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# Chromium depleted zone in nickel base alloy : experimental study of chromium diffusion between 350°C and 500°C

Josiane NGUEJIO<sup>1,2</sup>, Jérôme CREPIN<sup>2</sup>, Cécilie DUHAMEL<sup>2</sup>, Catherine GUERRE<sup>1</sup>, François JOMARD<sup>3</sup>

<sup>1</sup> : Den-Service de la Corrosion et du Comportement des Matériaux dans leur Environnement (SCCM), CEA, Université Paris-Saclay, F-91191, Gif-sur-Yvette, France

<sup>2</sup> : MINES ParisTech, PSL - Research University, Mat - Centre Des Matériaux, CNRS UMR 7633, BP 87, 91003 Evry, France

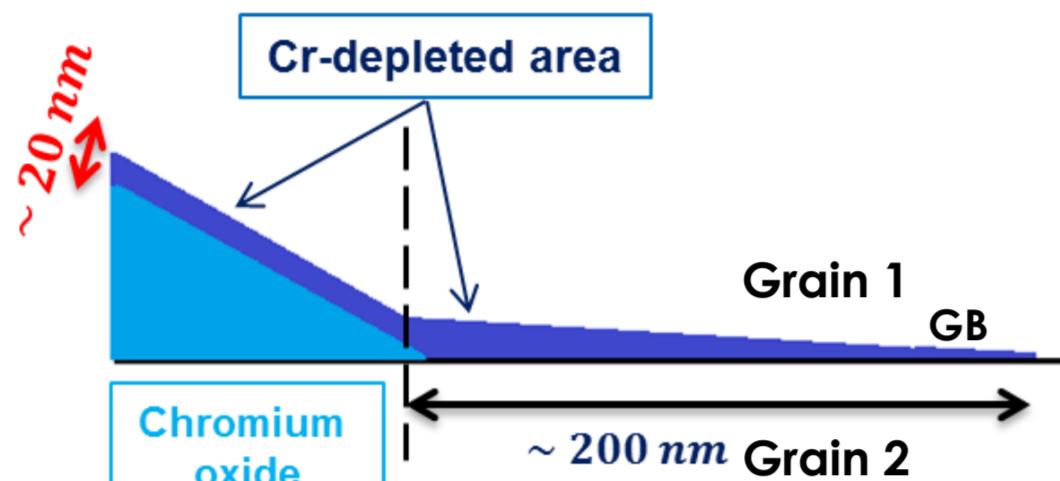
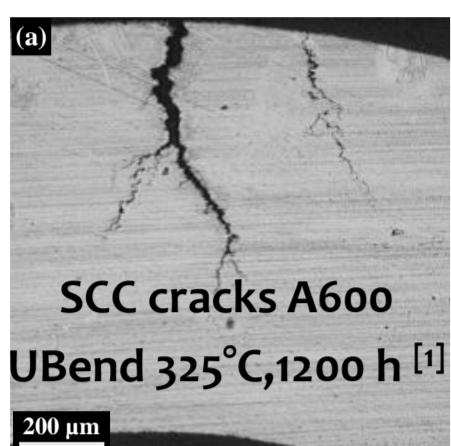
<sup>3</sup> : Laboratoire GEMaC, UMR 8635 CNRS – Université de Versailles - 45 Avenue Des Etats-Unis, 78035 Versailles Cedex, France

