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CORROSION BEHAVIOUR OF 9-12%CR AND 17-22%CR STEELS IN S-CO₂



[F. ROUILLARD \(CEA\), T. FURUKAWA \(JAEA\)](#)

B. DUPREY, G. MOINE

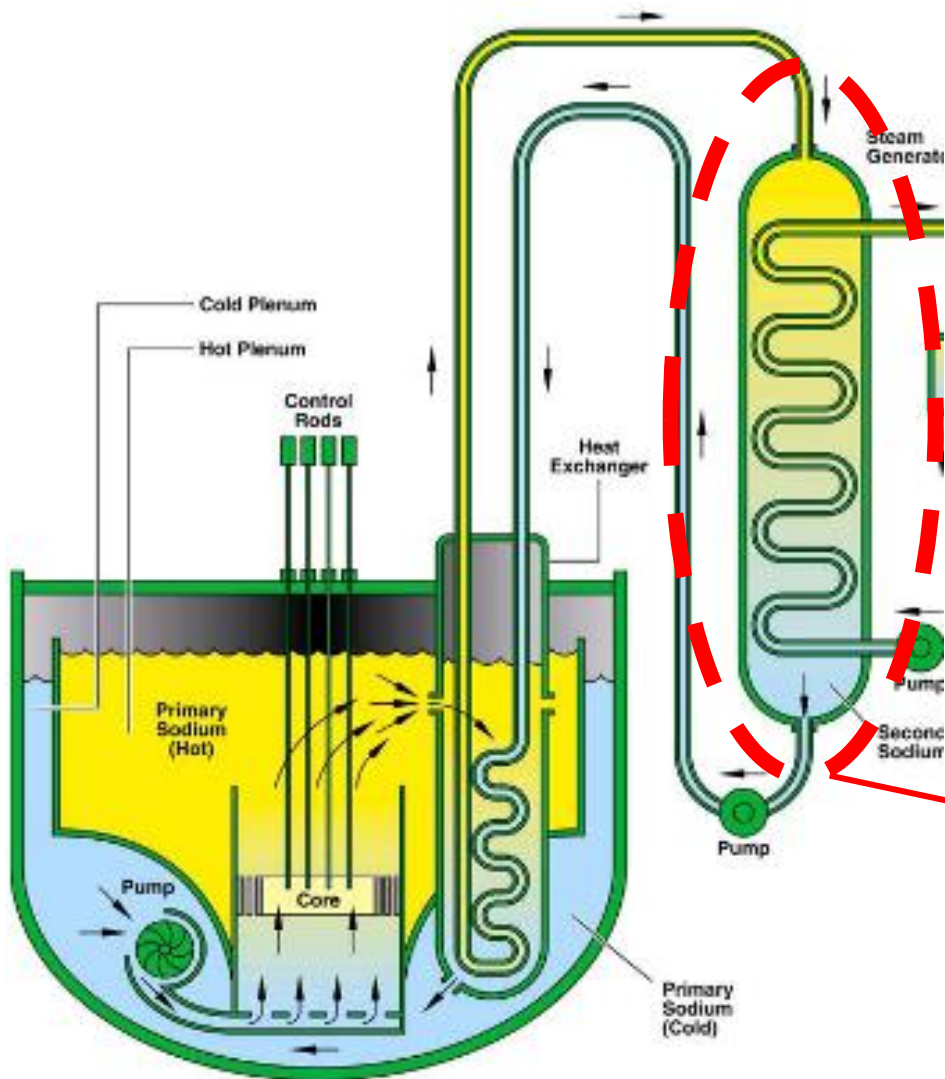
CEA/DEN/DANS/DPC/SCCME/LECNA (SACLAY)

JC RUIZ, P. VENDITTI

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

TMS2016
145th Annual Meeting & Exhibition

CONTEXT : S-CO₂ BRAYTON CYCLE COUPLED TO SFR



Advantages of S-CO₂ Brayton cycle :

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

International collaboration on S-CO₂ cycle coupled to Sodium Fast Reactor:
France, USA, South Korea, Japan

T : 400 - 550 °C
P : 80 - 250 bar

CORROSION IN CO₂ ?

FEEDBACKS FROM FORMER CO₂-COOLED NUCLEAR REACTORS (60-80'S)

CO₂ + 1% vol CO + up to a few hundreds of vpm H₂O, H₂, CH₄
Pressure = 3 – 4 MPa

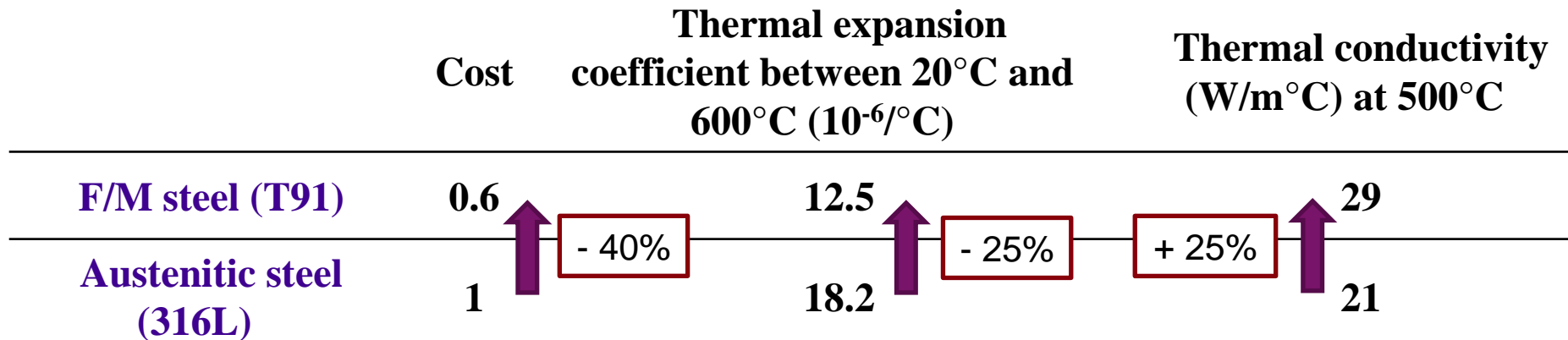
RECOMMANDATIONS :

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

T_{max} : 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-CO₂

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** CO₂ 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 (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

High pressure S-CO₂



Atmospheric pressure CO₂



Metallic coupons (25*15*1 mm)

« Industrial » CO₂ purity in JAEA and CEA tests (99,995%) :

- H₂O < 200 vpm
- O₂ < 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 = $f(T, P)$

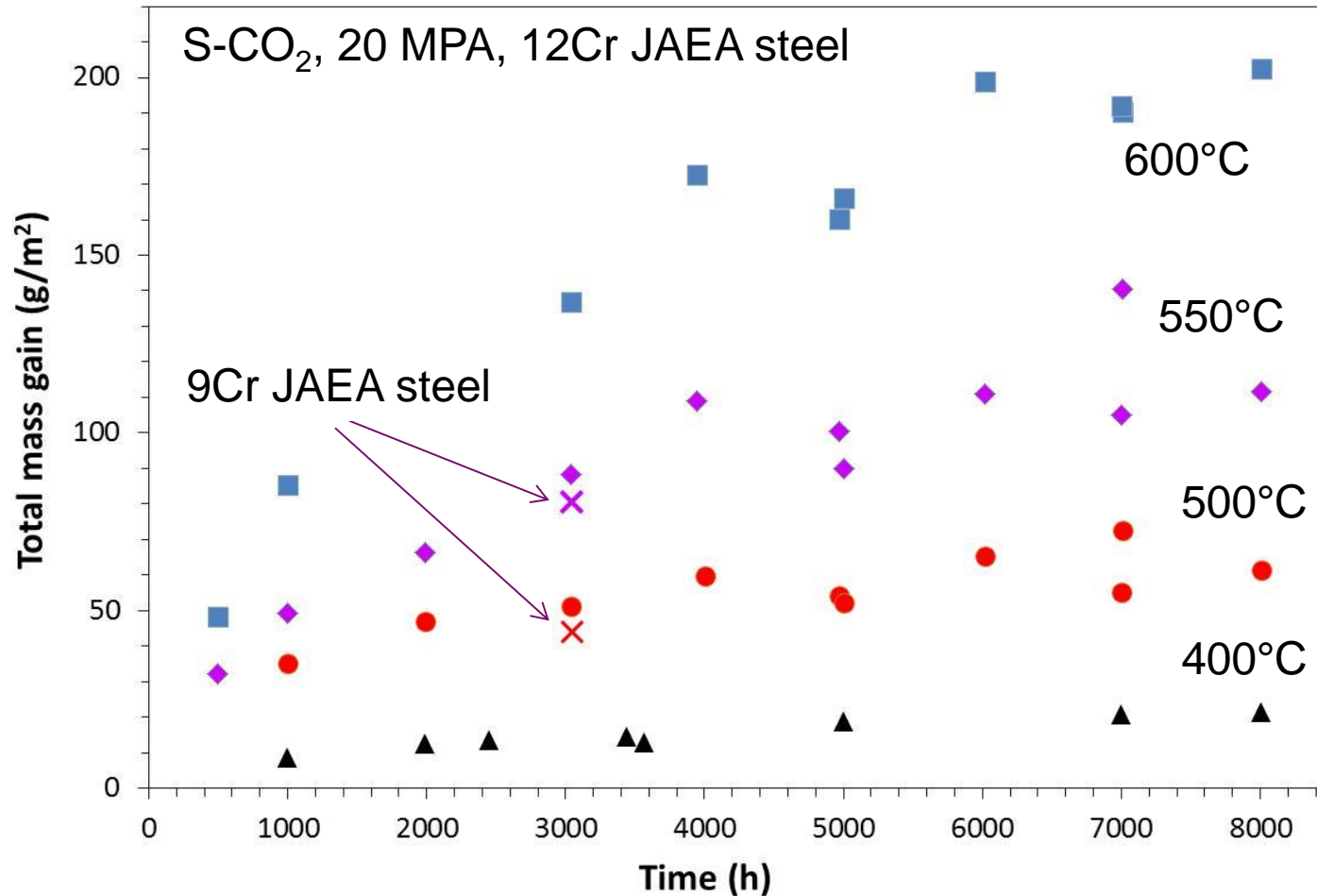


Proposed corrosion model : « Available Space Model »

