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.

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

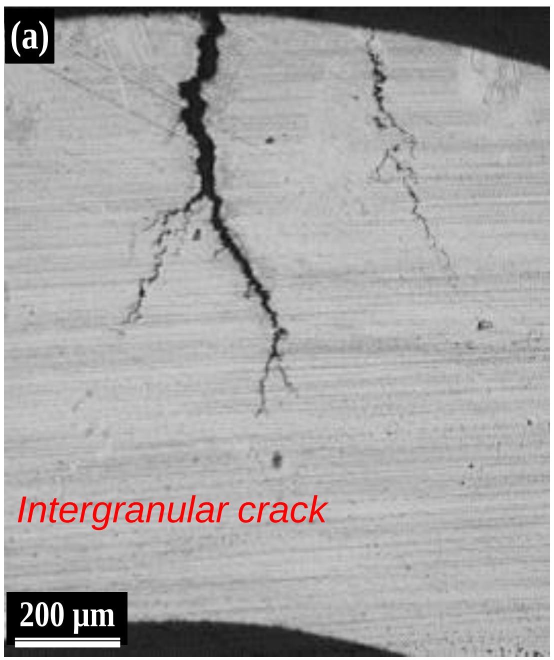
T. Couvant, J. Crépin, I. de Curières, C. Duhamel, F. Gaslain, C. Guerre, E. Héripre, M. Sennour

Workshop MIST, 12-15 Octobre 2015

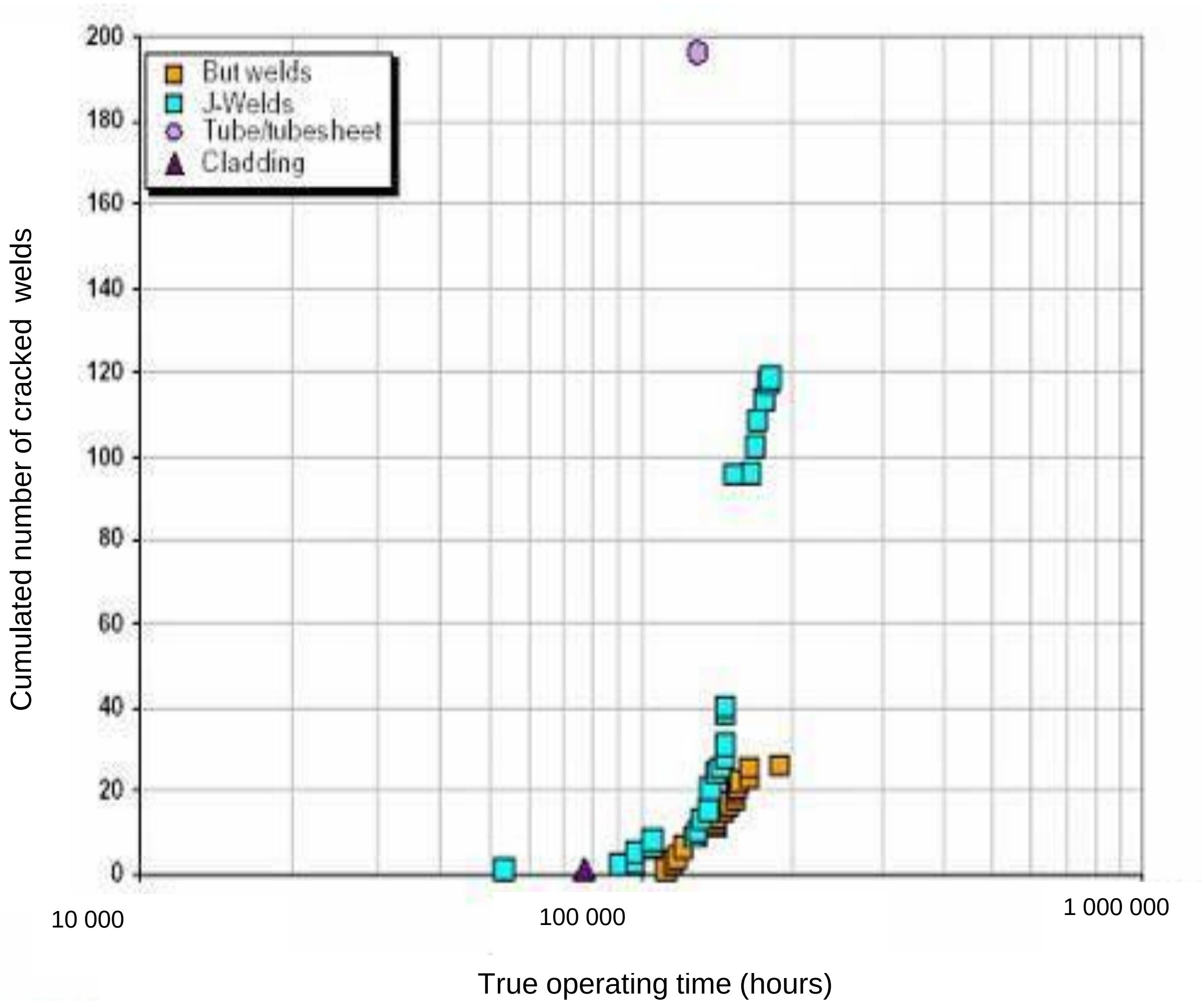
SCC cracks in Alloy 82 welds in J-Groove weld of Ringhals Steam Generator [2]

[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.

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



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

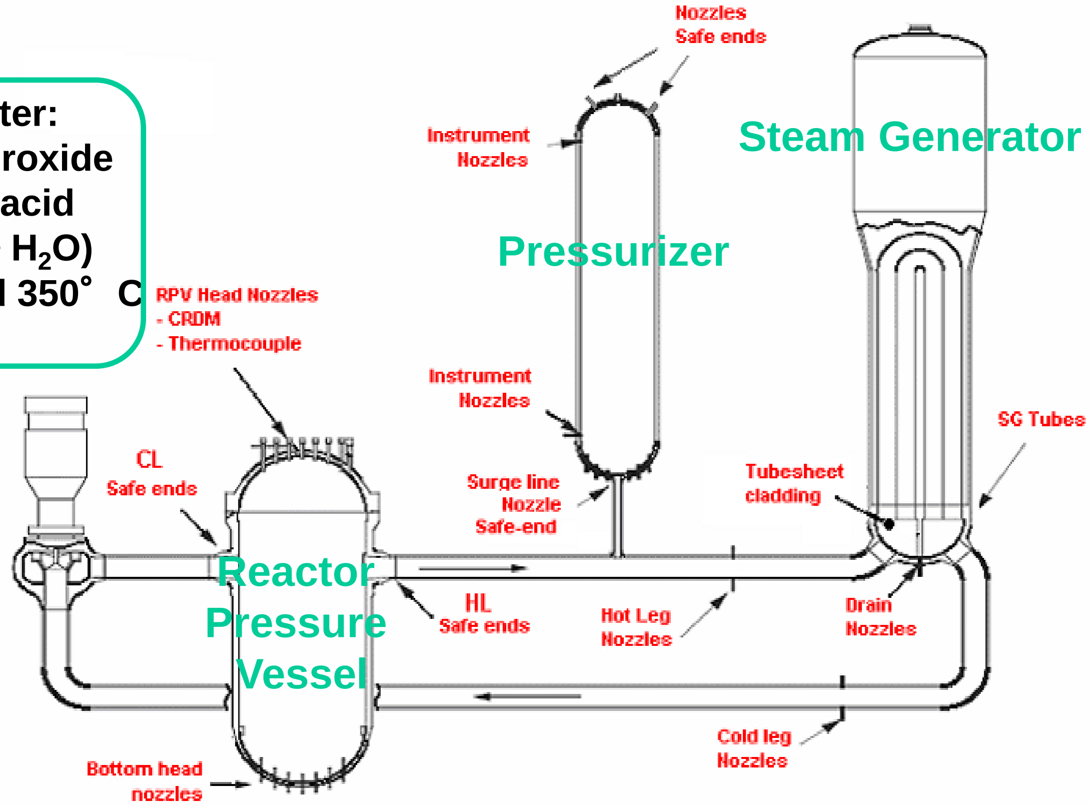


Life extension of PWR > 30 – 40 years

Nickel-base welds used in PWRs

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

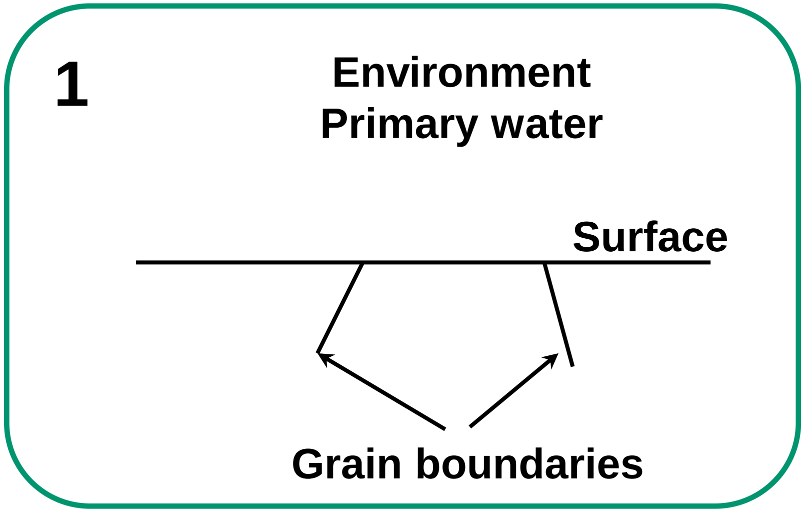
Nominal primary water:
2 ppm Li as lithium hydroxide
1000 ppm B as boric acid
Hydrogen (30 $cm^3.kg^{-1}$ H_2O)
Temperature: 290° C and 350° C

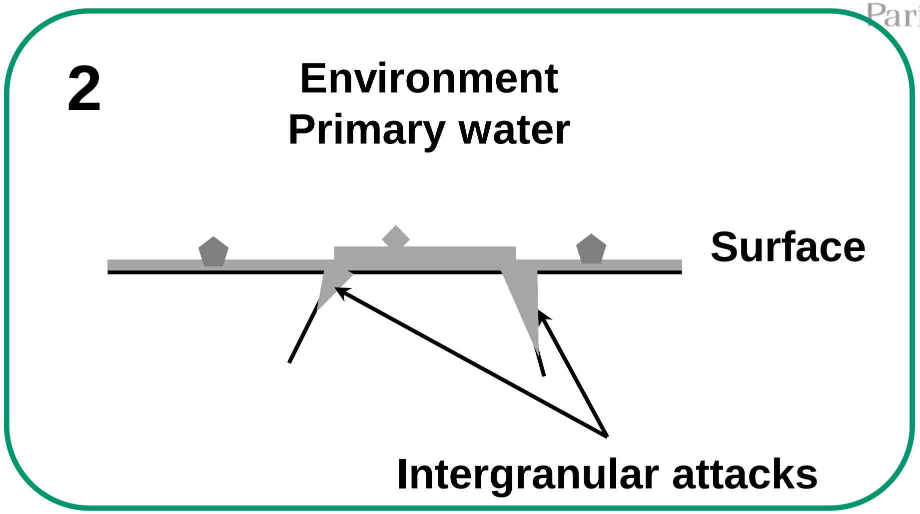


Scott, P., PWSCC of nickel base alloys & mitigation in PWRs, INL Seminar (2013)

CENTRE DES MATERIAUX
P.M FOURT

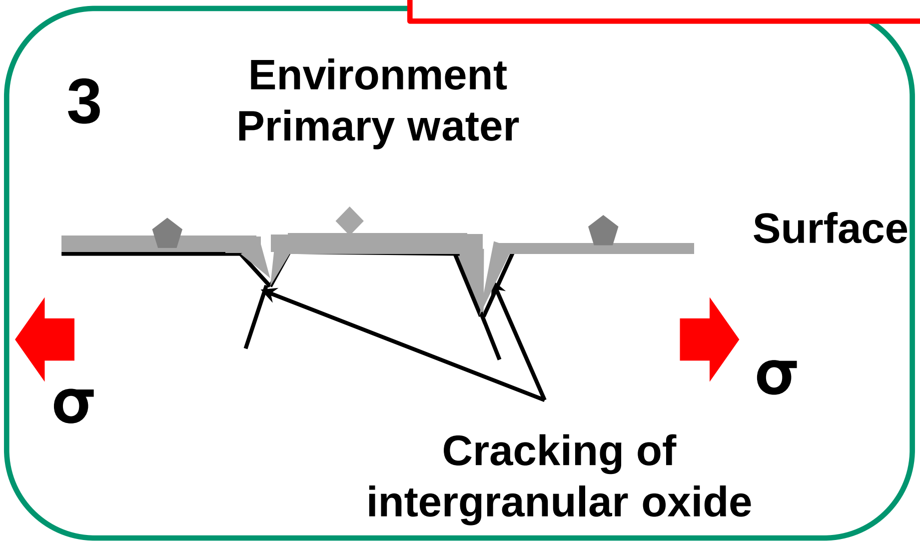
SCC initiation



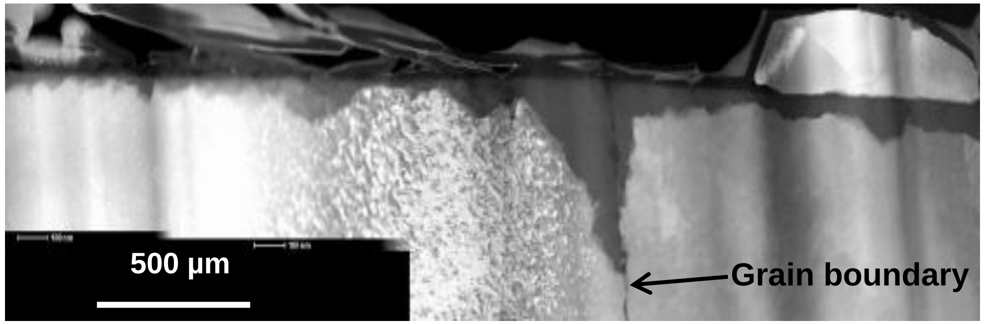


Critical oxide depth
Critical stress

Initiation = cracking of intergranular oxide

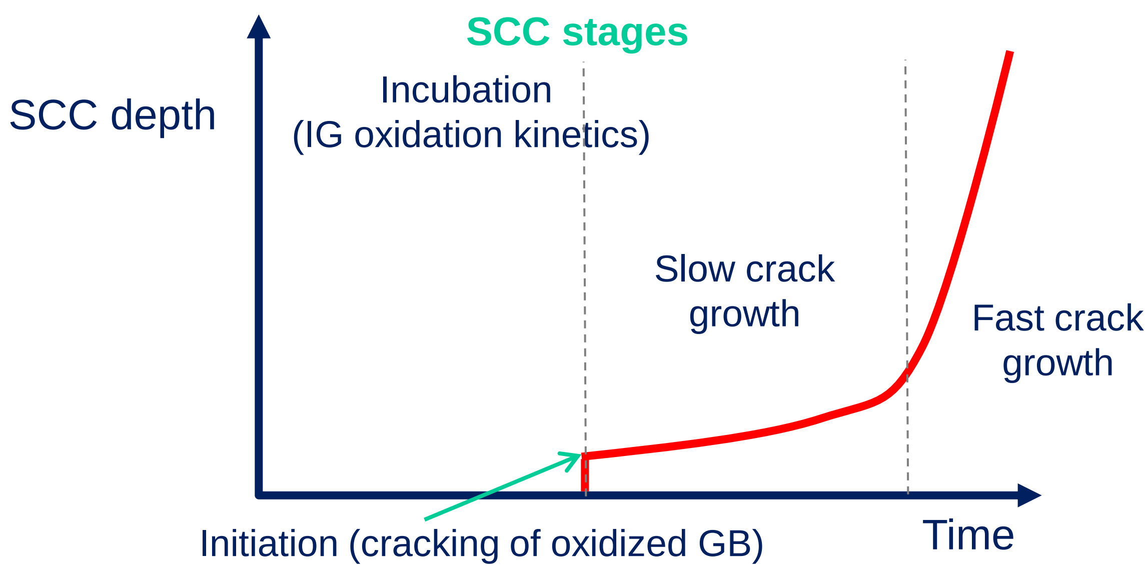


Cracking scenario



STEM HAADF image of the intergranular oxide penetration of Alloy 600

After 2000h in primary water at 360° C, DH= 30 mL H_2/kg H_2O



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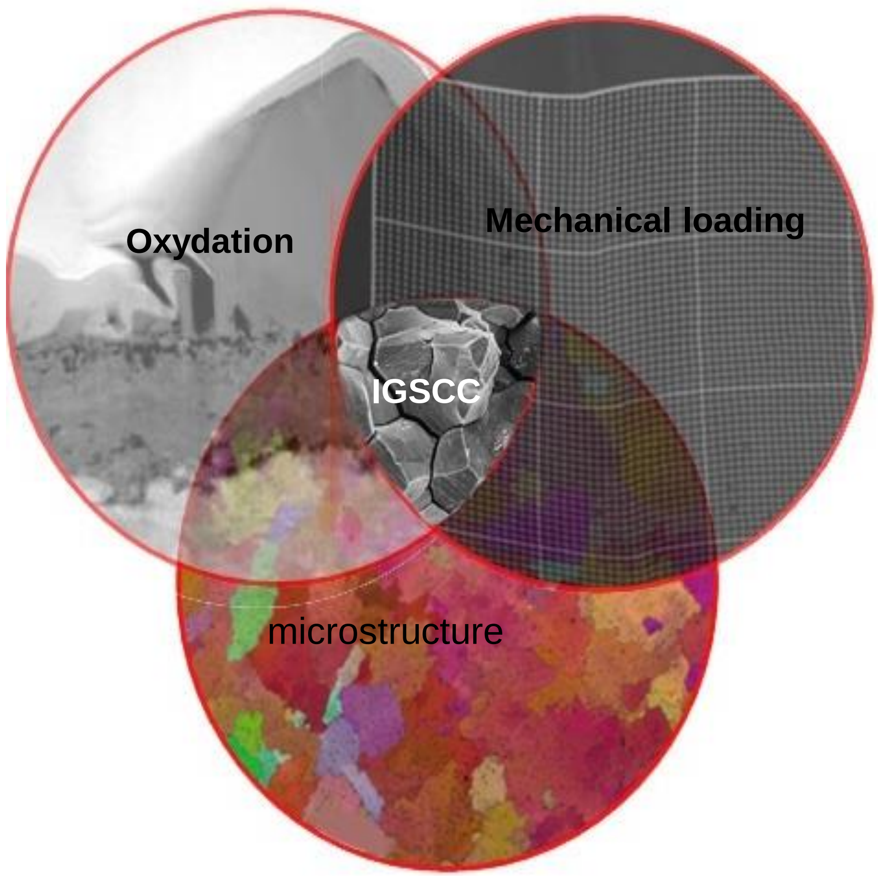
Intergranular stress corrosion cracking (IGSCC) results from the local interaction between microstructure, oxidation and mechanical loading



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 $cm^3.kg^{-1}$(TPN)**
O_2	**< 5 ppb**
$pH_{300°C}$	**≈ 7**

