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# DIFFUSION OF CHROMIUM IN NICKEL BASE ALLOYS: APPLICATION TO STRESS CORROSION CRACKING

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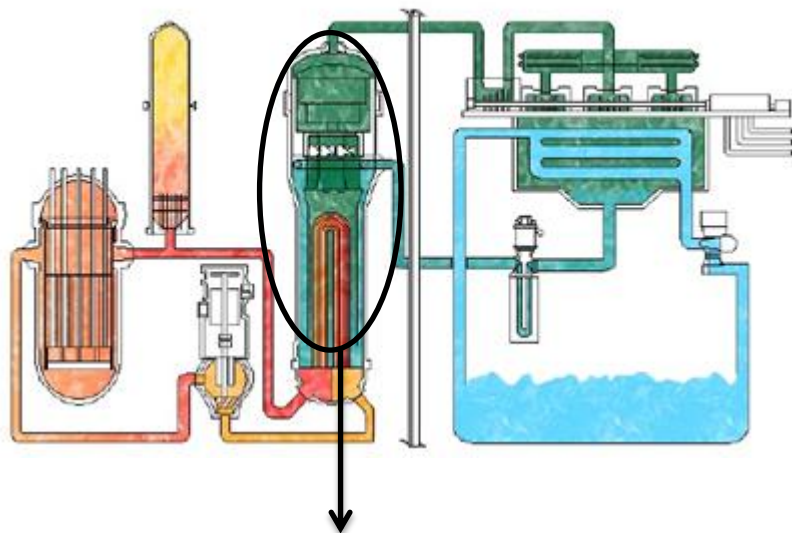
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25 JUNE 2015

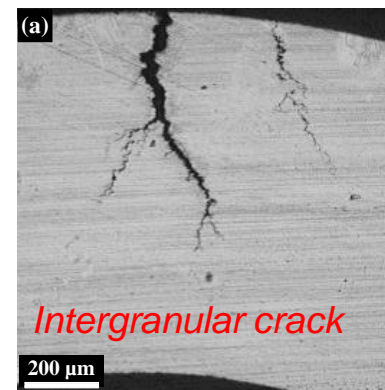
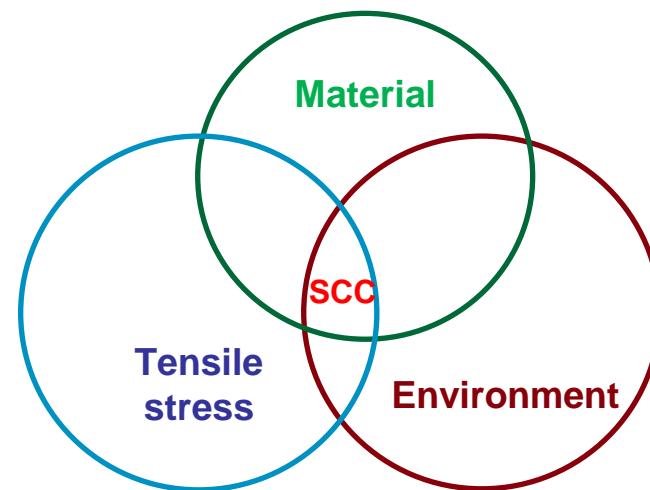
### Pressurized Water Reactor (PWR)



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

**Primary water conditions**

Temperature	285 - 325 °C
Pressure	155 bar
Boren (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



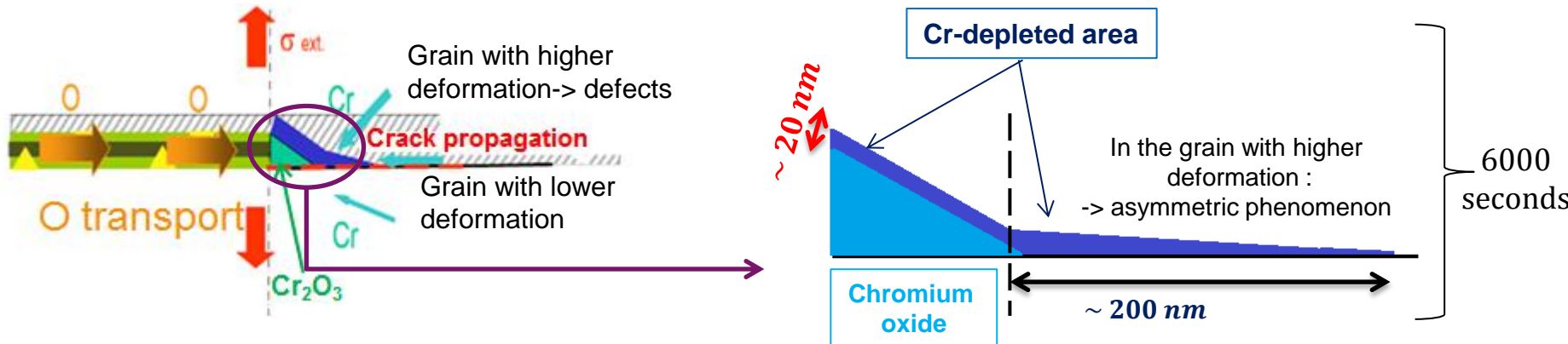
Stress corrosion cracking of Alloy 600 formed on U bend specimen at 325°C during 1200 hr [1]

