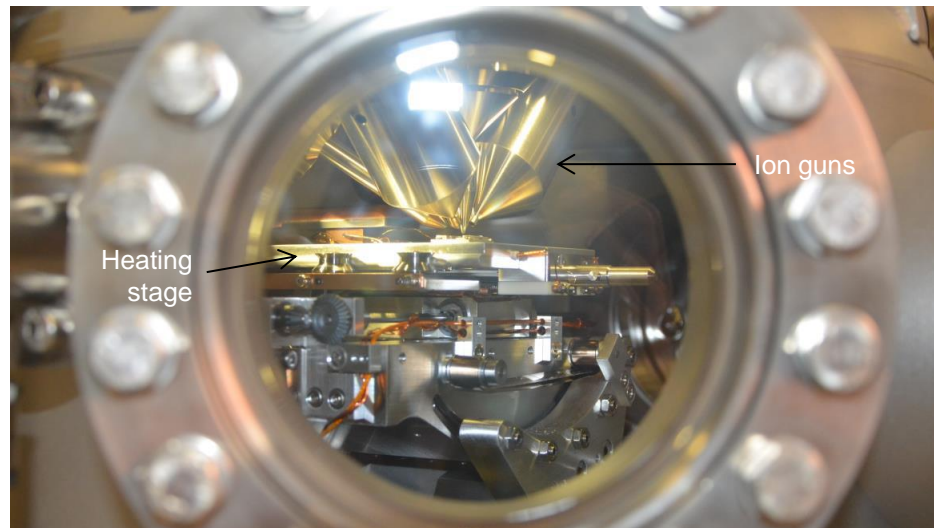
FIB Slice-and-View analyses confirm TEM observations:

- No significant effect of the mean local strain
- Strong effect of the strain gradient on IG oxide depth and scattering

- Metallurgical factors
  - Grain boundary character
  - Intergranular chromium carbides
  
- Environment
  - Temperature
  - Dissolved hydrogen content
  
- Mechanical factors
  - Pre-straining
  - Oxidation under stress

# Coupling oxidation and stress

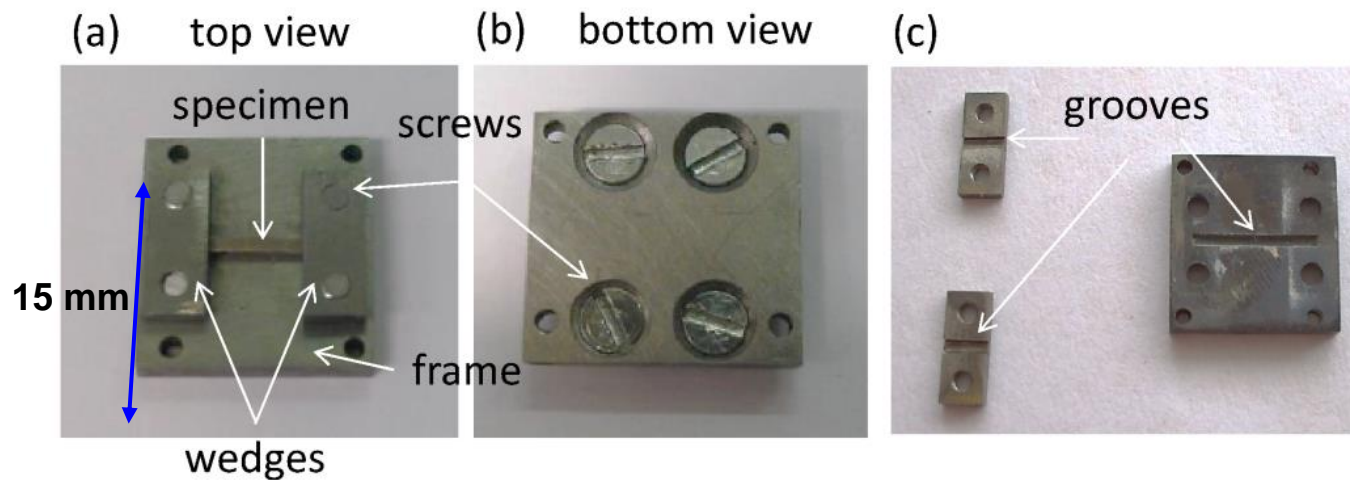
- Development of a device for studying oxidation under stress *in situ* in a ToF-SIMS
- MAI-SN project in collaboration with Chimie ParisTech:  
C. Poulain (post-doc), P. Marcus, A. Seyeux



