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## Chromium depletion in relation with oxidized grain boundaries at the SCC crack tip

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DE LA RECHERCHE À L'INDUSTRIE

**cea den**

# CHROMIUM DEPLETION IN RELATION WITH OXIDIZED GRAIN BOUNDARIES AT THE SCC CRACK TIP

JOSIANE NGUEJIO <sup>(1,2)</sup>

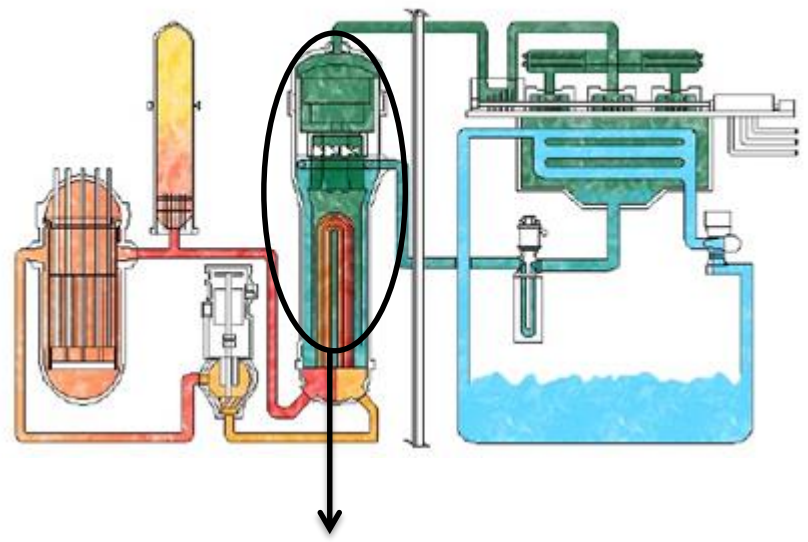
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CATHERINE GUERRE <sup>(2)</sup> , FRANÇOIS JOMARD <sup>(3)</sup>

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- (2) : MINES ParisTech, PSL Research University, MAT- Centre des matériaux, CNRS UMR 7633, BP 87 91003 Evry, France
- (3) : Laboratoire GEMaC, UMR 8635 CNRS - Université De Versailles

STRESS CORROSION CRACKING (SCC) OF A600 (Ni-15Cr-Fe) IN PWR

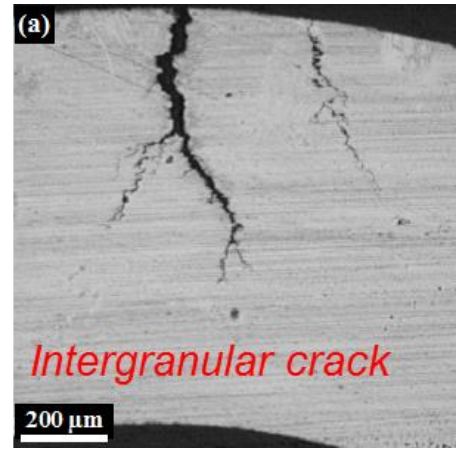
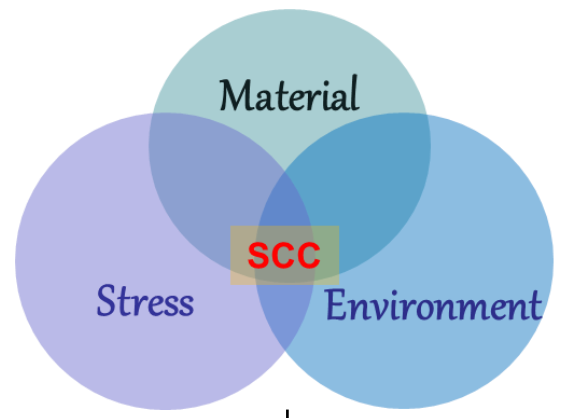
Pressurized Water Reactor (PWR)



Steam generator tubes : Nickel Base Alloy  
A 600-> Ni-15Cr-Fe

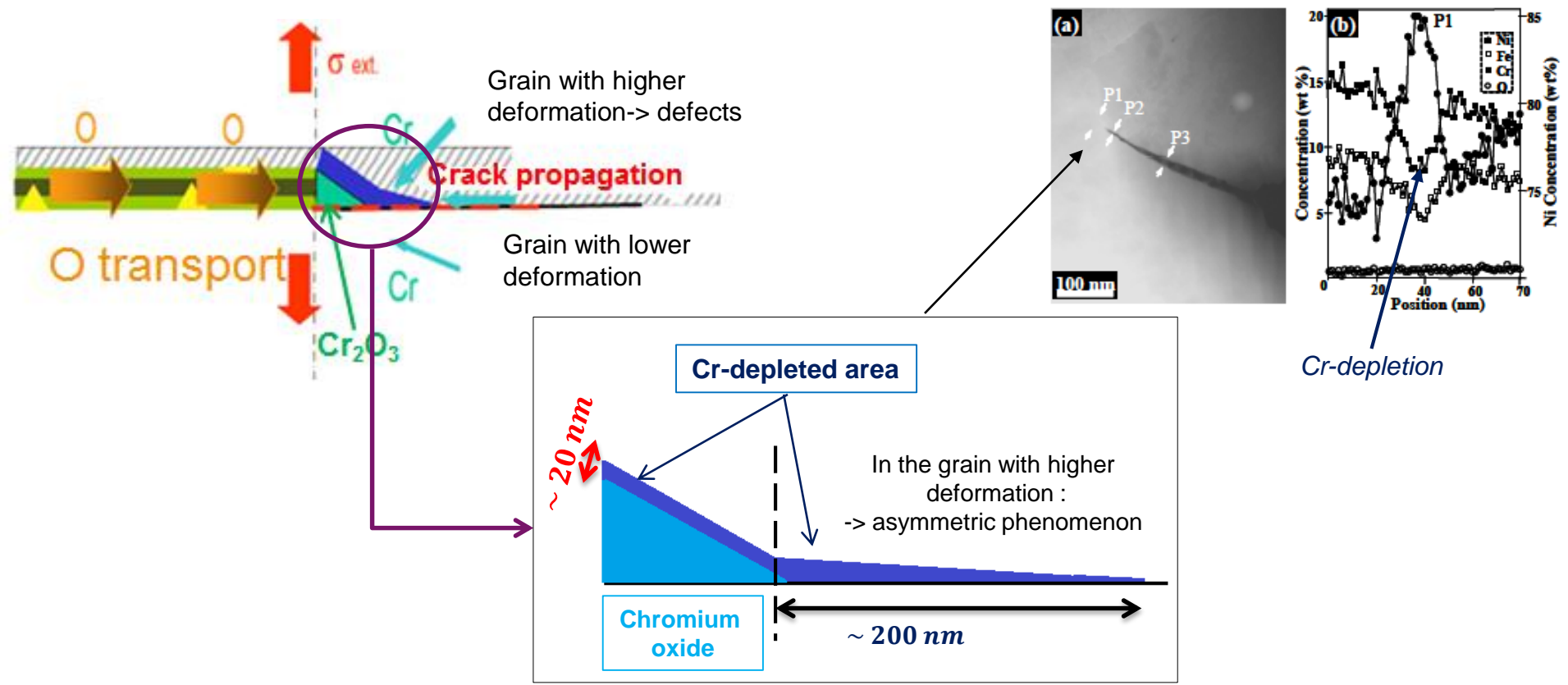
Primary water conditions

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



Understanding this mechanism is a key issue for the extension of PWR operation time  
> 30 – 40 years

CRACK PROPAGATION MODEL [1]



SCC propagation mechanism proposed by authors [1]

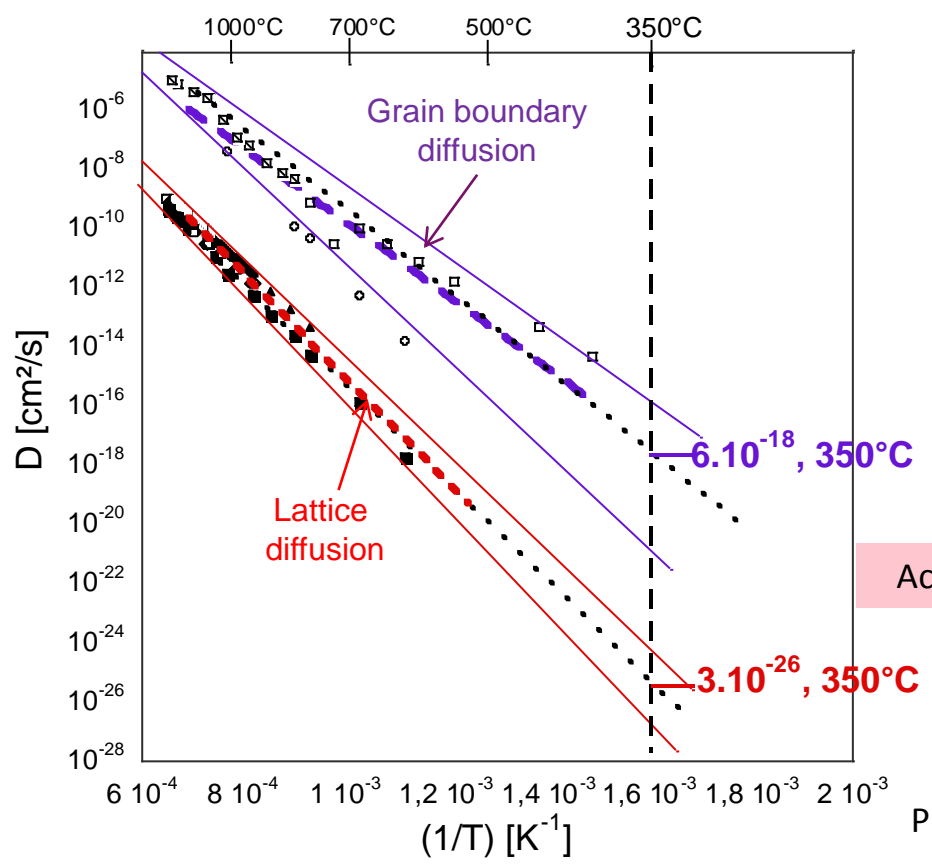
1. Chromium oxidation at the crack tip : weakens the grain boundary (GB)
2. Chromium depleted area of 20 nm in the grain and 200 nm along the GB
3. Chromium depletion is observed only in one side of GB
4. Assumptions :
  - Strain may be different in the vicinity of the grain boundary
  - Chromium diffusion is **the rate limiting step** of the SCC mechanism.