Life extension of PWR > 30 – 40 years

## Mechanisms of Stress Corrosion Cracking (SCC) [1]

Asymmetric and selective oxidation

Crack tip : Cr-depleted area observed only in one grain along the grain boundary

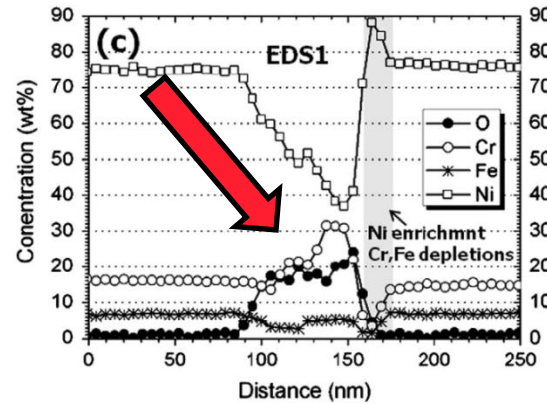
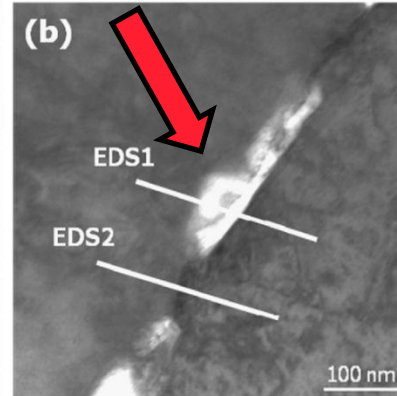
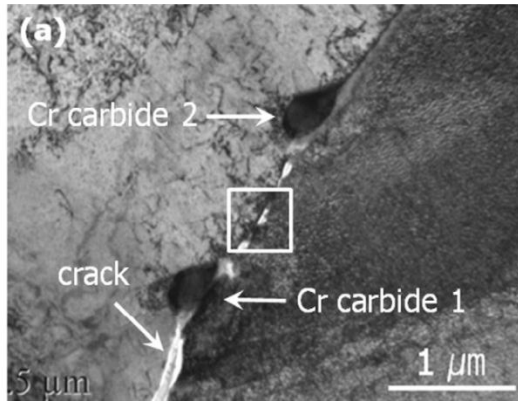


### Mechanisms proposed by authors [1]

1. Oxygen transport is not the rate-limiting step
2. Strain maybe heterogeneous in the vicinity of the crack tip
3. Formation of the chromium depleted area occurs in about 6000 seconds.

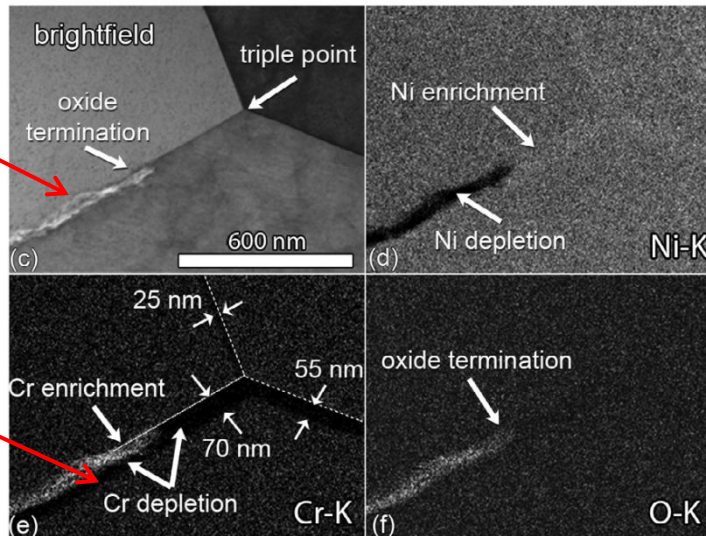
Chromium diffusion in Alloy 600 at low temperatures (around 350°C) : one of the key steps of the SCC mechanism

## Intergranular oxide and chromium depleted area in literature



Lim Yun Soo, Kim Hong Pyo, and Hwang Seong Sik.  
*Journal of Nuclear Materials*  
440, no. 1-3 (2013) : 46-54.

Chromium oxide



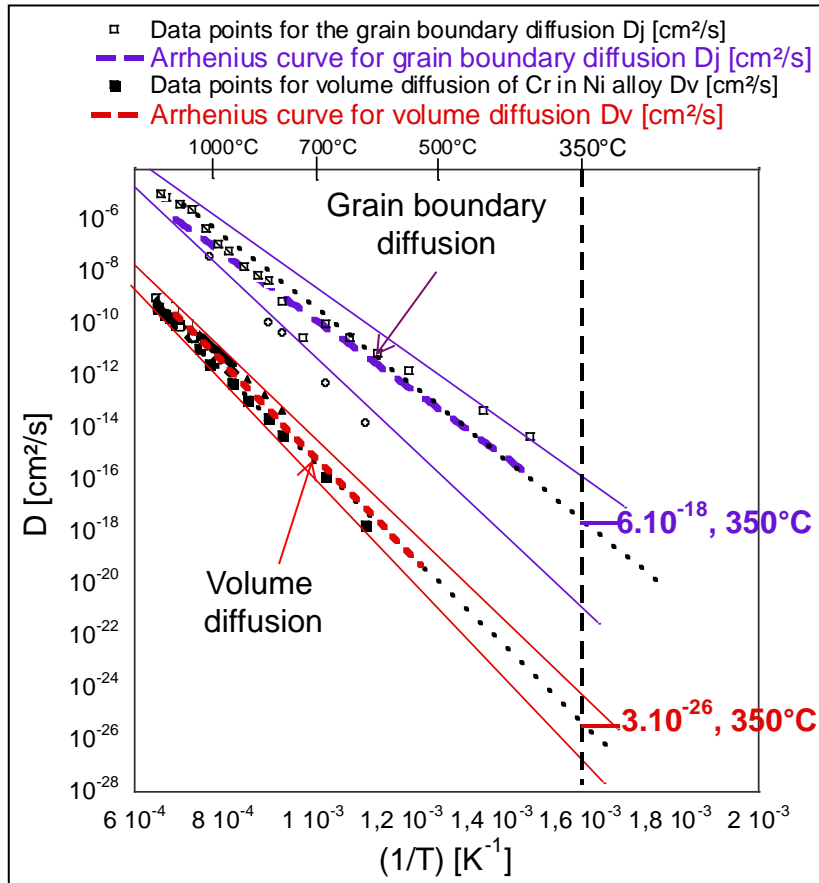
Cr-depleted area

Cr-depleted area at metal/oxide interface and ahead of the intergranular oxide.

