



## Corrosion behaviour of 9-12%Cr ferritic steels and 18-25%Cr austenitic steels in supercritical CO<sub>2</sub>

F. Rouillard, T. Furukawa, B. Duprey, G. Moine, J. C. Ruiz, P. Venditti

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# CORROSION BEHAVIOUR OF 9-12%CR AND 17-22%CR STEELS IN S-CO<sub>2</sub>



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**B. DUPREY, G. MOINE**

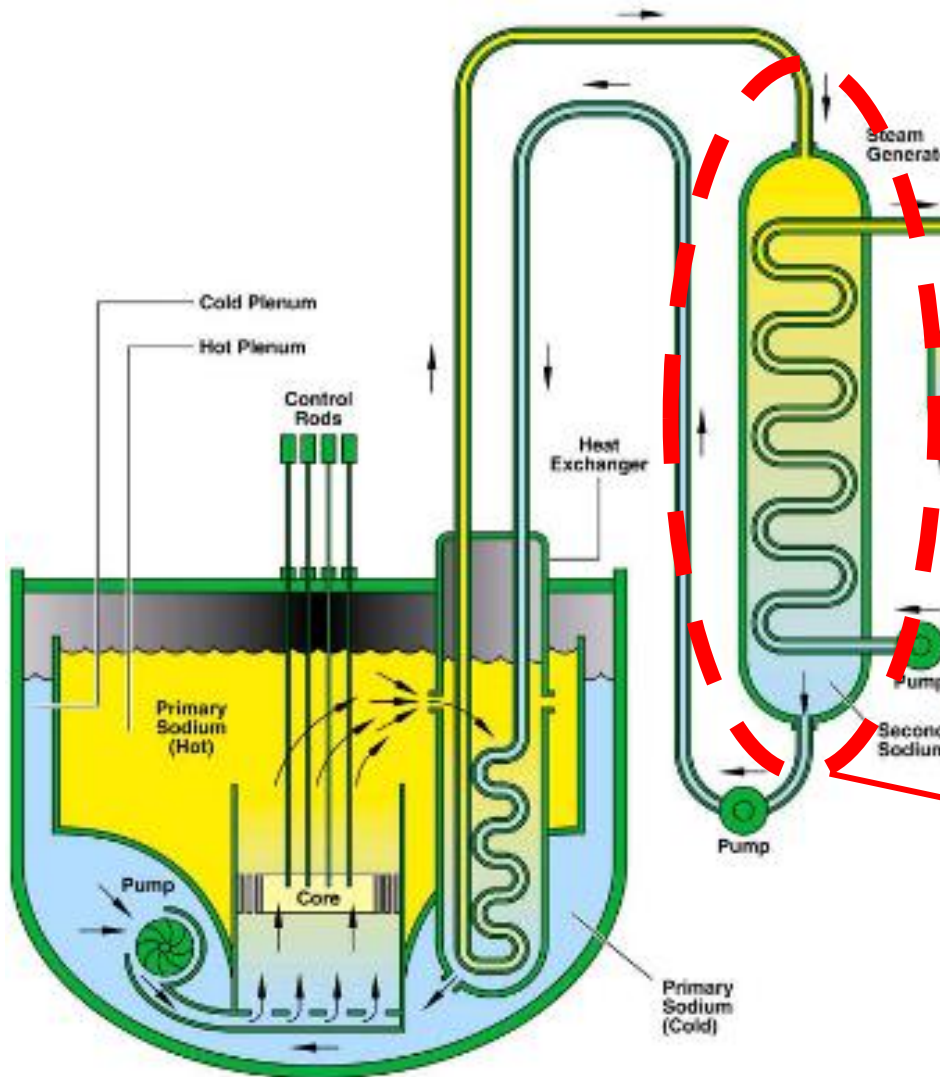
CEA/DEN/DANS/DPC/SCCME/LECNA (SACLAY)

**JC RUIZ, P. VENDITTI**

CEA/DEN/ DTCD/SPDE/LPSD (MARCOULE)

**TMS2016**  
145<sup>th</sup> Annual Meeting & Exhibition

# CONTEXT : S-CO<sub>2</sub> BRAYTON CYCLE COUPLED TO SFR



## Advantages of S-CO<sub>2</sub> Brayton cycle :

- Avoids the Sodium-Water reaction
- Increases the compactness of the cycle
- Increases the cycle efficiency

International collaboration on S-CO<sub>2</sub> cycle coupled to Sodium Fast Reactor:  
France, USA, South Korea, Japan

**T : 400 - 550 °C**  
**P : 80 - 250 bar**

# CORROSION IN CO<sub>2</sub> ?

## FEEDBACKS FROM FORMER CO<sub>2</sub>-COOLED NUCLEAR REACTORS (60-80'S)

CO<sub>2</sub> + 1% vol CO + up to a few hundreds of vpm H<sub>2</sub>O, H<sub>2</sub>, CH<sub>4</sub>  
Pressure = 3 – 4 MPa

RECOMMANDATIONS :

Grade	Mild steels	9Cr-1Mo steel	Austenitic steels (316L type)	Austenitic steels (310 type) or nickel base alloys
T <sub>max</sub>	< 350 °C	< 450 °C	< 660 °C	> 660 °C

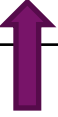




T<sub>max</sub> : strongly dependent on gas composition, steel composition, surface finish, ...

[D.R. Holmes, R.B. Hill, and L.M. Wyatt, Corrosion of steels in CO<sub>2</sub>, British Nuclear Energy Society, Reading University (1974)]

**9-12%Cr Ferritic/Martensitic steels**

**17-22%Cr Austenitic steels**

	Cost	Thermal expansion coefficient between 20°C and 600°C ( $10^{-6}/^{\circ}\text{C}$ )	Thermal conductivity (W/m°C) at 500°C
<b>F/M steel (T91)</b>	0.6	12.5	29
<b>Austenitic steel (316L)</b>	1	18.2	21
	 - 40%	 - 25%	 + 25%

❑ 9-12% Cr Ferritic/Martensitic steels : Physical Properties and Cost +

❑ 17-22% Cr Austenitic steels : Intrinsic Corrosion Behaviour +

## **Objectives : Technical exchanges for comprehensive understanding of corrosion mechanisms in S-CO<sub>2</sub>**

In both labs :

- more than **350** corroded samples
- **11** steel grades (F/M and austenitic steels)
- **5** temperatures from 400 °C to 600 °C
- **4** CO<sub>2</sub> pressures : from 0.1 MPa to 25 MPa
- Up to **8000 h** of exposure time
- Use of various experimental facilities (loop, autoclave, one-through furnace) : study of their impact ...

# STUDIED MATERIALS

F-M steels

Austenitic steels

Weigth %	%Cr	%Ni	%C	%Si	Other	Feedback
T91 (CEA)	9	0.2	0.1	0.3	Mo : 1%	SG in Fossil Power Plants
VM12 (CEA)	11	0.4	0.1	0.3	W : 2% Co : 2%	New generation of 9-12Cr steel
P122 (JAEA)	11	0.4	0.1	0.3	W : 2% Cu : 1%	New generation of 9-12Cr steel
316L (CEA)	17	11	0.02	0.6	Mo : 2%	« classic » austenitic steel
316FR (JAEA)	17	11	0.01	0.6	Mo : 2% N : 0.1%	« nuclear » grade austenitic steel
253MA (CEA)	21	11	0.1	1.6	Ce : 0.04%	Steel optimized for HT corrosion



## CORROSION FACILITIES

High pressure S-CO<sub>2</sub>

Loop, JAEA



One-through autoclave, CEA

Atmospheric pressure CO<sub>2</sub>

CEA



## Metallic coupons (25\*15\*1 mm)

« Industrial » CO<sub>2</sub> purity in JAEA and CEA tests (99,995%) :

- H<sub>2</sub>O < 200 vpm
- O<sub>2</sub> < 50 vpm



**CORROSION  
OF 9-12CR F/M  
STEELS**

□ The « short-term » corrosion kinetics of usual 9-12%Cr steels

- ✓ Oxidation rate =  $f(T, P)$
- ✓ Carburisation rate =  $f(T, P)$

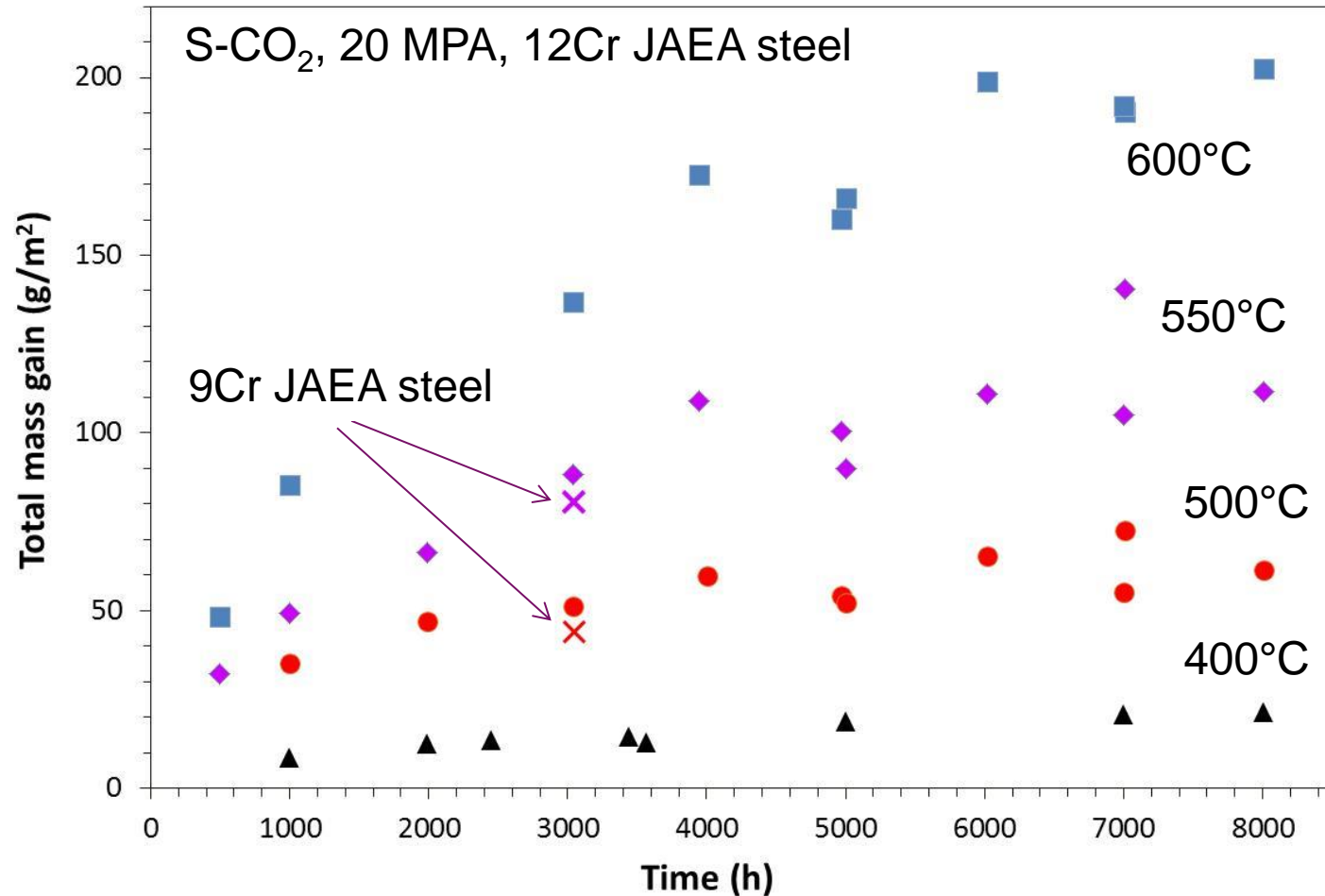


**Proposed corrosion model : « Available Space Model »**

- ✓ Influence of surface finish
- ✓ Influence of  $O_2$  impurities in  $CO_2$

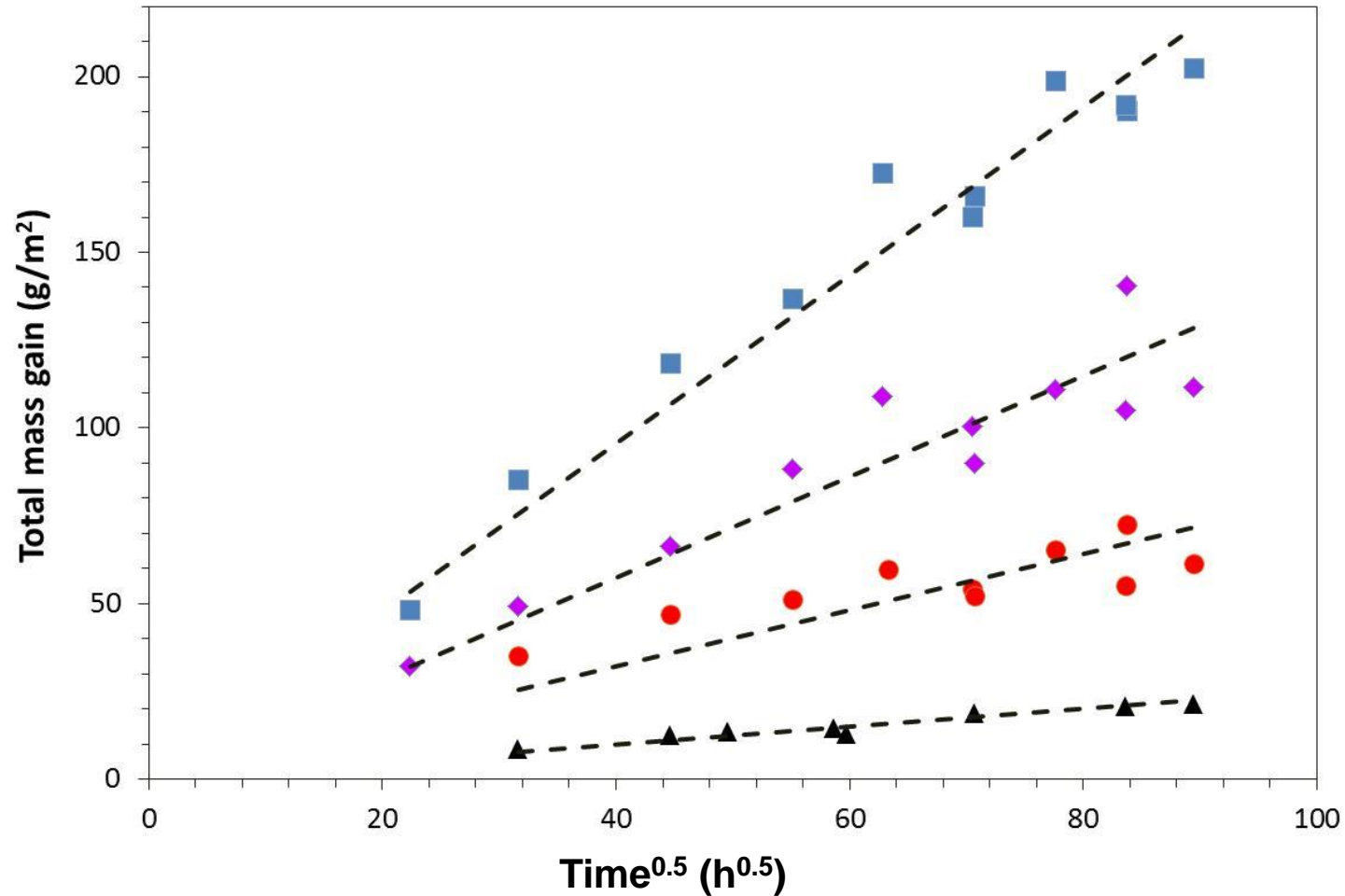
PhD thesis of S. Bouhieda  
(2009-2012)