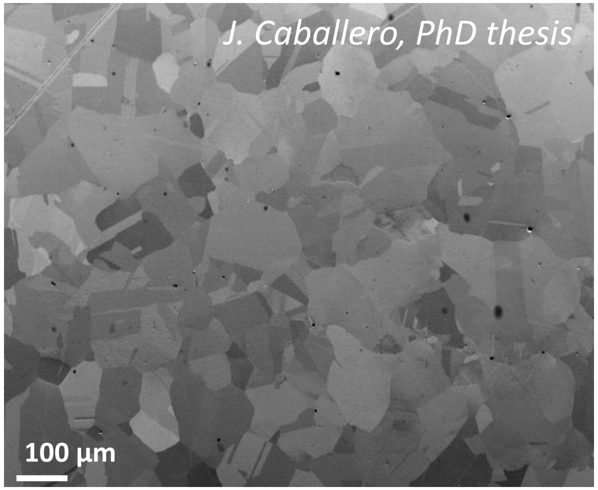
Materials

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

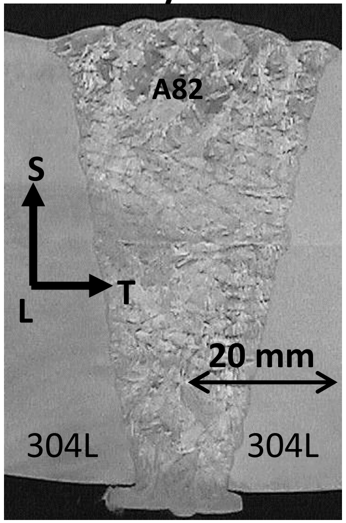
Cr content ↘

A600

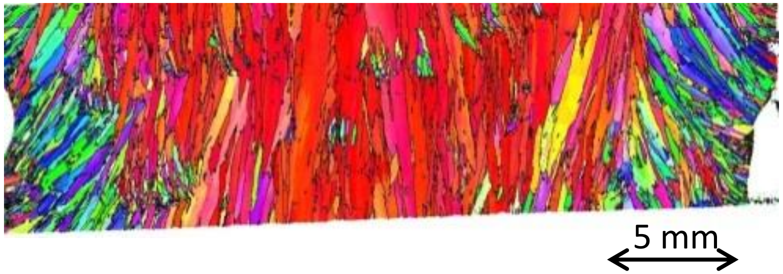


Possible IG chromium carbides

A182 / A82



E. Chaumun, PhD thesis

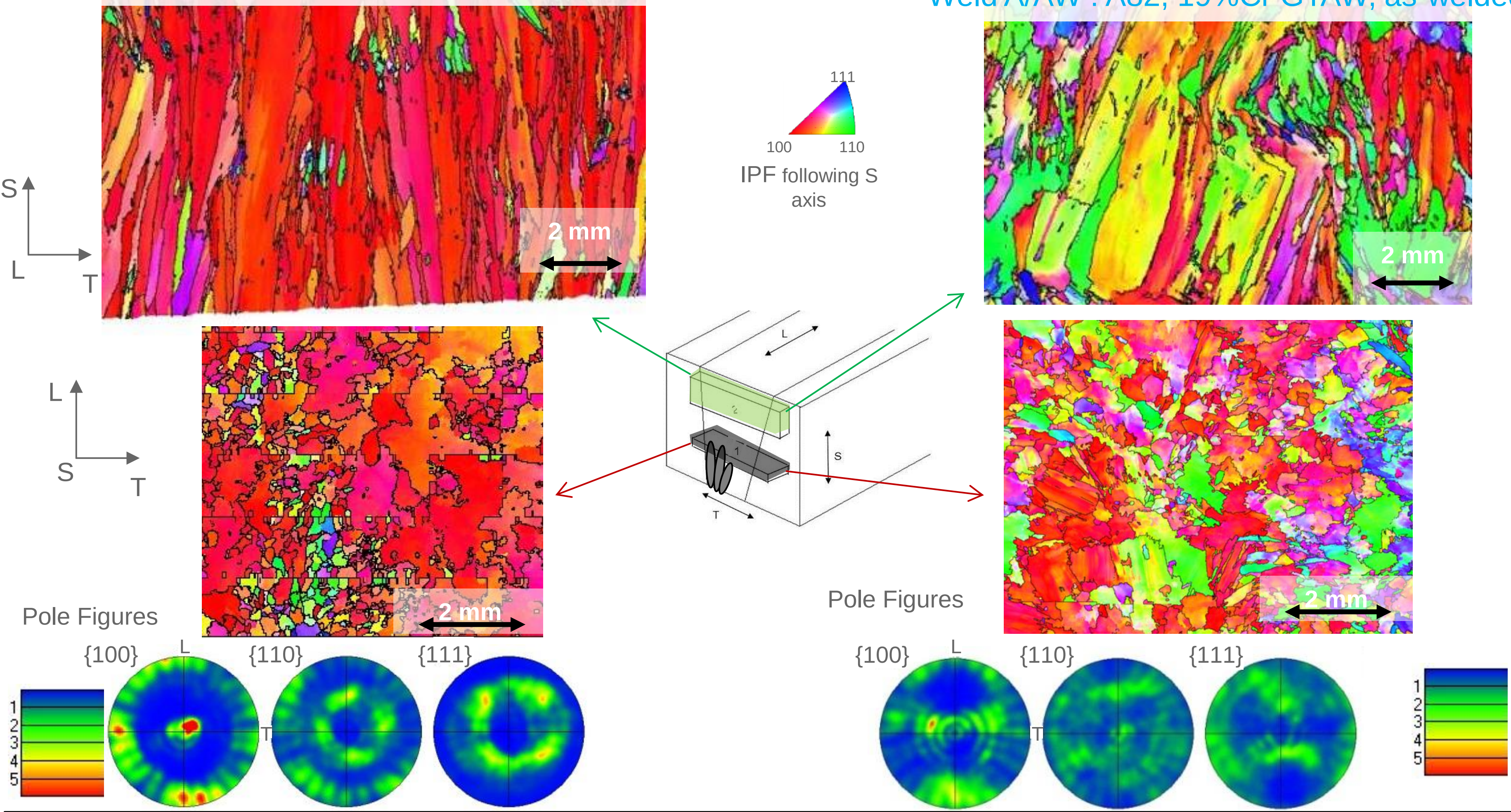


Possible IG niobium and chromium carbides

Microstructure features (EBSD)

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

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

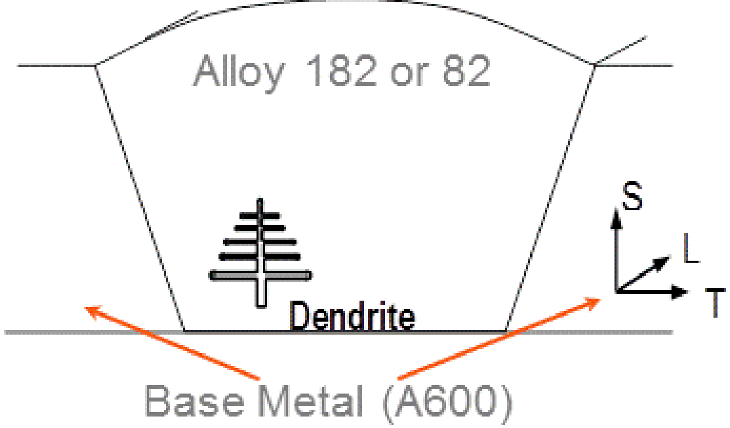


→ Crystallographic texture for weld B/AW, local texture for weld A/AW and no texture for weld A/HT

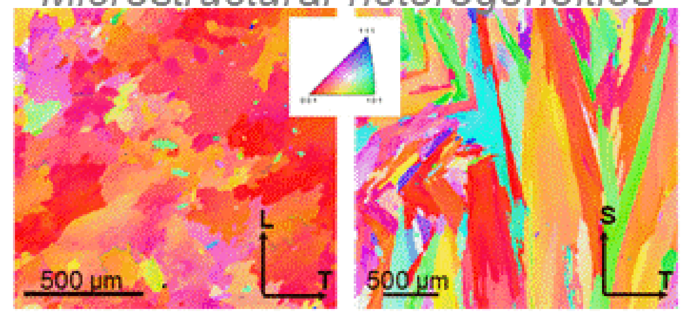
→ Morphology : Heterogeneous grain size and elongated grains along the S direction

Materials

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

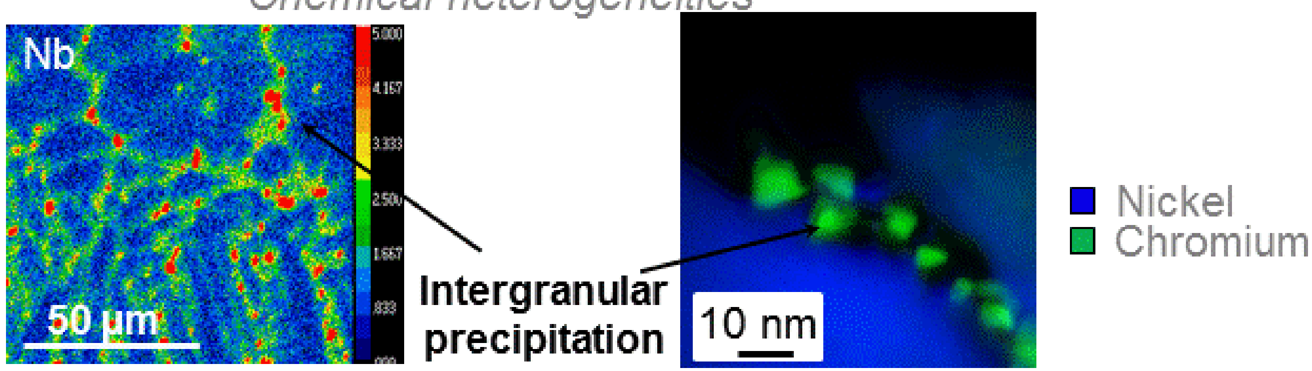


Microstructural heterogeneities



EBSD: Inverse Pole Figure (axis: S)   EBSD: Inverse Pole Figure (axis: L)

Chemical heterogeneities



Microprobe   EFTEM maps

Intragranular precipitation

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

Intergranular precipitation

Niobium carbides (NbC)
Chromium carbides

SCC initiation TESTs

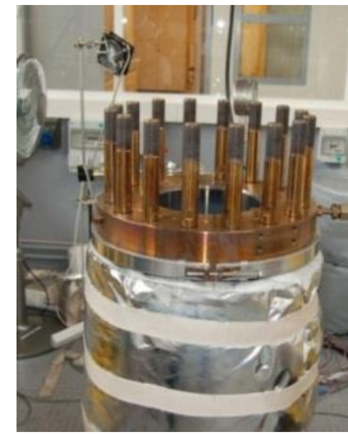
✓ Initiation tests

→ In an autoclave

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

Samples dimensions :
50mm x 9mm

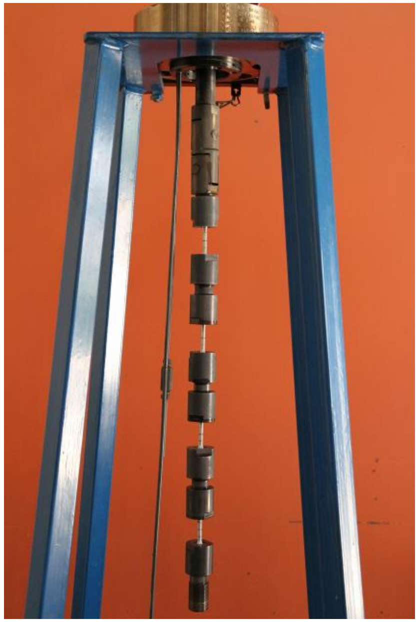
U-bend specimen



→ Test environment: **hydrogenated steam**

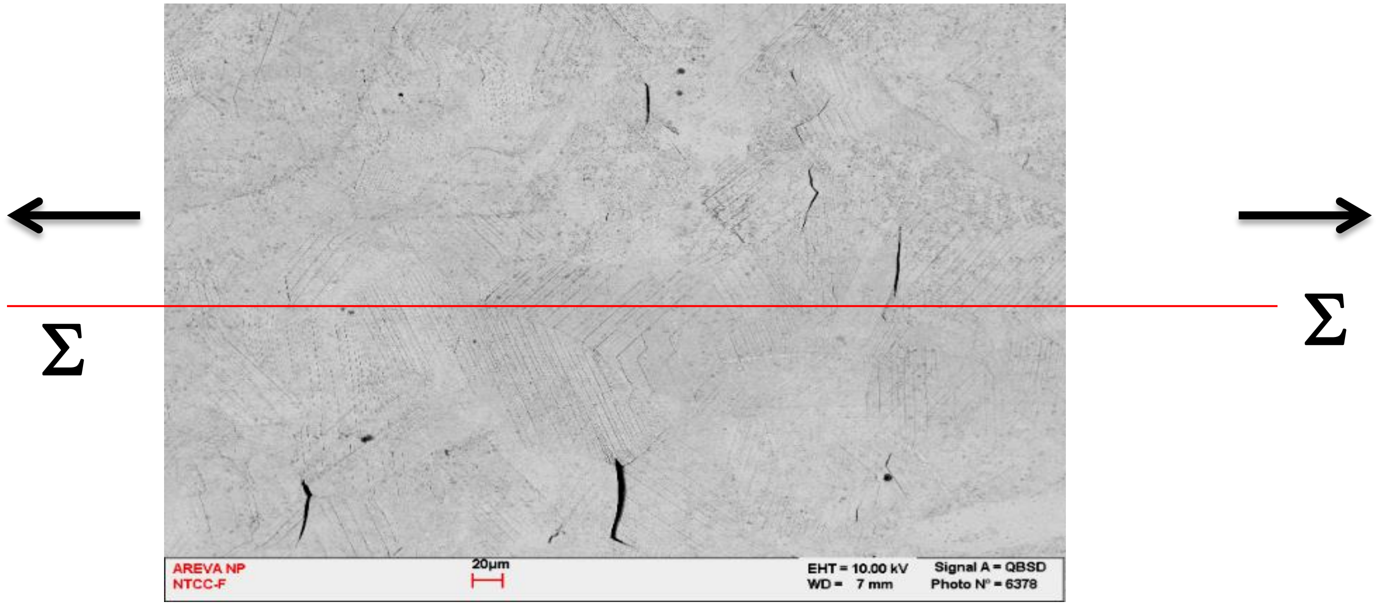
	Conditions
Temperature	400° C
Total pressure	188 bar
Hydrogen partial pressure	0.7 bar

Ligne d'amarrage



Autoclave

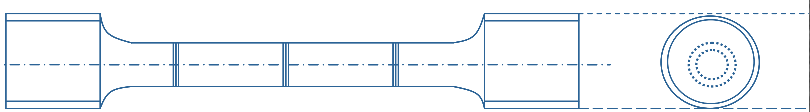
Machine de fluage modifiée

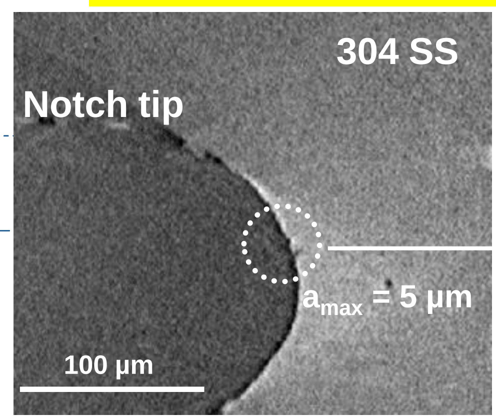


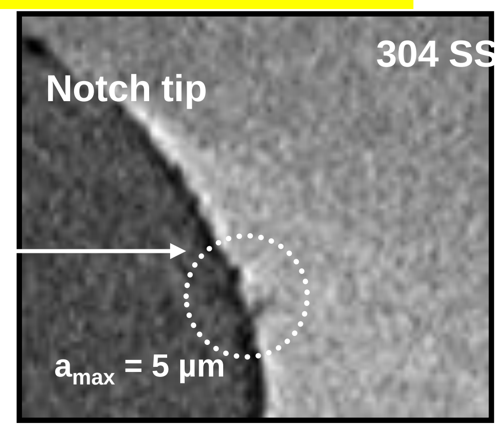
304 Stainless Steel, 5 dpa, 10%

Courtesy of M. Le Millier, chaire AREVA

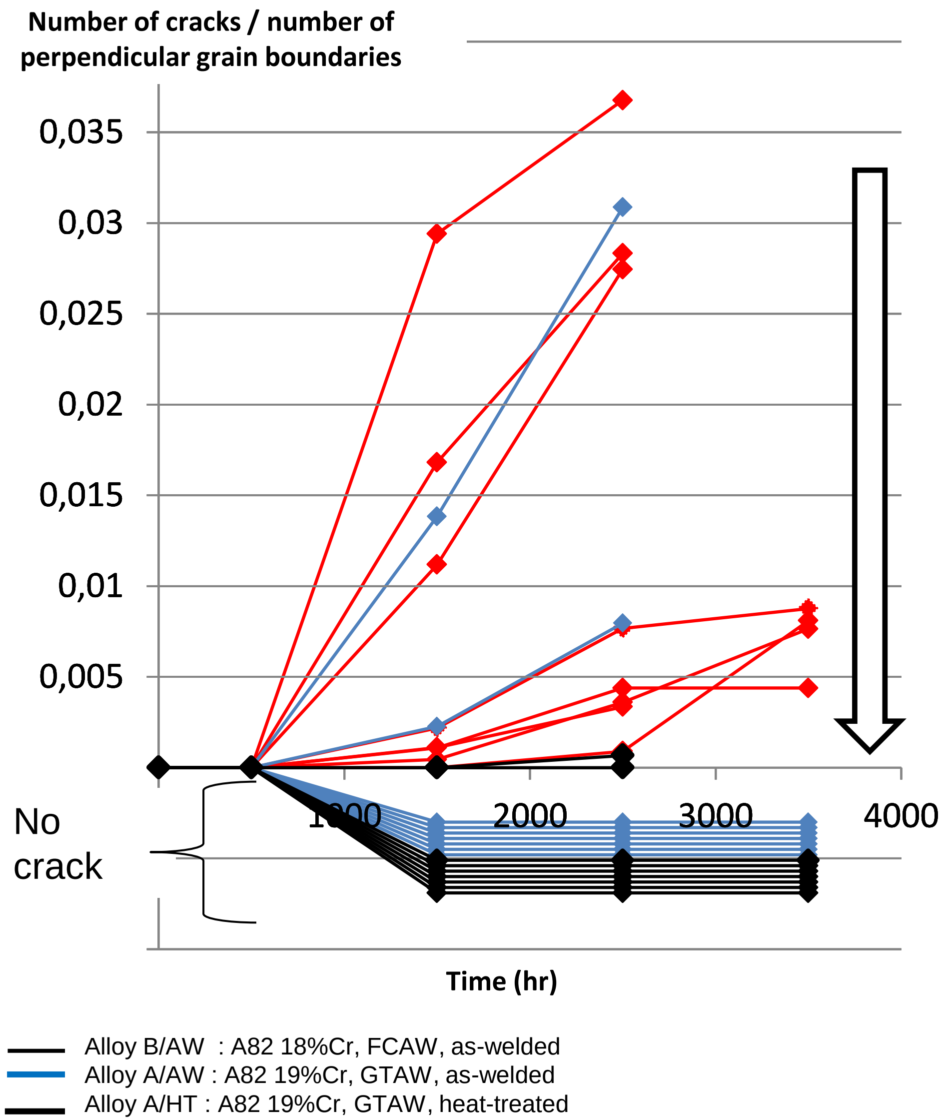
Laminographie : résolution = 0,77µm.pixel^{-1}







INITIATION TEST : RESULTS



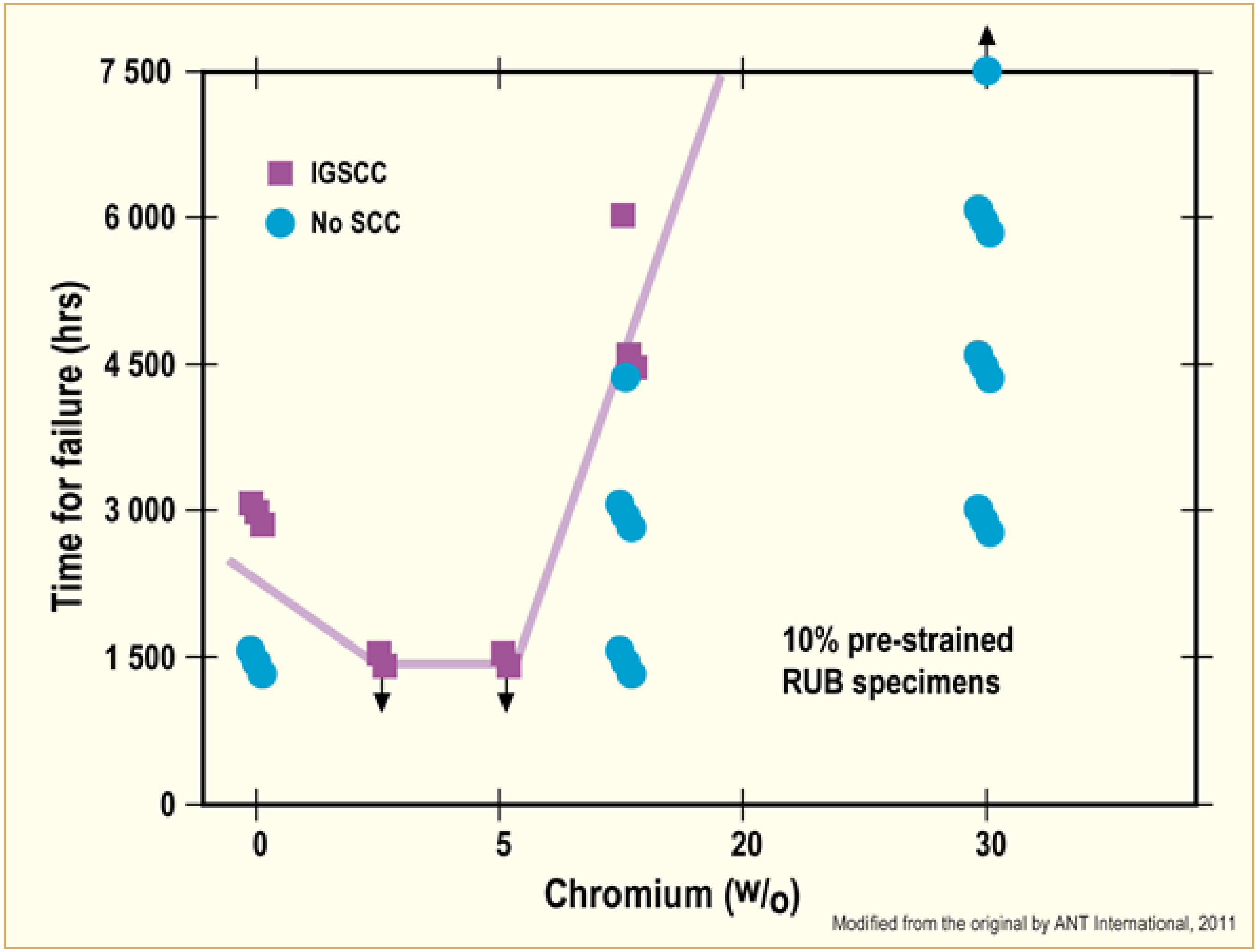
→ **B/AW is more susceptible** to SCC than **A/AW**