ToF-SIMS chamber [LEM 14]

*S. Lemaitre, internship (2014)*  
*A. Guillemain, internship (2015)*

- Stress imposed by differential thermal expansion using:
  - A molybdenum device ( $TEC \approx 5 \times 10^{-6} \text{ K}^{-1}$ )
  - Alloy 600 specimens ( $TEC \approx 14 \times 10^{-6} \text{ K}^{-1}$ )

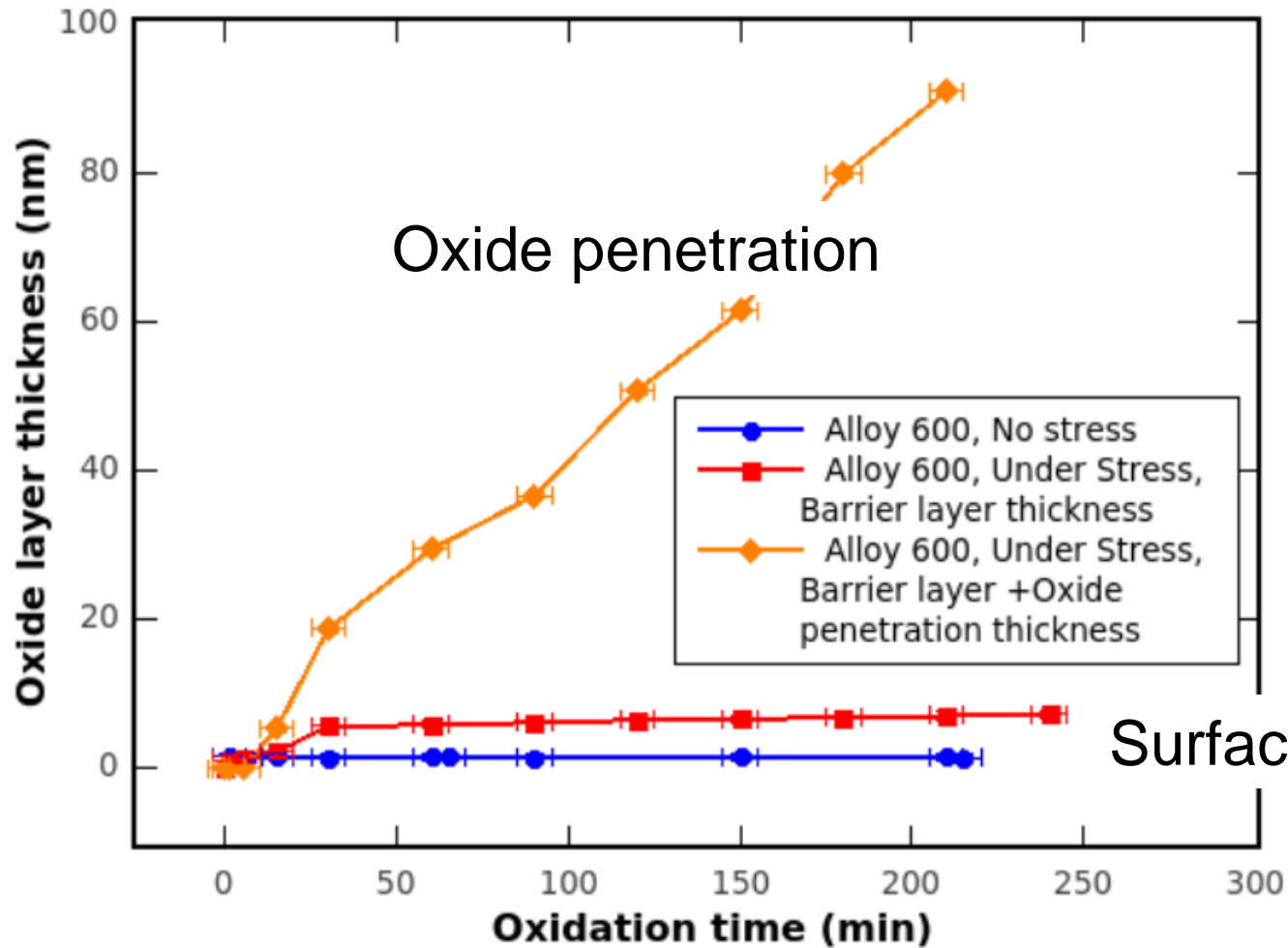


Specimen size:  $10 \times 1 \times 1 \text{ mm}^3$



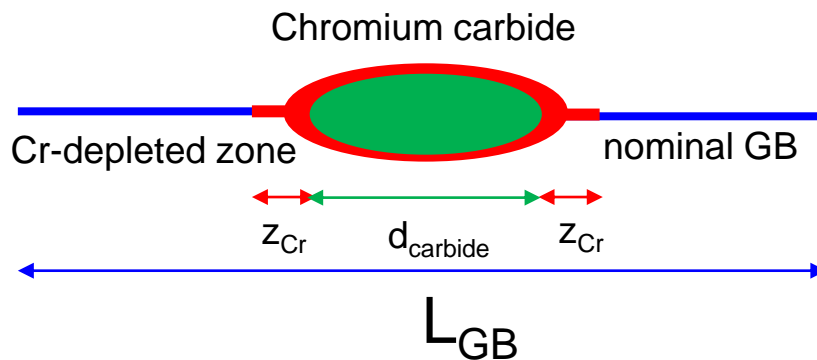
# Coupling oxidation and stress

## Surface oxidation of Alloy 600 single-crystal



# Intergranular oxidation model: approach

- 1) The grain boundary is constituted of 3 phases with different oxidation kinetics: nominal, chromium carbide, Cr-depleted zone.