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

CHROMIUM DIFFUSION : A KEY STEP OF THE SCC MECHANISM

**Aim** : determine which mechanism could explain the formation of Cr-depletion in one grain ahead of the crack tip ?

Study the lattice and grain boundary chromium diffusion at 350°C



$y = 2\sqrt{D}t$   
 -Grain boundary diffusion at 350°C  
 $\Rightarrow t = 3 \text{ days}$   
 -Lattice diffusion at 350°C  
 $\Rightarrow t = 1000 \text{ years}$

Diffusion time too high (compared to 6000 seconds [1])  
 Not sufficient...

Accelerating factor for chromium diffusion at the SCC crack tip ?

Assumption :

Plasticity at the crack tip could enhance chromium diffusion.

[1] D.D. Pruthi et al. Journal of Nuclear Materials 64 (1977) 206-210  
 [2] T.F. Chen et al. Materials Transactions 44 (2003) 40-46  
 [3] K. Monma, et al. The Japan Institute of Metals and Materials 28 (1964) 188-192  
 [4] B. Million, et al. Materials Science and Engineering 72 (1985) 85-100  
 [5] Moulin P., et al. Acta Metallurgica 77 (1979) : 1430-43.

EXPERIMENTAL APPROACH

Steps :

**1. Materials**

- Pure nickel - Single crystal - crystallographic orientation <101>

**2. Chromium deposition**

- Sample polishing
- Chromium evaporation under vacuum -> 20 nm layer (powder <sup>52</sup>Cr - 99,6% purity)

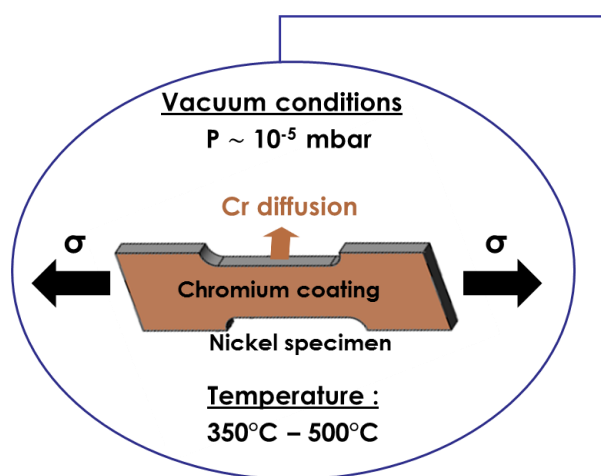
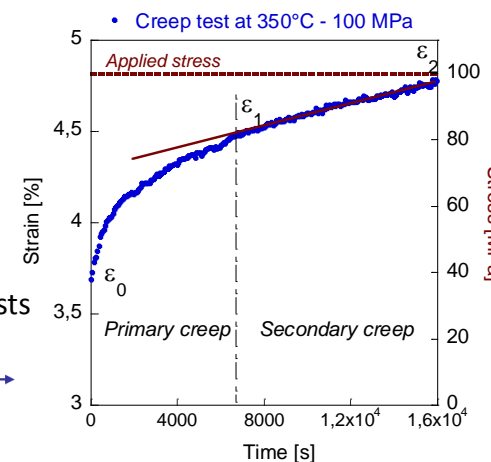
**3. Creep tests under secondary vacuum**

- Both diffusion and plastic deformation

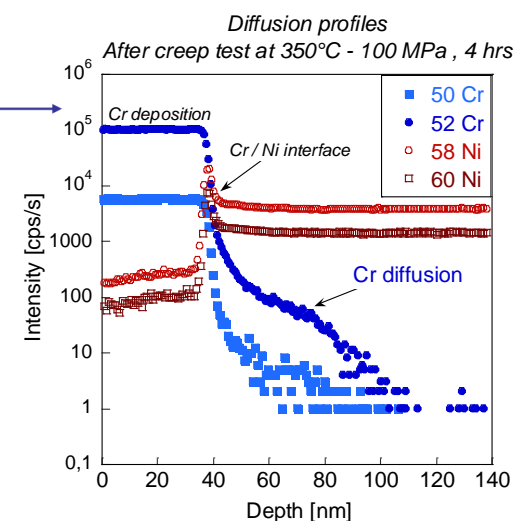
**4. Diffusion coefficients**

- Measured by Secondary Ion Mass Spectrometry (SIMS)

Mechanical measurements during creep tests  
(Average strain rate)



Diffusion profiling by SIMS  
(CAMECA IMS 7F – GEMaC laboratory)

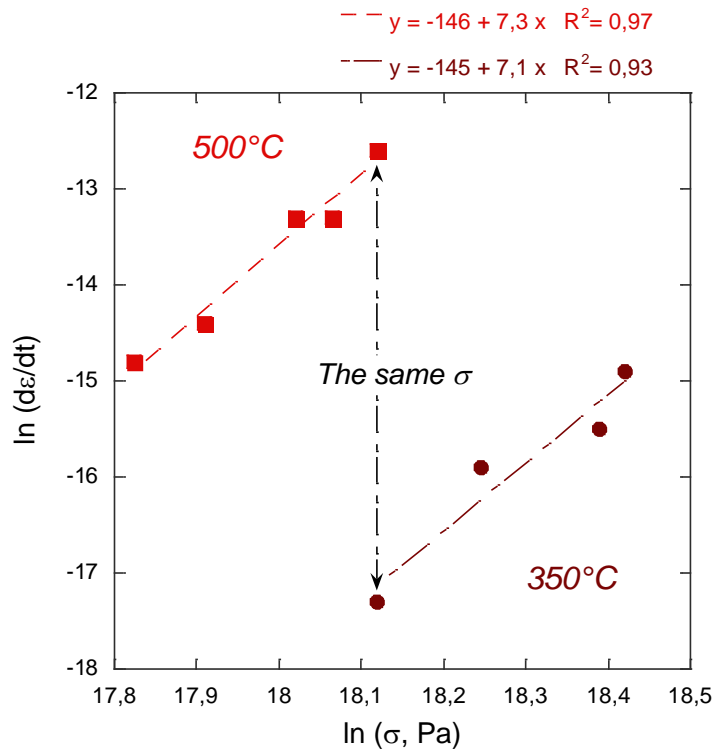


MECHANICAL RESULTS : CREEP TESTS ON PURE NICKEL

Loading at 500°C : 55-74 MPa (*yield stress 48 MPa*)

Loading at 350°C : 74-100 MPa (*yield stress 60 MPa*)

$$\text{Creep law : } \dot{\epsilon} = C. \exp\left(-\frac{\Delta H_{\text{creep}}}{RT}\right) \cdot \sigma^n$$



Power factor  $n \sim 7$   
Garofalo [1] :  $n = 5 - 6$

Mechanical results are in good agreement with literature.

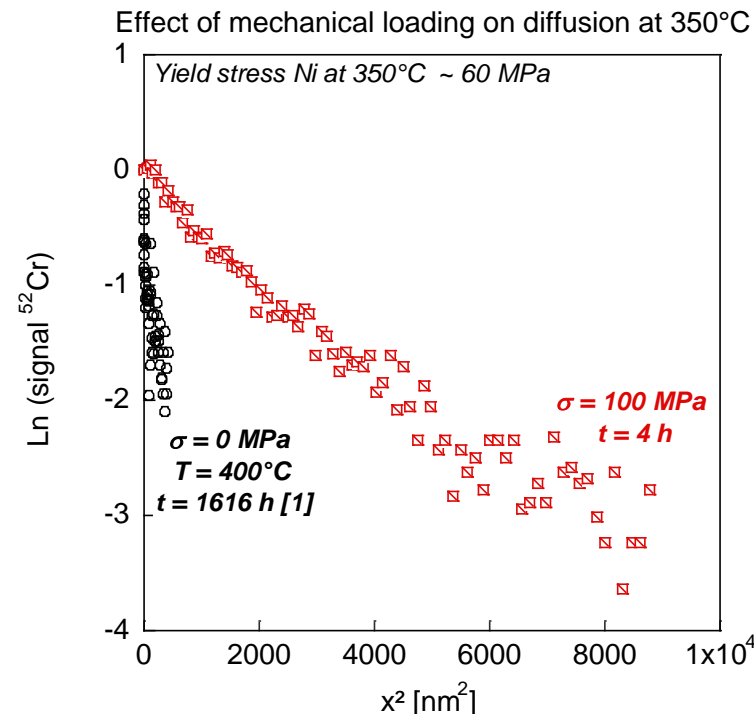
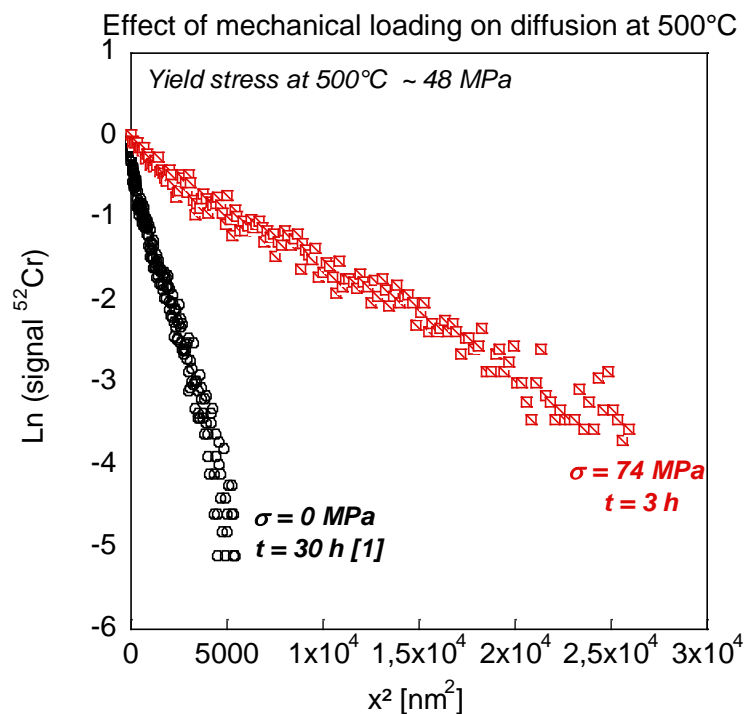
For a given  $\sigma$  :

$$\Delta H_{\text{creep}} = -R \frac{\delta \ln \epsilon}{\delta(1/T)}$$

$\Delta H_{\text{creep}} = 125 \text{ kJ/mol}$   
For  $T$  between  $350^\circ\text{C} - 500^\circ\text{C}$

