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F. Rouillard, T. Furukawa, B. Duprey, G. Moine, J. C. Ruiz, et al.. Corrosion behaviour of 9-12%Cr ferritic steels and 18-25%Cr austenitic steels in supercritical CO<sub>2</sub>. TMS 2016, Feb 2016, Nashville, United States. cea-02431803

**HAL Id: cea-02431803**

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Submitted on 8 Jan 2020

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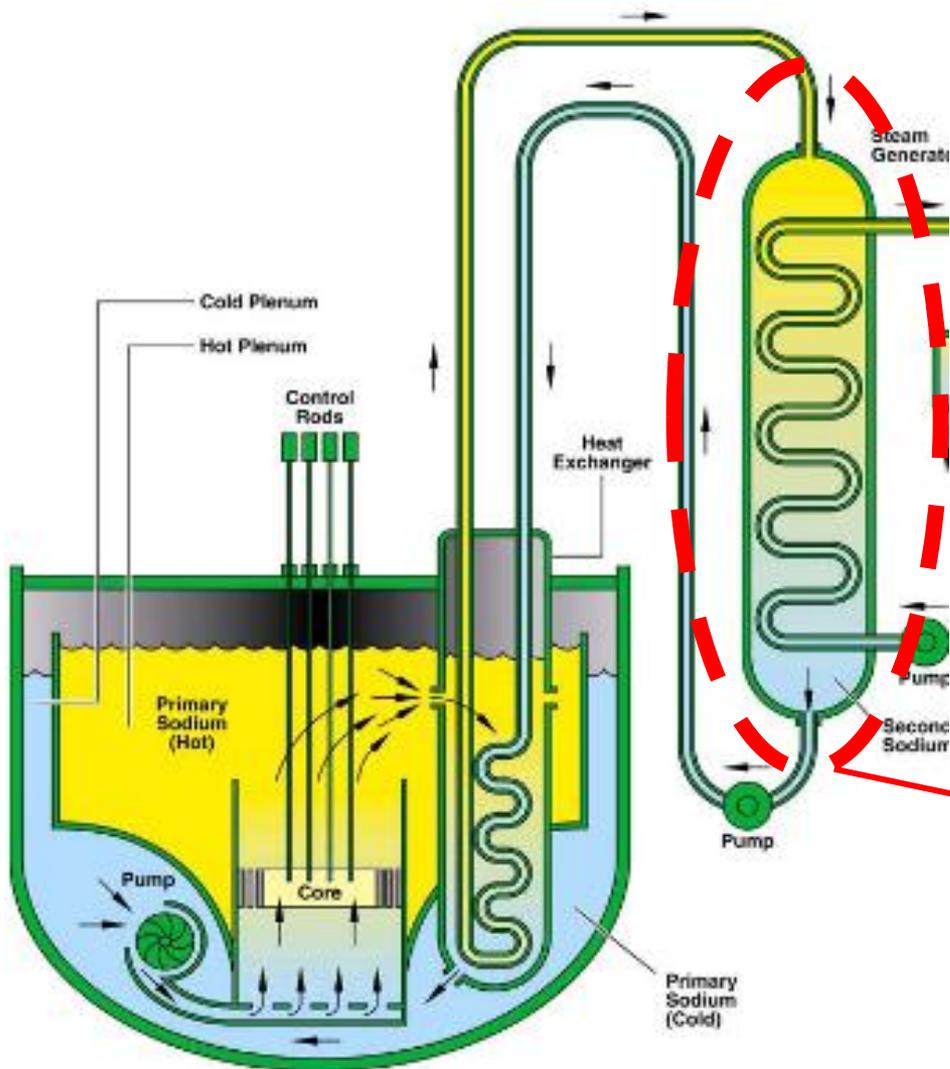
CEA/DEN/DANS/DPC/SCCME/LECNA (SACLAY)

[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

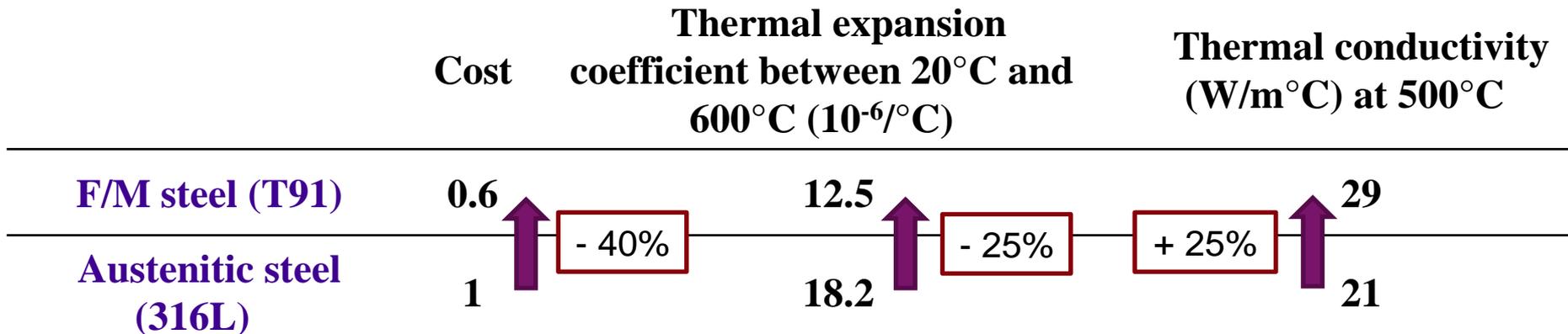
### RECOMMANDATIONS :

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

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

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

**17-22%Cr Austenitic steels**



- ❑ 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

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

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



## Atmospheric pressure CO<sub>2</sub>



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 =  $f(T, P)$

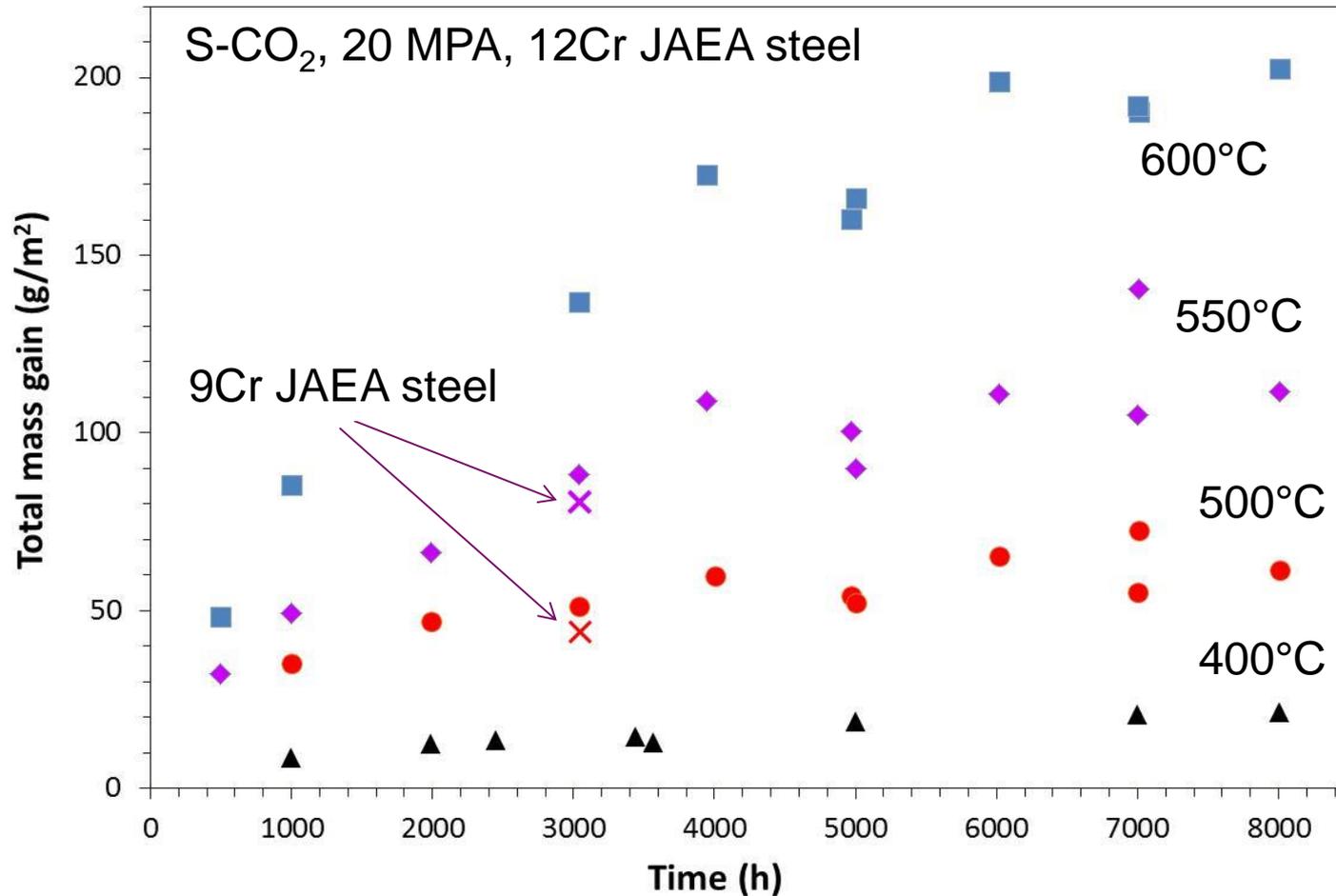


**Proposed corrosion model : « Available Space Model »**

- ✓ Influence of surface finish
- ✓ Influence of O<sub>2</sub> impurities in CO<sub>2</sub>

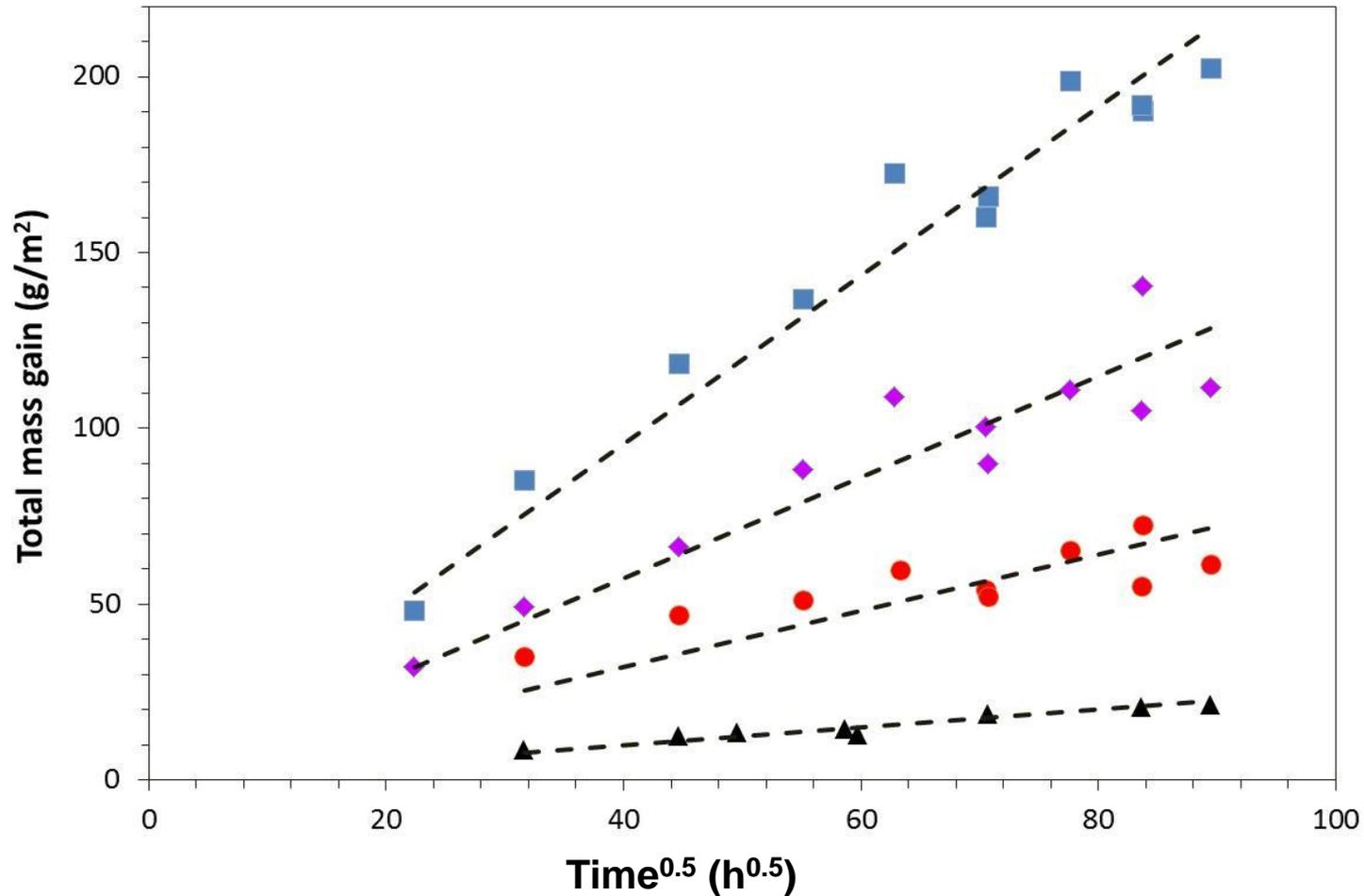
PhD thesis of S. Bouhieda  
(2009-2012)