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

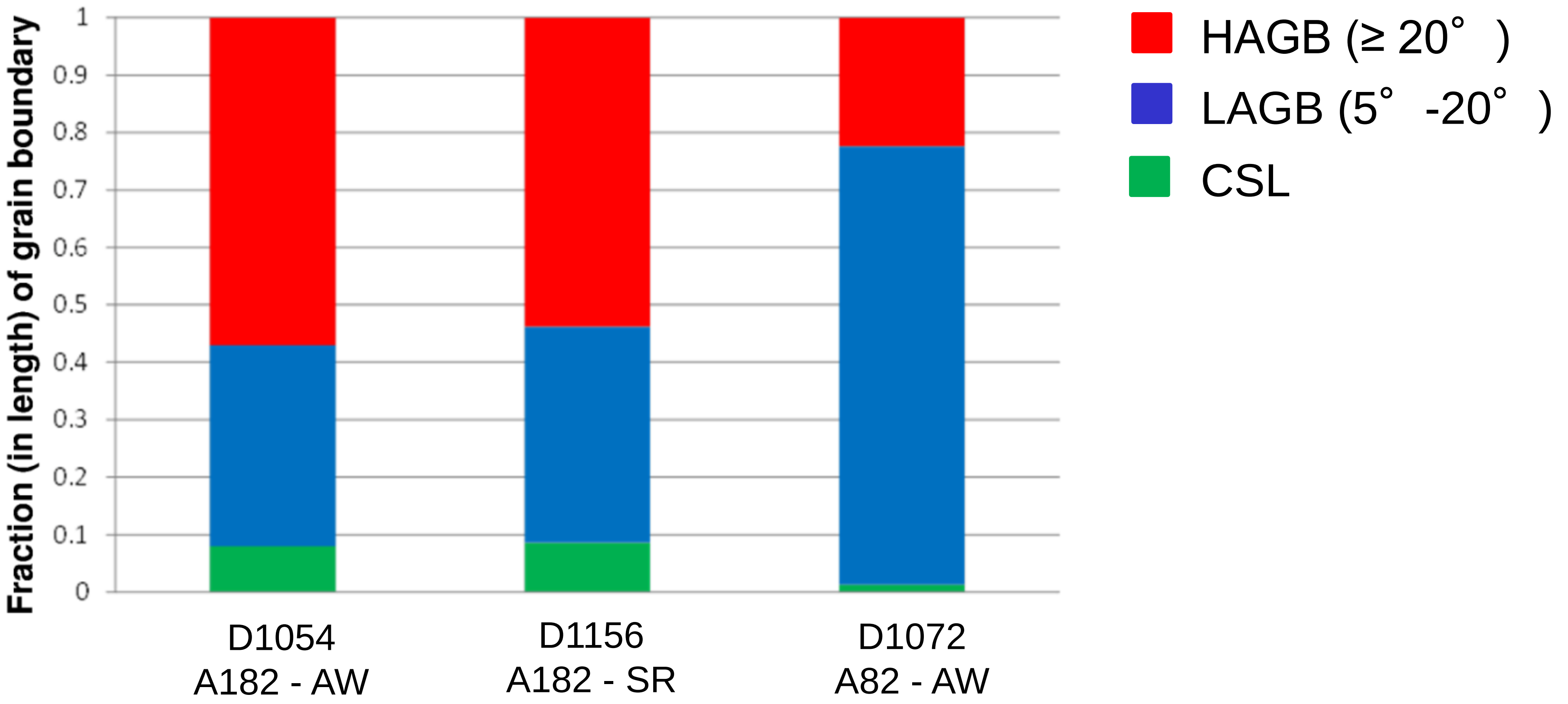
[Sennour2013] M. Sennour, E. Chaumun, J. Crépin, C. Duhamel, F. Gaslain, C. Guerre, I. de Curières, JNM, 2013

Chromium content and SCC

- Increasing the chromium content decreases the SCC susceptibility



Grain boundary character



LAGB (Δθ≤15°) HAGB (Δθ>15°)

SEM image

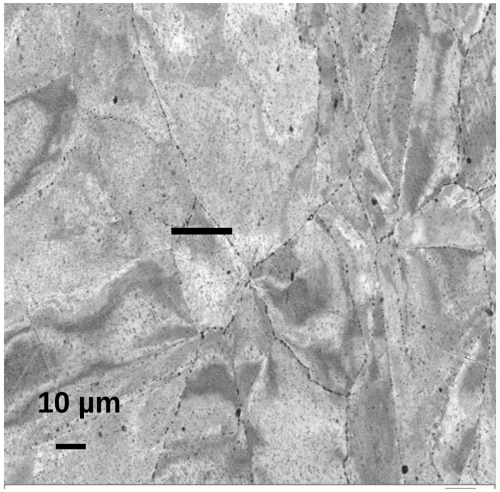
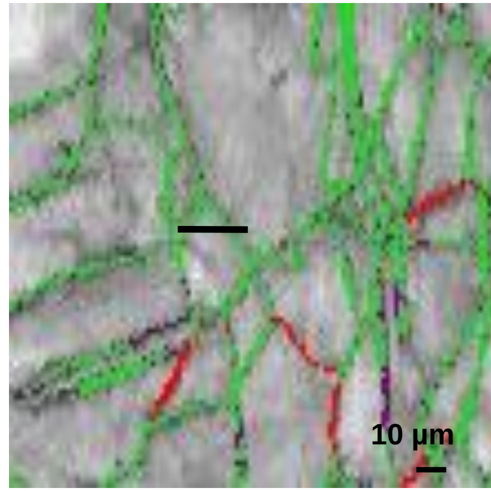


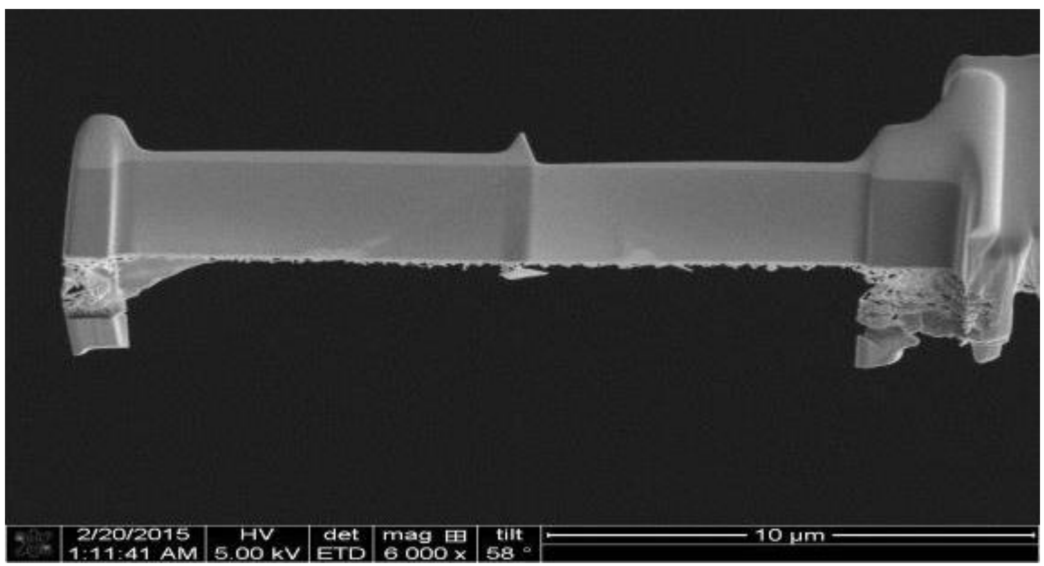
Image Quality map



S

T

Step size=1µm



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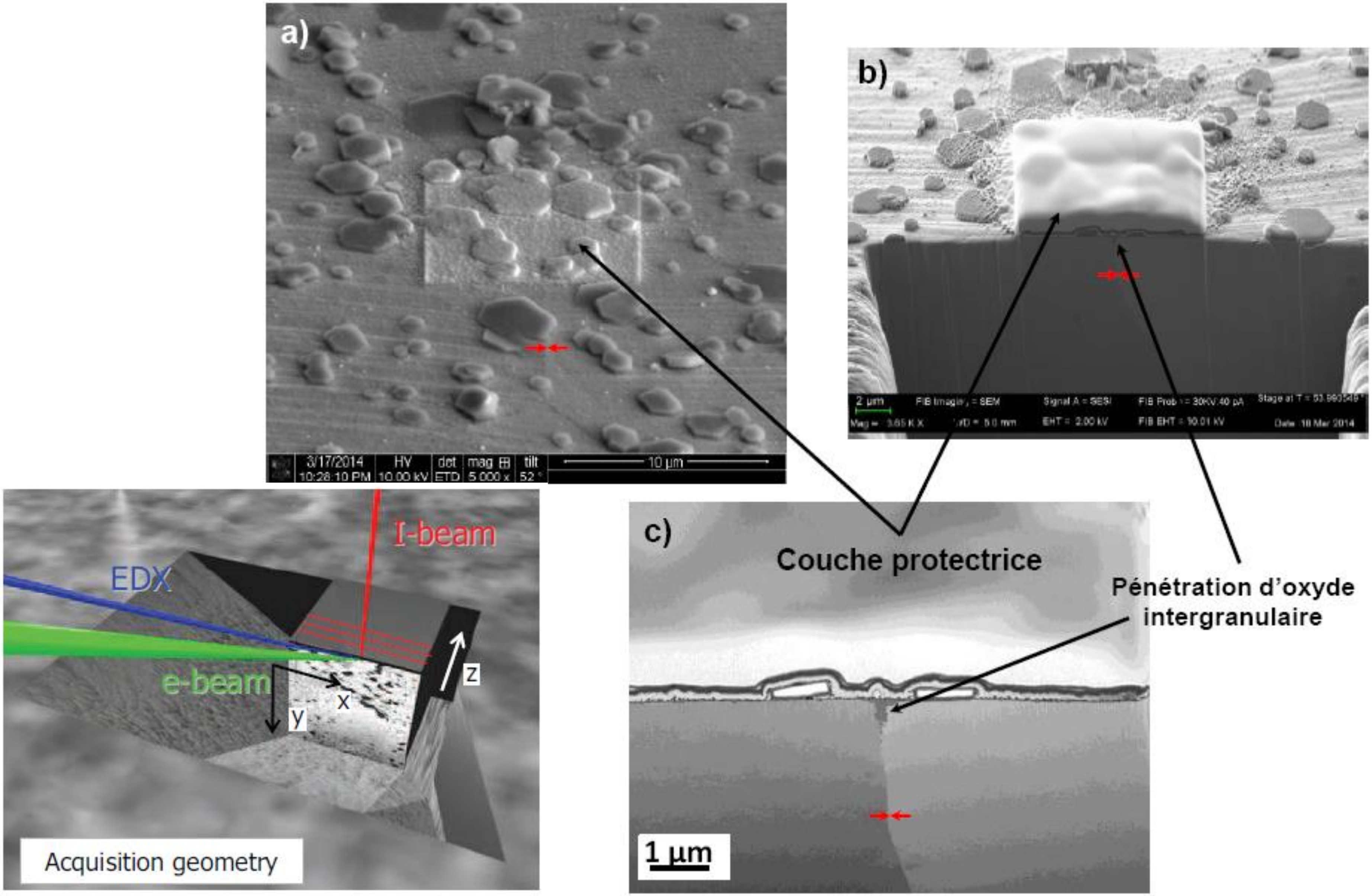
FIB/SEM tomography

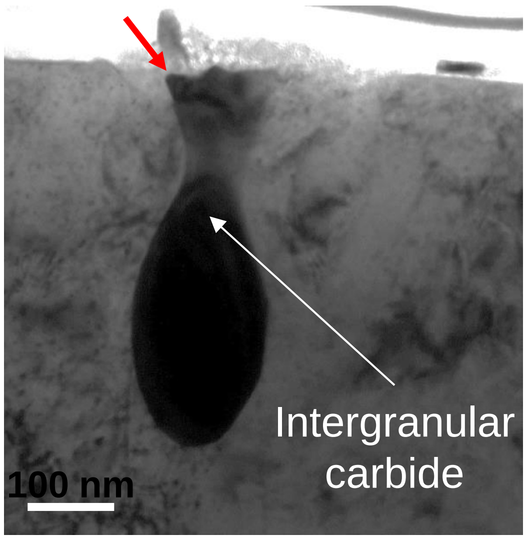


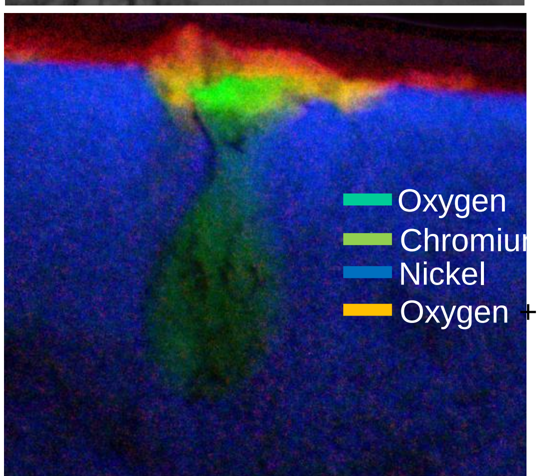
Oxidation and chromium carbides

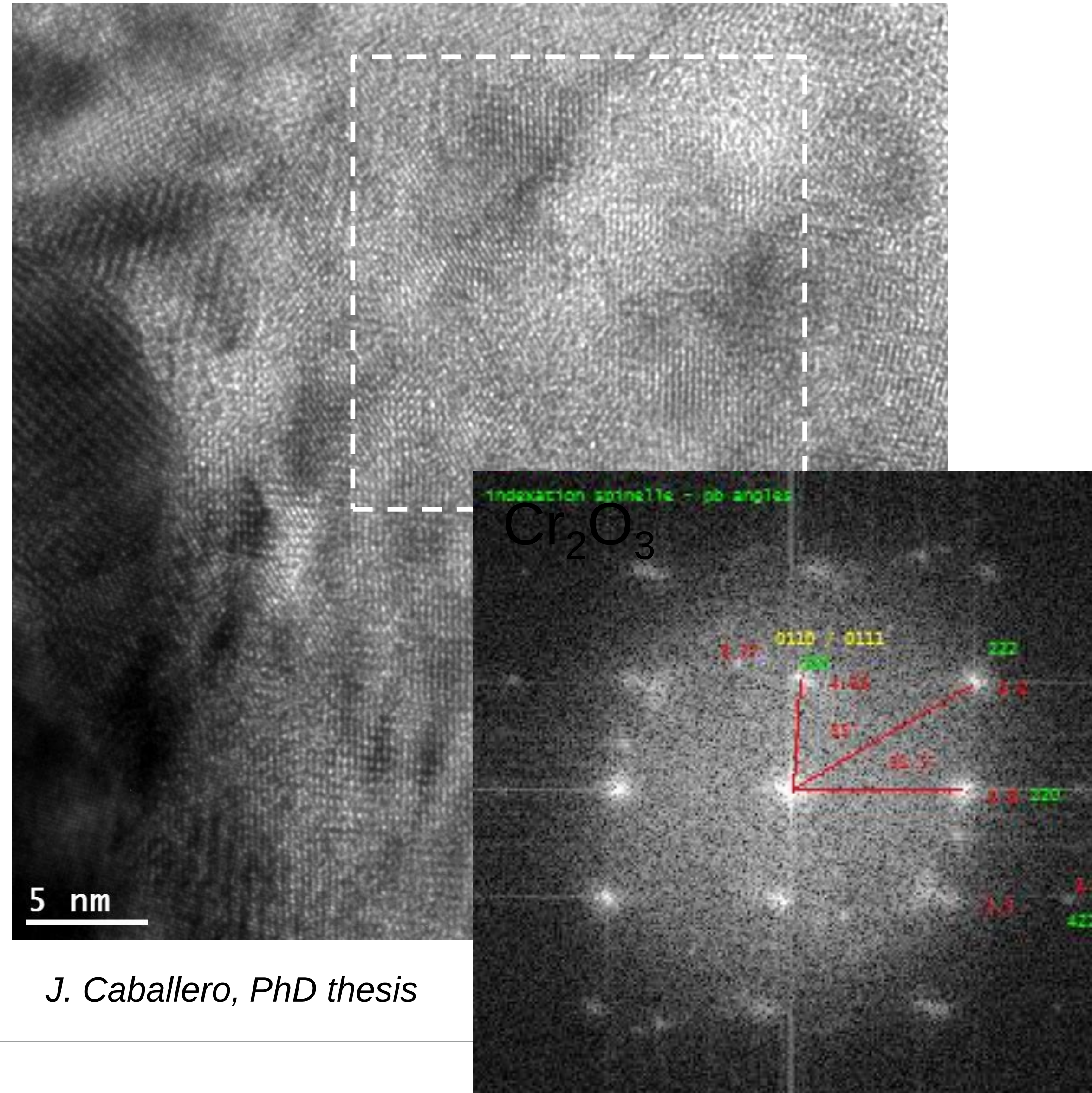
Alloy 600
325° C – 100h
30 mL H_2/kg H_2O

- **Formation of Cr_2O_3** around the carbide

Emerging carbide







J. Caballero, PhD thesis

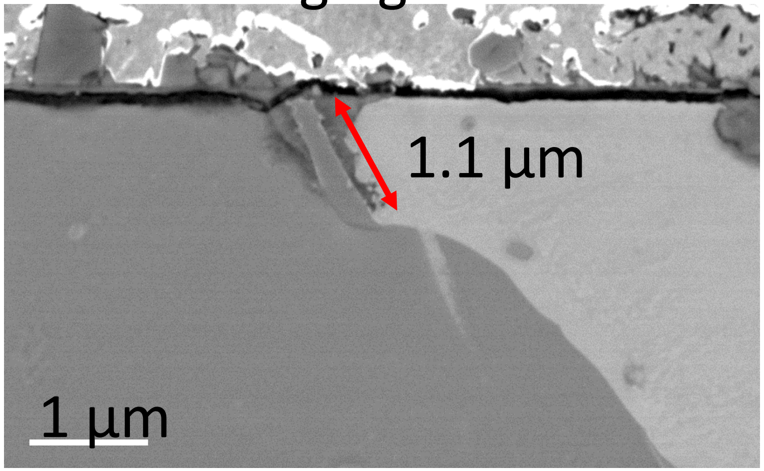
Emerging vs. non emerging carbides

Alloy 600
360° C – 1000h
20 mL H_2/kg H_2O

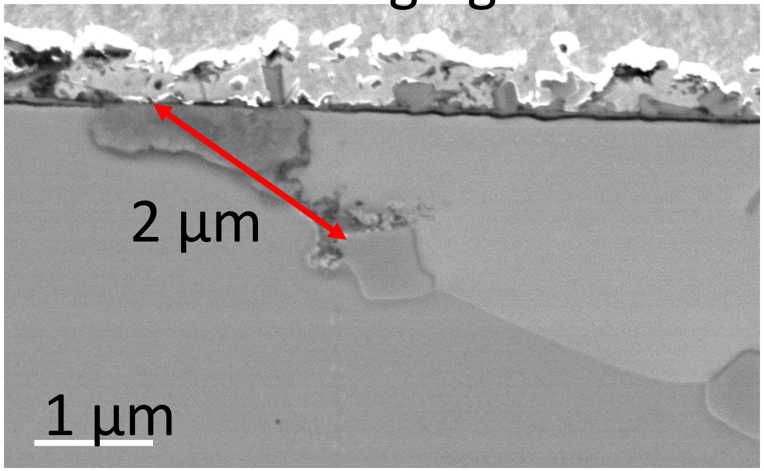
- Enhanced reactivity at the interfaces between carbide and matrix
- For long oxidation times , intergranular oxidation depth seems shorter in case of emerging carbides.