Creep mechanism : dislocation glide (low  $T$  and high  $\sigma$ )

CHROMIUM DIFFUSION PROFILES OBTAINED BY SIMS



1. Diffusion enhancement is observed, when the applied load is over the yield stress  
 ⇔ Accelerating effect of plasticity on diffusion at 500°C and 350°C
2. Calculation of apparent diffusion coefficients by the slope of diffusion profiles

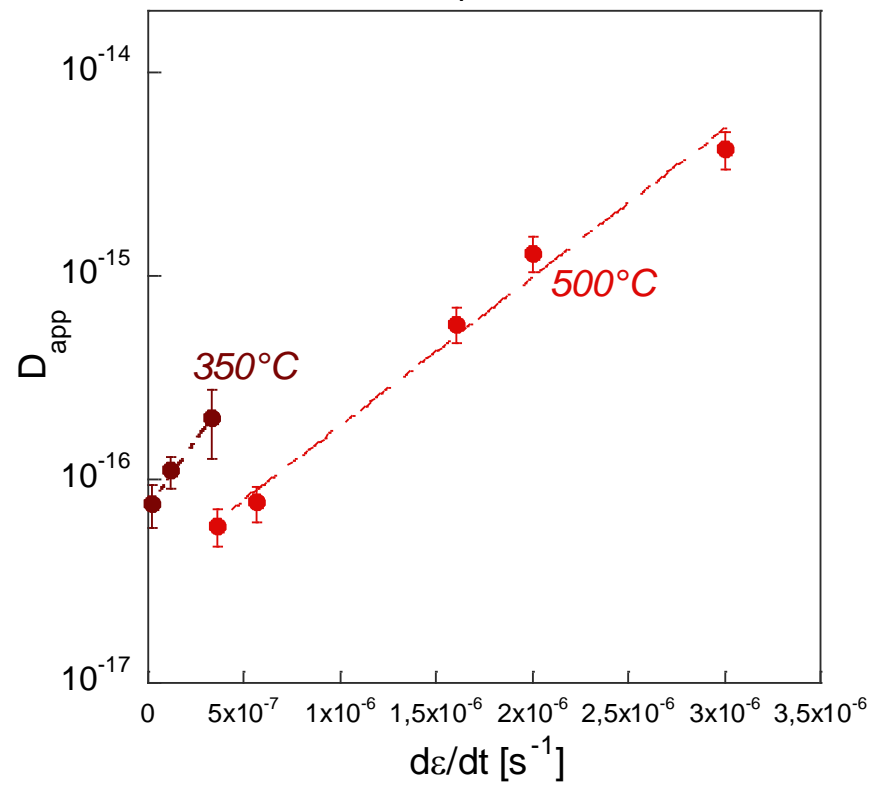
$$\frac{\partial^2 \ln C}{\partial x^2} = -\frac{1}{4 D_{app} t} \quad \text{Thin film solution of 2}^{nd} \text{ Fick law}$$

[1] Chetroui, B. "Stress corrosion cracking of Alloy 600 in primary water of PWR: study of chromium diffusion" Thesis MINES ParisTech 2015



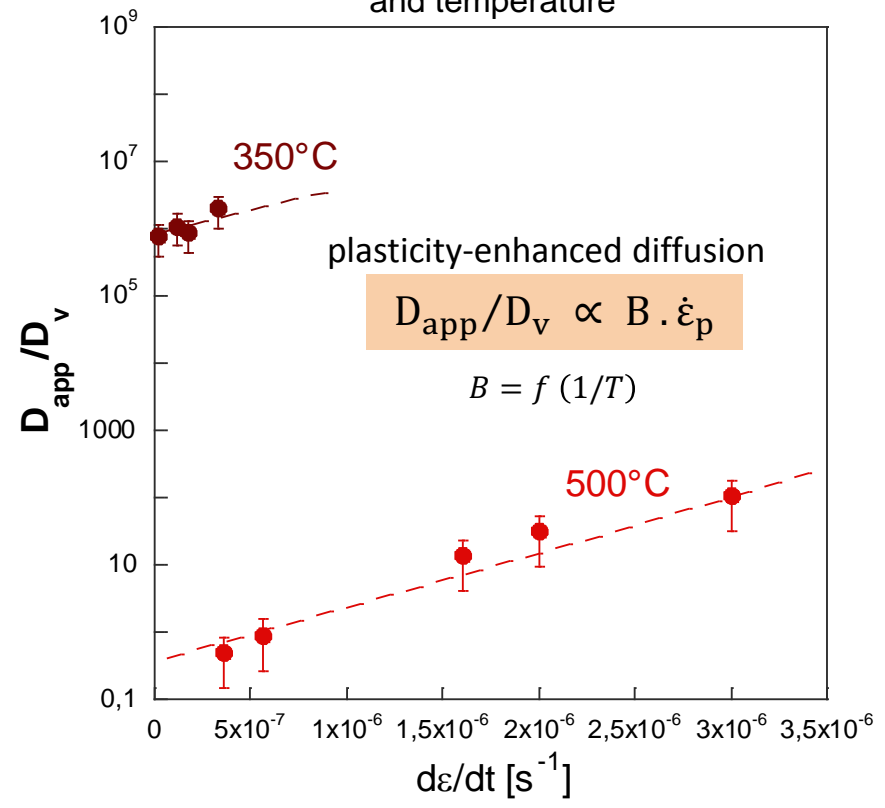
APPARENT DIFFUSION COEFFICIENTS AND PLASTICITY

Diffusion under plastic deformation



$D_{app}$  ↑ with  $\dot{\epsilon}$

Enhanced diffusion factor in function of strain rate and temperature



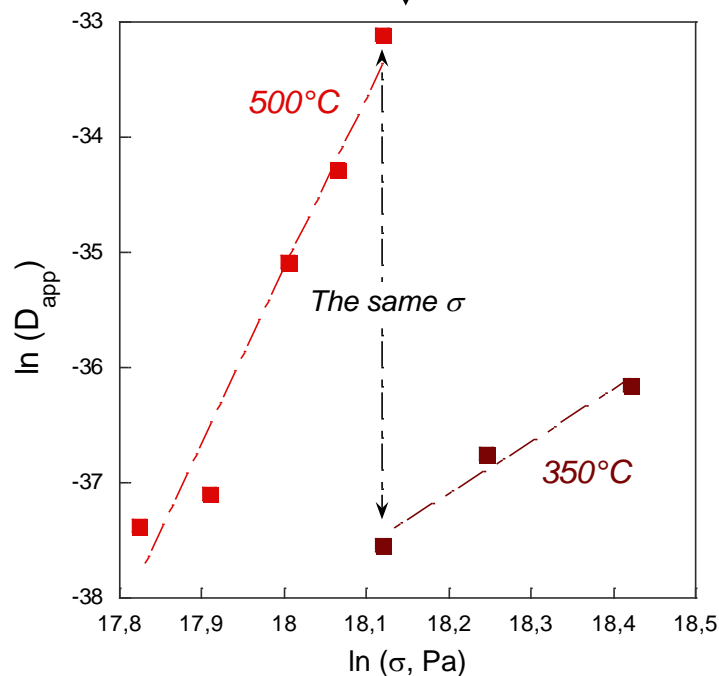
The enhanced diffusion factor

$$\left(\frac{D_{app}}{D_v}\right)_{350^\circ C} \gg \left(\frac{D_{app}}{D_v}\right)_{500^\circ C}$$

ACTIVATION ENERGY OF CHROMIUM DIFFUSION ENHANCED BY PLASTICITY

$D_{\dot{\epsilon}} = f[\dot{\epsilon}(T, \sigma)]$  then...  $D_{\dot{\epsilon}}$   
depend on temperature and **stress**

$$\text{For a given } \sigma : \Delta H_{\dot{\epsilon}} = -R \frac{\delta \ln D_{\dot{\epsilon}}}{\delta (1/T)}$$



The activation energy of chromium diffusion enhanced by plasticity is :

$$\Delta H_{\dot{\epsilon}} = 115 \text{ kJ/mol}$$

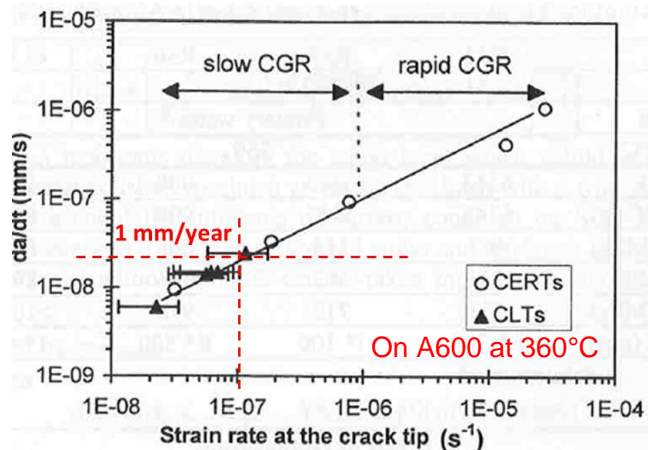
$$(\Delta H_{\text{lattice}} = 232 \text{ kJ/mol [1]})$$

This value is lower than activation energy of lattice diffusion

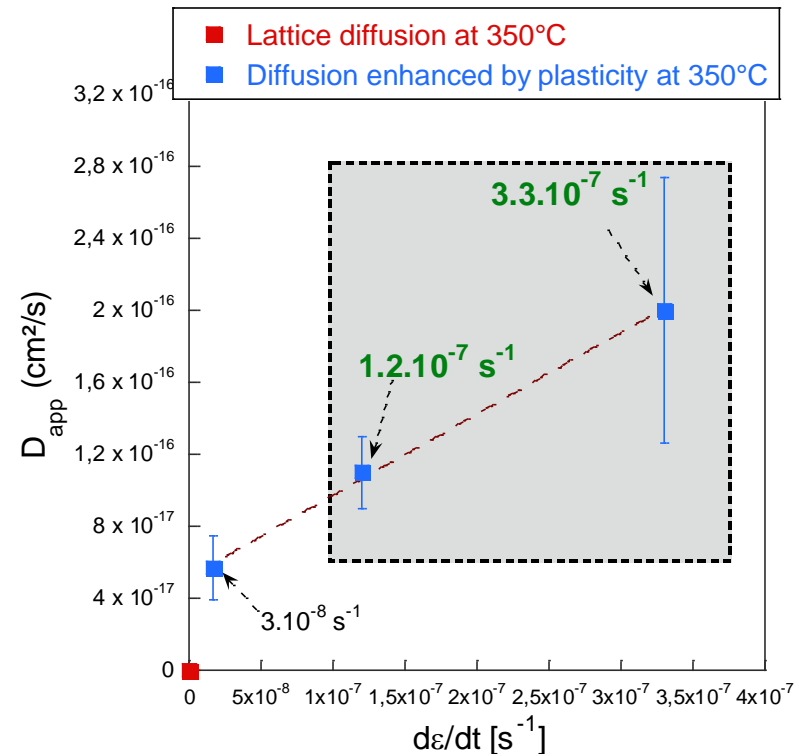
What about diffusion enhanced by the plasticity in front of the SCC crack tip ?