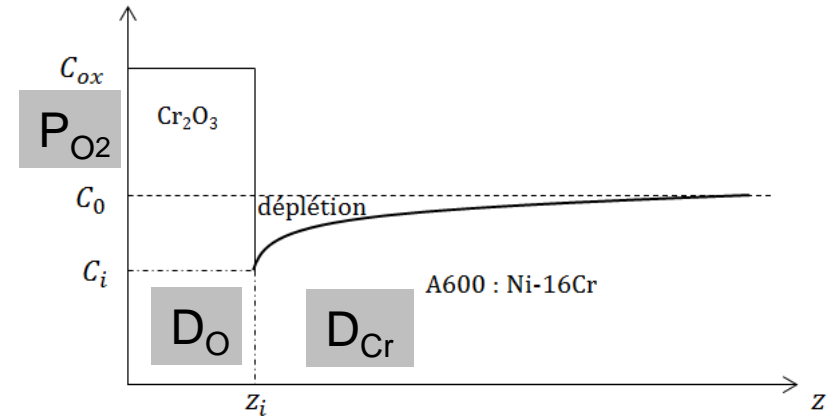
D.K. Schreiber, M.J. Olszta and S.M. Bruemmer, S., *Scripta Materiala* 89 (2014) 41-44

## Volume and grain boundary diffusion of chromium : literature

Arrhenius [1,2,3,4,5] 400°C et 1270°C



Calculation of chromium depletion time in Alloy 600



$$\frac{C - C_o}{C_i - C_o} = \frac{\text{erfc}\left(\frac{z}{2\sqrt{Dt}}\right)}{\text{erfc}\left(\frac{z_i}{2\sqrt{Dt}}\right)}$$

$z_i$  depend on :

- Oxygen diffusion coefficient
- Oxygen partial pressure
- Chromium diffusion coefficient

**Results :**

-Grain boundary diffusion

⇒ t = 3 days

-Volume diffusion

⇒ t = 100 years

- [1] D.D. Pruthi, M.S. Anand, and R.P. Agarwala, Journal of Nuclear Materials 64 (1977) 206-210  
 [2] T.F. Chen, G.P. Tiwari, Y. Iijima, and K. Yamauchi. Materials Transactions 44 (2003) 40-46  
 [3] K. Monma, O. Suto, and O. Hiroshi. The Japan Institute of Metals and Materials 28 (1964) 188-192  
 [4] B. Million, J. Ruzickova, and J. Vrestal. Materials Science and Engineering 72 (1985) 85-100  
 [5] Moulin P., Huntz A. M., and Lacombe P. Acta Metallurgica 77 (1979) : 1430-43.

These results are not sufficient to explain the chromium depleted area observed in literature (20 nm in 6000 seconds).

## For which conditions is chromium diffusion enhanced ?

### 1. Materials

- Pure nickel - Single crystal - crystallographic orientation  $\langle 101 \rangle$

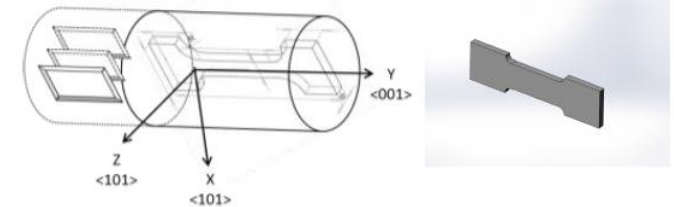
### 2. Chromium deposition

- Sample polishing
- Evaporating chromium under vacuum  
-> 20 nm thin layer (powder  $^{52}\text{Cr}$  - 99,6% purity)

### 3. Diffusion treatments in secondary vacuum

### 4. Measurement of diffusion coefficients

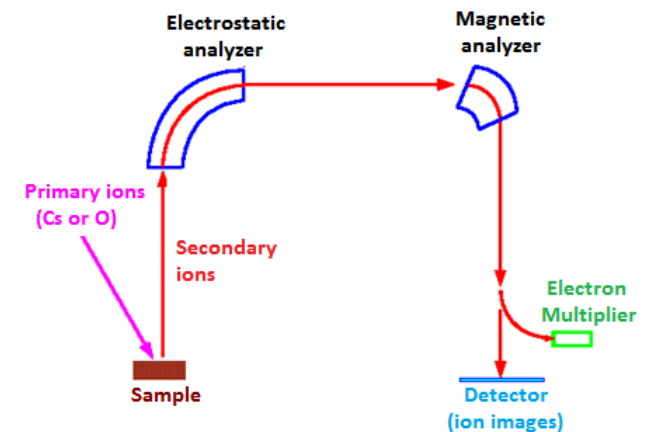
- By Secondary Ion Mass Spectrometry (SIMS)



**CAMECA - IMS 7F**

Detection limit : of ppb to ppm  
Lateral resolution : 0,5  $\mu\text{m}$   
Depth resolution : environ 1 nm

Analysis conditions :  
Primary ions :  $\text{O}_2^+$   
Partial pressure  $\text{O}_2$  :  $2 \cdot 10^{-6}$  mbar  
Primary ions intensity : 50 nA  
Crater Size : 150  $\mu\text{m}$  \* 150  $\mu\text{m}$   
Analysis area :  $\varnothing 33 \mu\text{m}$