1000h

Emerging carbide



Non emerging carbide

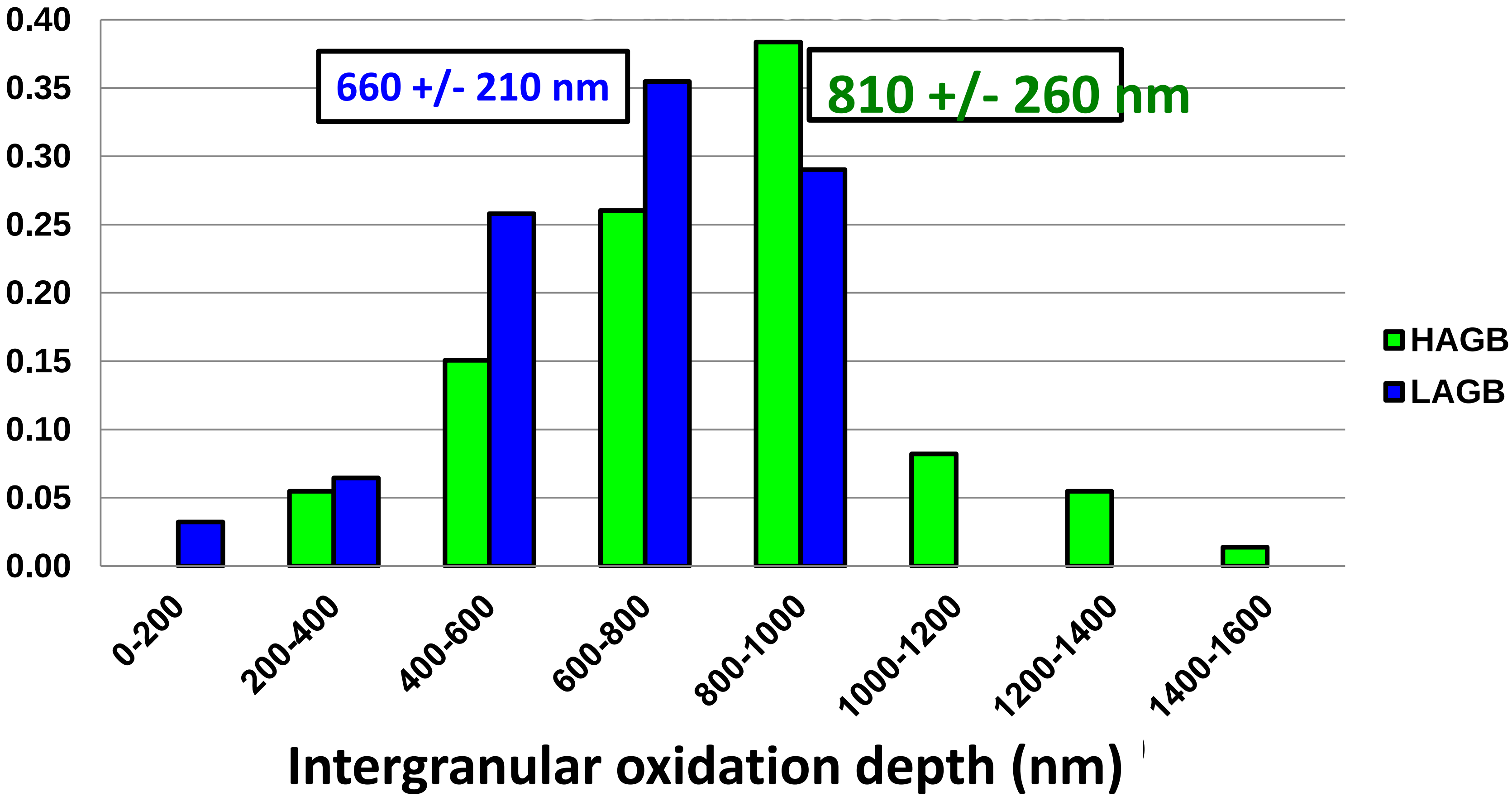


J. Caballero, PhD thesis

Grain boundary character and oxidation

Alloy 182
360° C – 1000h
30 mL H_2/kg H_2O

- Higher intergranular oxidation depth along HAGB than along LAGB



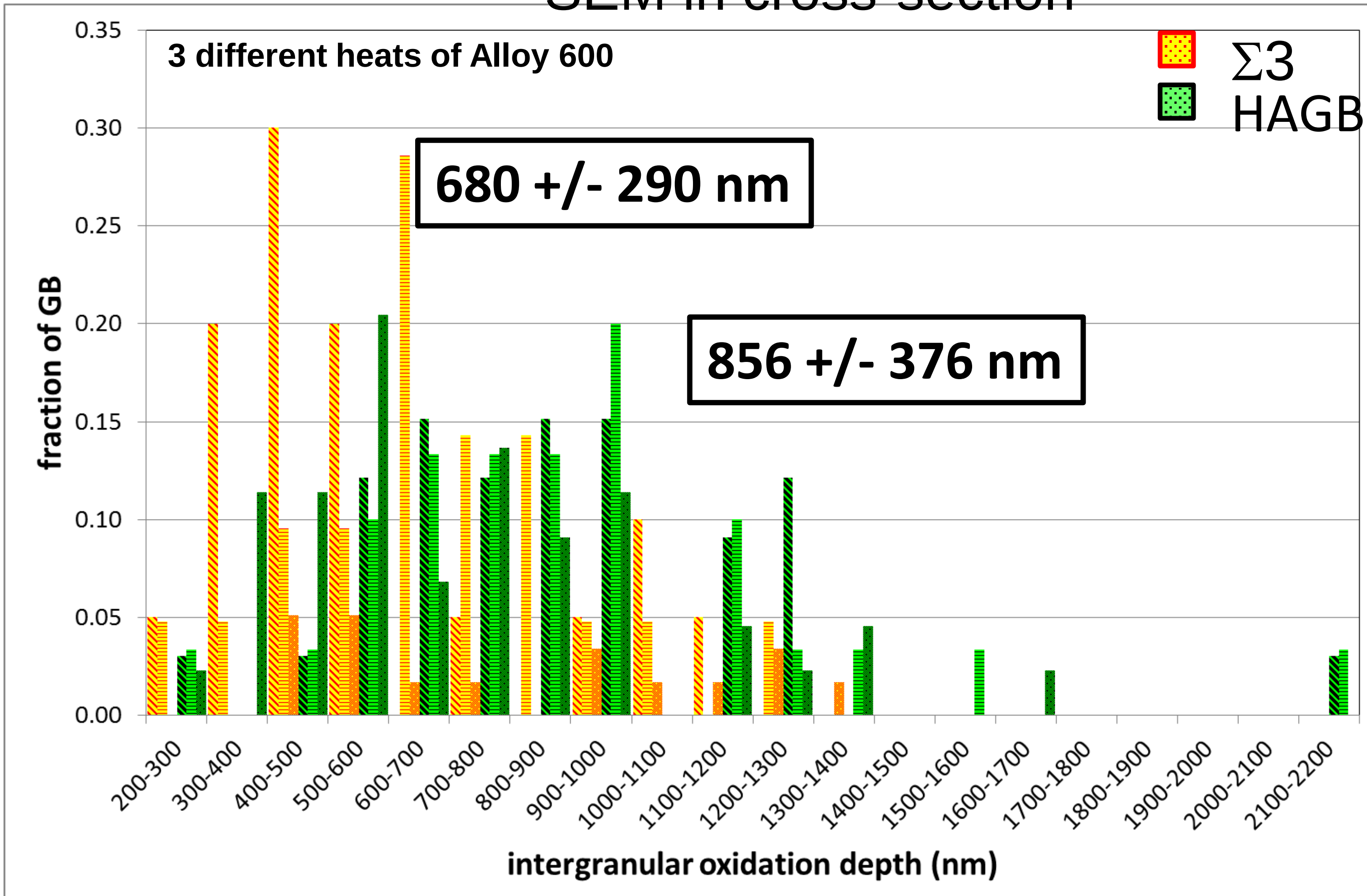
M. Wehbi, PhD thesis (2014)

Grain boundary character and oxidation

Alloy 600
360° C – 1000h
20 mL H_2/kg H_2O

- Higher intergranular oxidation depth along HAGB than along Σ3

SEM in cross-section

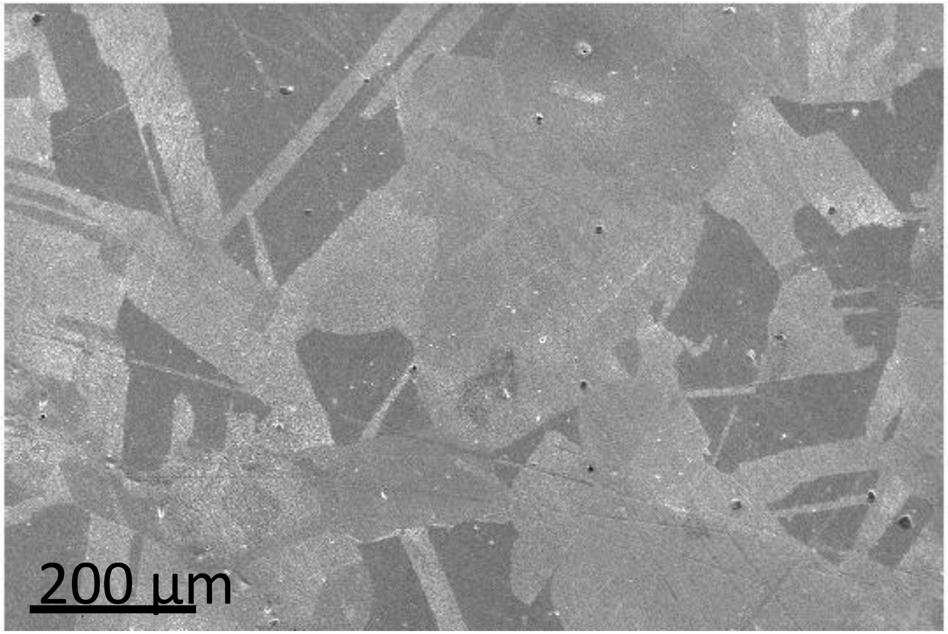


J. Caballero, PhD thesis

What about GB with no carbides?

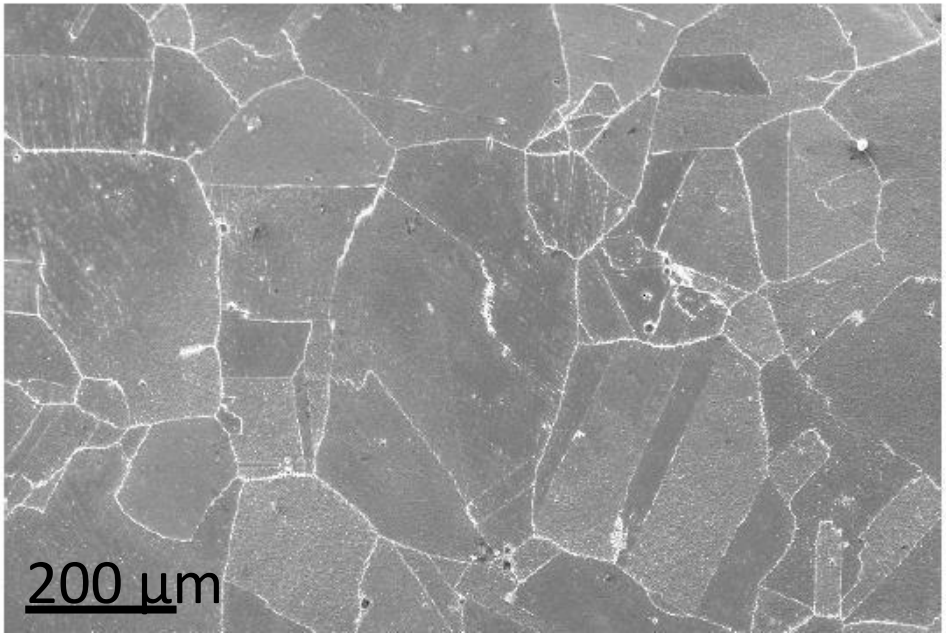
- Need for **model microstructures**
- Model microstructures prepared from a commercial heat of Alloy 600

SOLUTION-ANNEALED



Dissolution of chromium carbides

SOLUTION-ANNEALED + THERMALLY TREATED

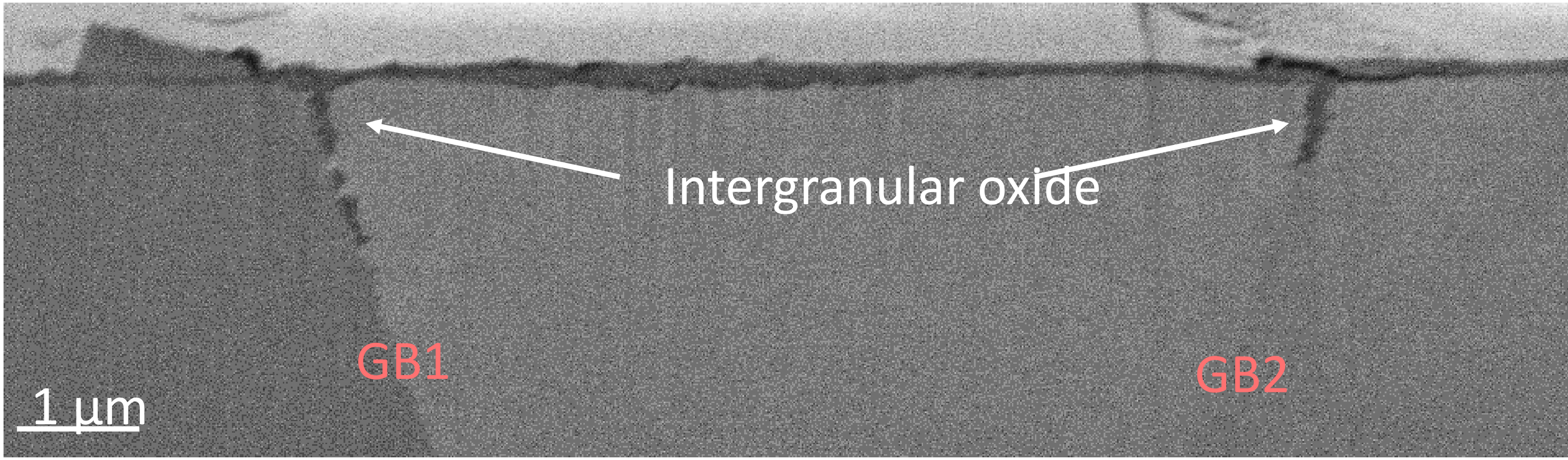


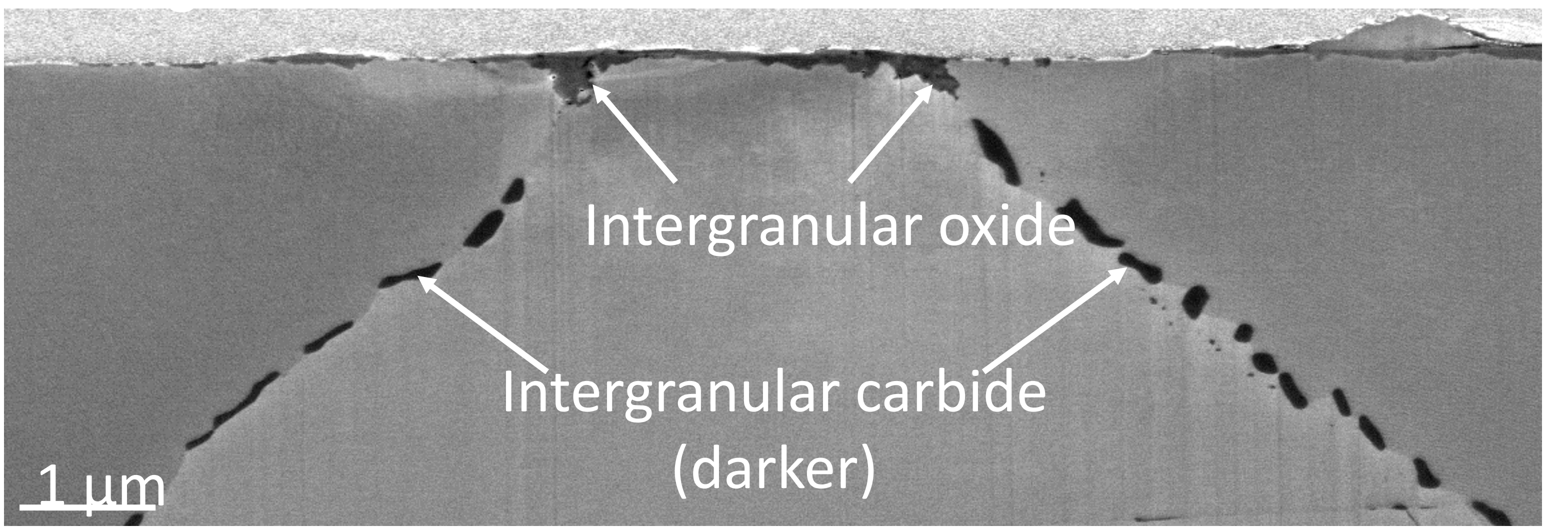
Quasi-continuous precipitation of intergranular chromium carbide

P. Laghoutaris, PhD thesis ENSMP (2009)

Alloys with model microstructures

Alloy 600
325° C – 1400h
30 mL H_2/kg H_2O

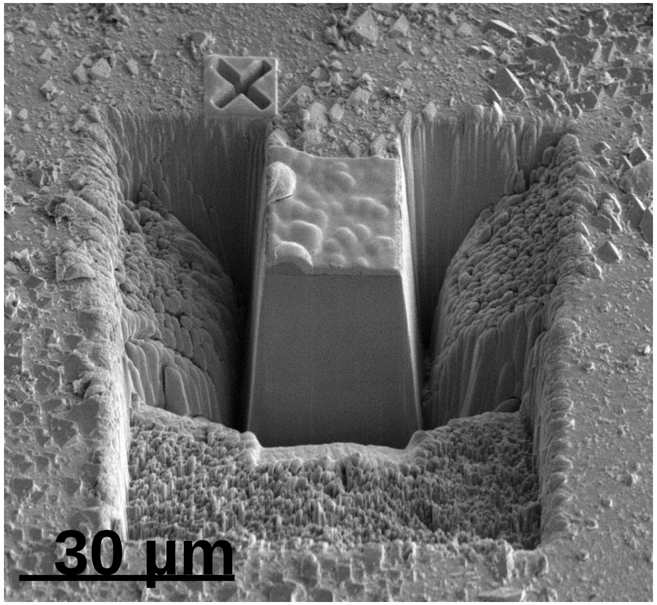


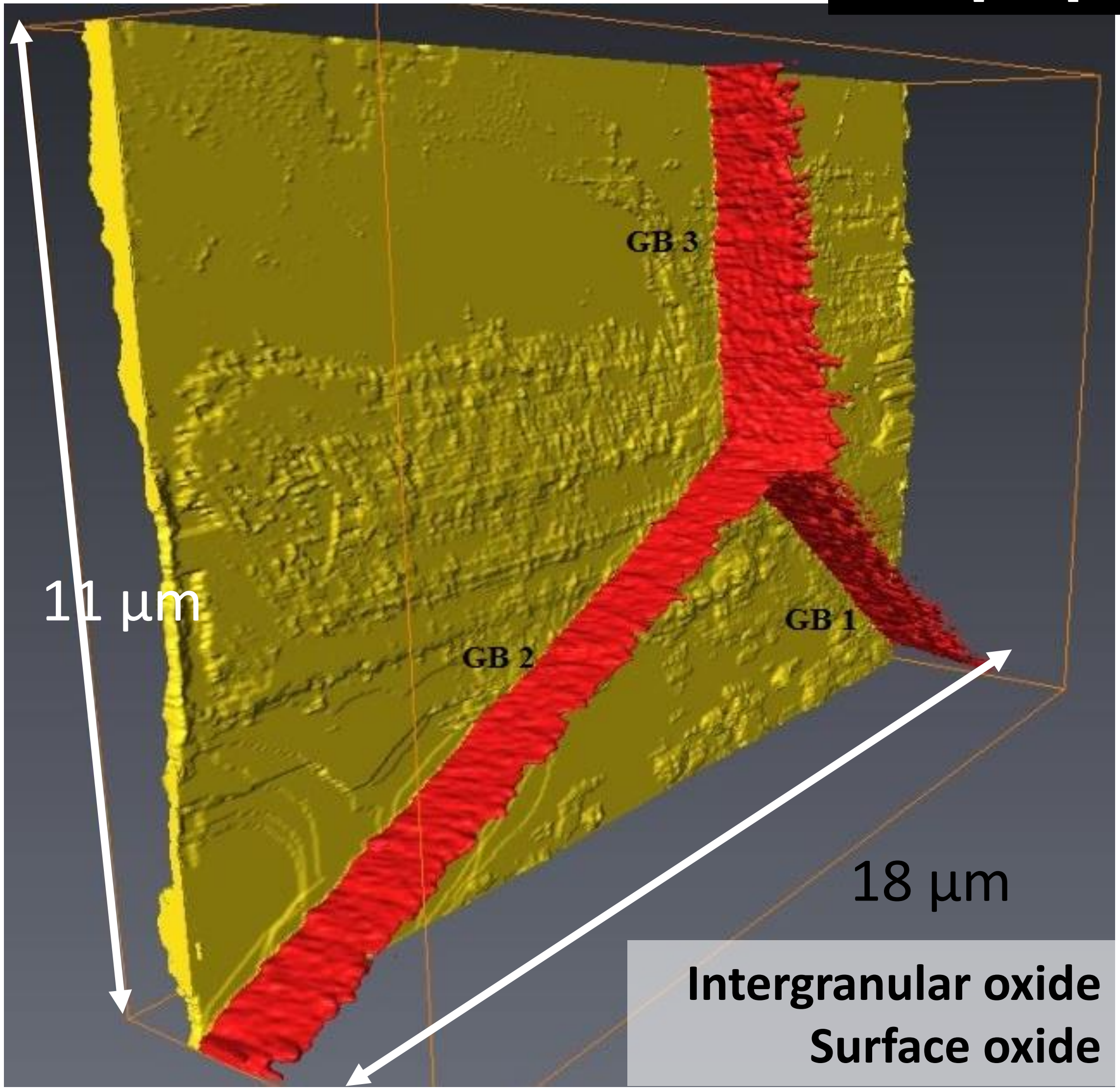


Alloy 600 without carbides

Alloy 600
325° C – 1400h
30 mL H_2/kg H_2O

FIB 3D Slicing





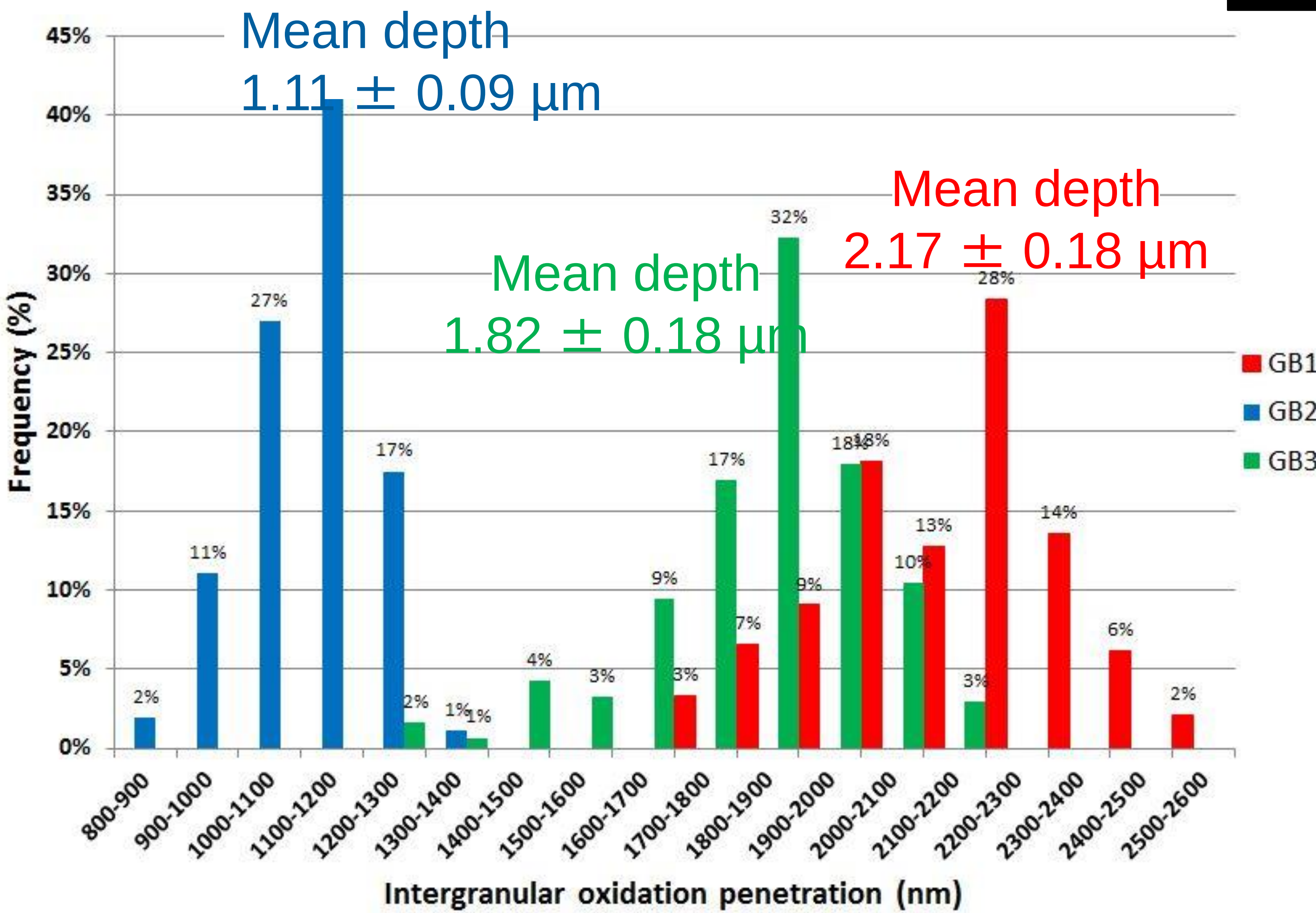
FIB/SEM facility
Equipex MATMECA

H.T. Le, internship (2015)