Microstructure :

- $L_{GB}$  (nm)
- $z_{Cr}$  (nm)
- $d_{carbide}$  (nm)
- $GBC \left( \frac{\sum d_{carbide}}{L_{GB}} \right)$

Limit conditions:

- time (h)
- $T$  ( $^{\circ}$  C)
- $[H_2]$ (cc/kg d'H<sub>2</sub>O)

- 2) The model generates randomly one grain boundary (1D) with the given properties ( $GBC$ ,  $d_{carbide}$ ,  $z_{Cr}$ ...)
- 3) Discretization (1 nm) and incremental calculation of the oxidation time of the discretized GB

# Intergranular oxidation kinetics

Assumption: for a given phase  $i$ , the IG oxidation kinetics follows a log-type law.

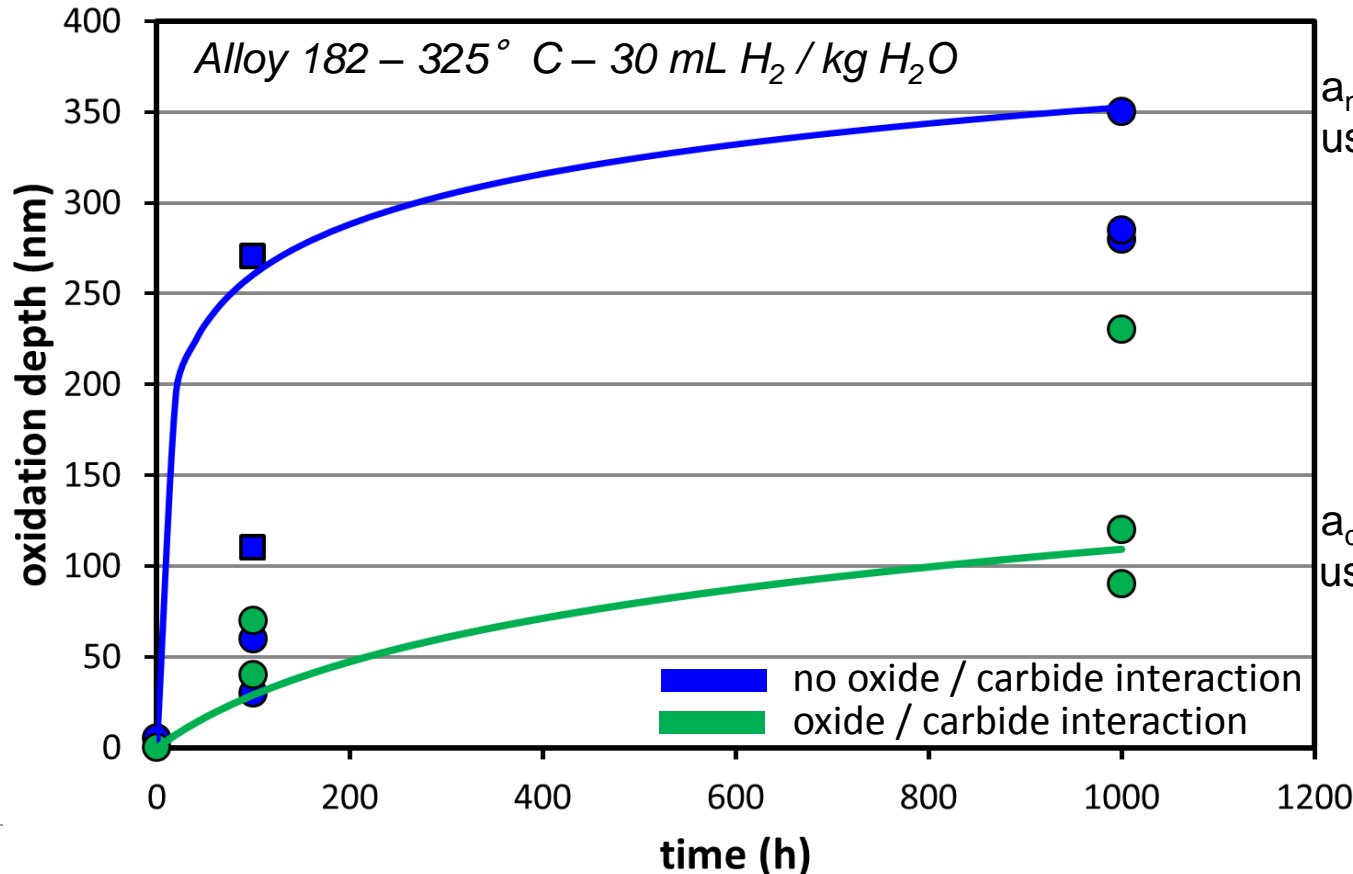
$$p_i = \frac{1}{a_i} \ln(1 + b_i \times t) \times f(\Delta E_{cP}) \times g(T)$$

