



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

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

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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. Chaumun, J. Nguejo, M. Wehbi

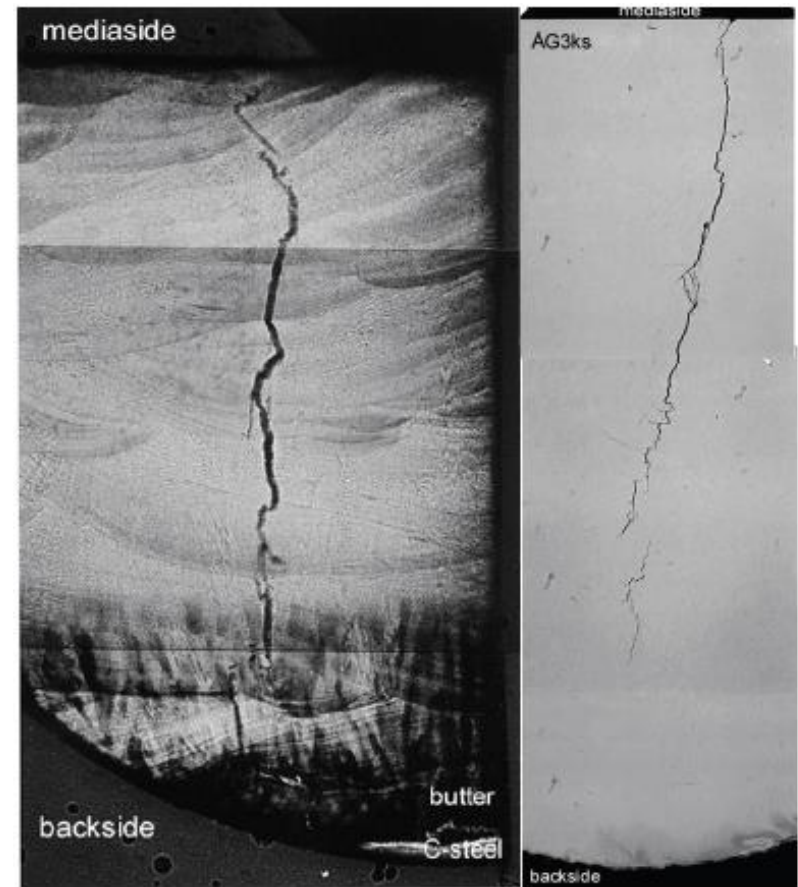
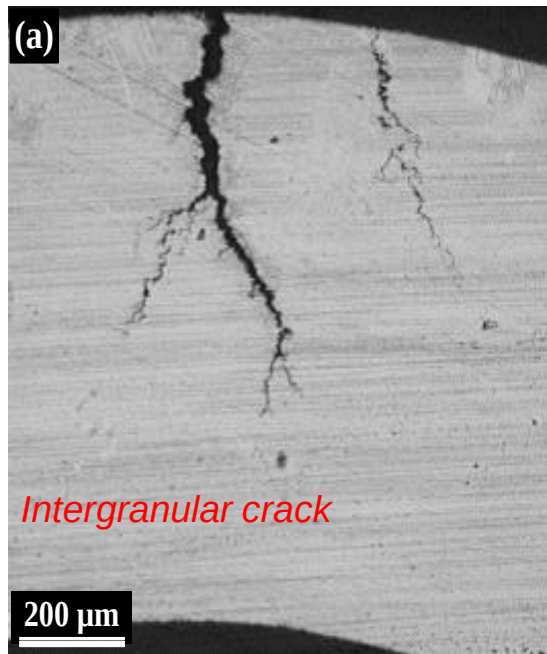
T. Couvant, J. Crépin, I. de Curières, C. Duhamel, F. Gaslain, C. Guerre, E. Hérippe, M. Sennour



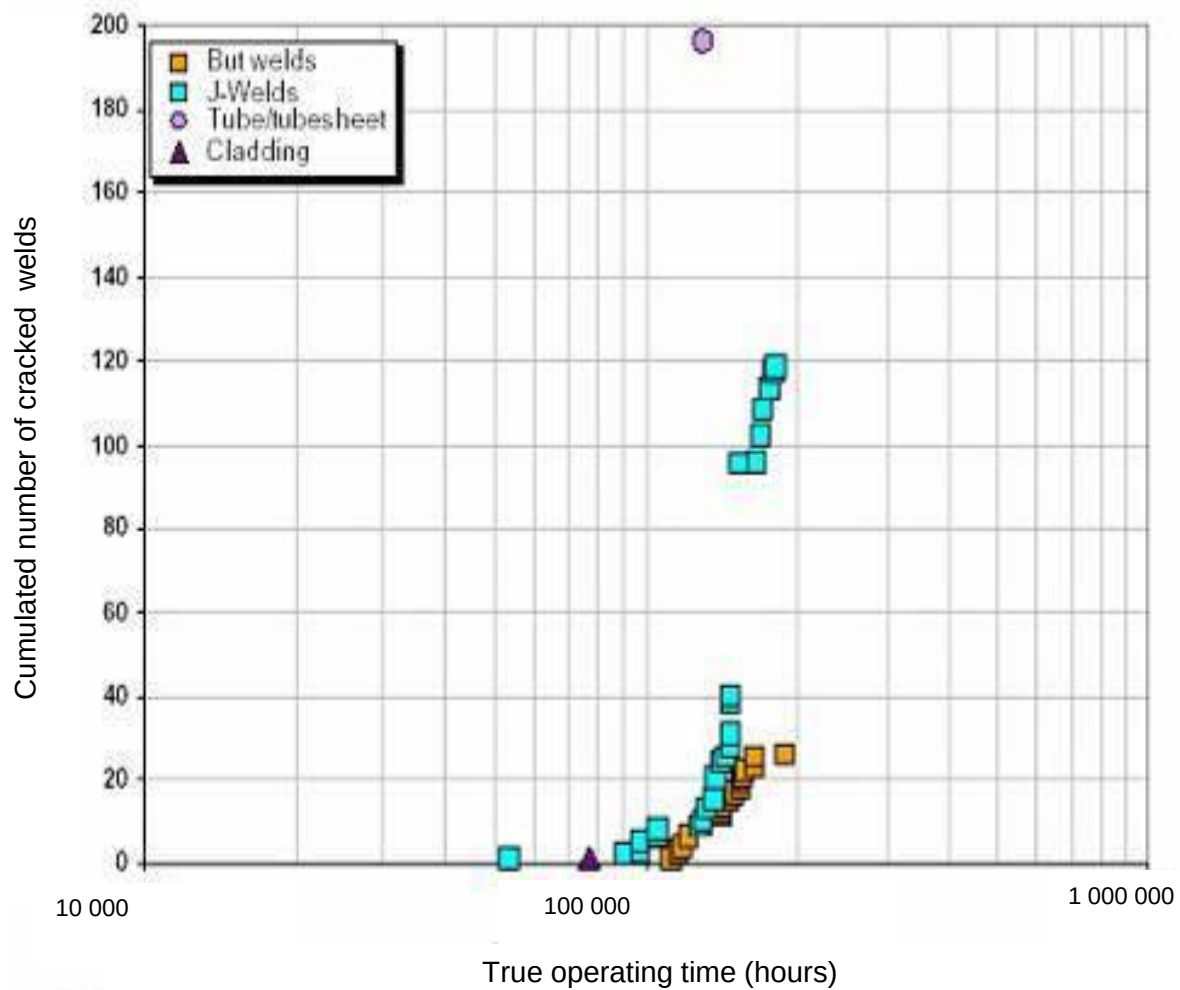
Workshop MIST, 12-15 Octobre 2015

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 12th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors”, TMS 2005.

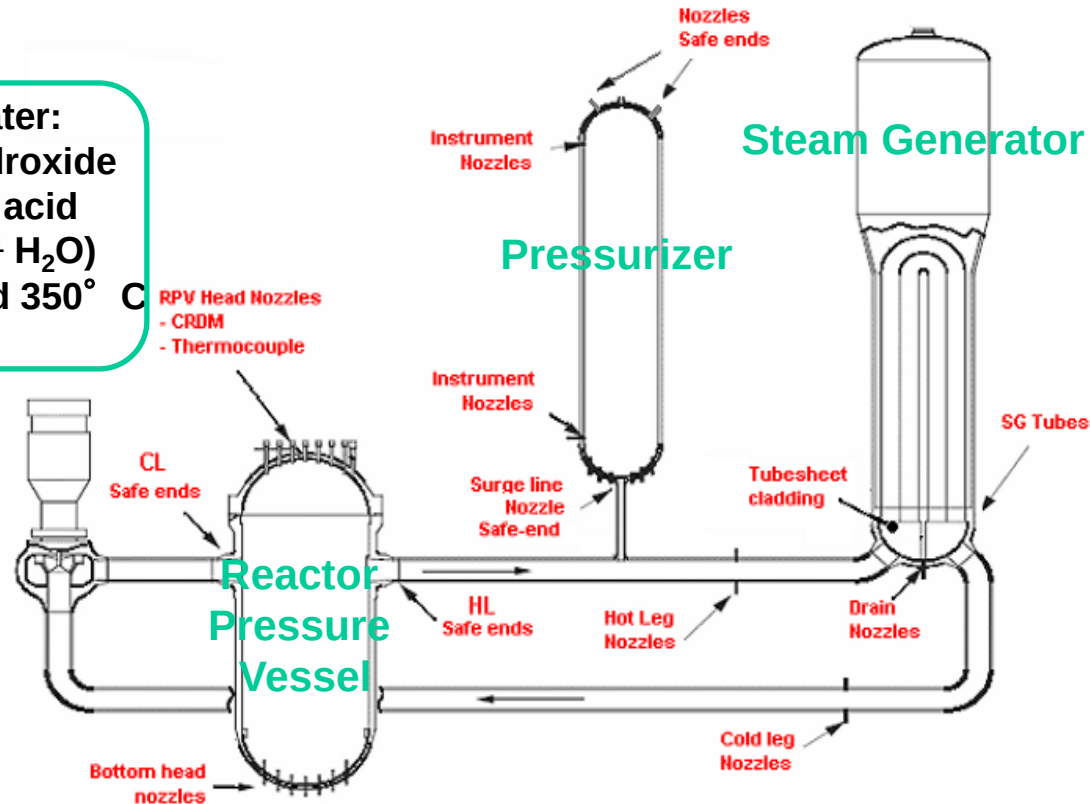


Life extension of PWR > 30 – 40 years

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 ($30 \text{ cm}^3.\text{kg}^{-1} \text{ H}_2\text{O}$)
Temperature: 290° C and 350° C

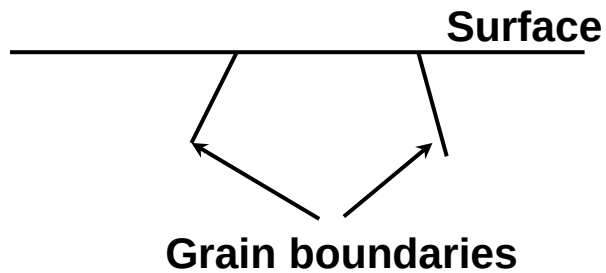


Scott, P., PWSCC of nickel base alloys & mitigation in PWRs, INL Seminar (2013)

SCC initiation

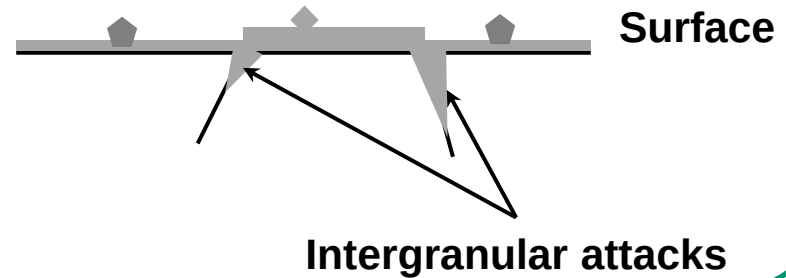
1

Environment
Primary water



2

Environment
Primary water



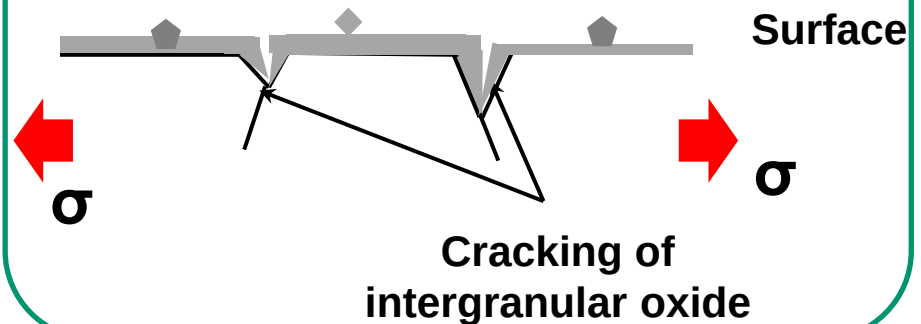
***Initiation = cracking of
intergranular oxide***



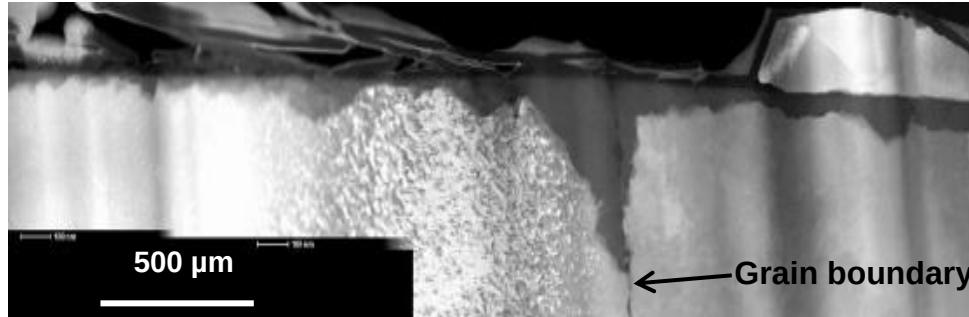
Critical oxide depth
Critical stress

3

Environment
Primary water

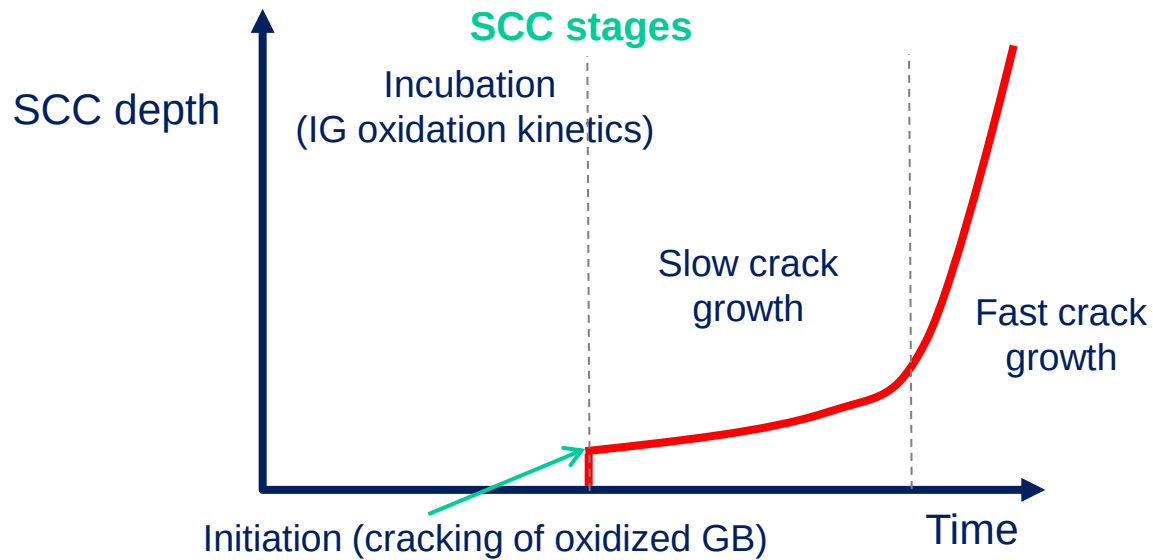


Cracking scenario

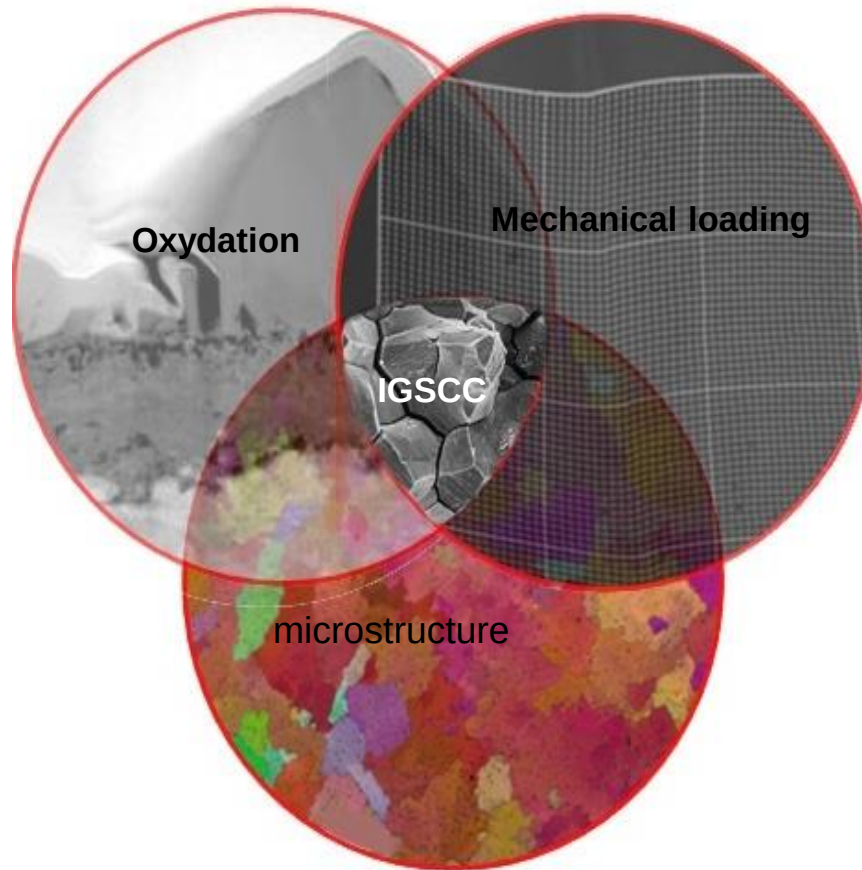


STEM HAADF image of the intergranular oxide penetration of Alloy 600

After 2000h in primary water at 360° C, DH= 30 mL H₂/kg H₂O



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

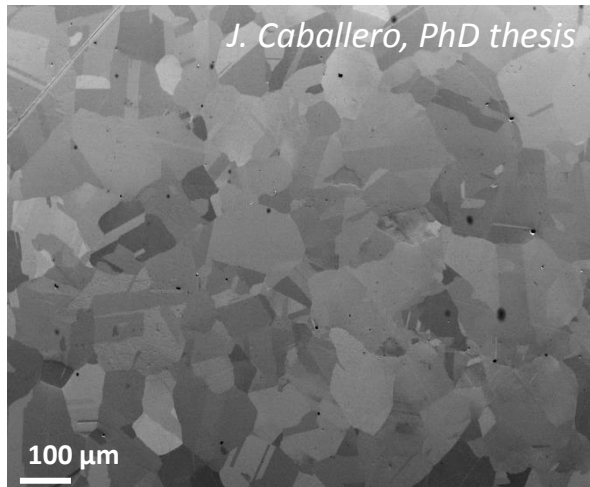
Temperature	285 - 325 ° C
Pressure	155 bar
Boren (H_3BO_3)	10 -1200 ppm
Lithium (LiOH)	0,7 - 2,2 ppm
H_2	25 - 50 $\text{cm}^3.\text{kg}^{-1}$(TPN)
O_2	< 5 ppb
$\text{pH}_{300^\circ \text{ C}}$	≈ 7

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

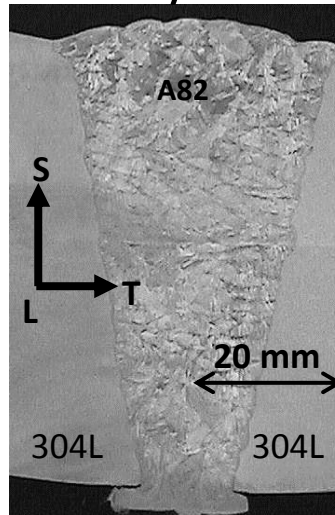
Cr content ↗

A600

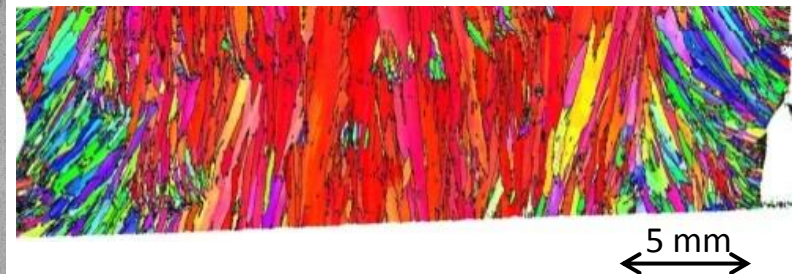


Possible IG chromium carbides

A182 / A82



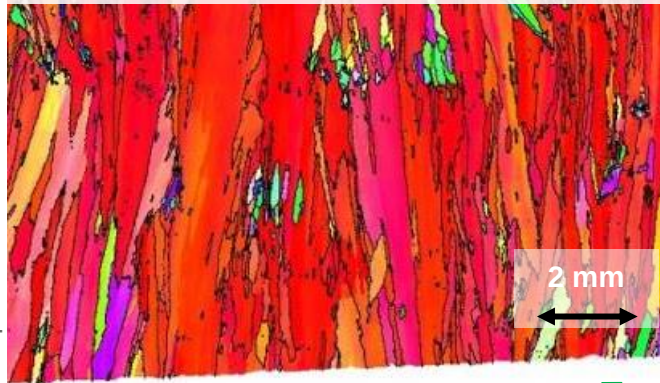
E. Chaumon, PhD thesis



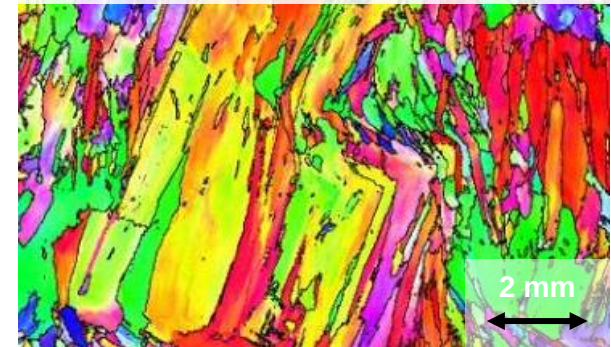
Possible IG niobium and chromium carbides

