Diffusion of Chromium in Nickel Base Alloys Application to Stress Corrosion Cracking

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DE LA RECHERCHE À L'INDUSTRIE

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

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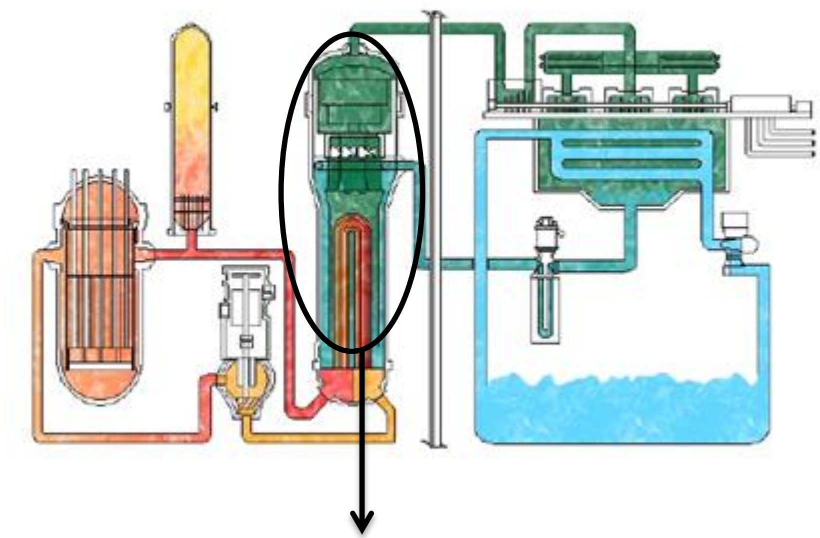
Stress corrosion cracking (SCC)

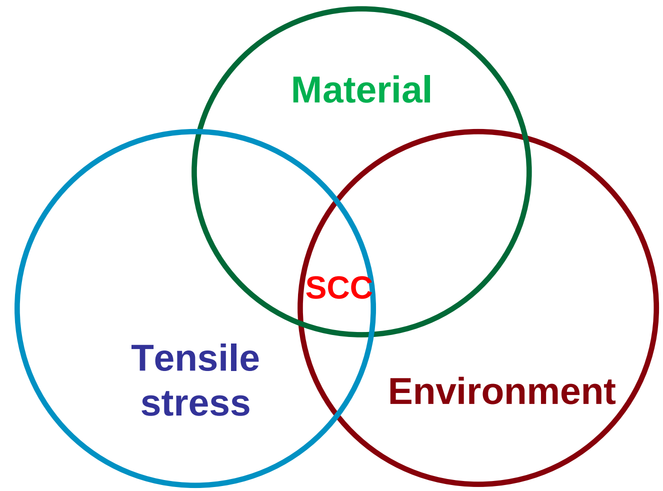
Pressurized Water Reactor (PWR)

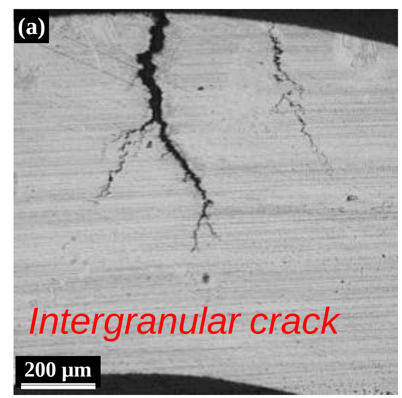


Steam generator tubes : Nickel Base Alloy
A 600-> Ni-15Cr-Fe

Primary water conditions

Temperature	285 - 325 °C
Pressure	155 bar
Boren (H_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





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

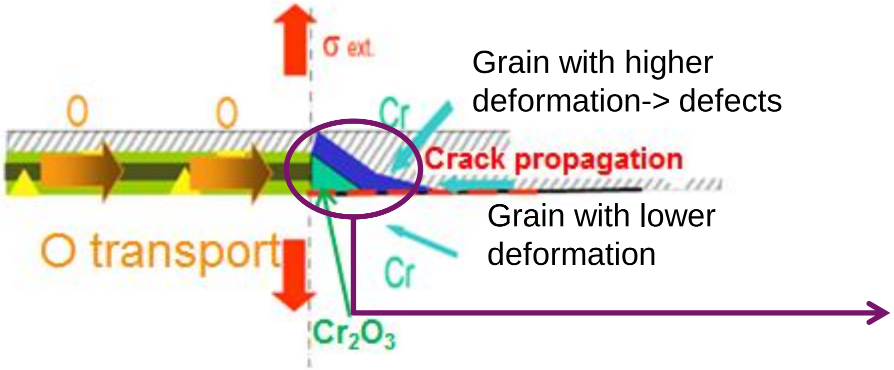
[1] M. Sennour, P. Laghoutaris, C. Guerre, R. Molins, Journal of Nuclear Materials, 393 (2009) 254-266