## CONTEXT AND OBJECTIVES

### Industrial context

#### Stress Corrosion Cracking (SCC)

Steam generator tubes : Nickel Base Alloy A600-> Ni-15Cr-Fe



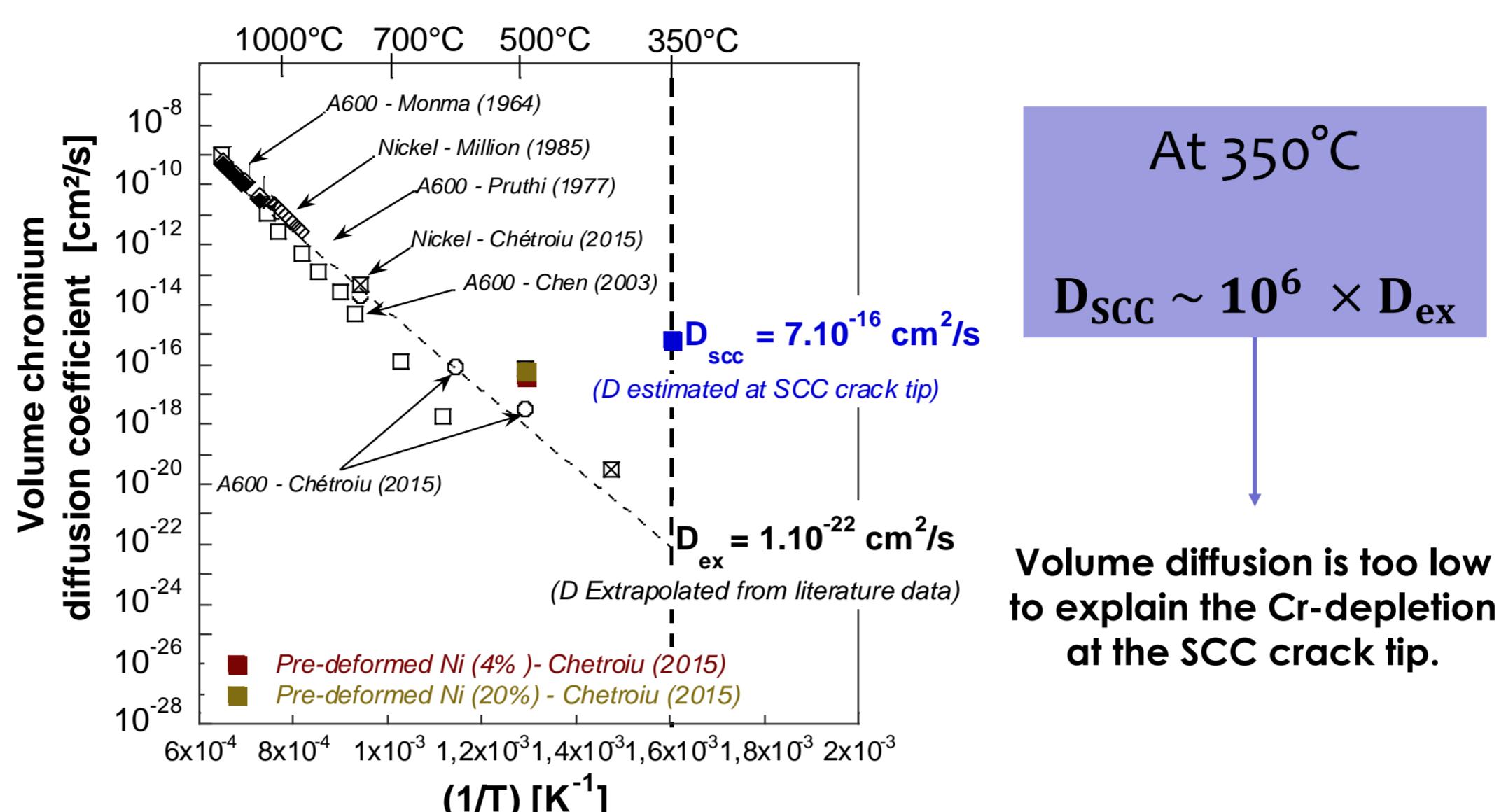
SCC crack tip [1] :  
Oxidation and/or Cr-depleted area leads to grain boundary embrittlement. The crack propagates until the end of the depleted zone.

~ 20 nm

Grain 1 GB  
Chromium oxide  
~ 200 nm Grain 2

### Scientific context

#### Chromium diffusion : a key step of the SCC mechanism



### Objectives

- To determine which mechanism explain the formation of the chromium-depleted area in the vicinity of grain boundary at low temperatures (350°C), in order to understand the propagation mechanism of the SCC crack.