- ✓ Influence of surface finish
- ✓ Influence of O₂ impurities in CO₂

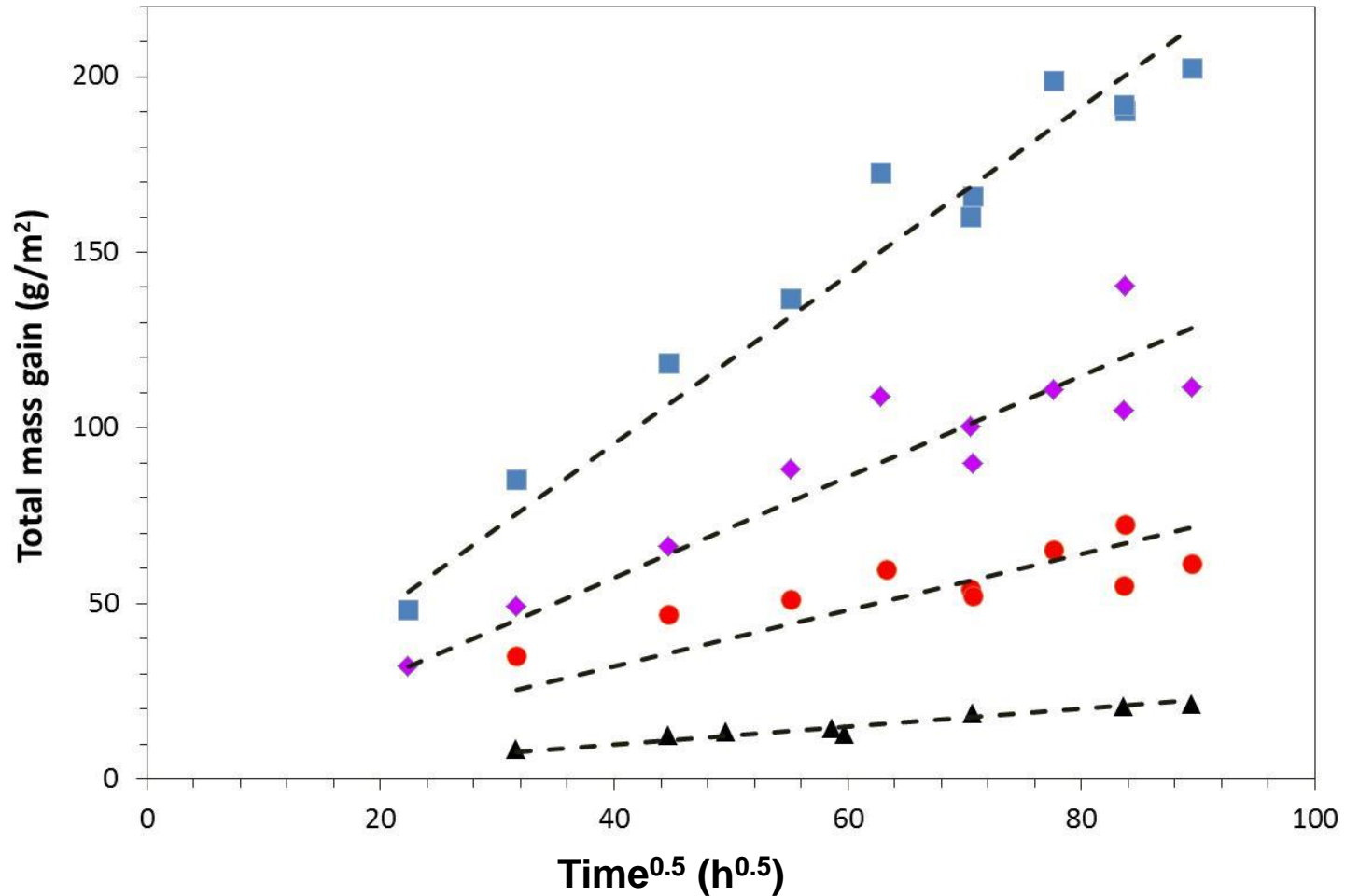
PhD thesis of S. Bouhieda
(2009-2012)

CORROSION KINETICS OF 9-12CR JAEA STEELS



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

CORROSION KINETICS OF 9-12CR JAEA STEELS

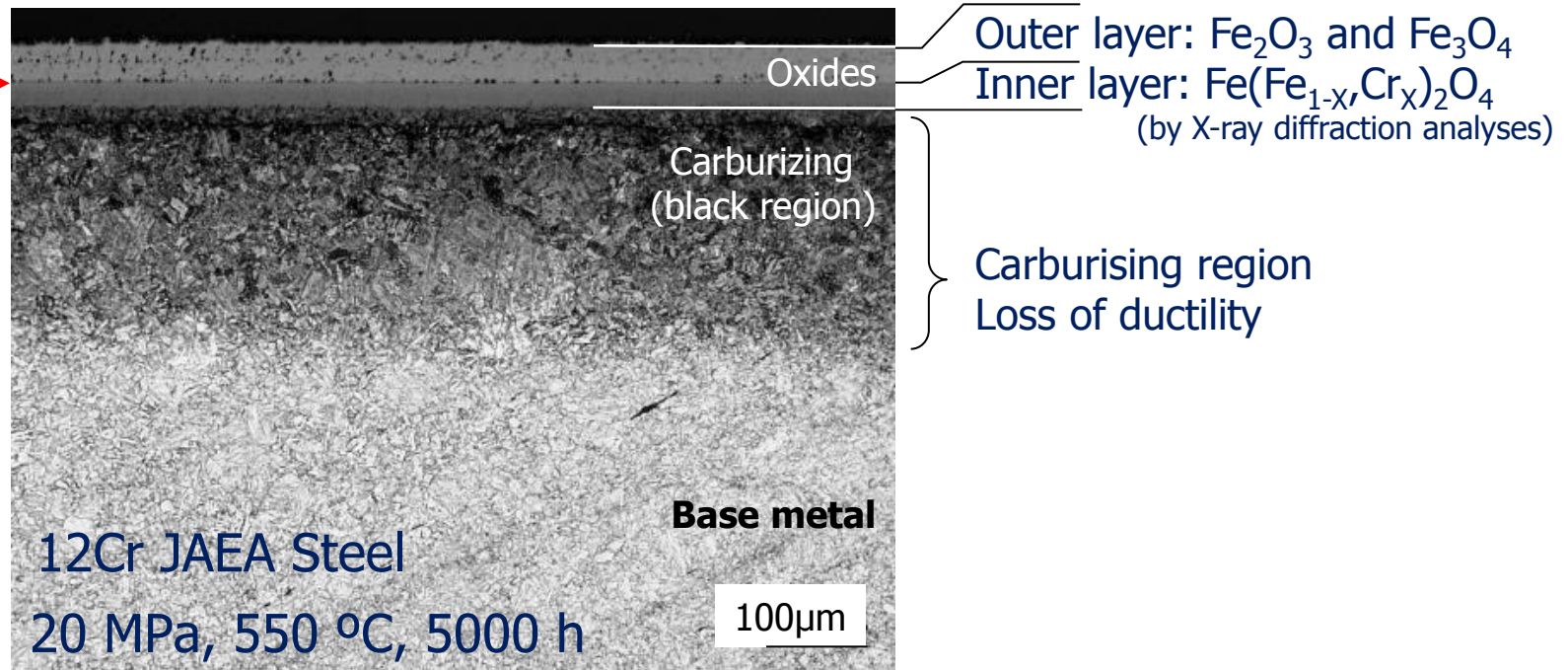


- Parabolic kinetics
- What does happen to the samples ?