Microstructure features (EBSD)

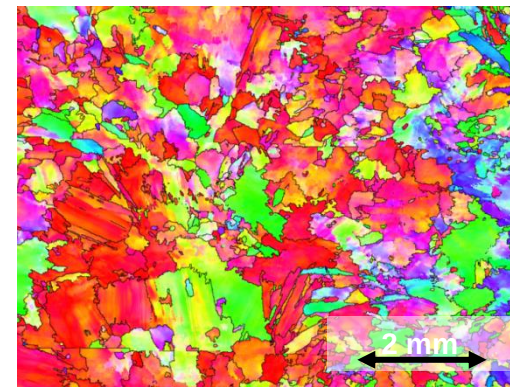
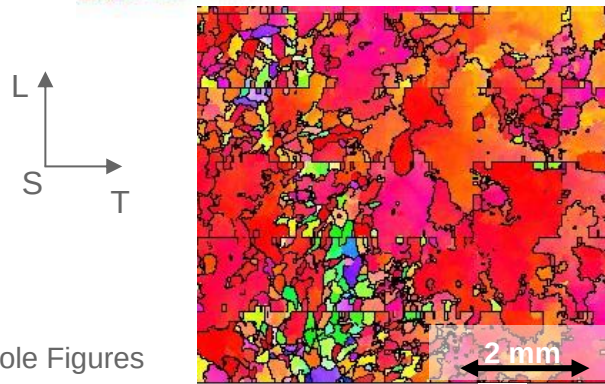
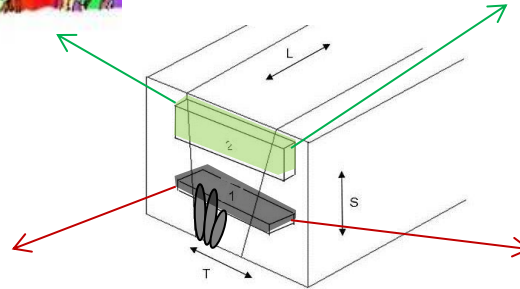
Weld B/AW : A82, 18%Cr, FCAW, as-welded



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

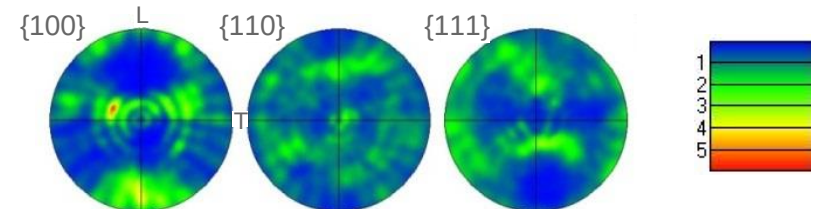
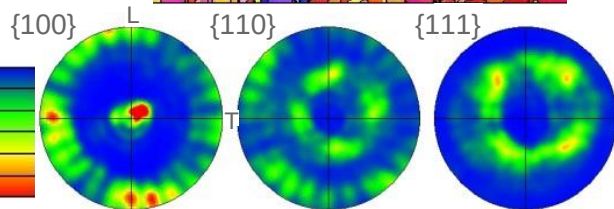


111
100 110
IPF following S
axis



Pole Figures

Pole Figures

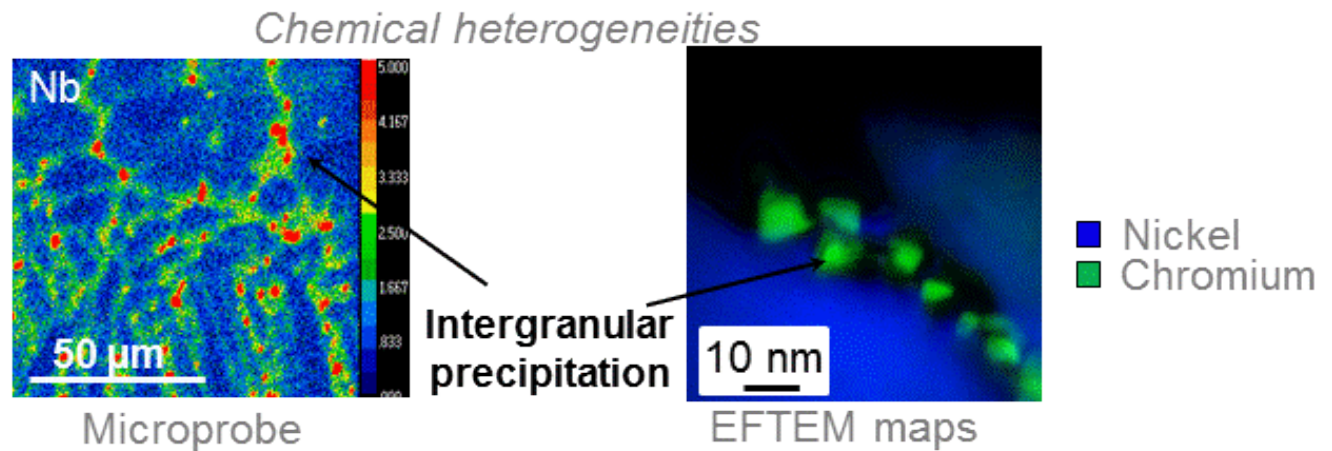
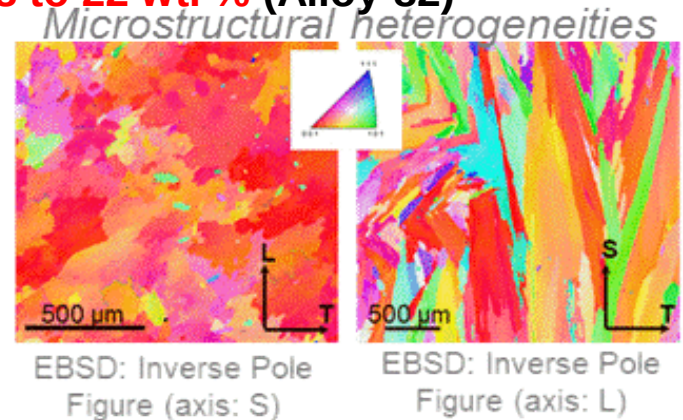
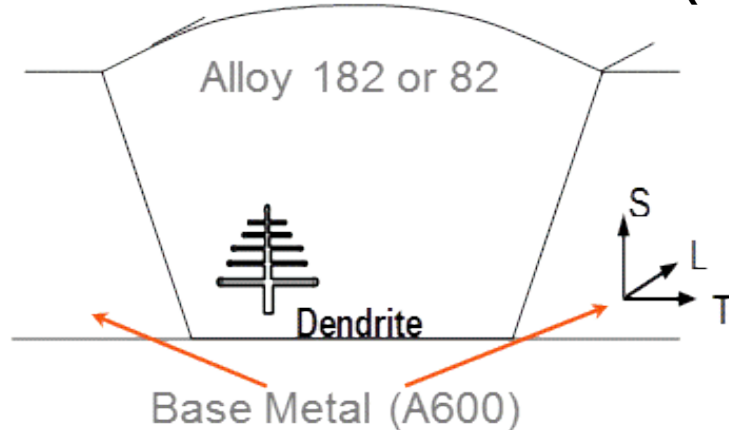


→ Crystallographic texture for weld B/AW, local texture for weld A/AW and no texture for weld A/HT

→ 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)



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



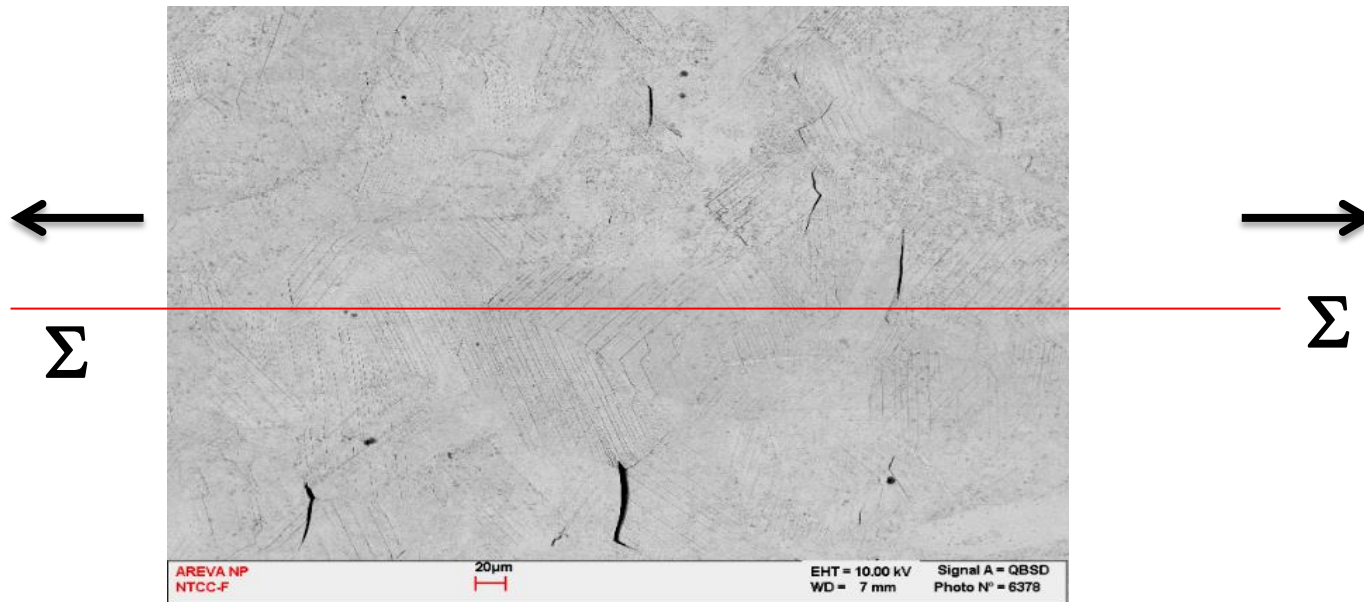
Autoclave



Machine de fluage



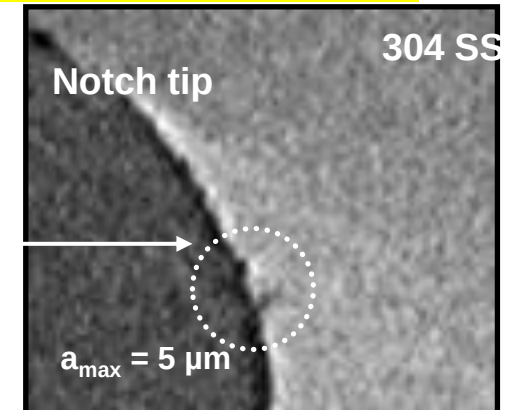
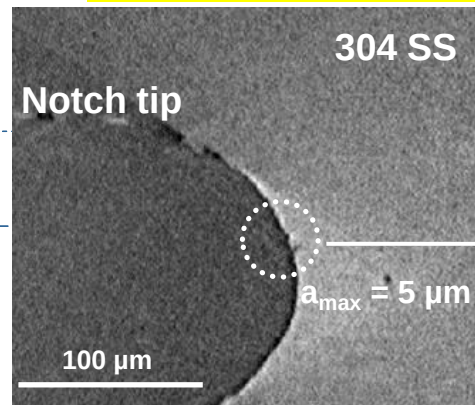
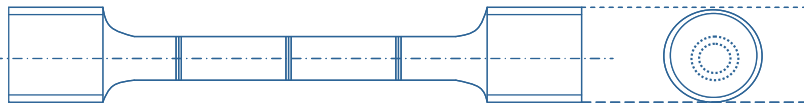
Load →



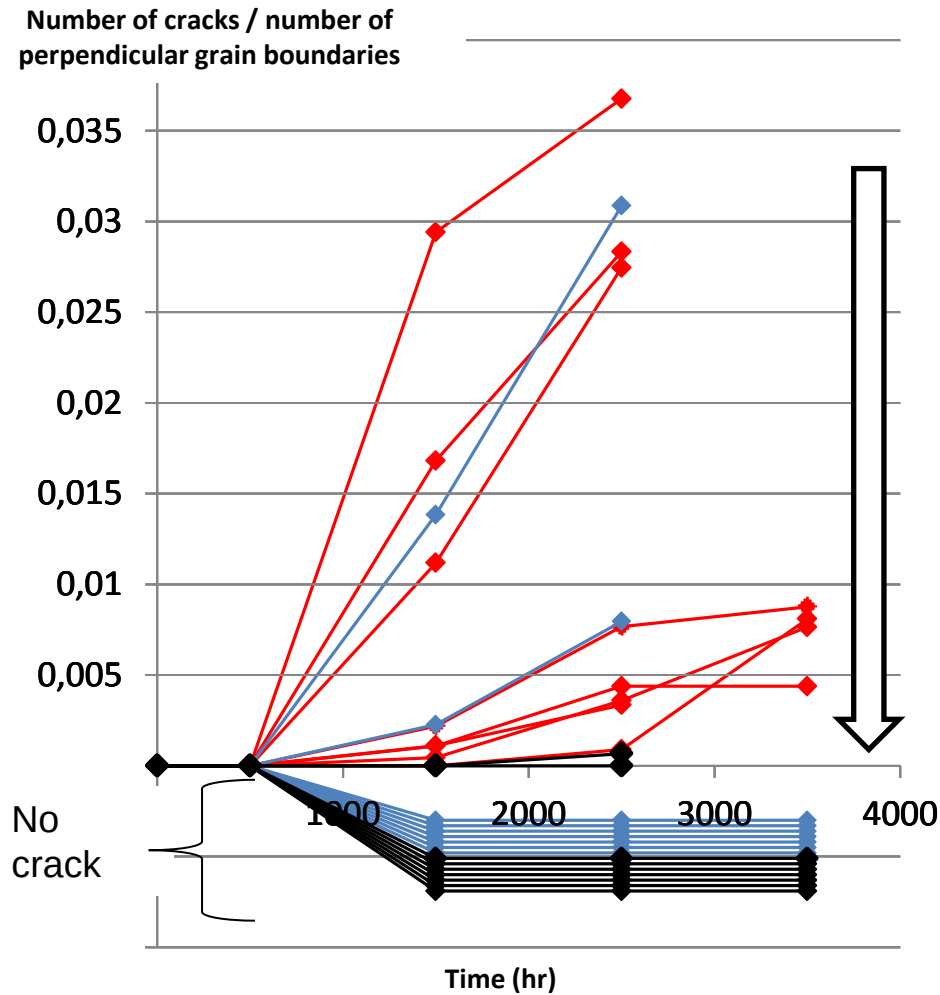
304 Stainless Steel, 5 dpa, 10%

Courtesy of M. Le Millier, chaire AREVA

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



INITIATION TEST : RESULTS



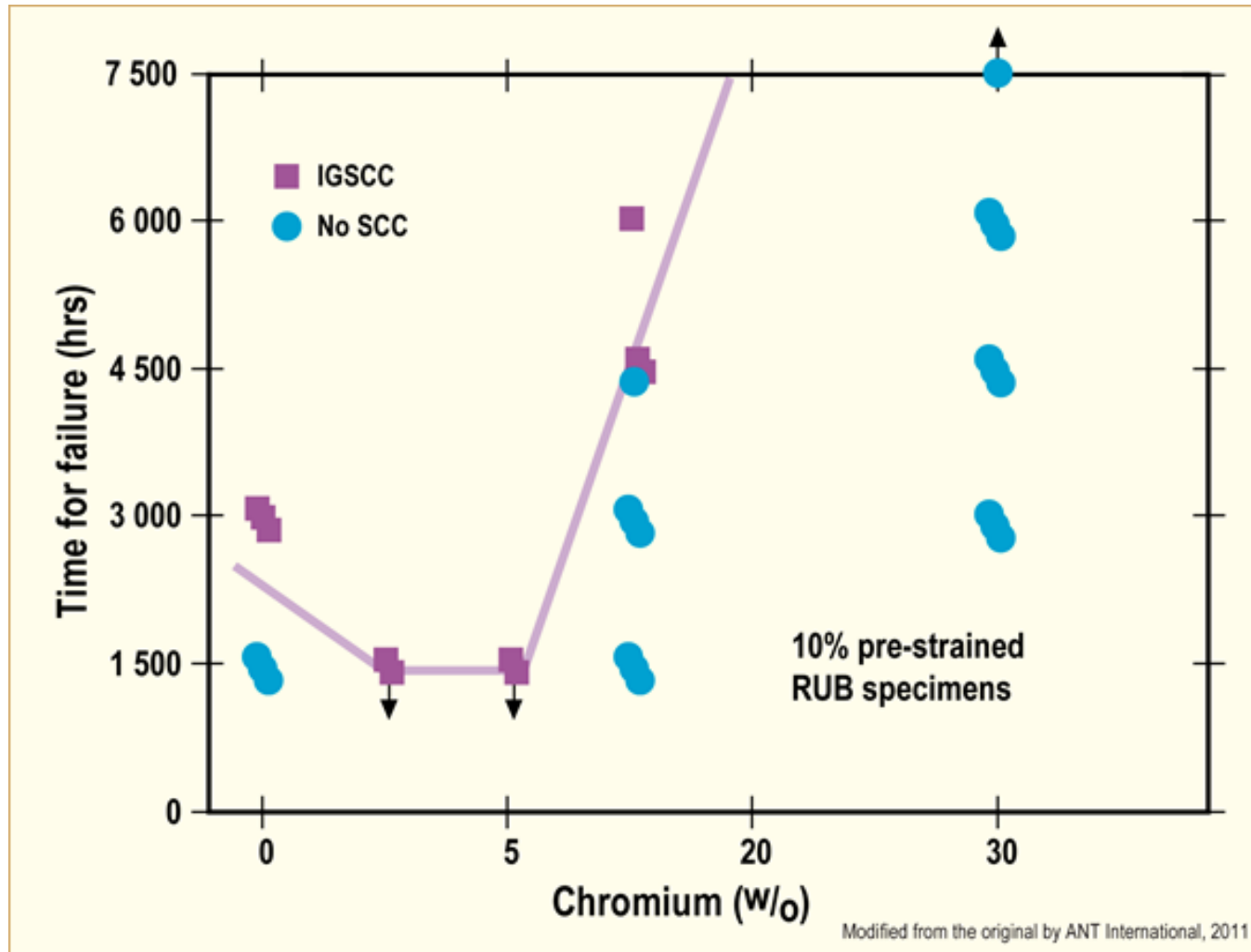
→ **B/AW is more susceptible to SCC than A/AW**

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

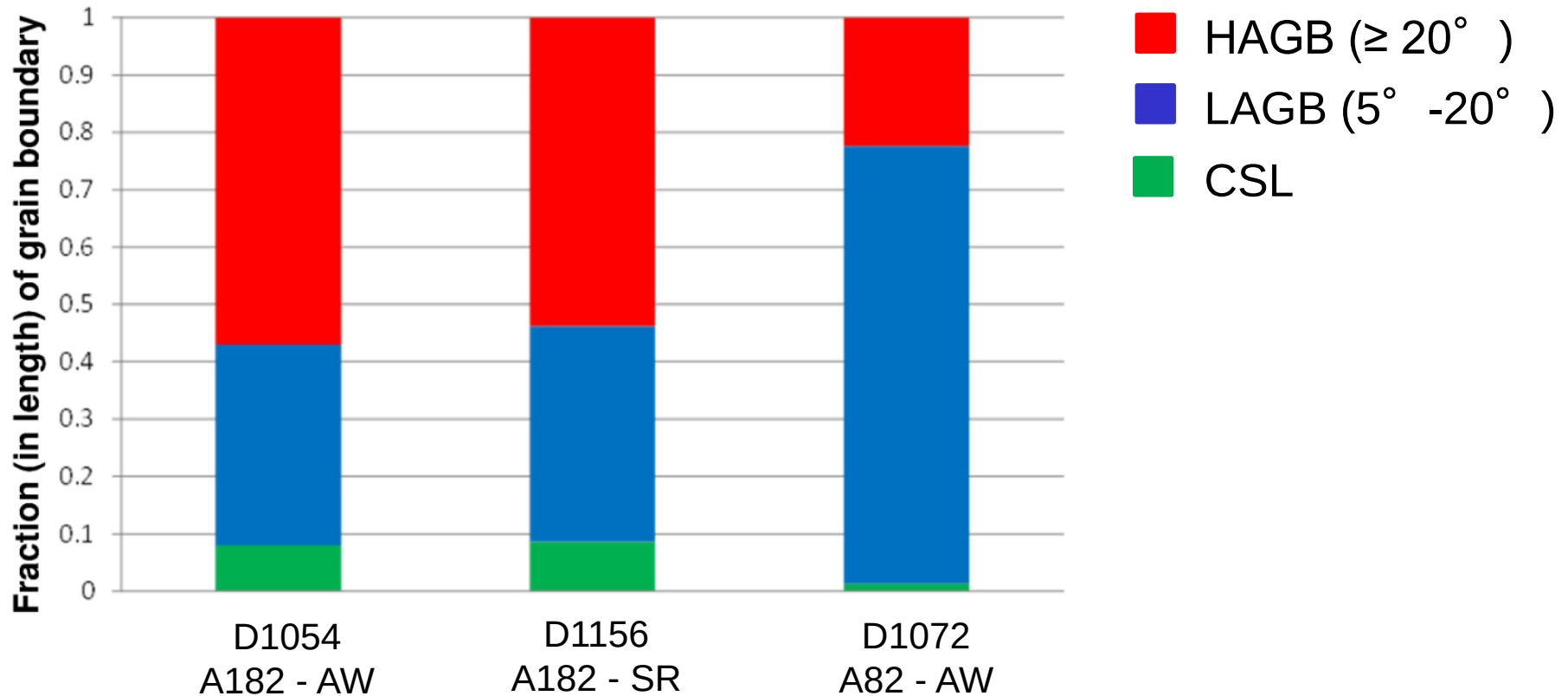
- Alloy B/AW : A82 18%Cr, FCAW, as-welded
- Alloy A/AW : A82 19%Cr, GTAW, as-welded
- Alloy A/HT : A82 19%Cr, GTAW, heat-treated