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

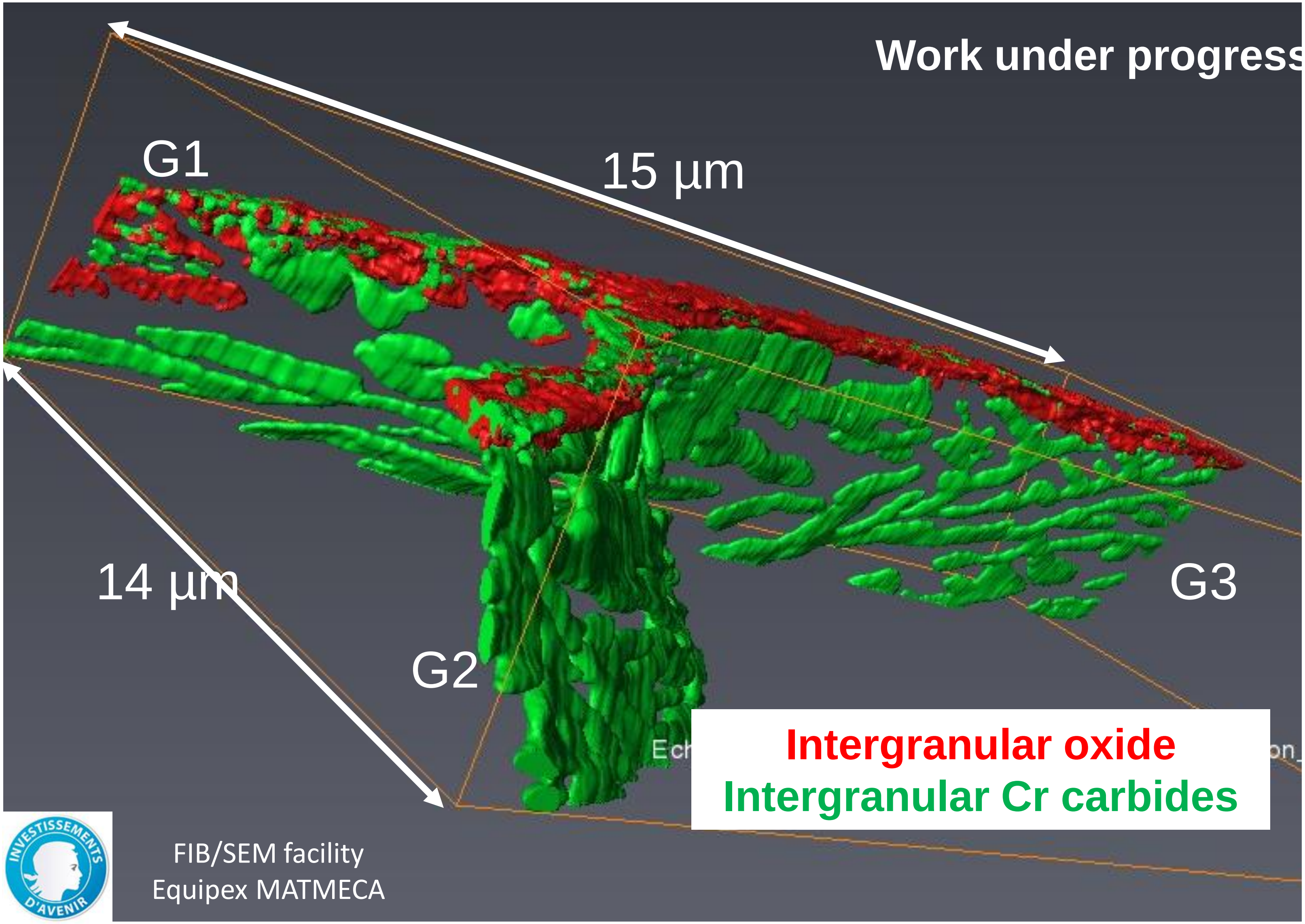
Alloy 600 without carbides

Alloy 600
325° C – 1400h
30 mL H_2/kg H_2O



Alloy 600 with carbide precipitation

Alloy 600
325° C – 1400h
30 mL H_2/kg H_2O

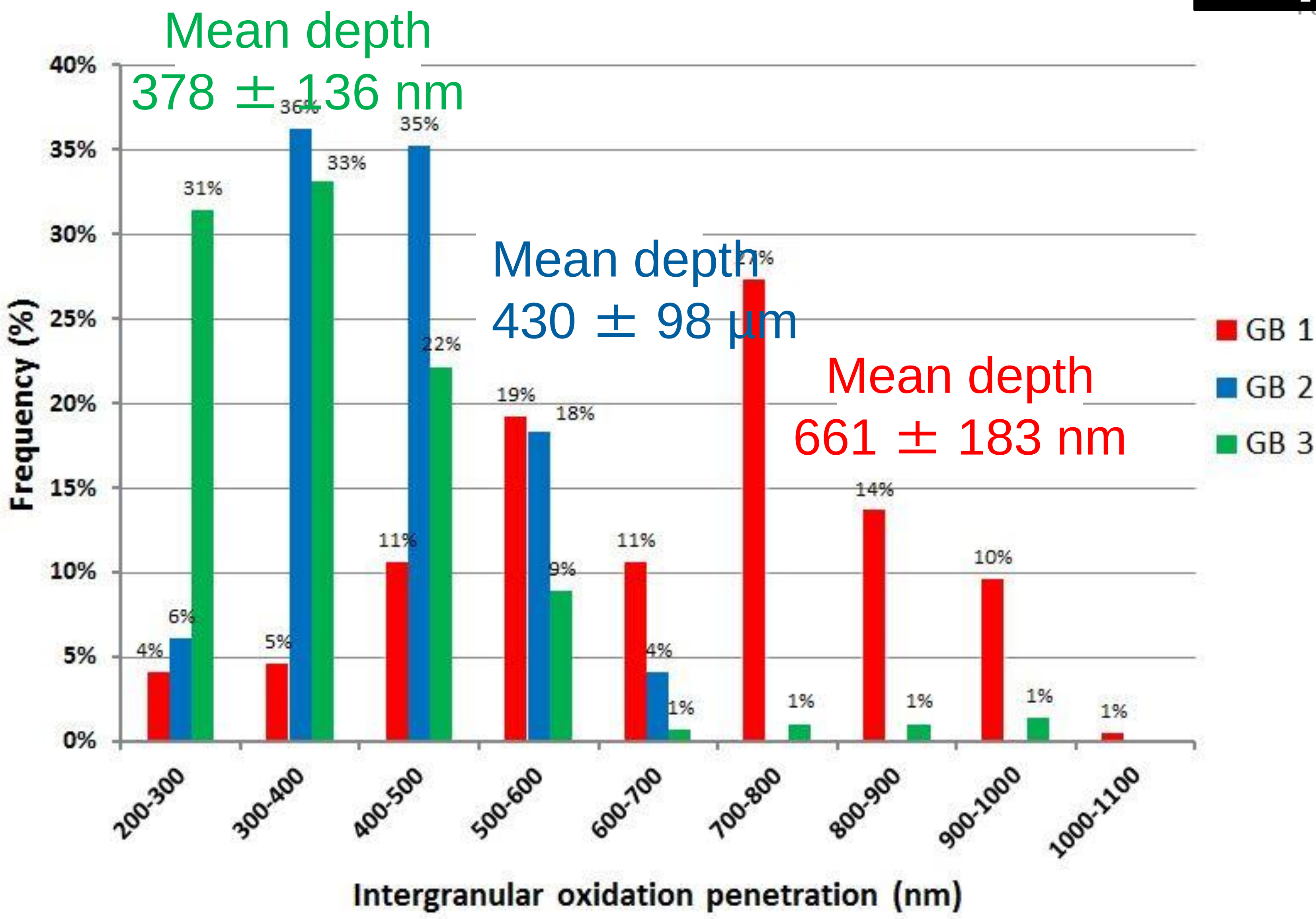


H.T. Le, internship (2015)

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

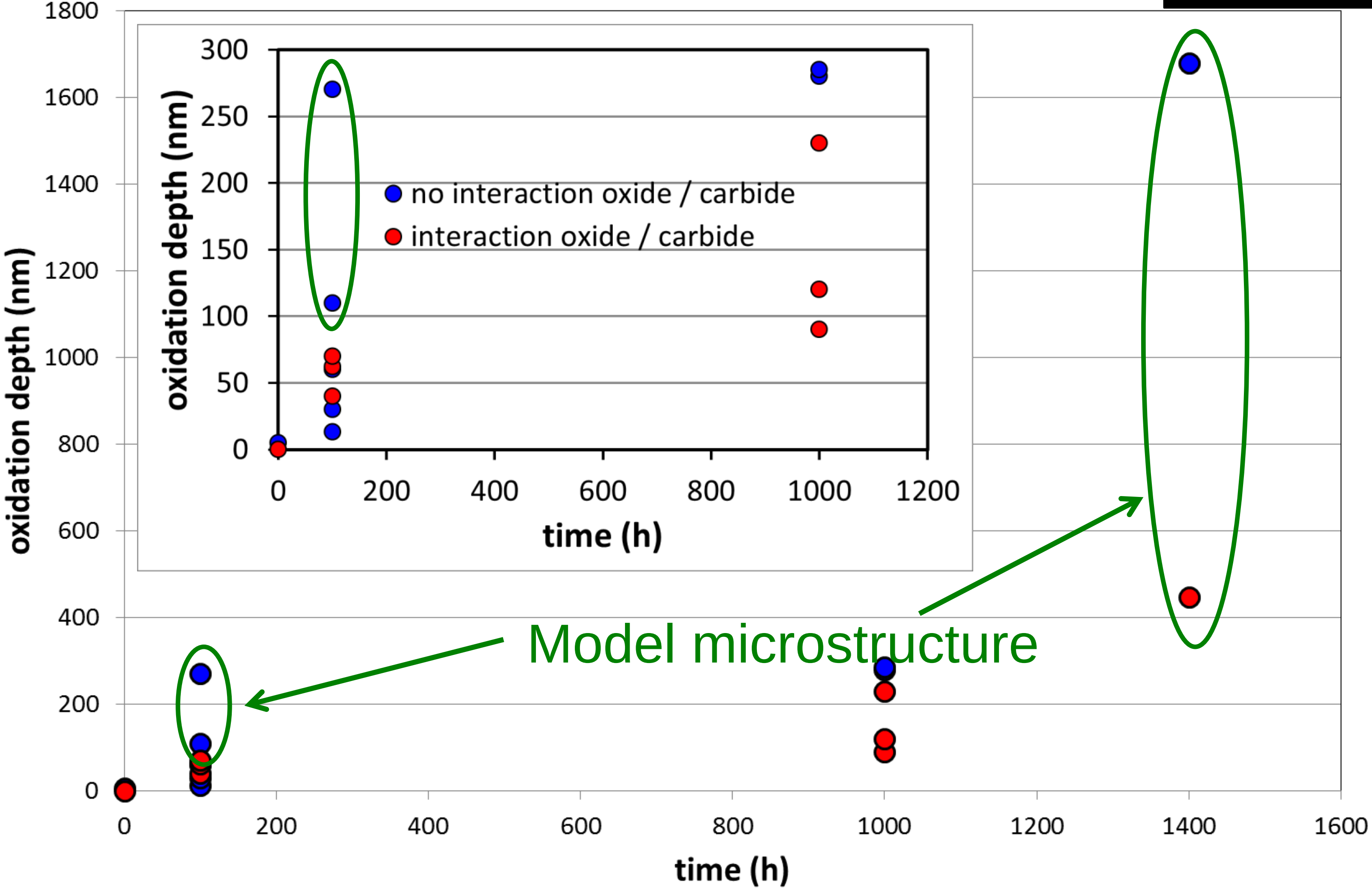
Alloy 600 with IG chromium carbides

Alloy 600
325° C – 1400h
30 mL H_2/kg H_2O



Oxidation kinetics at 325° C

Alloy 600 – Alloy 182
325° C
30 mL H_2/kg H_2O



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

Metallurgical factors: summary

- 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?

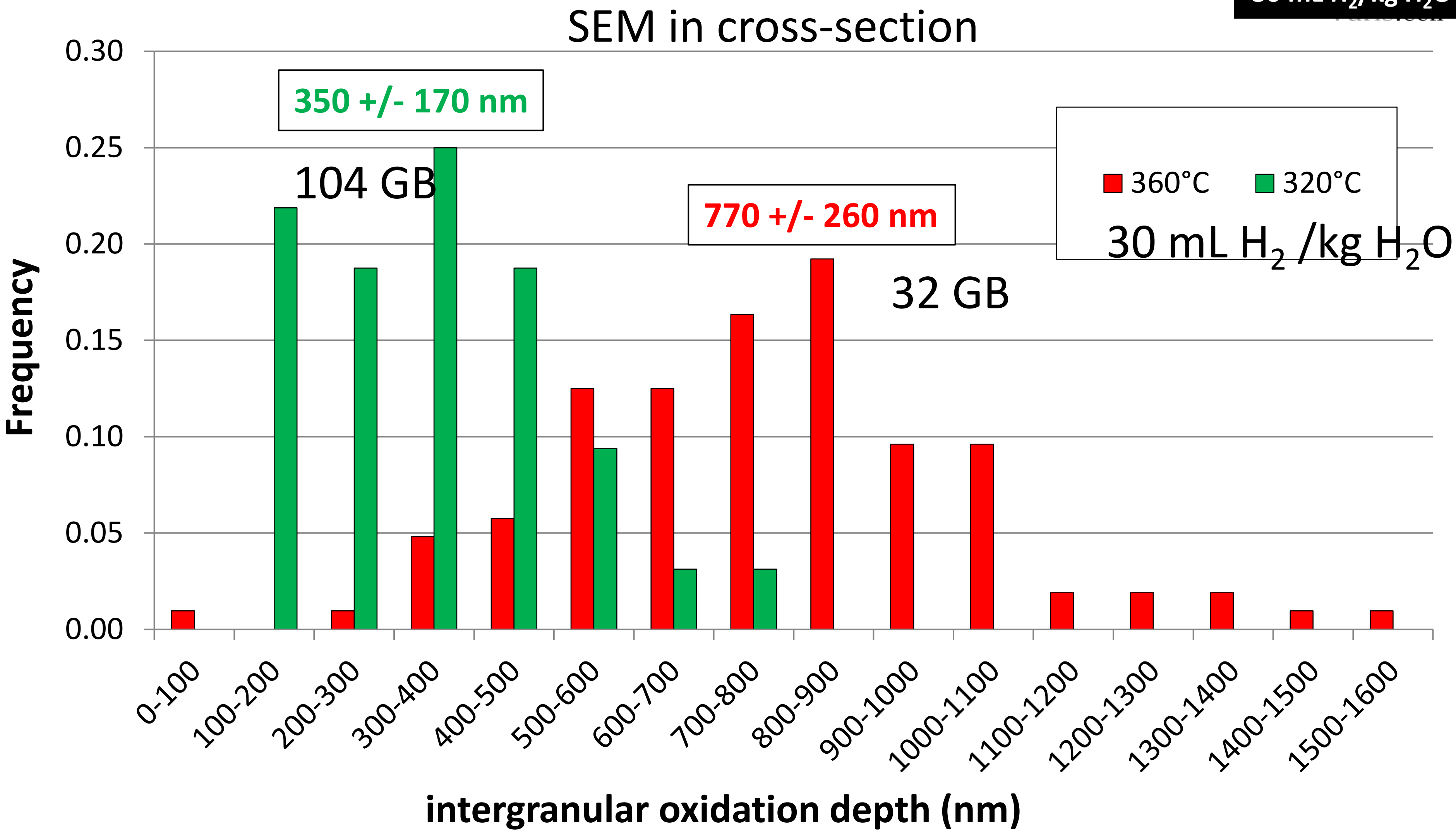
⇨ Need for more statistical data and model microstructures

Intergranular oxidation kinetics

- 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_2/kg H_2O



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

M. Wehbi, PhD thesis (2014)

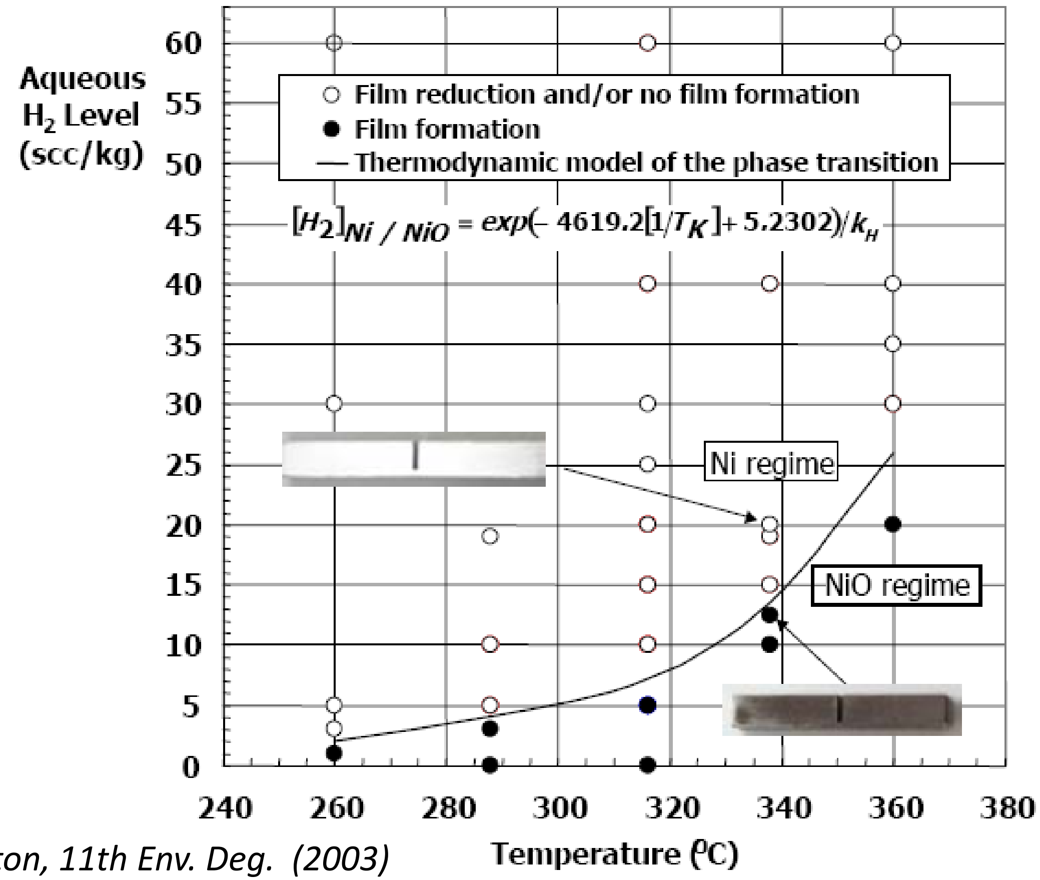
Environmental factors and SCC

Two main factors:

- Temperature
- Dissolved hydrogen content

Electrochemical potential (EcP)

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



S.A. Attanasio and D.S. Morton, 11th Env. Deg. (2003)

Environmental factors and SCC

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

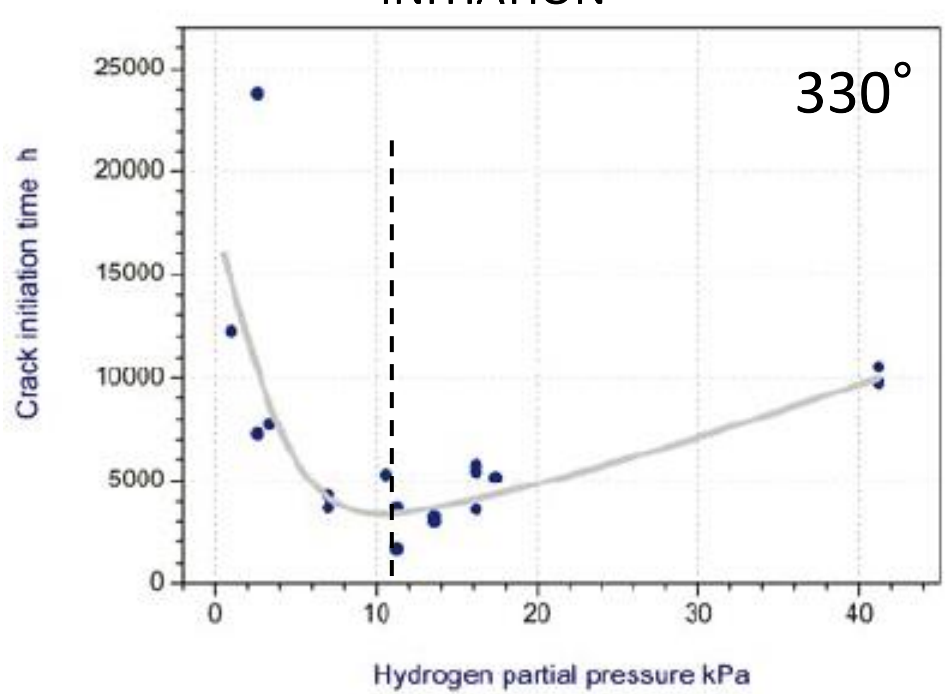
  Activation energy measured for a constant EcP: 140 ± 33 kJ.mol^{-1}