CORRODED SURFACE UNDER CO₂

Mass gain = Oxidation AND Carburisation

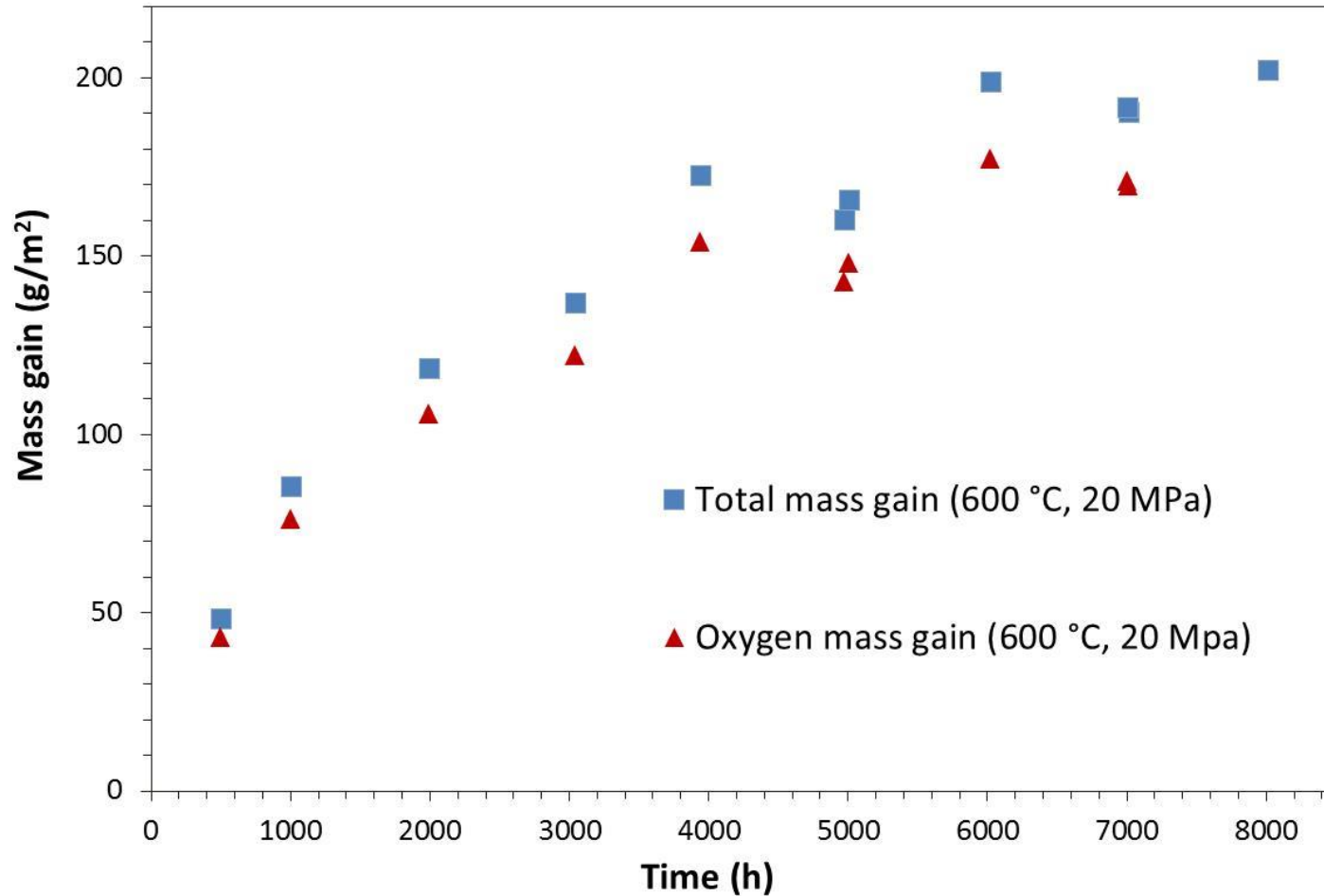
Original surface of base metal →



What are the proportion of the mass gain induced by :

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

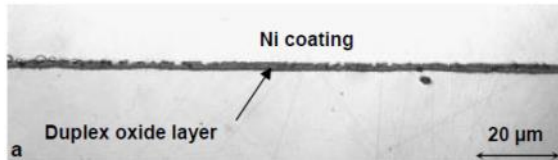
Oxidation mechanism of 9-12Cr steels in CO₂



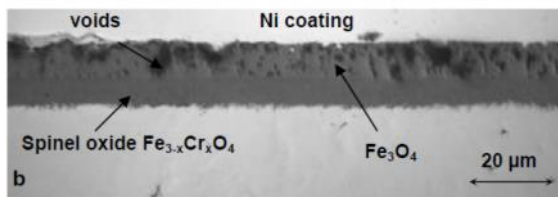
Parabolic oxidation rate = diffusion controlled

OXIDE FEATURES

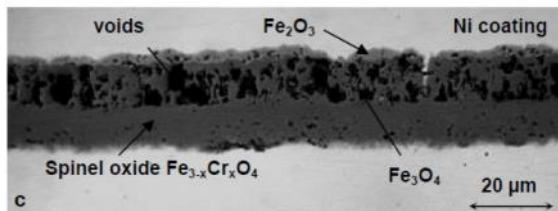
9Cr CEA steel in CO₂,
550 °C, 0.1 MPa



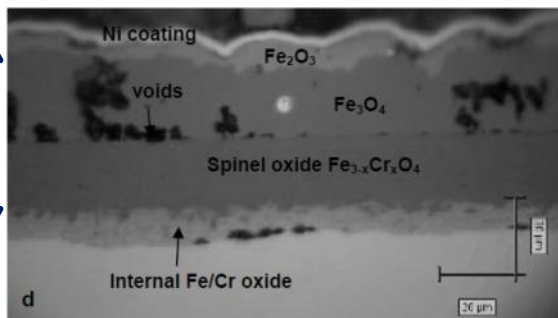
1 h



110 h



322 h



1000 h

- **Duplex** oxide layer : Fe oxides (Fe₃O₄ + Fe₂O₃) and Fe/Cr oxide (Fe_{2.3}Cr_{0.7}O₄)

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

- [Cr]_{spinel} (mol/cm³) ~ [Cr]_{substrate} (mol/cm³)

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

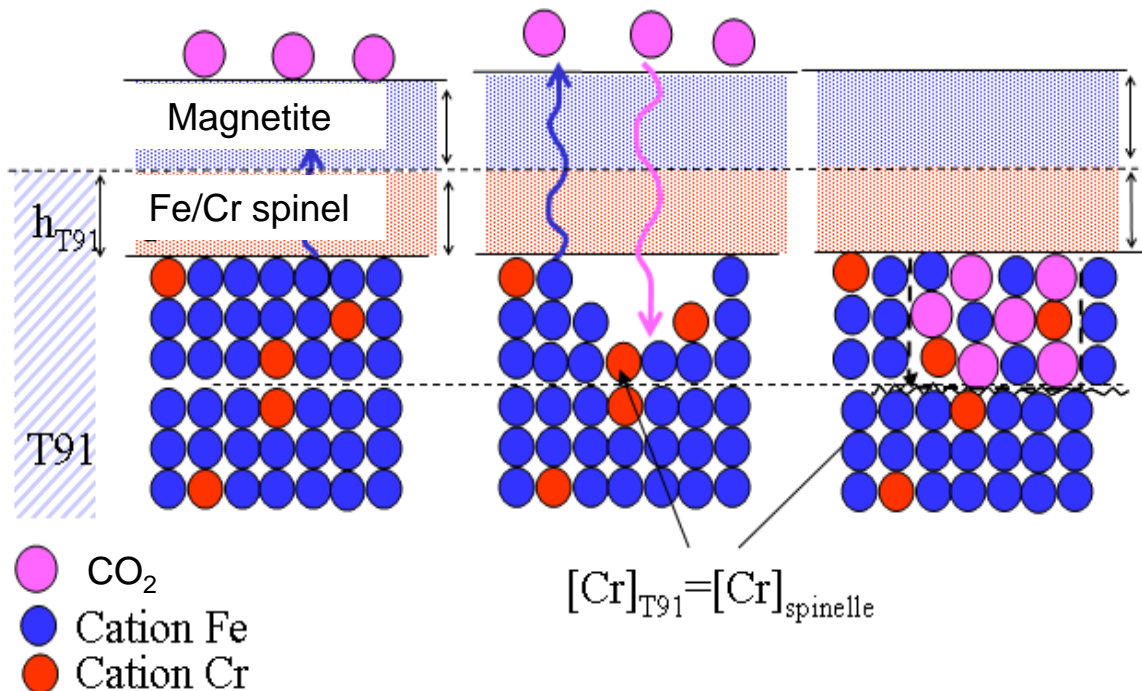
- **Carbon** enrichment at the O/M interface (GDOES analysis)

- Fe_{2.3}Cr_{0.7}O₄ grows at the metal/oxide interface and Fe₃O₄ at the oxide/gas interface (*Taylor et al. OxMet. 1980 : Tracers experiment*).

- **Parabolic** growth rate

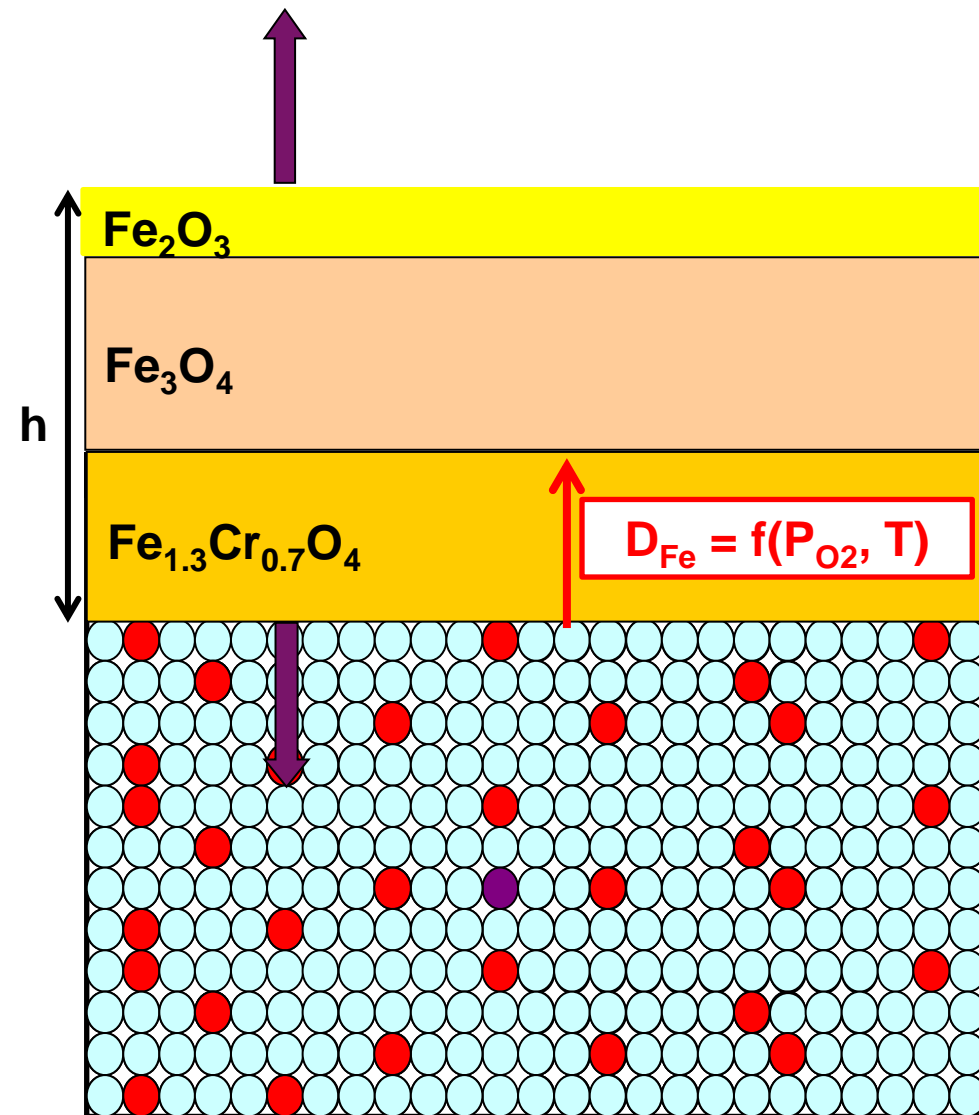
Oxidation model ?