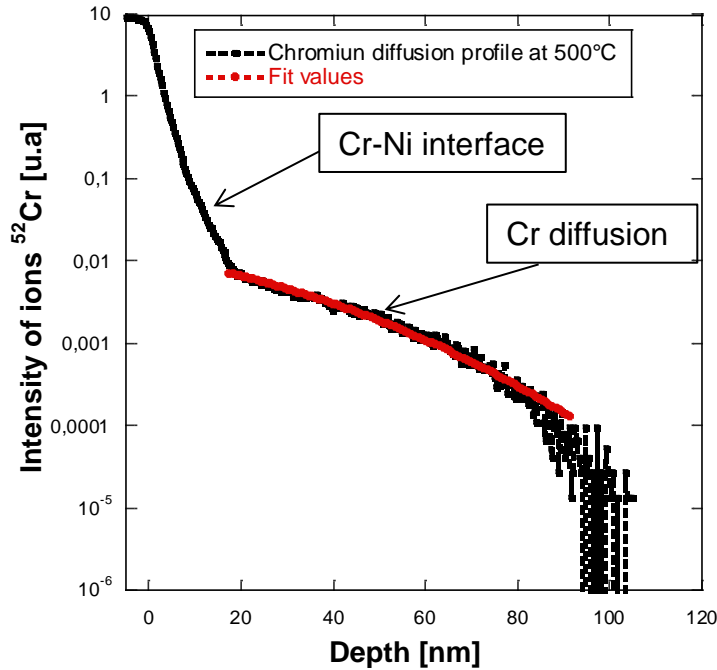


- Measurement of the final crater depth by profilometry technique

# RESULTS



## Secondary Ion Mass Spectrometry (SIMS)



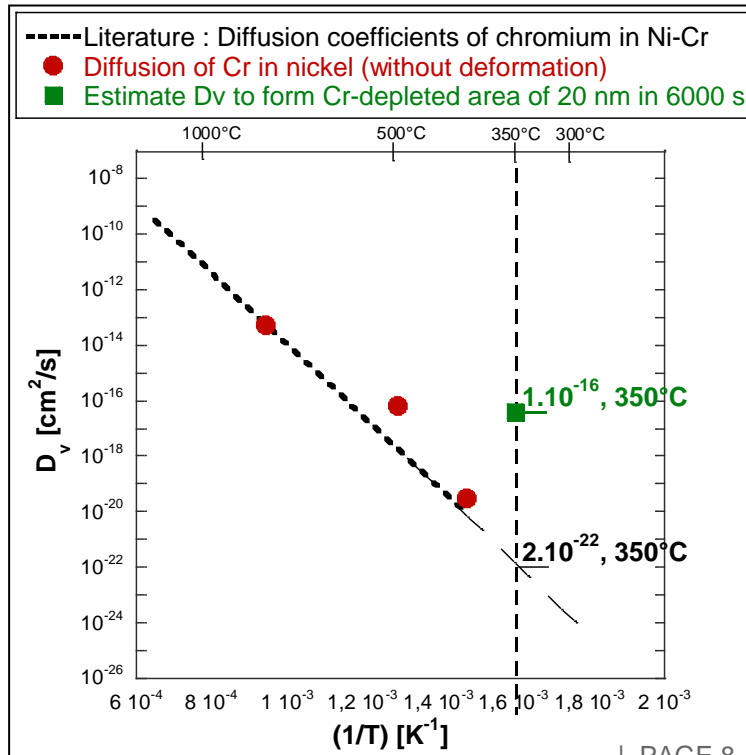
Fick's solution equation

$$C(x, t) = C_s \cdot \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)$$

Diffusion treatments	D [cm <sup>2</sup> /s]
787°C, 5h	(5±1).10 <sup>-14</sup>
500°C, 30h	(7±2).10 <sup>-17</sup>
405°C, 1616h	(3±2).10 <sup>-20</sup>

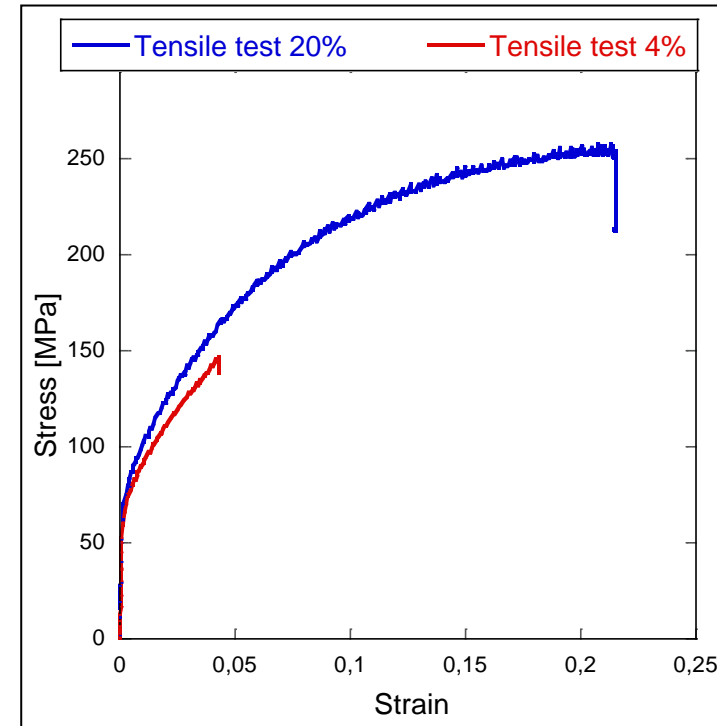
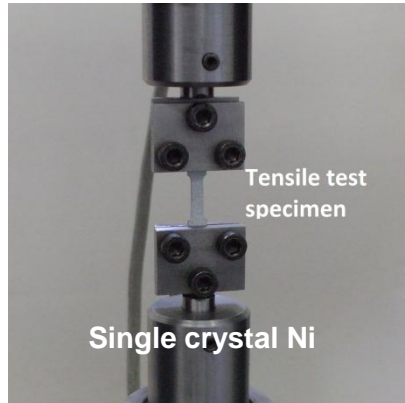
⇒ Results consistent with literature data.  
 ⇒ Volume diffusion is not sufficient to explain the asymmetric Cr depletion observed in literature (20 nm in 6000 sec).