# CORROSION KINETICS OF 9-12CR JAEA STEELS



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

# CORROSION KINETICS OF 9-12CR JAEA STEELS

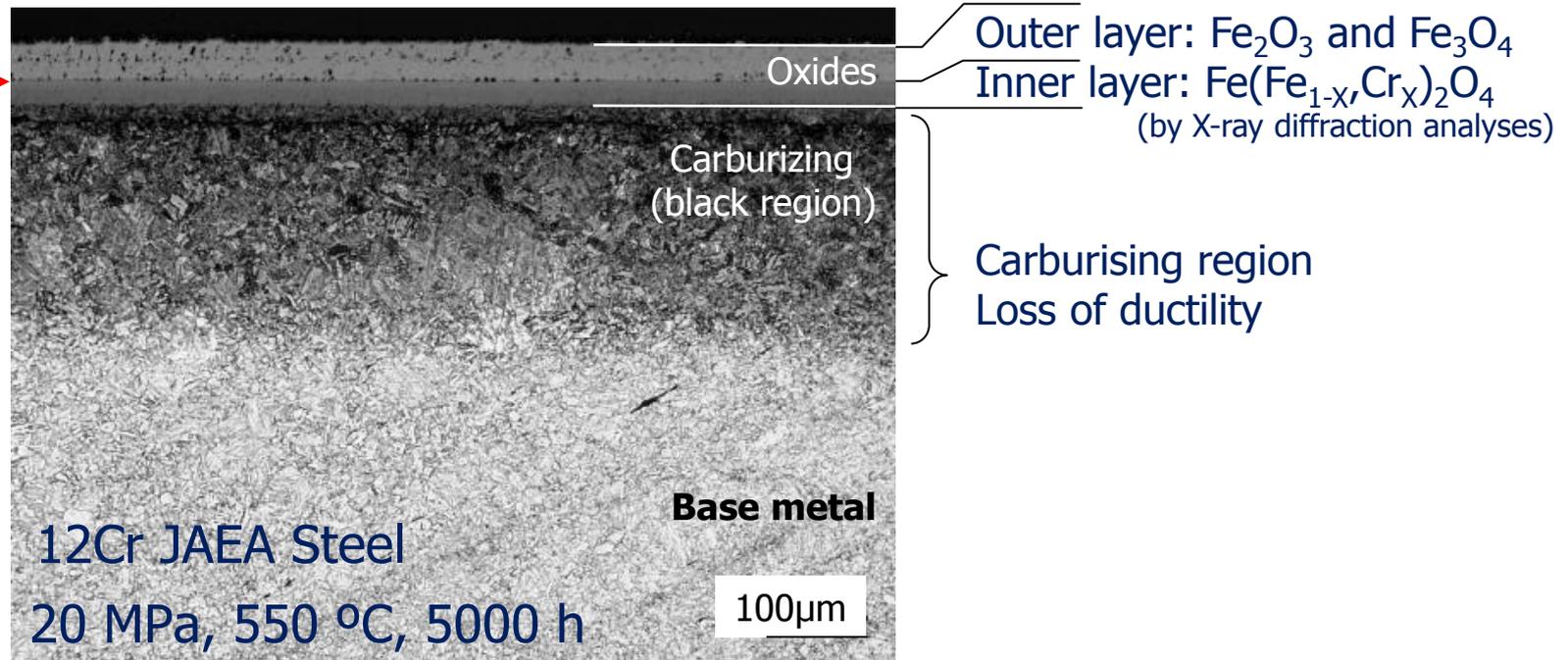


- Parabolic kinetics
- What does happen to the samples ?

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

Mass gain = Oxidation AND Carburisation

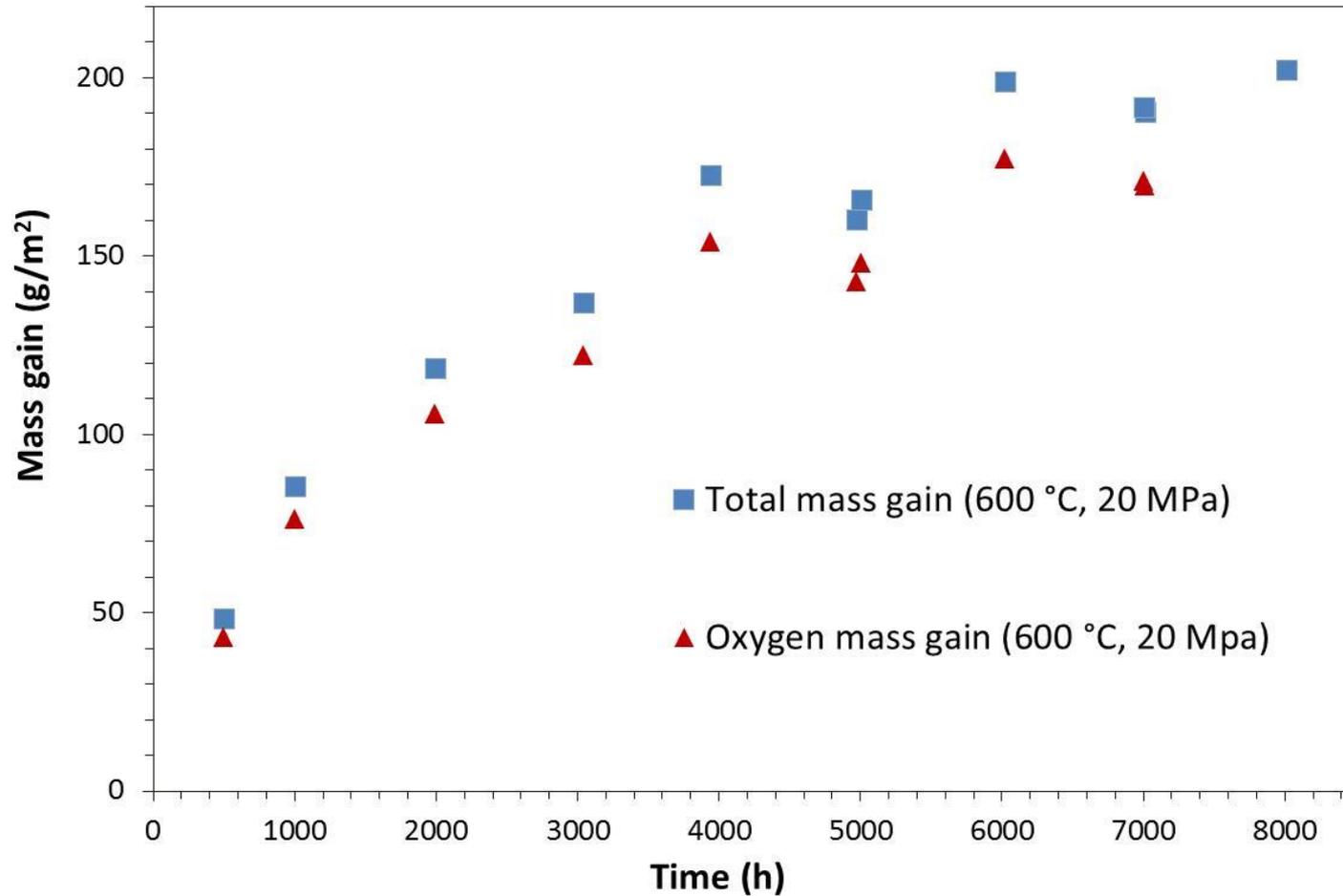
Original surface of base metal →



What are the proportion of the mass gain induced by :

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

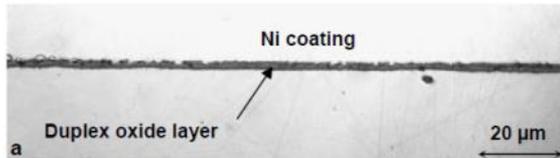
# Oxidation mechanism of 9-12Cr steels in CO<sub>2</sub>



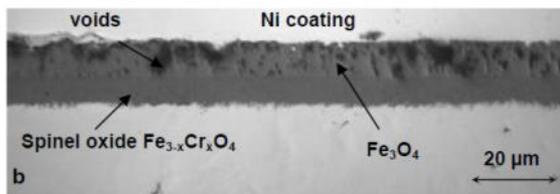
Parabolic oxidation rate = diffusion controlled

## OXIDE FEATURES

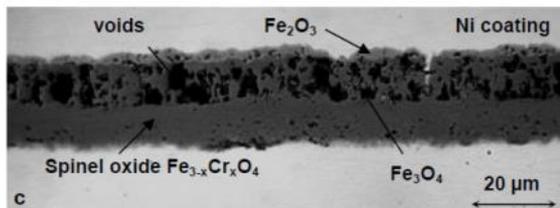
9Cr CEA steel in CO<sub>2</sub>,  
550 °C, 0.1 MPa



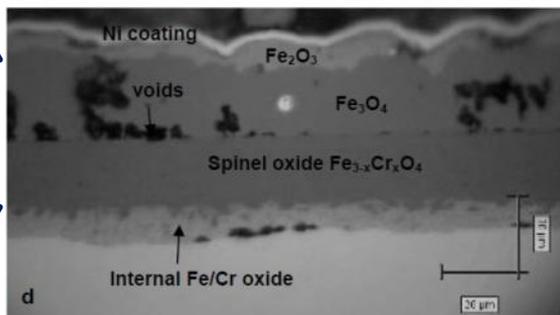
1 h



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]<sub>spinel</sub> (mol/cm<sup>3</sup>) ~ [Cr]<sub>substrate</sub> (mol/cm<sup>3</sup>)

**Chromium does not diffuse and is oxidized in the substrate.**

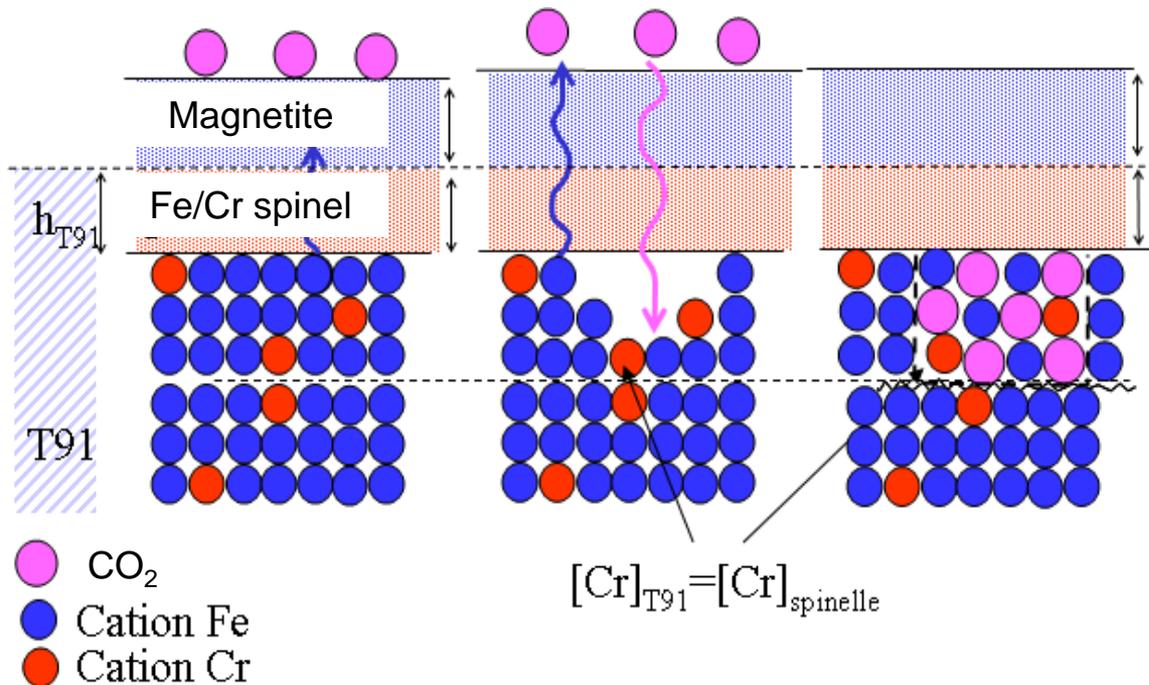
- **Carbon** enrichment at the O/M interface (GDOES analysis)