### Assumptions

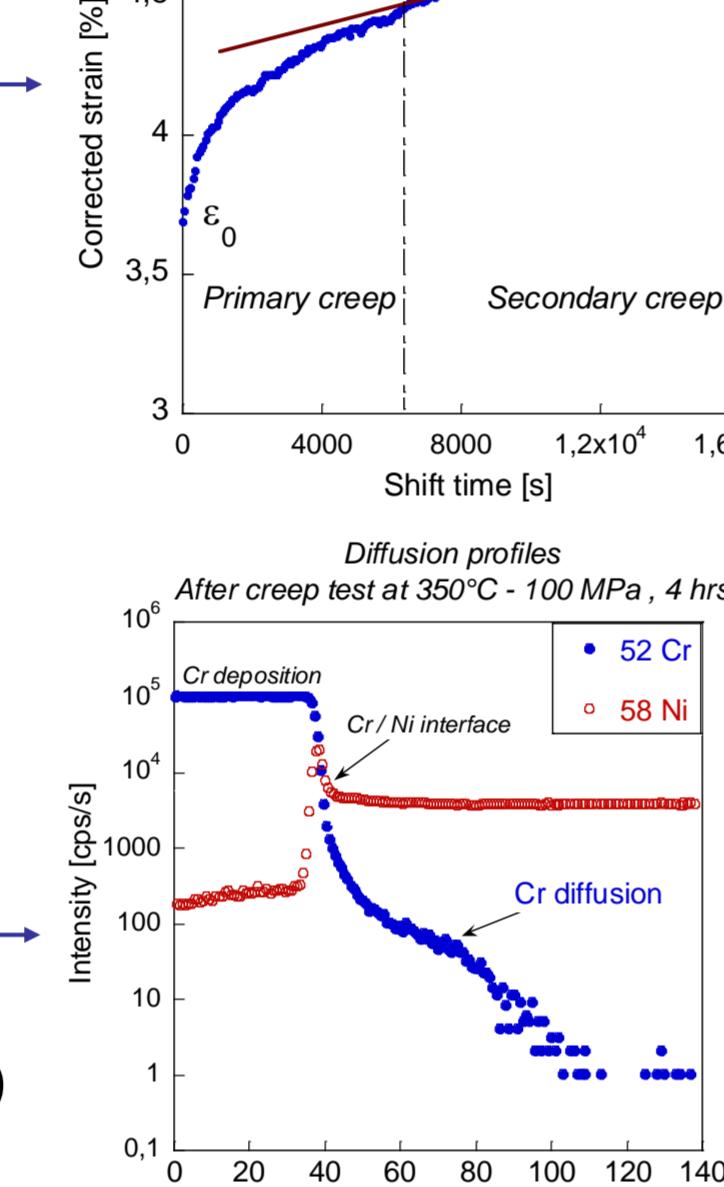
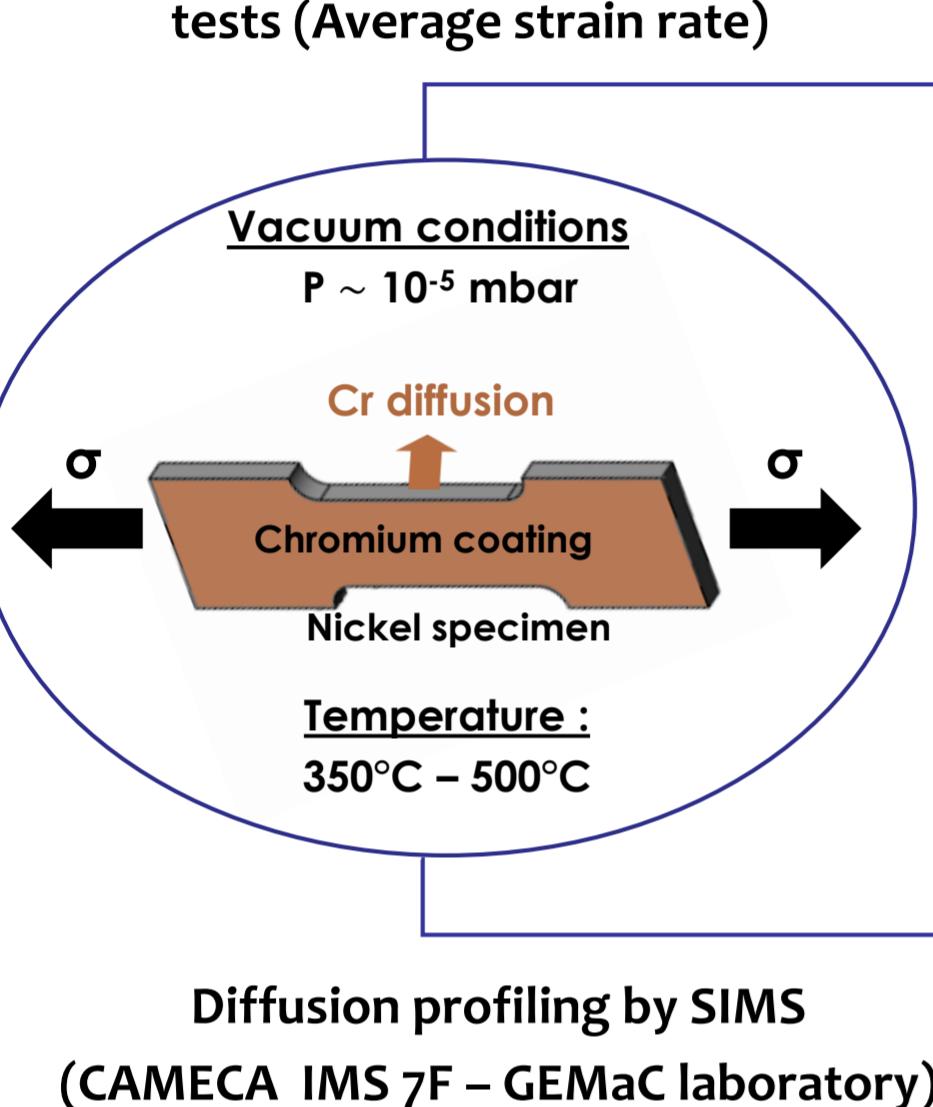
- Plasticity-enhanced diffusion
- Diffusion induced grain boundary migration (DIGM).