**Effect of pre-deformation ?**



Aim : influence of pre-deformation on diffusion coefficient

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



Samples conditions	Diffusion treatments	D [cm <sup>2</sup> /s]
Non-deformed	30h, 500°C	$(7\pm 2).10^{-17}$
$\varepsilon_p = 4 \%$	30h, 487°C	$(3,5\pm 0,9).10^{-17}$
$\varepsilon_p = 20 \%$	30h, 487°C	$(3\pm 3).10^{-17}$

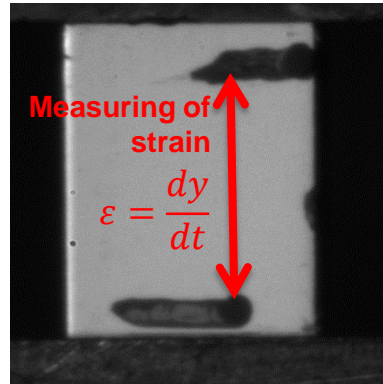
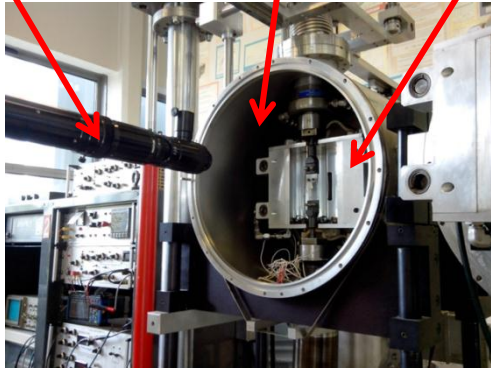
⇒ No significant effect of the pre-deformation on chromium diffusion.

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

**Coupling of diffusion and deformation ?**

*Aim : the effect of dislocations mobility*

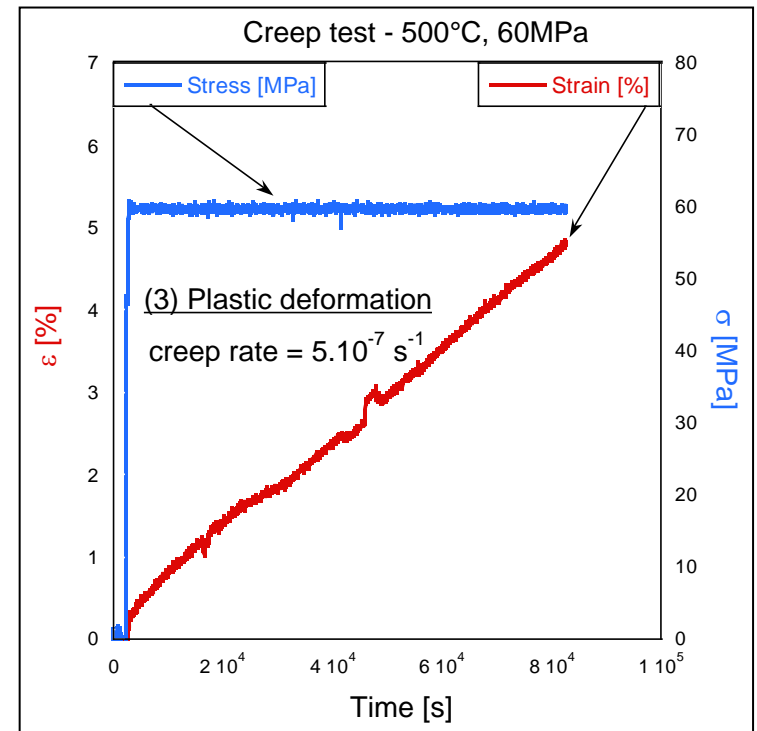
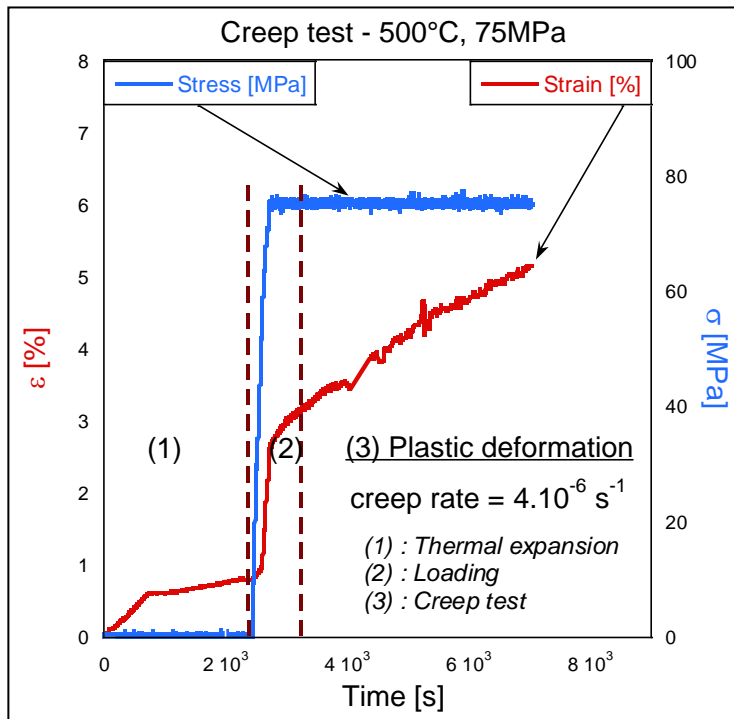
Camera Chamber Furnace