- 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

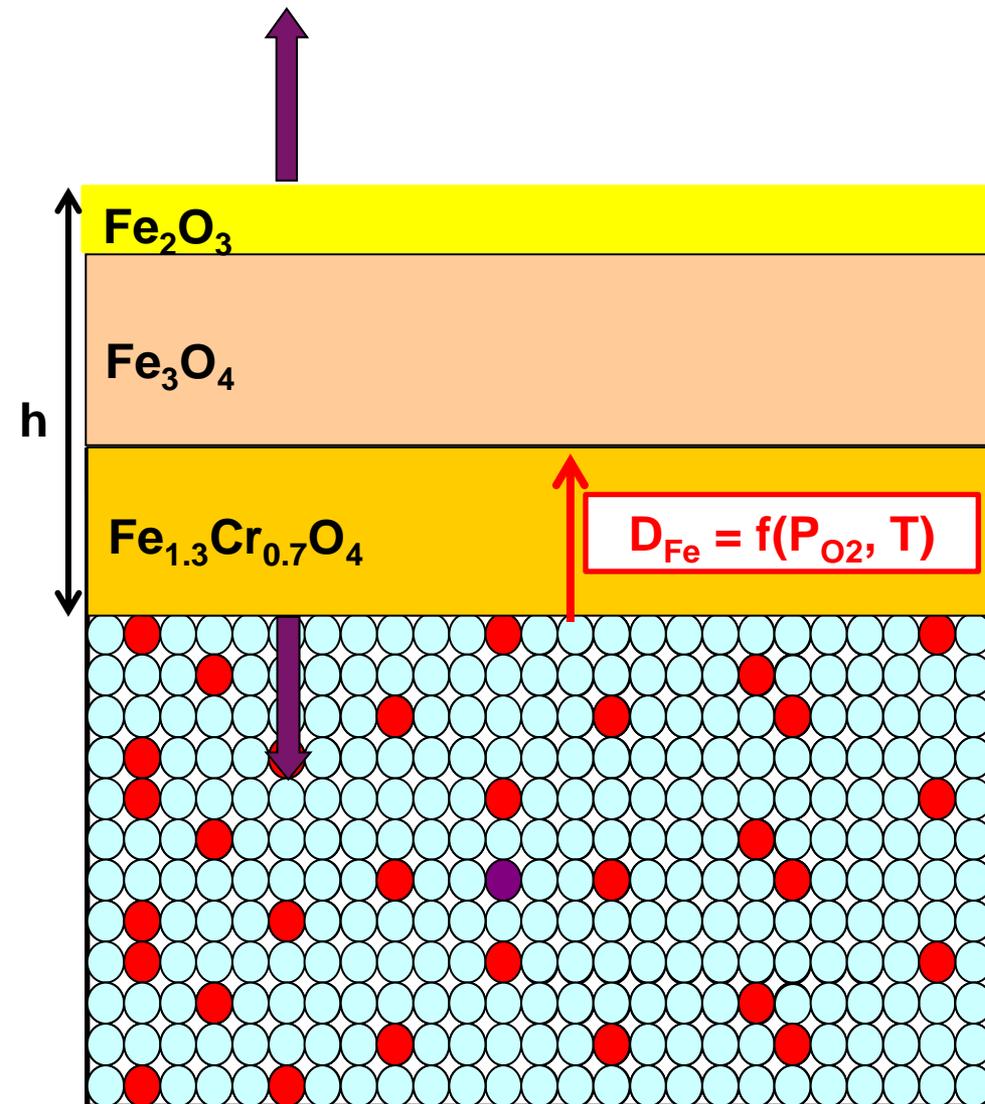
Oxidation model ?

## « 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

 $P_{\text{O}_2}^{\text{ext}}$ 

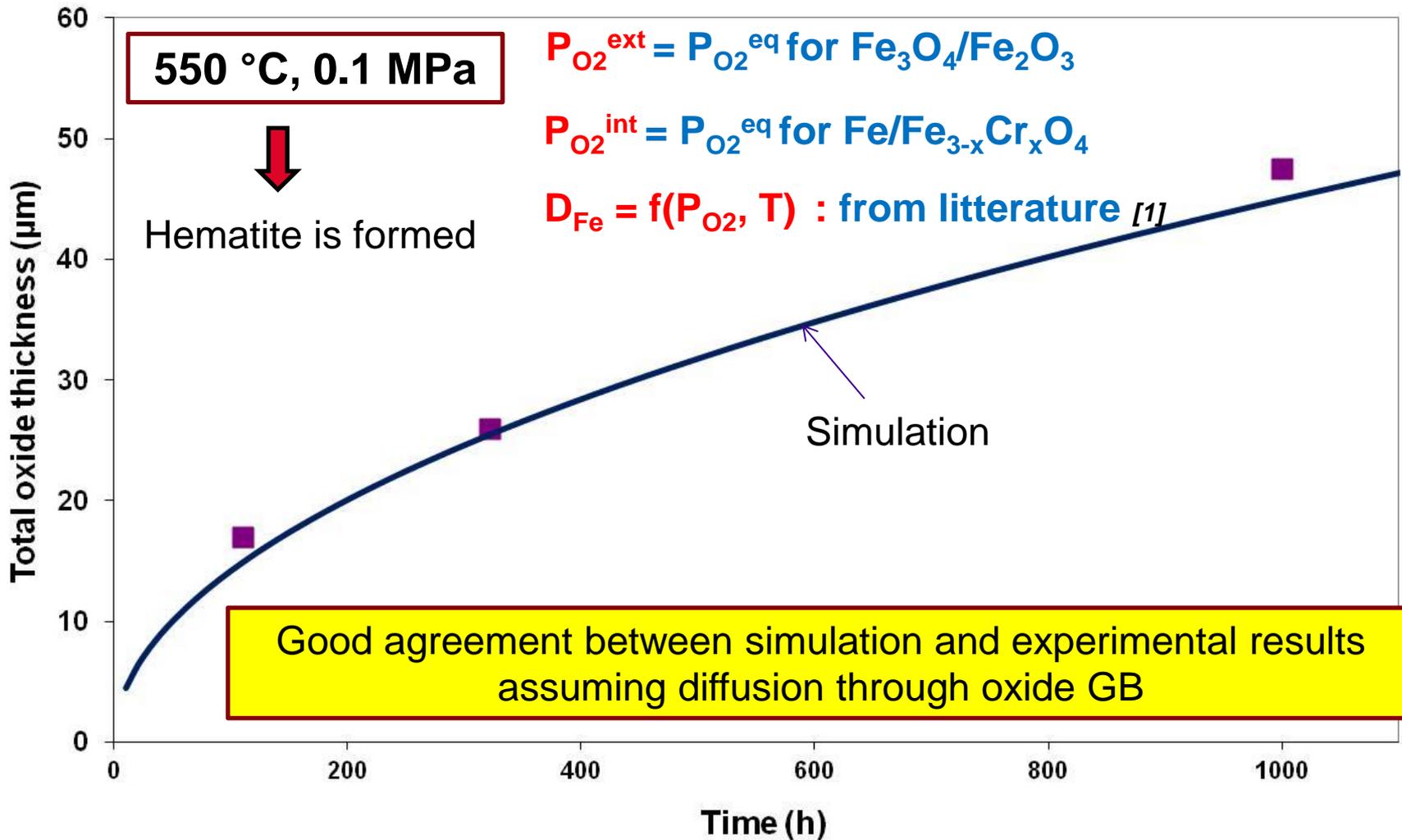
- calculated from the gas phase composition ( $P_{\text{CO}_2}/P_{\text{CO}}$  ratio) or
- $= P_{\text{O}_2}^{\text{eq}}$  for  $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$  if  $\text{Fe}_2\text{O}_3$  stable

$P_{\text{O}_2}^{\text{int}} = P_{\text{O}_2}^{\text{eq}}$  for  $\text{Fe}/\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$   
 = Rate limiting oxide layer

$$h(t) = f(D_{\text{Fe}}, P_{\text{O}_2}^{\text{int}}, P_{\text{O}_2}^{\text{ext}})$$

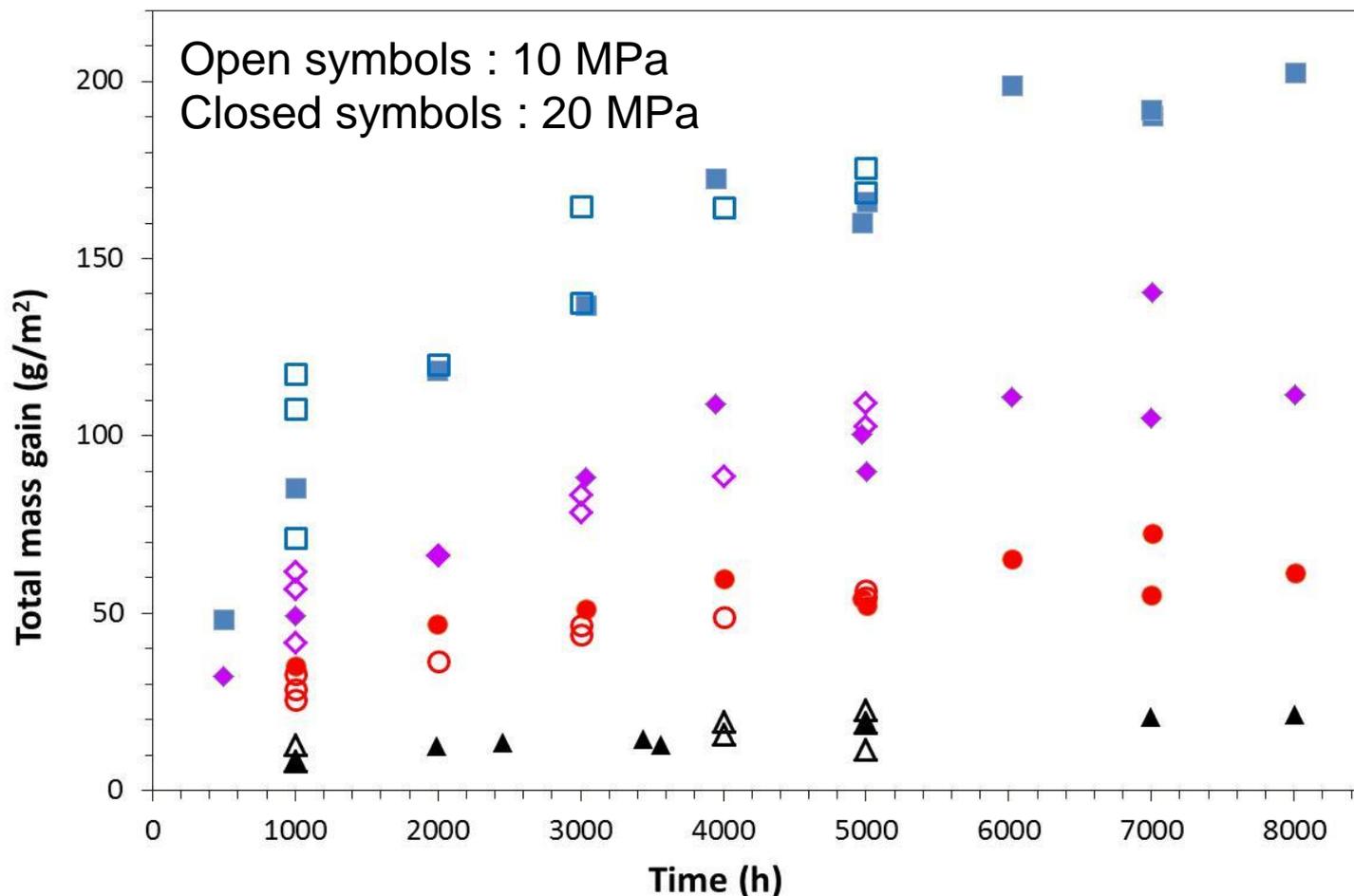
$D_{\text{Fe}}, P_{\text{O}_2}^{\text{int}}, P_{\text{O}_2}^{\text{ext}}$  : input parameters  
 (from literature review)

# OXIDE GROWTH MODELING AND SIMULATION



[1] : Topfer et al. Solid State Ionics 81 (1995)