Chromium content and SCC

- Increasing the chromium content decreases the SCC susceptibility



Grain boundary character



SEM image

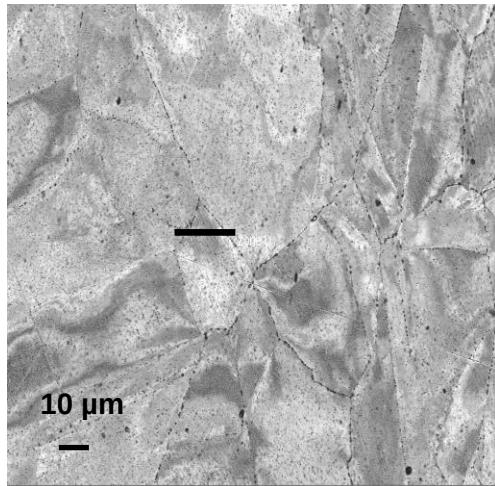
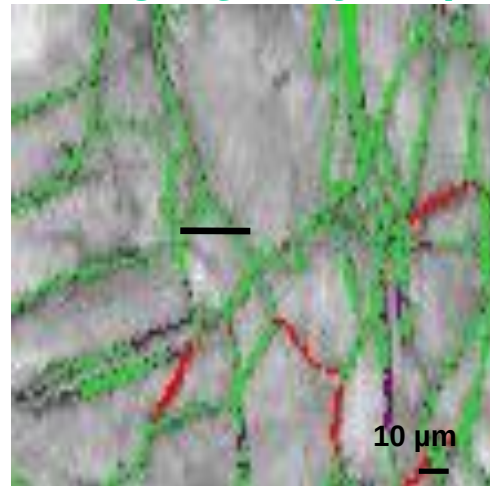
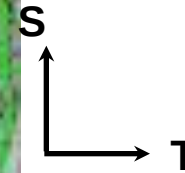


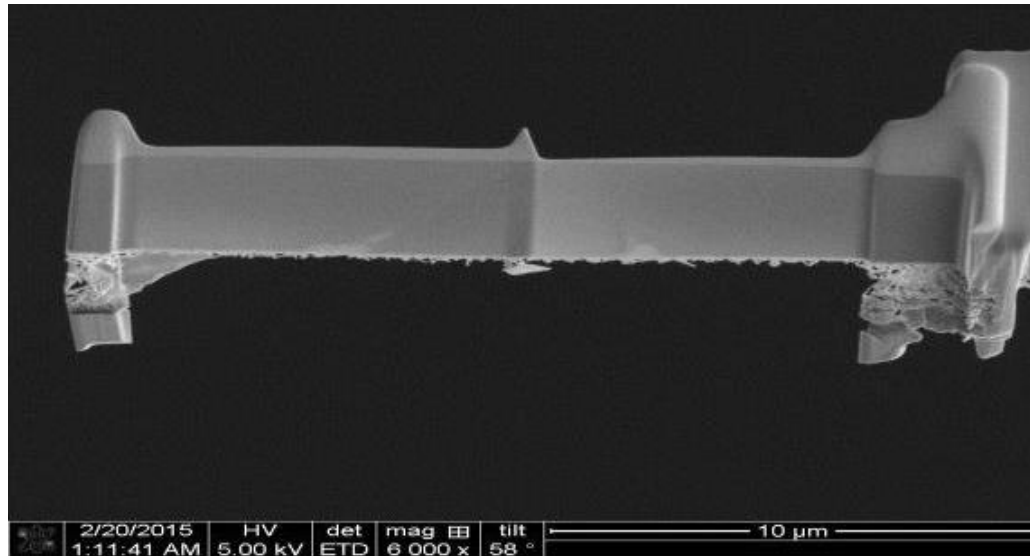
Image Quality map



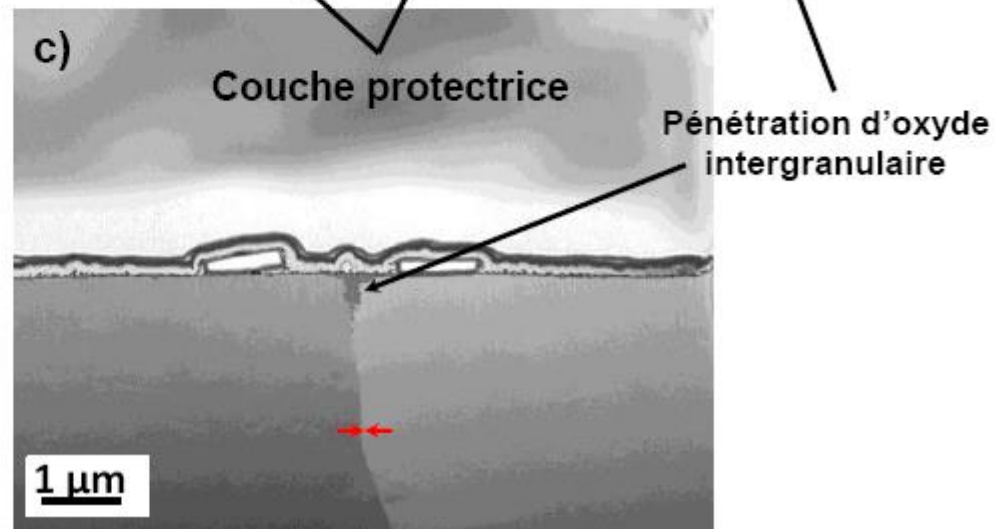
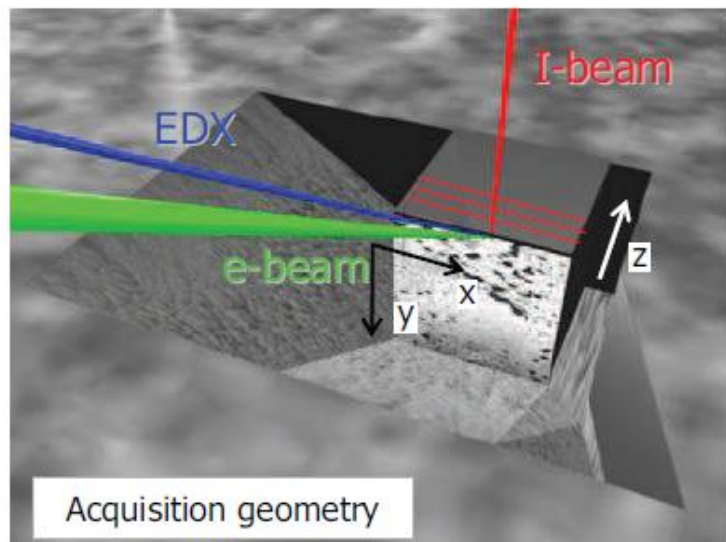
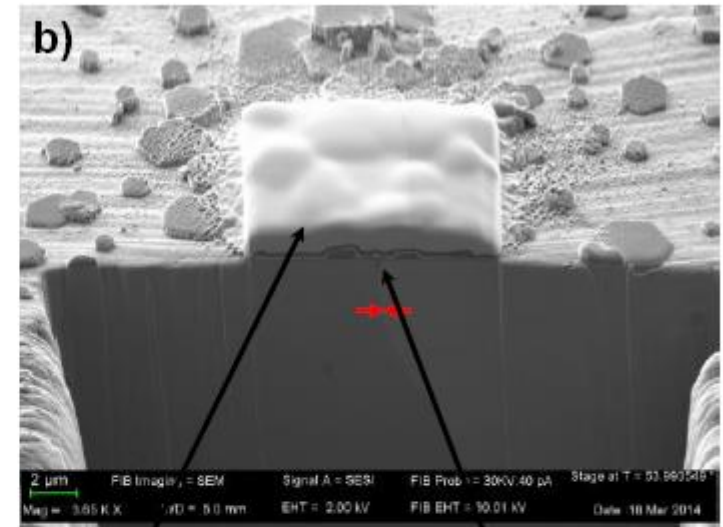
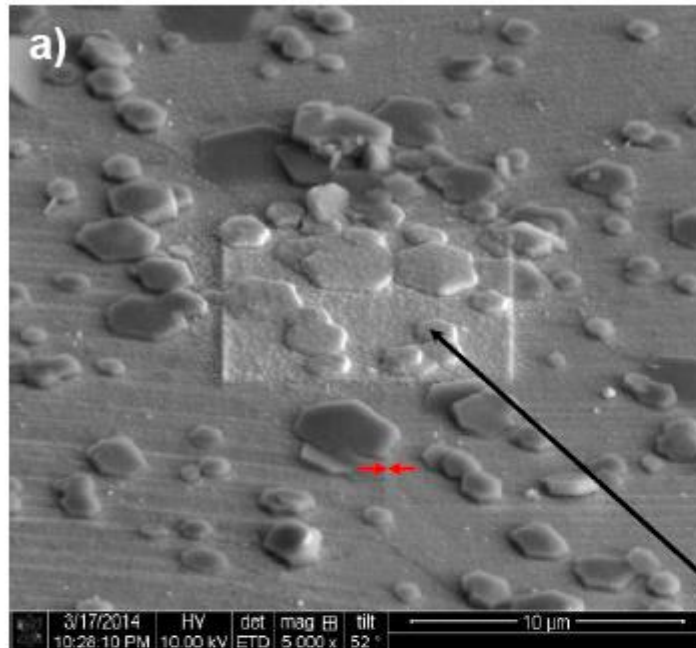
— LAGB ($\Delta\theta \leq 15^\circ$) — HAGB ($\Delta\theta > 15^\circ$)



Step size = $1\mu\text{m}$



FIB/SEM tomography

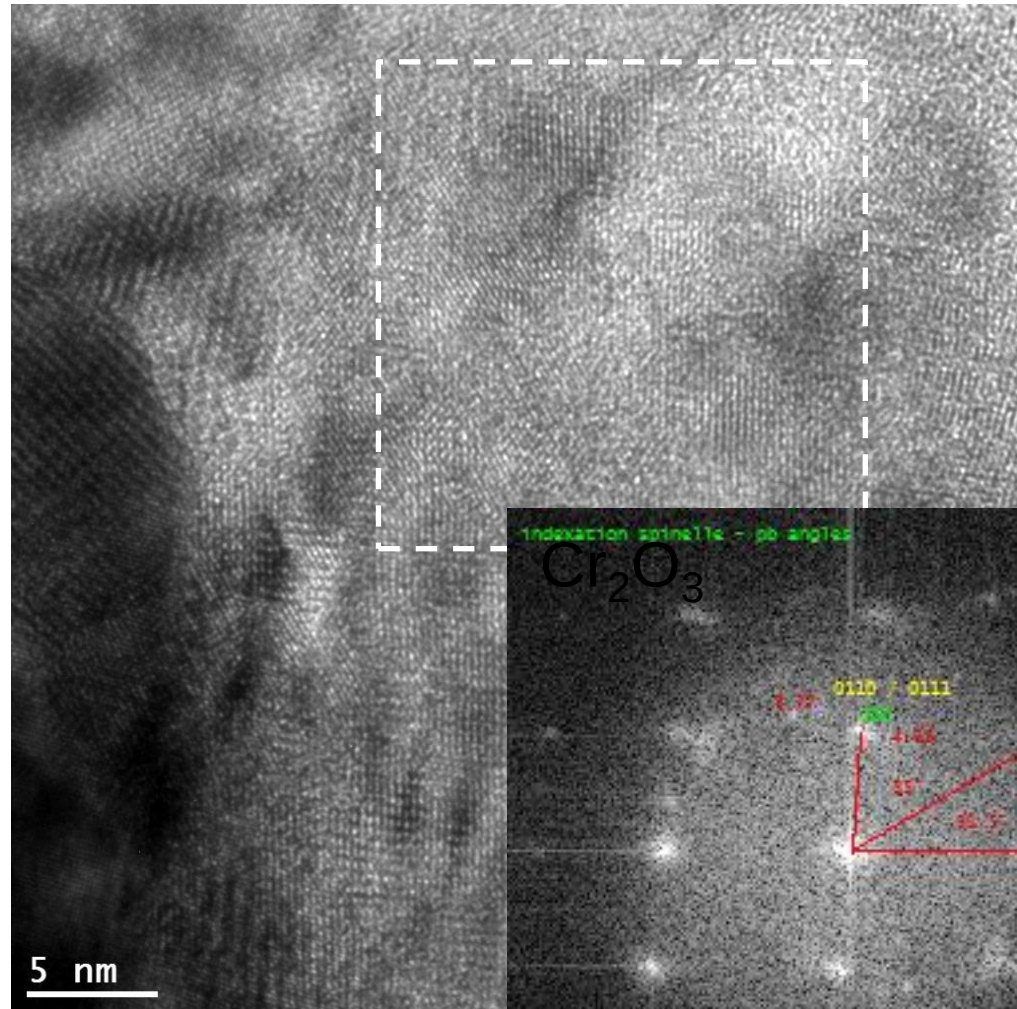
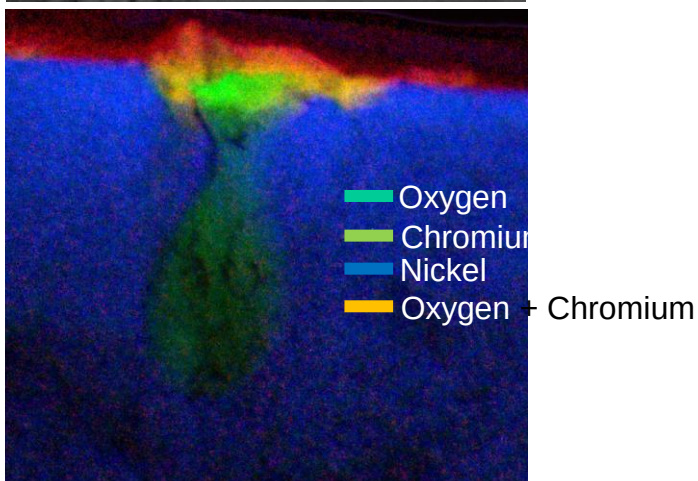
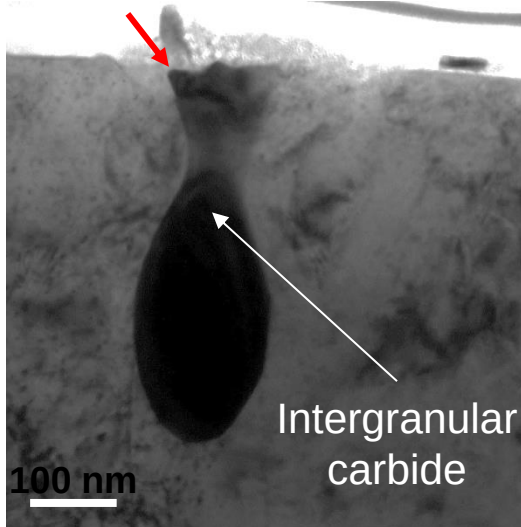


Oxidation and chromium carbides

Alloy 600
325° C – 100h
30 mL H₂/kg H₂O

- Formation of Cr₂O₃ around the carbide

Emerging carbide



J. Caballero, PhD thesis

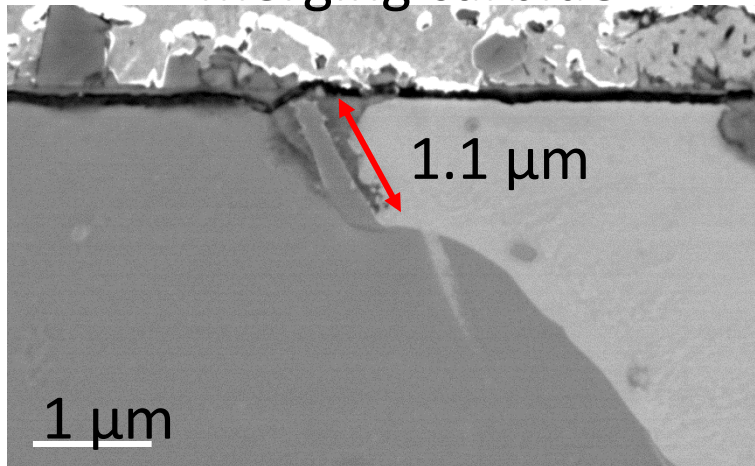
Emerging vs. non emerging carbides

Alloy 600
360° C – 1000h
20 mL H₂/kg H₂O

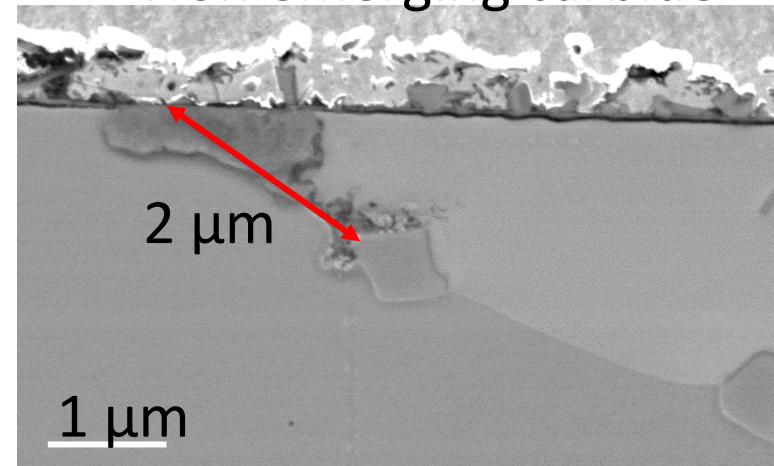
- Enhanced reactivity at the interfaces between carbide and matrix
- For long oxidation times , intergranular oxidation depth seems shorter in case of emerging carbides.