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

- Effect of H_2 content

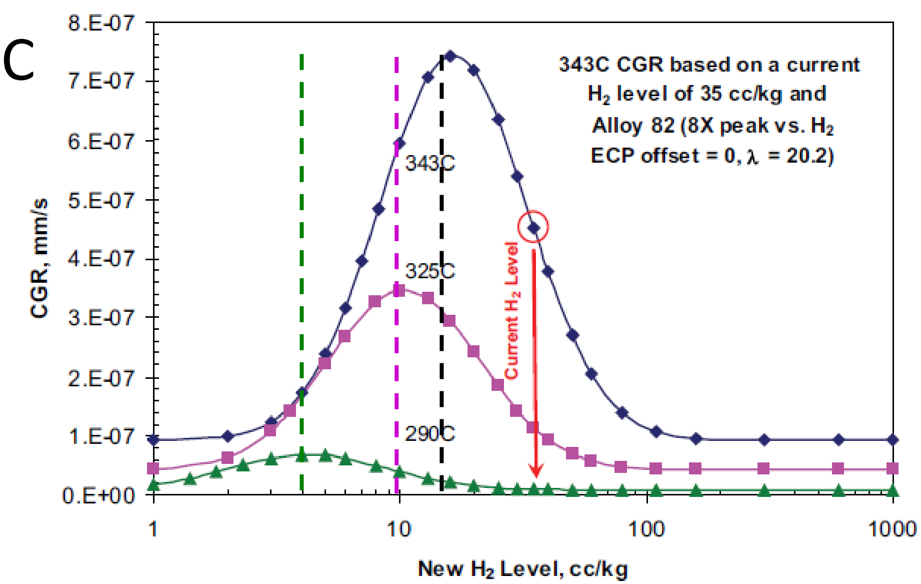
P. Andresen (2007)

INITIATION



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

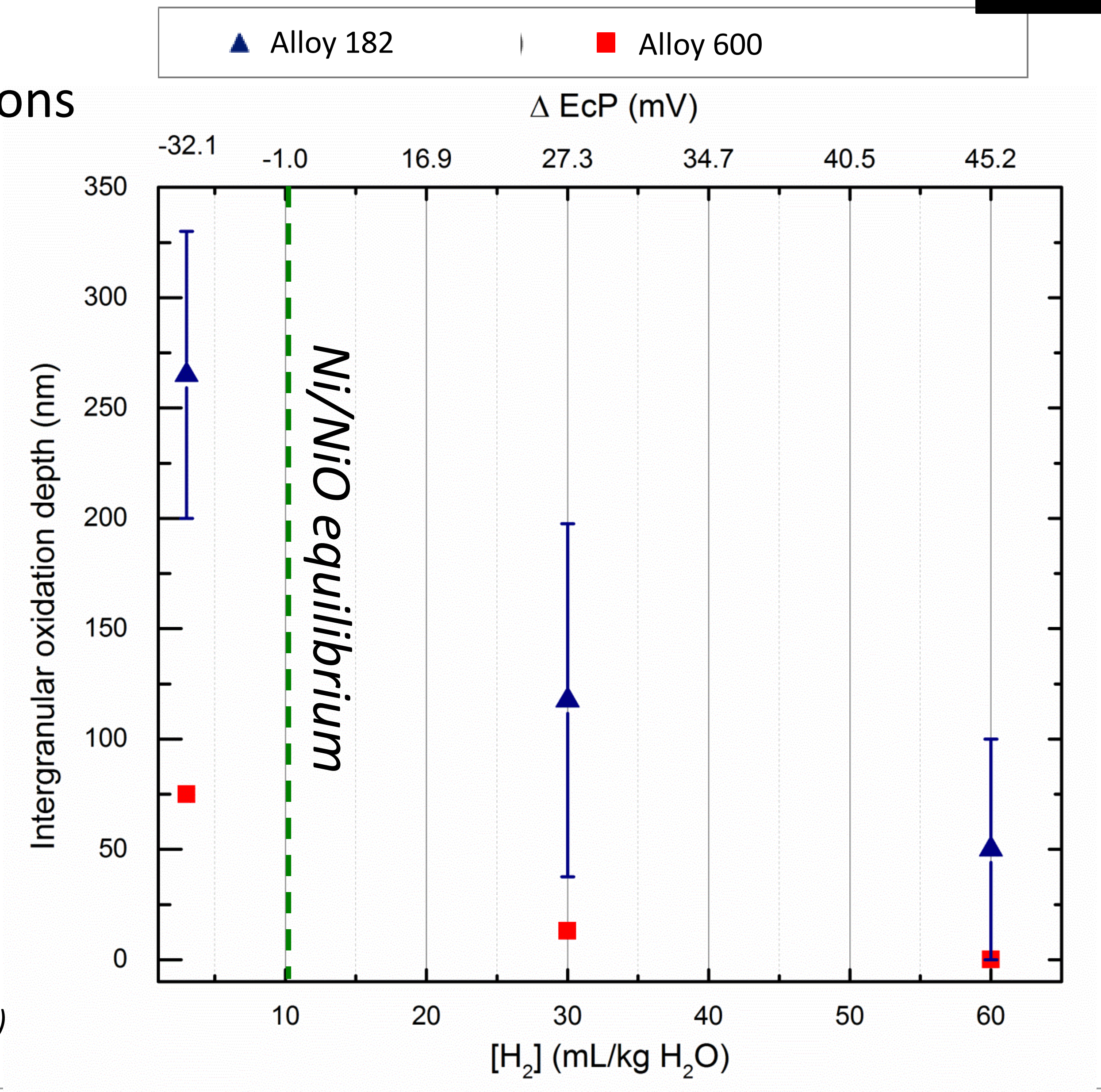
PROPAGATION



Maximum crack growth rate at the Ni/NiO equilibrium

Dissolved hydrogen content

325° C - 100h
TEM observations

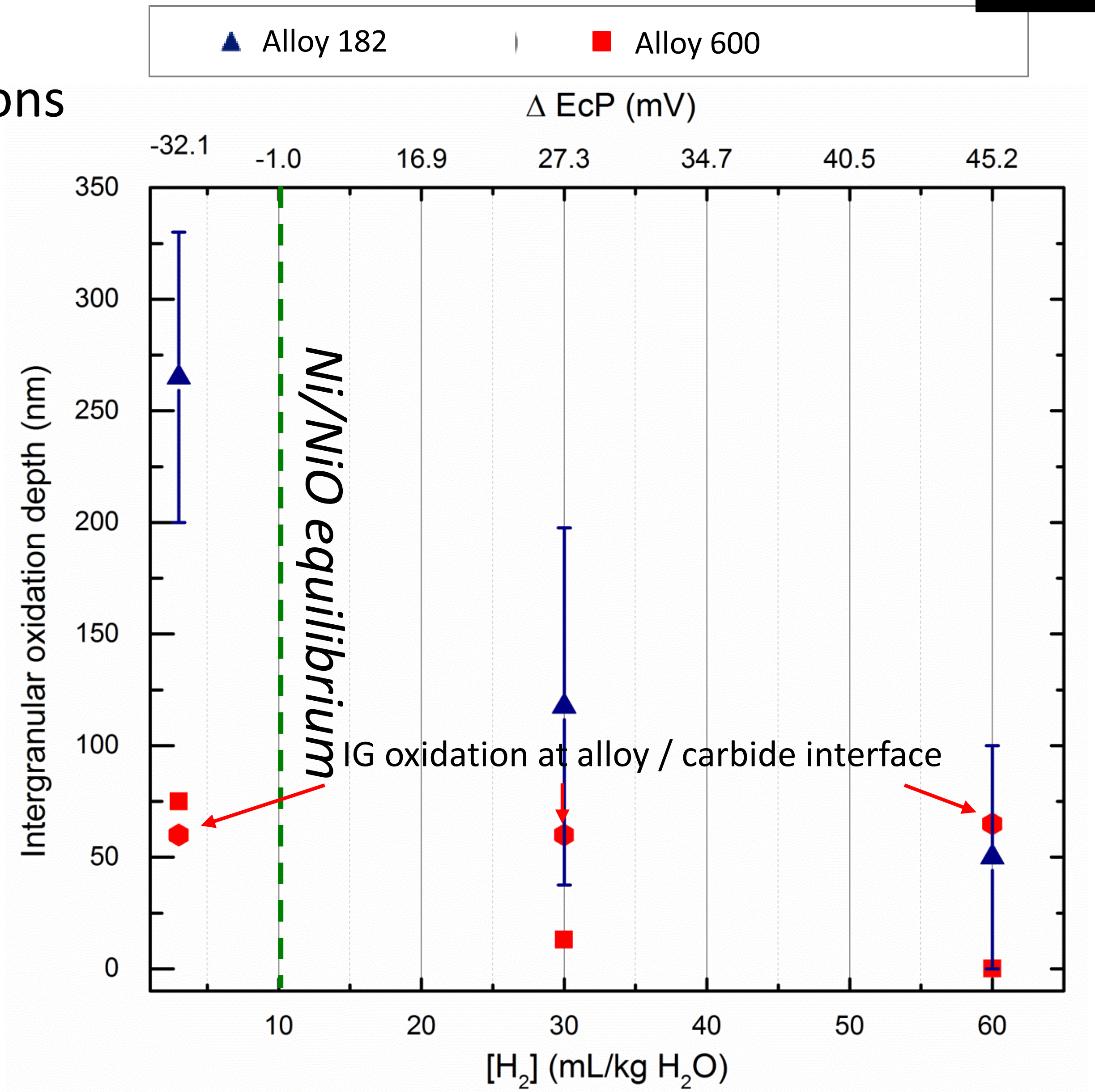


M. Wehbi, PhD thesis (2014)
J. Caballero, PhD thesis

Dissolved hydrogen content

Alloy 182 – Alloy 600
325° C
100h

325° C - 100h
TEM observations

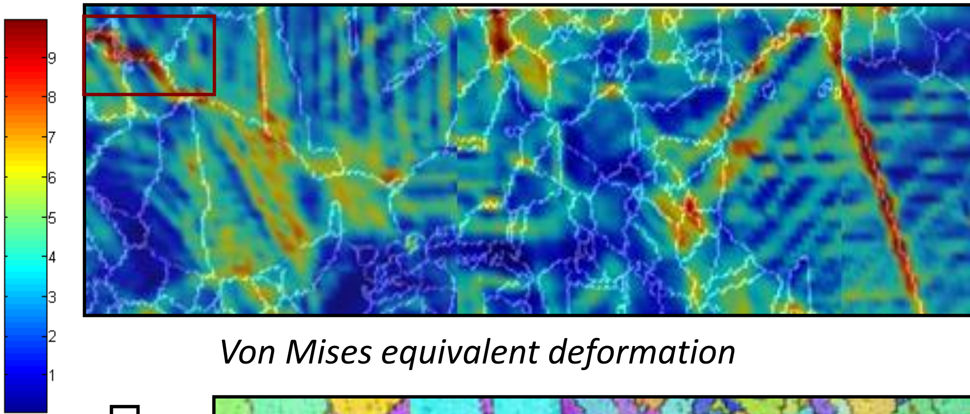


M. Wehbi, PhD thesis (2014)
J. Caballero, PhD thesis

Intergranular oxidation kinetics

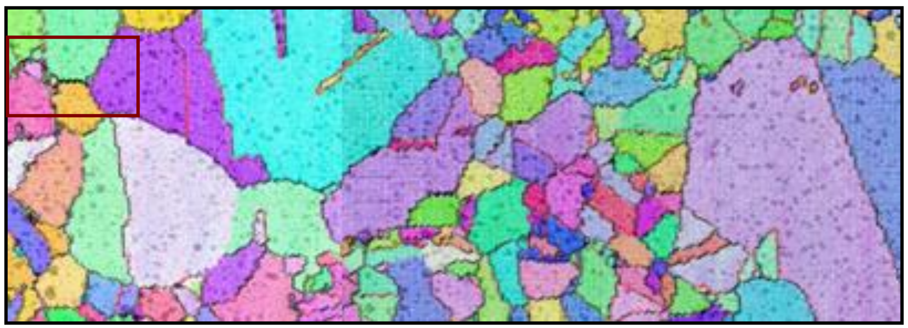
- Metallurgical factors
  - Grain boundary character
  - Intergranular chromium carbides
- Environment
  - Temperature
  - Dissolved hydrogen content
- Mechanical factors
  - Pre-straining
  - Oxidation under stress

Coupling between microstructure and strain fields



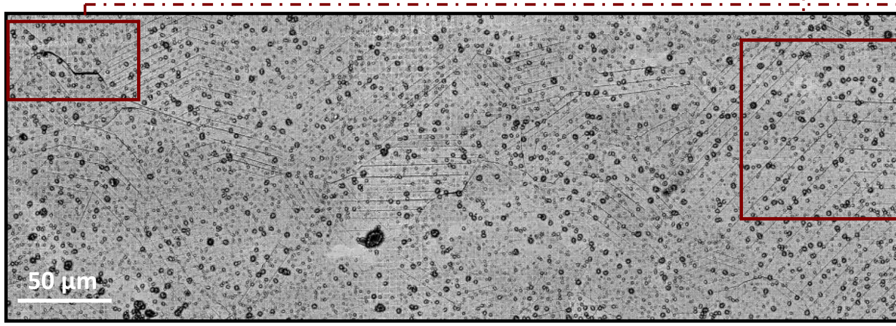
Von Mises equivalent deformation

Strain field measurements
(Von Mises equivalent deformation)

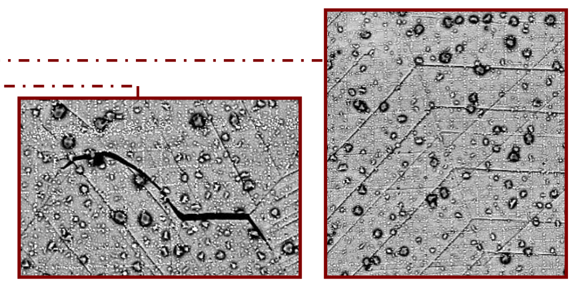


EBSD orientation mapping of the same area

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

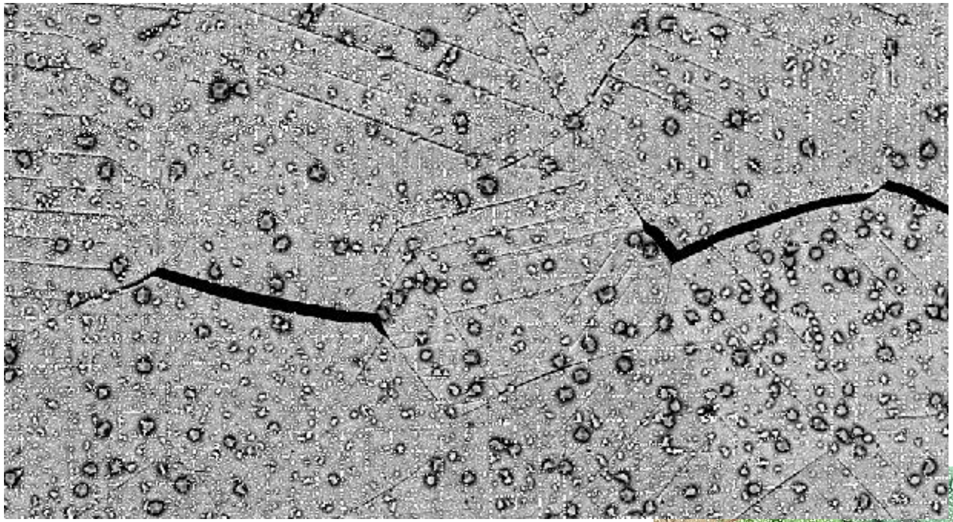


Cracking network (SEM observations)

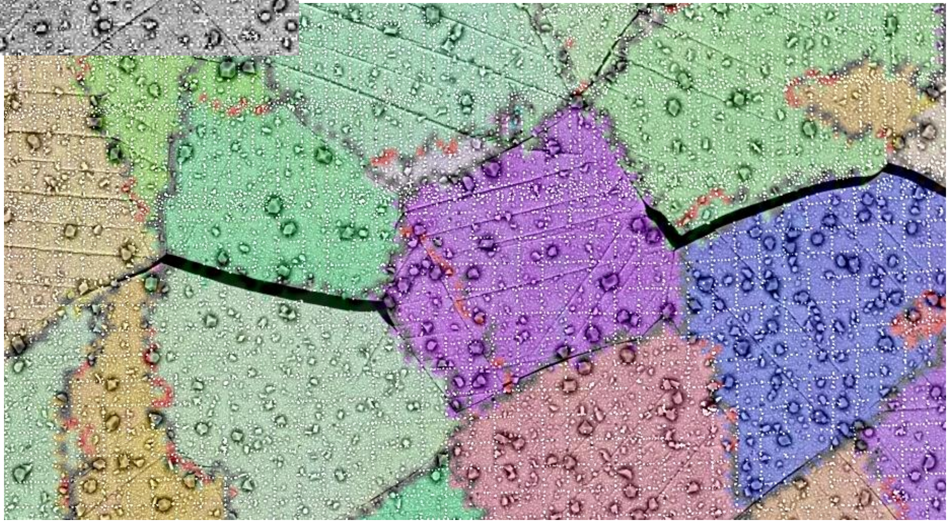


- Cracking features
- Oxidation
- Slip bands

→ Application to IASCC of austenitic stainless steels



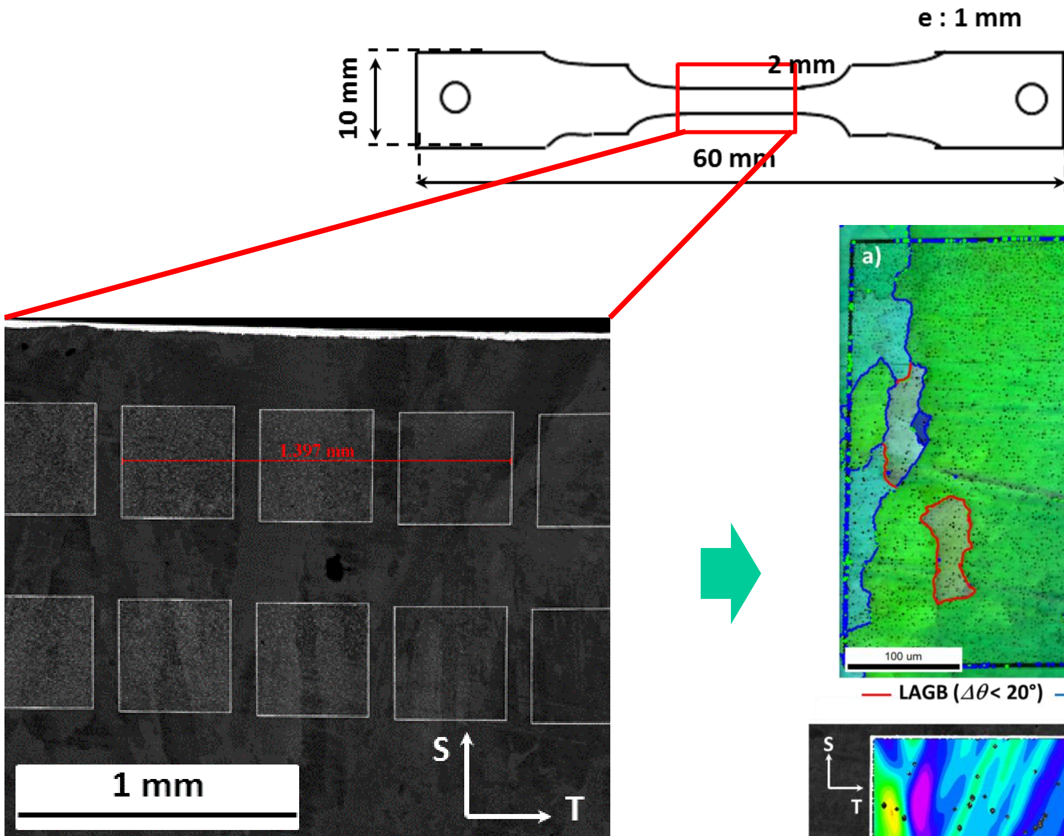
5 dpa, 2% macroscopic srain



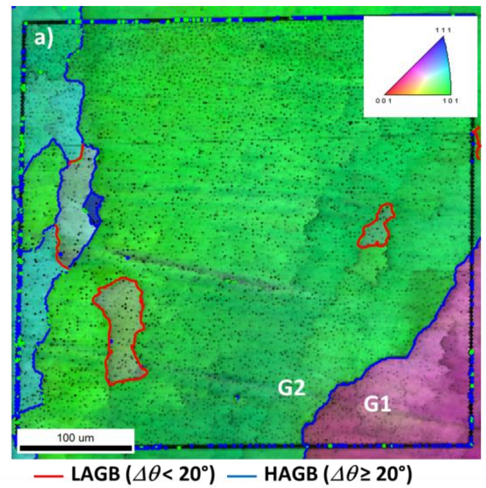
Effect of pre-straining

Alloy 82
360° C - 1000h
30 mL H_2 / kg H_2O

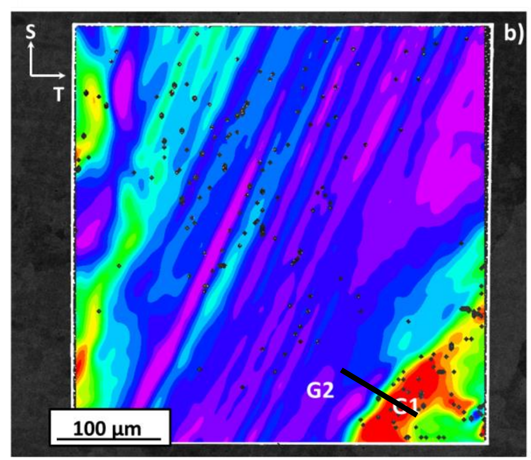
Tensile specimens – mirror finish
Macroscopic deformation: 0, 7, 20%

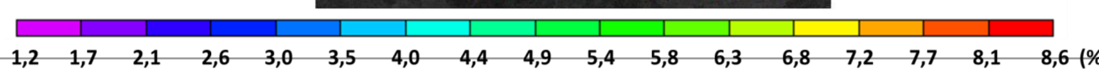


8 fields (400 µm x 400 µm)
gold speckle (diameter : 1 µm)



EBSD orientation maps





Strain field measurement

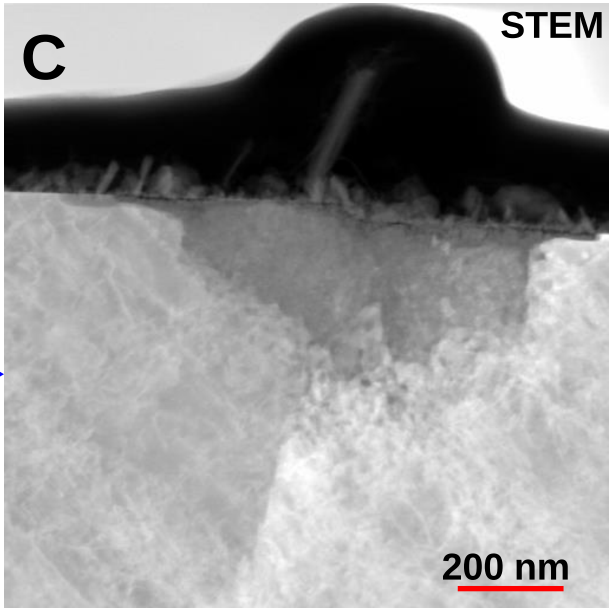
M. Wehbi, PhD thesis (2014)