## PLASTICITY AT THE SCC CRACK TIP

Literature :  $\dot{\epsilon}_{ct} \sim 1.10^{-7} \text{ s}^{-1}$



Correlation between crack propagation rate and the strain rate at the SCC crack tip (by Le Hong)



The strain rate estimated by the study is in good agreement with the strain rate at the SCC crack tip

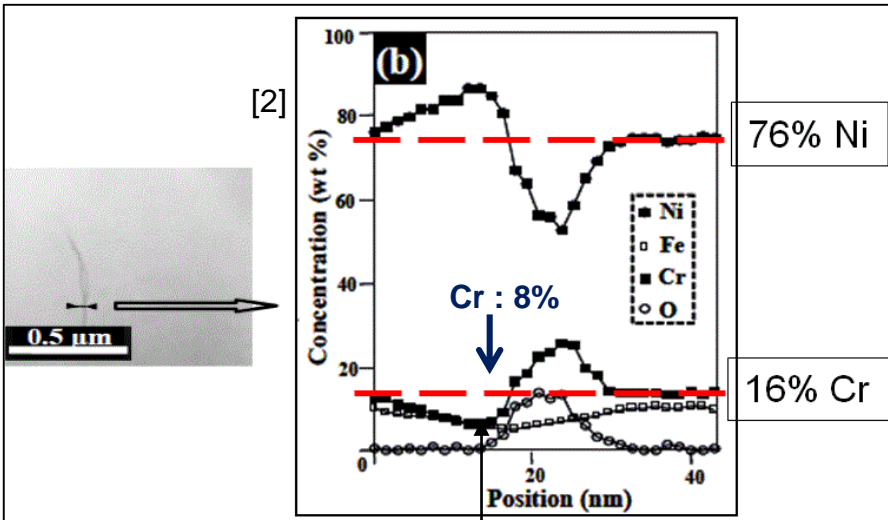
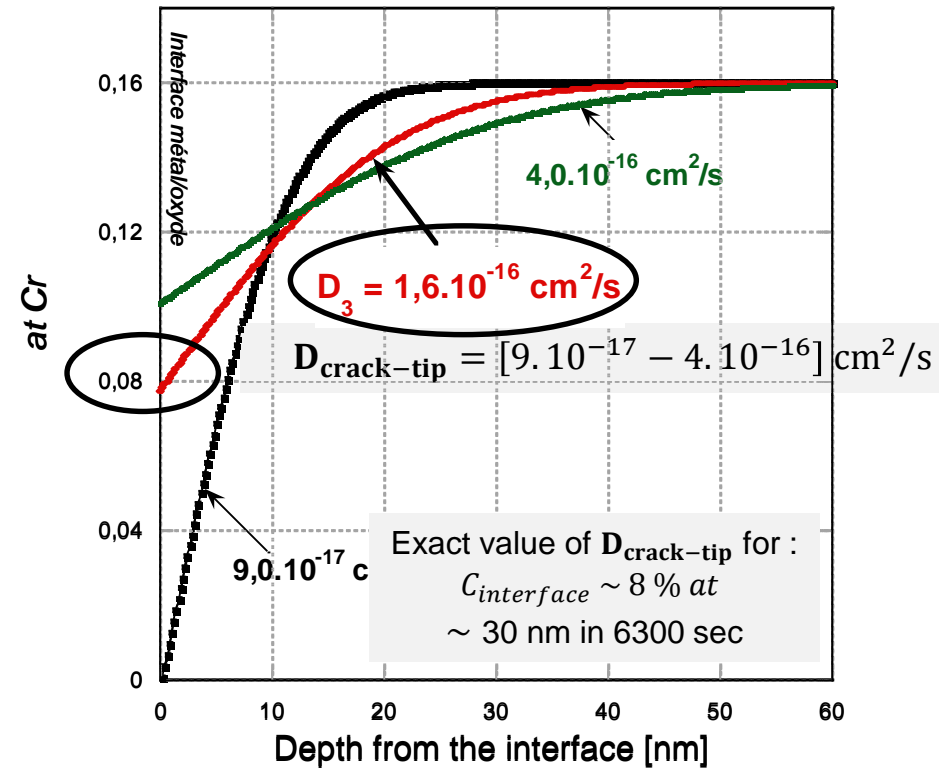
Diffusion coefficient in front of the SCC crack tip is between :

$$D_{\text{crack-tip}} = [9.10^{-17} - 4.10^{-16}] \text{ cm}^2/\text{s}$$

Wagner [1] calculation at 350°C

$$Cr(x,t) = C_i + (C_0 - C_i) \times \left( \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{D_{Cr} \times t}}\right) - \operatorname{erf}\left(\sqrt{\frac{k_c}{2D_{Cr}}}\right)}{\operatorname{erfc}\left(\sqrt{\frac{k_c}{2D_{Cr}}}\right)} \right)$$

Cr depletion in Ni-Cr alloy by Wagner modelling



Literature Cr-depleted area :  
20 nm in 6300 sec

The minimum diffusion coefficient in the interval :

$C_{interface} \sim 0\%$  at  
Cr-depleted area : 20 nm

The maximum diffusion coefficient in the interval

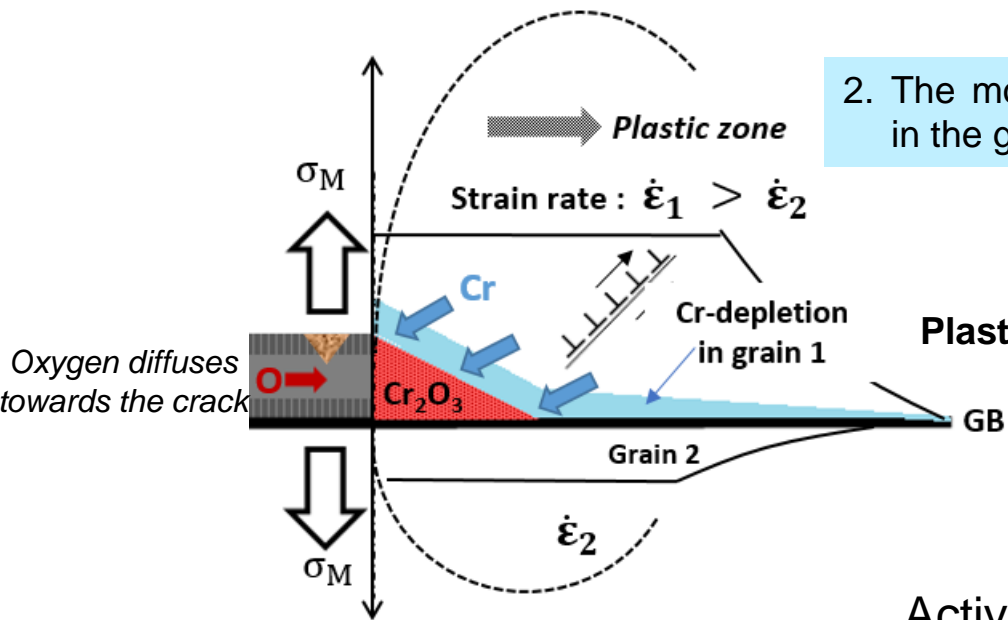
$C_{interface} \sim 10\%$  at  
Cr-depleted area : 50 nm

[1] Wagner, C. (1952). *Journal of the Electrochemical Society* **99**(10): 369-380.

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

## CHROMIUM DIFFUSION AND SCC CRACK PROPAGATION

1. A plastic zone ( $\dot{\epsilon}_{ct} = 1 \cdot 10^{-7} \text{ s}^{-1}$ ), is generated in front of the crack tip.



2. The moving dislocations accelerate the chromium diffusion in the grain 1, with a higher strain rate ( $\dot{\epsilon}_1 > \dot{\epsilon}_2$ )