# CORROSION KINETICS OF 9-12CR JAEA STEELS



Same corrosion kinetics for 9 and 12Cr steel (JAEA)

# CORROSION KINETICS OF 9-12CR JAEA STEELS

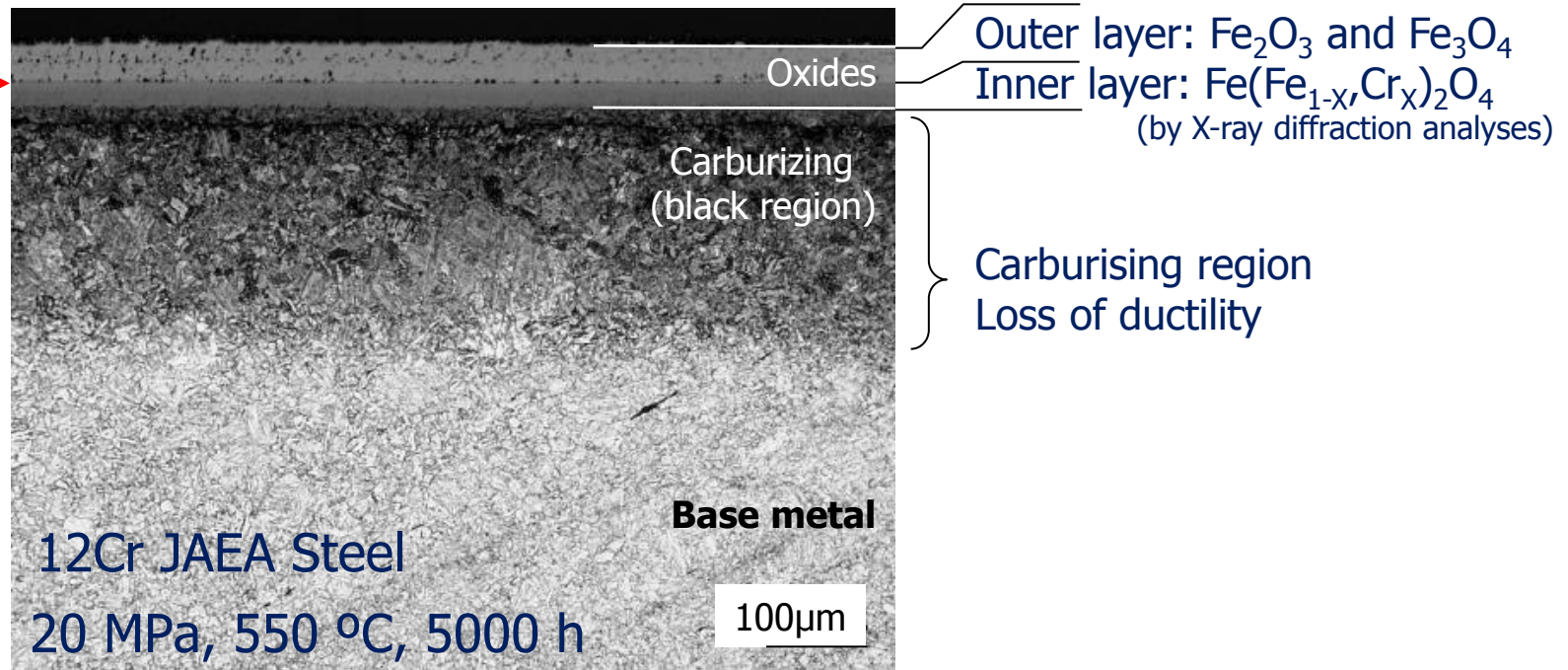


- ☐ Parabolic kinetics
- ☐ What does happen to the samples ?

# CORRODED SURFACE UNDER CO<sub>2</sub>

Mass gain = Oxidation AND Carburisation

Original  
surface  
of base  
metal →



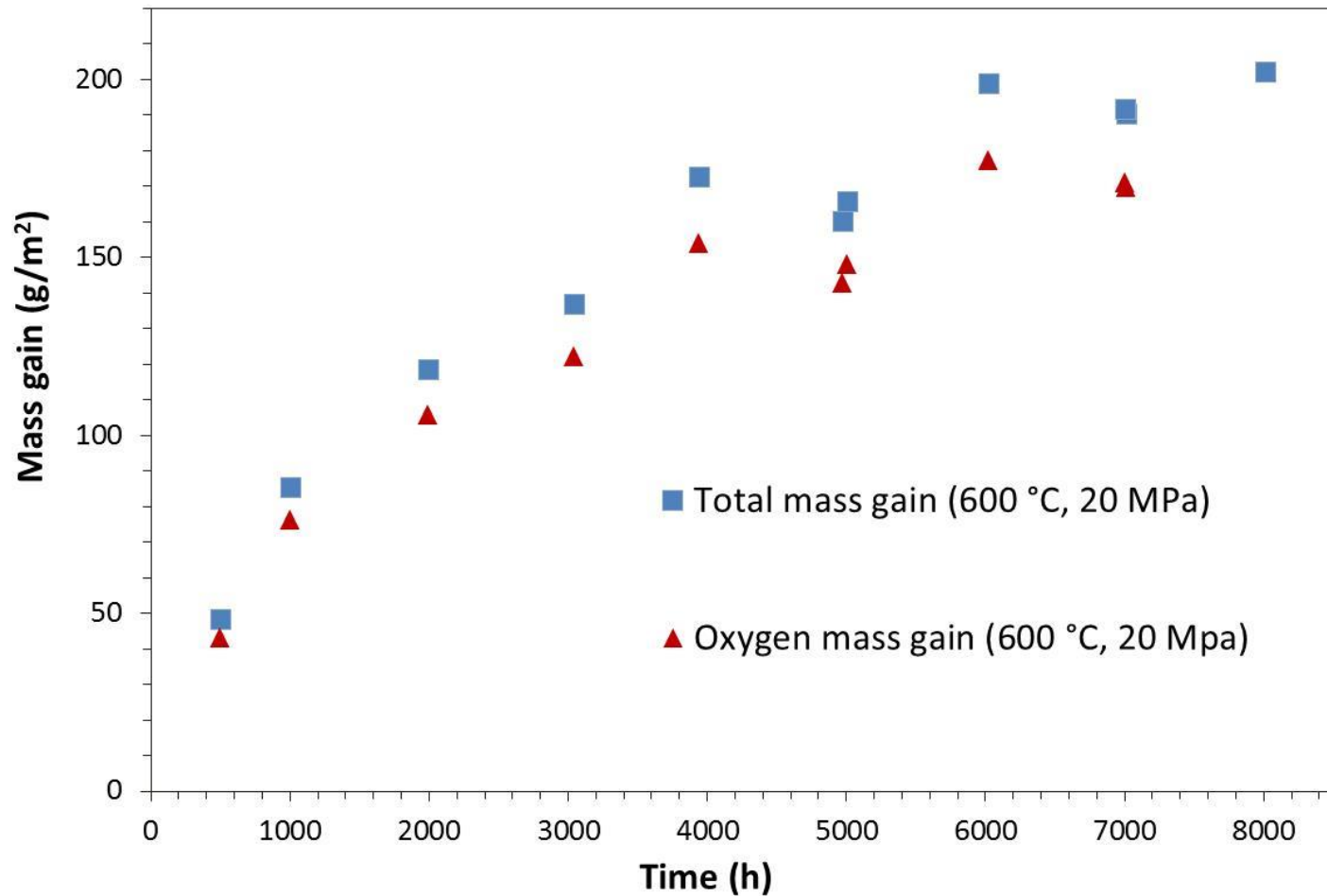
What are the proportion of the mass gain induced by :

- Oxidation : Mechanism ? Driving Force ?
- Carbon transfer : Mechanism Driving Force ?

# **Oxidation mechanism of 9-12Cr steels in CO<sub>2</sub>**



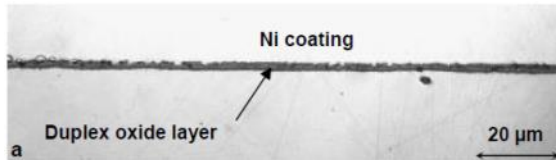
# OXIDATION KINETICS



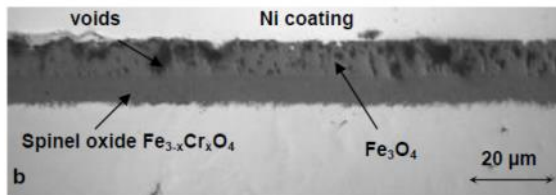
Parabolic oxidation rate = diffusion controlled

# OXIDE FEATURES

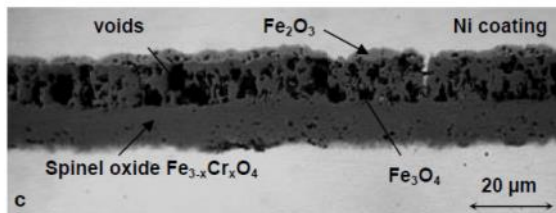
9Cr CEA steel in CO<sub>2</sub>,  
550 °C, 0.1 MPa



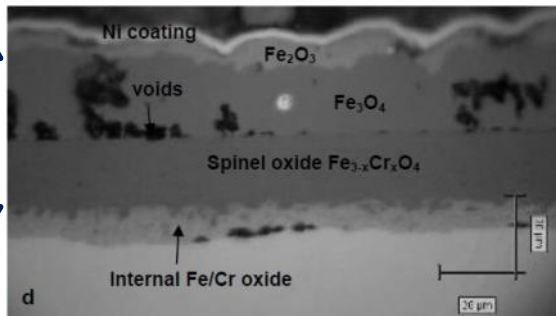
1 h



110 h



322 h



1000 h

- **Duplex** oxide layer : Fe oxides (Fe<sub>3</sub>O<sub>4</sub> + Fe<sub>2</sub>O<sub>3</sub>) and Fe/Cr oxide (Fe<sub>2.3</sub>Cr<sub>0.7</sub>O<sub>4</sub>)

- The oxide/oxide interface = **original** metallic surface (gold markers)

- $[Cr]_{\text{spinel}}(\text{mol/cm}^3) \sim [Cr]_{\text{substrate}}(\text{mol/cm}^3)$   
**Chromium does not diffuse and is oxidized in the substrate.**

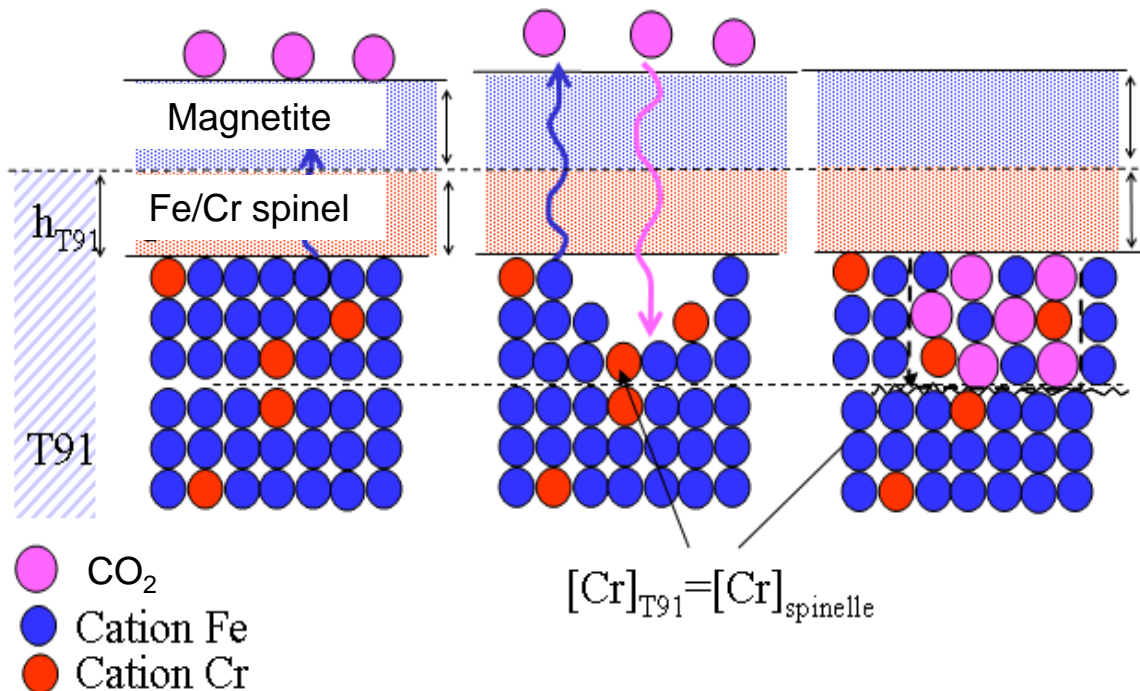
- **Carbon** enrichment at the O/M interface (GDOES analysis)

- Fe<sub>2.3</sub>Cr<sub>0.7</sub>O<sub>4</sub> grows at the metal/oxide interface and Fe<sub>3</sub>O<sub>4</sub> at the oxide/gas interface  
(Taylor et al. OxMet. 1980 : Tracers experiment).