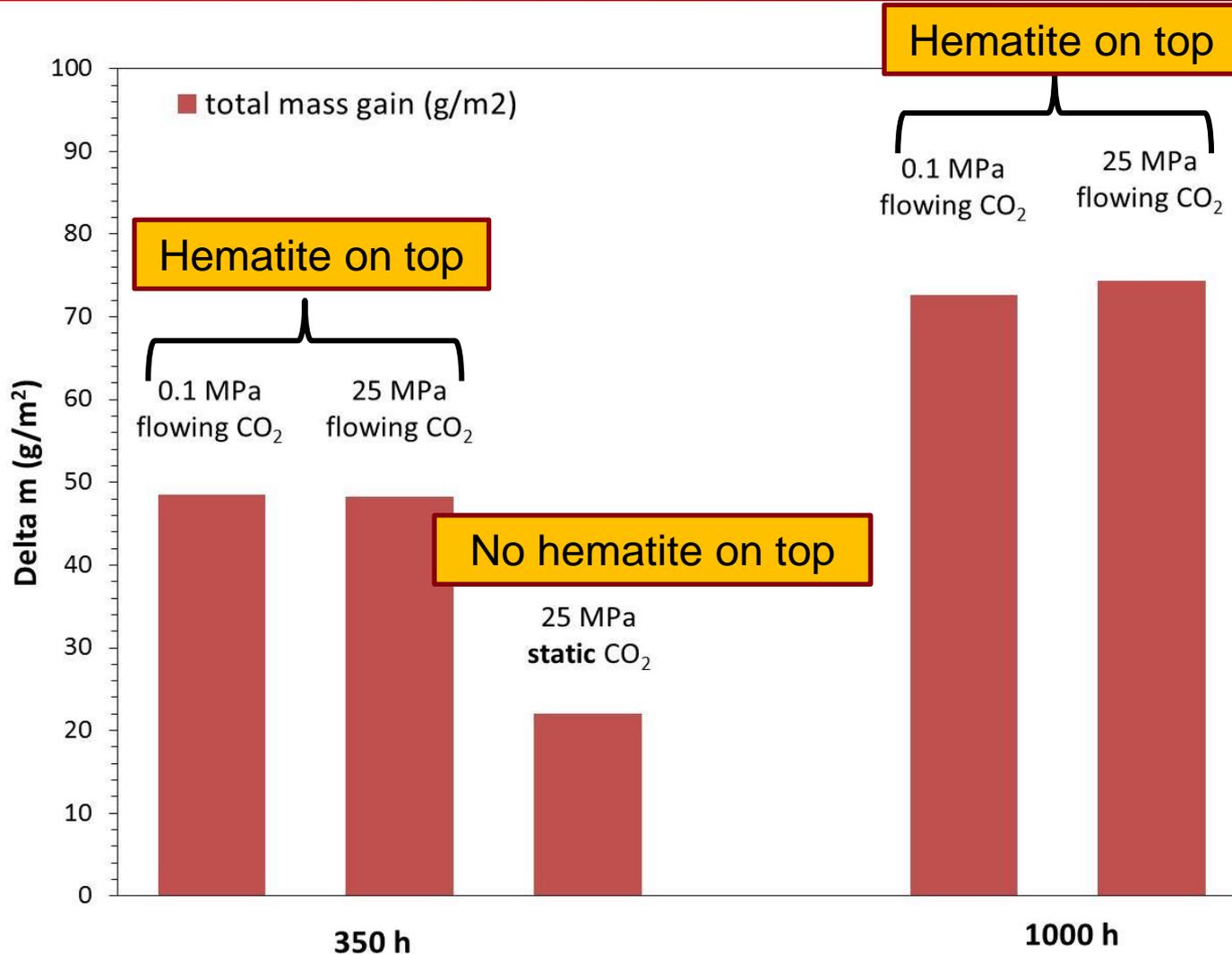
# EFFECT OF $P_{CO_2}$ ON OXIDATION



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

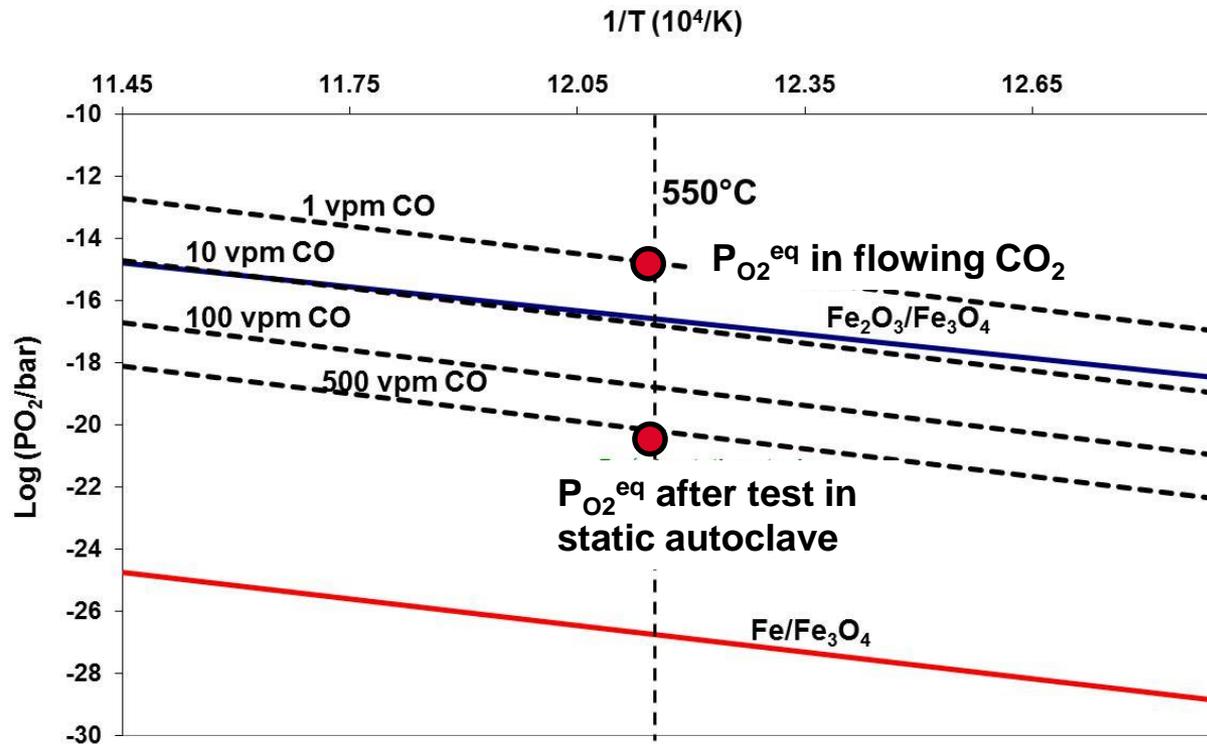
With higher  $P_{CO_2}$  difference : 0.1 MPa and 25 MPa ?

# 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 $Fe_2O_3$ ?

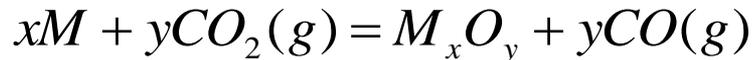


The formation of  $Fe_2O_3$  is controlled by the  $P_{CO_2}/P_{CO}$  ratio in the gas phase :



$$P_{O_2}^{ext} = \left( \frac{K * P_{CO_2}}{P_{CO}} \right)^2$$

CO(g) in the gas phase is mainly formed from oxidation of the metallic substrate :



As a consequence, the driving force for oxidation  $P_{CO_2}/P_{CO}$  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  $P_{\text{CO}_2}$  ?

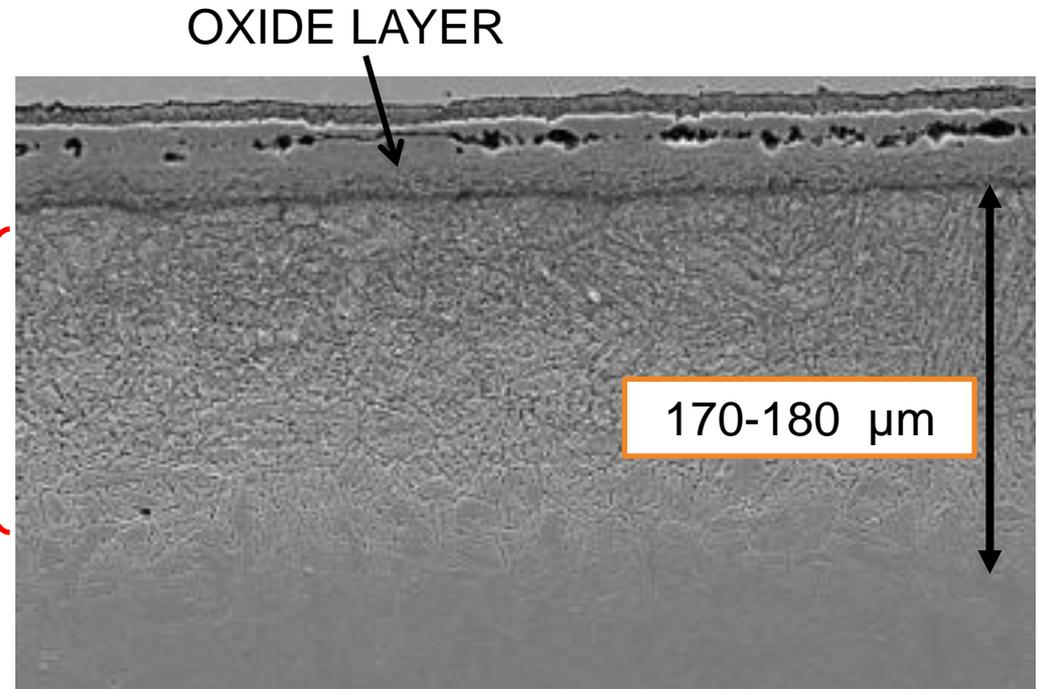
Could we model the carburisation  
propagation into the steel ?

Why does the steel  
carburise ?

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

## CARBURISED ZONE :

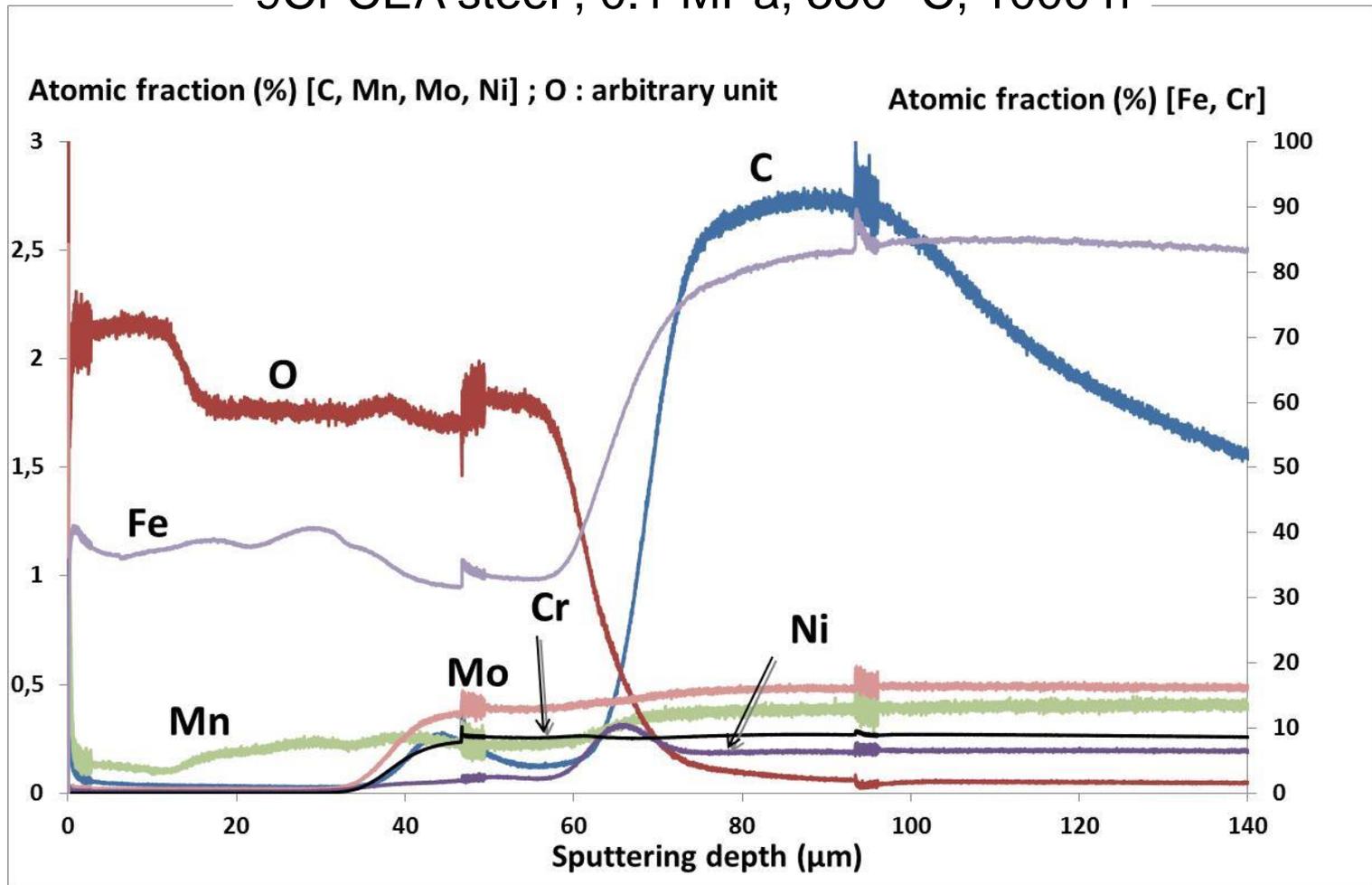
On martensitic laths  
and old primary austenitic GB