« 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. CO₂ 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



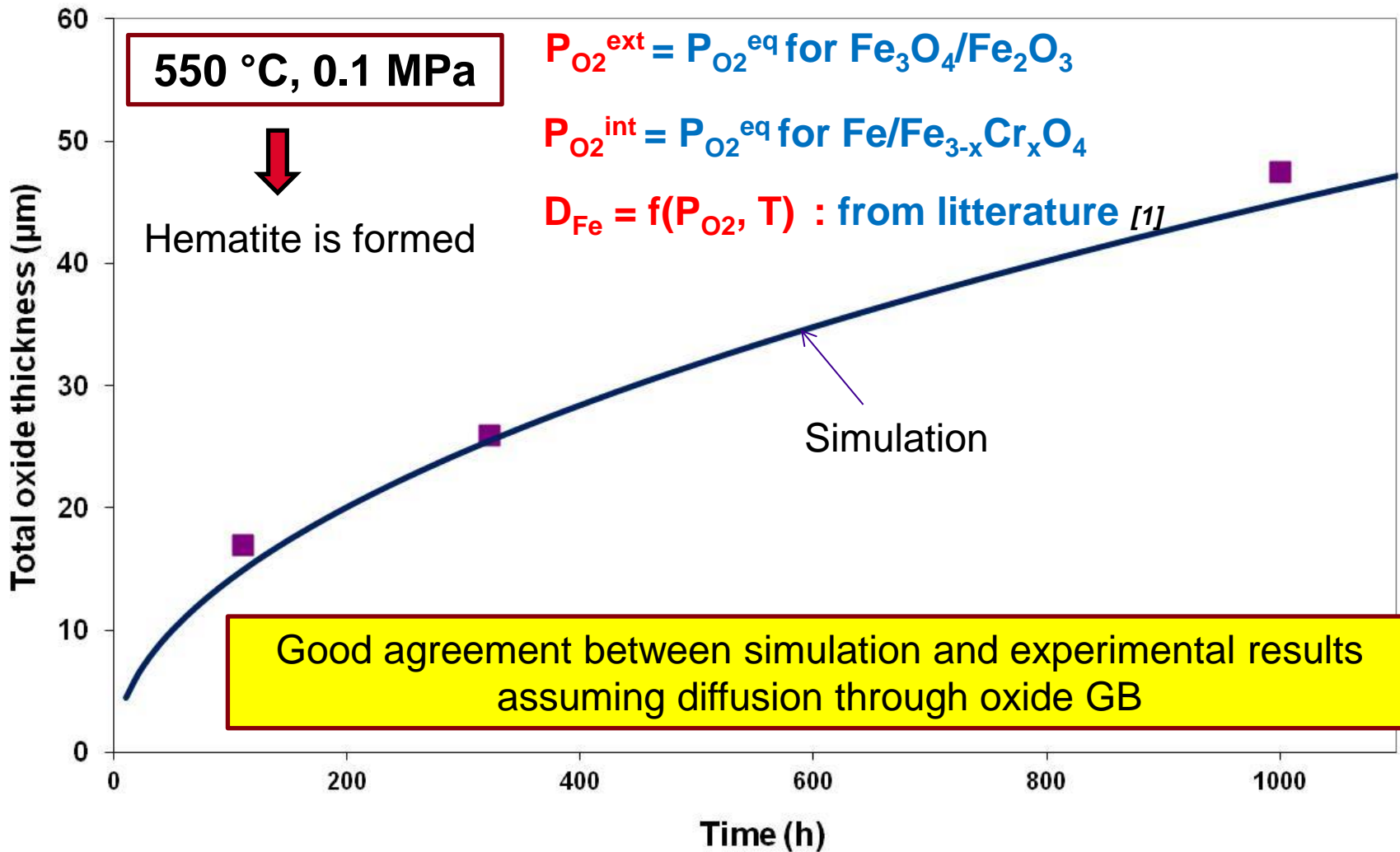
- $P_{\text{O}_2}^{\text{ext}}$
- calculated from the gas phase composition ($P_{\text{CO}_2}/P_{\text{CO}}$ ratio)
or
 - $= P_{\text{O}_2}^{\text{eq}}$ for $\text{Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3$
if Fe_2O_3 stable

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

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

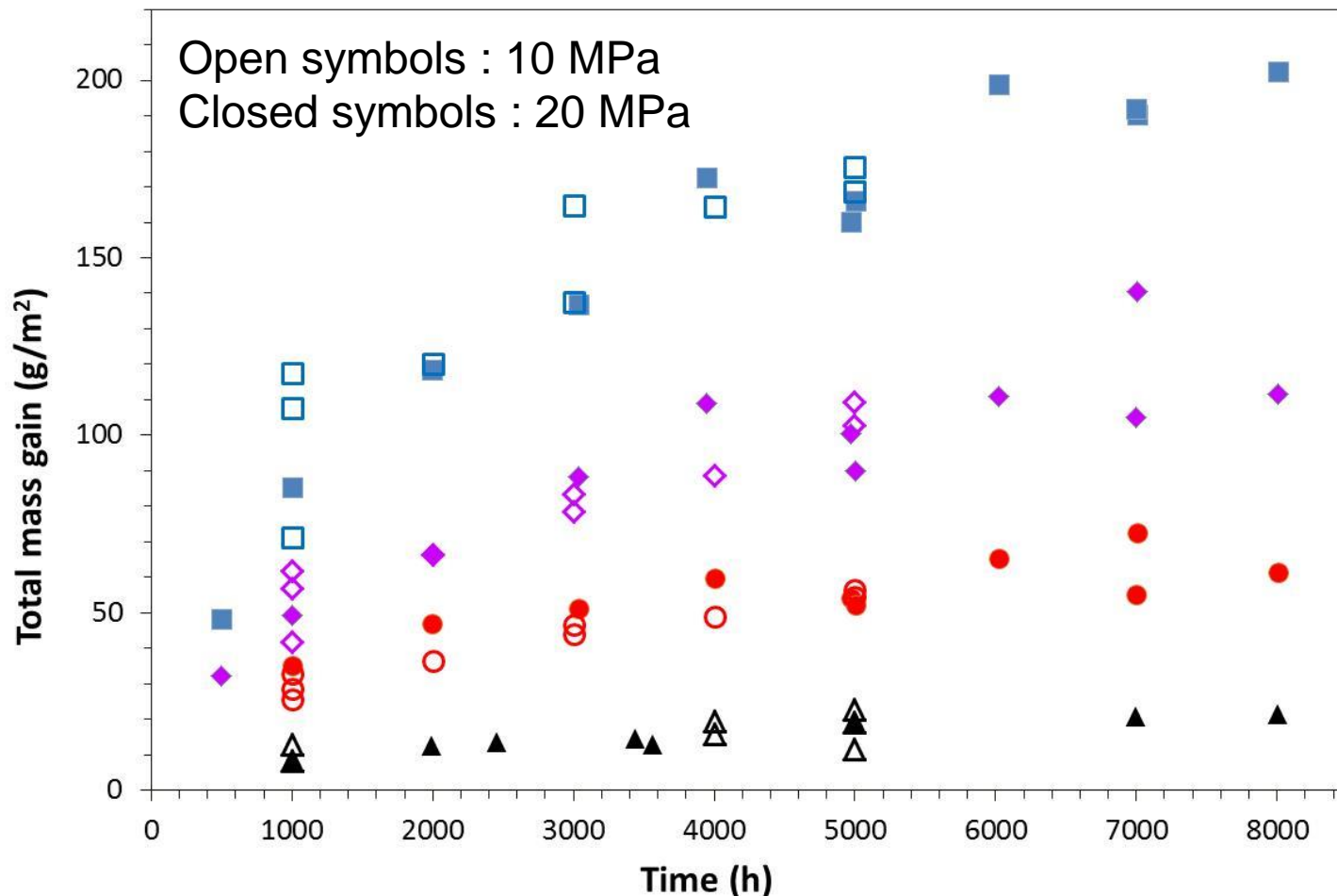
$D_{\text{Fe}}, P_{\text{O}_2}^{\text{int}}, P_{\text{O}_2}^{\text{ext}}$: input parameters
(from literature review)