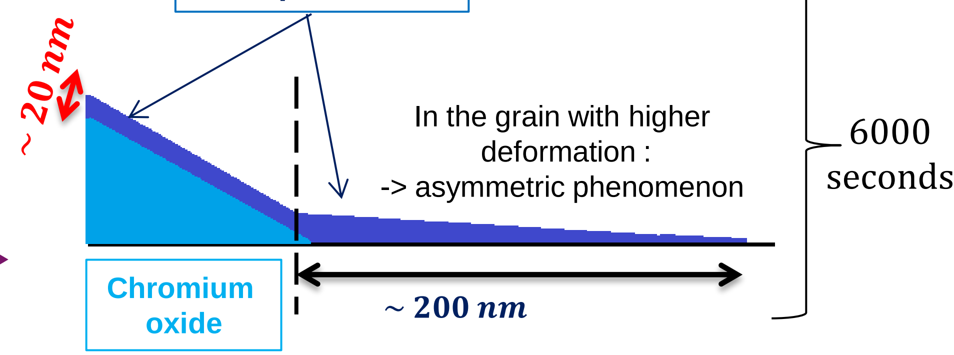
CONTEXT

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]

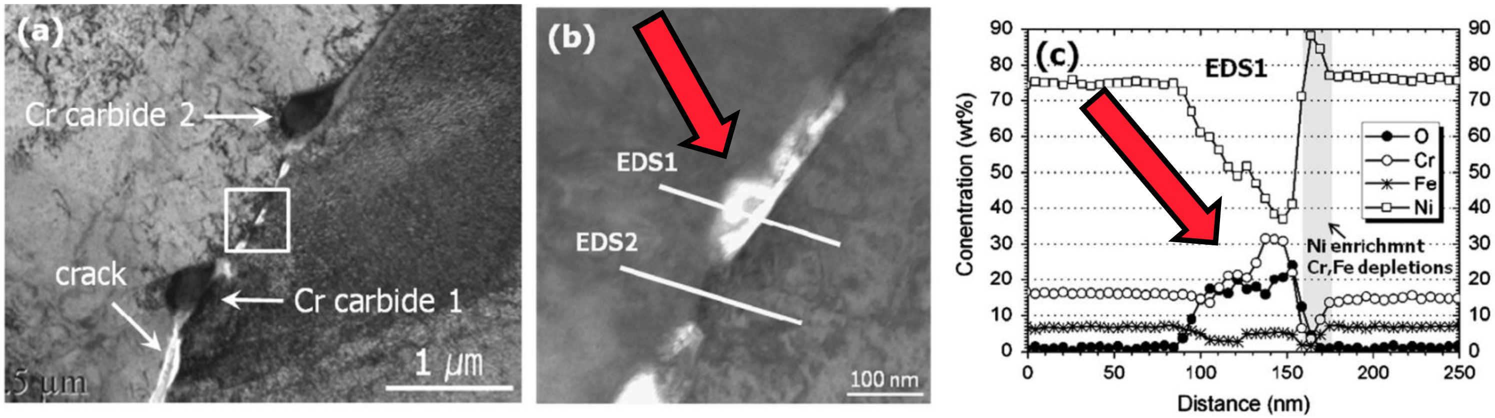
1. Oxygen transport is not the rate-limiting step
2. Strain maybe heterogeneous in the vicinity of the crack tip
3. Formation of the chromium depleted area occurs in about 6000 seconds.

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

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

CONTEXT

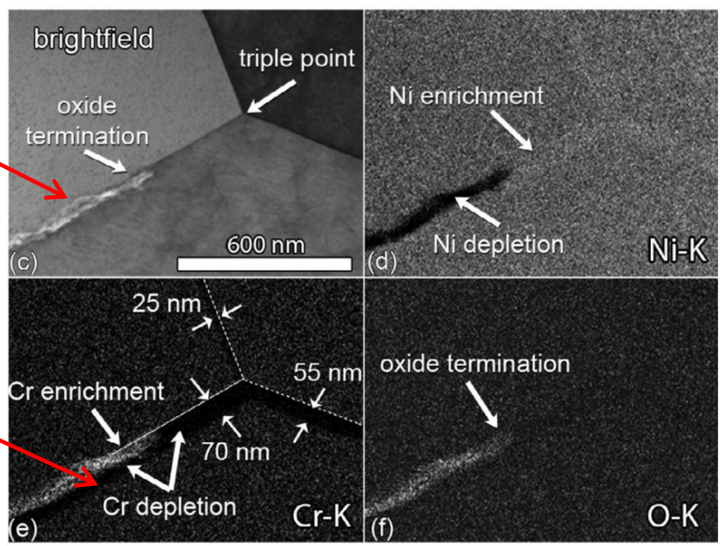
Intergranular oxide and chromium depleted area in literature