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

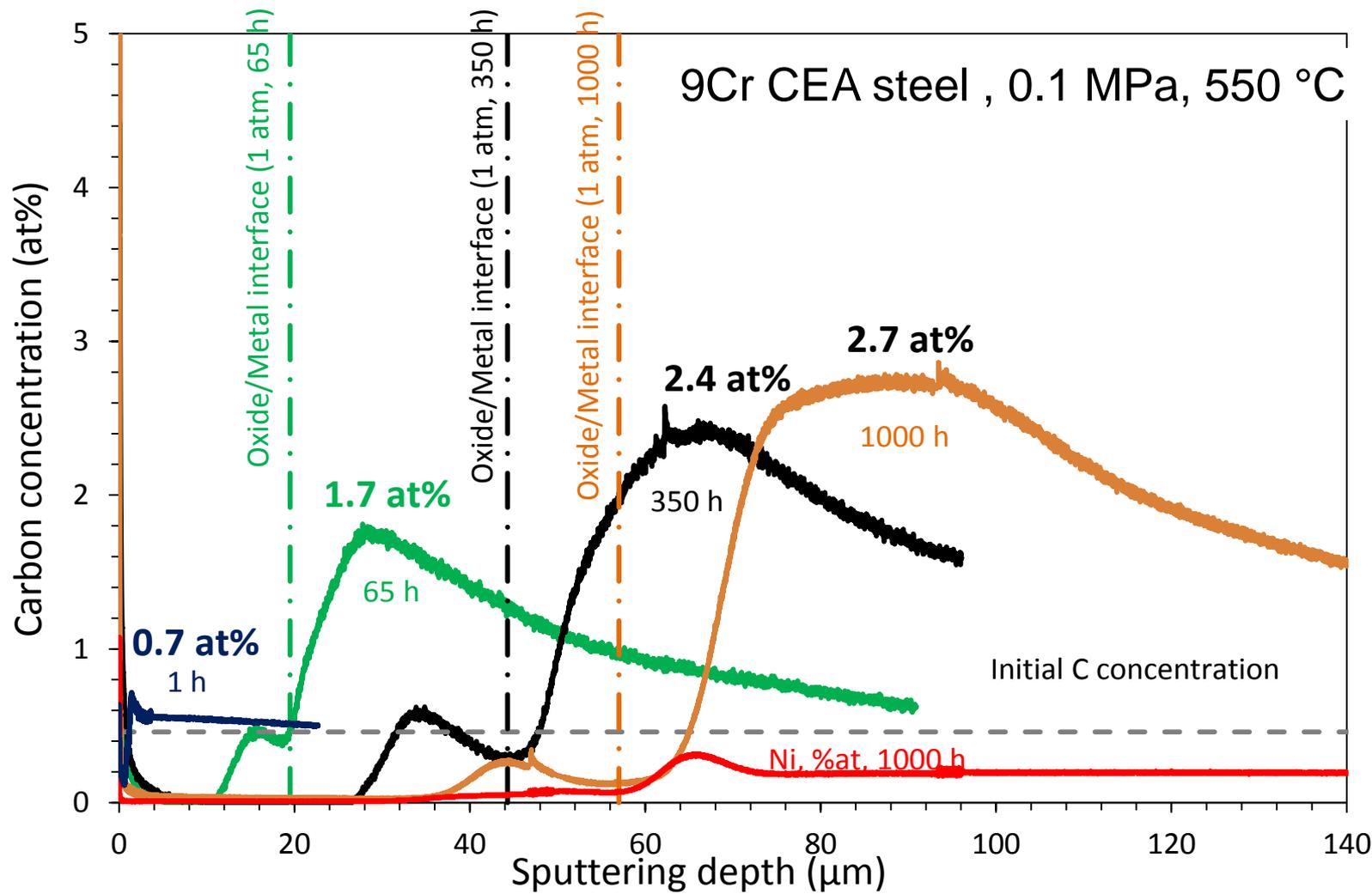
# CARBON PROFILE BY GDOES

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 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 :

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

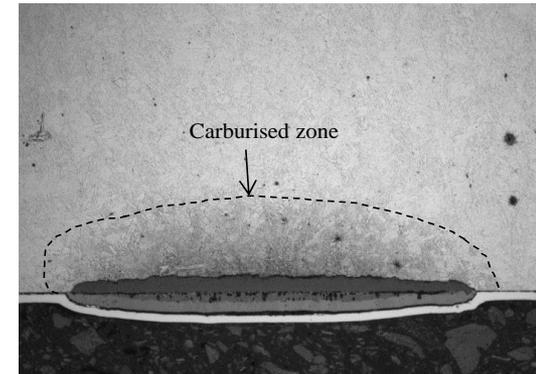
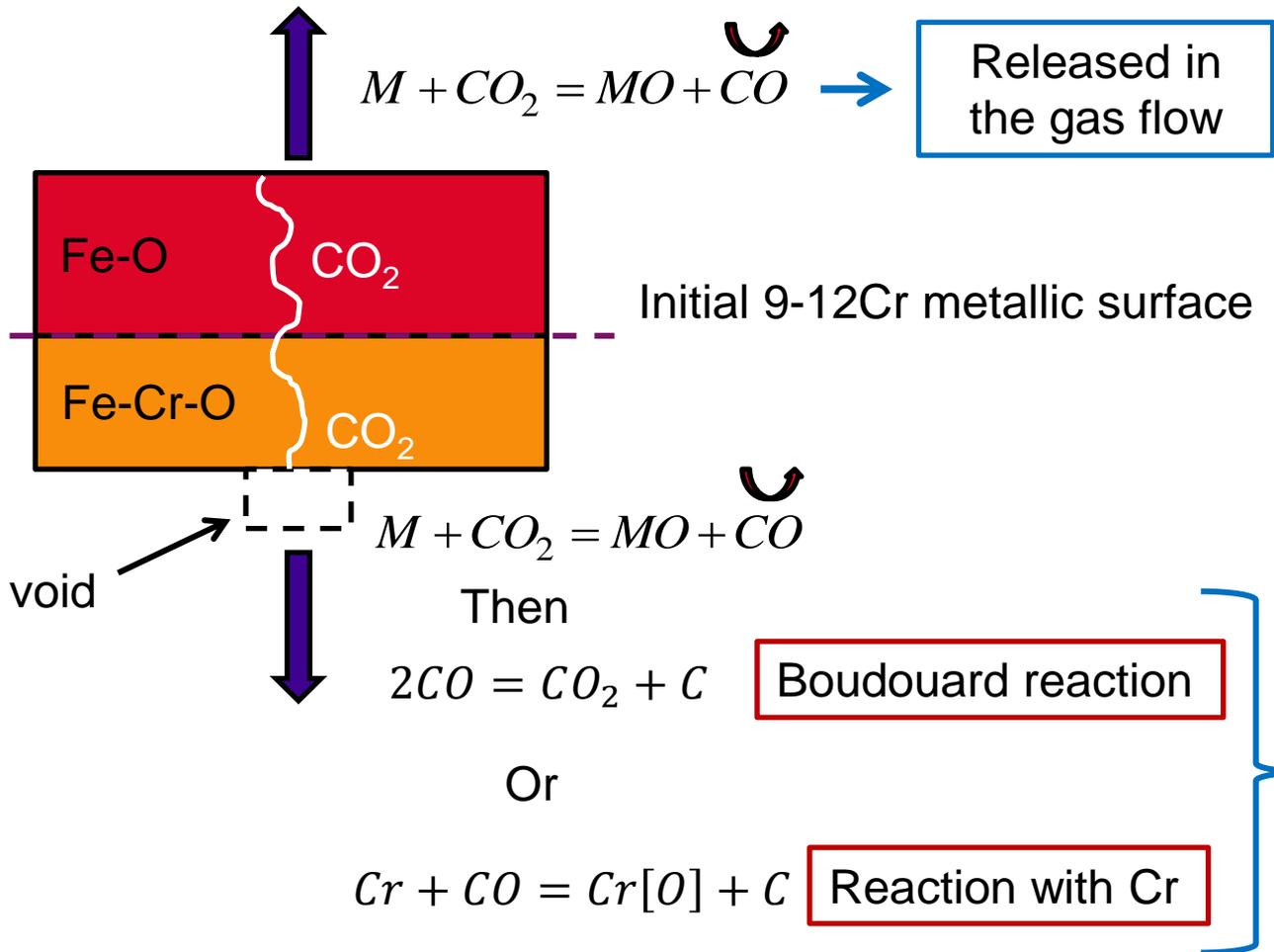
With  $C^{eq}$  the concentration of carbon in equilibrium with **the carbon activity of the gas phase**