1000h

Emerging carbide



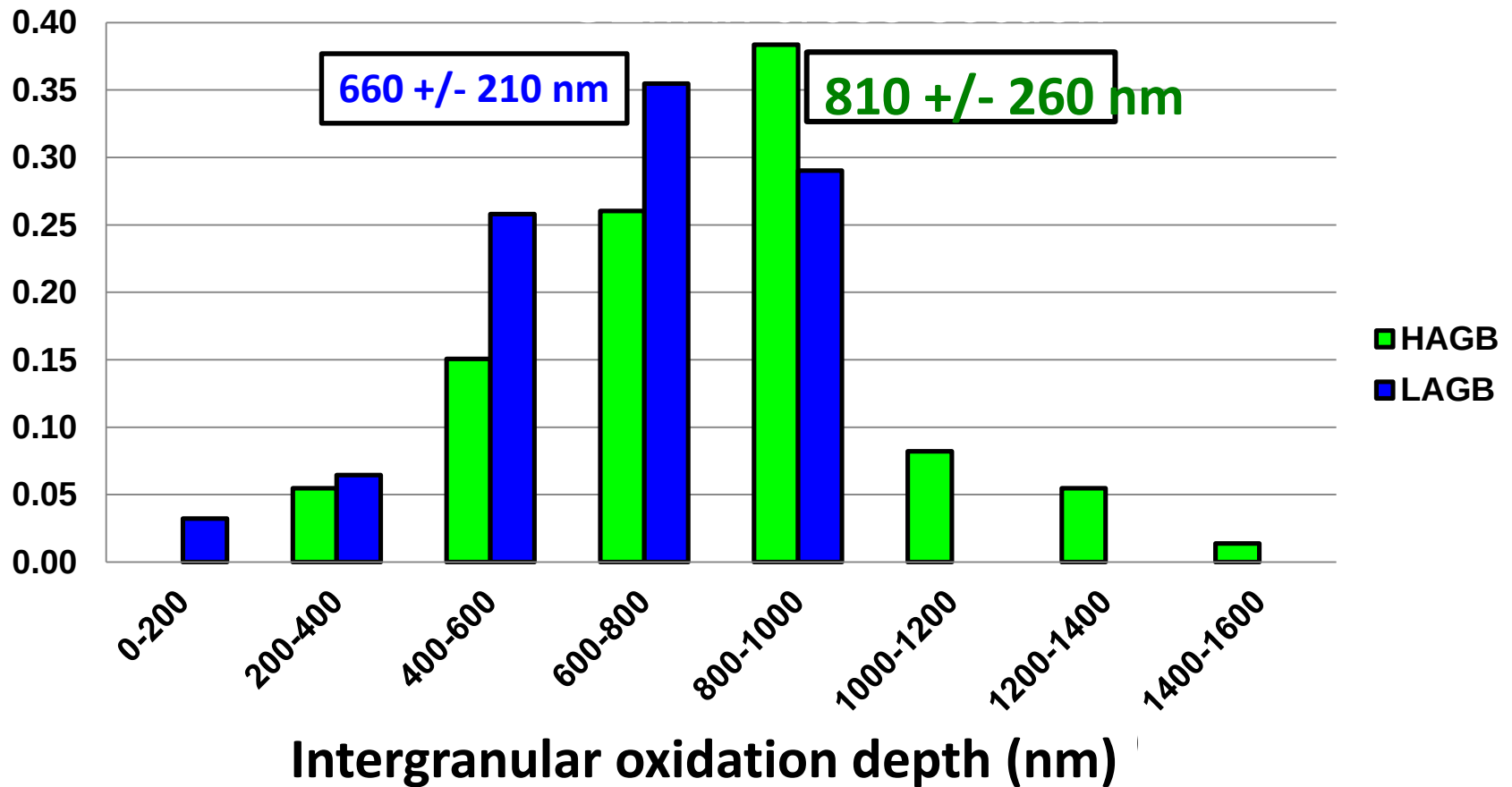
Non emerging carbide



Grain boundary character and oxidation

Alloy 182
360° C – 1000h
30 mL H₂/kg H₂O

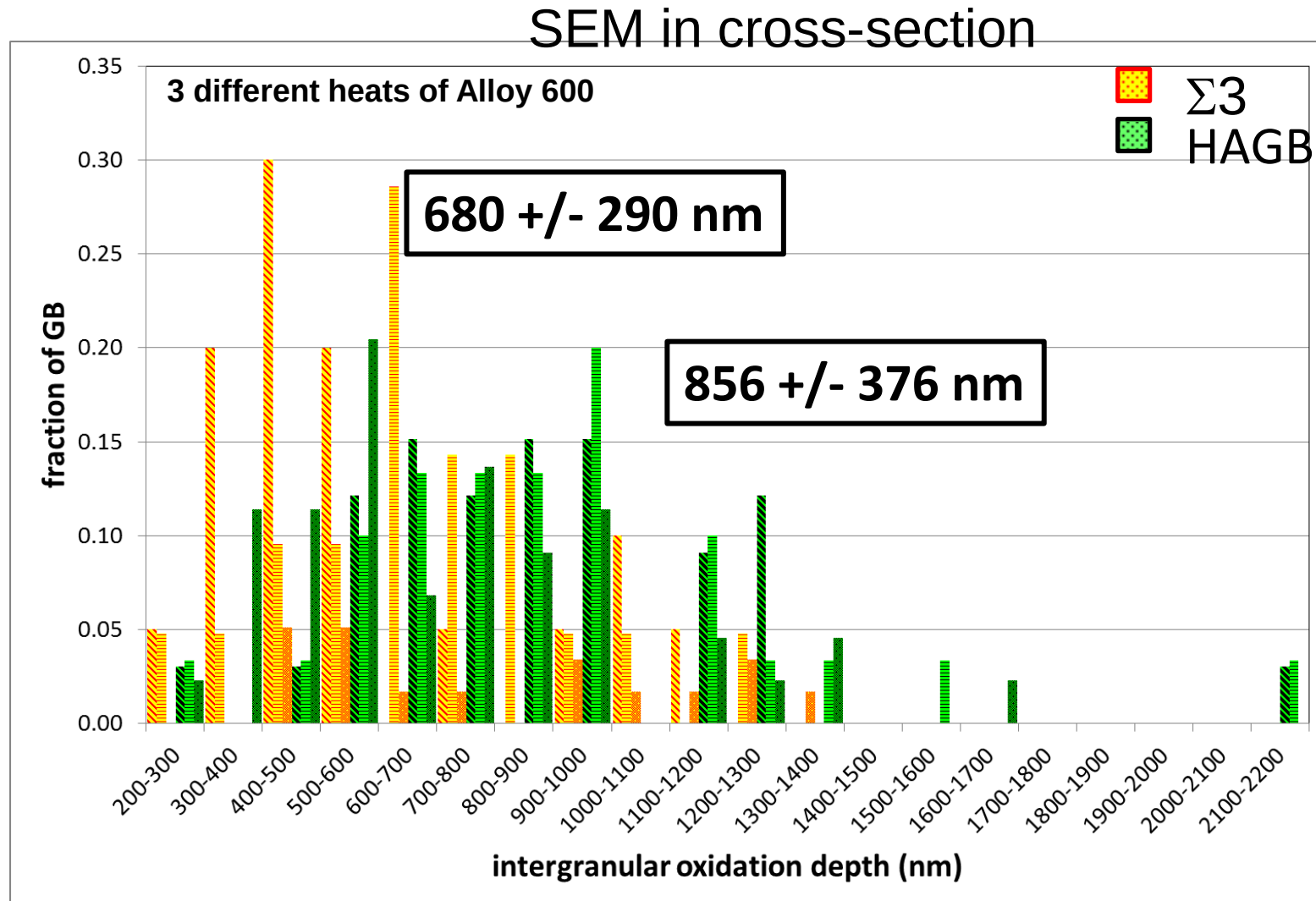
- Higher intergranular oxidation depth along HAGB than along LAGB



Grain boundary character and oxidation

Alloy 600
360° C – 1000h
20 mL H₂/kg H₂O

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

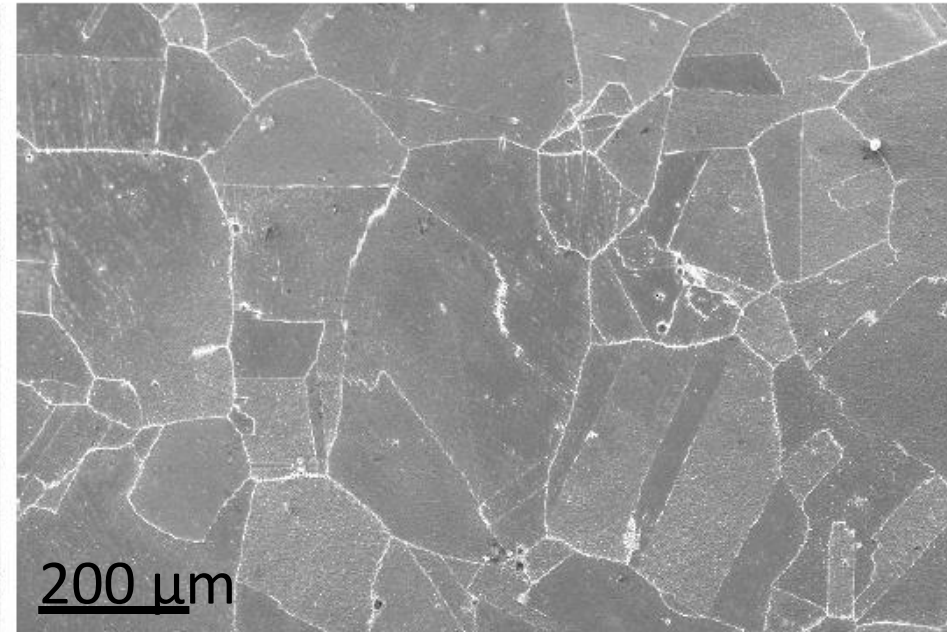
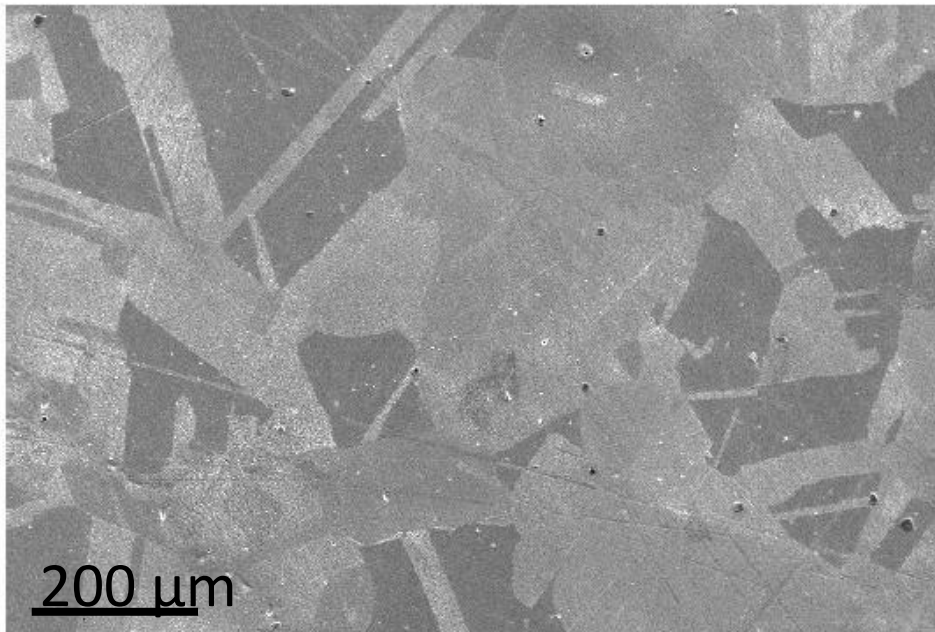


What about GB with no carbides?

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

SOLUTION-ANNEALED

SOLUTION-ANNEALED + THERMALLY TREATED

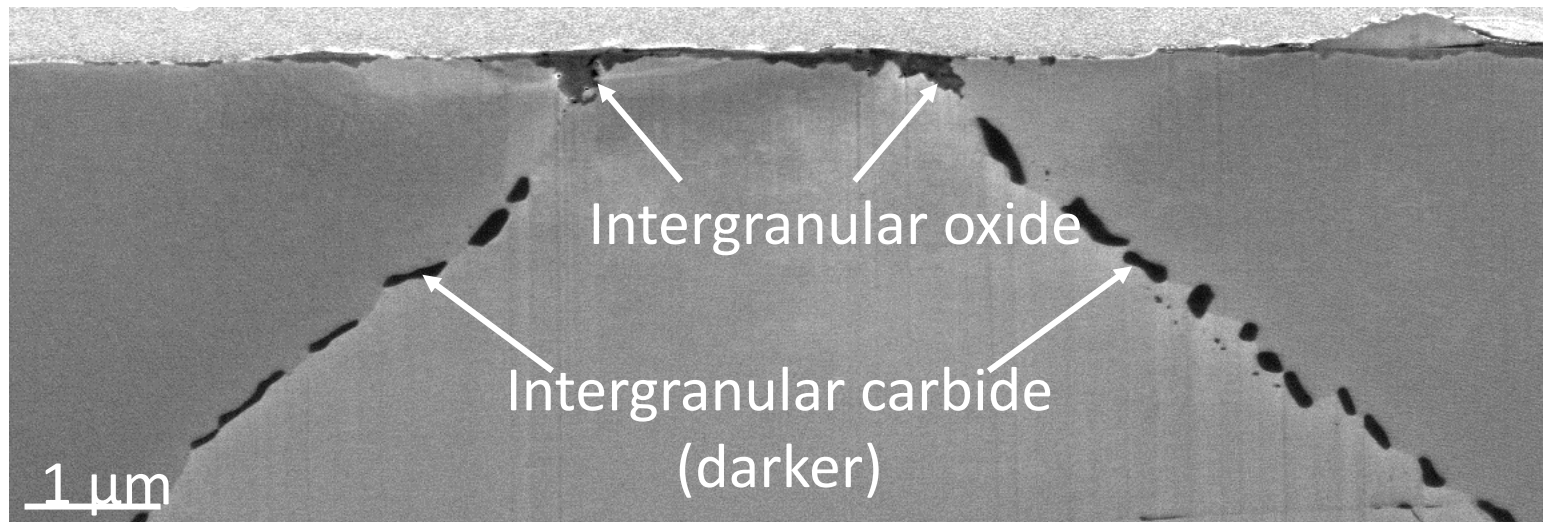
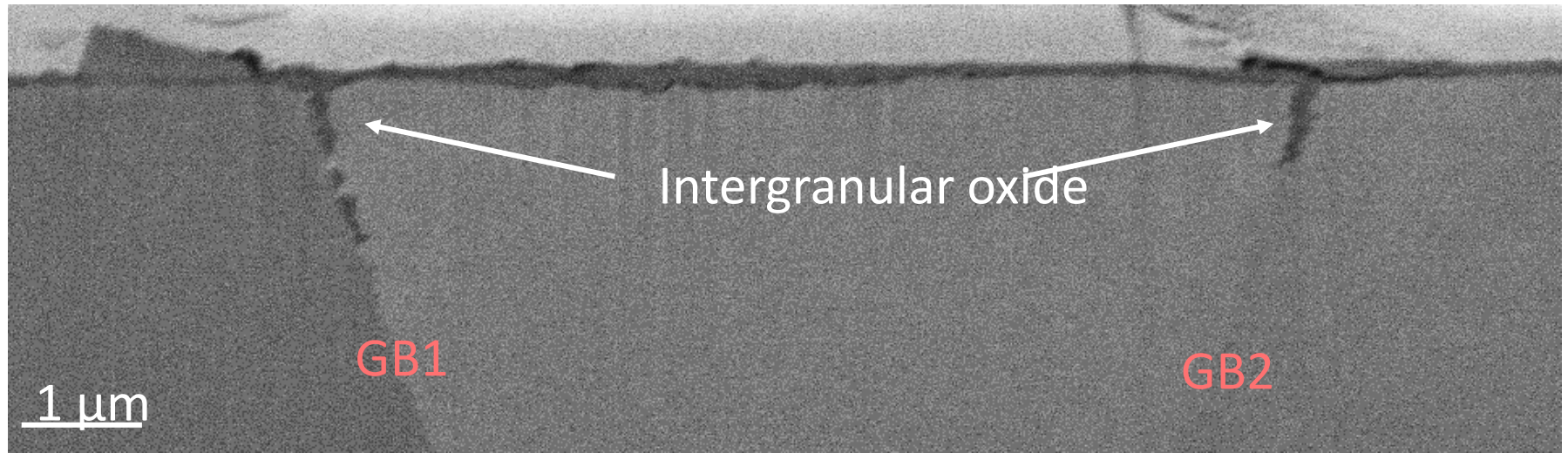


Dissolution of chromium
carbides

Quasi-continuous
precipitation of intergranular
chromium carbide

Alloys with model microstructures

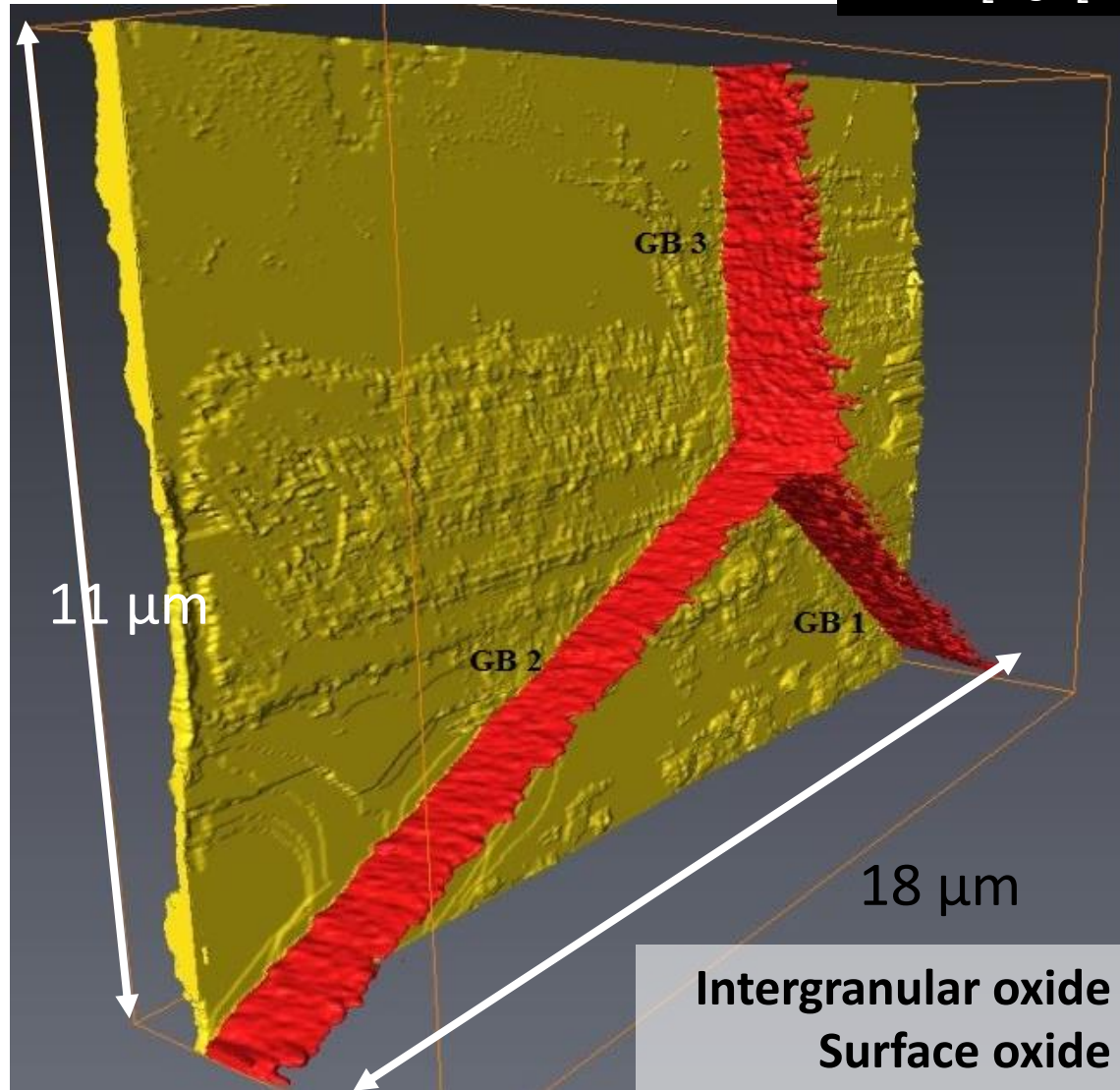
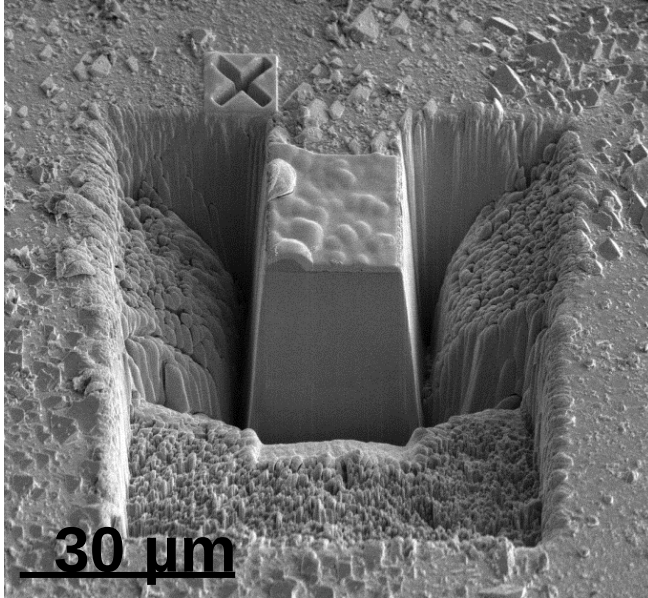
Alloy 600
325° C – 1400h
30 mL H₂/kg H₂O



Alloy 600 without carbides

Alloy 600
325° C – 1400h
30 mL H₂/kg H₂O

FIB 3D Slicing



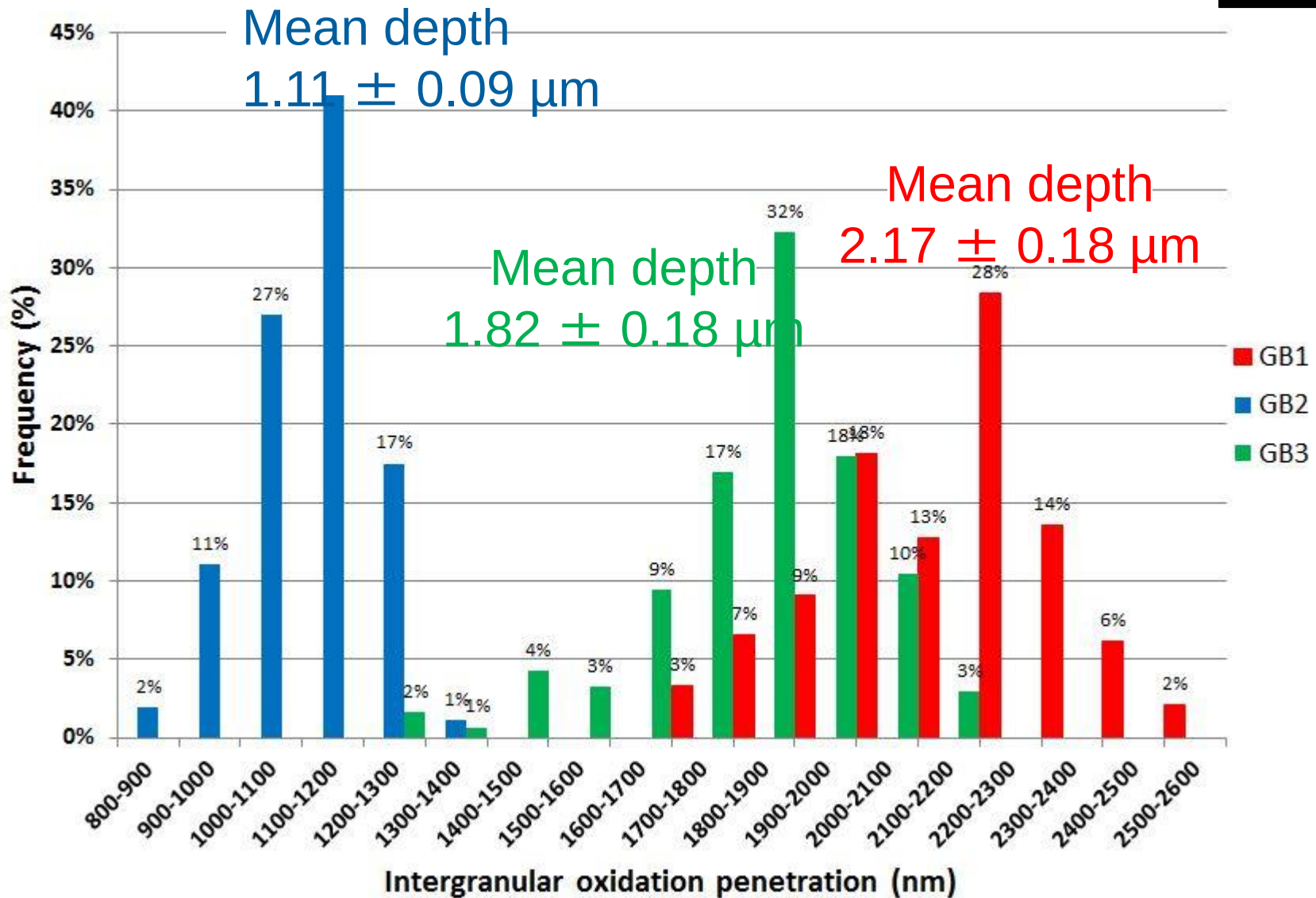
FIB/SEM facility
Equipex MATMECA

H.T. Le, internship (2015)