## PLASTICITY ENHANCED DIFFUSION OF CHROMIUM IN PURE NICKEL

### Experimental approach

#### Both diffusion and plastic deformation

Mechanical measurements during creep tests (Average strain rate)



#### strain-enhanced diffusion

$$(\varepsilon \neq 0 \text{ and } \dot{\varepsilon} \neq 0) [2-3]$$

$$\frac{\partial C}{\partial t} = D_p \frac{\partial C}{\partial x^2} - \dot{\varepsilon} x \frac{\partial C}{\partial x}$$

$$\frac{\partial \ln C}{\partial x^2} = - \frac{1}{4 D_p t} \left[ \frac{2\varepsilon}{\exp(2\varepsilon) - 1} \right]$$

Diffusion profiles

After creep test at 350°C - 100 MPa, 4 hrs

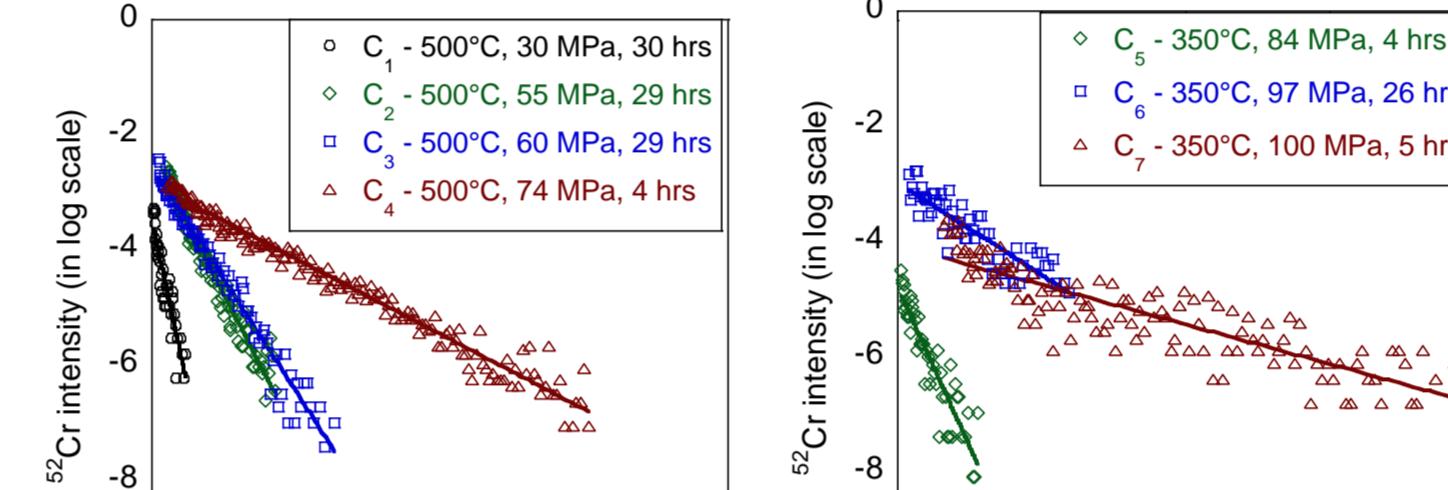
• 52 Cr

○ 58 Ni

Intensity [cps]

Depth [nm]

### Results



Mechanical state	Diffusion	Final strain ε [%]	Average strain rate [10^-7 s^-1]	D [cm/s]	Enhanced diffusion $D_p/D_v$
Without plasticity	500°C, 30 hrs	-	-	$(3.0 \pm 1) \cdot 10^{-17}$	1.0
Below the yield stress	500°C, 30 hrs	2.5	4.7	$(4.6 \pm 1) \cdot 10^{-17}$	1.5
	500°C, 29 hrs	5.0	5.2 ± 0.7	$(7.6 \pm 1) \cdot 10^{-17}$	2.5
	500°C, 29 hrs	5.4	5.7 ± 0.1	$(8.3 \pm 1) \cdot 10^{-17}$	2.8
Plasticity-enhanced diffusion	500°C, 4 hrs	7.5	46 ± 13	$(2.2 \pm 1) \cdot 10^{-15}$	73
	350°C, 4 hrs	1.4	1.9	$(1.7 \pm 1) \cdot 10^{-16}$	$1 \times 10^6$
	350°C, 26 hrs	5.9	3.1 ± 2.0	$(2.0 \pm 1) \cdot 10^{-16}$	$2 \times 10^6$
	350°C, 5 hrs	4.8	7.0 ± 3.6	$(3.9 \pm 1) \cdot 10^{-16}$	$4 \times 10^6$