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

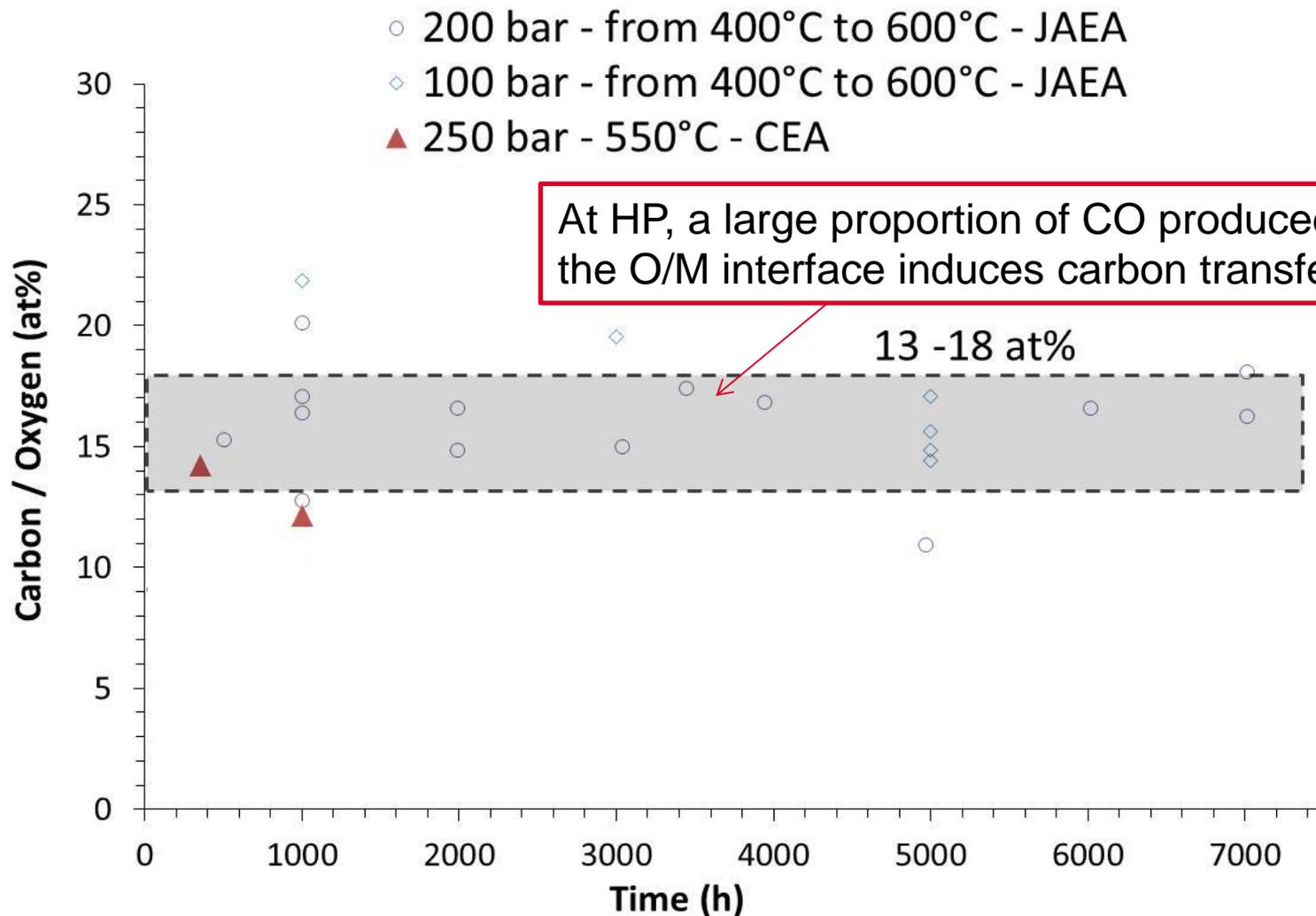
# CARBON TRANSFER

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



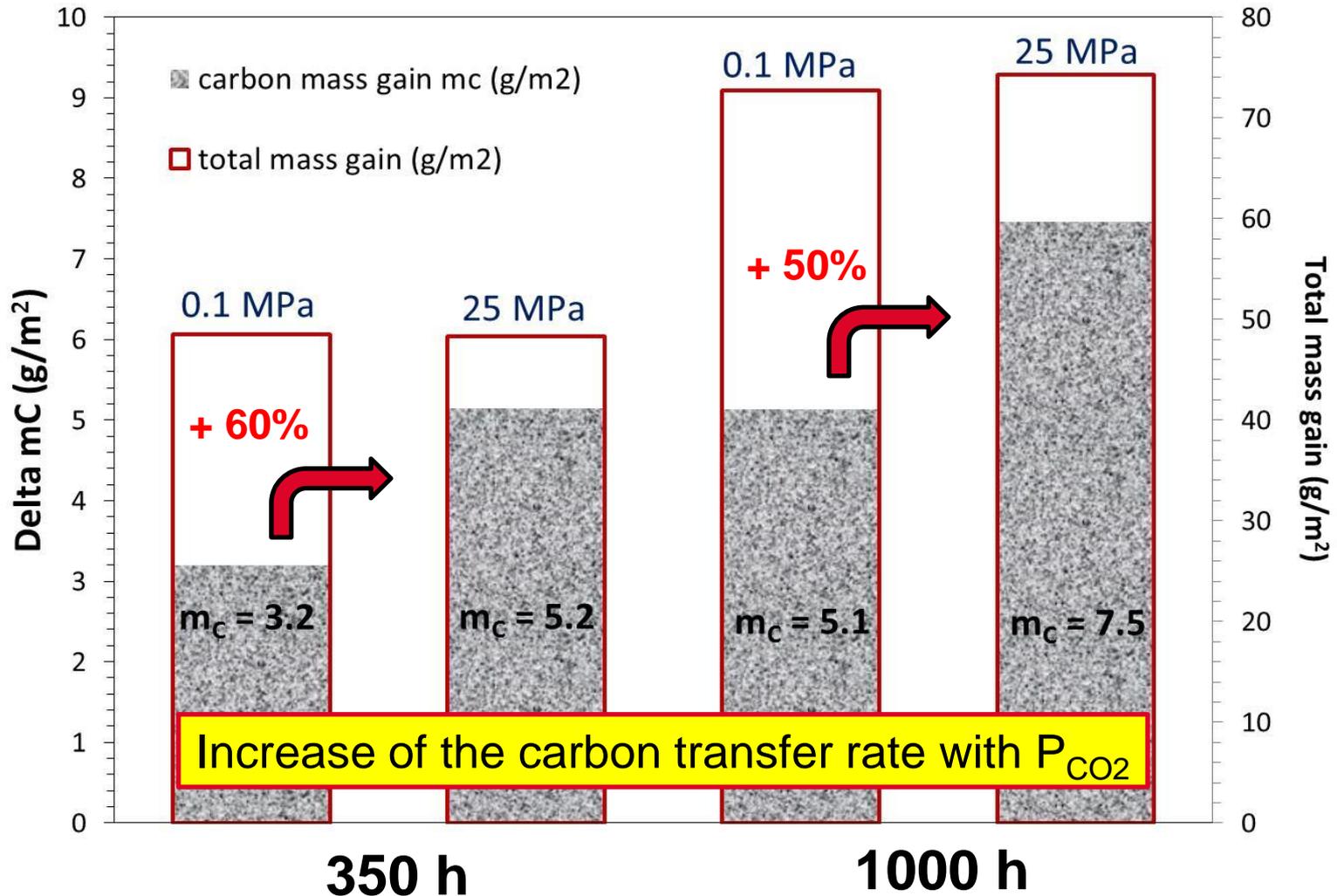
If all CO molecules carburise then %C/%O = 20 at%

## CARBON TRANSFER

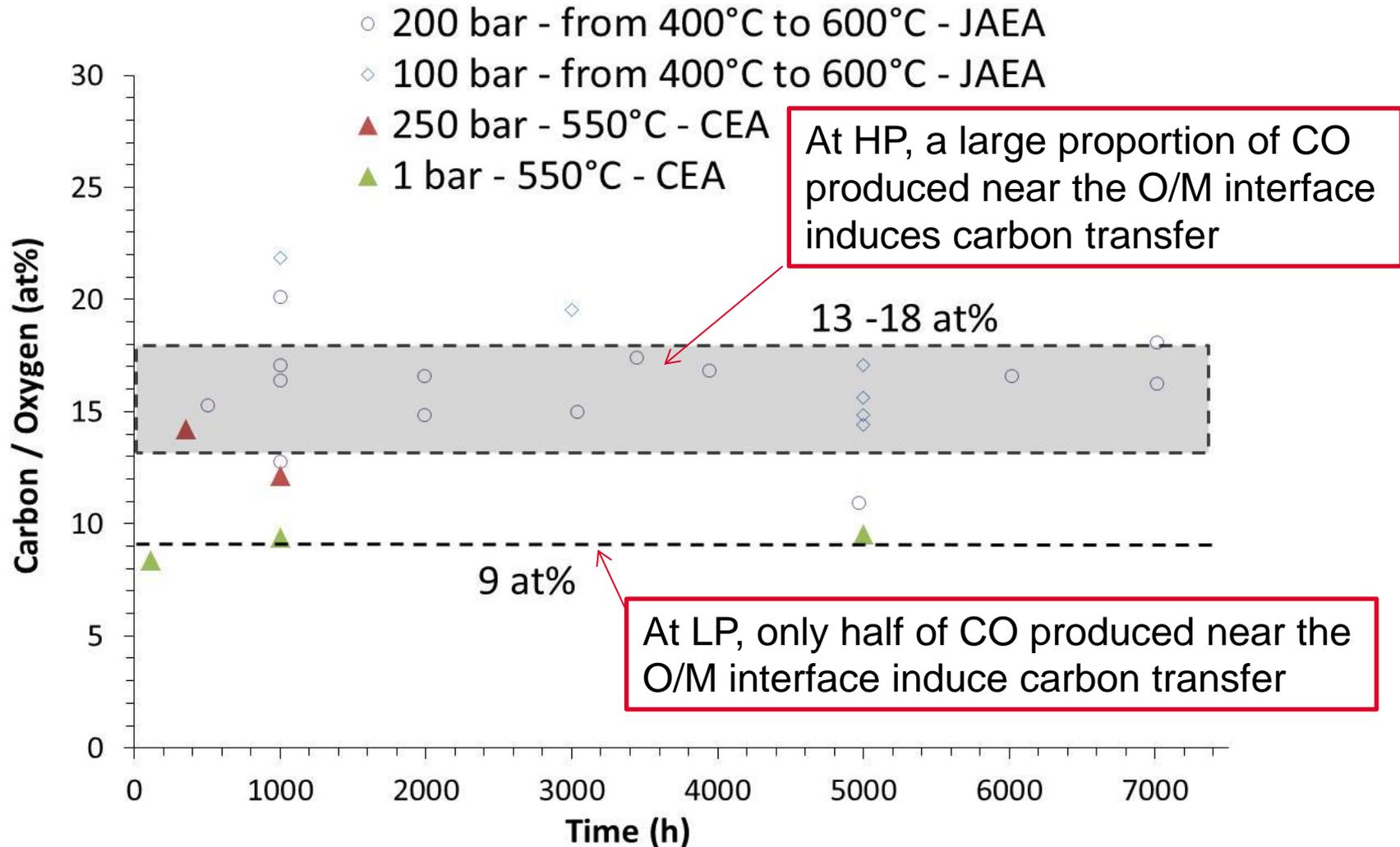


# INFLUENCE OF $P_{CO_2}$ ON CARBON TRANSFER

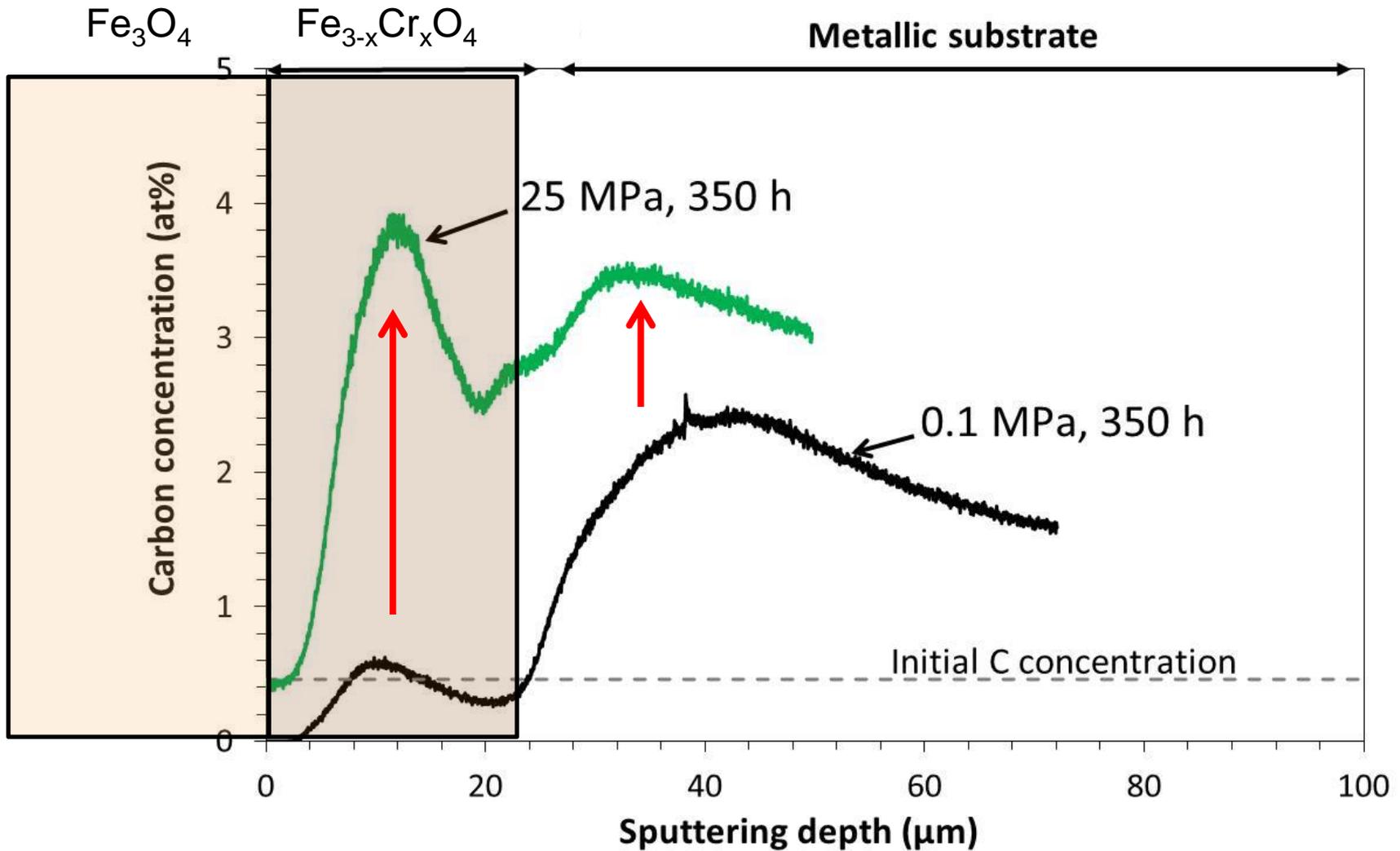
❑ No « detectable » influence of  $P_{CO_2}$  between 10 and 20 MPa ...  
... but higher carbon transfer rate detectable when increasing from 0.1 to 25 MPa



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



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



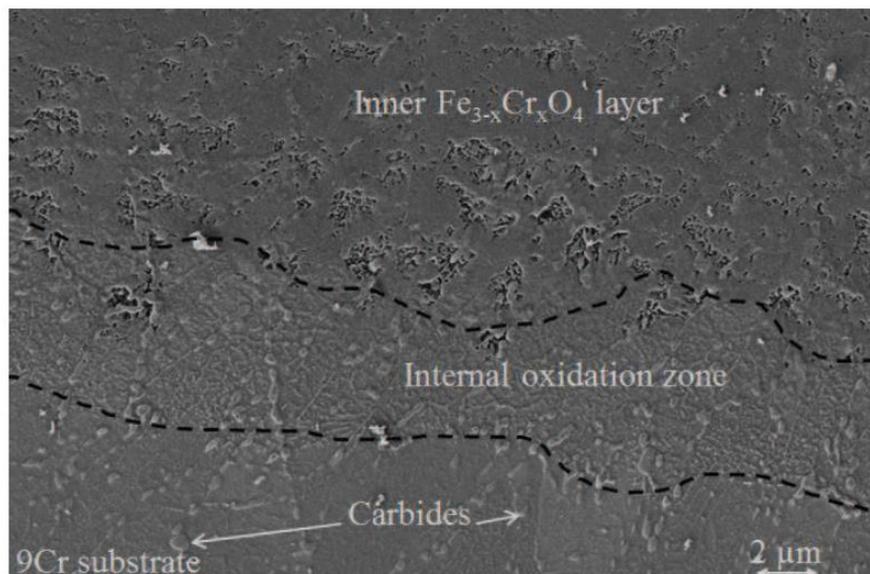
- %C at the O/M interface increases
- %C in the inner oxide scale increases