Plasticity could explain the Cr-depleted area in grain 1

$$\dot{\epsilon} = \rho_m b v$$

Activation energy

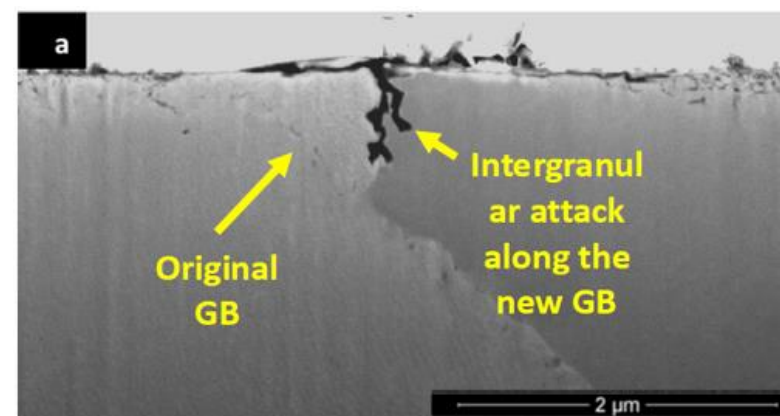
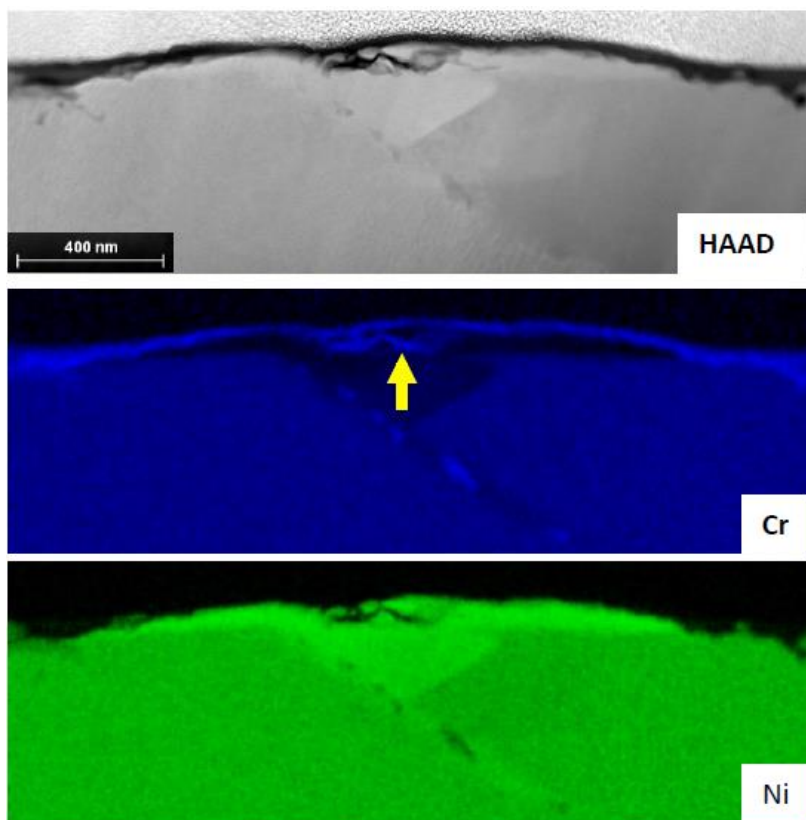
$$\Delta H_{\text{diffusion-plasticity}} = 115 \text{ kJ/mol}$$

~

$$\Delta H_{\text{SCC-propagation}} = 130 \text{ kJ/mol} \quad [2]$$

The SCC crack propagation is linked to the mechanism of the chromium diffusion enhanced by the plasticity.

[1] M. Sennour, P. Laghoutaris, C. Guerre, R. Molins, Journal of Nuclear Materials, 393 (2009) 254-266  
 [2] Lorho, N. (2013). "SCC susceptibility in Alloy 600 with different strain histories." Thèse de l'Université de Manchester.

Cr – DEPLETION ALSO OBSERVED WITHOUT PLASTICITYA600 – exposed in hydrogenated steam at 480°C, 130h*G. Bertali, F. Scenini, M.G. Burke, 16<sup>th</sup> Environmental degradation, (2013).*

The author assumes that the depletion is due to the diffusion induced grain boundary migration phenomenon (DIGM)

2<sup>nd</sup> assumption

Cr-depletion is due to DIGM

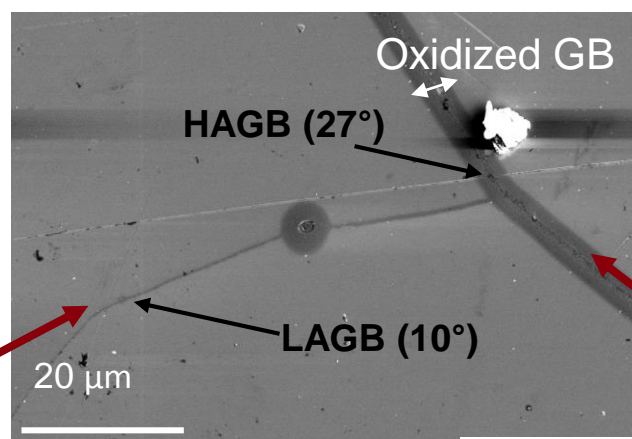
Heat treatments are performed :

on A600 – polycrystal (1 mm)

at 500°C, 30 hrs in vacuum

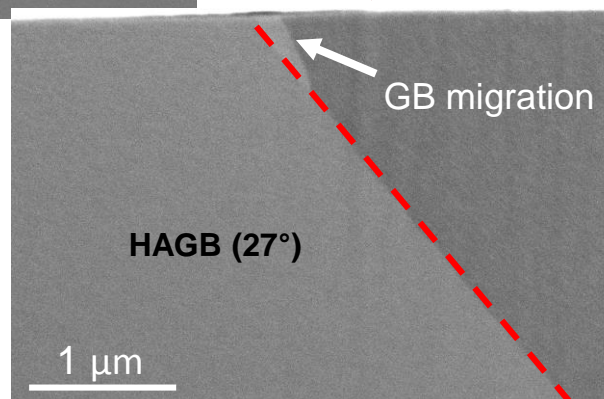
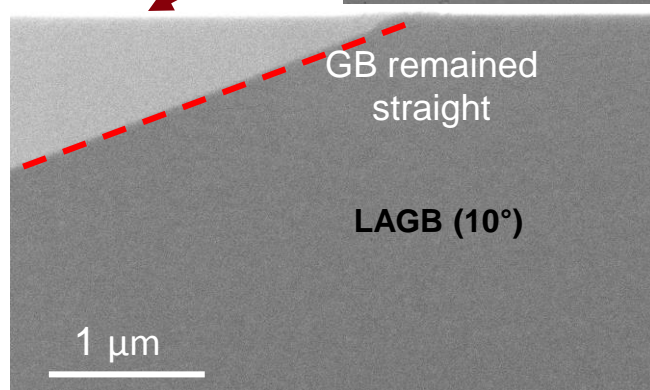
Grain boundary observations : SEM/FIB and TEM in cross-section

### Effect of GB misorientation



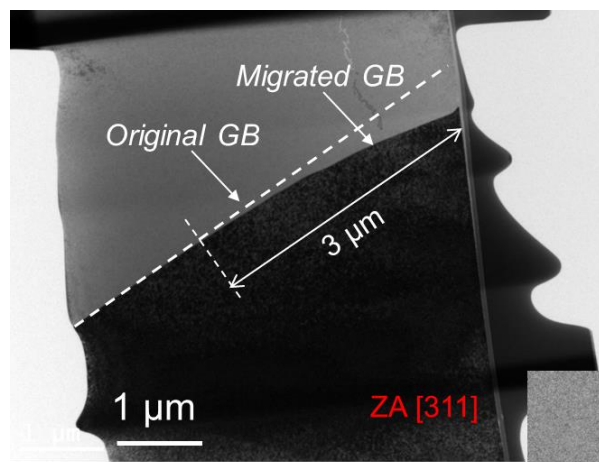
The DIGM is observed only for high angle grain boundaries ( $>15^\circ$ ) [1].

Oxidation is associated with the migration of the GB.

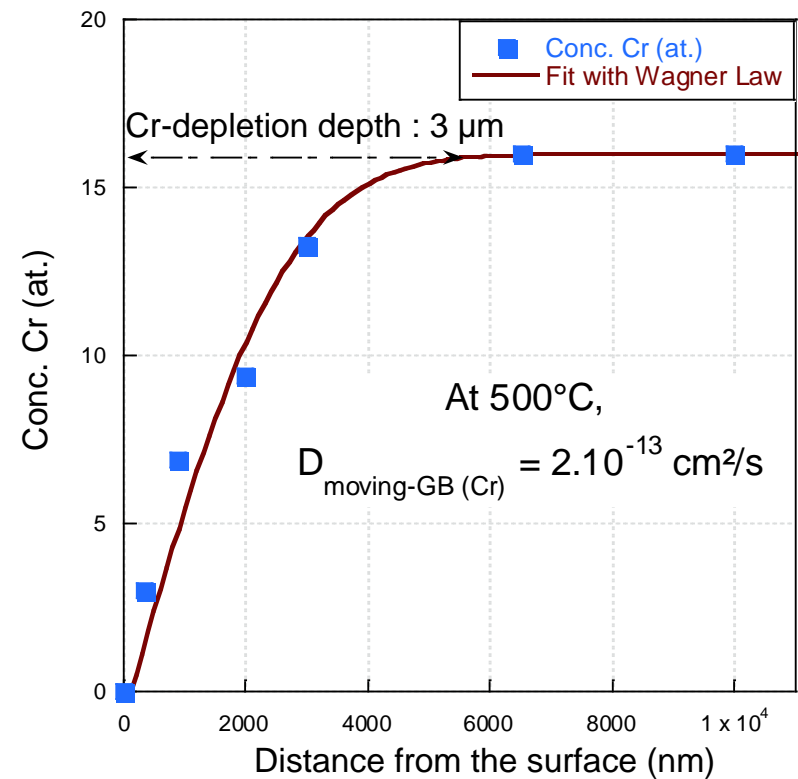
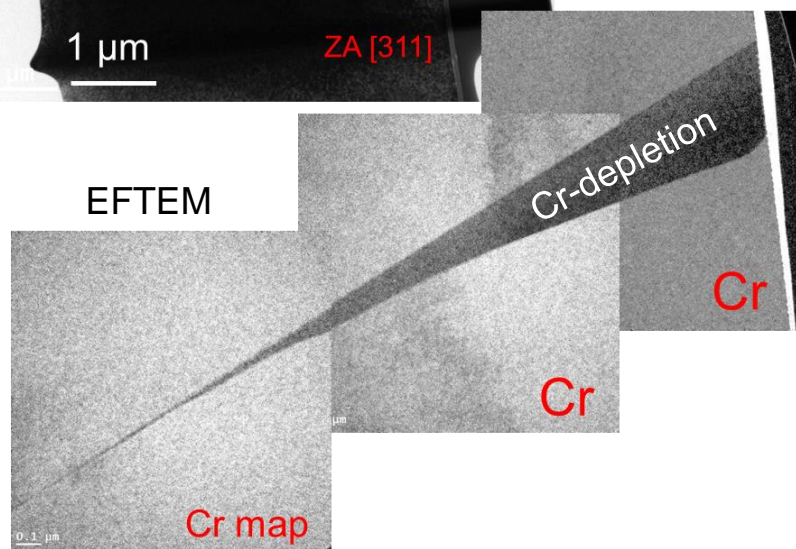


TEM CHARACTERIZATIONS

TEM bright field (BF) image



Migrated grain boundary leaves in its wake a Cr-depleted area.