OXIDE GROWTH MODELING AND SIMULATION



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

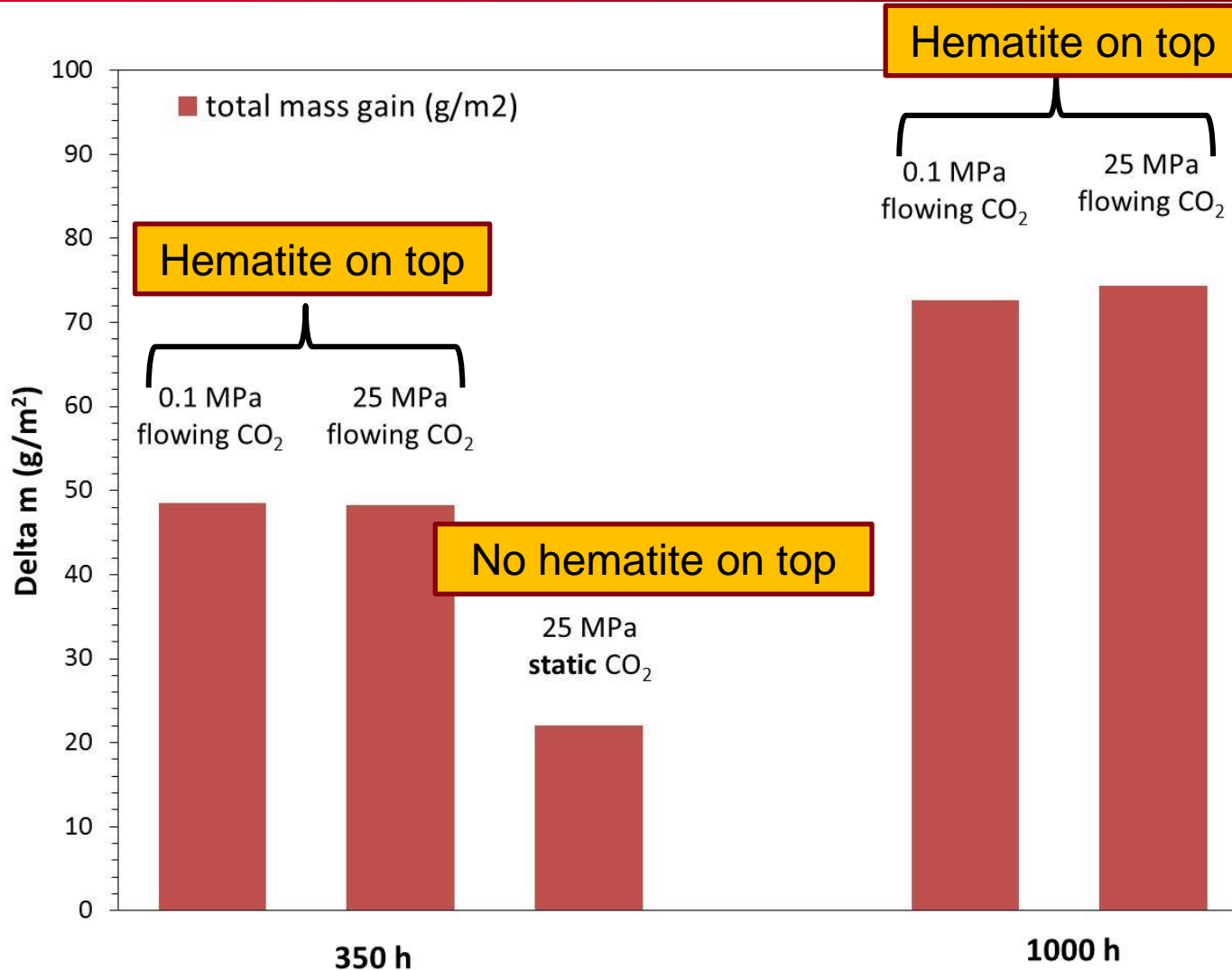
EFFECT OF P_{CO_2} ON OXIDATION



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

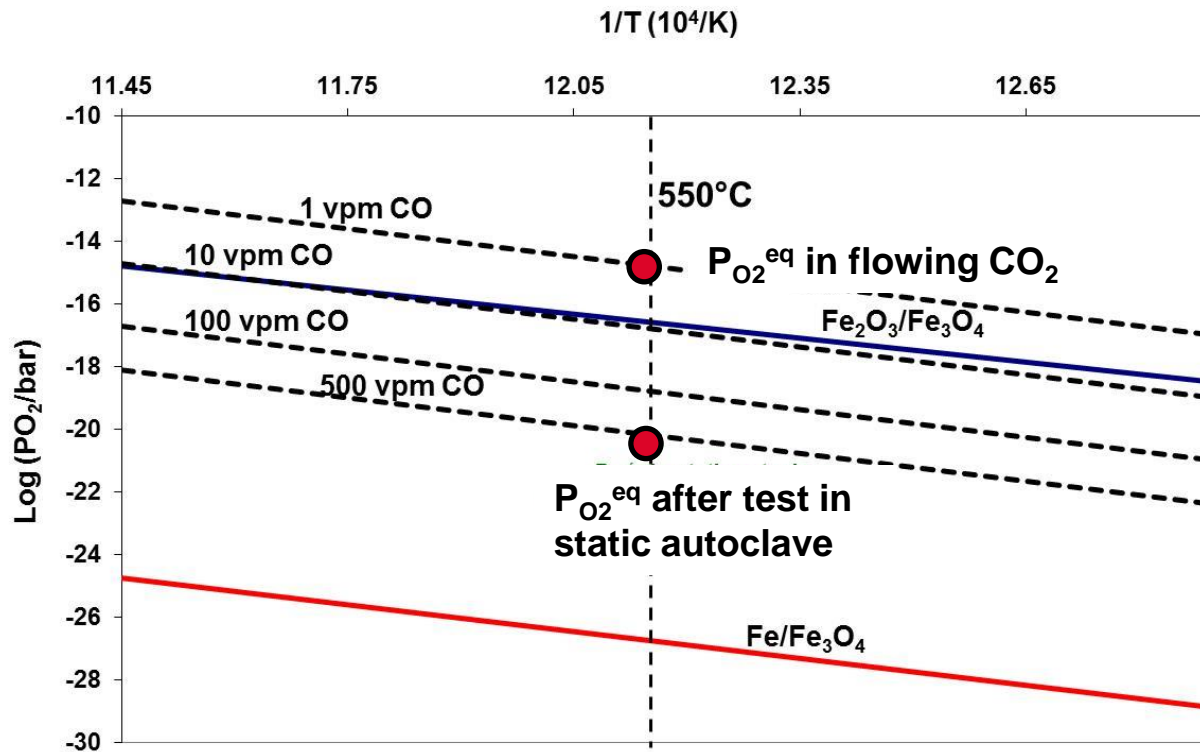
With higher P_{CO_2} difference : 0.1 MPa and 25 MPa ?

EFFECT OF P_{CO_2} ON OXIDATION

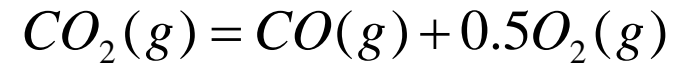


The oxidation rate does not depend on P_{CO_2} : the external driving force for oxide growth $P_{O_2}^{ext}$ is « buffered » by the presence of hematite

FORMATION OF Fe_2O_3 ?

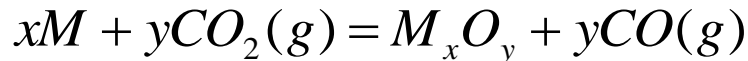


The formation of Fe_2O_3 is controlled by the P_{CO_2}/P_{CO} ratio in the gas phase :



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

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 CO₂

What is the carburisation kinetics ?
Is there any effect of P_{CO_2} ?

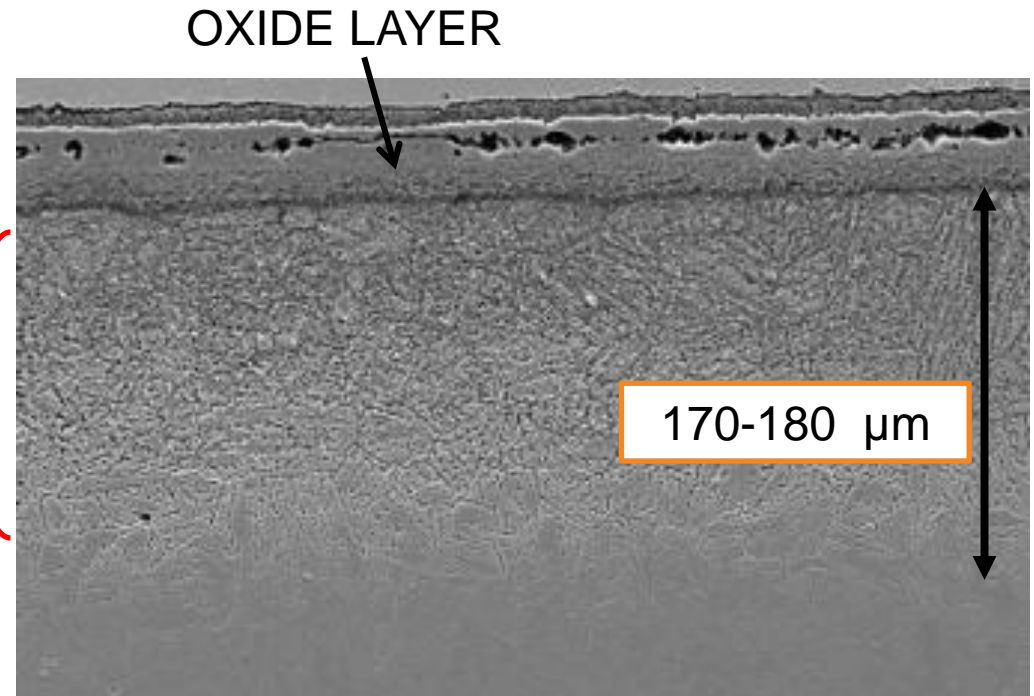
Could we model the carburisation
propagation into the steel ?