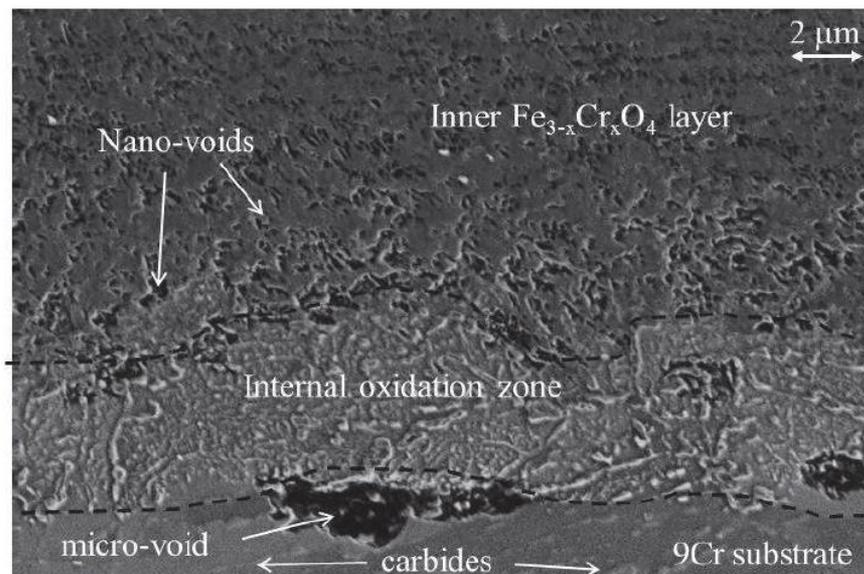
Carburisation rate increases

# INFLUENCE OF CARBURISATION ON THE INNER OXIDE MICROSTRUCTURE

T91, **0.1 MPa**, 550 °C, 350 h



T91, **25 MPa**, 550 °C, 350 h



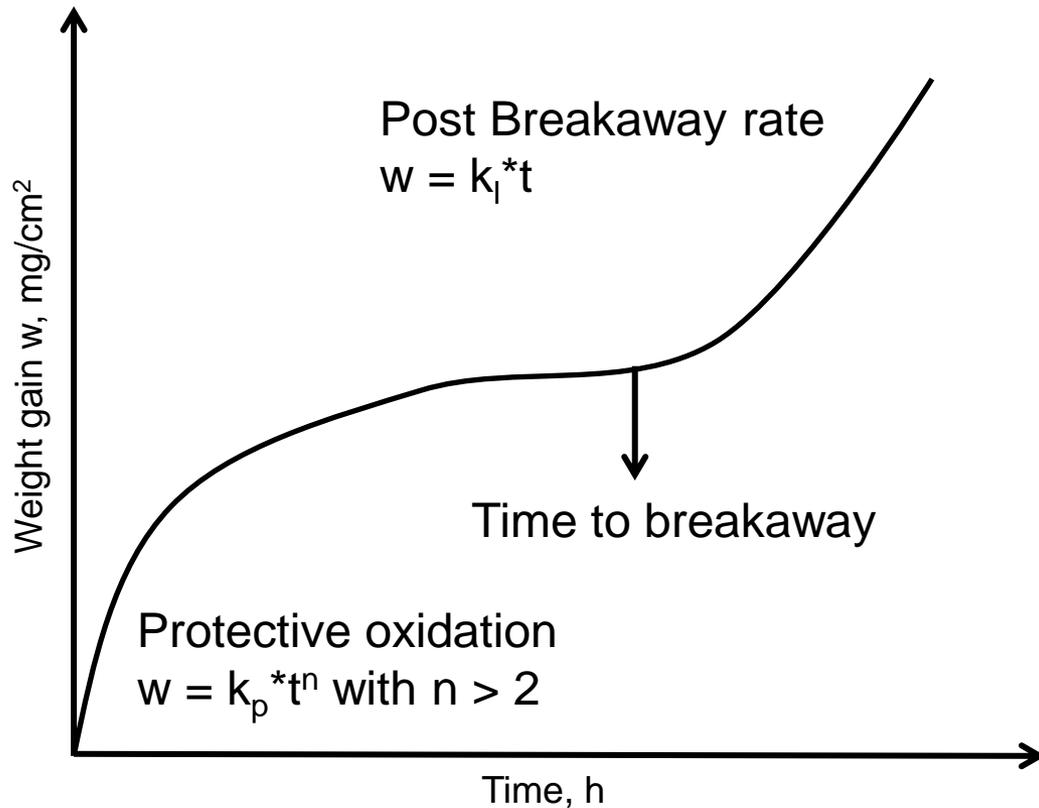
At high  $P_{CO_2}$  :

- 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 ?



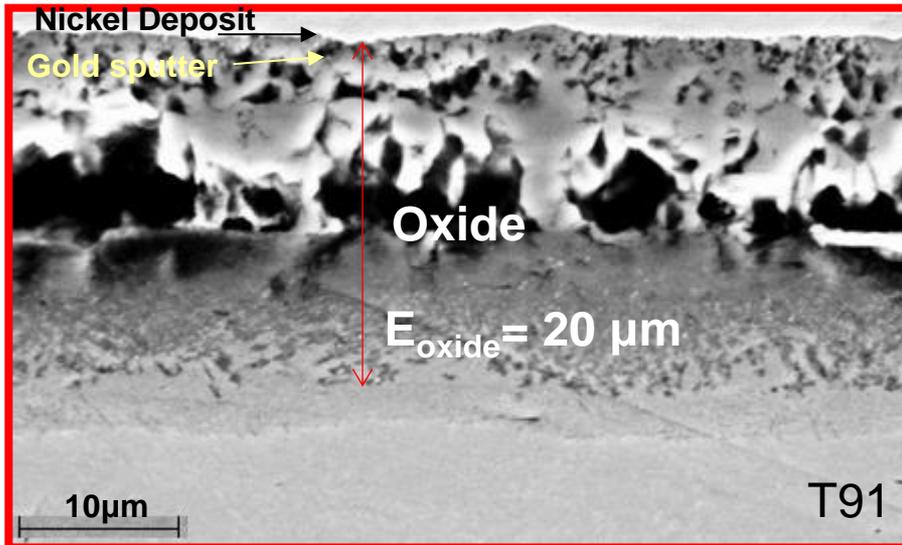
Feedbacks from  $\text{CO}_2$ -cooled nuclear reactors\*:

- Known for mild steels in S- $\text{CO}_2$  at  $T > 350 \text{ }^\circ\text{C}$
- 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 ?

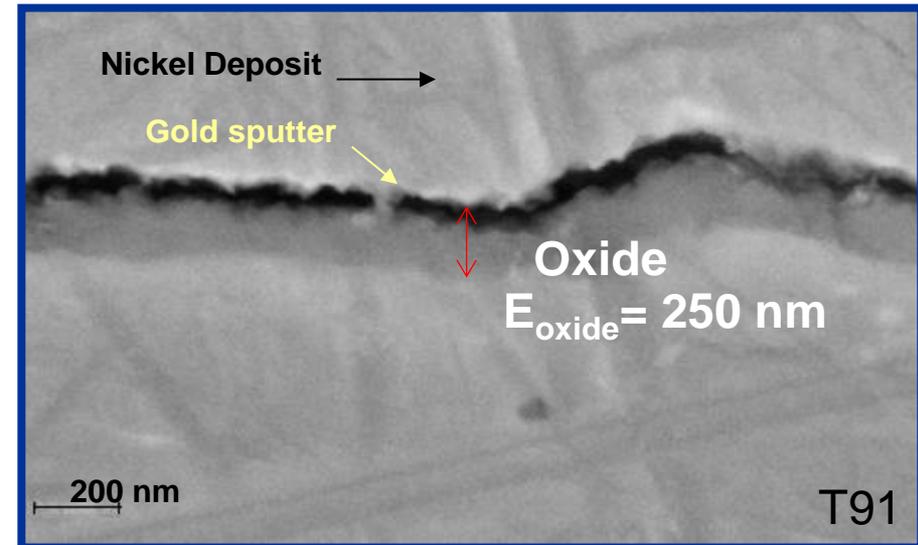
« Industrial » CO<sub>2</sub> purity (with O<sub>2</sub> ~ 100 μbar)



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%**

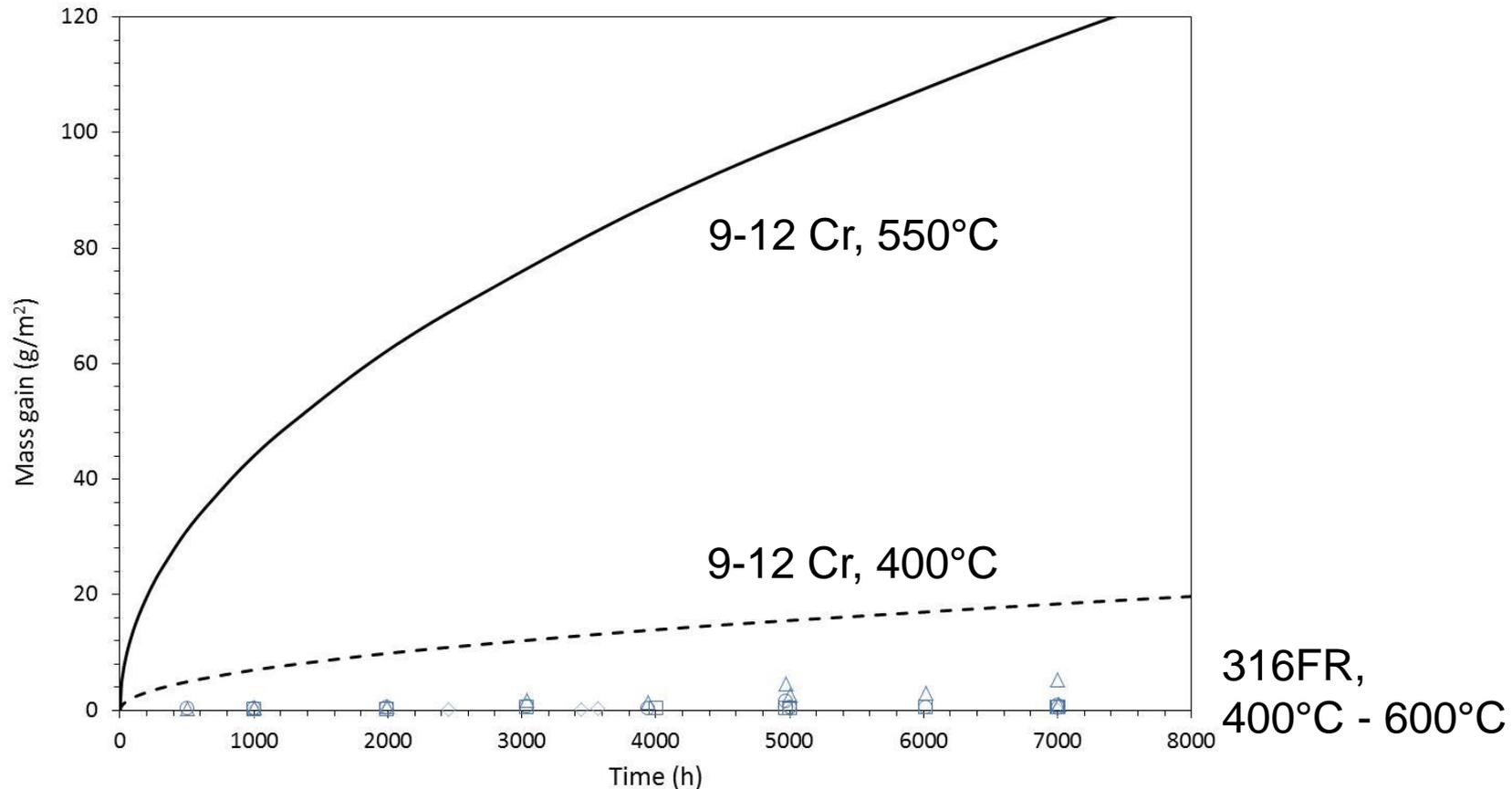
Still protective after 5000 h

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

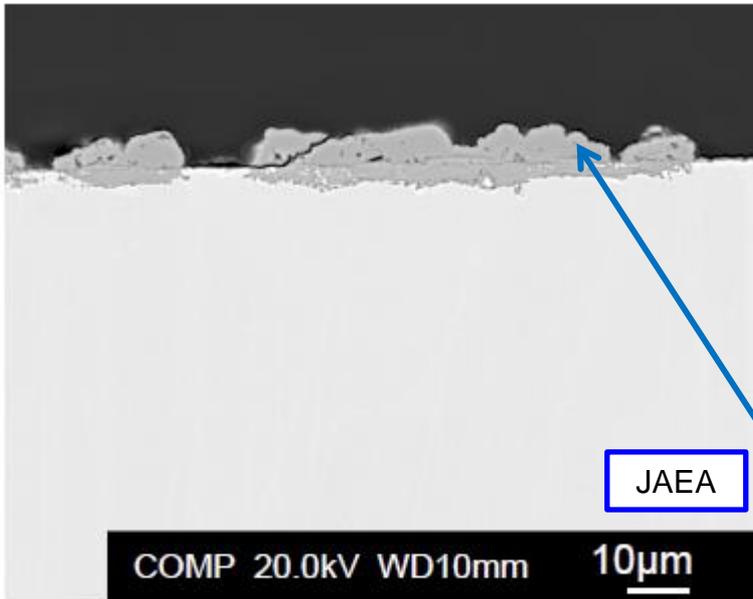
- O<sub>2</sub> impurities (μbar) react first during the thermal ramp
  - Its level in CO<sub>2</sub> impacts on the surface oxide composition (Cr enrichment)
- The surface finish (mainly roughness?) impacts on the critical O<sub>2</sub> partial pressure