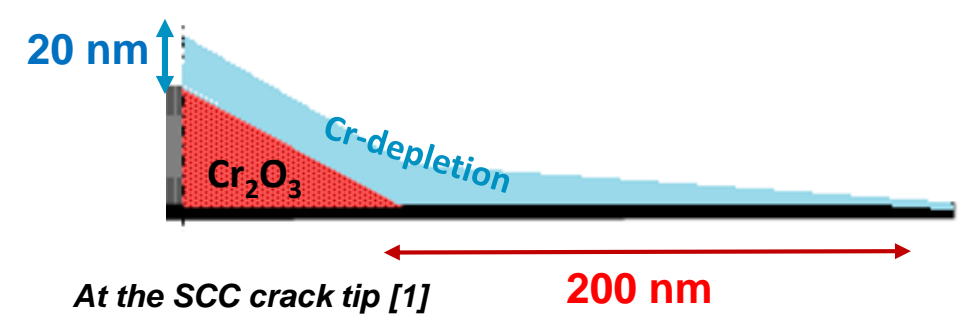
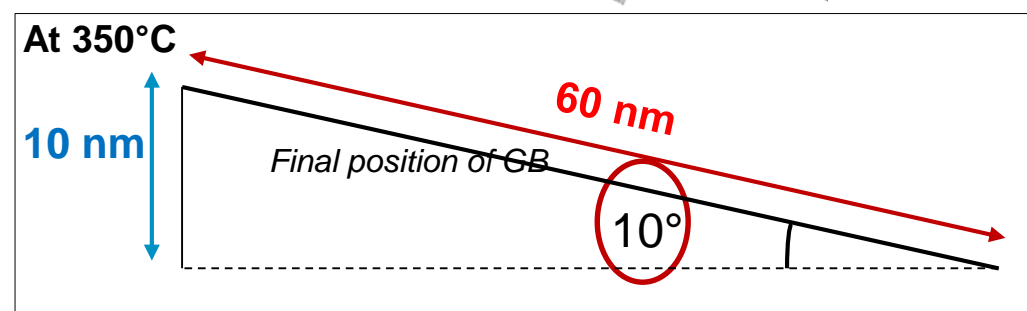
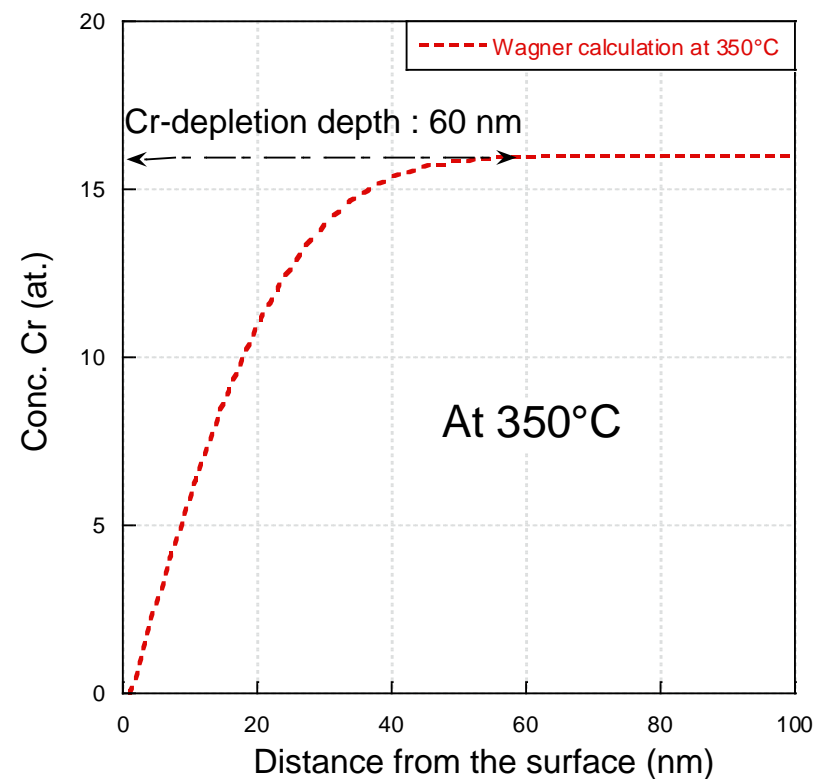
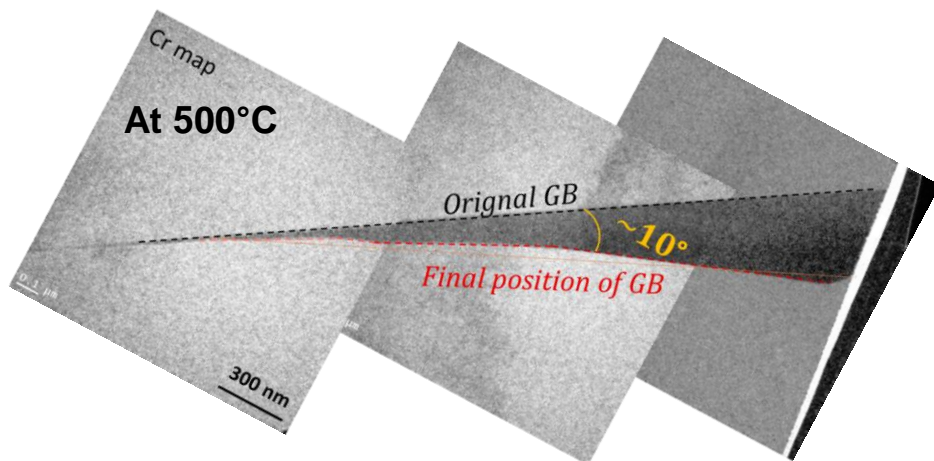


At 500°C,  
 $D_{\text{moving-GB (Cr)}} = 2.10^{-13} \text{ cm}^2/\text{s}$   
 $D_{\text{moving-GB (Cr)}} \sim D_{\text{stationary-GB (Cr)}}$   
 (6.10<sup>-13</sup> cm<sup>2</sup>/s at 500°C by Pruthi)

$D_{\text{mobile-GB (Cr)}}$  can be extrapolated at 350°C.



TEM CHARACTERIZATIONS



$$D_{\text{moving-GB}}(\text{Cr}) \sim D_{\text{stationary-GB}}(\text{Cr})$$

(6.10<sup>-13</sup> cm<sup>2</sup>/s at 500°C by Pruthi)

D<sub>mobile-GB</sub>(Cr) can be extrapolated at 350°C.

The DIGM can also account for the Cr-depleted area at the SCC crack tip.

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

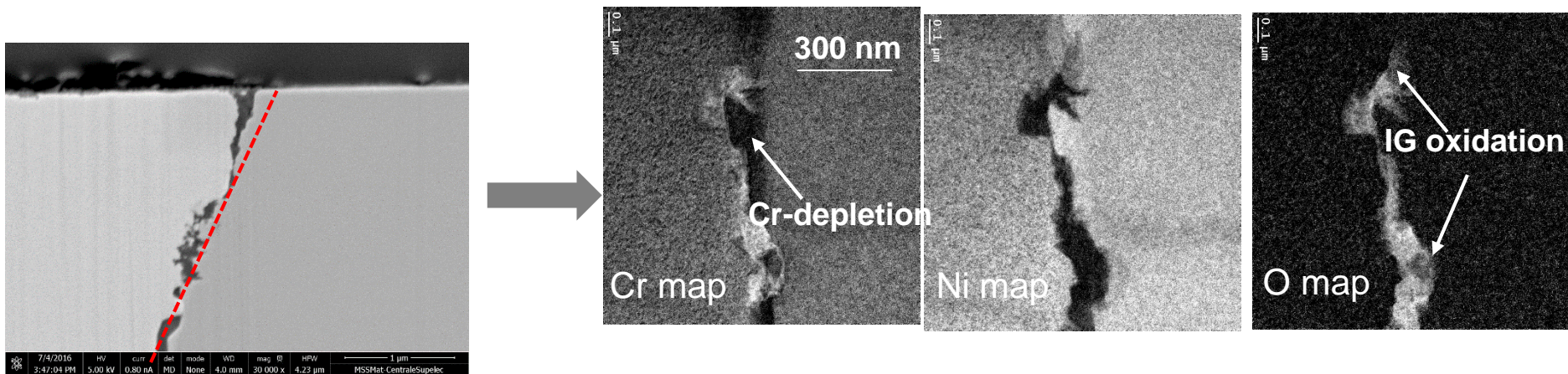
## 1. Cr – depletion at the crack tip

- ✓ Without plasticity, lattice and grain boundary diffusion coefficients cannot explain the asymmetrical depletion observed in one grain at the crack tip.
- ✓ Enhanced diffusion by plasticity is observed at 500°C and 350°C.
- ✓ Strain rate estimated in this study at 350°C is very close to the known strain rate at the SCC crack tip.
- ✓ Activation energy of chromium diffusion enhanced by the plasticity, is also in good agreement with the activation energy of the SCC crack propagation.
- ✓ Plasticity-enhanced diffusion can explain the dimension and the asymmetrical morphology of Cr-depleted area at the crack tip.

## 2. Cr – depletion along the intergranular oxide penetration

- ✓ This study showed that the DIGM is observed only for HAGBs, known to be more susceptible to SCC.
- ✓ DIGM can explain the Cr-depletion along the intergranular oxide penetration
- ✓ This phenomenon can also account for the Cr-depleted area at the crack tip.