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

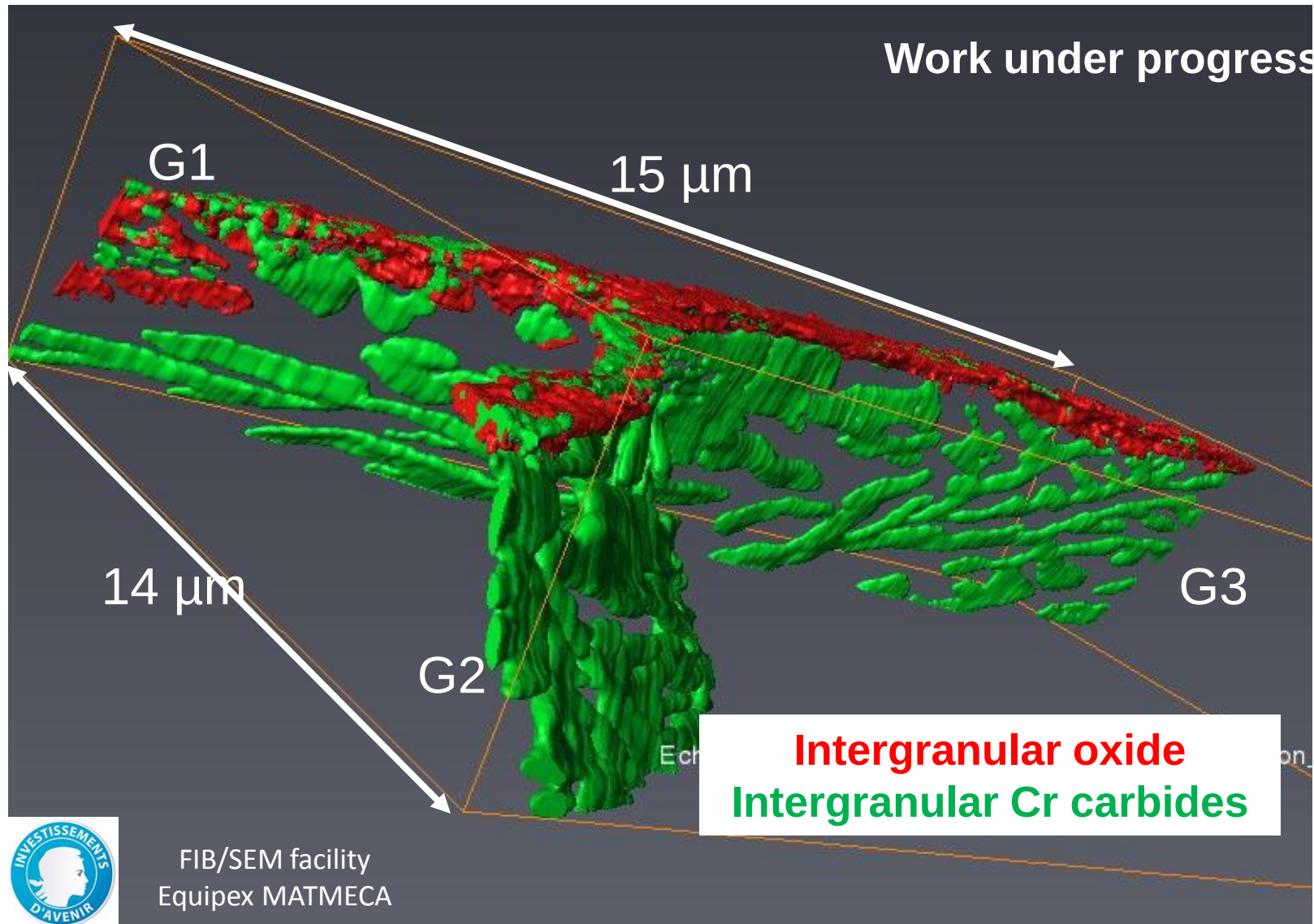
Alloy 600 without carbides

Alloy 600
325° C – 1400h
30 mL H₂/kg H₂O



Alloy 600 with carbide precipitation

Alloy 600
325° C – 1400h
30 mL H₂/kg H₂O

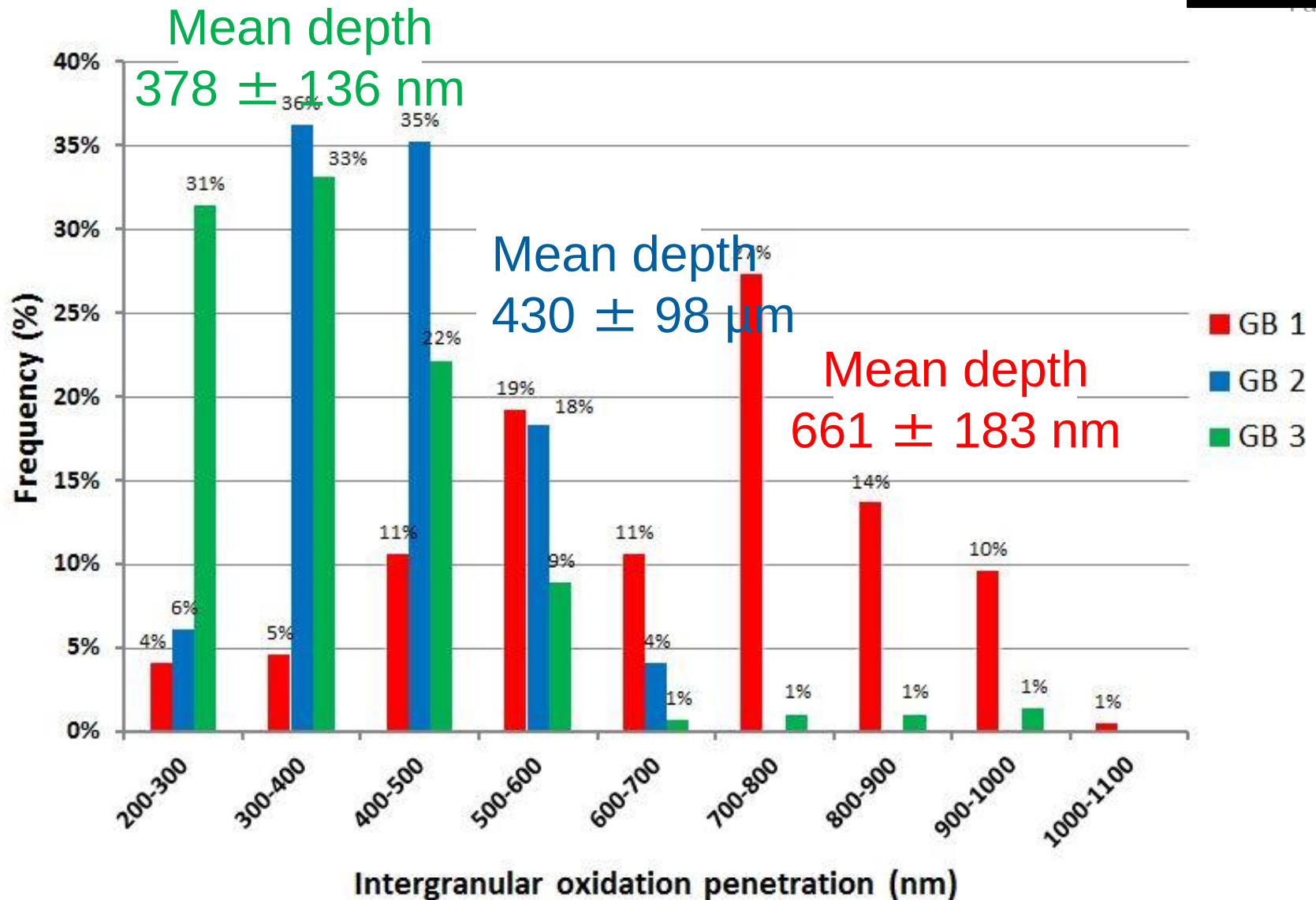


H.T. Le, internship (2015)

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

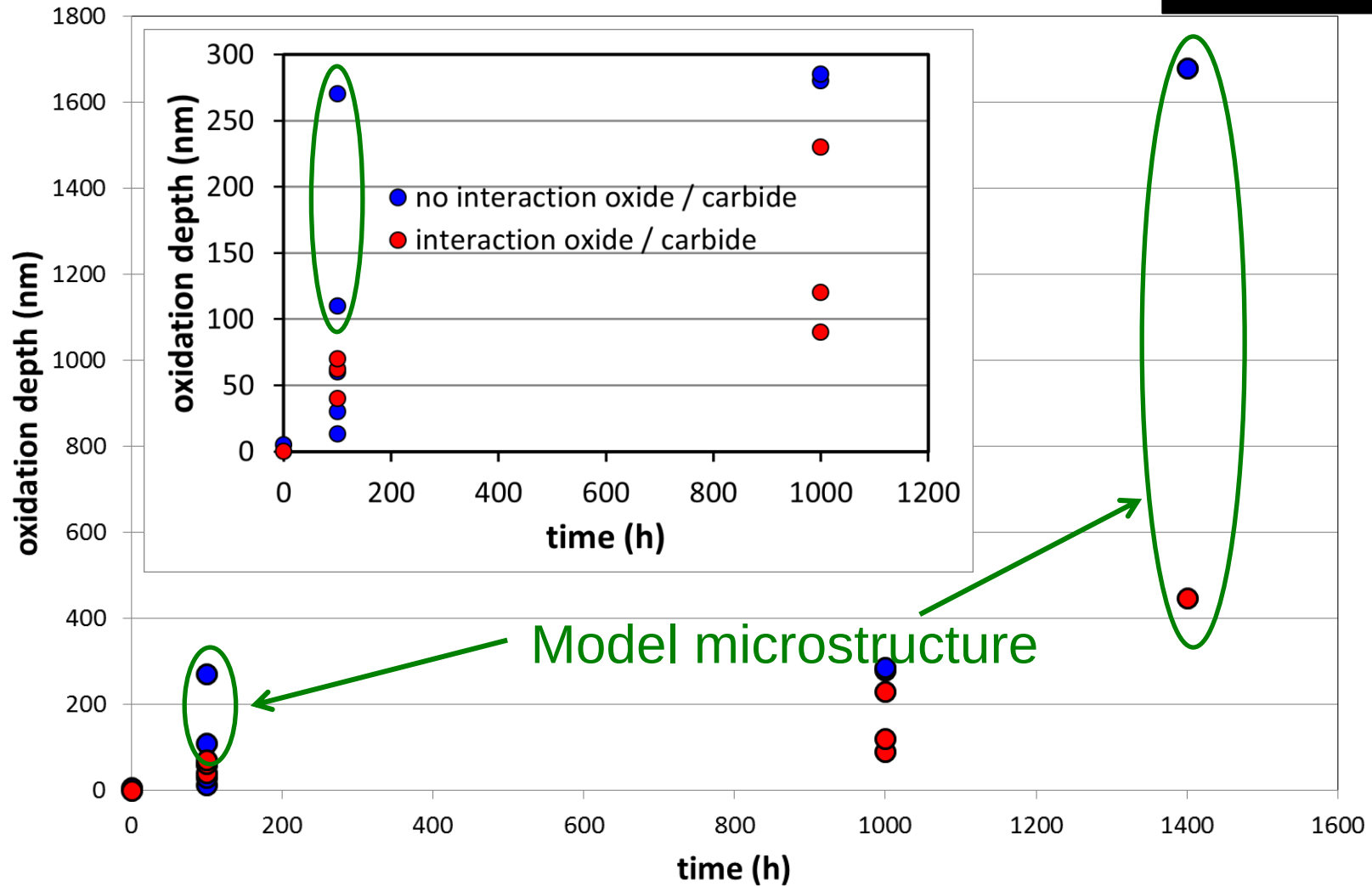
Alloy 600 with IG chromium carbides

Alloy 600
325° C – 1400h
30 mL H₂/kg H₂O



Oxidation kinetics at 325° C

Alloy 600 – Alloy 182
325° C
30 mL H₂/kg H₂O



- **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 ($t = 100\text{h}$)

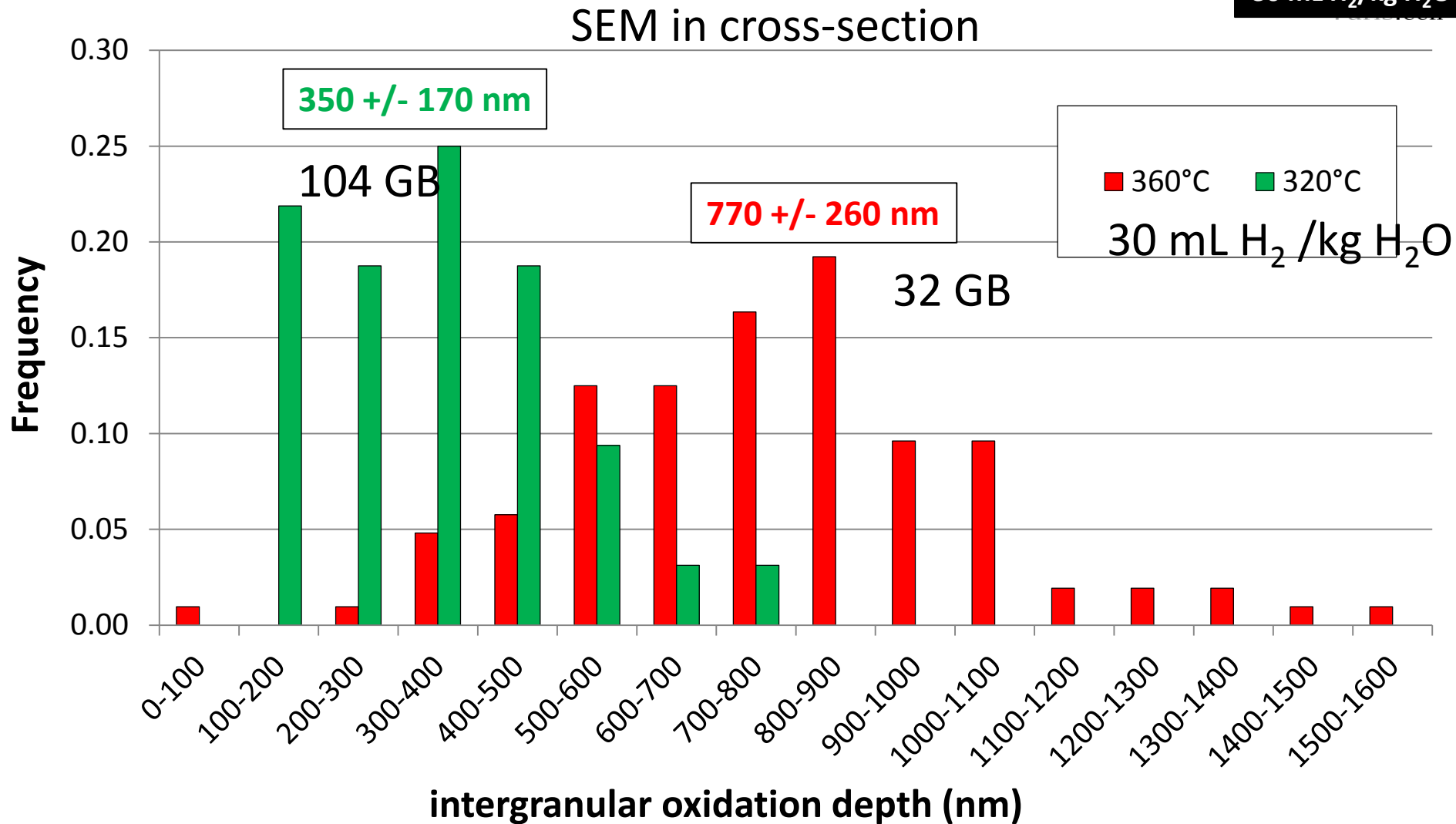
- IG oxidation deeper along:
 - HAGB than LAGB
 - HAGB than $\Sigma 3$
- Beneficial effect of intergranular chromium carbides on IG oxidation
- What is the effects of carbide type (Cr_7C_3 , Cr_{23}C_6), carbide distribution, carbide size on IG oxidation?
- Coupled effect grain boundary character / IG carbide precipitation?
- What is the nature of the oxide / carbide interaction?
 - Change in the nature of the oxide: Cr_2O_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 H₂/kg H₂O



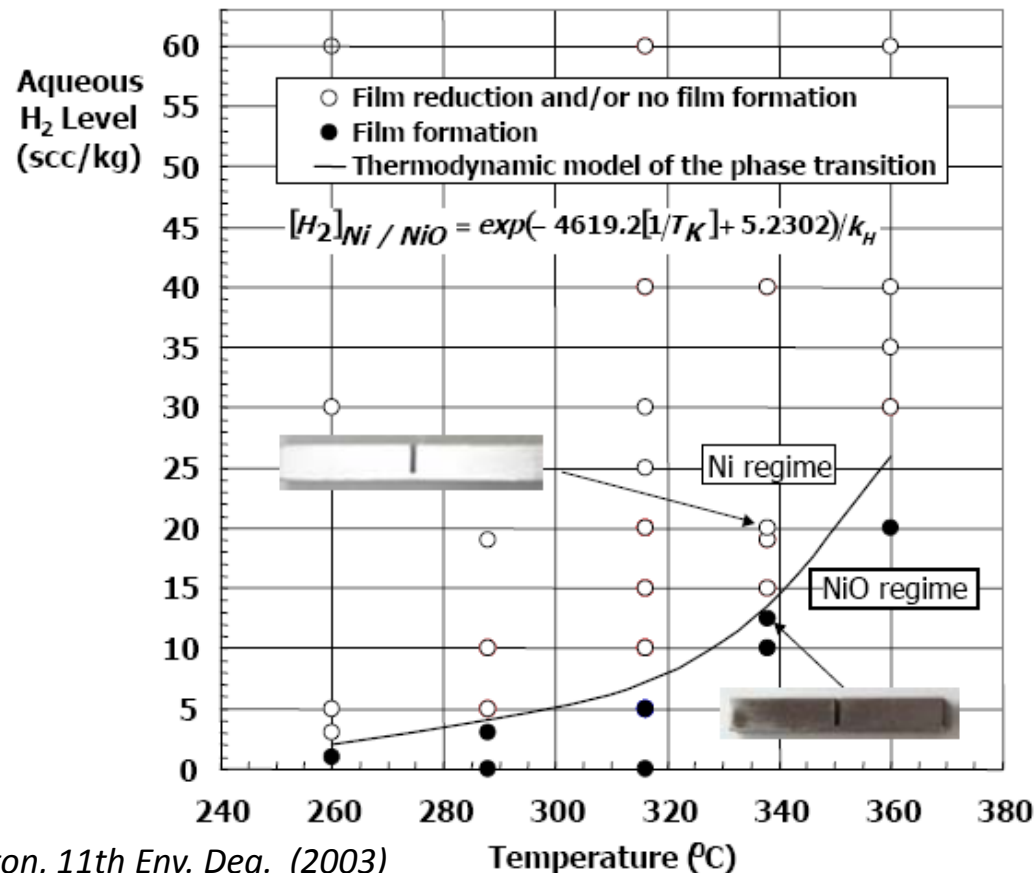
Estimated activation energy for intergranular oxidation: $Q \approx 57 \text{ kJ.mol}^{-1}$

Environmental factors and SCC

Two main factors:

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

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



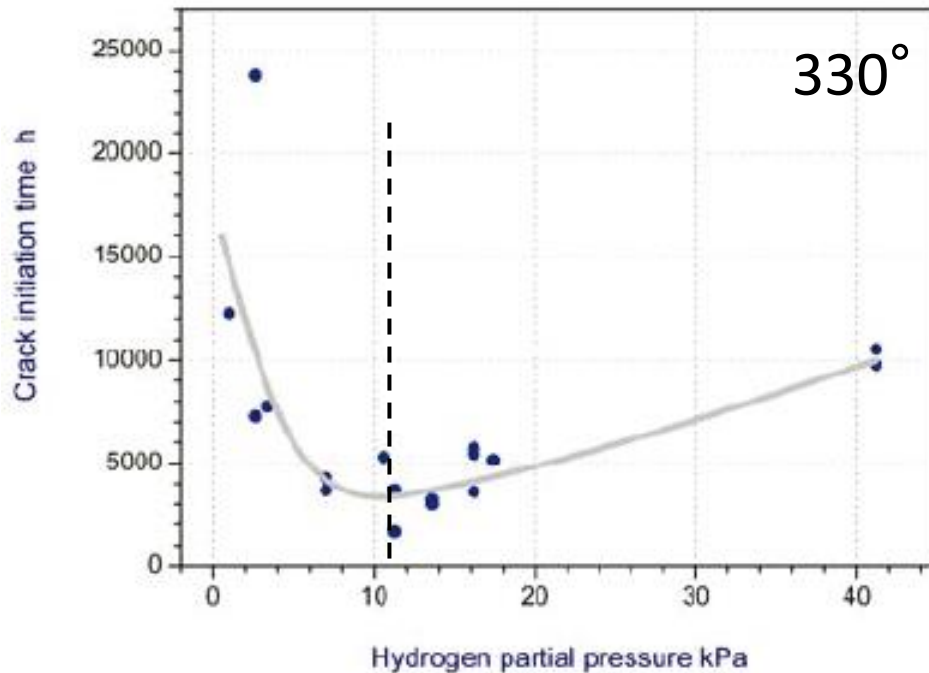
Environmental factors and SCC

- Activation energy for crack initiation: $30 - 220 \text{ kJ.mol}^{-1}$

Activation energy measured for a constant EcP: $140 \pm 33 \text{ kJ.mol}^{-1}$

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

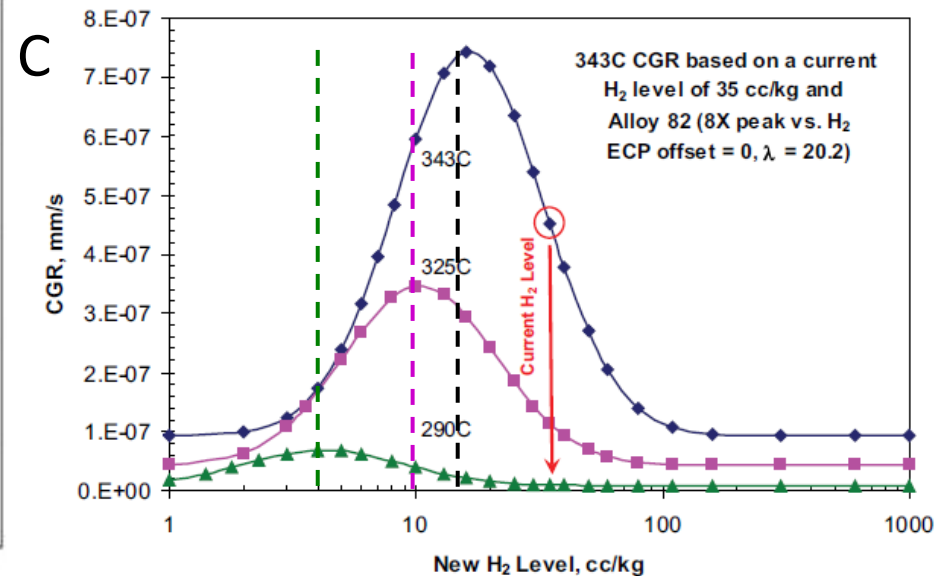
- Effect of H_2 content
INITIATION



A. Molander et al., 15th Env. Deg. (2011)

P. Andresen (2007)

PROPAGATION



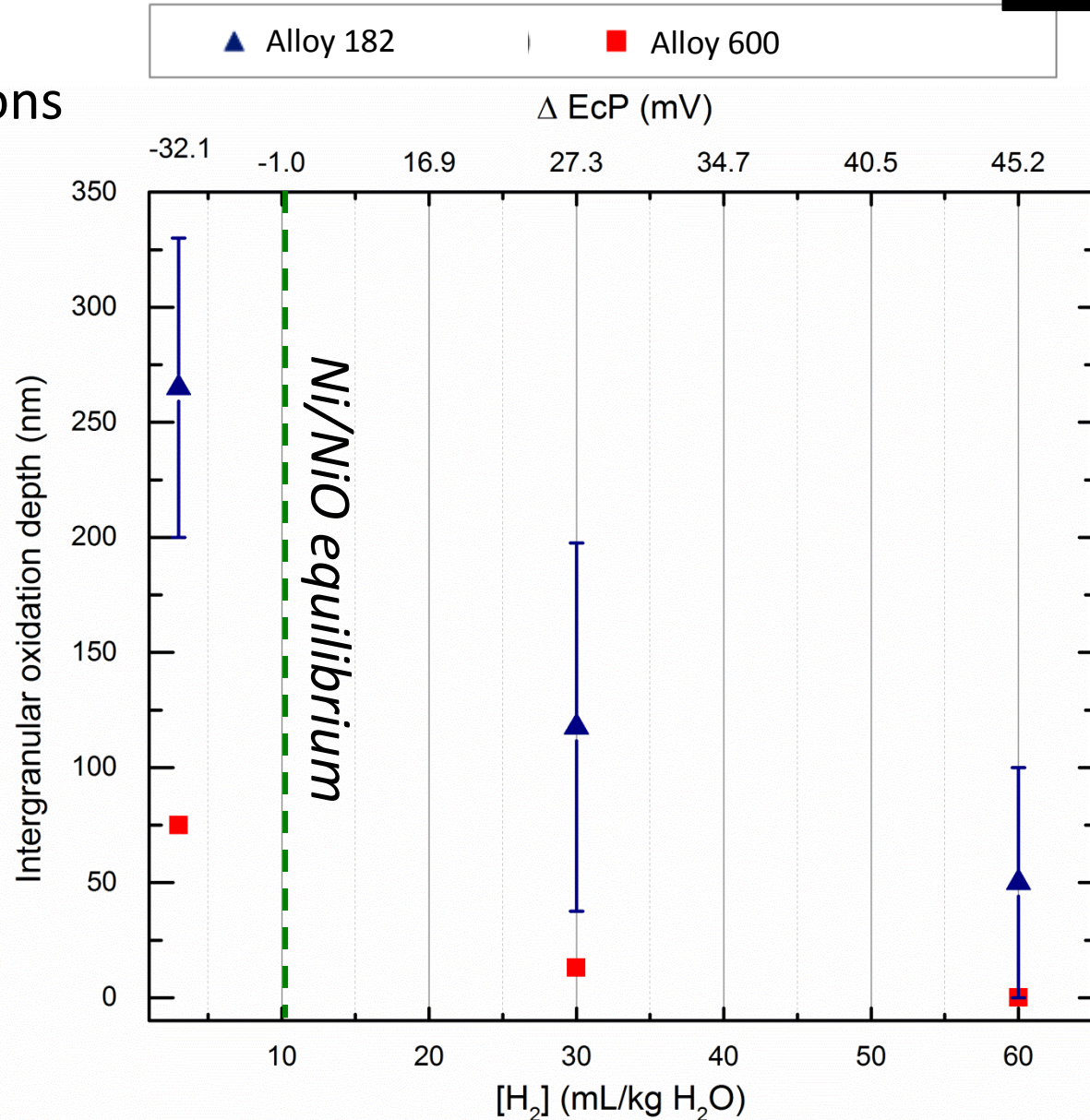
Maximum crack growth
rate at the Ni/NiO
equilibrium

Dissolved hydrogen content

Alloy 182 – Alloy 600
325° C
100h

325° C - 100h

TEM observations



M. Wehbi, PhD thesis (2014)

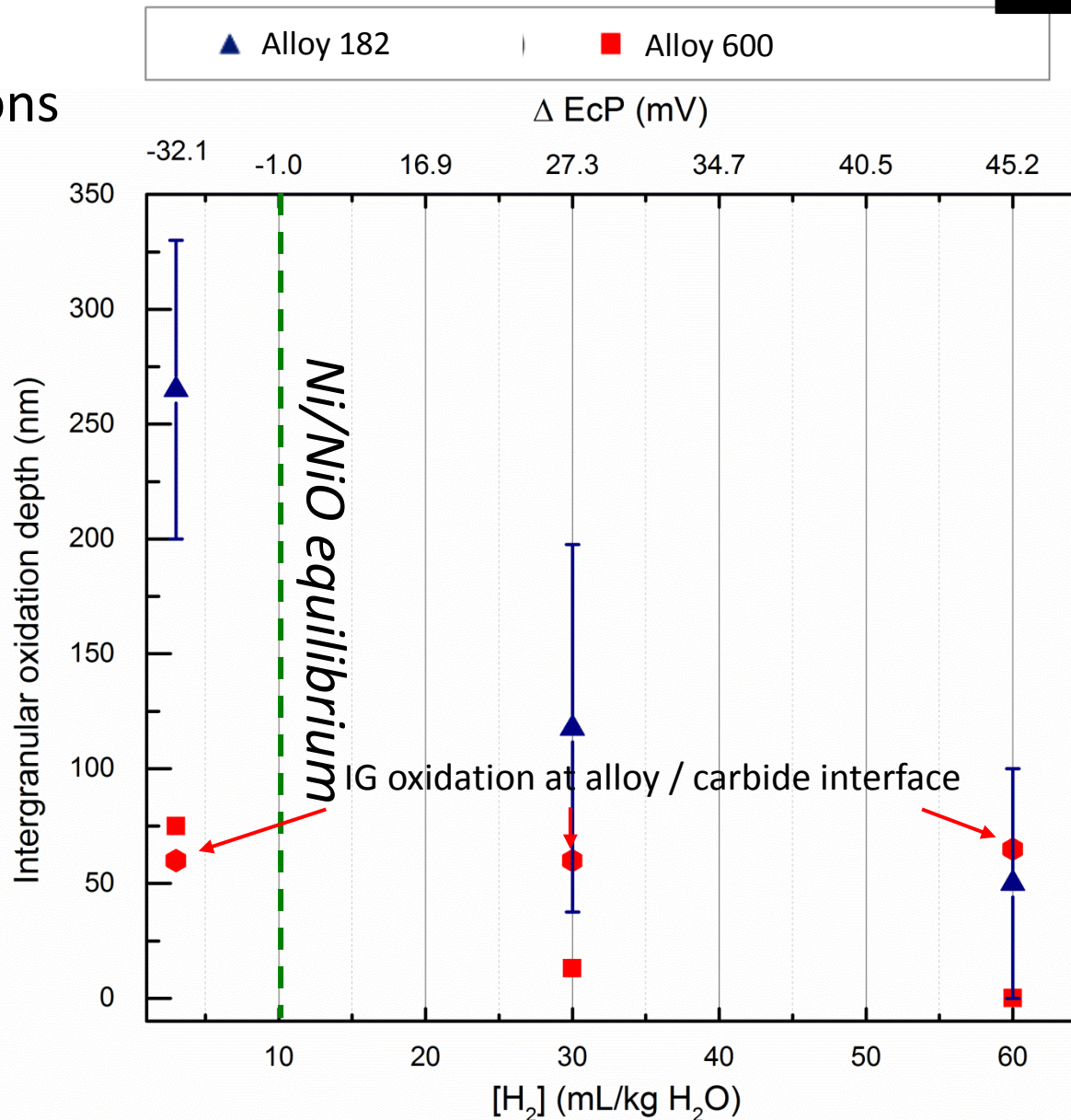
J. Caballero, PhD thesis

Dissolved hydrogen content

Alloy 182 – Alloy 600
325° C
100h

325° C - 100h

TEM observations

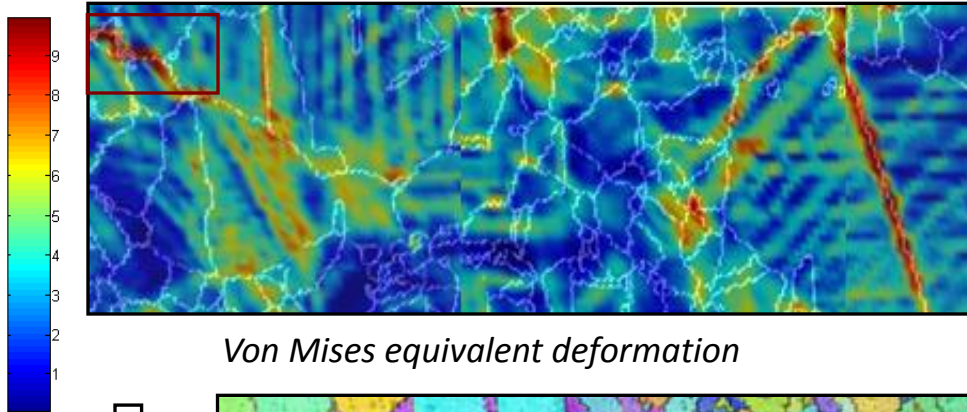


M. Wehbi, PhD thesis (2014)

J. Caballero, PhD thesis

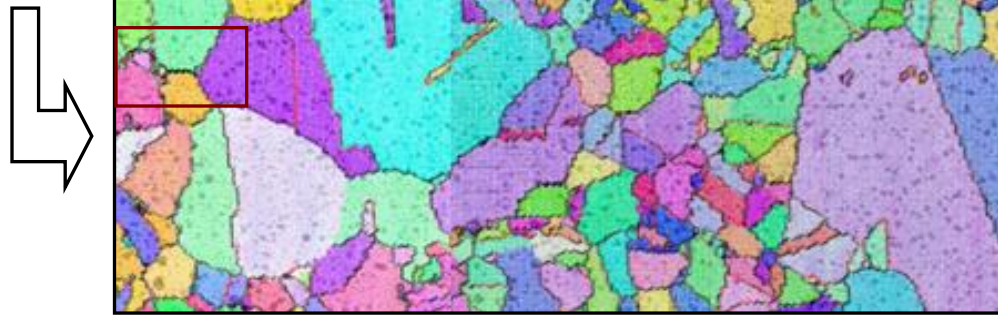
- Metallurgical factors
 - Grain boundary character
 - Intergranular chromium carbides
- Environment
 - Temperature
 - Dissolved hydrogen content
- Mechanical factors
 - Pre-straining
 - Oxidation under stress

Coupling between microstructure and strain fields



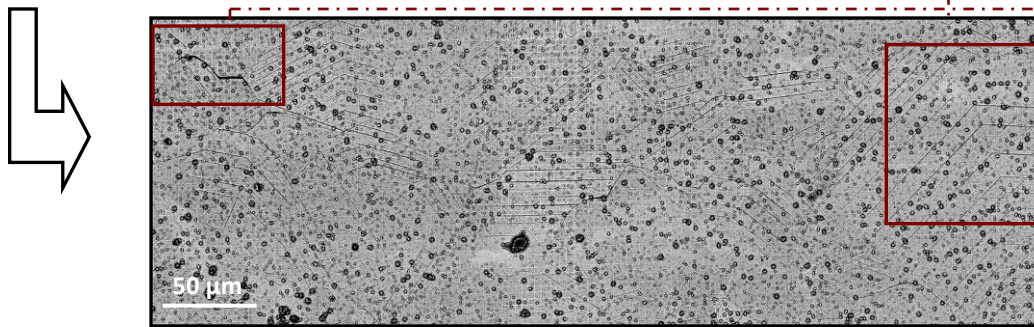
Strain field measurements
(Von Mises equivalent deformation)

Von Mises equivalent deformation

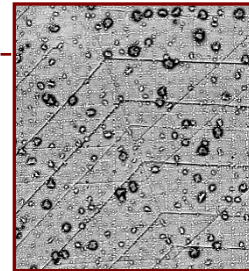
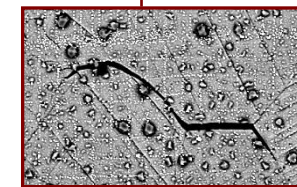


EBSD orientation mapping of the same area

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

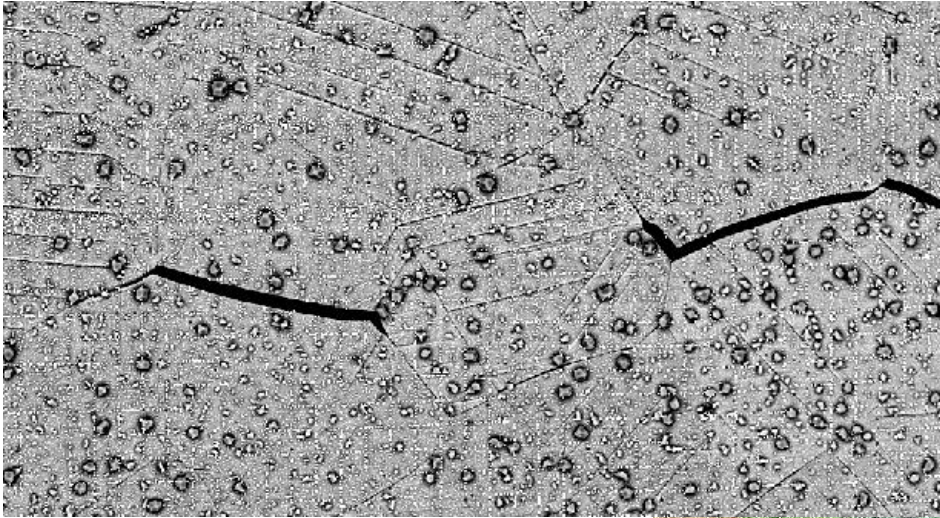


Cracking network (SEM observations)

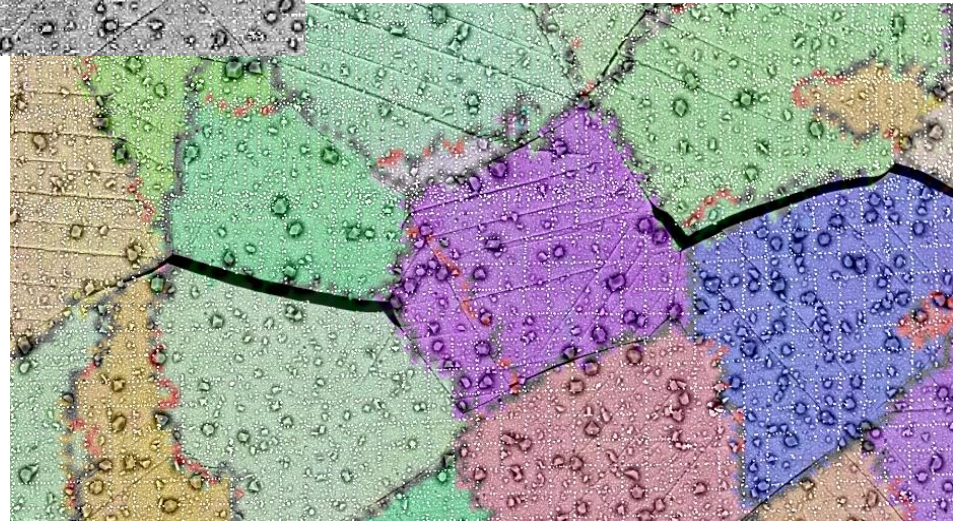


- Cracking features
- Oxidation
- Slip bands

→ Application to IASCC of austenitic stainless steels

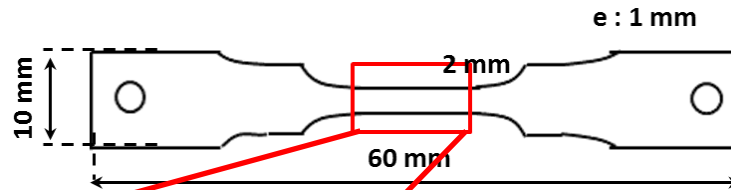


5 dpa, 2% macroscopic strain

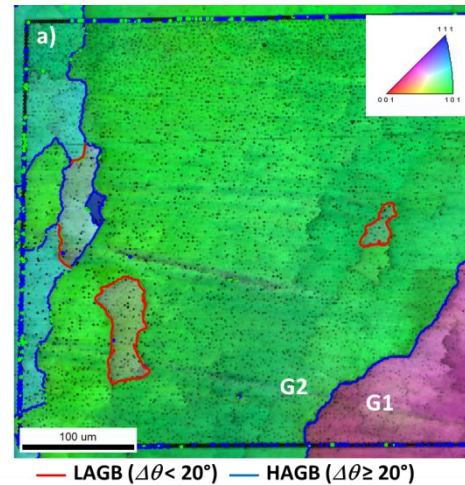
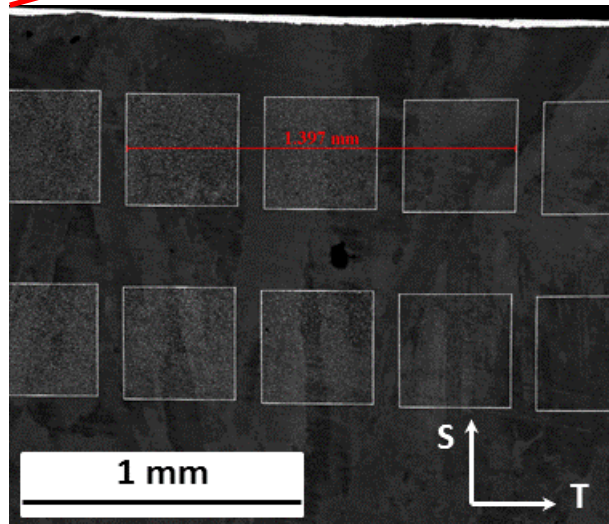


Effect of pre-straining

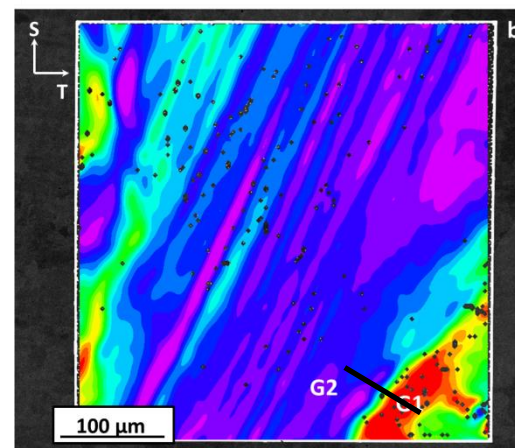
Alloy 82
360° C - 1000h
30 mL H₂ / kg H₂O



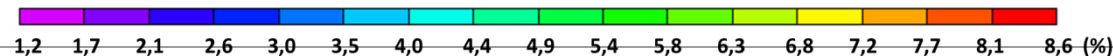
Tensile specimens – mirror finish
Macroscopic deformation: 0, 7, 20%