Effect of pre-straining

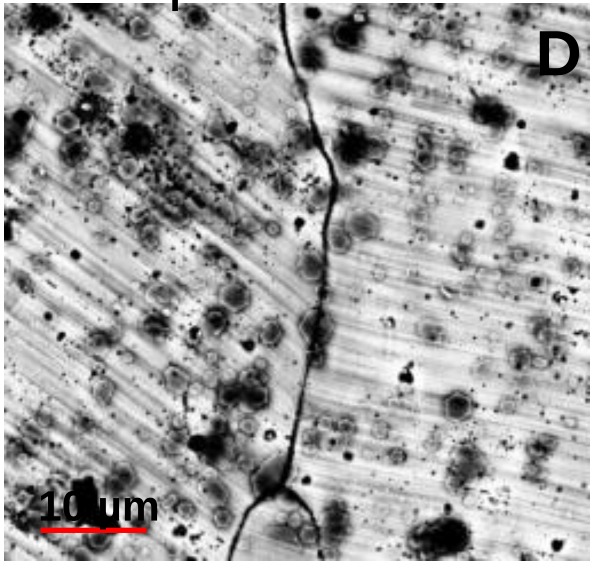
Alloy 82
360° C - 1000h
30 mL H_2 / kg H_2O

Grain boundaries studied after oxidation

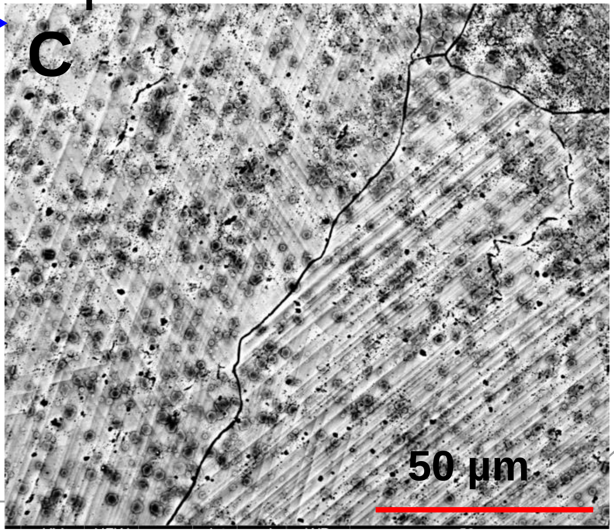
GB	GB misorientation (°)	Mean local strain (%)	Local strain gradient (%)
A	40	0	-
B	5	7	0
C	40	6	6
D	30	13	0



Slip band continuity



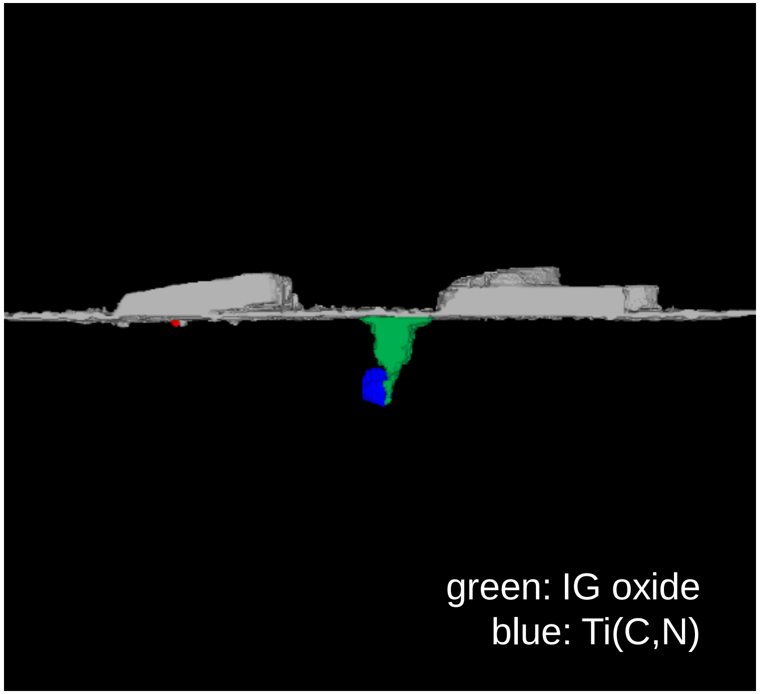
Slip band discontinuity



Effect of pre-straining

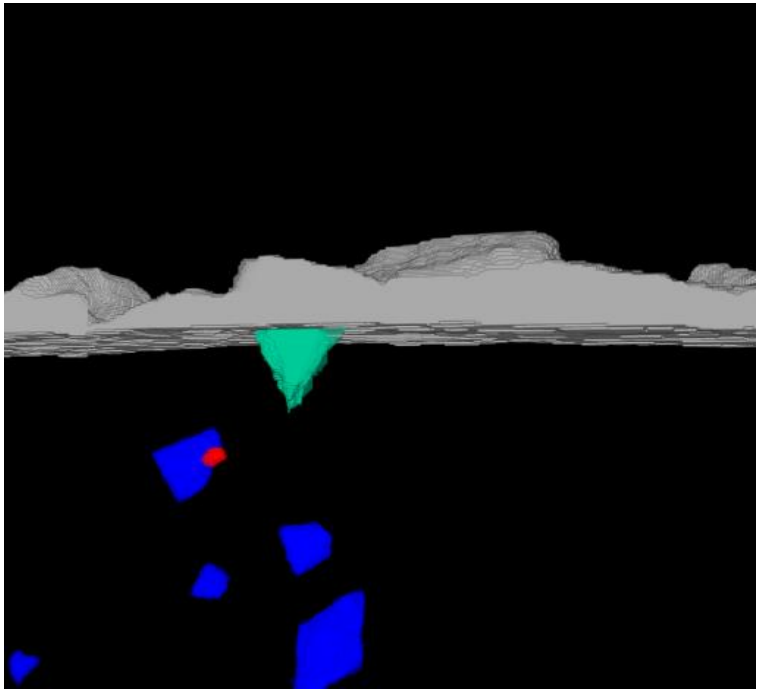
Alloy 82
360° C - 1000h
30 mL H_2 / kg H_2O

Grain boundary D
Grain boundary length: 6 µm
$\varepsilon_{\text{von Mises}}$: 0,13 – strain discrepancy: 0 %



Mean oxidation depth:
550 +/- 50 nm

Grain boundary C
Grain boundary length : 3 µm
$\varepsilon_{\text{von Mises}}$: 0,06 – strain discrepancy: 6 %



Mean oxidation depth:
1050 +/- 180 nm

A strain gradient between neighbouring grains seems to promote:

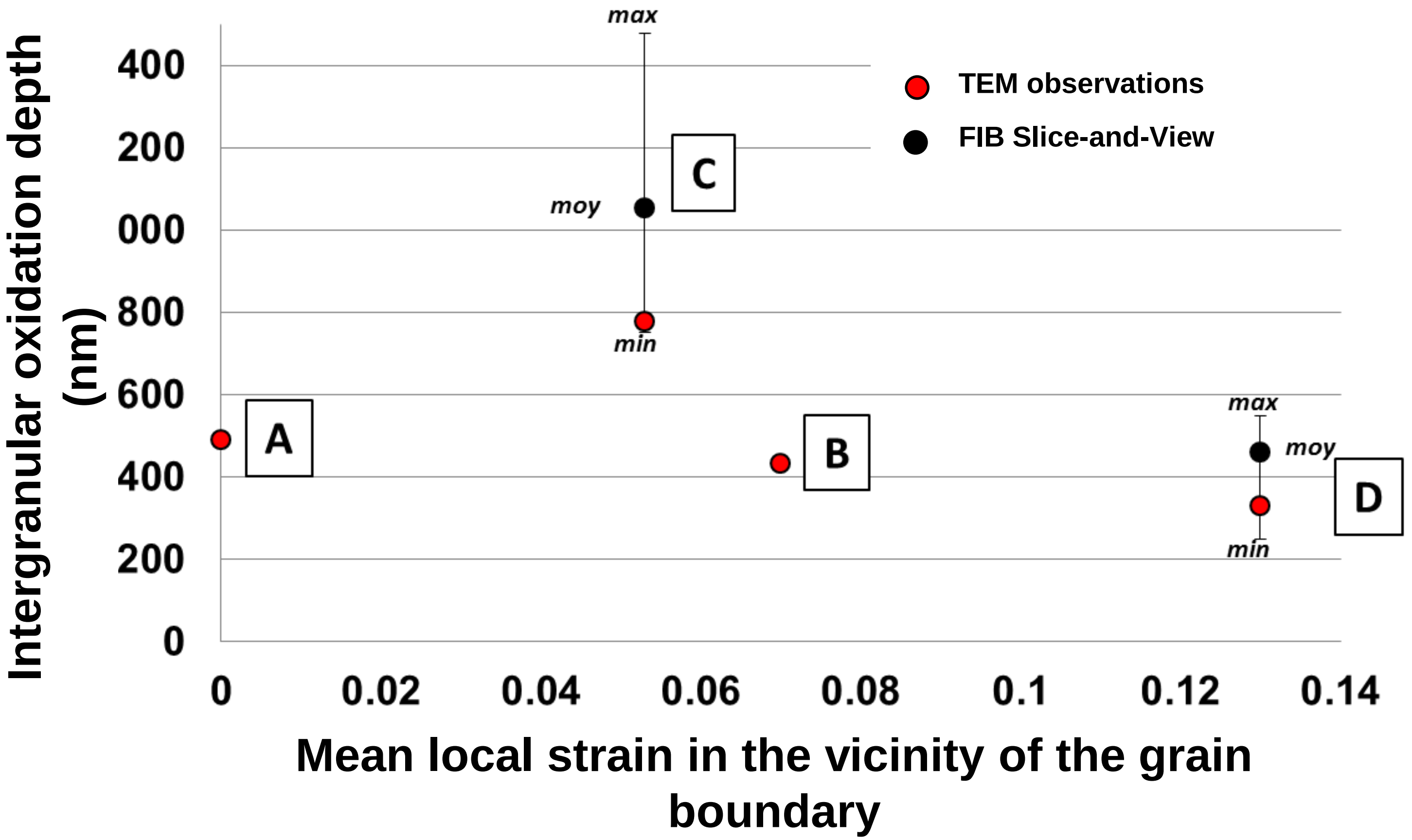
- Intergranular oxidation
- Oxide depth scattering along the GB

FIB 3D Slicing performed by K. Rousseau, SERMA Technologies (Grenoble)

Effect of pre-straining

Alloy 82
360° C - 1000h
30 mL H_2 / kg H_2O

ParisTech



FIB Slice-and-View analyses confirm TEM observations:

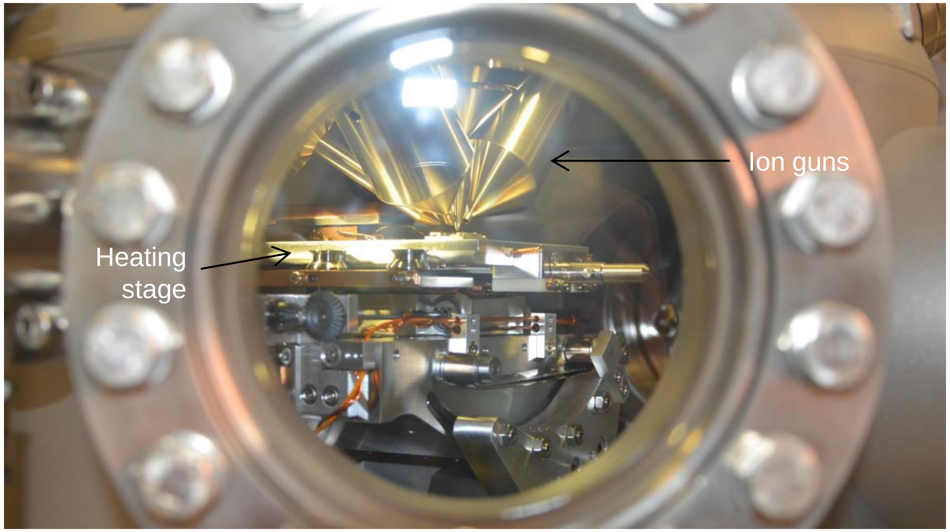
- No significant effect of the mean local strain
- Strong effect of the strain gradient on IG oxide depth and scattering

Intergranular oxidation kinetics

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

Coupling oxidation and stress

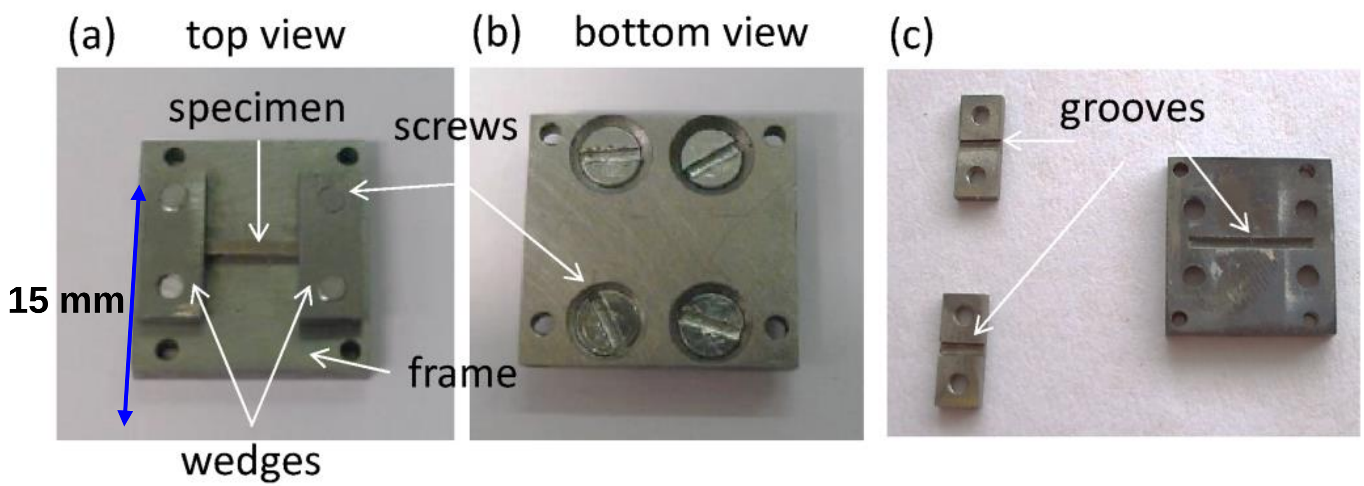
- Development of a device for studying oxidation under stress *in situ* in a ToF-SIMS
- MAI-SN project in collaboration with Chimie ParisTech:
  C. Poulain (post-doc), P. Marcus, A. Seyeux



ToF-SIMS chamber [LEM 14]

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

- Stress imposed by differential thermal expansion using:
  - A molybdenum device (TEC ≈ 5×10^{-6} K^{-1})
  - Alloy 600 specimens (TEC ≈ 14×10^{-6} K^{-1})

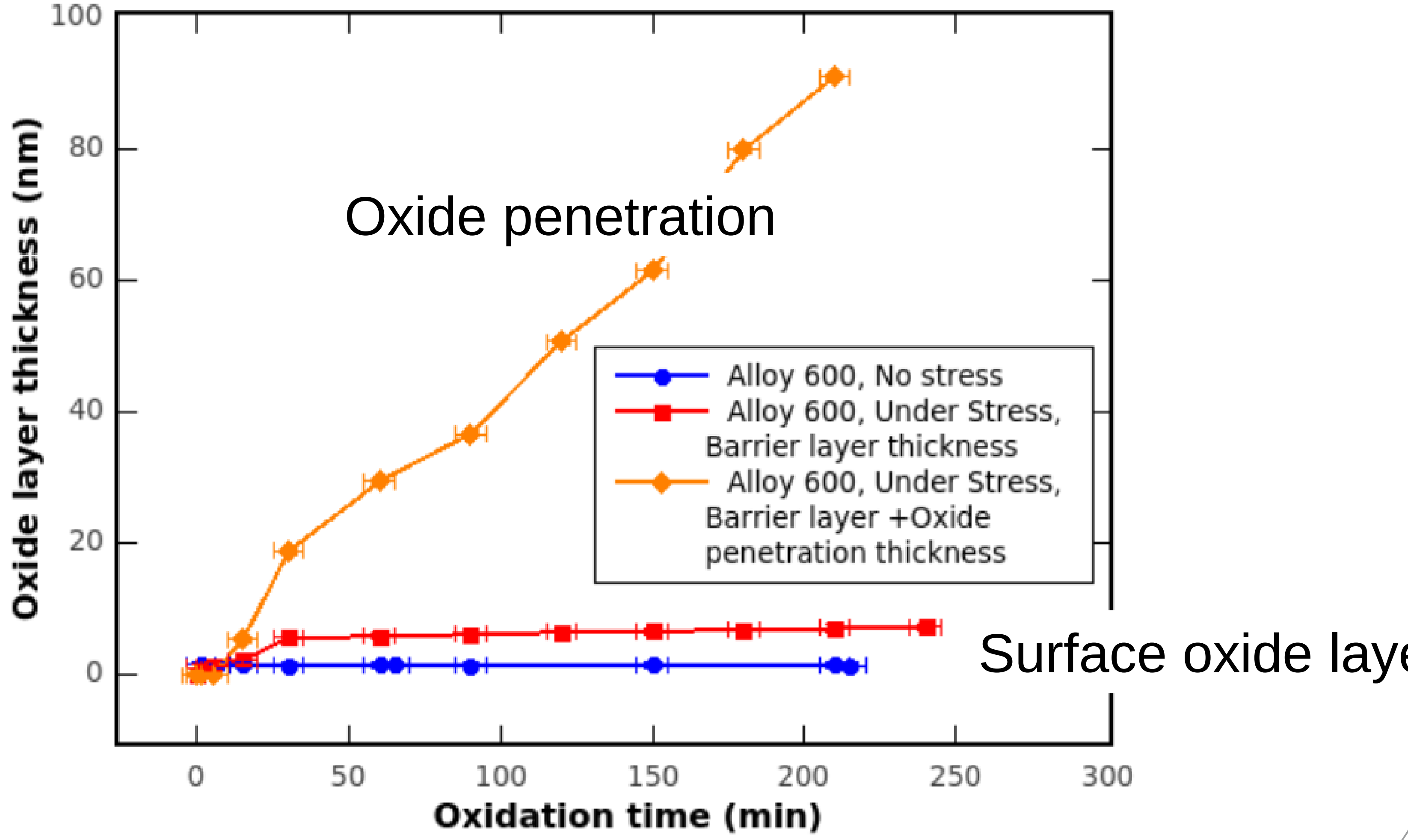


Specimen size: $10\times1\times1mm^3$

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

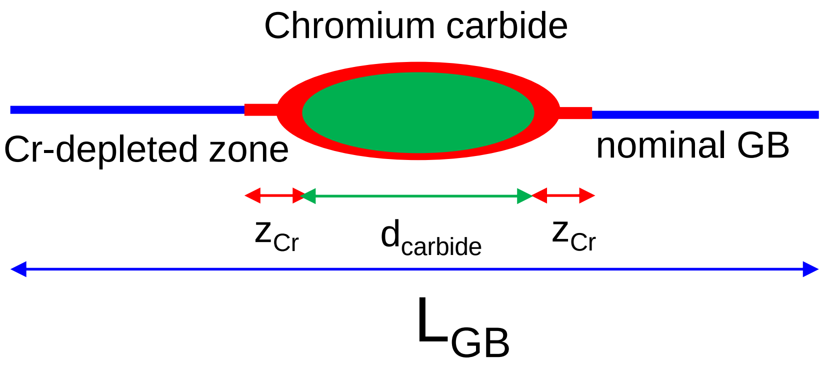
Coupling oxidation and stress

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-depled zone.



Microstructure :

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

Limit conditions:

- time (h)
- T (° C)
- [H_2](cc/kg 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

<u>Assumption:</u> for a given phase *i*, the IG oxidation kinetics follows a log-type law.