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

# MASS GAIN KINETICS OF 316 AUSTENITIC STEEL

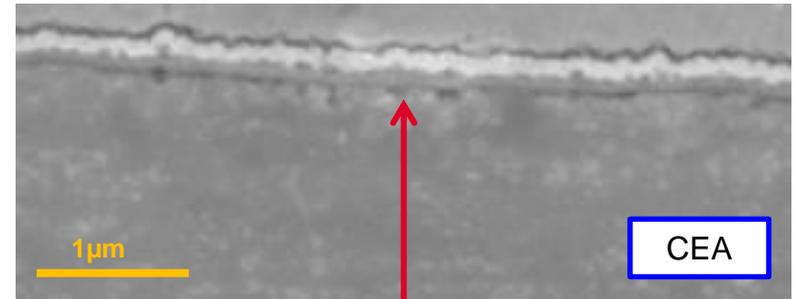


- Very low mass gain : mass gain (316FR) < 100\*mass gain (9-12Cr)
- No detectable effect of total pressure
- Larger mass gain is detectable after 5000 h at T = 600°C



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)

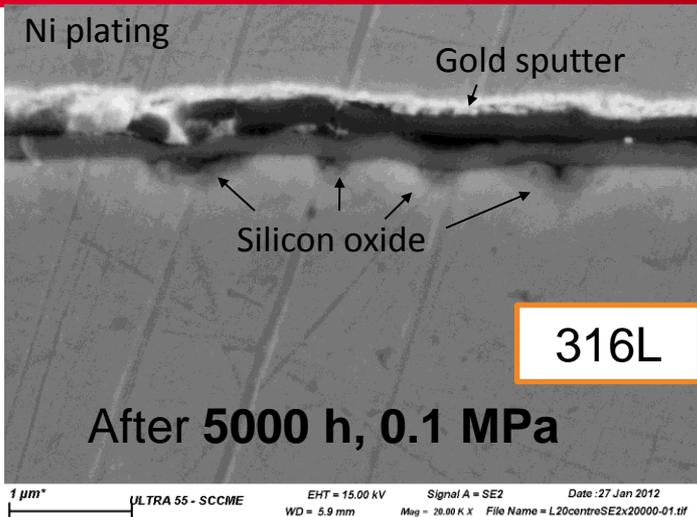
The « short-term » resistance of Cr rich austenitic steels is evaluated by its ability to form thin Cr rich oxide scale

8 µm thick

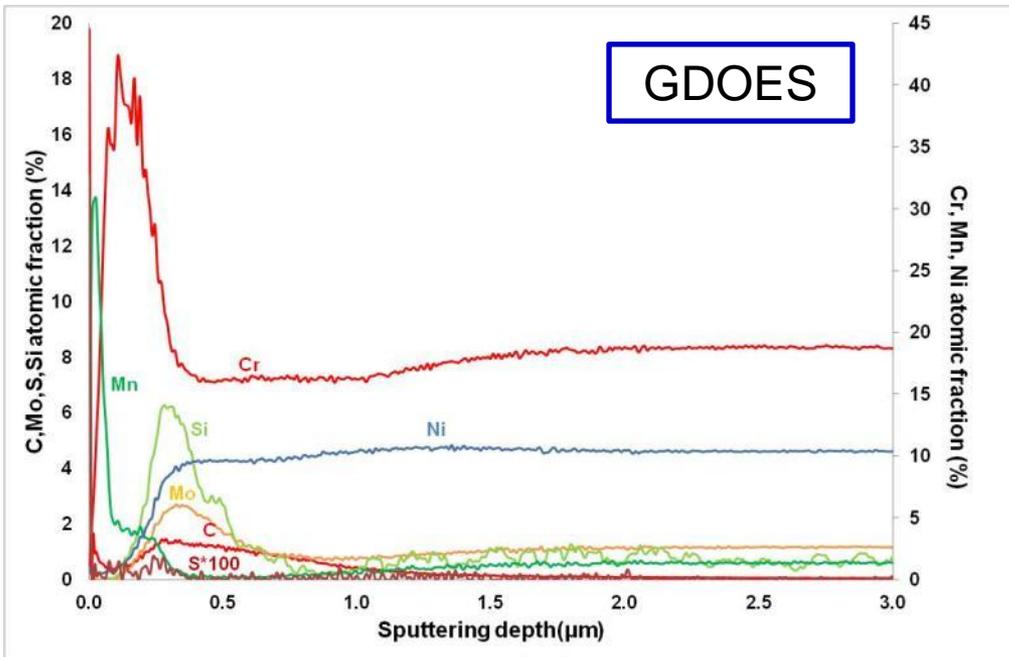
316L, 550 °C, 25 MPa, 1000 h

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)

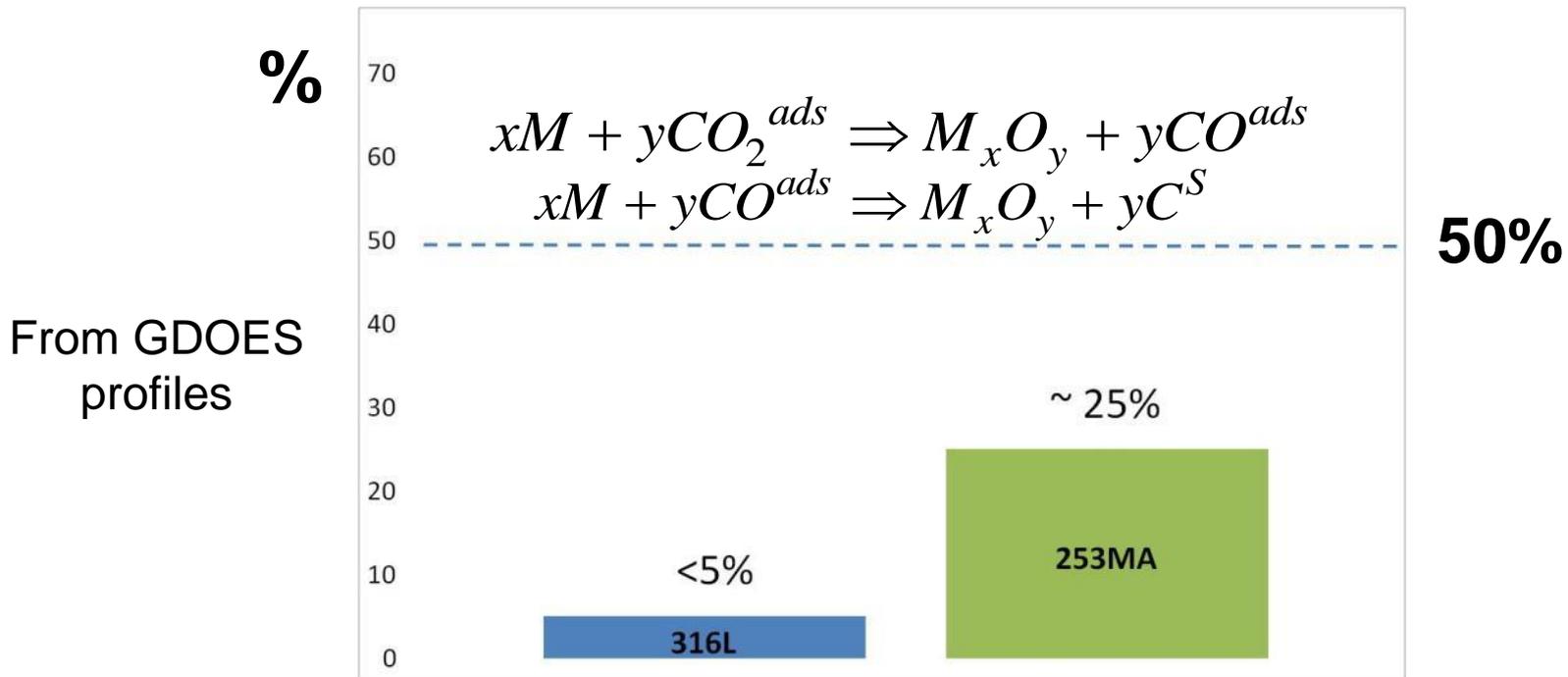


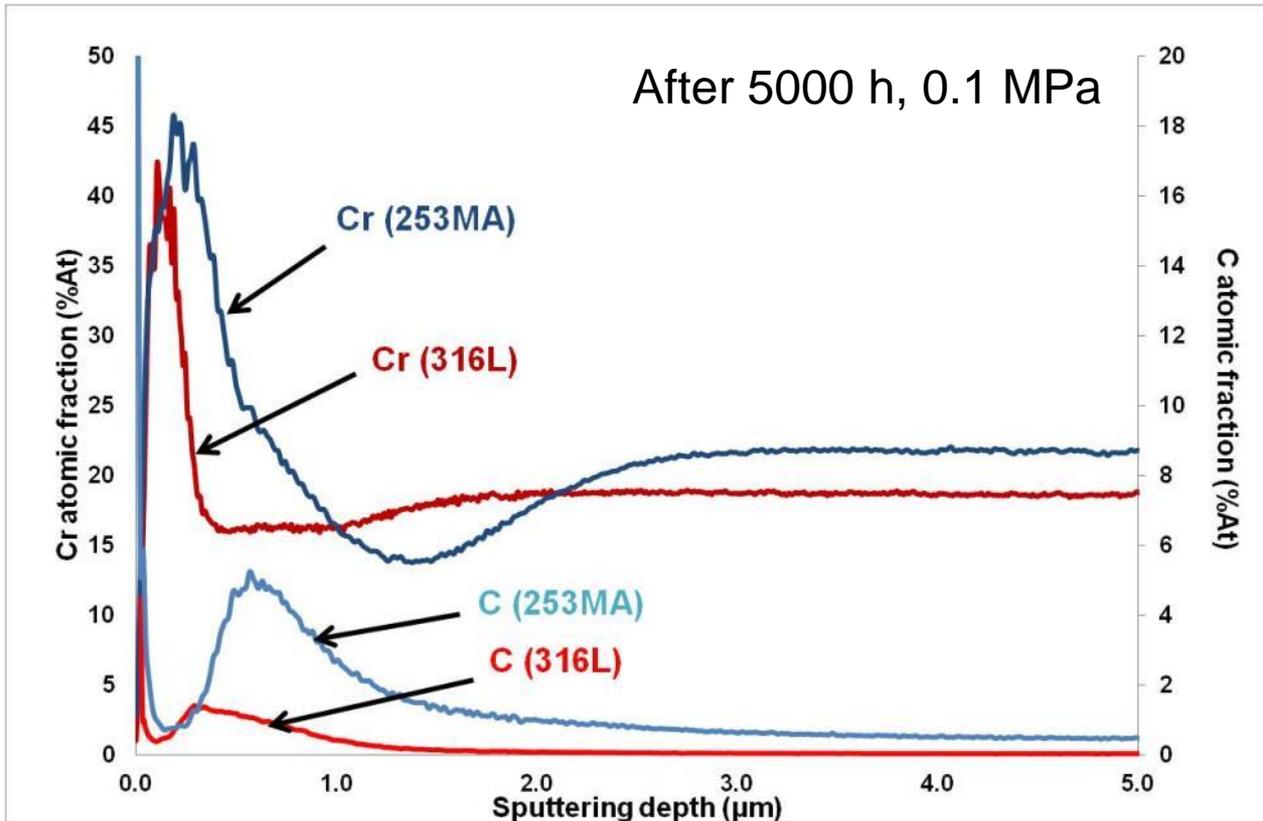
- ✓ **Substrate :**
  - **C** enrichment below the oxide layer and diffusion profile

# 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



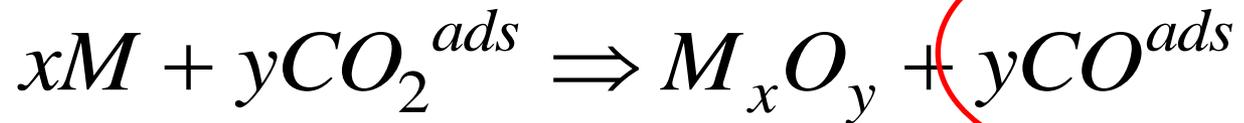


*ThermoCalc*

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

# CARBURIZATION PROCESS ?

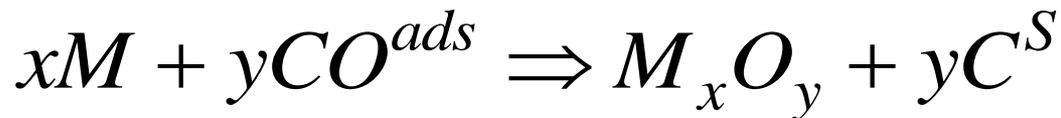
Oxidation



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**