### Interpretation

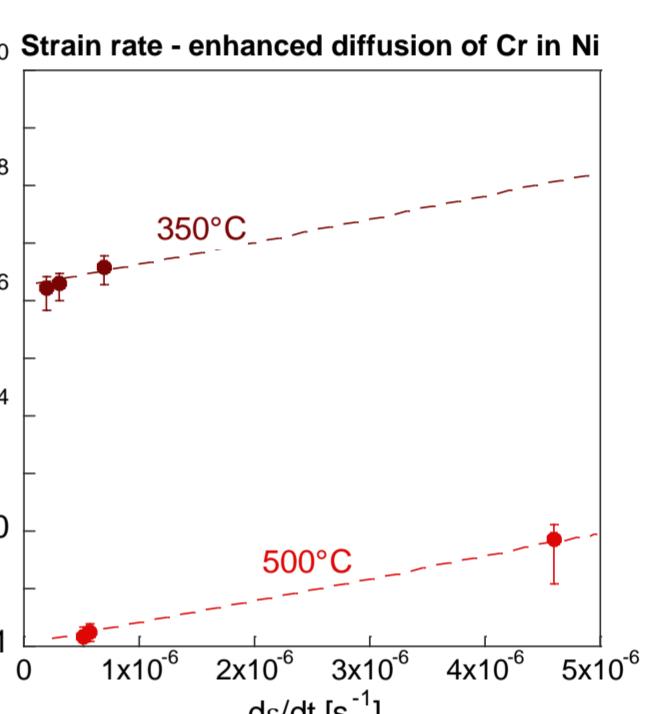
- Diffusion is enhanced by plasticity at 350°C and 500°C
- Diffusion depends on the strain rate and temperature.

$$D_p/D_v = 1 + B(1/T) \dot{\varepsilon}_p$$

Accelerating factor

Condition for plasticity-enhanced diffusion

High strain rate And/or Low temperature



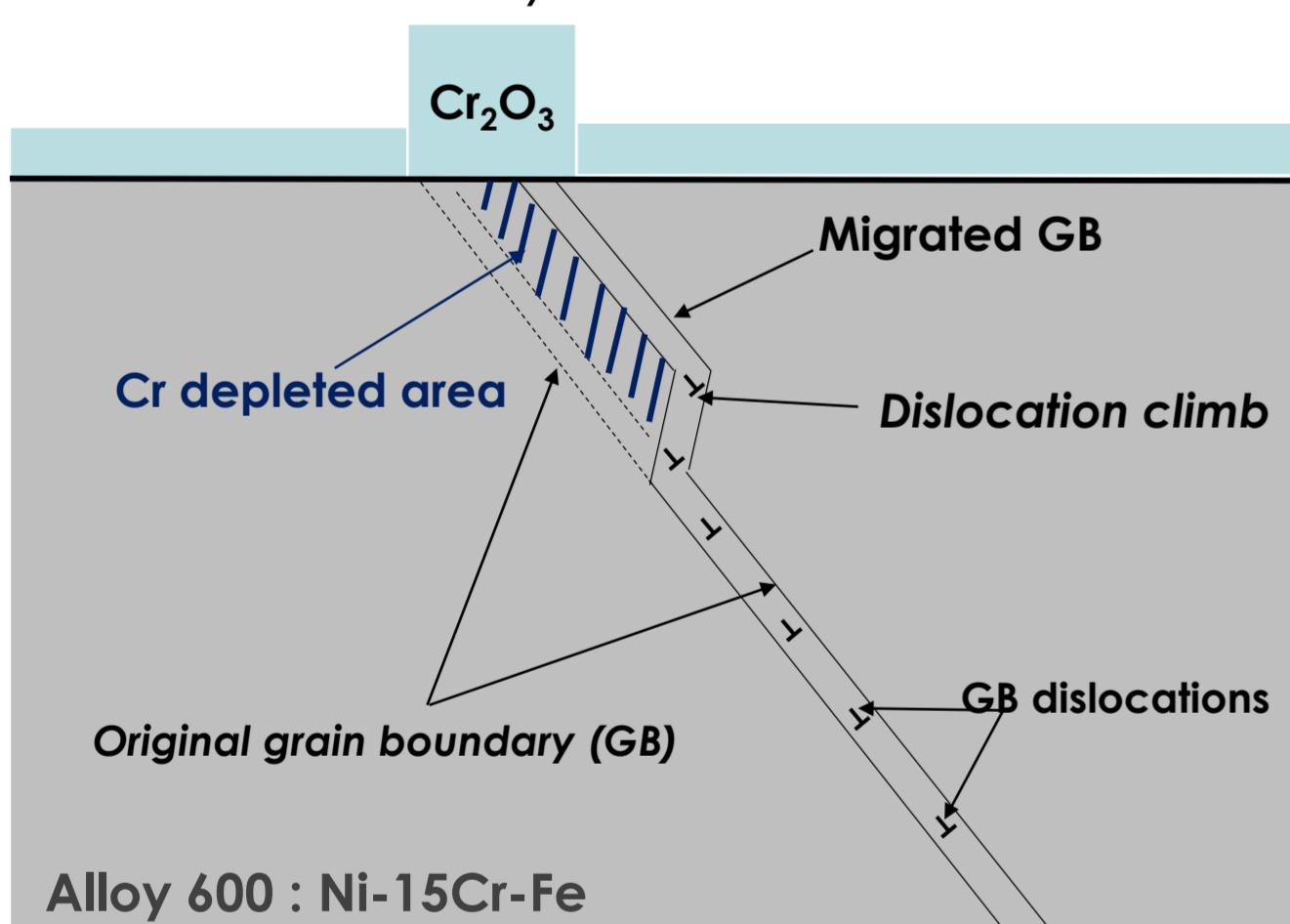
Mechanism : Dislocation-assisted diffusion along moving short-circuiting.