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

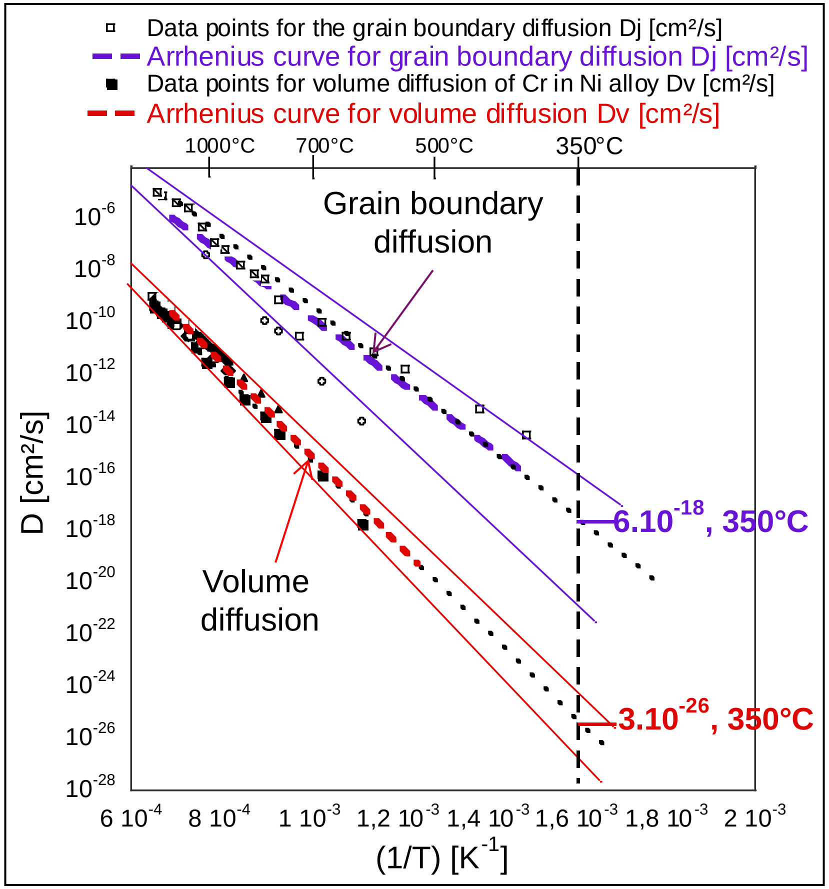


D.K. Schreiber, M.J. Olszta and S.M. Bruemmer, S., Script Materiala 89 (2014) 41-44

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

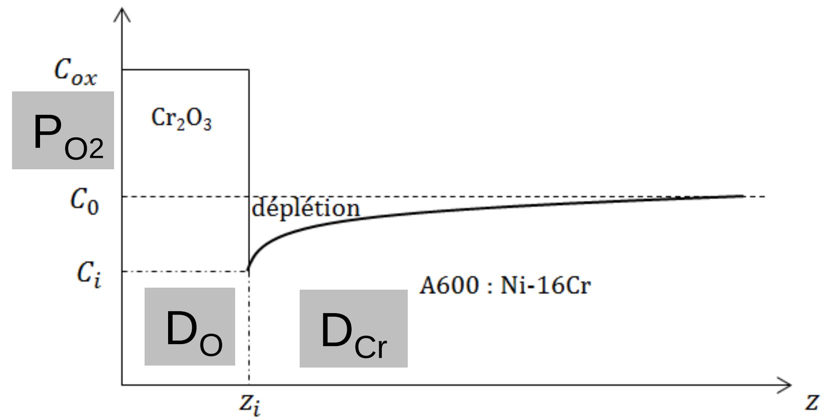
Volume and grain boundary diffusion of chromium : literature

Arrhenius [1,2,3,4,5] 400°C et 1270°C



[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. Iljima, 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.

Calculation of chromium depletion time in Alloy 600



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

z_i depend on :

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

Results :

-Grain boundary diffusion

$\Rightarrow$ t = 3 days

-Volume diffusion

$\Rightarrow$ t = 100 years

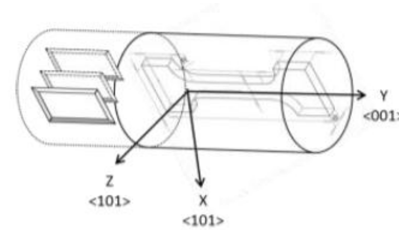
These results are not sufficient to explain the chromium depleted area observed in literature *(20 nm in 6000 seconds)*.

EXPERIMENTAL PROCEDURE

For which conditions is chromium diffusion enhanced ?

1. Materials

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



2. Chromium deposition

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

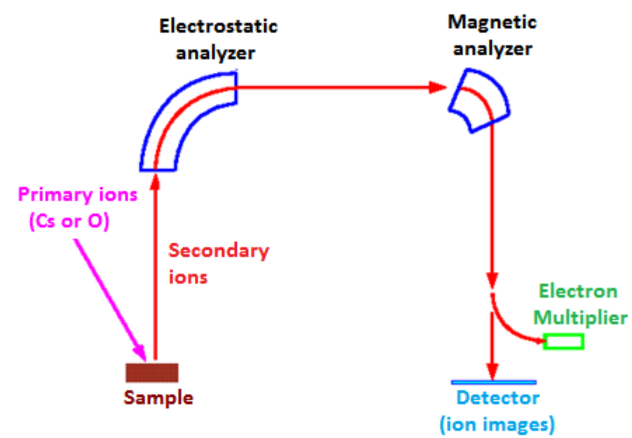
3. Diffusion treatments in secondary vacuum

4. Measurement of diffusion coefficients

- ❑By Secondary Ion Mass Spectrometry (SIMS)

CAMECA - IMS 7F
Detection limit : of ppb to ppm
Lateral resolution : 0,5 µm
Depth resolution : environ 1 nm

Analysis conditions :
Primary ions : O2+
Partial pressure O_2 : 2.10^{-6} mbar
Primary ions intensity : 50 nA
Crater Size : 150 µm*150 µm
Analysis area : Ø33µm