Why does the steel
carburise ?

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

CARBURISED ZONE :

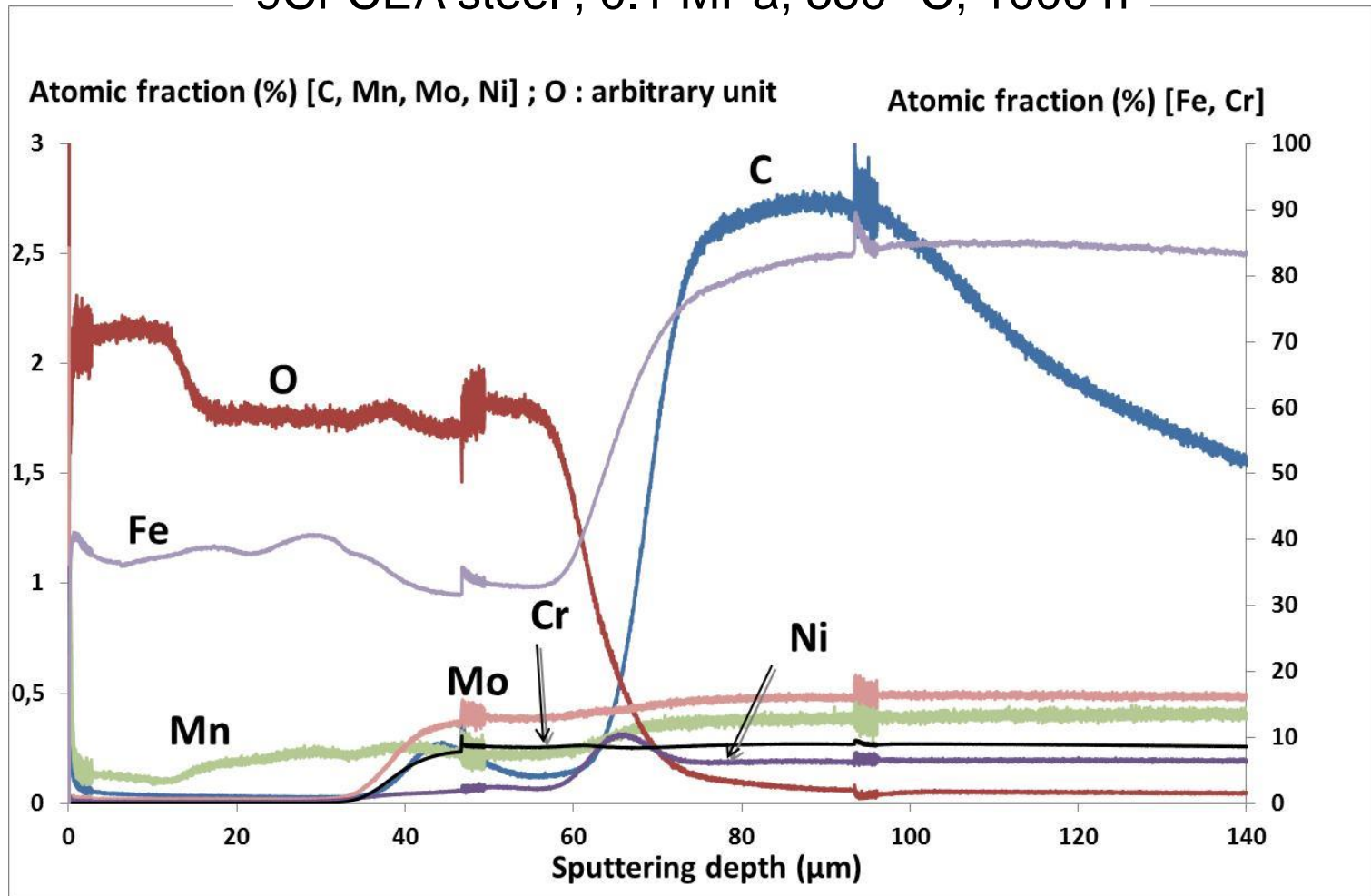
On martensitic laths
and old primary austenitic GB



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

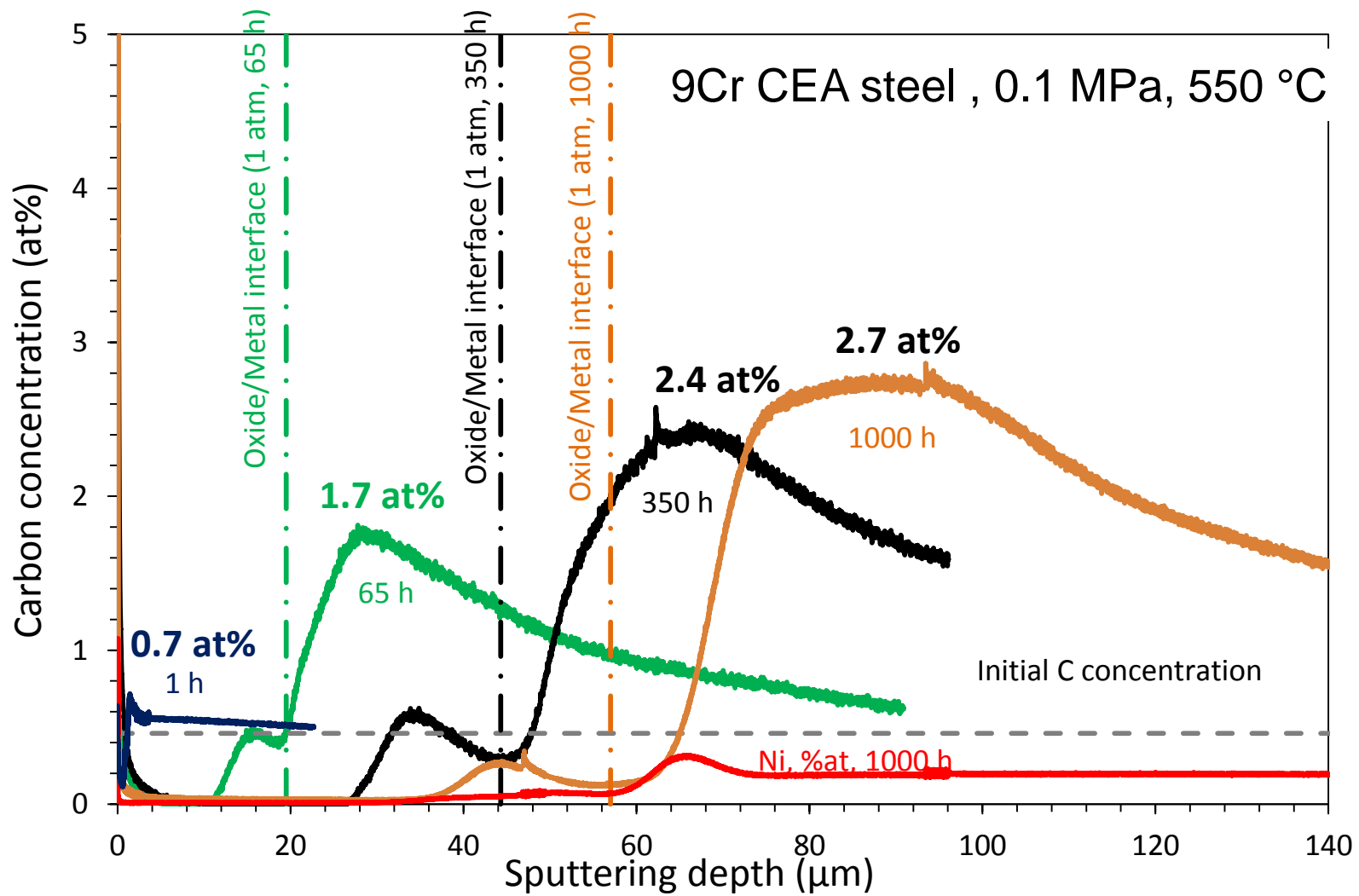
CARBON PROFILE BY GDOES

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 CO₂ 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 :