Consistent with the Hart model assuming that the dislocations pipes move and facilitate the diffusion.

## DIFFUSION INDUCED GRAIN BOUNDARY MIGRATION (DIGM)

### DIGM Mechanism

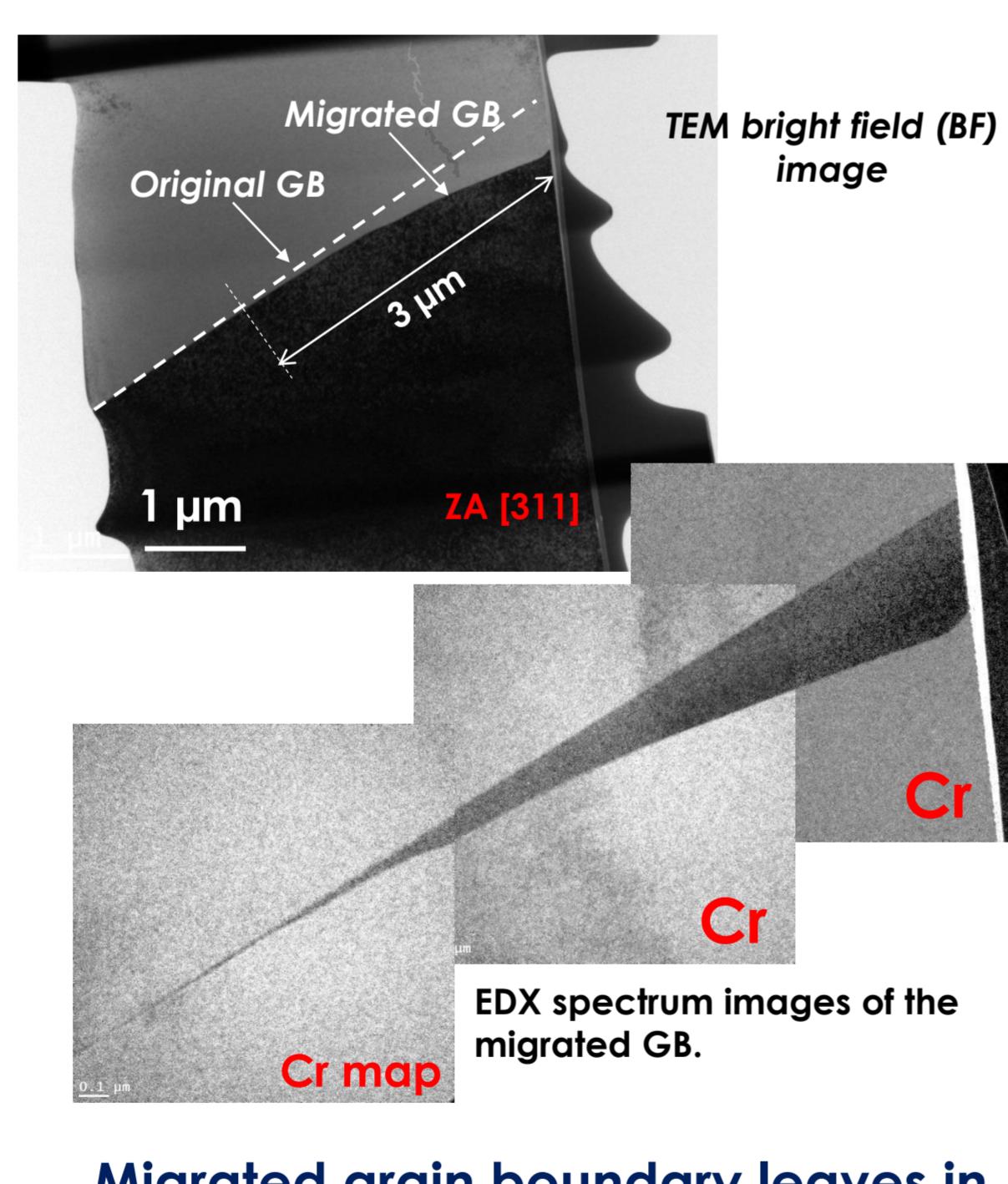
Grain boundary dislocation climb [4]