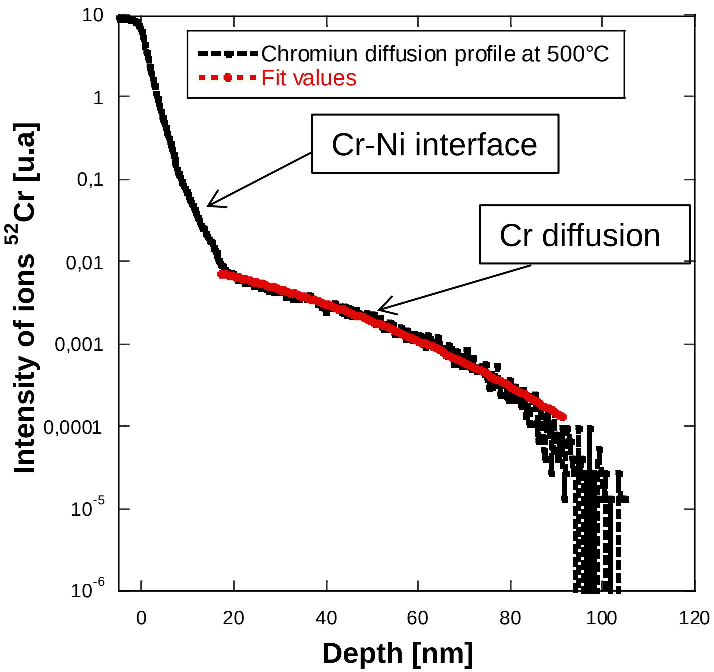
- ❑Measurement of the final crater depth by profilometry technique

RESULTS

DIFFUSION IN NON-DEFORMED MATERIAL

Aim : obtain volume diffusion coefficients at low temperatures

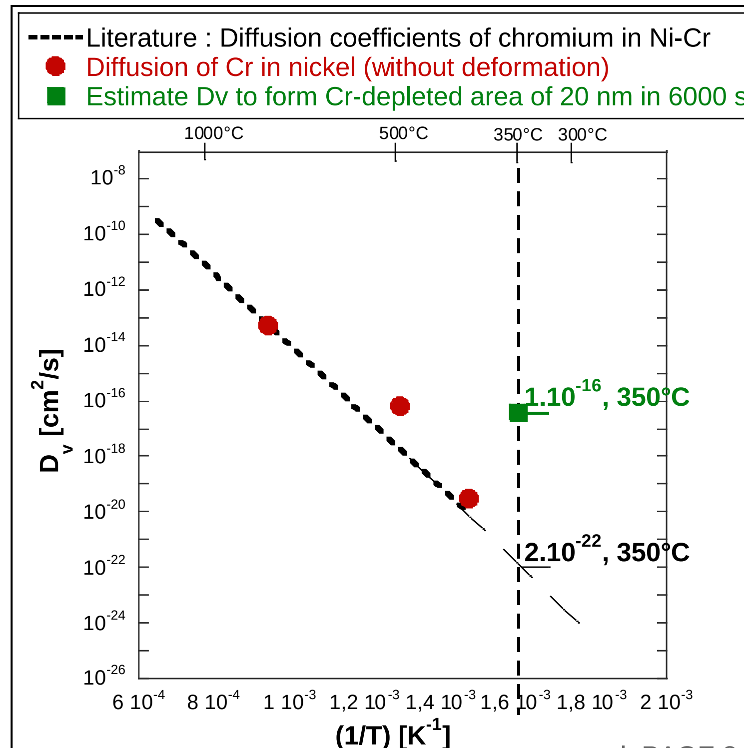
Secondary Ion Mass Spectrometry (SIMS)



Fick's solution equation

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

Diffusion treatments	D $[cm^2/s]$
787°C, 5h	$(5\pm1).10^{-14}$
500°C, 30h	$(7\pm2).10^{-17}$
405°C, 1616h	$(3\pm2).10^{-20}$



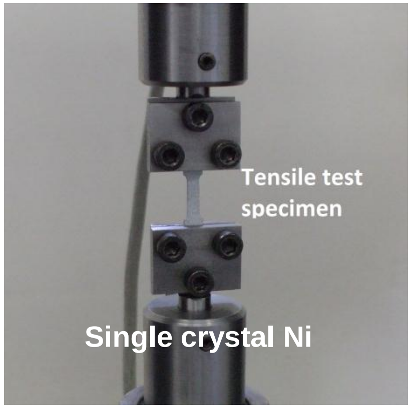
⇒Results consistent with literature data.
⇒Volume diffusion is not sufficient to explain the asymmetric Cr depletion observed in literature *(20 nm in 6000 sec)*.

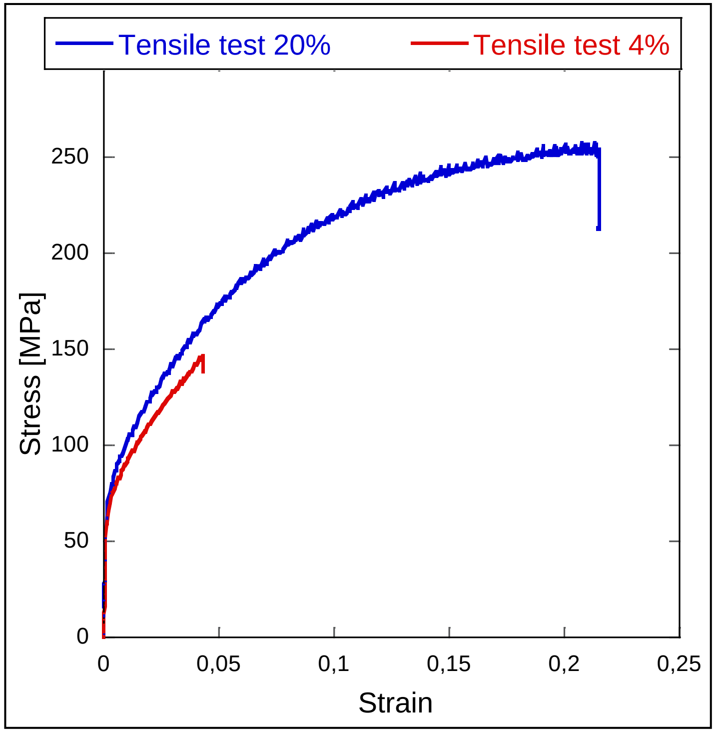
Effect of pre-deformation ?