IG oxide depth

constant

electrochemical potential

temperature



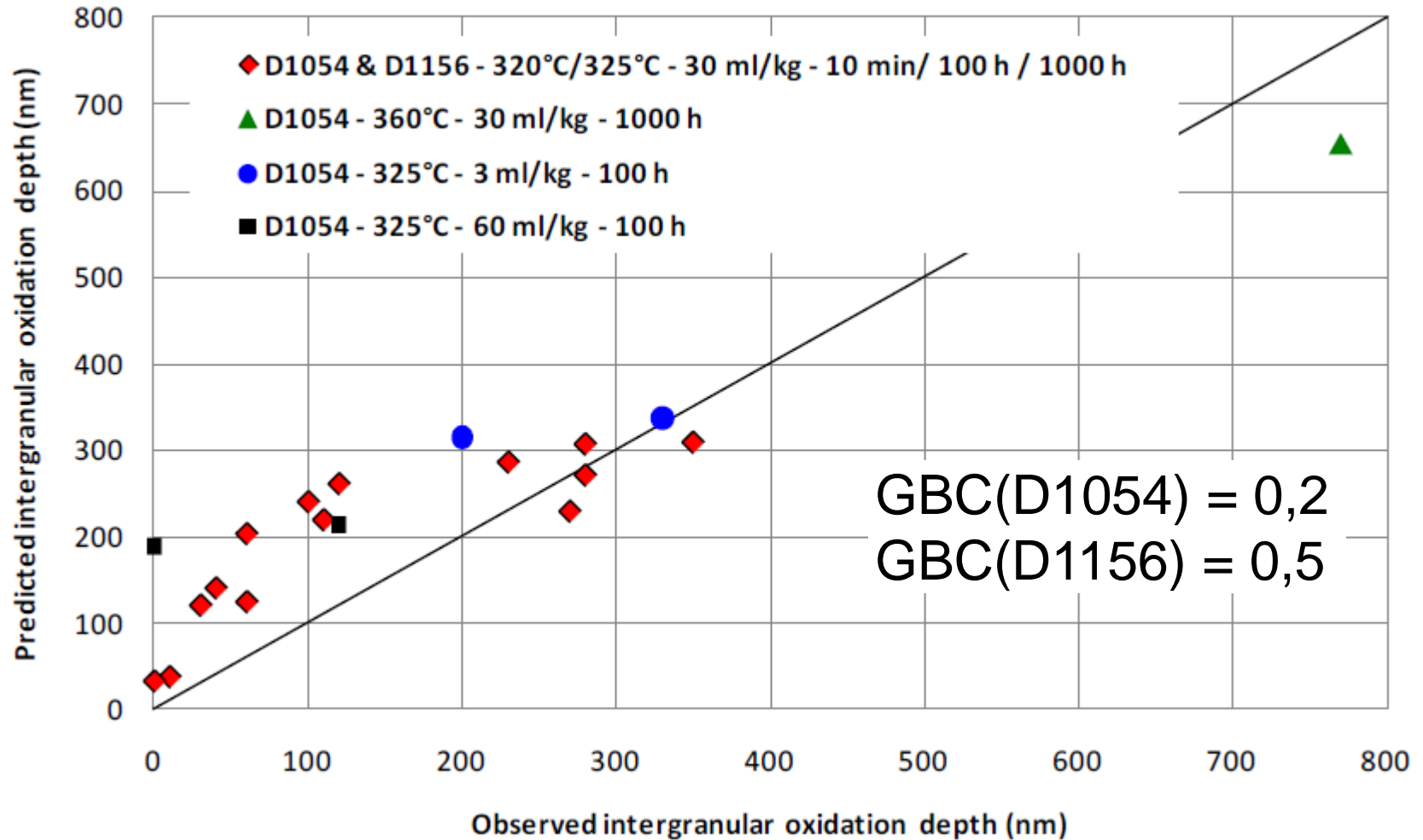
$a_{\text{nominal}}$  and  $b_{\text{nominal}}$  identified using the **maximum** depths