- Steps of mechanism :
1. Intergranular diffusion
  2. Kirkendall effect (vacancies flow) along the GB
  3. Lead to the self-sustaining climb of GB dislocations
  4. Steps of climb cause the GB migration.

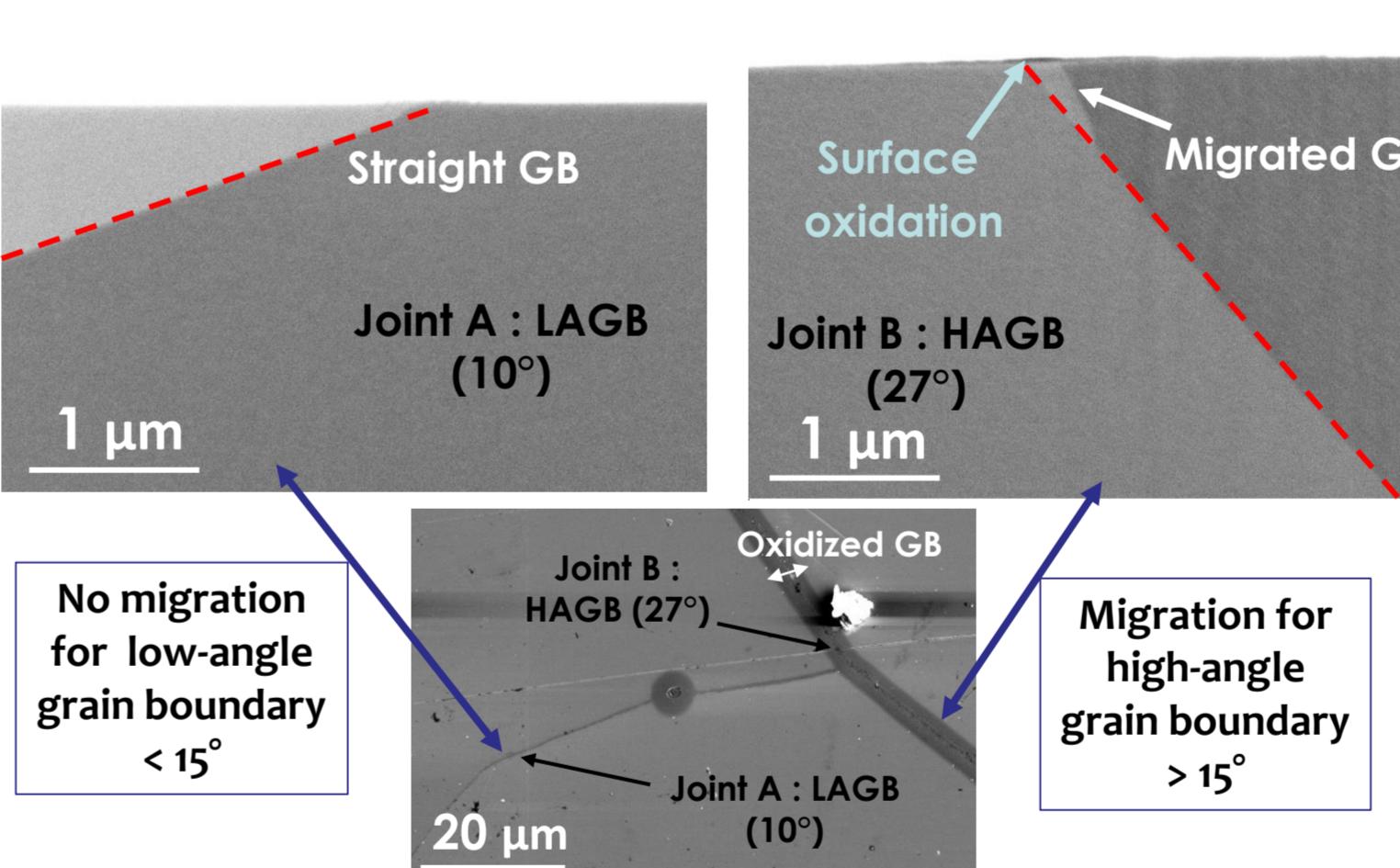
### DIGM characterizations

Heat treatments at 360°C and 500°C on A600 (under vacuum).



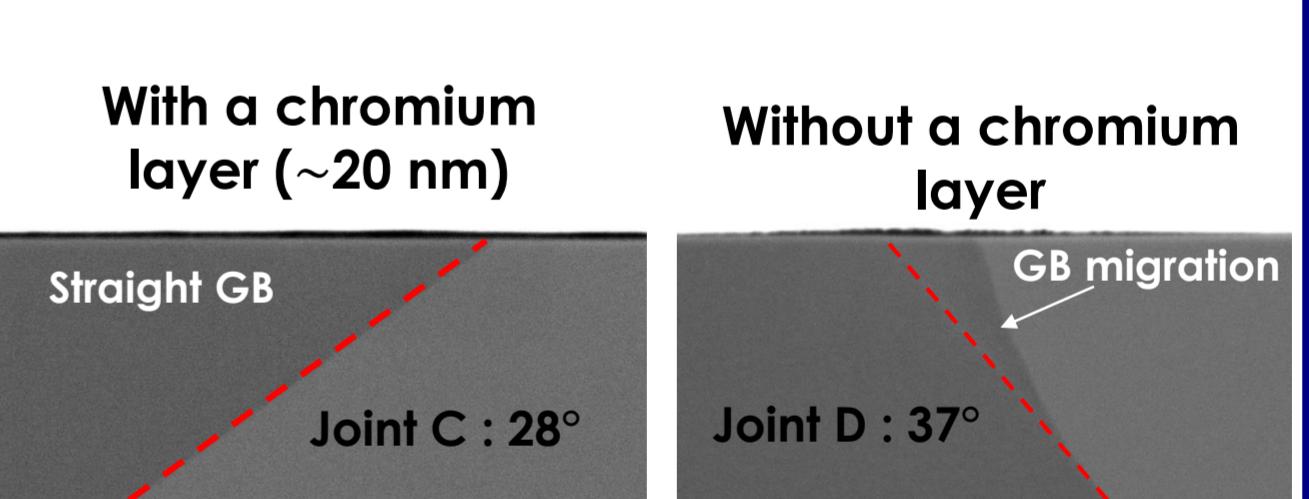
### Effect of grain boundary misorientation on DIGM

Results obtained on A600 sample after 30 hrs at 500°C, in vacuum ( $P = 10^{-6}$  mbar)



### DIGM : a result of oxidation process

Results obtained on A600 sample after heating at 500°C, 30 hrs in vacuum.



GB migration is possible only if the oxidation contribute to the intergranular diffusion mechanism.

## CONCLUSION

### First assumption

Enhanced diffusion by plastic deformation

$$\text{At } 350^\circ\text{C} : D_p \sim D_{SCC}$$

$$\text{Calculated Cr-depleted area} \Leftrightarrow 30 \text{ nm}$$

A dynamic strain rate could accelerate the chromium diffusion at the SCC crack tip and could explain the formation of the Cr-depleted area.

### Second assumption

Diffusion induced grain boundary migration

$$\text{At } 500^\circ\text{C} :$$

$$\text{Measured Cr-depleted area} \Leftrightarrow 600 \text{ nm}$$

Without any external stresses, GB migration could explain the remarkable extent of Cr depletion on A600 at low temperatures (PWR primary water)

## PERSPECTIVES

- To perform the same tests (diffusion during creep) on Alloy 600
- To model the mechanism of dislocation-assisted diffusion
- To highlight the DIGM phenomenon in PWR conditions.

## References

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