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

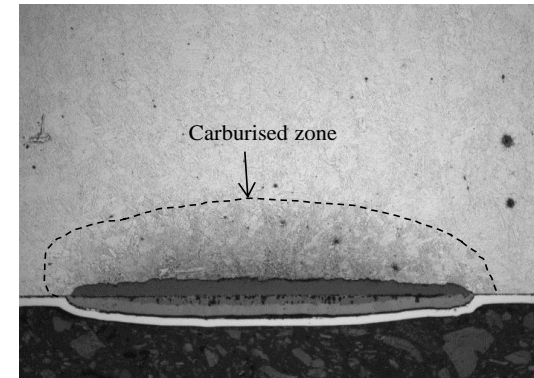
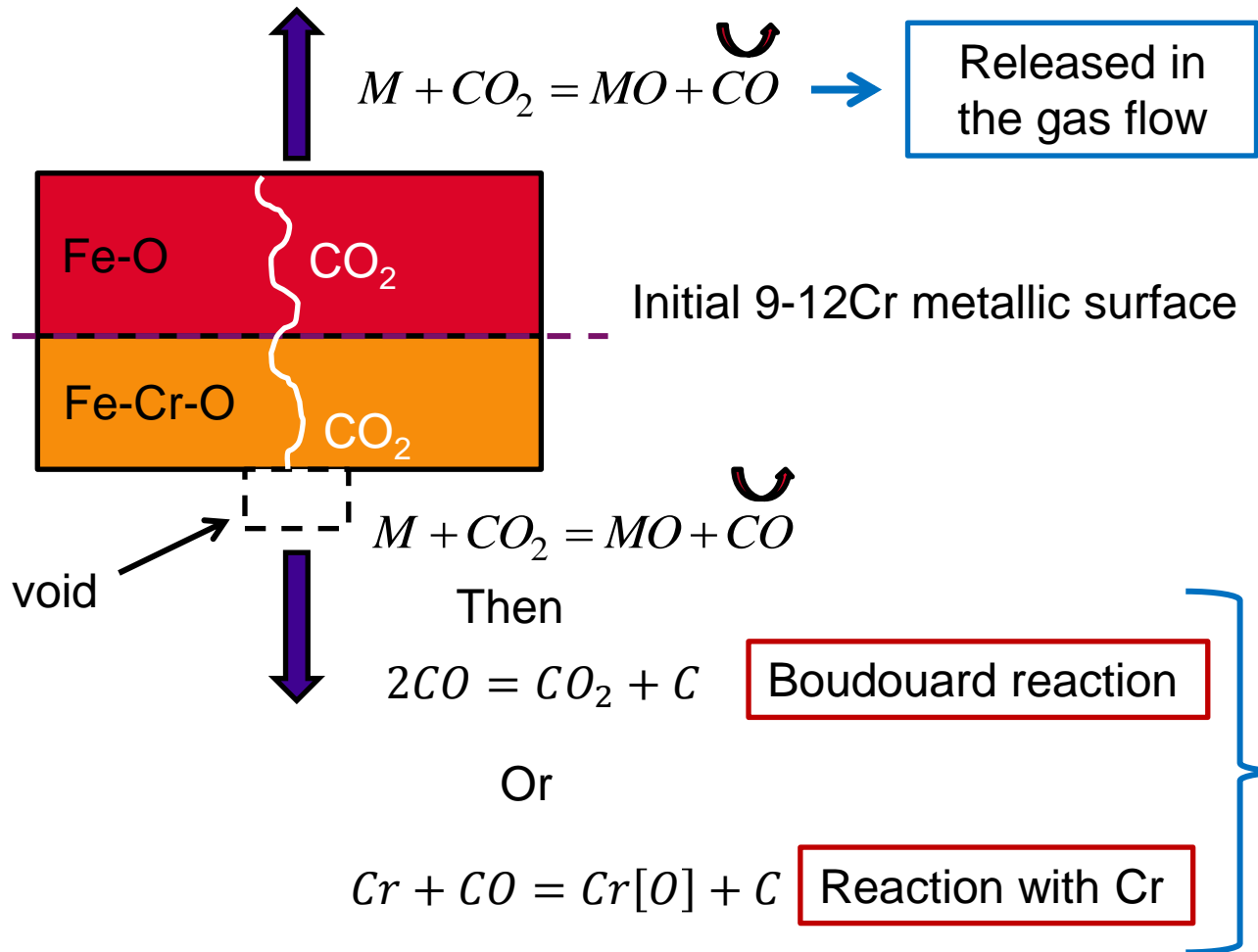
With C^{eq} the concentration of carbon in equilibrium with **the carbon activity of the gas phase**