DIFFUSION IN PRE-DEFORMED MATERIAL

Aim : influence of pre-deformation on diffusion coefficient

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





Samples conditions	Diffusion treatments	D [cm^2/s]
Non-deformed	30h, 500°C	$(7\pm2).10^{-17}$
ε_p = 4 %	30h, 487°C	$(3,5\pm0,9).10^{-17}$
ε_p = 20 %	30h, 487°C	$(3\pm3).10^{-17}$

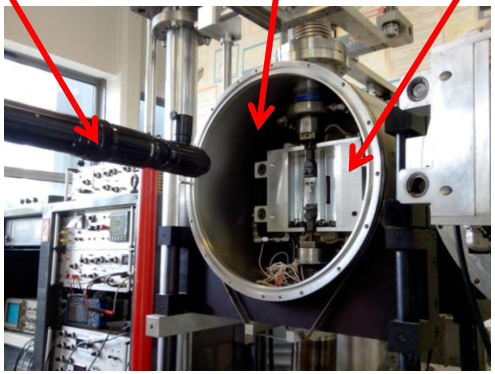
⇒No significant effect of the pre-deformation on chromium diffusion.
⇒Pre-deformation can not explain the asymmetric oxidation and depletion along grain boundary.

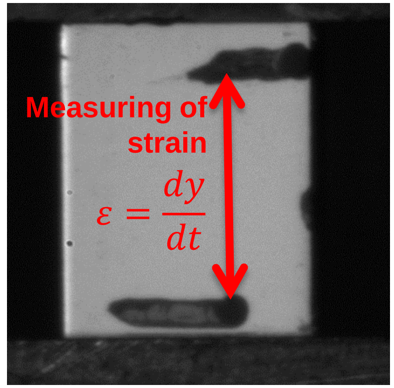
Coupling of diffusion and deformation ?

COUPLING DIFFUSION-PLASTICITY

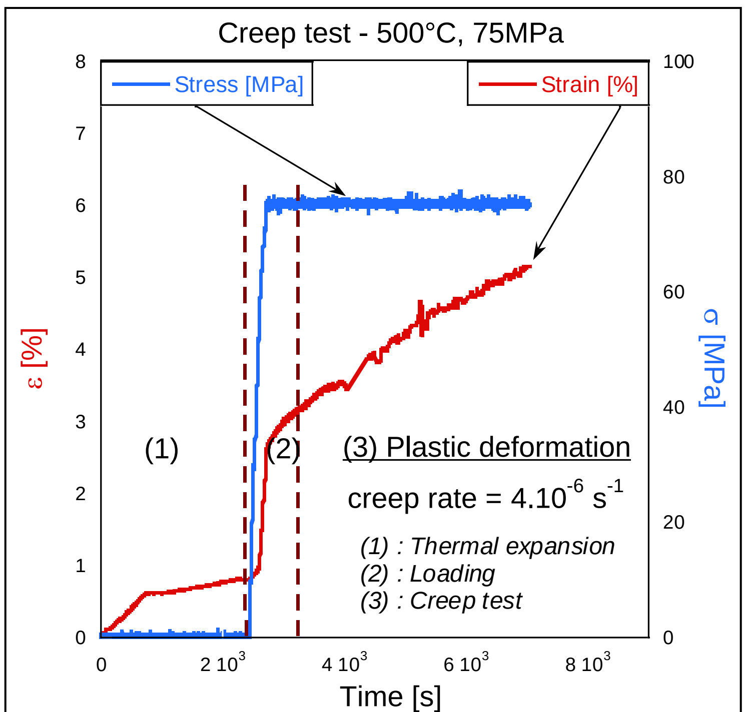
Aim : the effect of dislocations mobility