EBSD orientation maps



Strain field measurement



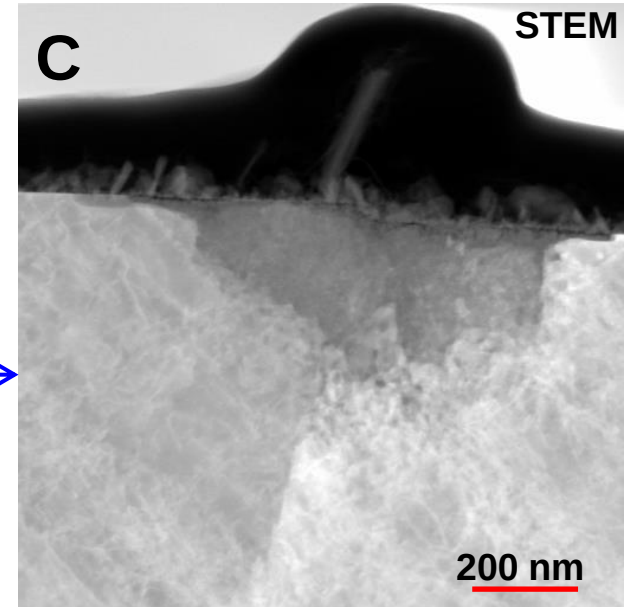
8 fields (400 μm x 400 μm)
gold speckle (diameter : 1 μm)

Effect of pre-straining

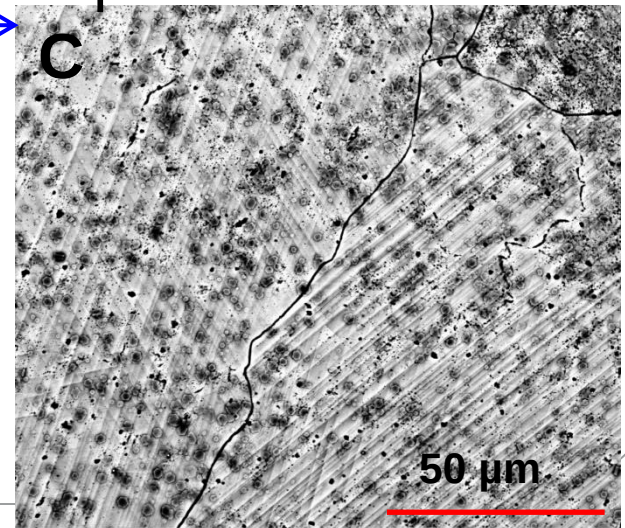
Alloy 82
360° C - 1000h
30 mL H₂ / kg H₂O

Grain boundaries studied after oxidation

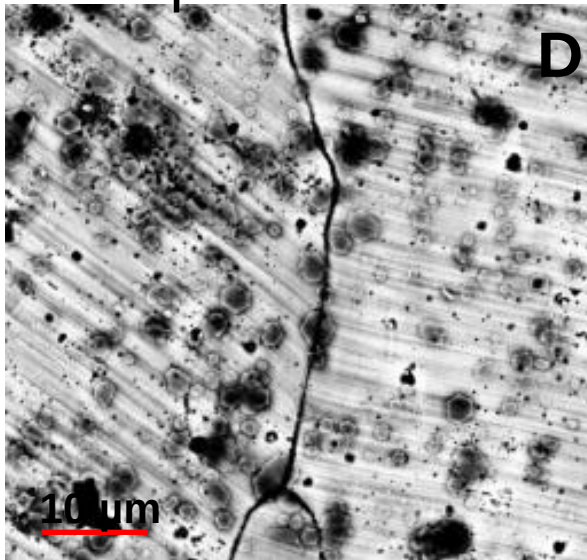
GB	GB misorientation (°)	Mean local strain (%)	Local strain gradient (%)
A	40	0	-
B	5	7	0
C	40	6	6
D	30	13	0



Slip band discontinuity



Slip band continuity



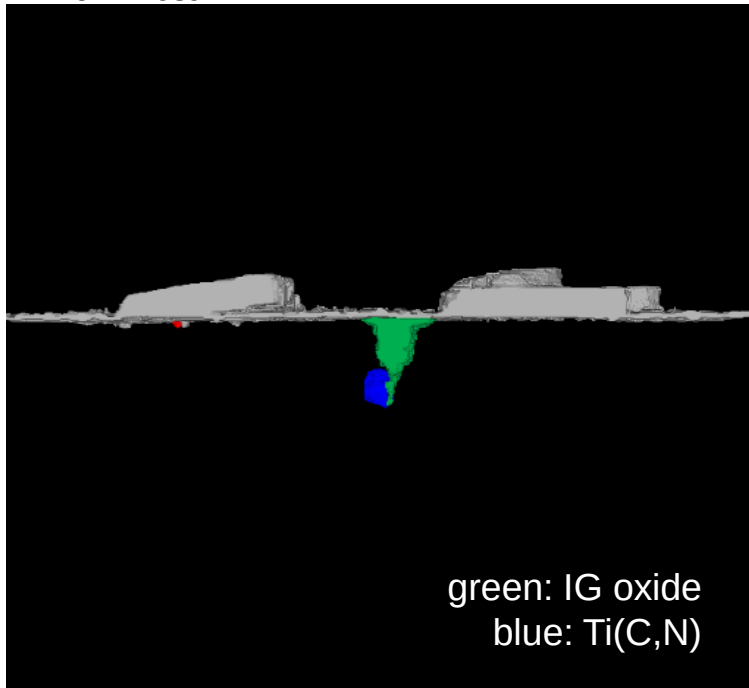
Effect of pre-straining

Alloy 82
360° C - 1000h
30 mL H₂ / kg H₂O

Grain boundary D

Grain boundary length: 6 μm

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

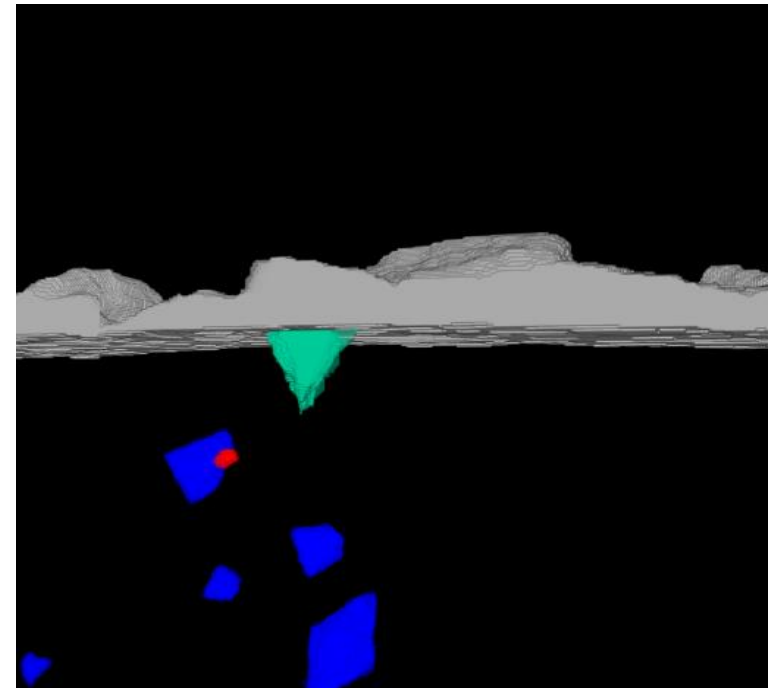


Mean oxidation depth:
550 +/- 50 nm

Grain boundary C

Grain boundary length : 3 μm

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

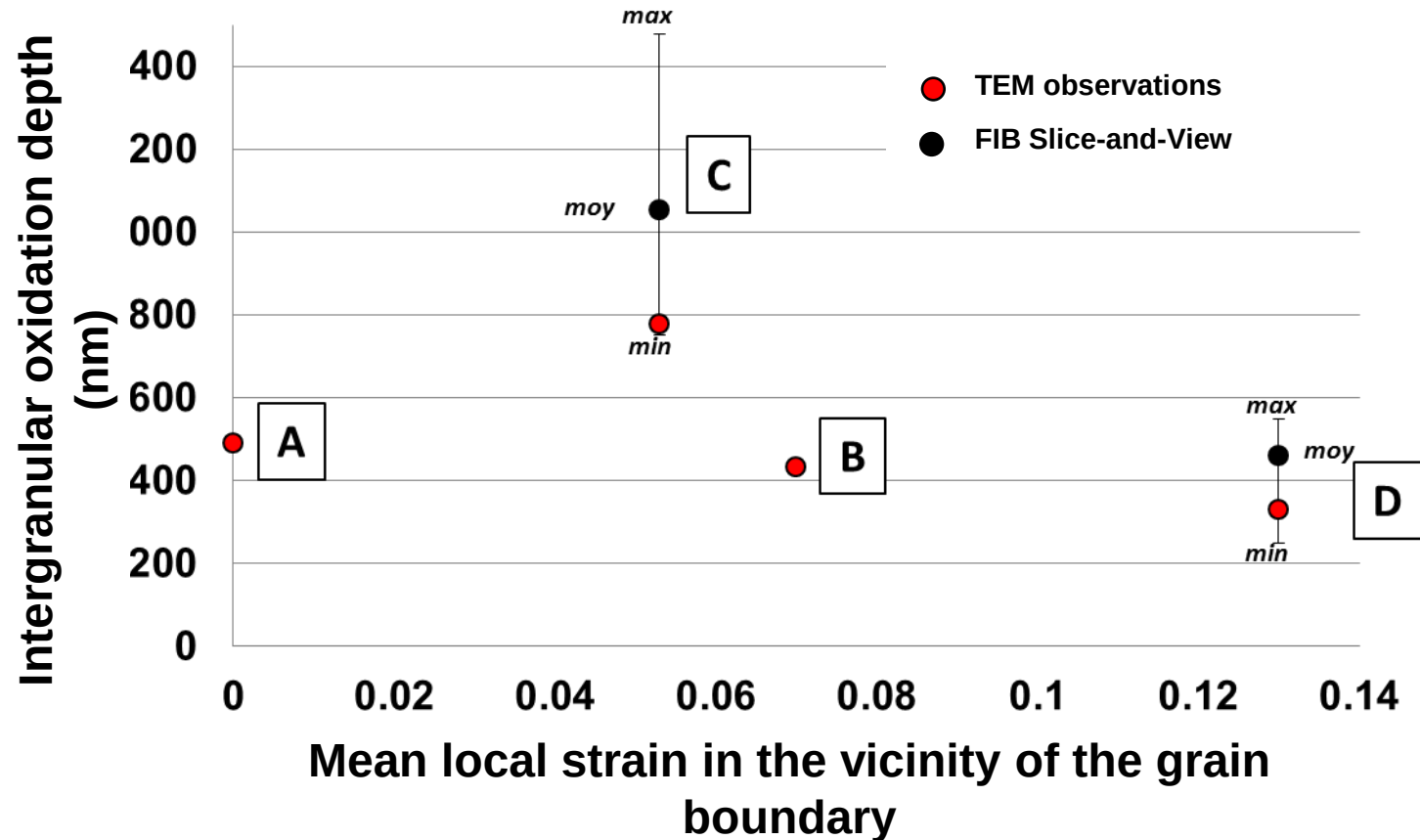


Mean oxidation depth:
1050 +/- 180 nm

A strain gradient between neighbouring grains seems to promote:

- Intergranular oxidation
- Oxide depth scattering along the GB

Effect of pre-straining



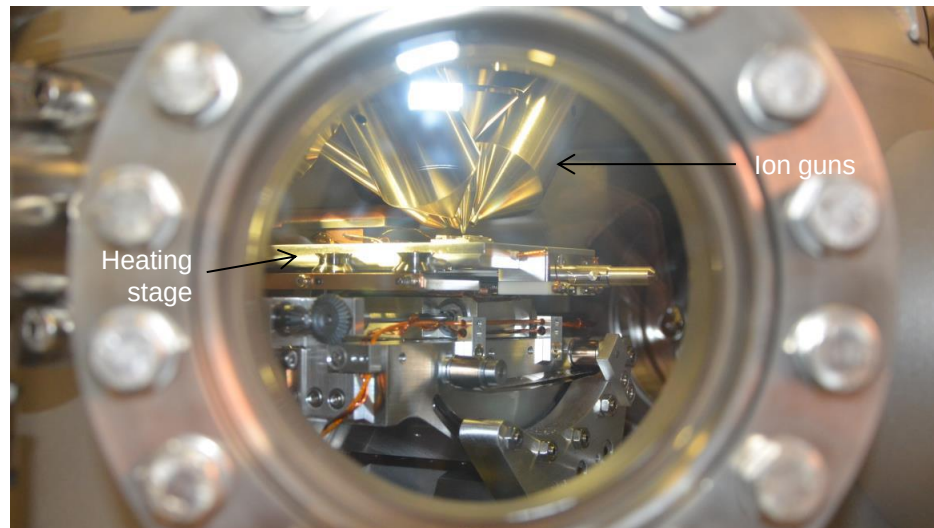
FIB Slice-and-View analyses confirm TEM observations:

- 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

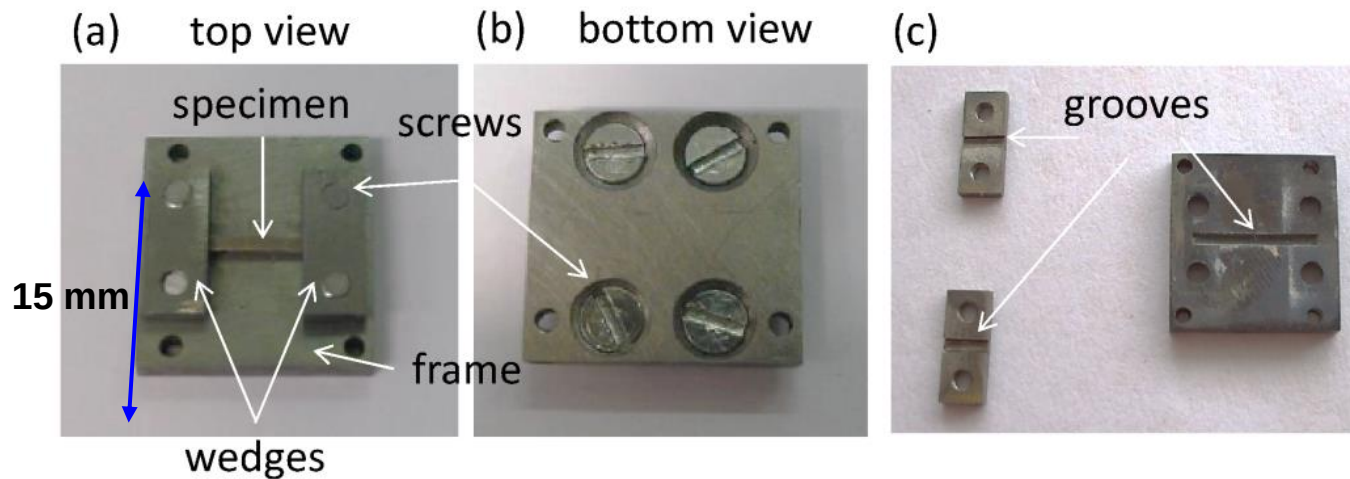
Coupling oxidation and stress

- 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]

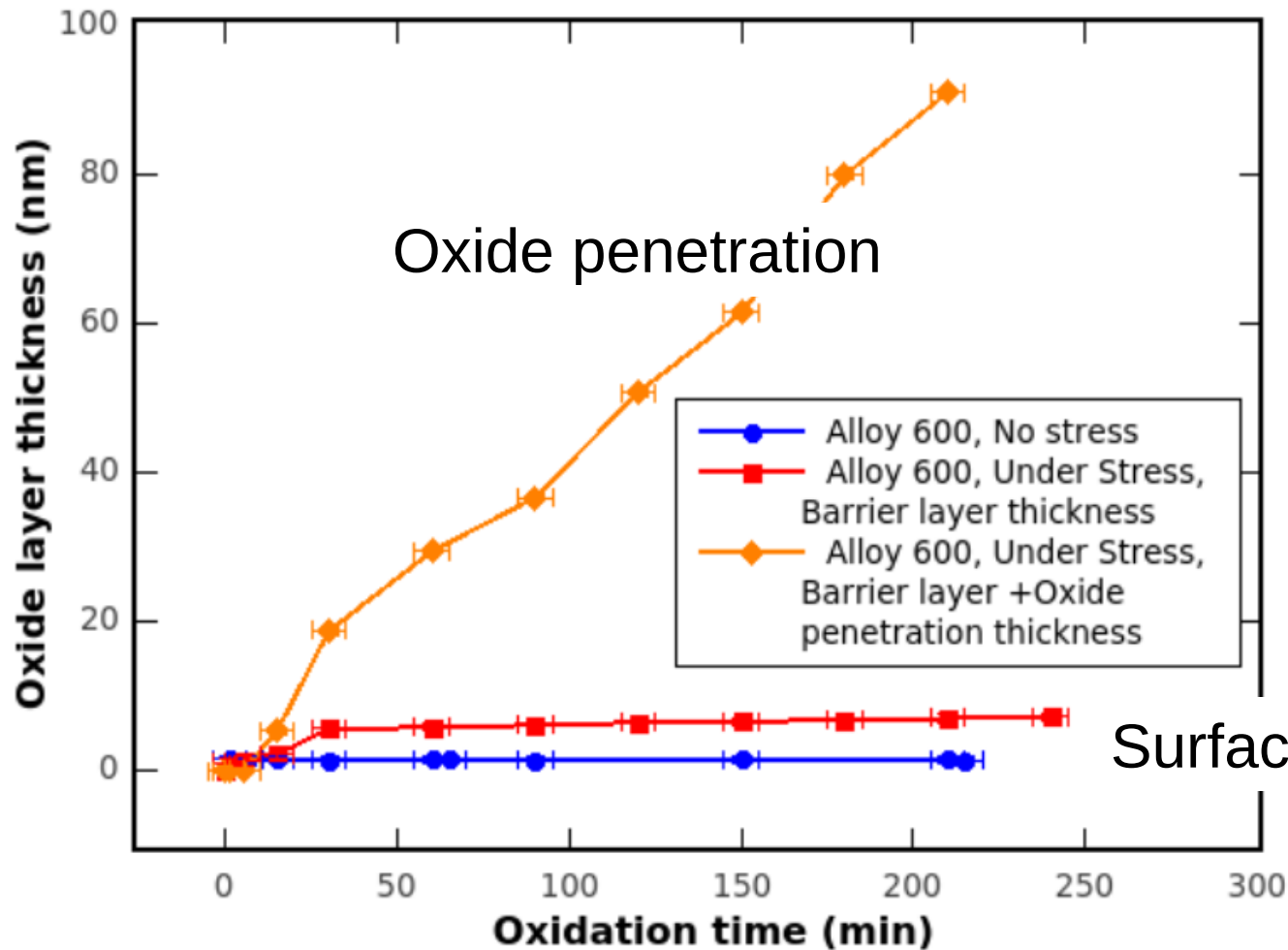
- Stress imposed by differential thermal expansion using:
 - A molybdenum device ($\text{TEC} \approx 5 \times 10^{-6} \text{ K}^{-1}$)
 - Alloy 600 specimens ($\text{TEC} \approx 14 \times 10^{-6} \text{ K}^{-1}$)



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

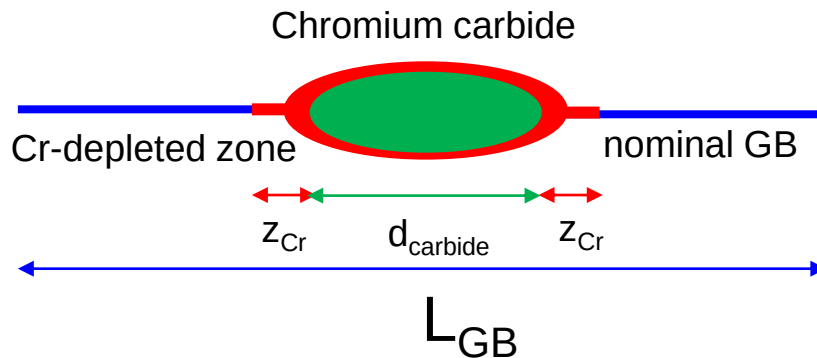
Coupling oxidation and stress

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 ($^{\circ}C$)
- $[H_2](cc/kg \text{ d'H}_2O)$

- 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.