$a_{\text{carbide}}$  and  $b_{\text{carbide}}$  identified using the **minimum** depths

# Application to Alloy 182

- Random sampling of 100 GB

GBC = Grain boundary coverage with chromium carbides



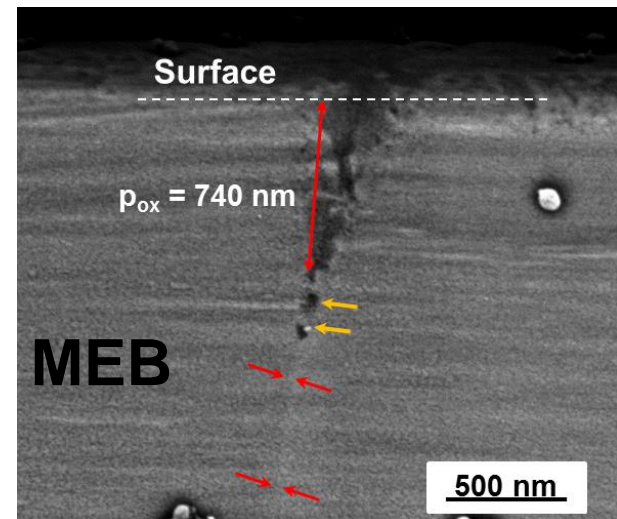
# Crack initiation criterion : methodology

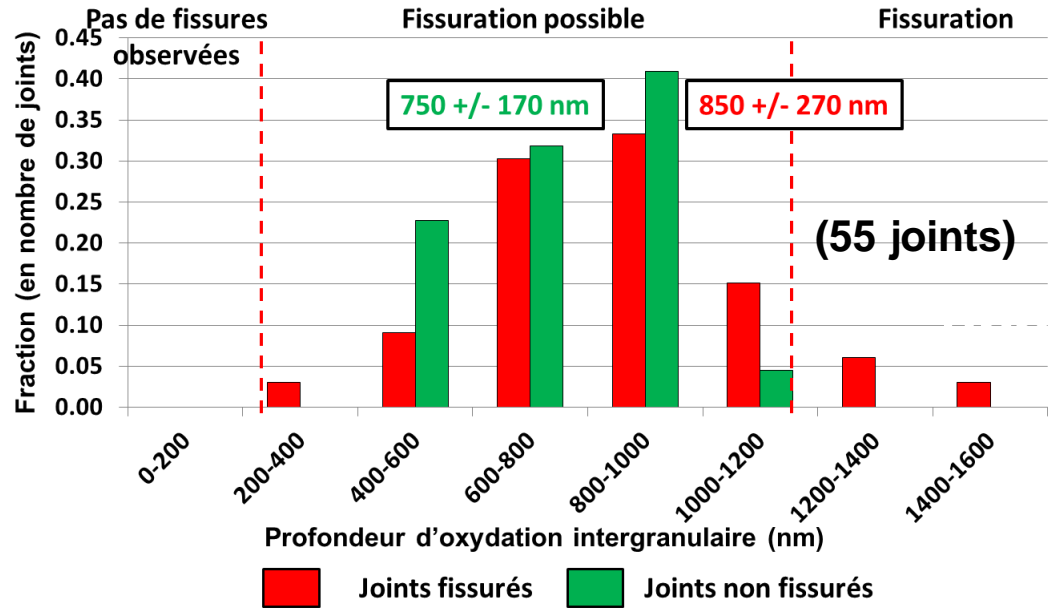
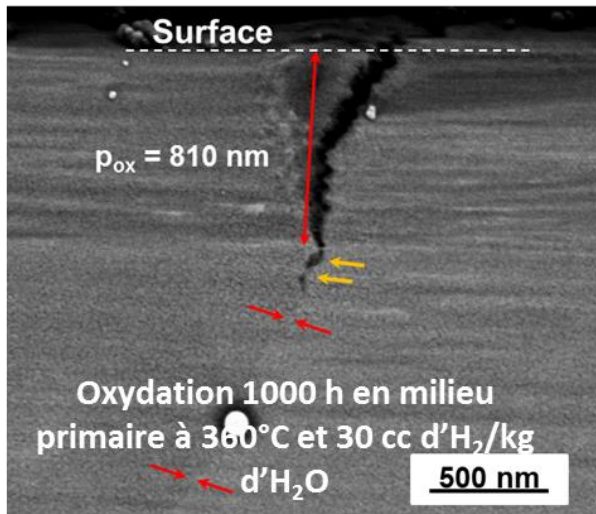
Alloy 182 1000 hours primary water at 360° C, 30 mL d'H<sub>2</sub>/kg  
d'H<sub>2</sub>O