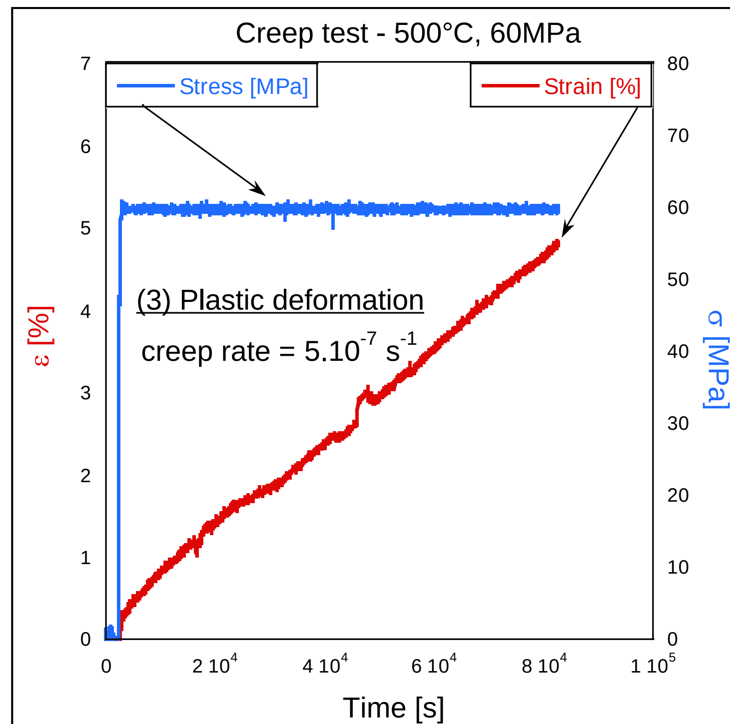
Camera Chamber Furnace





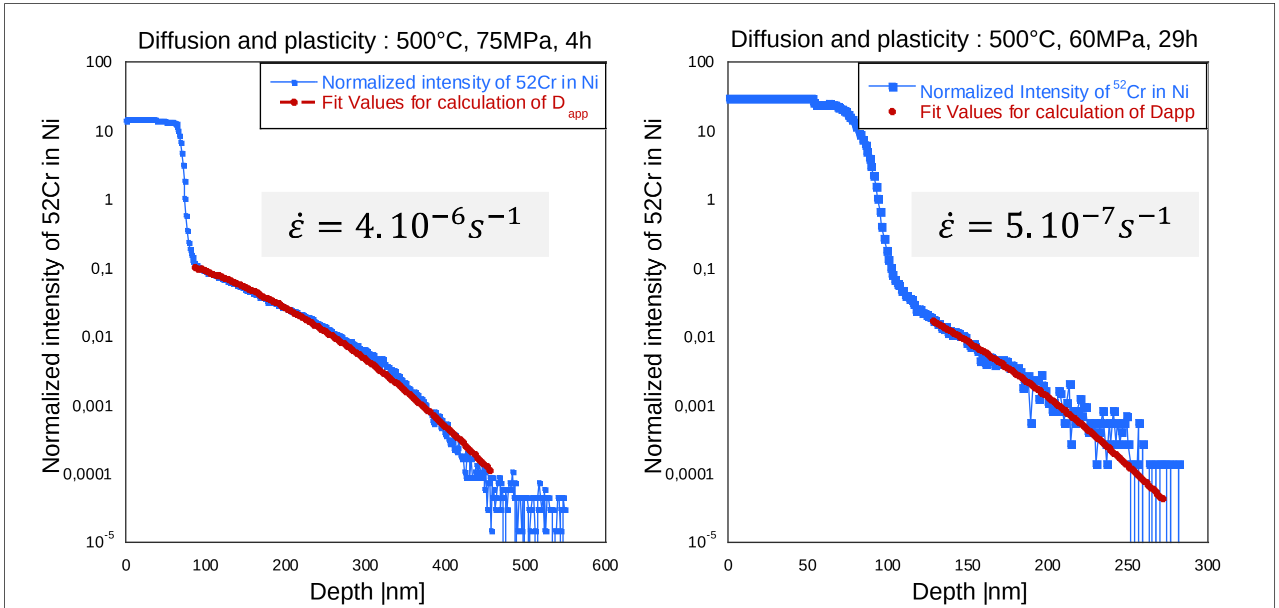
Creep tests
500°C, 60 MPa, 29h *Creep rate :* $\mathbf{5.10^{-7} s^{-1}}$
500°C, 75 MPa, 4h *Creep rate :* $\mathbf{4.10^{-6} s^{-1}}$





COUPLING DIFFUSION-PLASTICITY

The effect of dislocations mobility at 500°C



Analytic solution [1] :

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

Experiments	D_{app} [cm^2/s]
500°C, 60 MPa, 29h *Creep rate :* $\mathbf{5.10^{-7} s^{-1}}$	$2{,}8.10^{-16}$
500°C, 75 MPa, 4h *Creep rate :* $\mathbf{4.10^{-6} s^{-1}}$	$6{,}4.10^{-15}$
(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 :* $\dot{\varepsilon} = \rho . b . v$).

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

[1] A. D. Le Claire, and A. Rabinovitch. "A Mathematical Analysis of Diffusion in Dislocations ." Journal of Physics C: Solid State Physics 15 (1982): 3455-71.

COUPLING DIFFUSION-PLASTICITY

Aim : the effect of dislocations mobility at 350°C

Creep law :