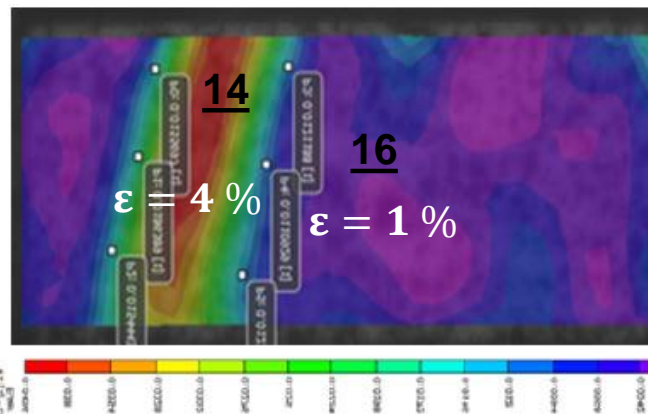
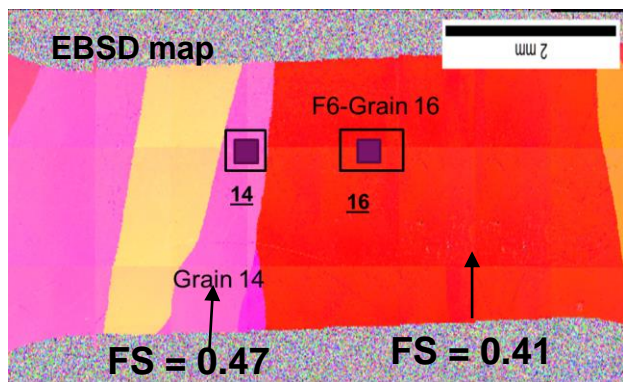
- To evidence the DIGM phenomenon in **PWR conditions** (A600 - 340°C, 1000 hrs)



- Coupling plasticity and DIGM

Perform creep tests on A600 (grain size ~ 1 mm) : study the asymmetrical diffusion

Strain field measured by digital image correlation



## Acknowledgments

Fabrice GASLAIN (Centre des Matériaux)  
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Régis CLEMENT (Centre des Matériaux)  
Loic NAZE (Centre des Matériaux)

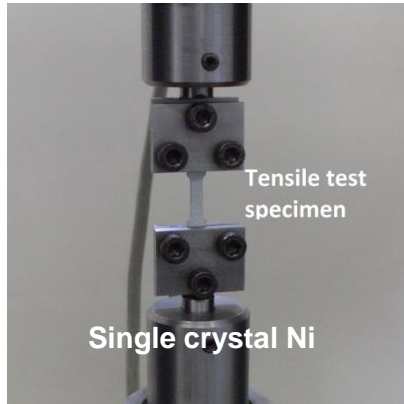
Laure MARTINELLI (CEA)  
Marc MAISONNEUVE (CEA)



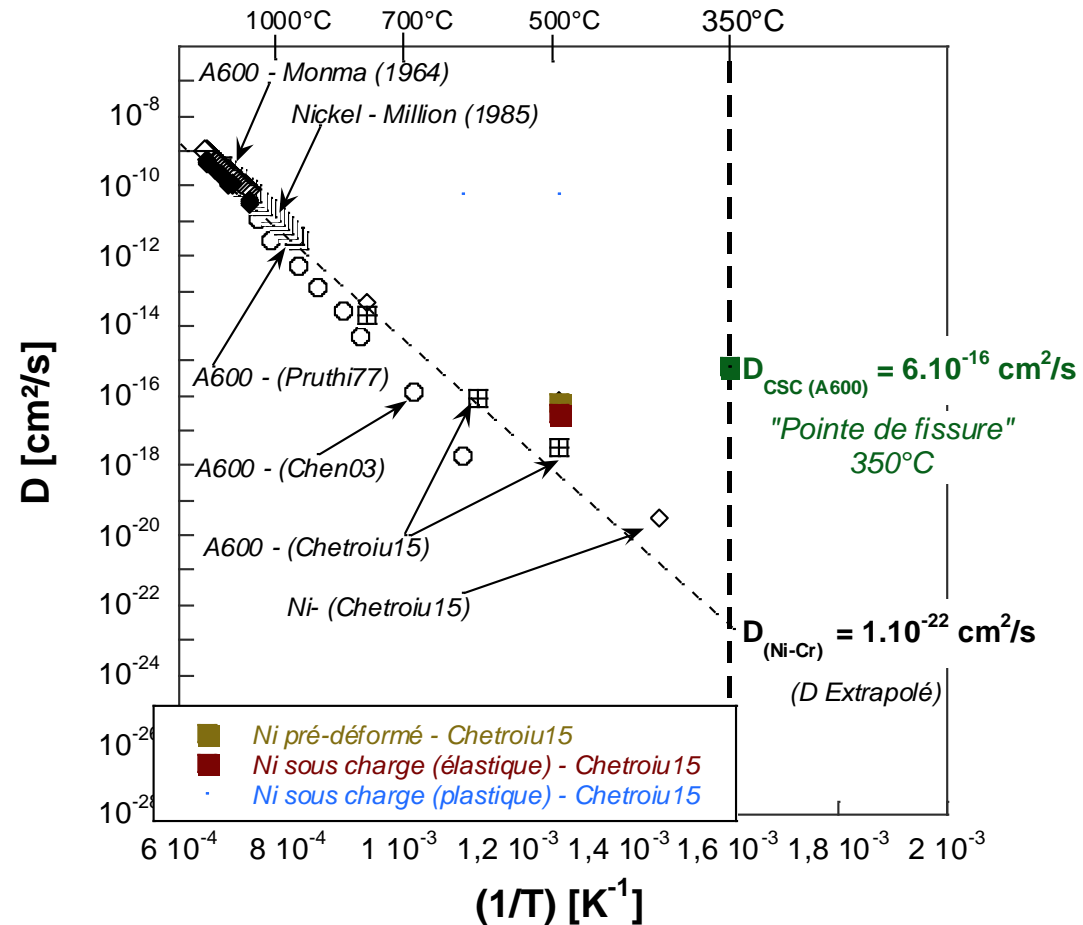
Financial support by EDF (Thierry Couvant) is gratefully acknowledged

# Thanks !

## Diffusion in pre-deformed material : diffusion treatments after tensile tests



Samples conditions	Diffusion treatments
Non-deformed	30h, 500°C
$\varepsilon_p = 4 \%$	30h, 487°C
$\varepsilon_p = 20 \%$	30h, 487°C



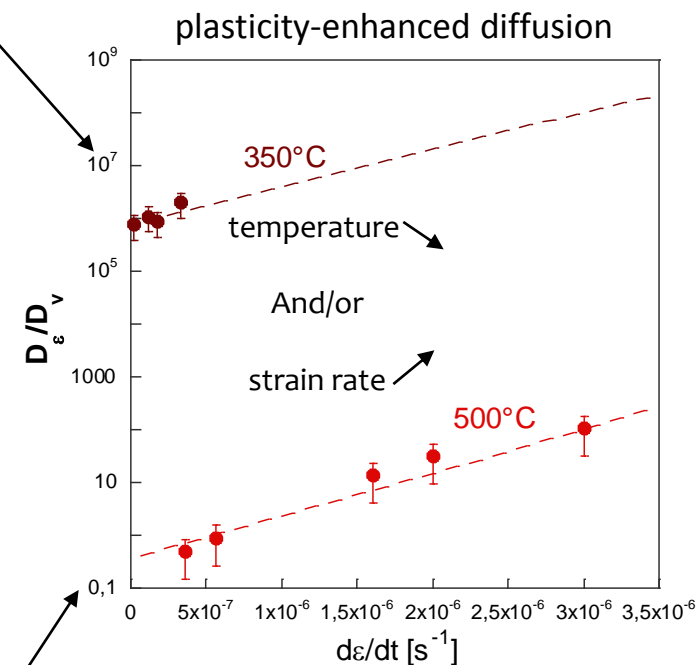
⇒ No significant effect of the pre-deformation on chromium diffusion.

⇒ Pre-deformation can not explain the asymmetric oxidation and depletion along grain boundary.

## APPARENT DIFFUSION COEFFICIENTS

Diffusion at 500°C			
Mechanical state	Strain rate ( $10^{-7} \text{ s}^{-1}$ )	$D_{app}$ ( $10^{-17} \text{ cm}^2/\text{s}$ )	Enhanced diffusion $D_{app}/D_v(500^\circ\text{C})$
Without plasticity	-	$4.0 \pm 0.2$	1.0
30 MPa [1] (below the yield stress)	-	$4.6 \pm 1.0$	1.1
Plasticity 55 MPa	3.8	$5.9 \pm 0.6$	1.5
Plasticity 60 MPa	5.6	$7.7 \pm 0.1$	1.9
Plasticity 65 MPa	16	$58 \pm 1.6$	4.5
Plasticity 70 MPa	19	$100 \pm 8.0$	25
Plasticity 74 MPa	33	$420 \pm 10$	105

Diffusion at 350°C			
Mechanical state	Strain rate ( $10^{-7} \text{ s}^{-1}$ )	$D_{app}$ ( $10^{-17} \text{ cm}^2/\text{s}$ )	Enhanced diffusion $D_{app}/D_v(350^\circ\text{C})$
Without plasticity [1] (400°C, 1616 hrs)	-	0.003	-
Plasticity 74 MPa	0.3	$5.7 \pm 2.0$	$8 \cdot 10^5$
Plasticity 84 MPa	1.2	$11 \pm 0.1$	$1 \cdot 10^6$
Plasticity 100 MPa	3.3	$20 \pm 1.6$	$2 \cdot 10^6$