- **Parabolic** growth rate

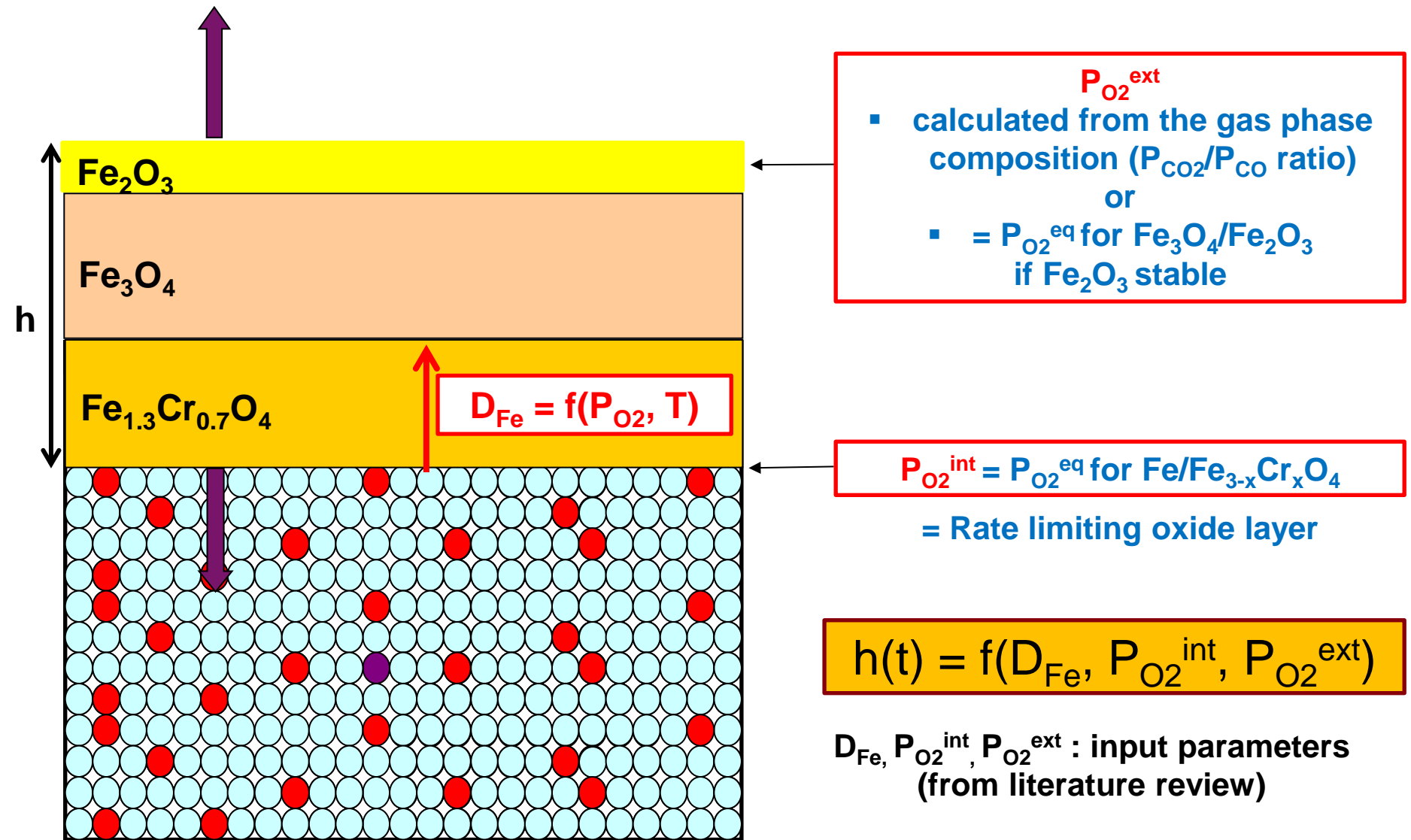
Oxidation model ?

## « Available Space Model » or « void-induced oxide growth »

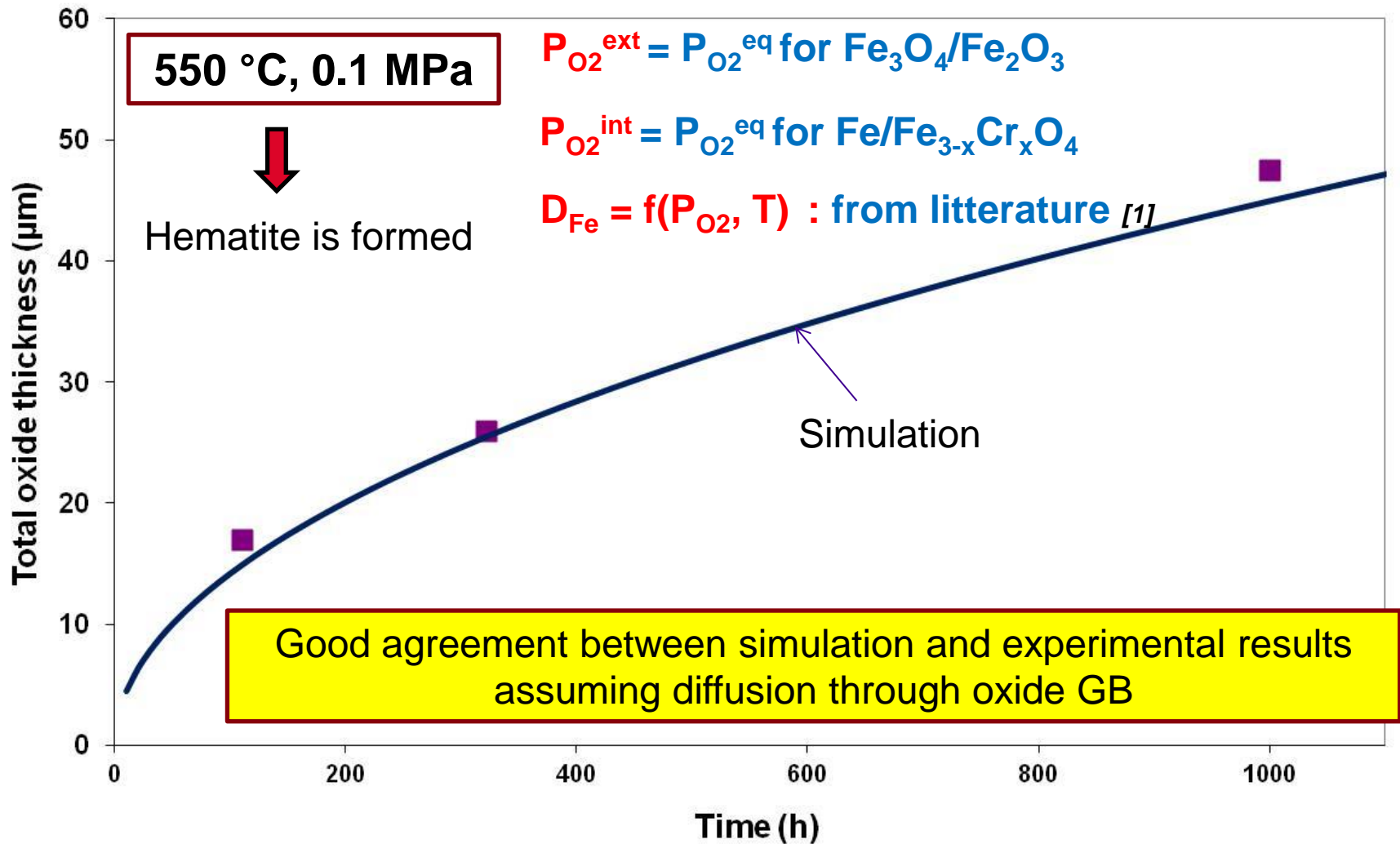


1. Outwards diffusion of Fe cations
  - ✓ Injection of vacancies at the O/M interface
  - ✓ **Formation of voids**
2. CO<sub>2</sub> diffusion to the O/M interface
  - through high diffusion paths (nanochannels) in the oxide layer
  - Atkinson et al. Rev. Mod. Phys. 57 (1985)*
3. Filling of the voids by new oxide formation

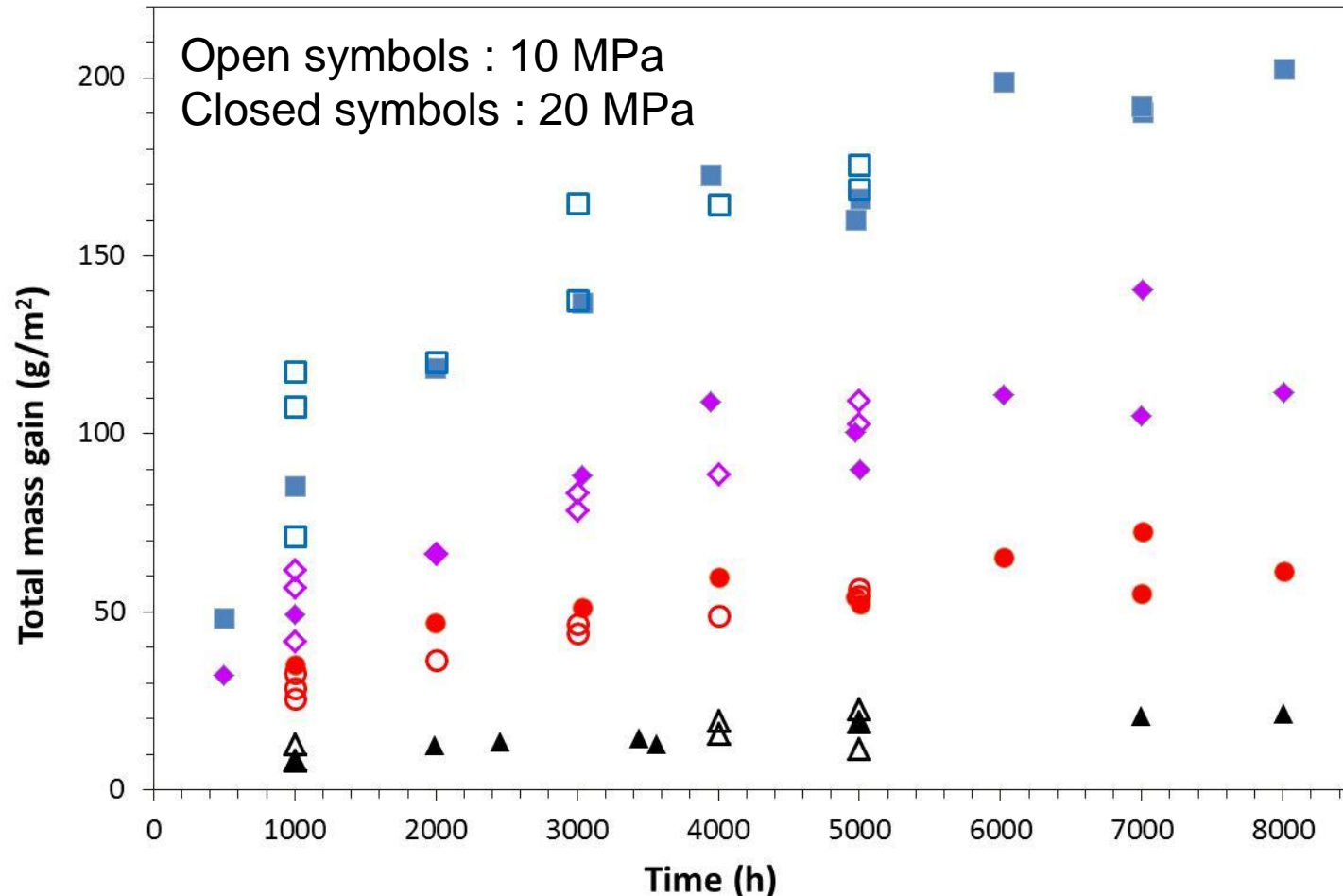
# OXIDE KINETICS MODELING AND SIMULATION