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

$S = \text{constant}$

$\Delta H \sim 66 kcal/mol$

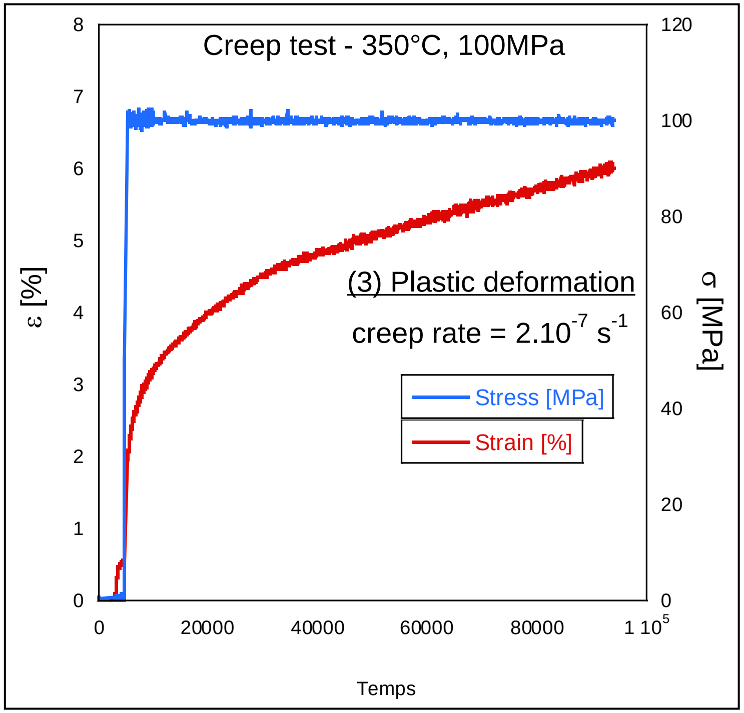
$\beta = 1.10^{-7}$

Estimation of stress at 350°C

$$\sigma_{350°C} = 41 + 5\ln\left(\frac{\dot{\varepsilon}_{350°C}}{\dot{\varepsilon}_{500°C}}\right) + \sigma_{500°C}$$ **en MPa**

Same creep rate : $\dot{\varepsilon}_{500°C} = \dot{\varepsilon}_{350°C}$	
T = 500°C	$\sigma_{500°C} = 60\text{MPa}$
T = 350°C	$\boldsymbol{\sigma_{350°C} = 100\text{MPa}}$

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



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

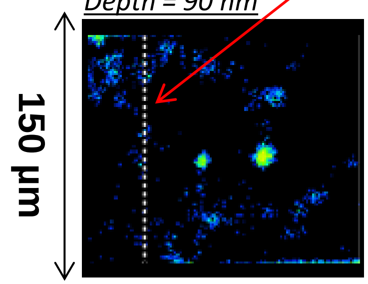
Measurement of diffusion coefficient of chromium after the creep test at 350°C.

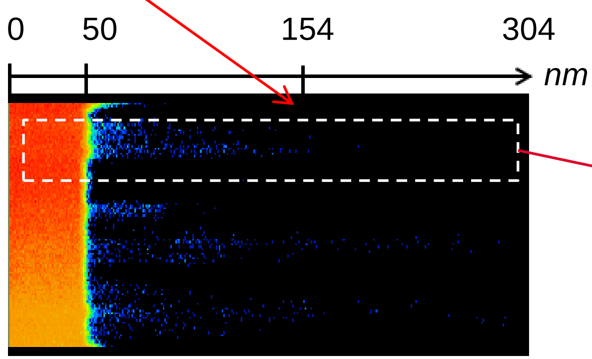
[1] *Garofalo Franck « Fundamentals of Creep and Creep rupture in Metals » 1965 , p.104*

COUPLING DIFFUSION-PLASTICITY

Aim : the effect of dislocations mobility at 350°C

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

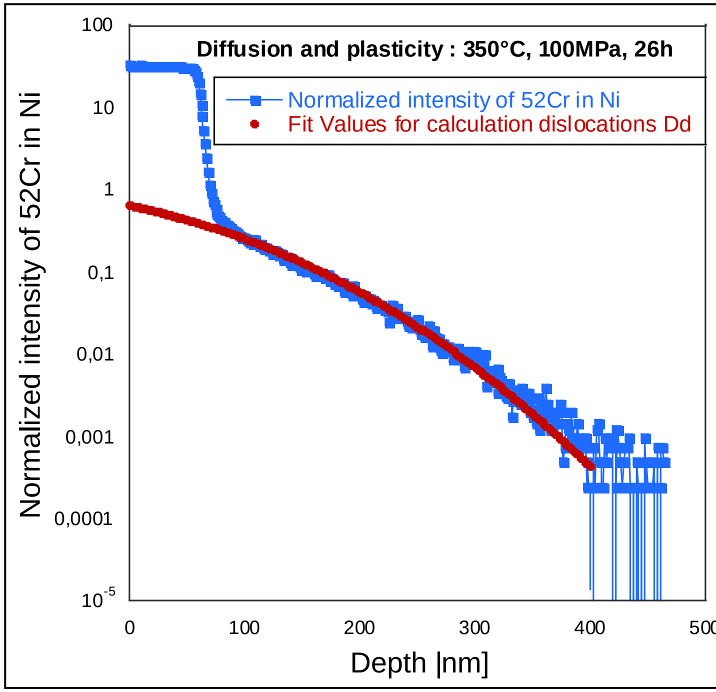




SIMS crater area

Cr deposit

Chromium diffusion in nickel up to 300 nm of depth.



Optical image

Experiment	D [cm²/s]
350°C, 100 MPa, 26h *Creep rate :* $\mathbf{2.10^{-7}s^{-1}}$	7,4.10^{-16}
(Without plasticity) at 350°C (extrapolated value)	1,9.10^{-22}