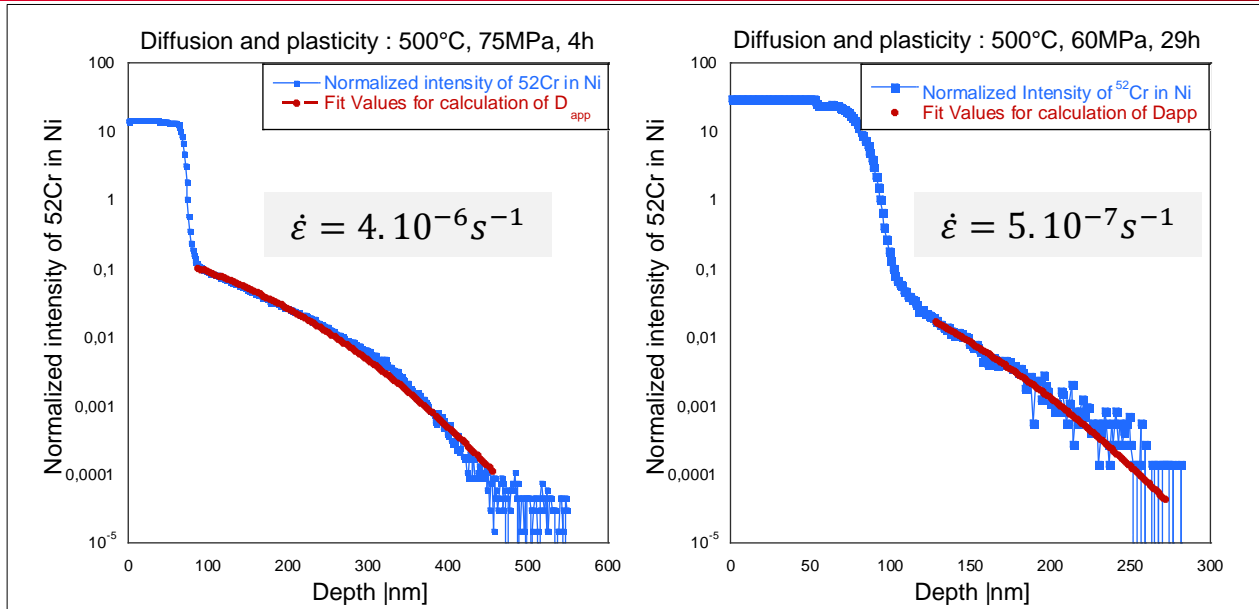
## Creep tests

500°C, 60 MPa, 29h Creep rate :  $5 \cdot 10^{-7} \text{ s}^{-1}$

500°C, 75 MPa, 4h Creep rate :  $4 \cdot 10^{-6} \text{ s}^{-1}$



## The effect of dislocations mobility at 500°C



Analytic solution [1] :

$$C(x) = C_o \left[ \operatorname{erfc} \left( \frac{x}{2\sqrt{D_{app} \times t}} \right) \right]$$

Experiments	$D_{app}$ [ $cm^2/s$ ]
500°C, 60 MPa, 29h Creep rate : $5.10^{-7} s^{-1}$	$2,8.10^{-16}$
500°C, 75 MPa, 4h Creep rate : $4.10^{-6} s^{-1}$	$6,4.10^{-15}$
(Without plasticity) at 500°C, 30h	$7,0.10^{-17}$

⇒ Enhanced chromium diffusion at 500°C with plasticity effect.

⇒ The diffusion coefficient increases with creep rate (or dislocations mobility  $v$  ; *Orowan's law* :  $\dot{\epsilon} = \rho \cdot b \cdot v$ ).

Creep test at 350°C for the same dislocations mobility as at 500°C !

Aim : the effect of dislocations mobility at 350°C

Creep law :

$$[1] \quad \dot{\epsilon}_s = S. \exp\left(\frac{-\Delta H}{RT} + \beta\sigma\right)$$

$S = \text{constant}$   
 $\Delta H \sim 66 \text{ kcal/mol}$   
 $\beta = 1.10^{-7}$

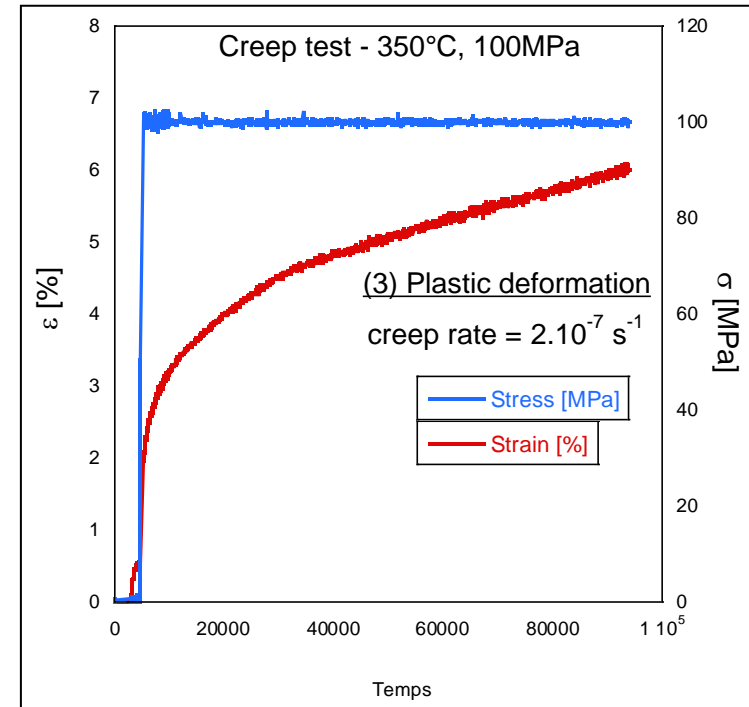
Estimation of stress at 350°C

$$\sigma_{350^\circ\text{C}} = 41 + 5 \ln\left(\frac{\dot{\epsilon}_{350^\circ\text{C}}}{\dot{\epsilon}_{500^\circ\text{C}}}\right) + \sigma_{500^\circ\text{C}} \text{ en MPa}$$