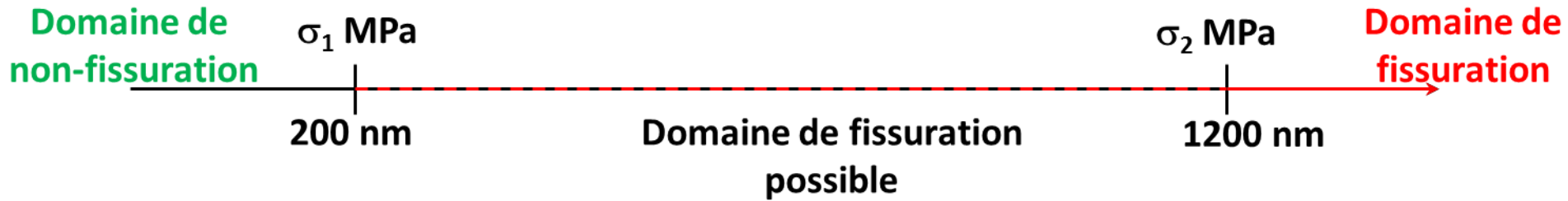
Tensile test at 360° C (strain rate : 10<sup>-5</sup> s<sup>-1</sup>)



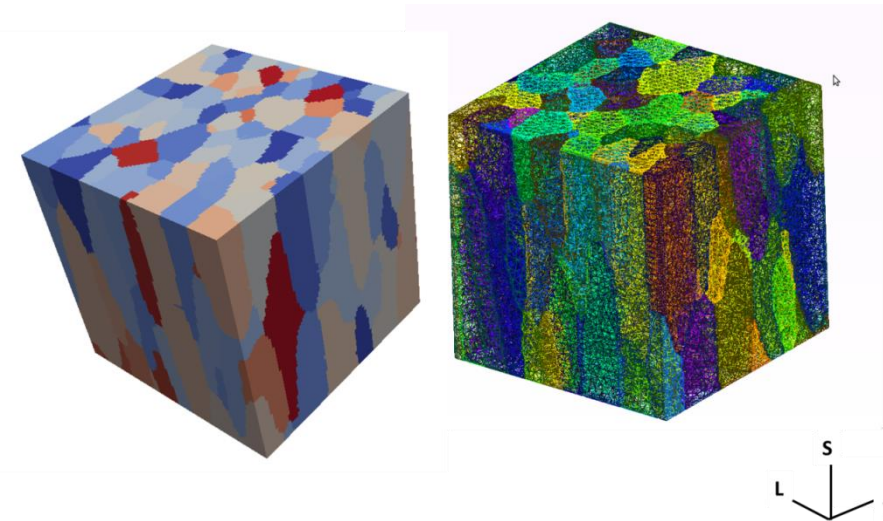
Study of the length of the intergranular oxyde penetration  
in relation with cracked or uncracked grain boundary