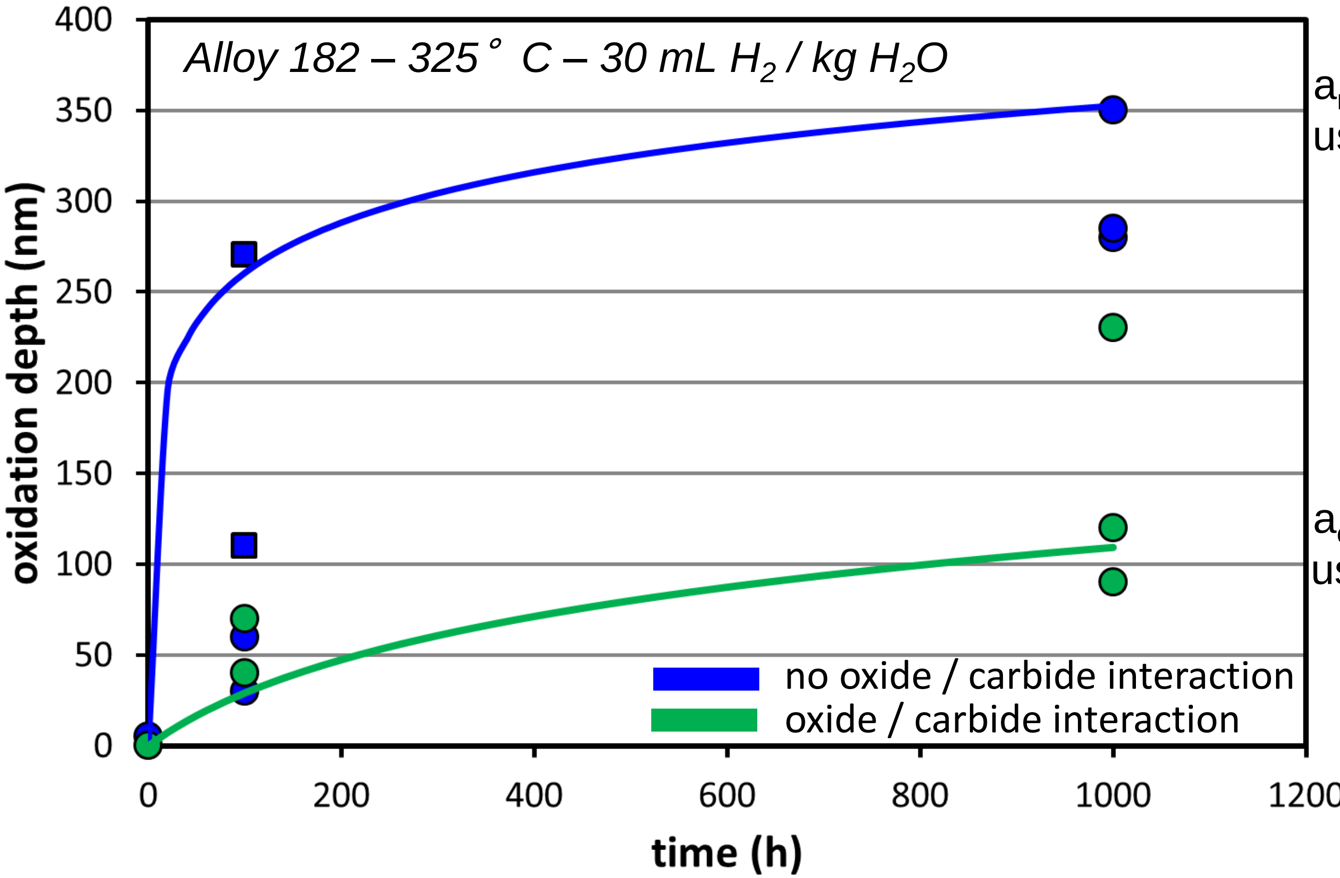
$$p_i = \frac{1}{a_i} \mathrm{Ln}(1 + b_i \times t) \times f(\Delta EcP) \times g(T)$$

IG oxide depth

constant

electrochemical potential

temperature

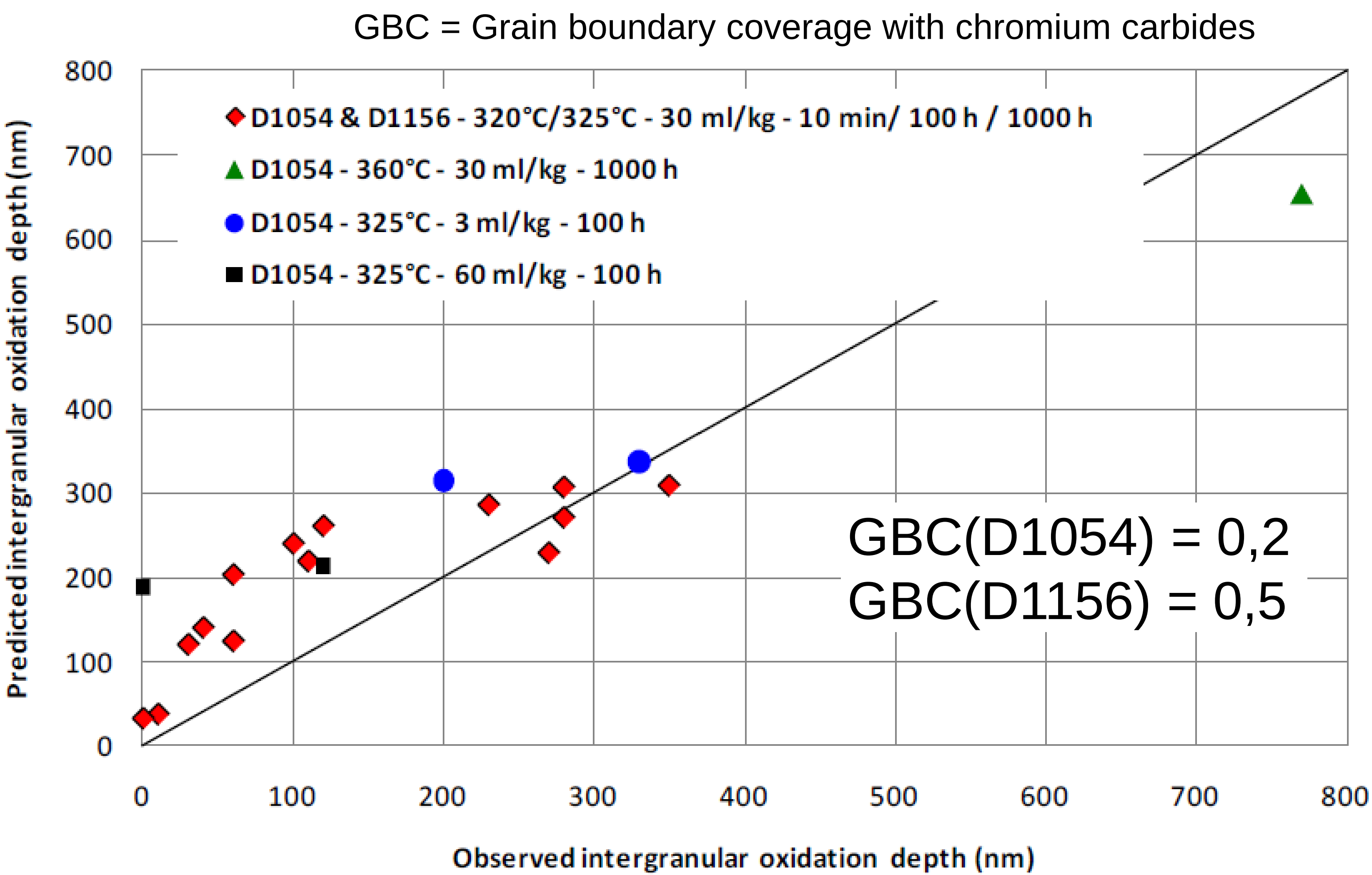


$a_{nominal}$ and $b_{nominal}$ identified using the **maximum** depths

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

Application to Alloy 182

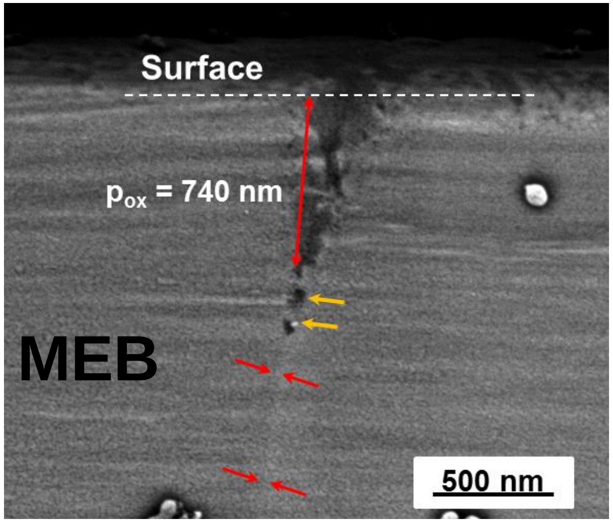
- Random sampling of 100 GB

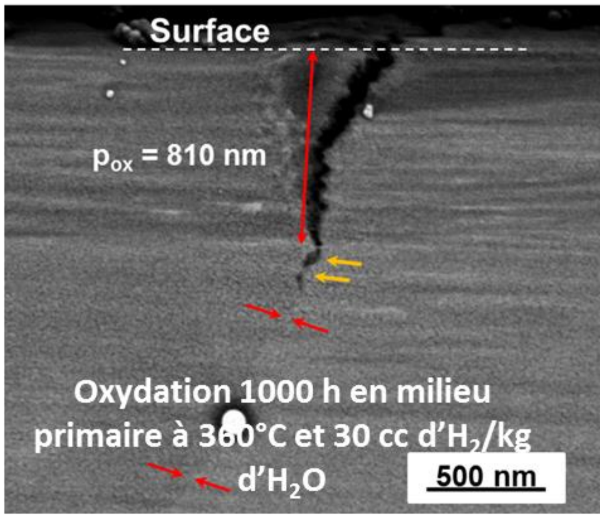


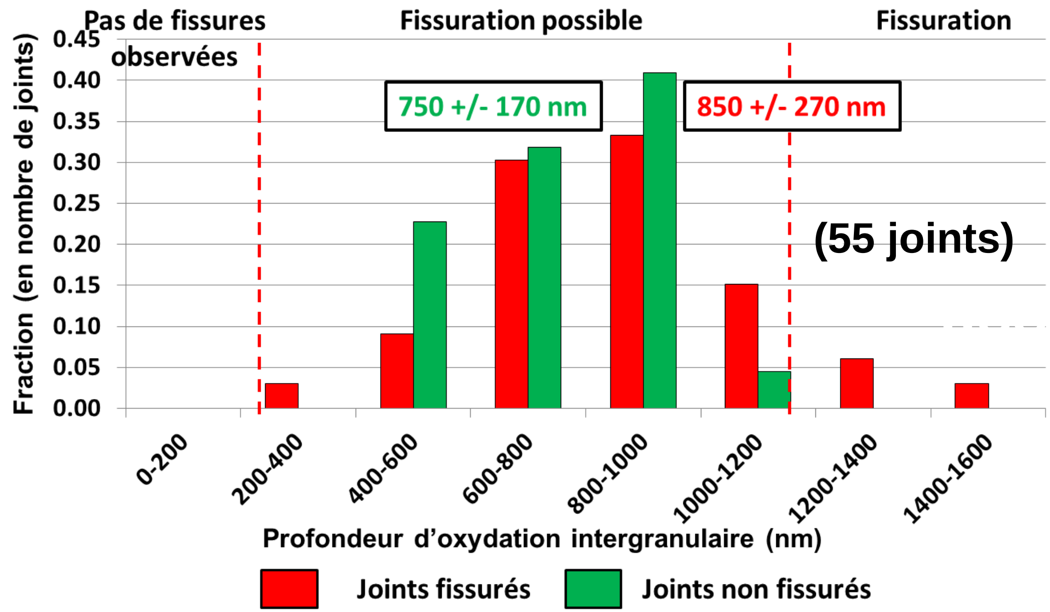
Crack initiation criterion : methodology

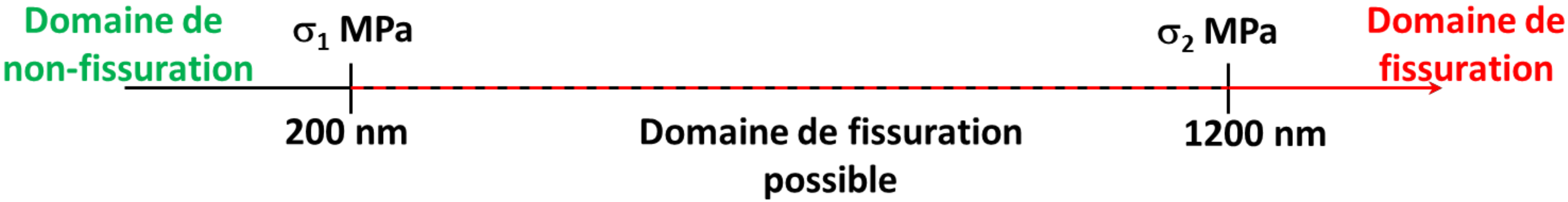
Alloy 182 1000 hours primary water at 360°C, 30 mL d'H_2/kg d'H_2O
Tensile test at 360°C (strain rate : 10^{-5} s^{-1})

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

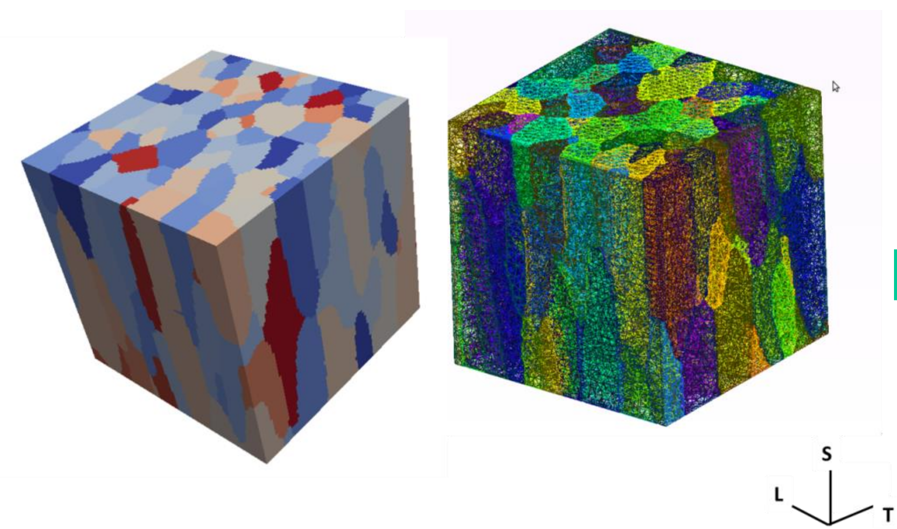



Surface
p_{ox} = 810 nm
Oxydation 1000 h en milieu primaire à 360°C et 30 cc d'H_2/kg d'H_2O
500 nm

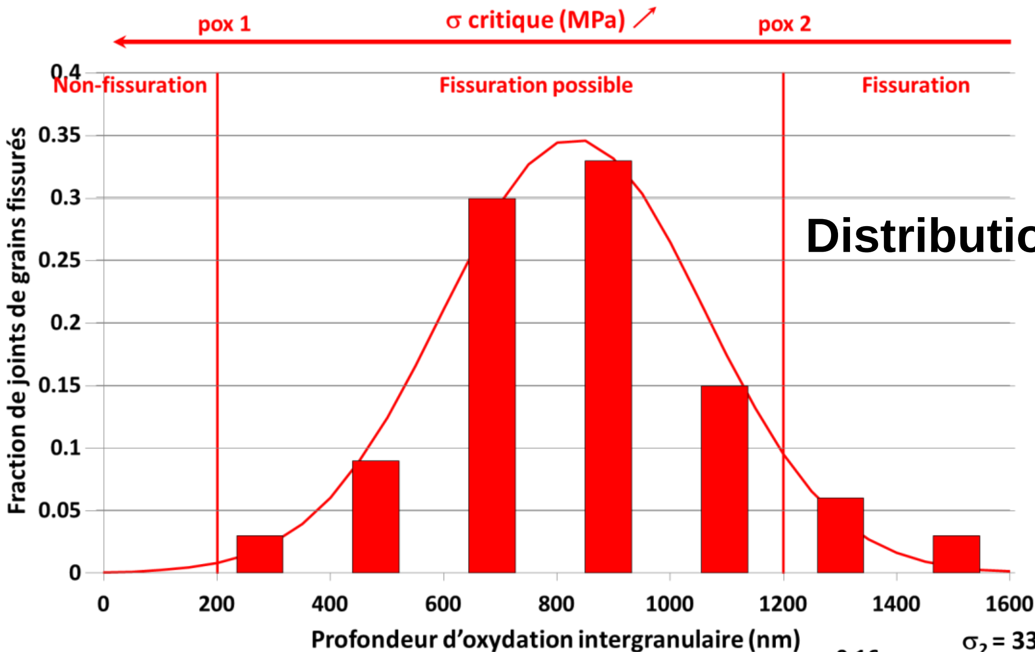

Pas de fissures observées
Fissuration possible
Fissuration
750 +/- 170 nm
850 +/- 270 nm
(55 joints)
Fraction (en nombre de joints)
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0-200
200-400
400-600
600-800
800-1000
1000-1200
1200-1400
1400-1600
Profondeur d'oxydation intergranulaire (nm)
Joints fissurés
Joints non fissurés



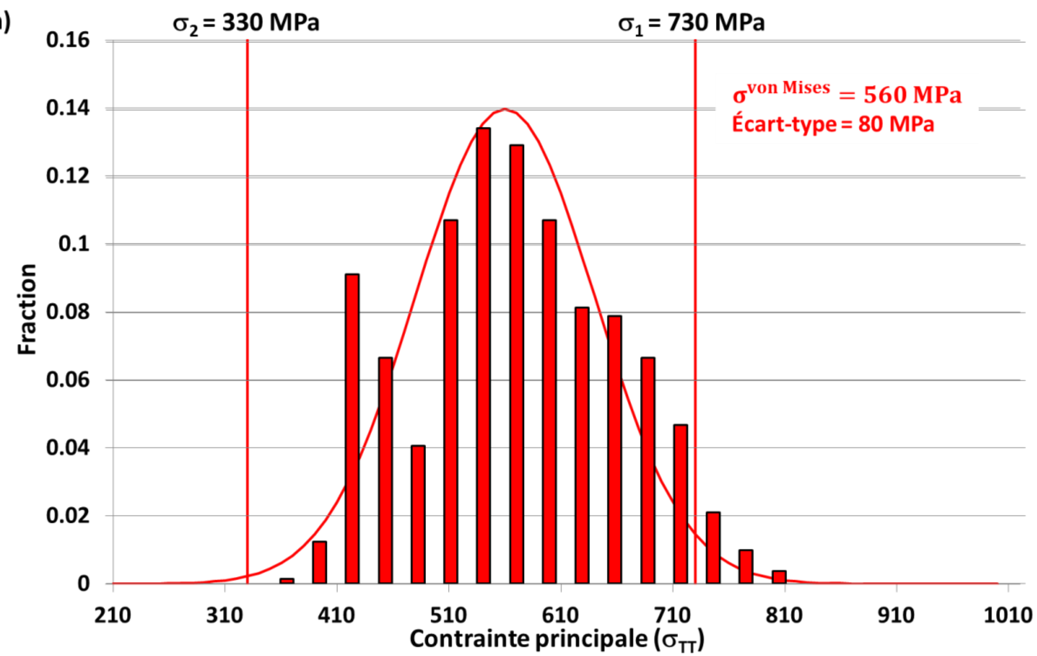
EVP crystallographic constitutive equation
Virtual microstructure representative of the columnar microstructure texture <001>



Stress distribution along the grain boundaries



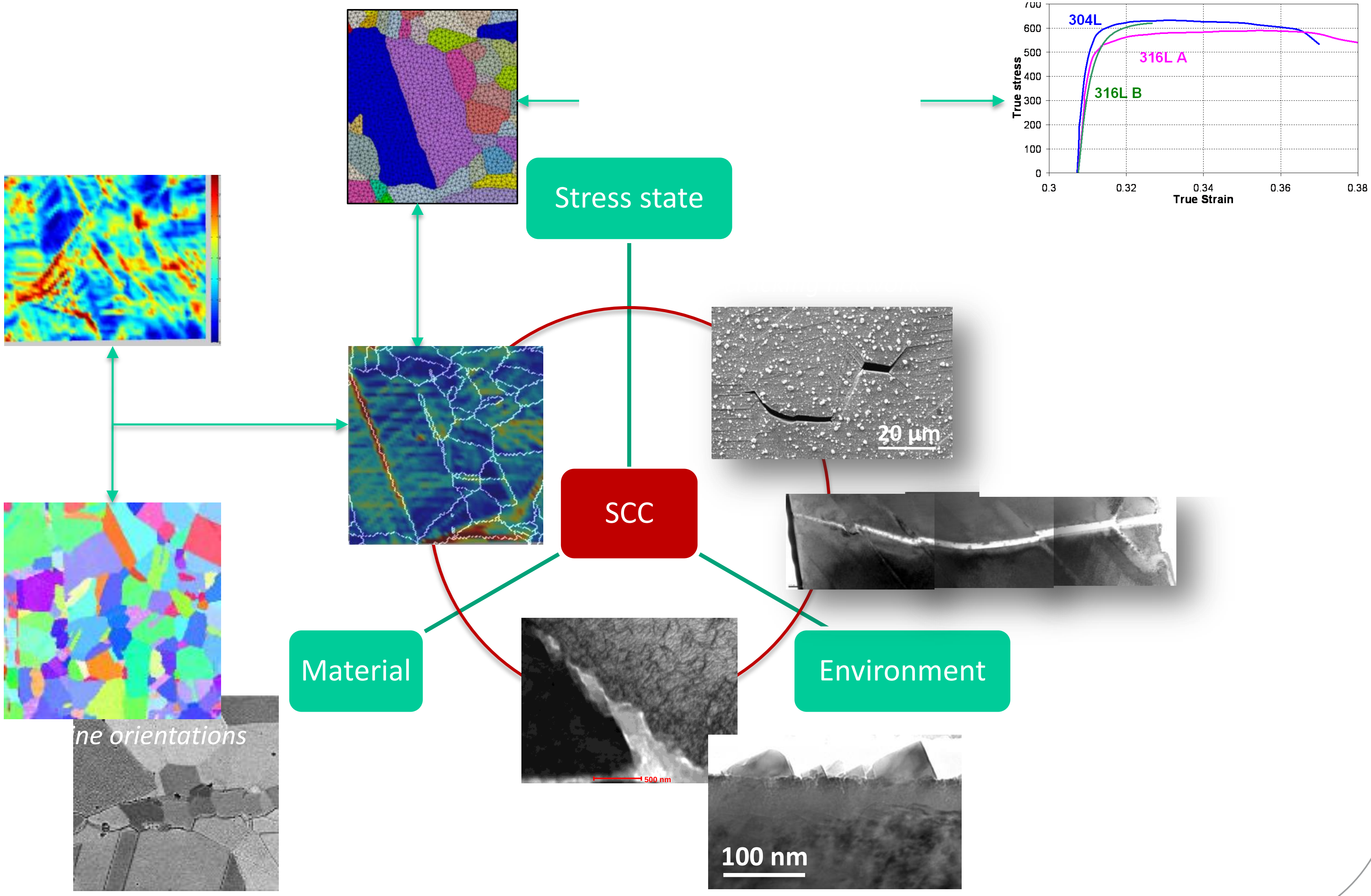
Distribution of the cracked grain boundaries



σ_{TT} distribution for 7 % macroscopic strain

Criteria:
pox ≥ 200 nm
σcrit ≥ 730 MPa

Development of a combined approach



Thank you for your attention