<b>Same creep rate : <math>\dot{\epsilon}_{500^\circ\text{C}} = \dot{\epsilon}_{350^\circ\text{C}}</math></b>	
T = 500°C	$\sigma_{500^\circ\text{C}} = 60 \text{ MPa}$
T = 350°C	$\sigma_{350^\circ\text{C}} = 100 \text{ MPa}$

Creep test at 350°C

**350°C, 100 MPa, 26h Creep rate :  $2.10^{-7} \text{ s}^{-1}$**

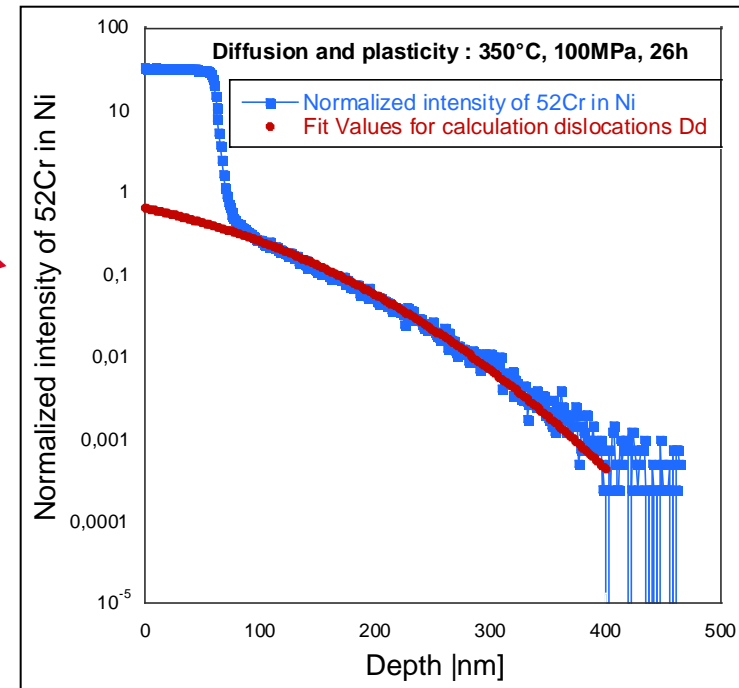
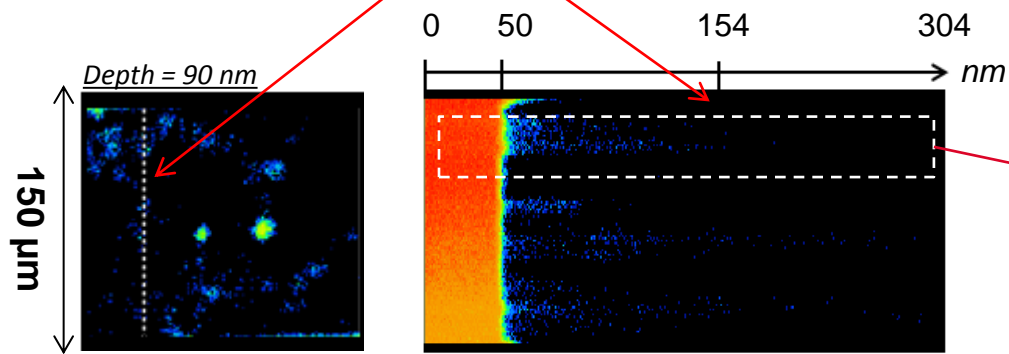


✓ Viscoplasticity is observed at 350°C in these conditions.

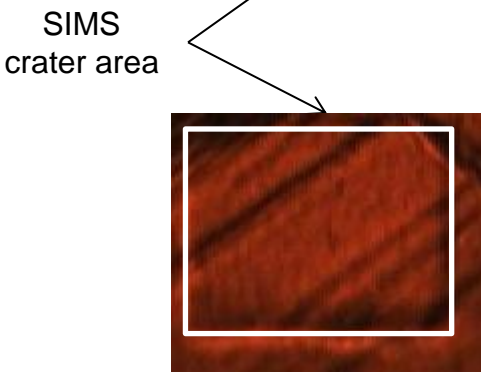
Measurement of diffusion coefficient of chromium after the creep test at 350°C.

Aim : the effect of dislocations mobility at 350°C

SIMS analysis : Cr-ionic image  
at cross-section in the deep



Cr deposit  
Chromium diffusion in nickel  
up to 300 nm of depth.