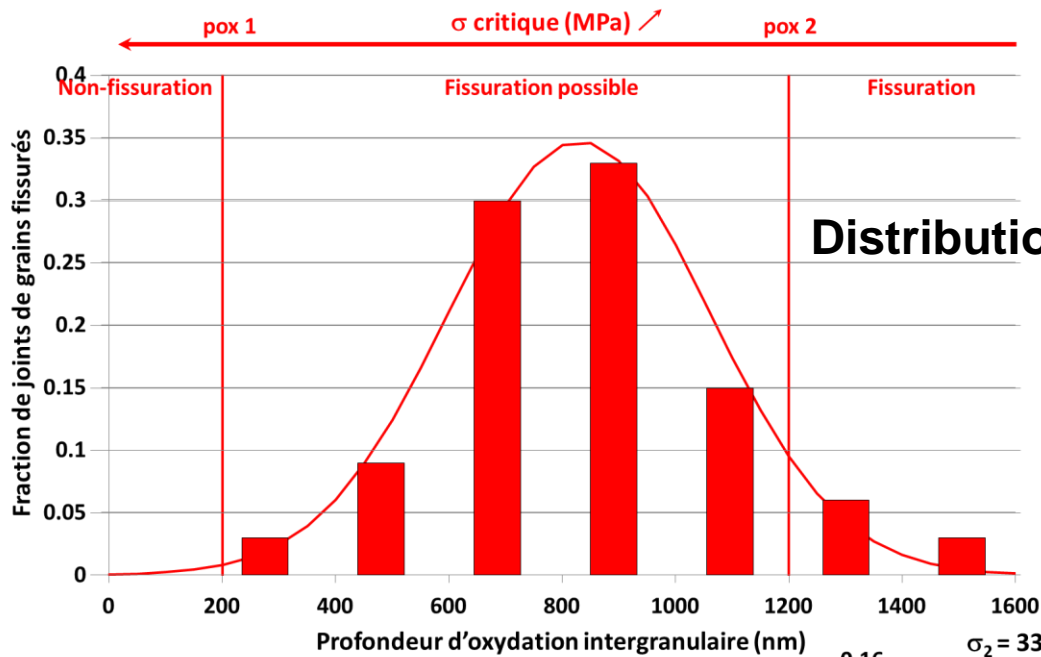




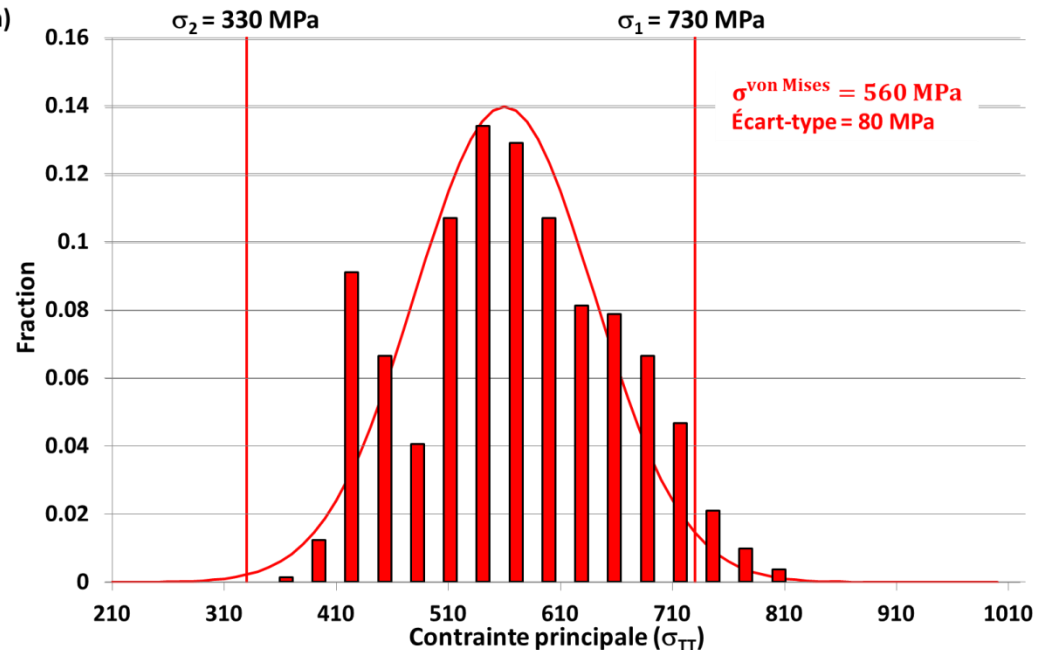
**EVP crystallographic constitutive equation**  
**Virtual microstructure representative of the columnar**  
**microstructure texture  $\langle 001 \rangle$**