# OXIDE GROWTH MODELING AND SIMULATION



# EFFECT OF $P_{CO_2}$ ON OXIDATION

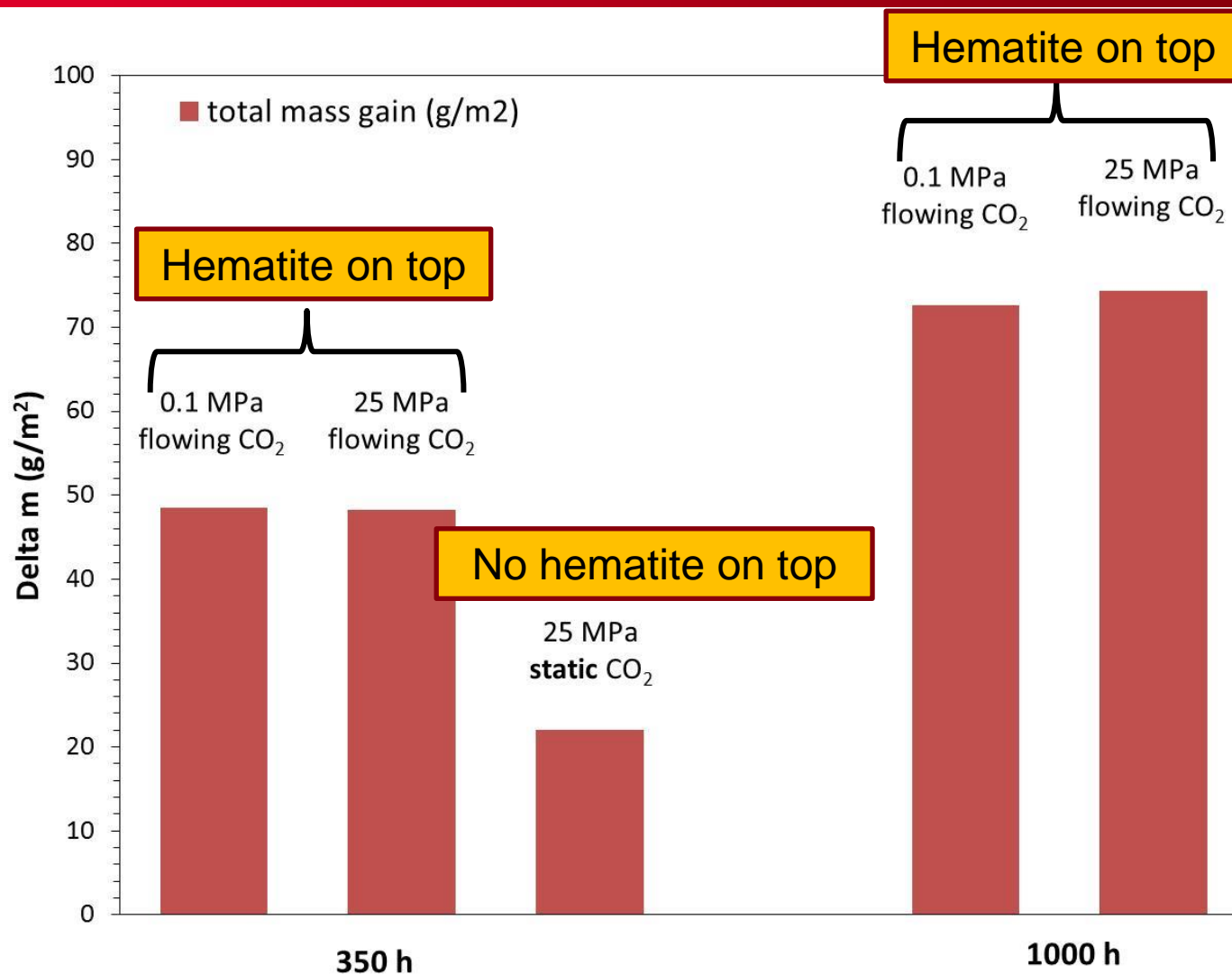


No detectable effect of  $P_{CO_2}$  between 10 and 20 MPa

With higher  $P_{CO_2}$  difference : 0.1 MPa and 25 MPa ?

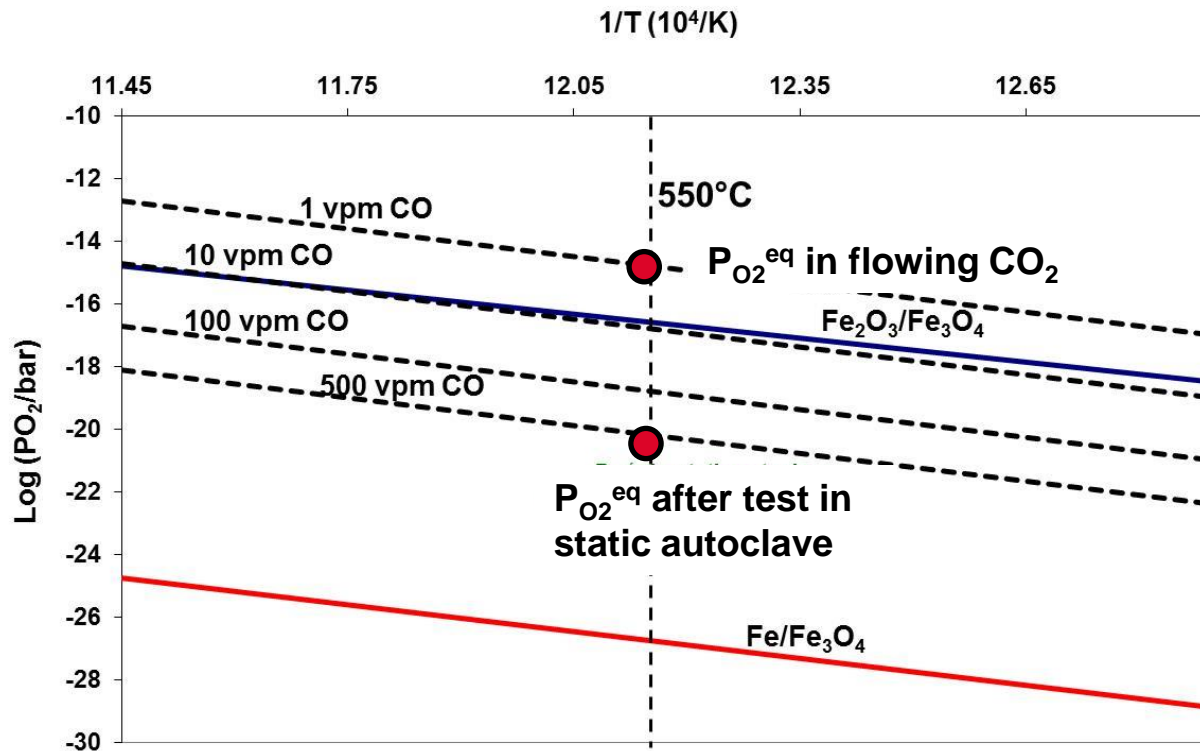


# EFFECT OF $P_{CO_2}$ ON OXIDATION



**The oxidation rate does not depend on  $P_{CO_2}$ :** the external driving force for oxide growth  $P_{O_2}^{ext}$  is « buffered » by the presence of hematite

# FORMATION OF $\text{Fe}_2\text{O}_3$ ?

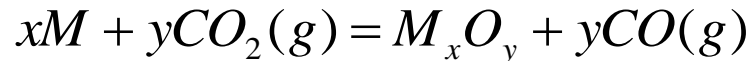


The formation of  $\text{Fe}_2\text{O}_3$  is controlled by the  $P_{\text{CO}_2}/P_{\text{CO}}$  ratio in the gas phase :



$$P_{\text{O}_2}^{\text{ext}} = \left( \frac{K * P_{\text{CO}_2}}{P_{\text{CO}}} \right)^2$$

$\text{CO}(\text{g})$  in the gas phase is mainly formed from oxidation of the metallic substrate :



As a consequence, the driving force for oxidation  $P_{\text{CO}_2}/P_{\text{CO}}$  is driven by any **CO accumulation** encountered along the flow :

- Depends on the hydrodynamics encountered in the channel or the tube
- Oxidation kinetics in static autoclave < Oxidation kinetics in tube furnace with gas flow

# Carburisation mechanism of 9-12Cr steels in CO<sub>2</sub>

What is the carburisation kinetics ?  
Is there any effect of  $P_{\text{CO}_2}$  ?

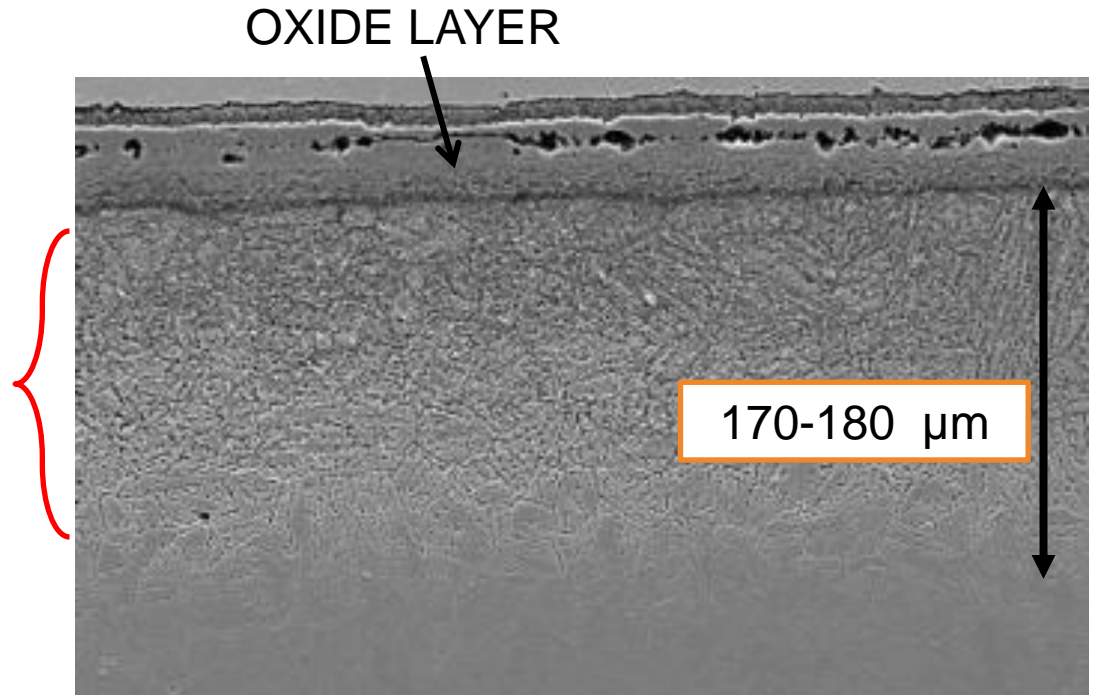
Could we model the carburisation  
propagation into the steel ?

Why does the steel  
carburise ?

What are the driving  
force and the  
mechanism for carbon  
transfer ?

## CARBURISED ZONE :

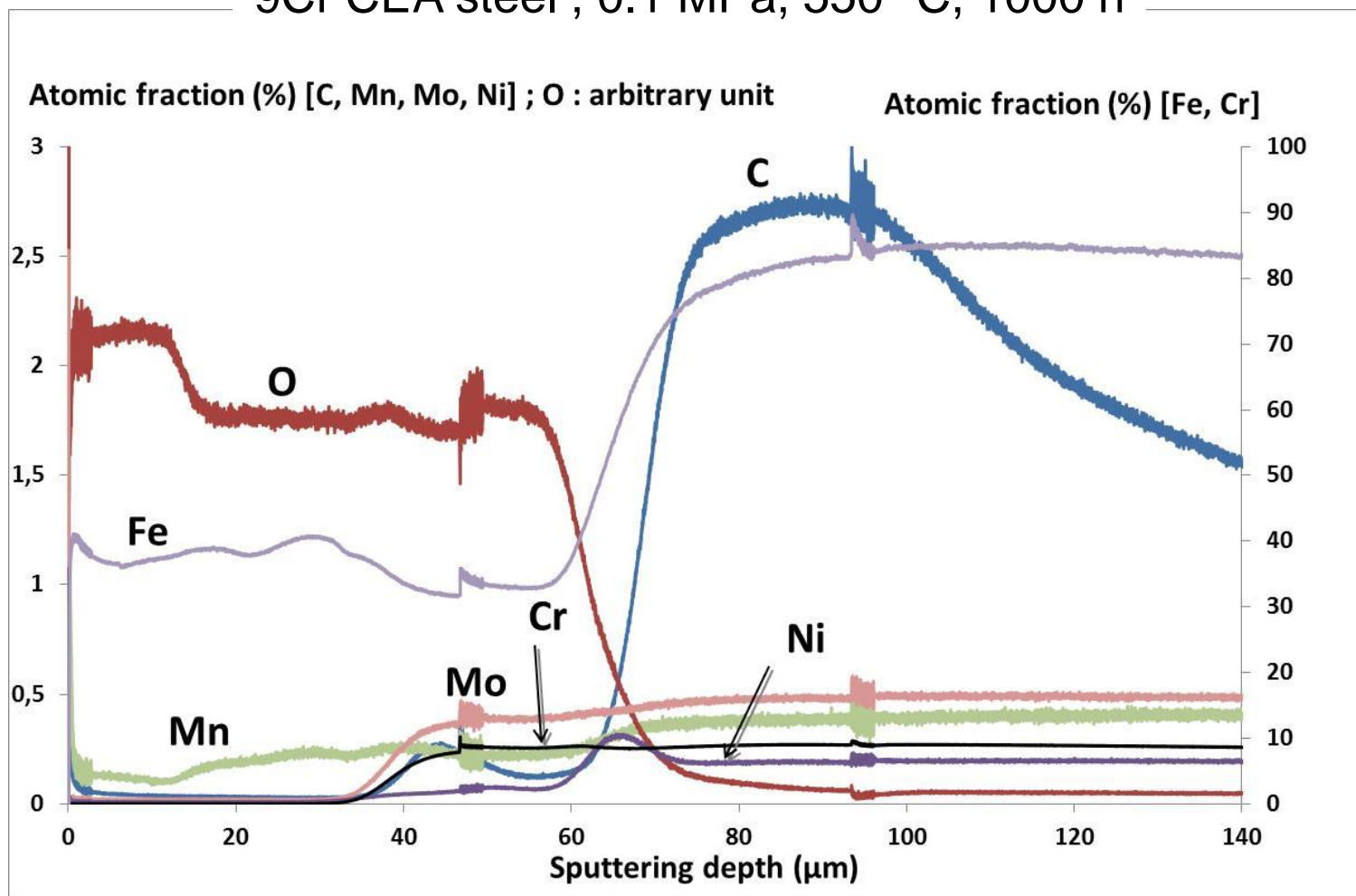
On martensitic laths  
and old primary austenitic GB