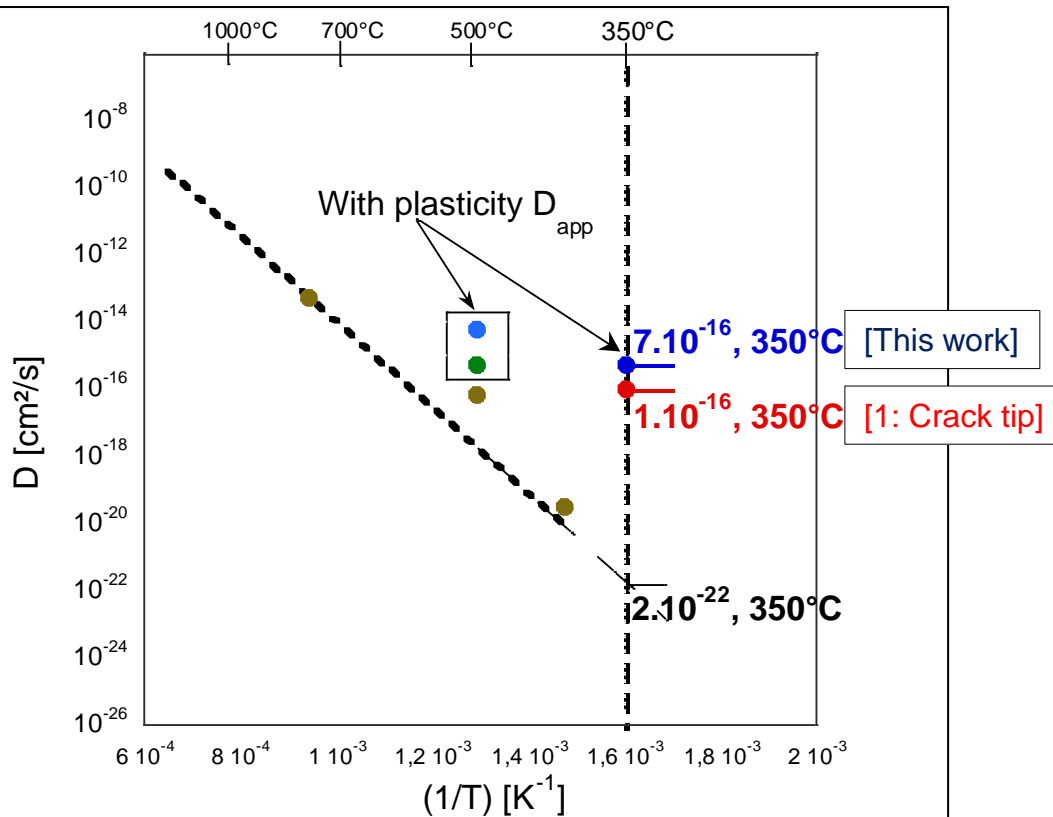


Experiment	$D$ [ $\text{cm}^2/\text{s}$ ]
350°C, 100 MPa, 26h Creep rate : $2 \cdot 10^{-7} \text{s}^{-1}$	$7,4 \cdot 10^{-16}$
(Without plasticity) at 350°C (extrapolated value)	$1,9 \cdot 10^{-22}$
500°C, 60 MPa, 29h Creep rate : $5 \cdot 10^{-7} \text{s}^{-1}$	$2,8 \cdot 10^{-16}$

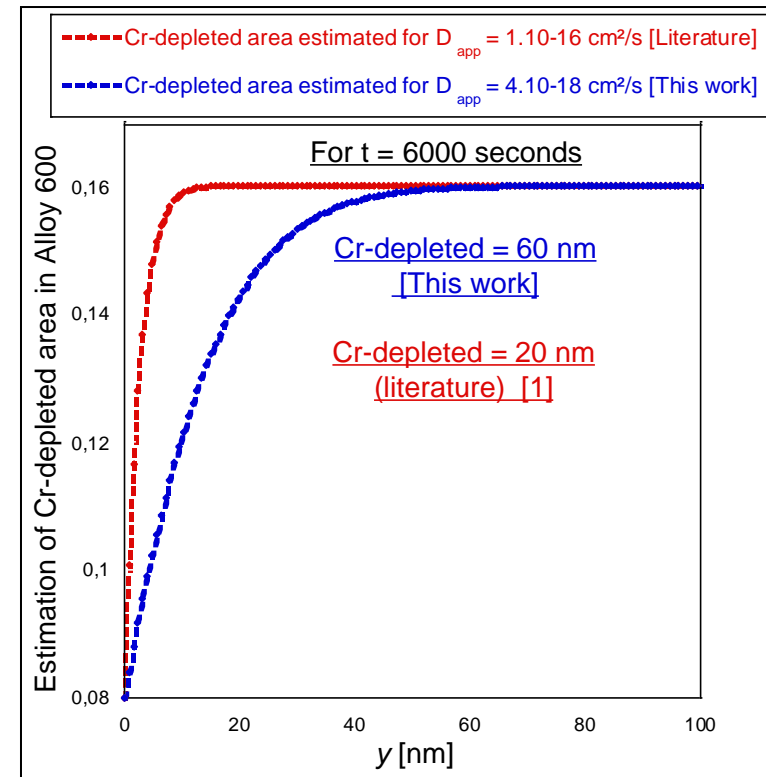
⇒ Plasticity can accelerate the chromium diffusion at low temperatures.

⇒ This phenomenon seems to depend on the creep rate.

## Summary : Cr-depleted area at the SCC crack tip



- Literature : Diffusion coefficients of Cr in alloy nickel  $D$  [cm<sup>2</sup>/s]
- Diffusion of Cr in nickel (without deformation)  $D$  [cm<sup>2</sup>/s]
- Diffusion coupling with plasticity :  $4.10^{-6} s^{-1}$  - 500°C  $D_{app}$  [cm<sup>2</sup>/s]
- Diffusion coupling with plasticity :  $5.10^{-7} s^{-1}$  - 500°C  $D_{app}$  [cm<sup>2</sup>/s]
- Diffusion coupling with plasticity :  $2.10^{-7} s^{-1}$  - 350°C  $D_{app}$  [cm<sup>2</sup>/s]
- Estimate D to form Cr-depleted area of 20 nm in 6000 s



Chromium diffusion assisted by moving dislocations can explain Cr-depleted area, observed at SCC crack tip.

## ➤ Conclusions

- ❑ No effect of pre-deformation on chromium diffusion coefficient in nickel.
- ❑ The accelerating effect of plasticity on chromium diffusion in nickel has been showed at 500°C and 350°C. Diffusion is enhanced by dislocations mobility for the tested conditions.
- ❑ Diffusion along moving dislocations could take place at the SCC crack tip and could allow the formation of chromium depleted area.

## ➤ Prospects

- ❖ Perform more experiments at low temperatures (350°C) and for different dislocation velocities.
- ❖ Similar experiments with A600.
- ❖ Define a model which describes the formation of chromium depleted area at the SCC crack tip.



# Thank you for your attention

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