**Stress distribution along the**  
**grain boundaries**



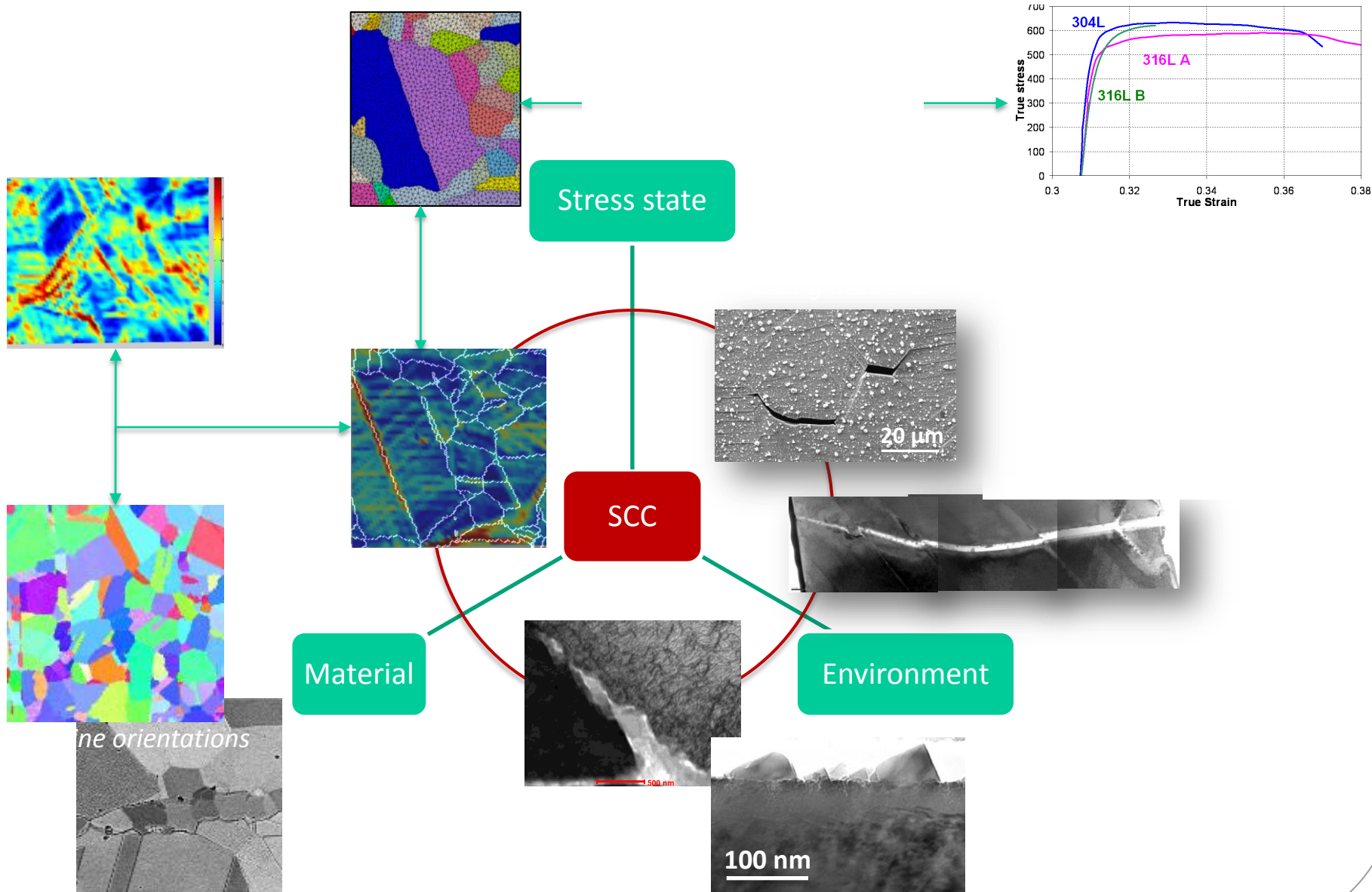
**$\sigma_{TT}$  distribution for 7 % macroscopic strain**



**Criteria:**  
 $pox \geq 200 \text{ nm}$   
 $\sigma_{crit} \geq 730 \text{ MPa}$



# Development of a combined approach



Thank you for your attention