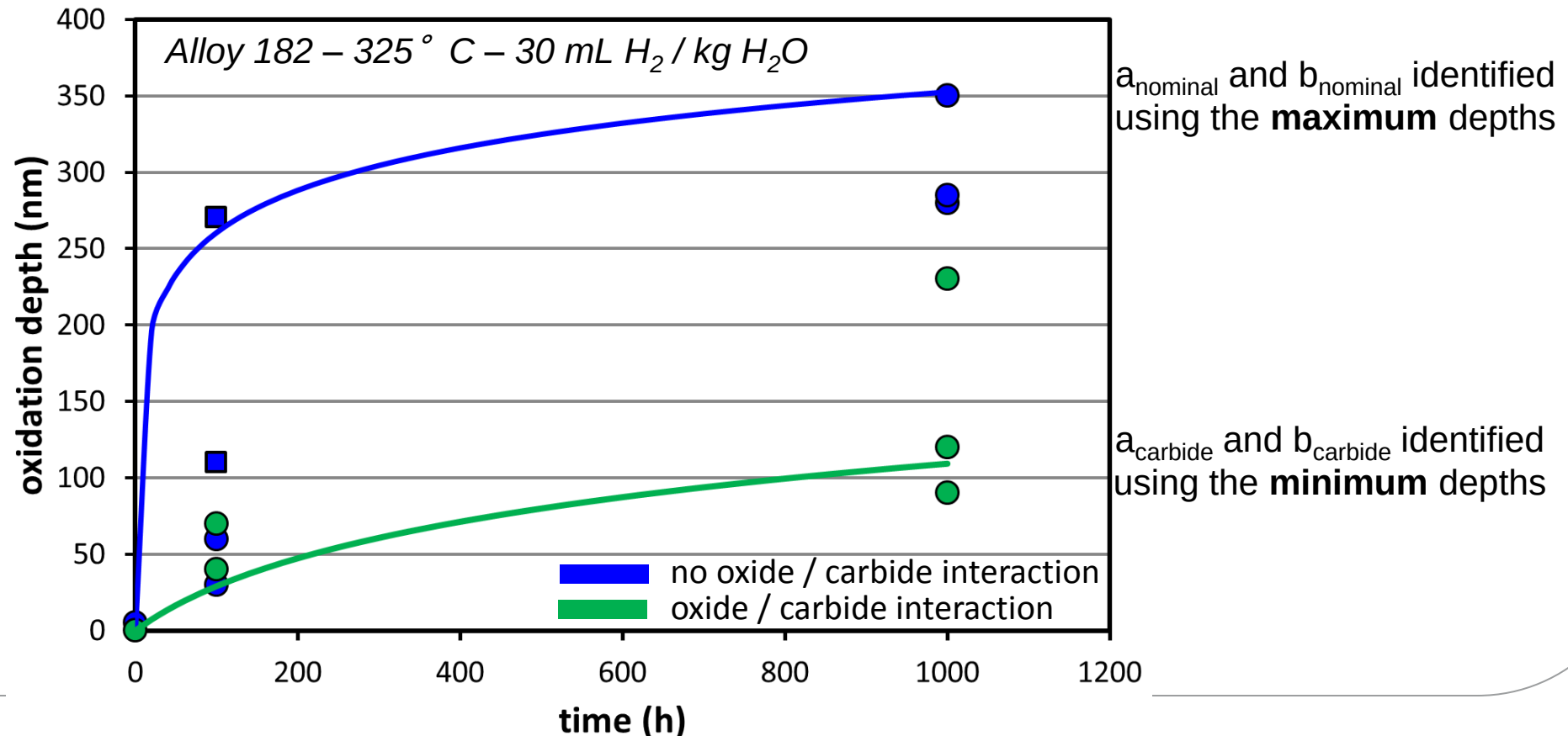
$$p_i = \frac{1}{a_i} \ln(1 + b_i \times t) \times f(\Delta E_{cP}) \times g(T)$$

IG oxide depth

constant

electrochemical potential

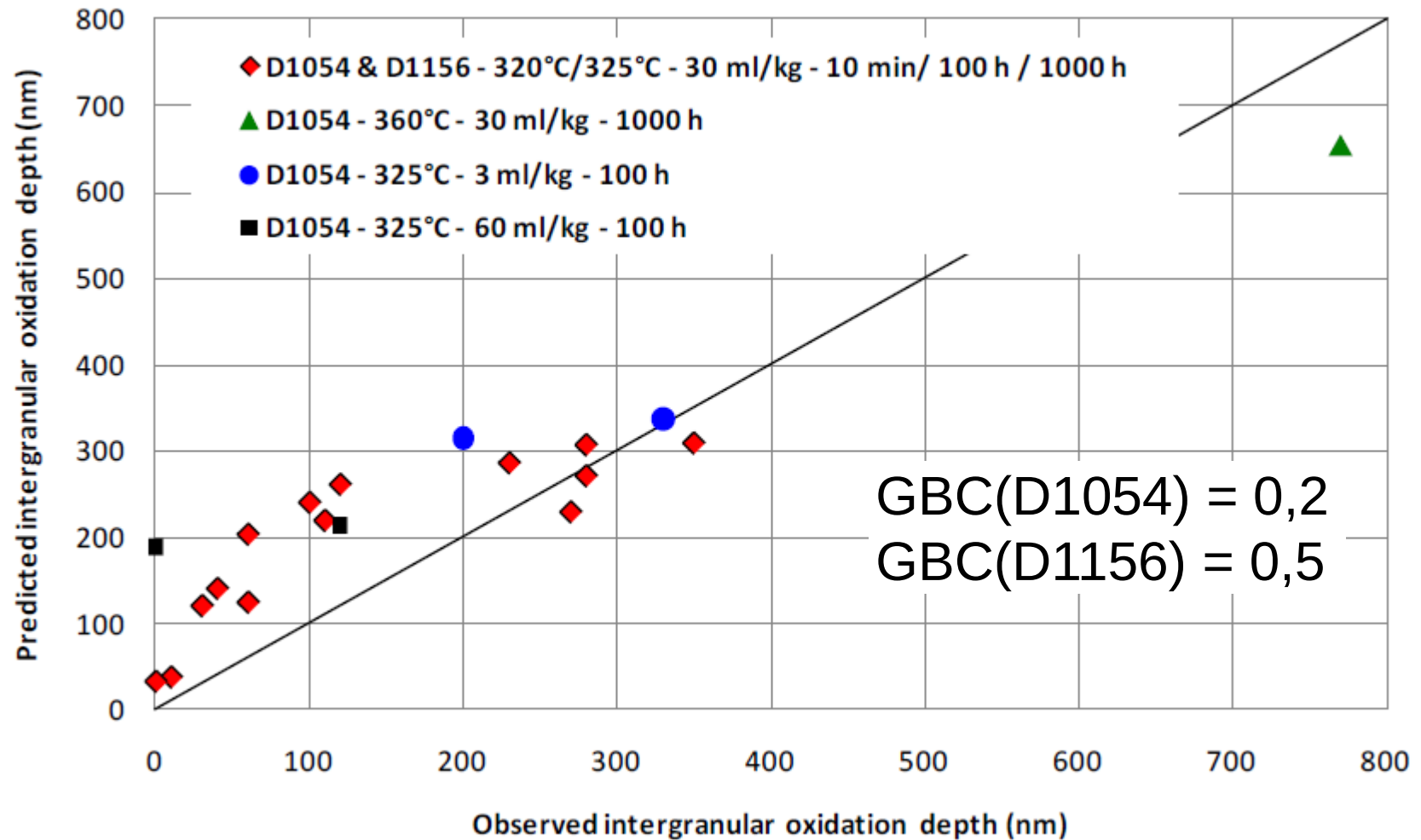
temperature



Application to Alloy 182

- Random sampling of 100 GB

GBC = Grain boundary coverage with chromium carbides



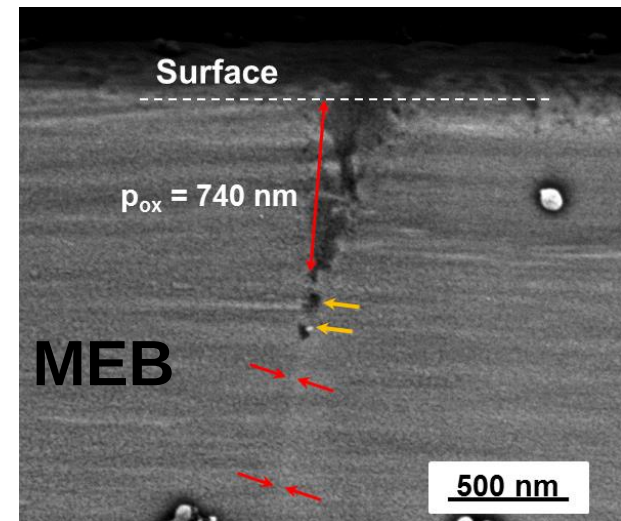
Crack initiation criterion : methodology

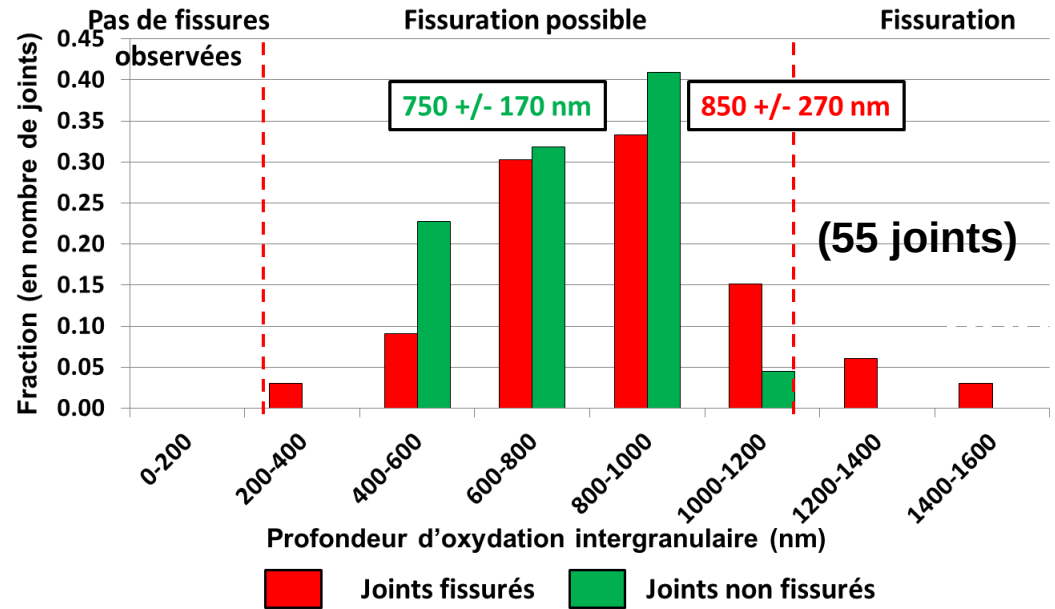
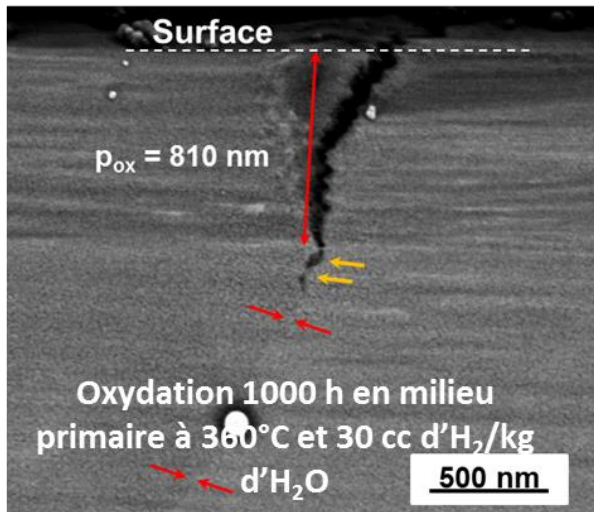
Alloy 182 1000 hours primary water at 360° C, 30 mL d'H₂/kg
d'H₂O

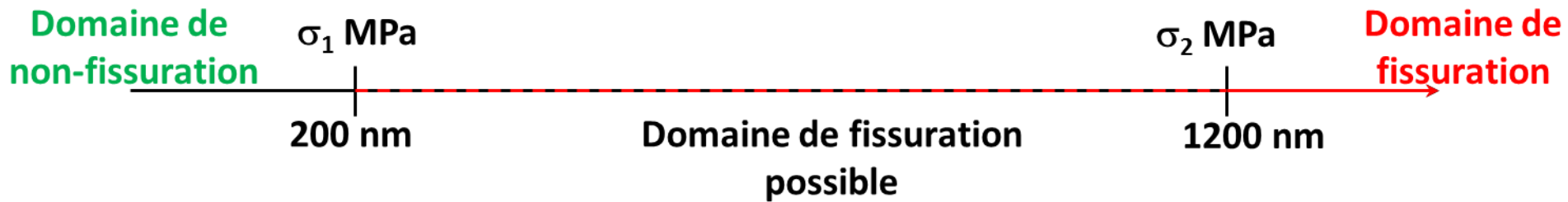
Tensile test at 360° C (strain rate : 10⁻⁵ s⁻¹)



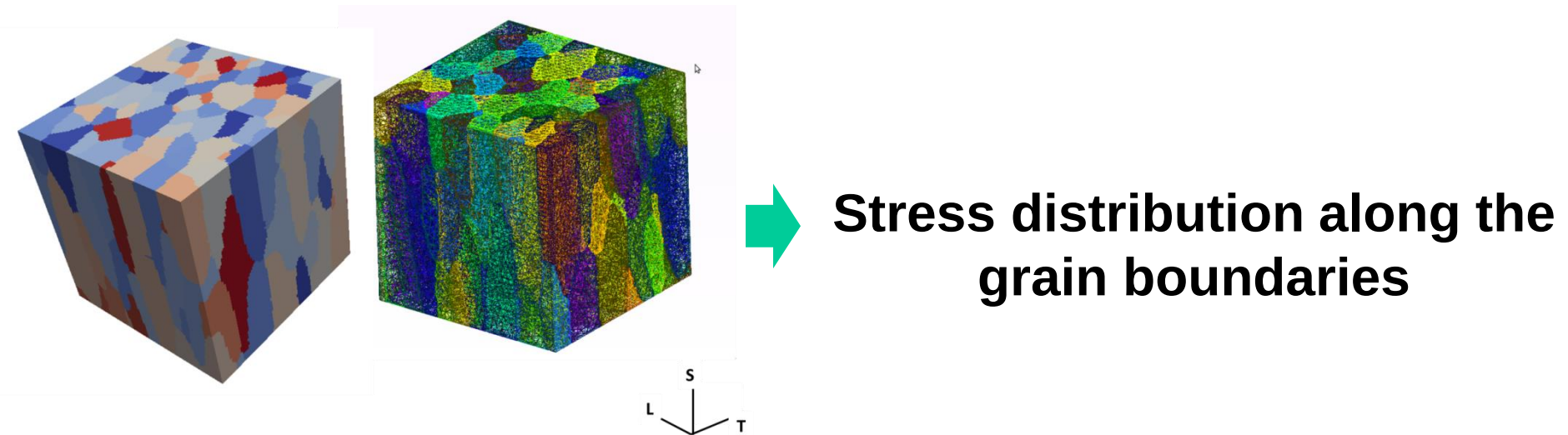
Study of the length of the intergranular oxyde penetration
in relation with cracked or uncracked grain boundary

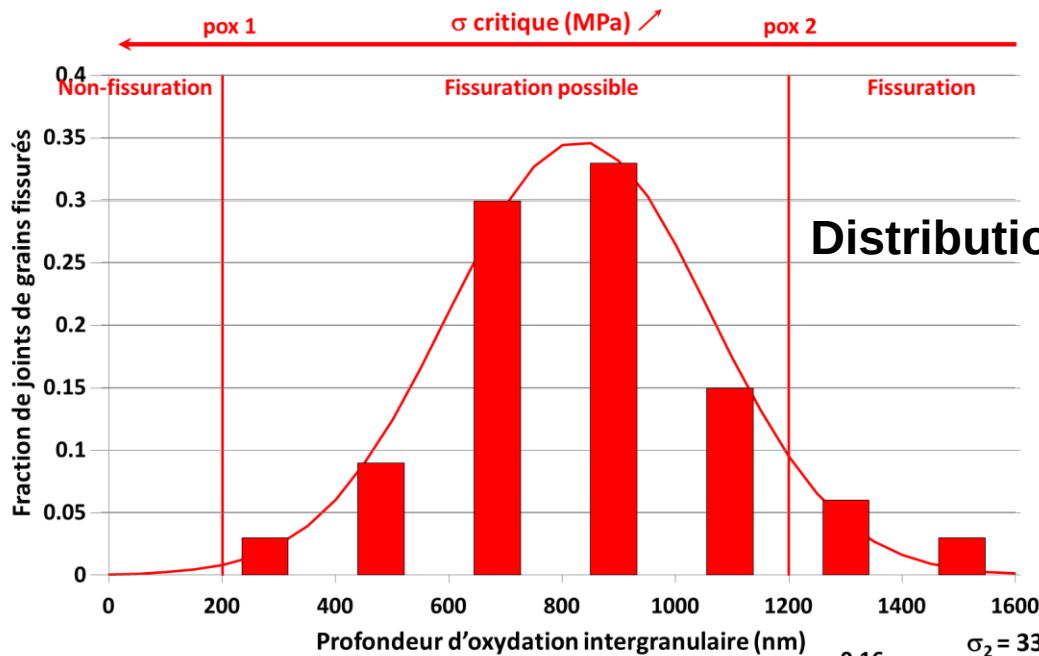






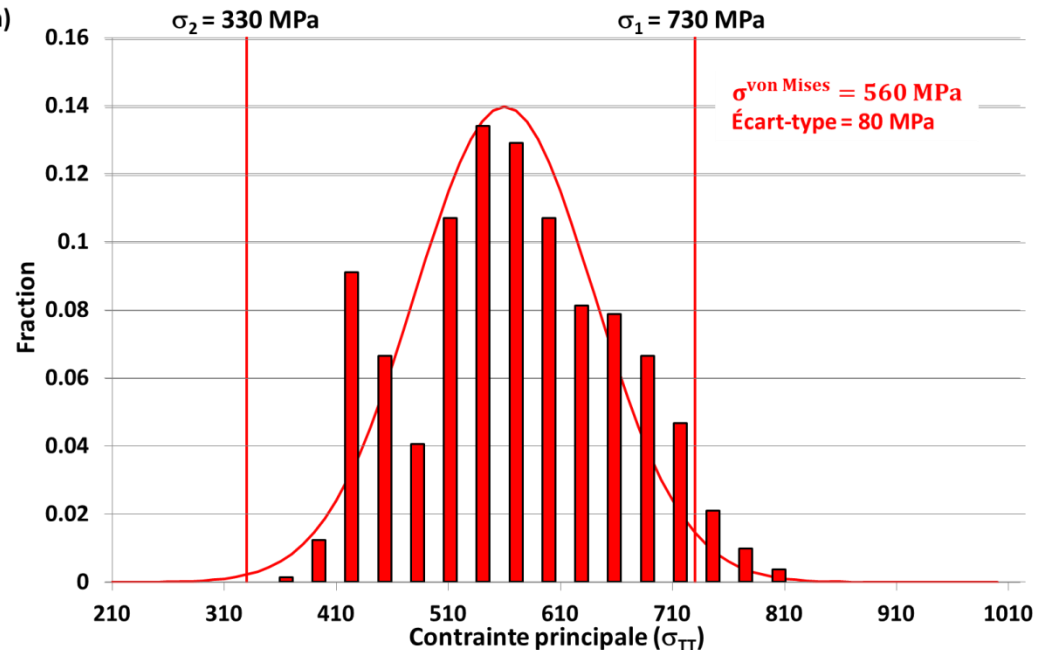
EVP crystallographic constitutive equation
Virtual microstructure representative of the columnar microstructure texture $\langle 001 \rangle$



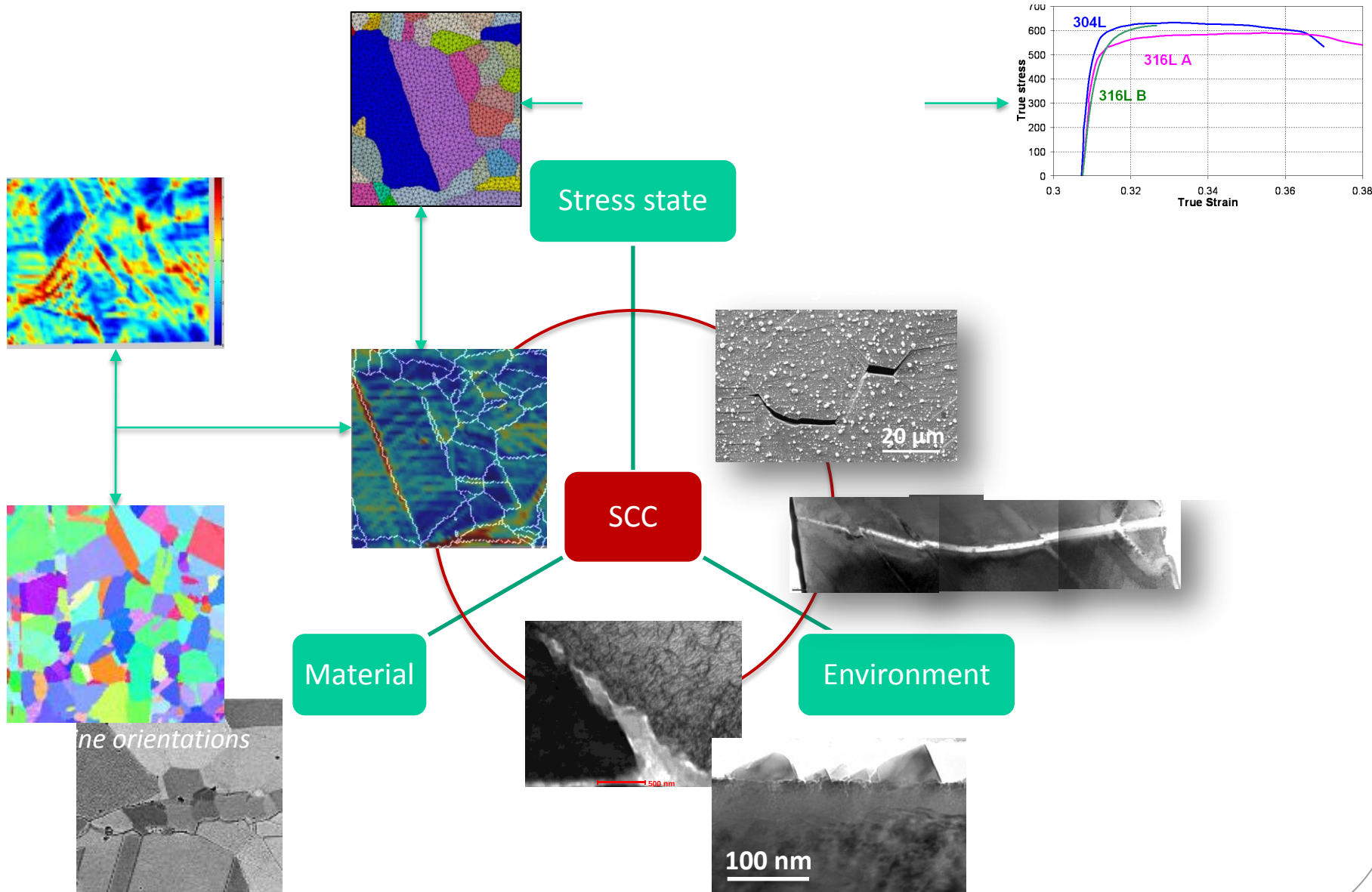


σ_{TT} distribution for 7 % macroscopic strain

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



Development of a combined approach



Thank you for your attention