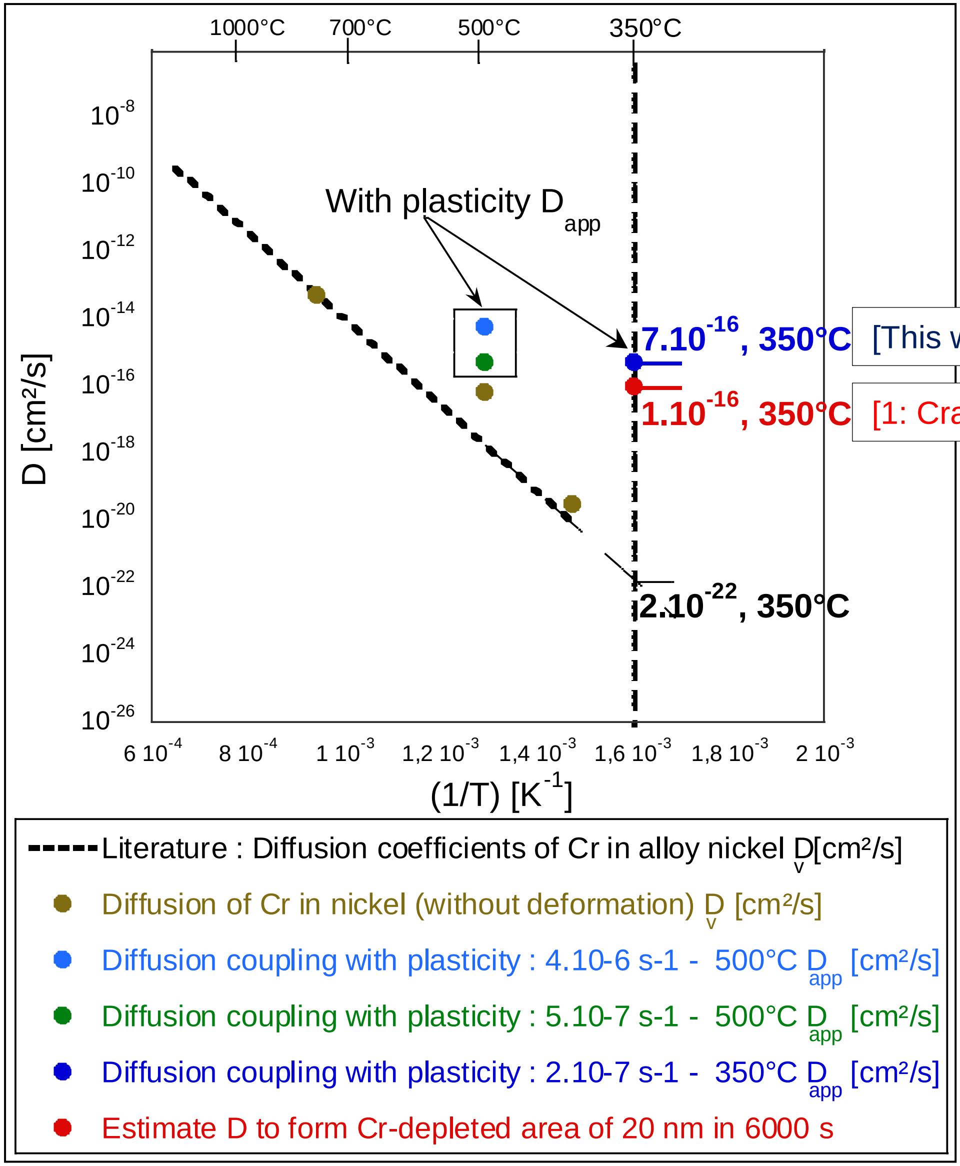
500°C, 60 MPa, 29h *Creep rate :* $\mathbf{5.10^{-7}s^{-1}}$	2,8.10^{-16}

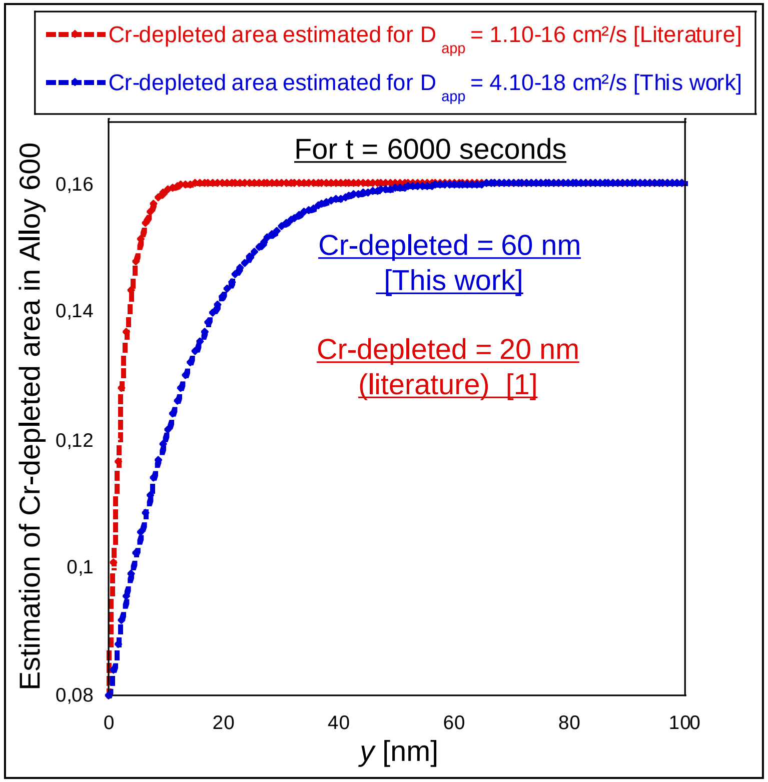
⇒ Plasticity can accelerate the chromium diffusion at low temperatures.

⇒This phenomenon seems to depend on the creep rate.

COUPLING DIFFUSION-PLASTICITY

Summary : Cr-depleted area at the SCC crack tip





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

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

CONCLUSIONS AND PROSPECTS

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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