9Cr CEA steel , 0.1 MPa, 550 °C, 1000 h

# CARBON PROFILE BY GDOES

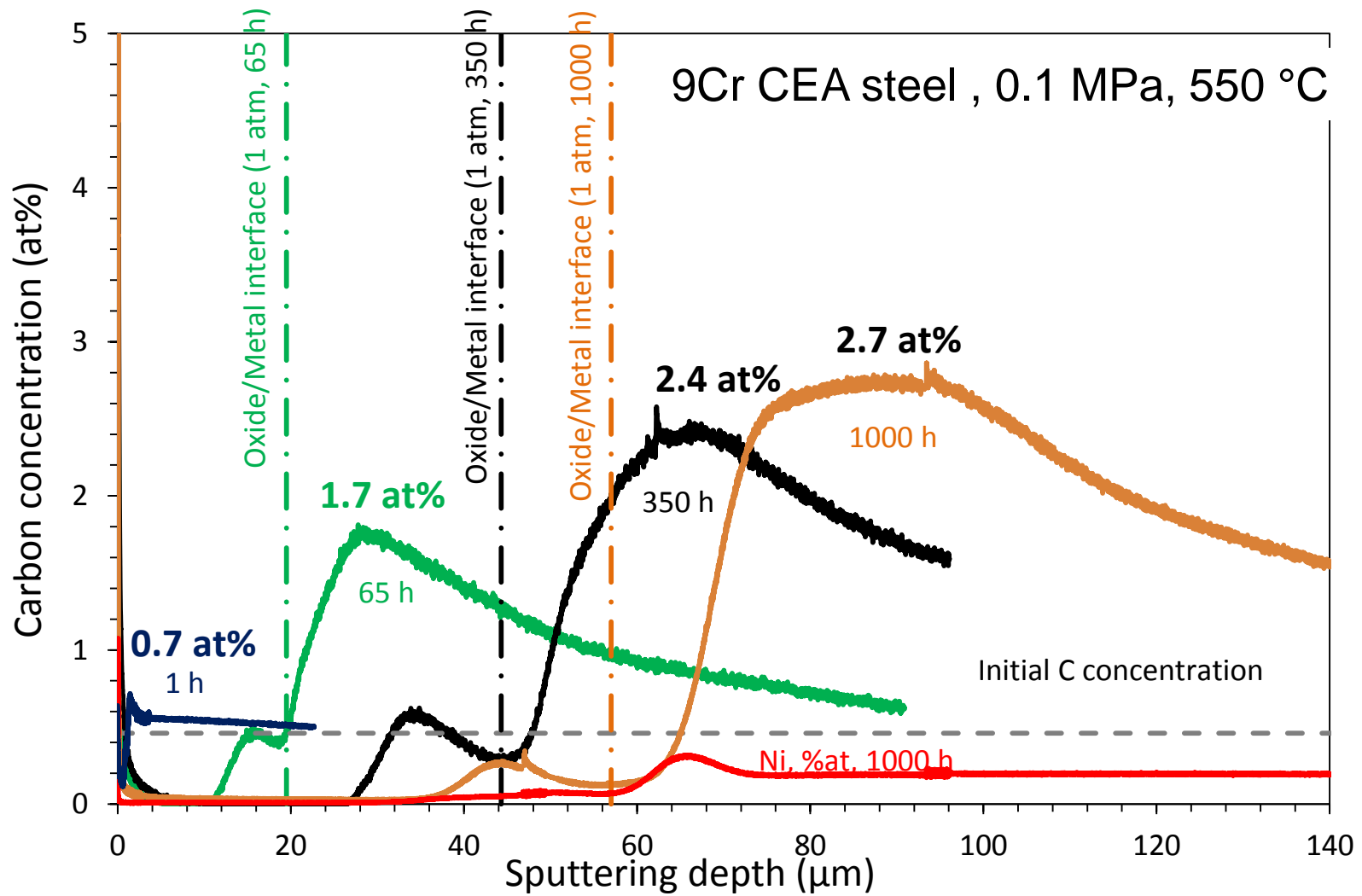
9Cr CEA steel , 0.1 MPa, 550 °C, 1000 h



- ❑ Strong carbon enrichment below the O/M interface
- ❑ No carbon in magnetite. Only small content in the spinel oxide layer



# NON STEADY STATE CARBURISATION



□ %C at the O/M interface increases with time  
= Non steady state carburisation

# CARBURISATION PROPAGATION INTO THE SUBSTRATE

- ❑ Carburisation depth kinetics = Parabolic ...
- ❑ ... even if increase of %C at the oxide/metal interface with time ?
- ❑ The carburisation depth kinetics is :
  - lower than expected by simple C diffusion in ferrite
  - higher than expected by C diffusion in ferrite and reaction with all Cr atoms to form carbides (according to Wagner theory)



Similar results than observed by Young et al.

*Non-steady state carburisation of martensitic 9 – 12%Cr steels  
in CO<sub>2</sub> rich gases at 550 °C,  
Young et al. Corrosion Science 88 (2014)*

## YOUNG'S CARBURISATION MODEL ASSUMPTIONS

- ❑ Normal diffusion of solute carbon within the metal phase, coupled with rapid carbide precipitation and **equilibrium partitioning** of carbon between the metal and precipitate phases (Thermodynamic calculations)
- ❑ Slow rate of carbon transfer :

$$v_c = \alpha(C^{eq} - C^s)$$

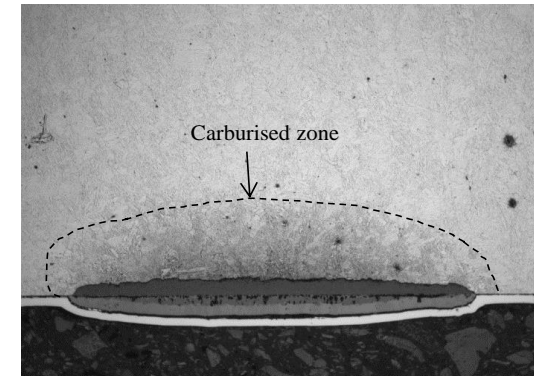
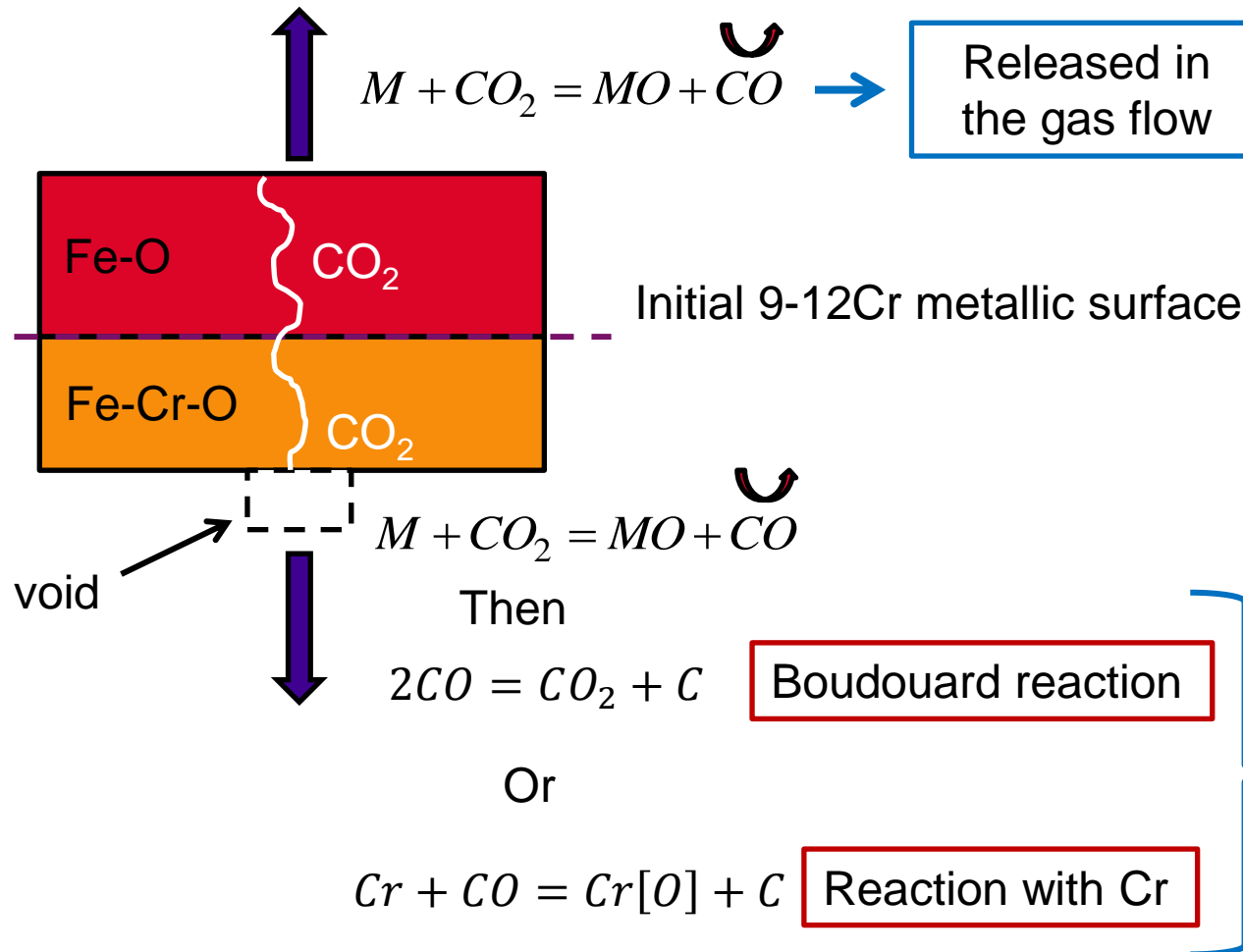
With  $C^{eq}$  the concentration of carbon in equilibrium with **the carbon activity of the gas phase**



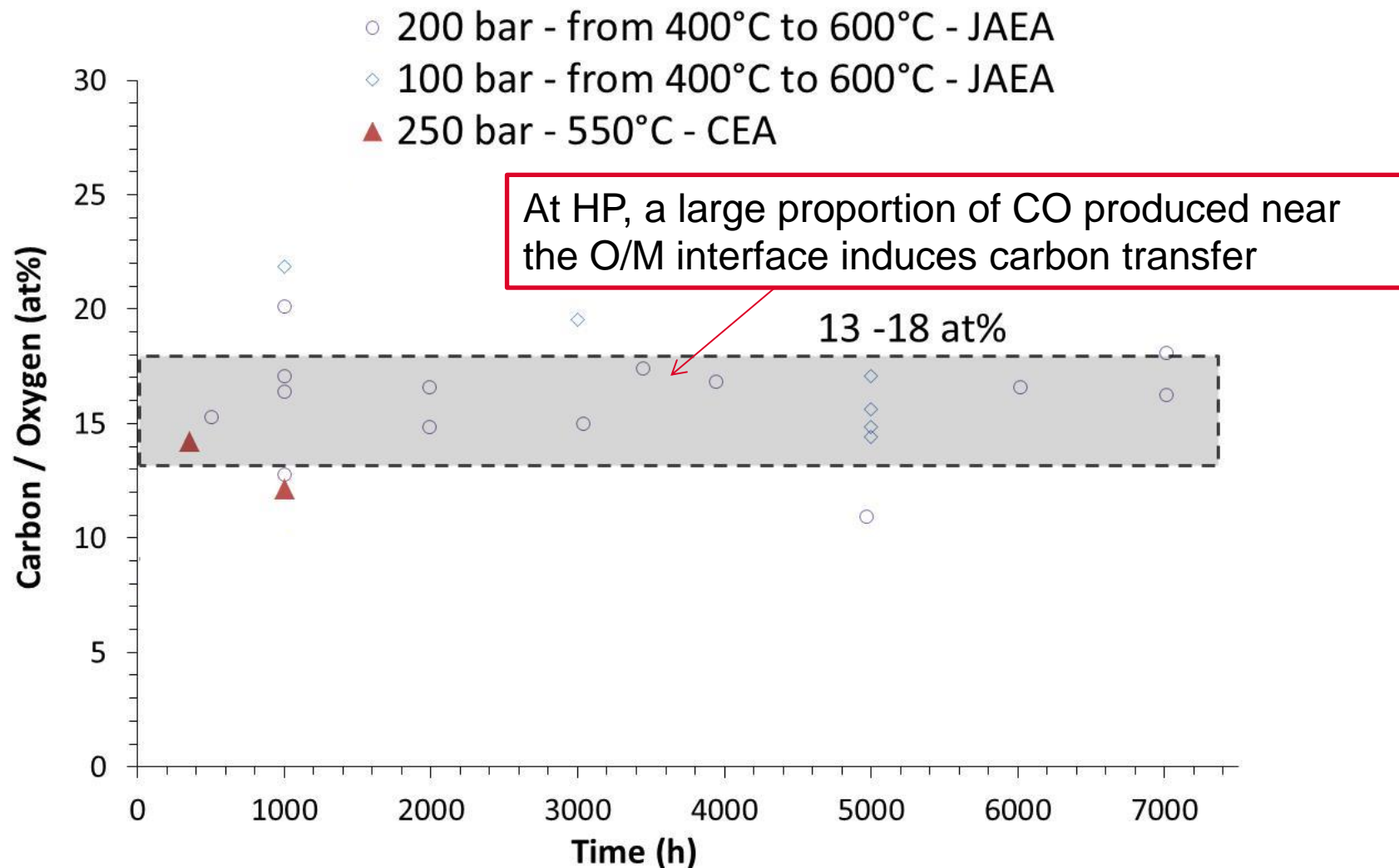
There are still questions about the carbon transfer mechanism and its rate expression

# CARBON TRANSFER

We believed that the carbon transfer is **intrinsically** induced by the way the steel oxidizes = the « Available Space Model » allows carbon reaching the O/M interface easily