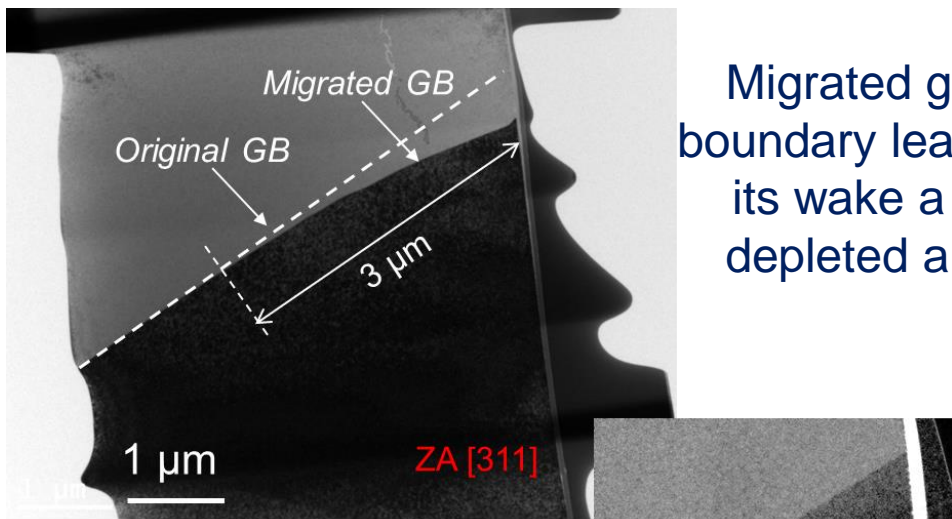
*Accelerating factor*

$$D_{app}/D_v \propto B \cdot \dot{\epsilon}_p$$

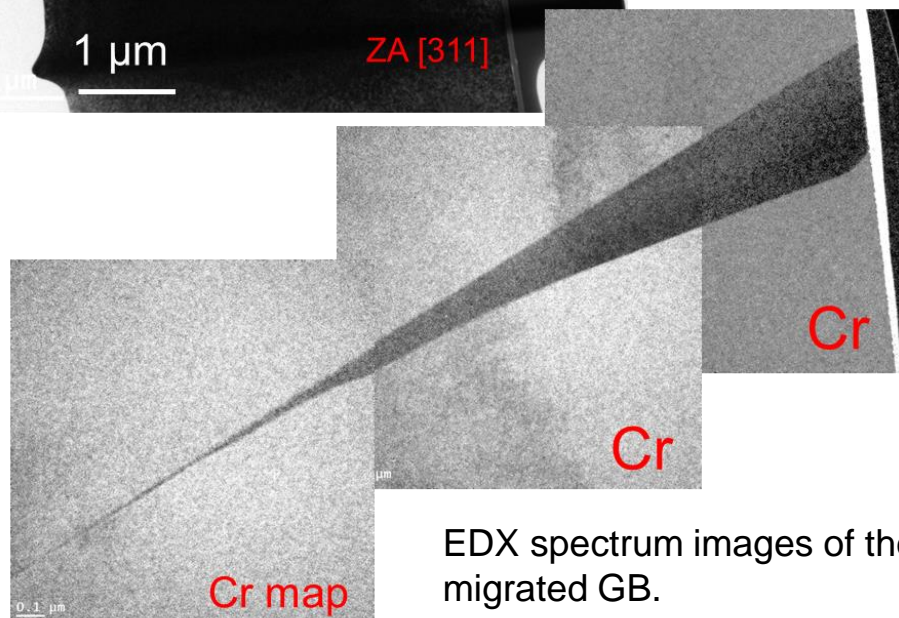
$$B = f(1/T)$$

## MET CHARACTERIZATIONS AFTER HEAT TREATMENT AT 500°C

TEM bright field (BF)  
image

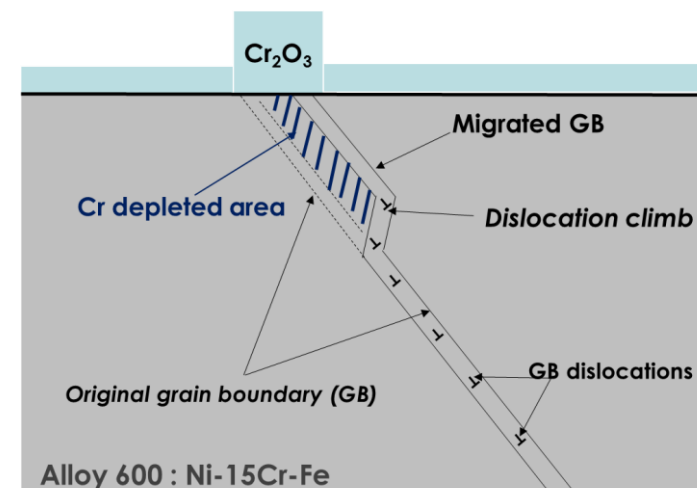


Migrated grain boundary leaves in its wake a Cr-depleted area.



EDX spectrum images of the migrated GB.

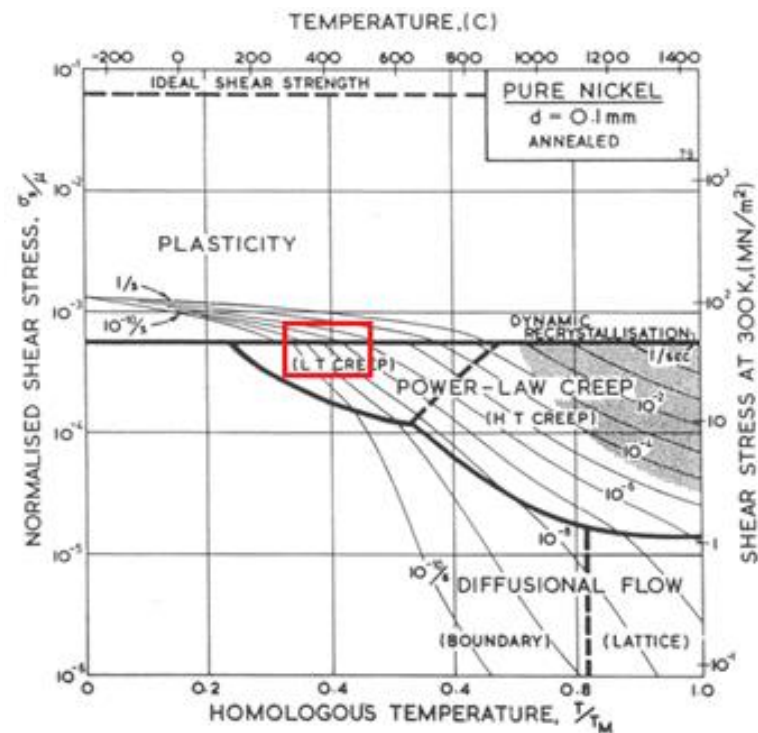
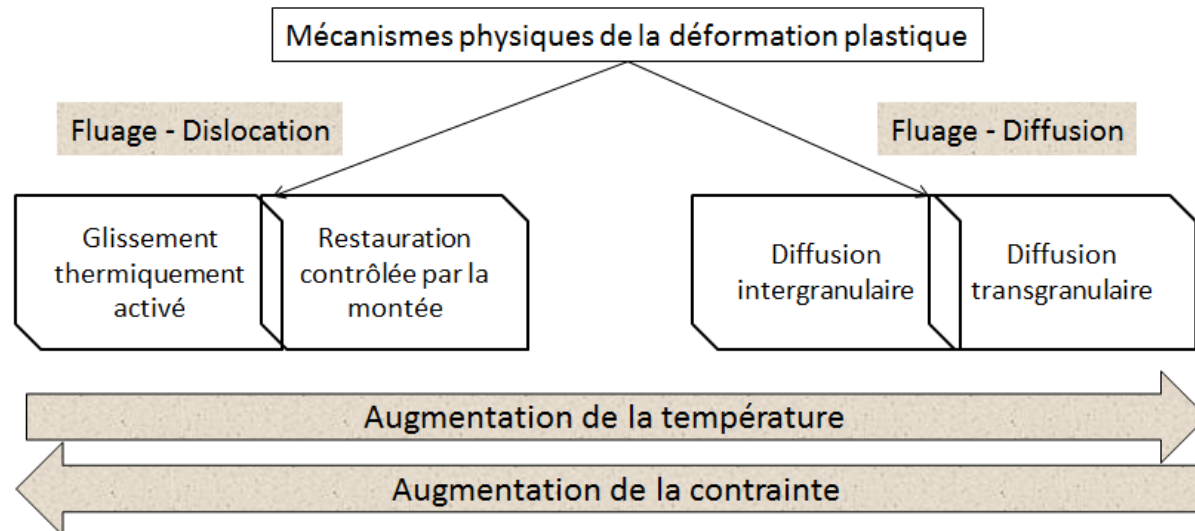
## DIGM Mechanism



### Steps of mechanism :

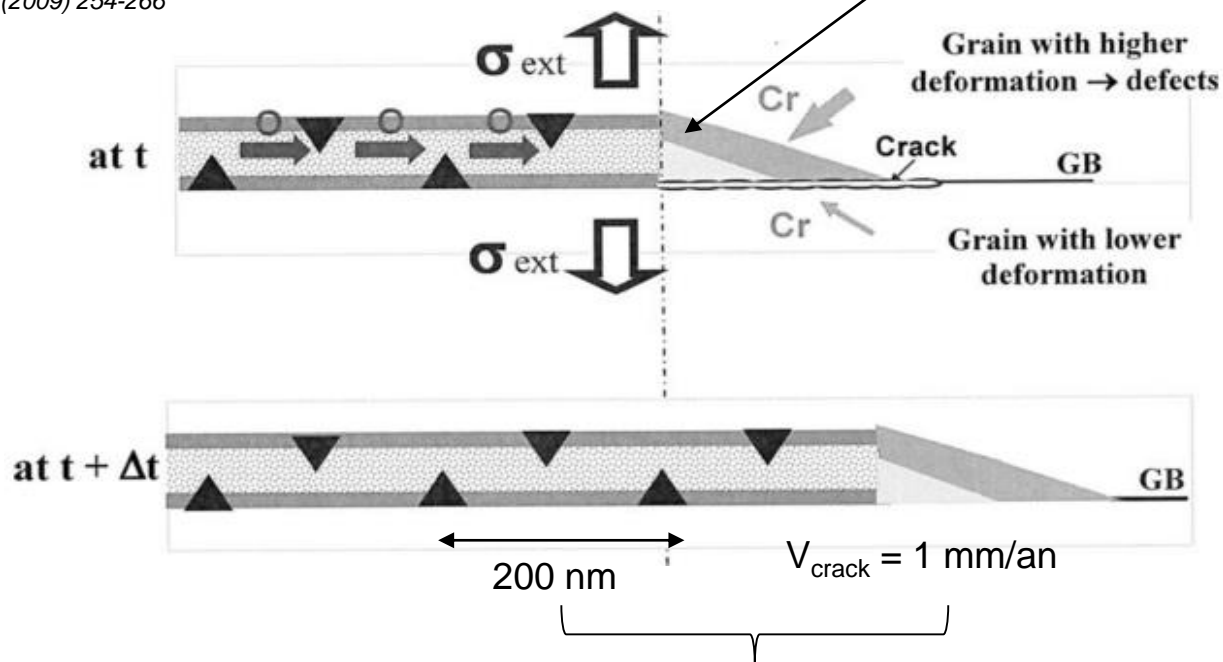
1. Intergranular diffusion
2. Kirkendall effect (vacancies flow) along the GB
3. Lead to the self-sustaining climb of GB dislocations
4. Steps of climb cause the GB migration
5. Depleted area is formed during the migration





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

*Cr-depletion in one grain*



Step time of cracking ~ time of oxidation = 6300 sec

*Summary : Chromium depletion of 20 nm in 6300 sec*