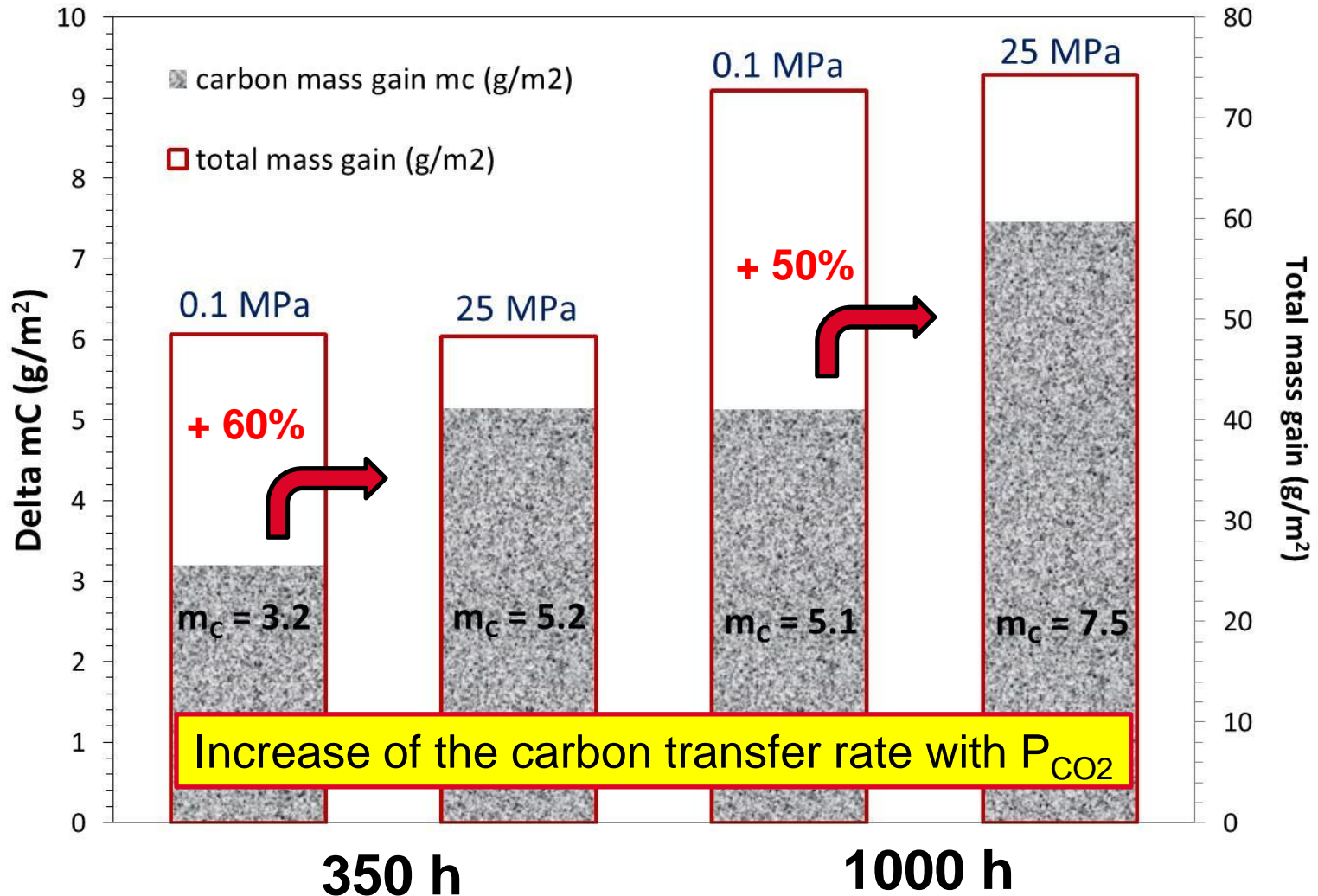


# CARBON TRANSFER



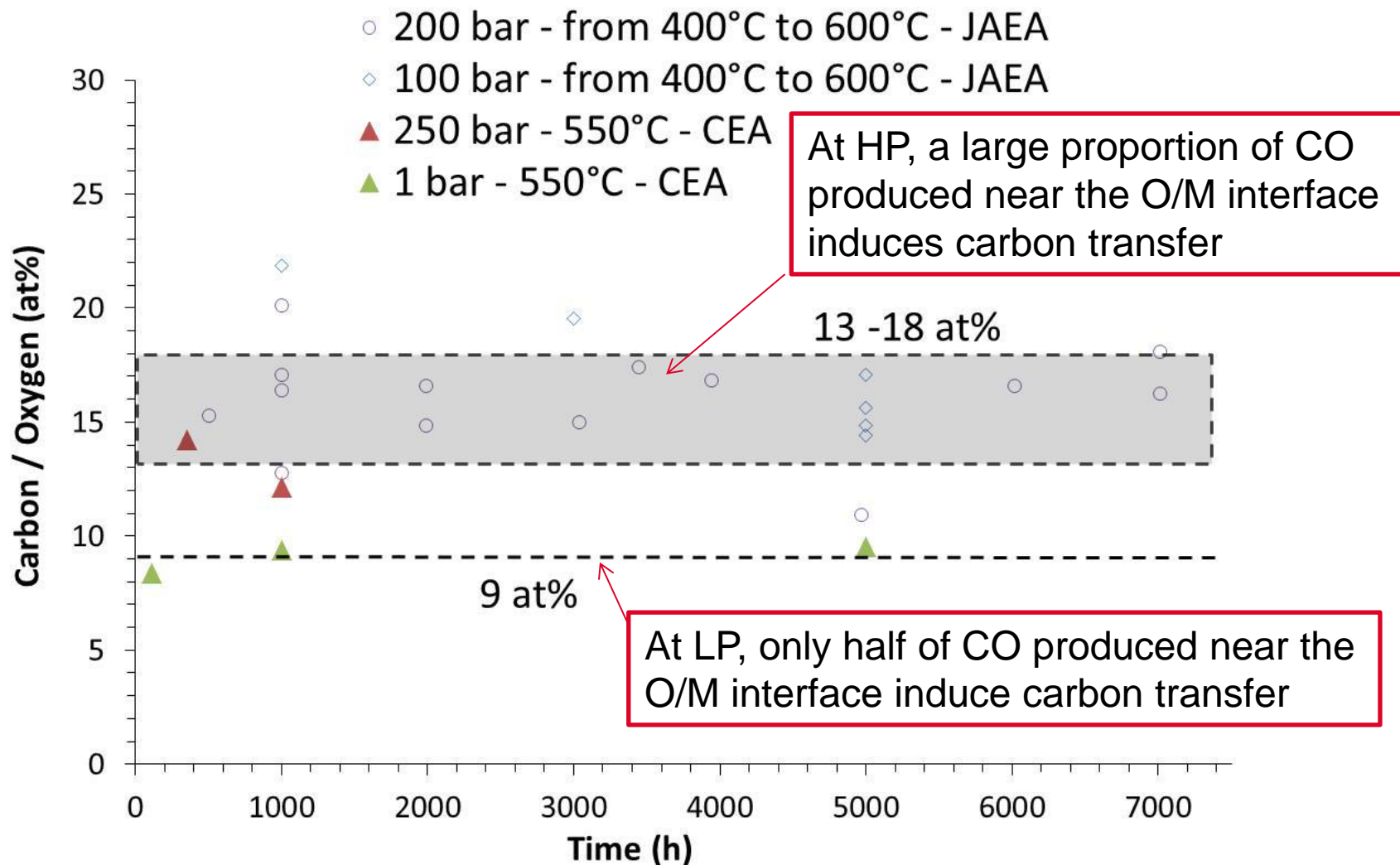
# INFLUENCE OF $P_{CO_2}$ ON CARBON TRANSFER

❑ No « detectable » influence of  $P_{CO_2}$  between 10 and 20 MPa ...  
... but higher carbon transfer rate detectable when increasing from 0.1 to 25 MPa

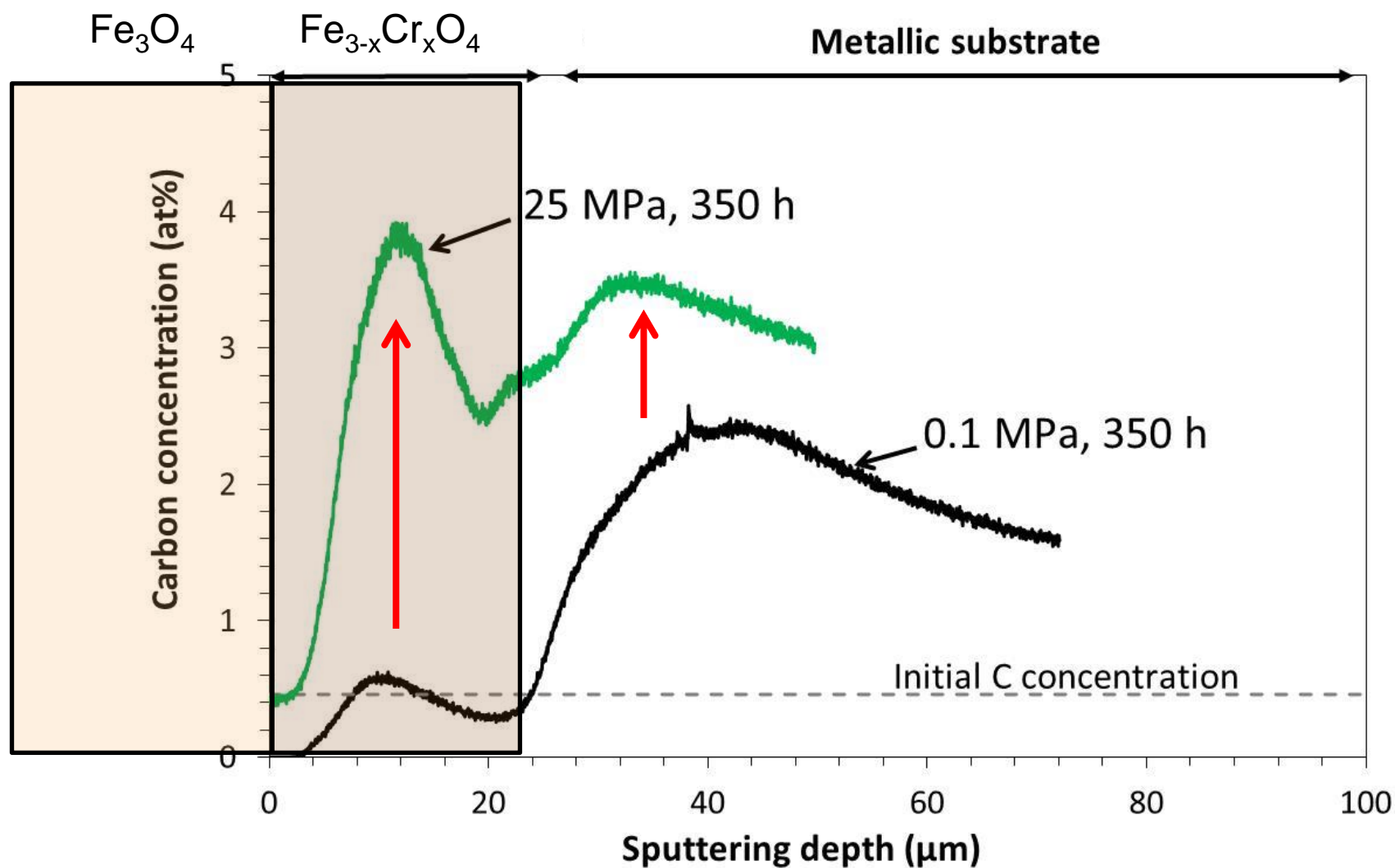




# INFLUENCE OF $P_{CO_2}$ ON CARBON TRANSFER



# INFLUENCE OF $P_{CO_2}$ ON CARBON TRANSFER



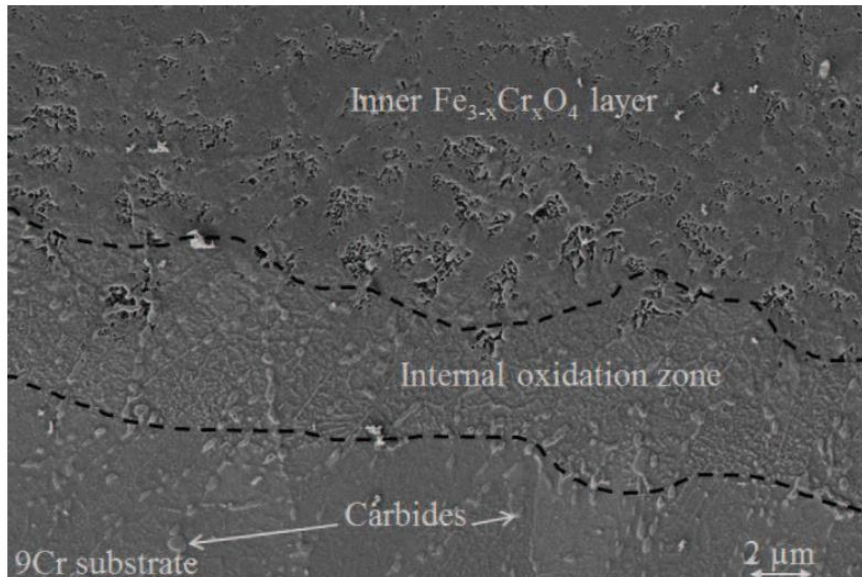
- ☐ %C at the O/M interface increases
- ☐ %C in the inner oxide scale increases



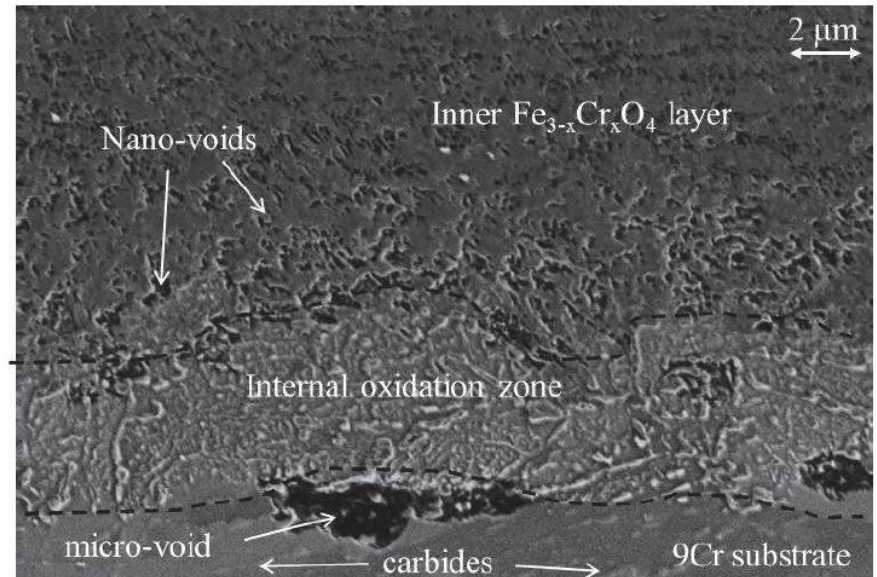
Carburisation rate increases

# INFLUENCE OF CARBURISATION ON THE INNER OXIDE MICROSTRUCTURE

T91, **0.1 MPa**, 550 °C, 350 h



T91, **25 MPa**, 550 °C, 350 h



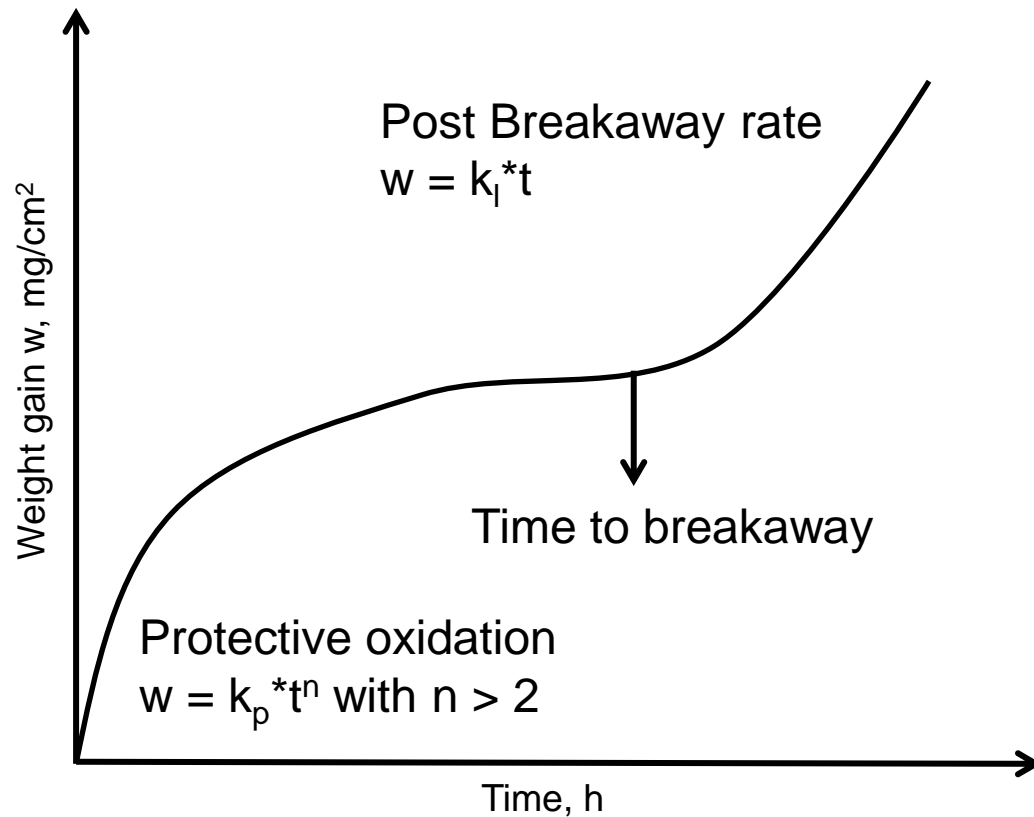
At high  $P_{CO_2}$  :

- ☐ Carbide density is higher below the inner spinel oxide scale
- ☐ The void density in the inner spinel oxide scale is higher

Voids are formed around former carbide precipitates while oxide grows inwards ?

Inner oxide porosity may depend on carbide density

# CAN « BREAKAWAY » OXIDATION BE POSSIBLE ON USUAL 9-12%CR STEELS ?

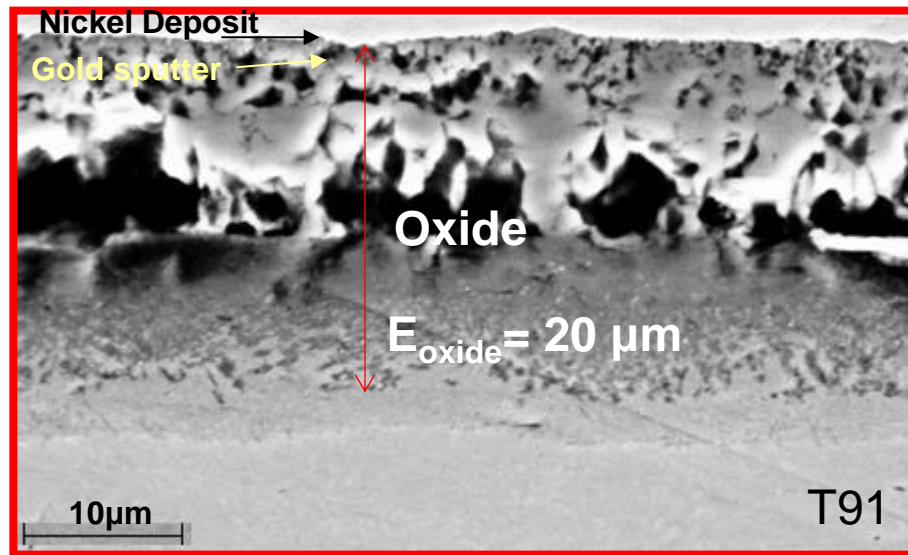


Feedbacks from  $\text{CO}_2$ -cooled nuclear reactors\*:

- Known for mild steels in S- $\text{CO}_2$  at  $T > 350^\circ\text{C}$
- But already observed on 9Cr steel in  $\text{CO}_2$  – 40 bar at  $550^\circ\text{C}$  (first in 1971)
- Favored at HP  $\text{CO}_2$  with high water vapour content ( $>0.1\%$ ) and low Si content

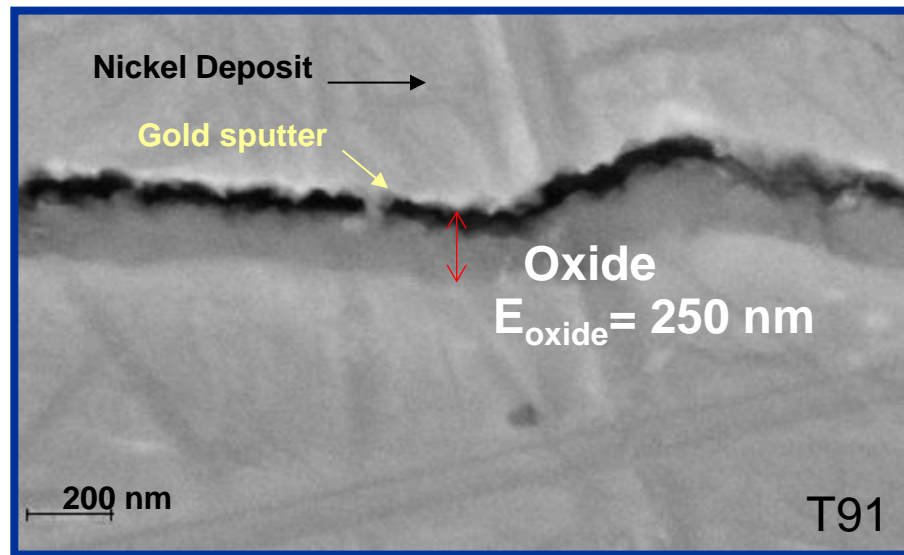
\*D.R. Holmes, R.B. Hill, and L.M. Wyatt, *Corrosion of steels in  $\text{CO}_2$* , British Nuclear Energy Society, Reading University (1974)

What is the exact mechanism ?  
Influenced by the carburisation state of the substrate ?

INFLUENCE OF CO<sub>2</sub> PURITY ON THE SURFACE OXIDE COMPOSITION« Industrial » CO<sub>2</sub> purity (with O<sub>2</sub> ~ 100 µbar)

Fast growing iron rich duplex oxide scale

%Cr oxide ~ 9 at%

High CO<sub>2</sub> purity (with O<sub>2</sub> ~ 1 µbar)

Slow growing chromium rich oxide scale

%Cr oxide ~ 20 at%

Still protective after 5000 h

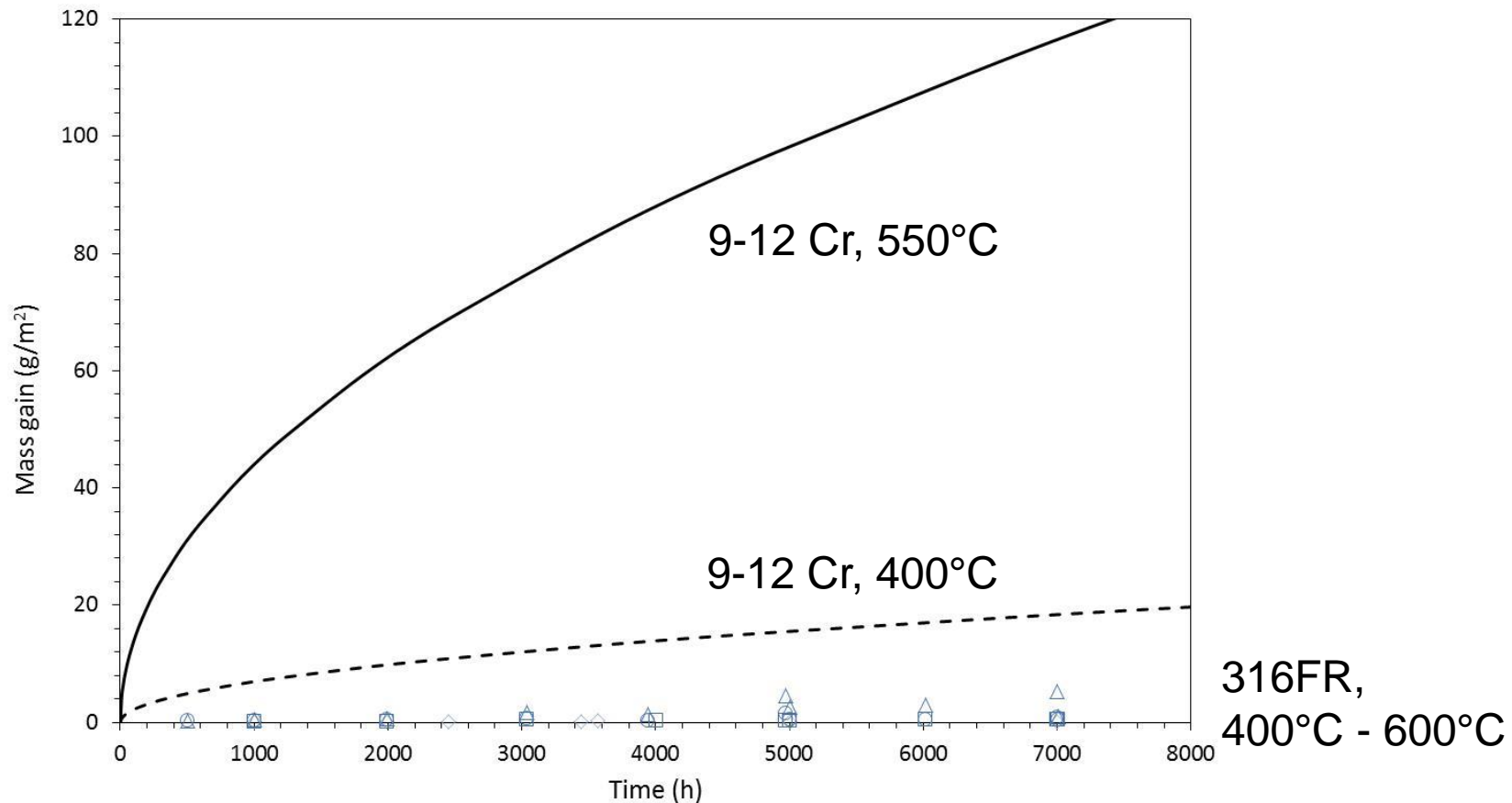
**Conclusions of PhD thesis (S. Bouhieda 2012) :**

- O<sub>2</sub> impurities (µbar) react first during the thermal ramp
  - Its level in CO<sub>2</sub> impacts on the surface oxide composition (Cr enrichment)
- The surface finish (mainly roughness?) impacts on the critical O<sub>2</sub> partial pressure

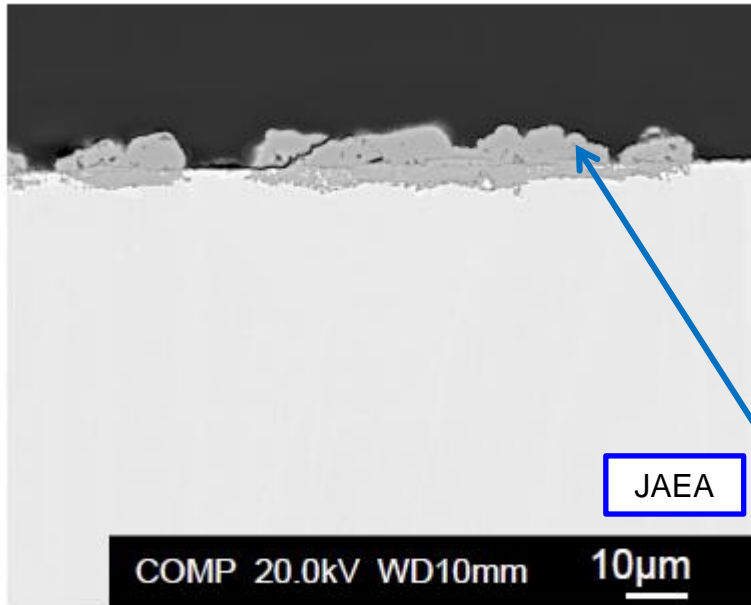
# **CORROSION MECHANISM OF 17-21CR AUSTENITIC STEELS**



# MASS GAIN KINETICS OF 316 AUSTENITIC STEEL

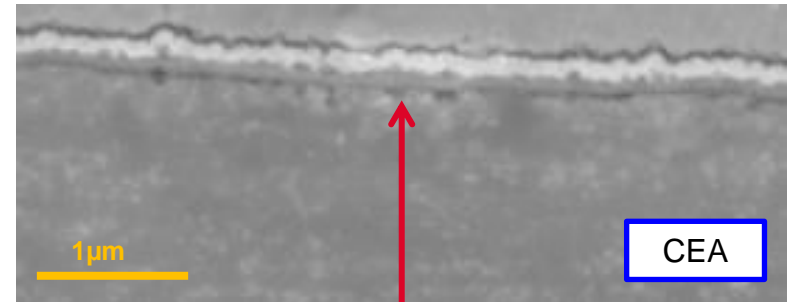


- ❑ Very low mass gain :  $\text{mass gain (316FR)} < 100 \times \text{mass gain (9-12Cr)}$
- ❑ No detectable effect of total pressure
- ❑ Larger mass gain is detectable after 5000 h at  $T = 600^\circ\text{C}$



316FR, 600 °C, 20 MPa, 4000 h

316L – 0.1 MPa – 550°C – 1000 h



< 200 nm

Formation of thin « protective » Cr rich oxide scale and thick nodules of duplex oxide scale (as on 9-12Cr steel but higher %Cr)

The « short-term » resistance of Cr rich austenitic steels is evaluated by its ability to form thin Cr rich oxide scale

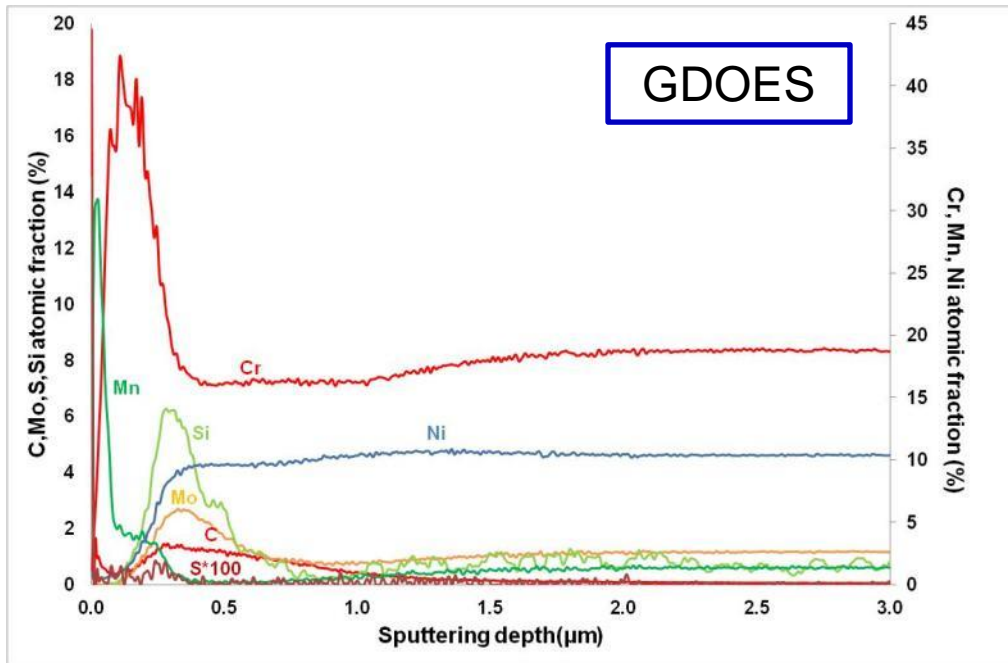
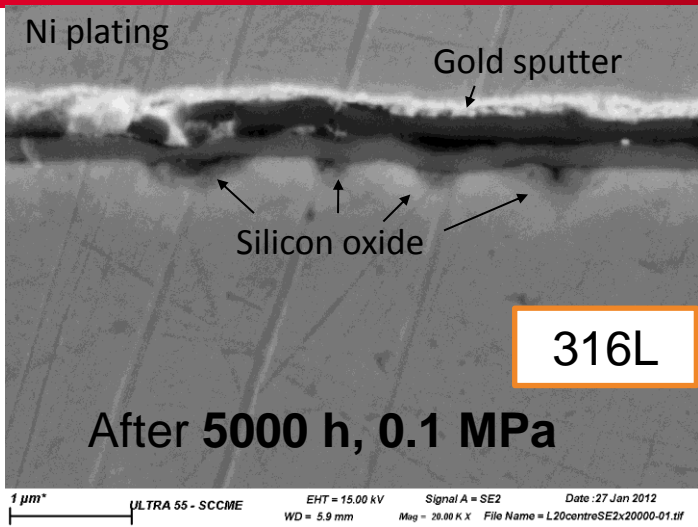
8 μm thick

316L, 550 °C, 25 MPa, 1000 h

CEA

200μm





✓ **Oxide layer :**

- **Cr** rich oxide layer
- **Mn** enrichment in the external part (30 at%) and internal part (4 at%)
- **Si** oxide at the O/M interface (discontinuous)

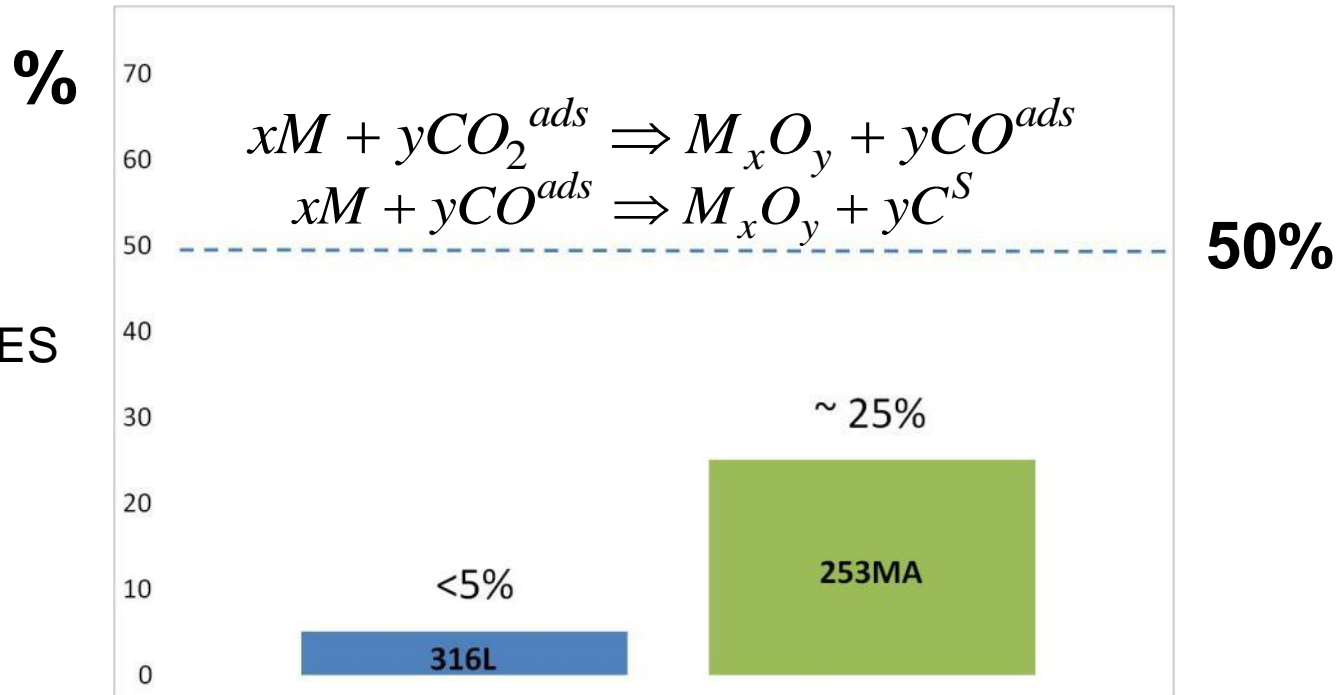
✓ **Substrate :**

- **C** enrichment below the oxide layer and diffusion profile

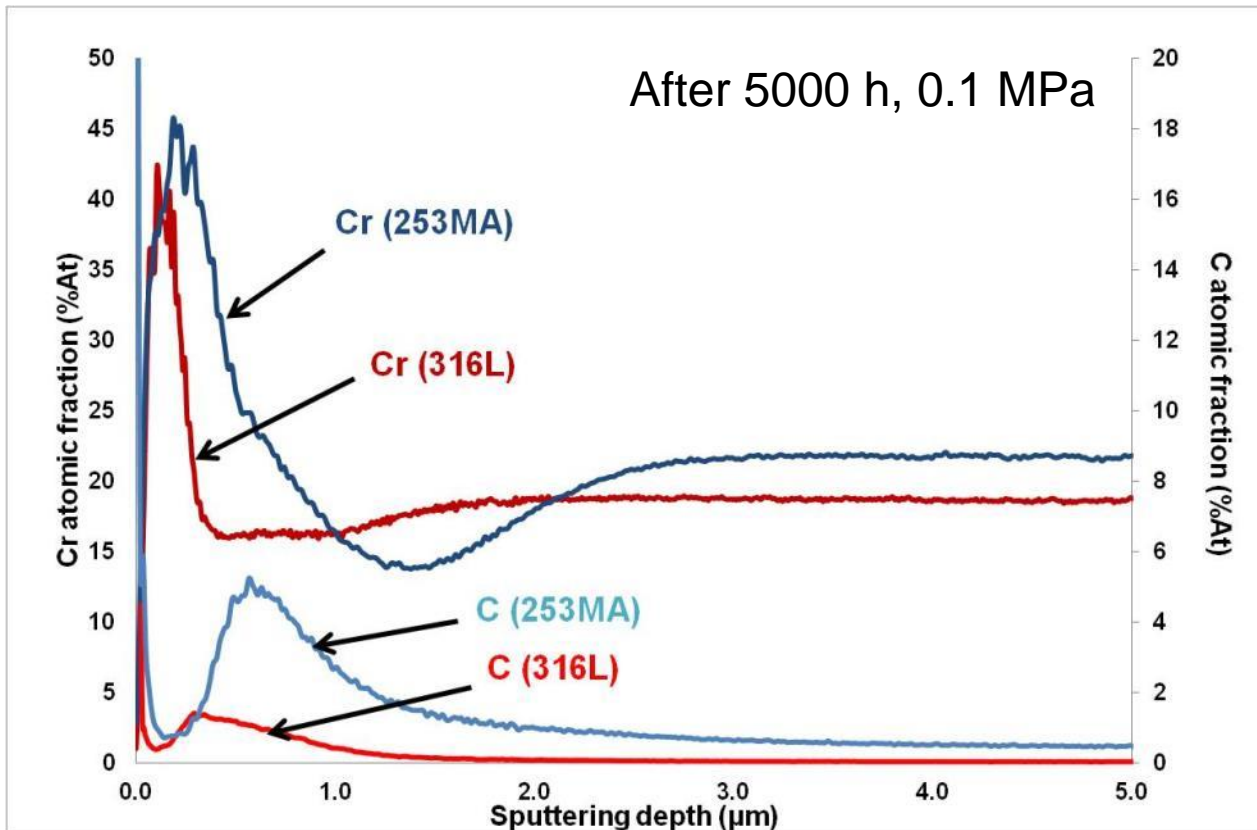
# INFLUENCE OF STEEL GRADE ON CARBON TRANSFER

At%	%Cr	%Ni	Other
316L	19%	10%	/
253MA	22%	10%	Si : 3%, Ce

**C content / O content ratio for two grades at any time**



## INFLUENCE OF STEEL GRADE ON CARBON TRANSFER

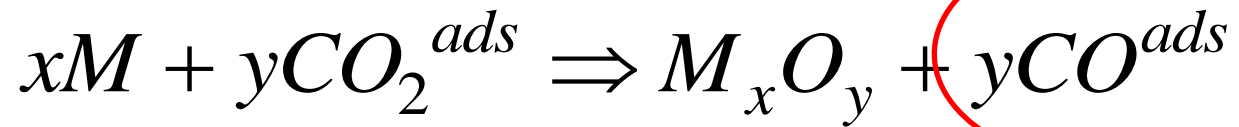


ThermoCalc

At%	Max %at C at the O/M interface	Volume fraction $f_v$ of $M_{23}C_6$
316L	1.3%	5%
253MA	5%	21%

# CARBURIZATION PROCESS ?

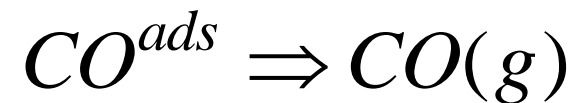
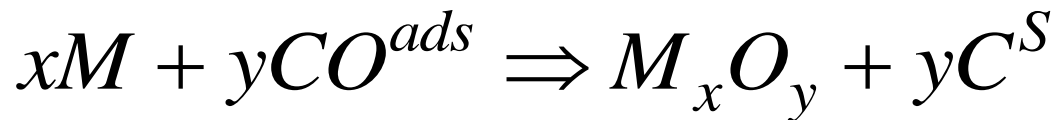
Oxidation



Carburisation

Or

Desorption



## Carburisation degree of austenitic steels :

Depends on the catalytic properties of the surface for CO dissociation ?

- ✓ increases with Cr content [*Anghel et al. Applied Surface Science 233 (2004)*]
- ✓ with other elements ?



Influence on long-term corrosion behaviour ?

## 9Cr F/M Steels

### ➤ Thick duplex oxide scale

*[Fe-oxides + Fe/Cr oxide]*

### ➤ Fast parabolic growth rate

*Driving force =  $P_{O_2}^{eq} Fe_3O_4/Fe_2O_3$*

### ➤ Strong Carburisation rate

*[via Boudouard reaction ?]*

*Carbon transfer rate increases with  $P_{CO_2}$*

## 17-25Cr Austenitic Steels

### ➤ Thin oxide scale

*[Cr rich oxide]*

### ➤ Slow growth rate

*[exact mechanism to be determined]*

### ➤ Low Carburisation rate

*[via CO dissociation ?]*

*Increases with %at Cr ?*

*Impact on long-term exposure ?*

*Is Breakaway Oxidation possible ??  
One should look for it ...*



*Formation of oxide nodules on the  
lowest Cr rich austenitic steels (17Cr)  
which grow faster*

**THANK YOU FOR  
YOUR ATTENTION**