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

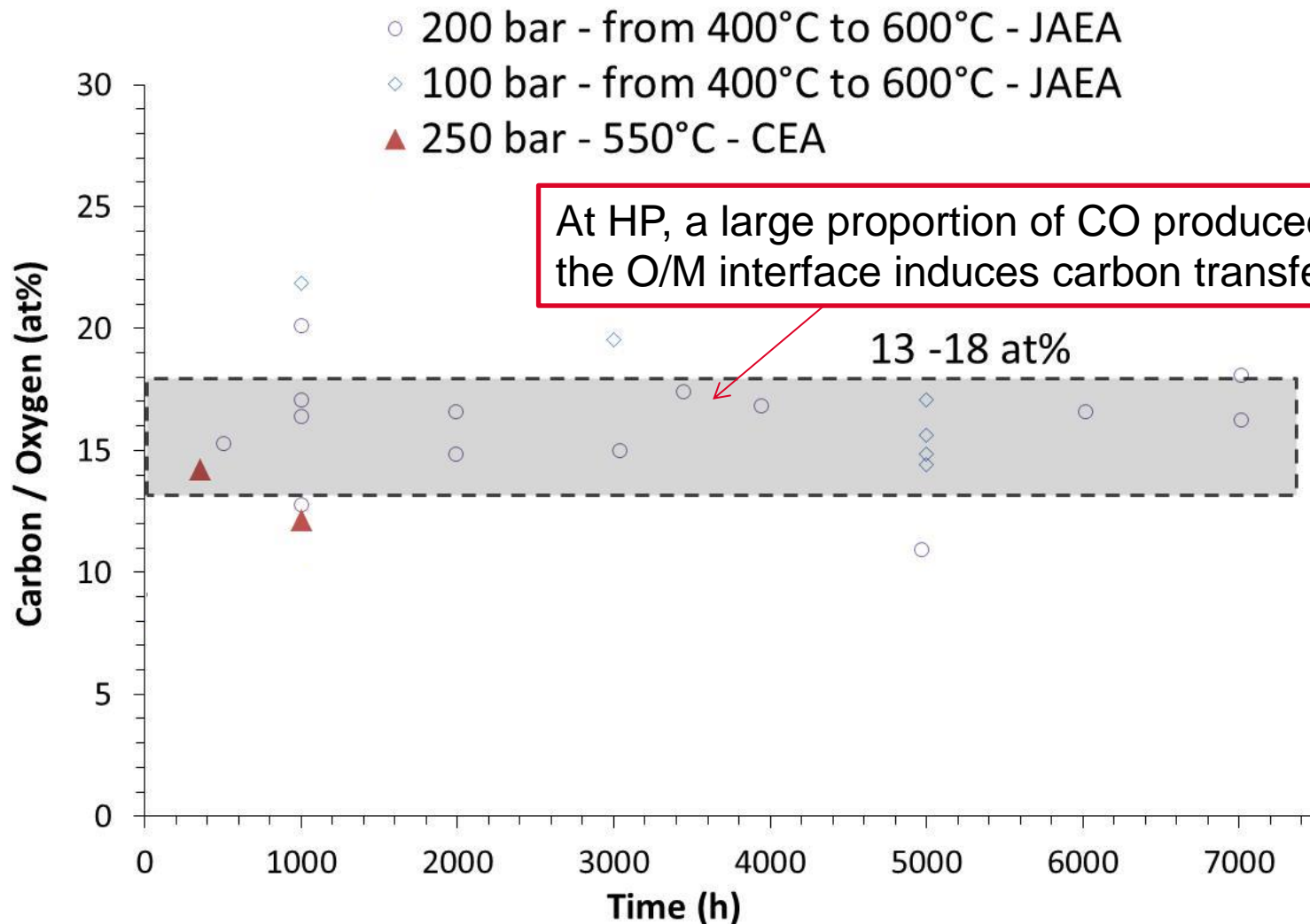
CARBON TRANSFER

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%

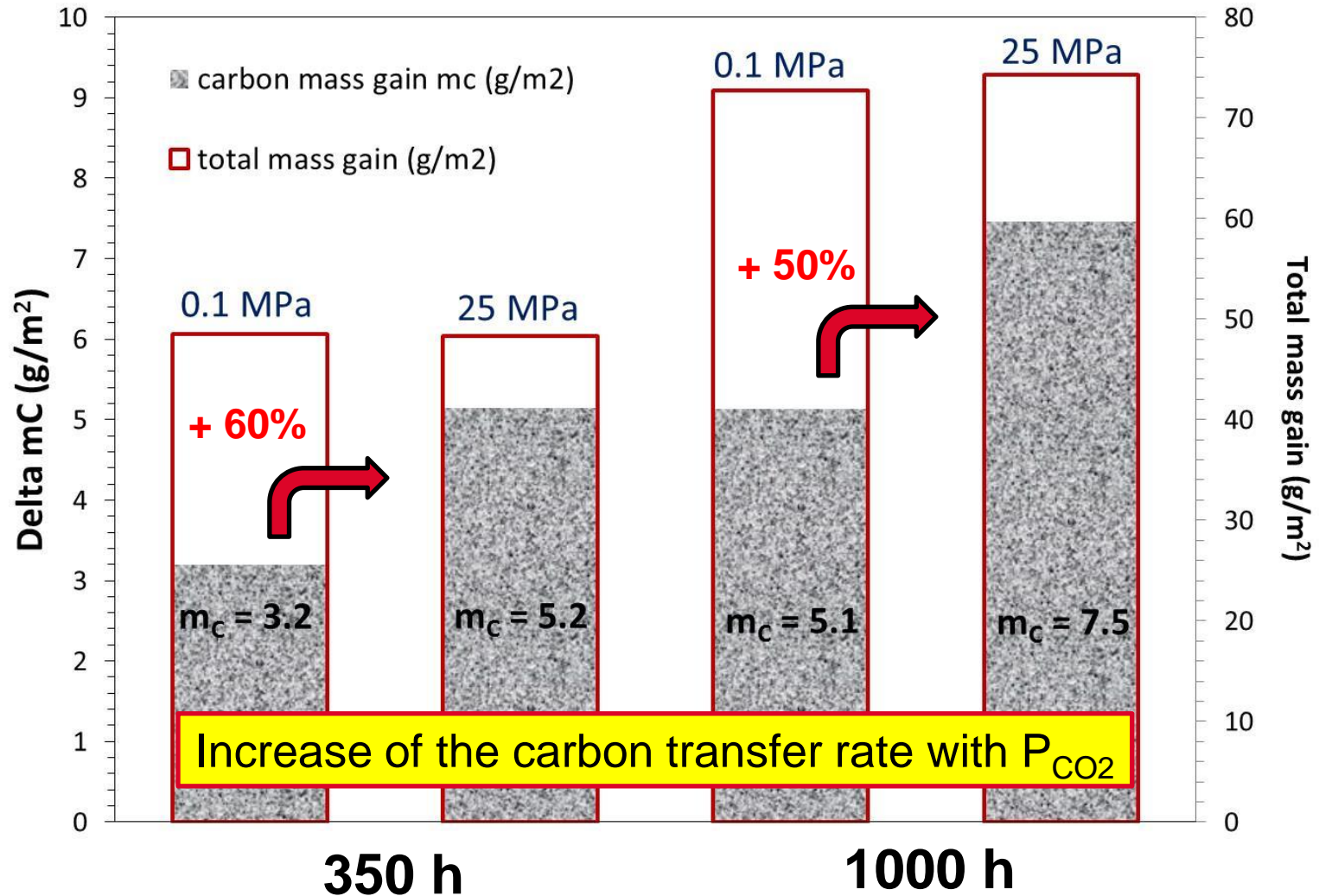
CARBON TRANSFER



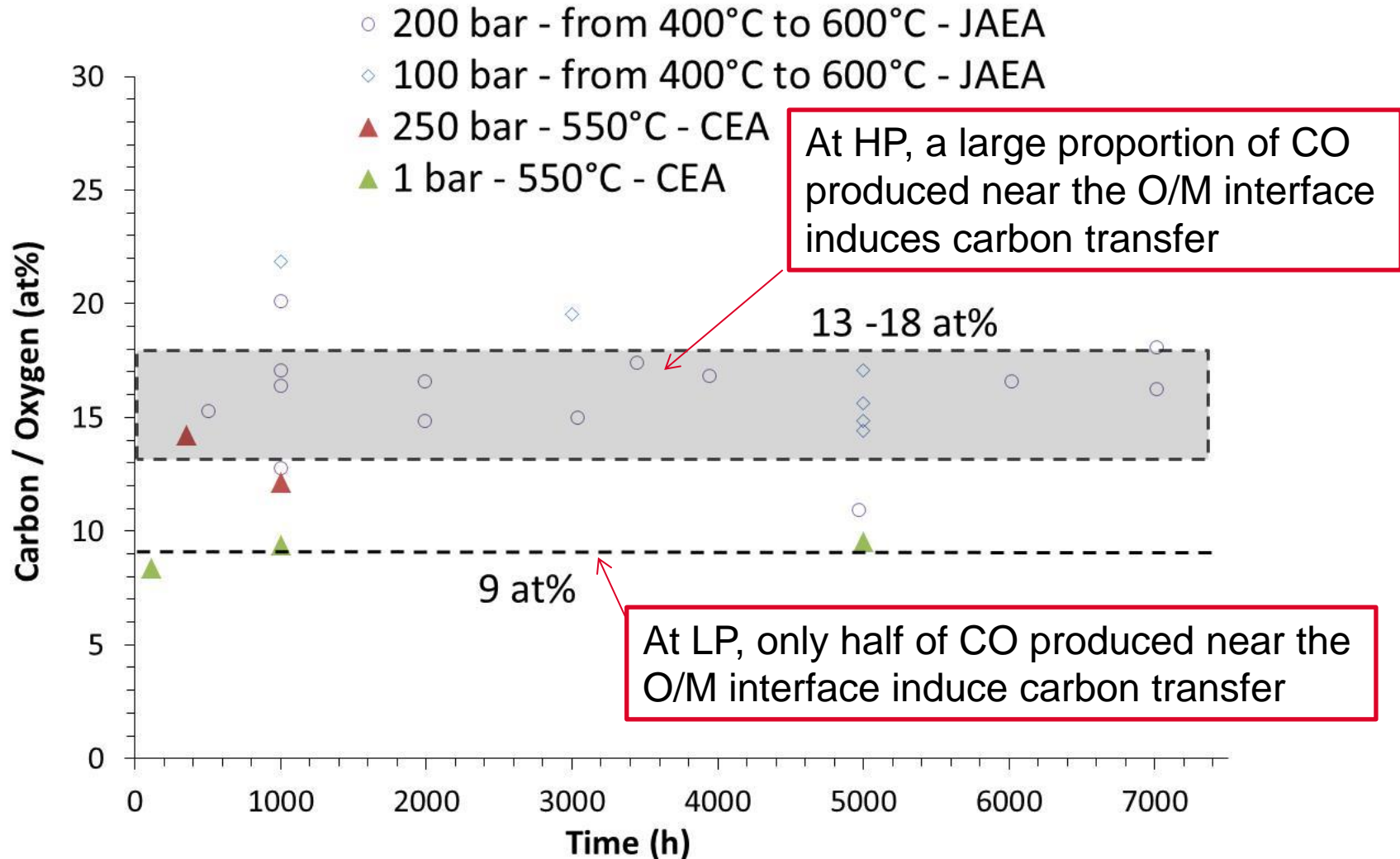
INFLUENCE OF P_{CO_2} ON CARBON TRANSFER

❑ No « detectable » influence of P_{CO_2} between 10 and 20 MPa ...

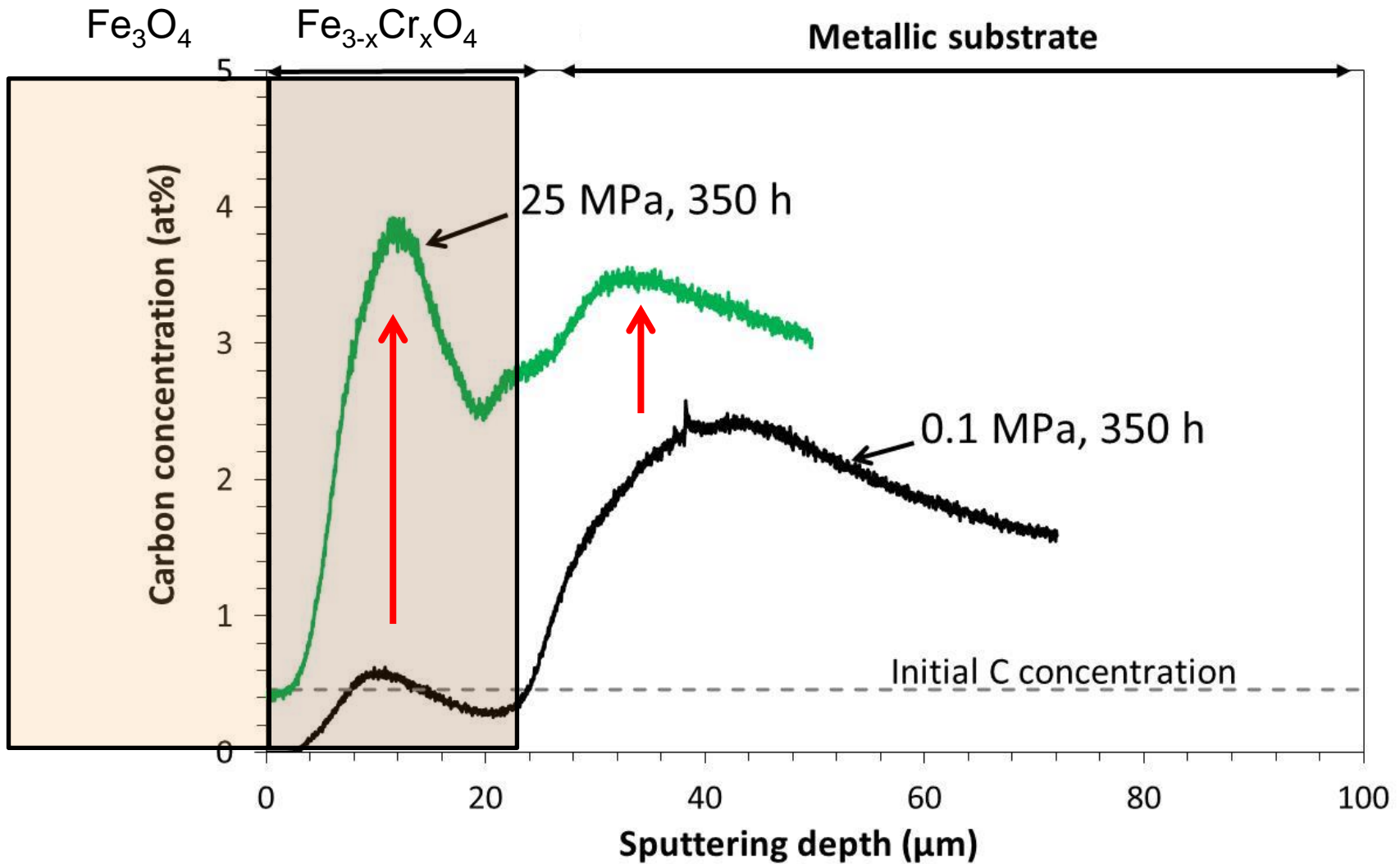
... but higher carbon transfer rate detectable when increasing from 0.1 to 25 MPa



INFLUENCE OF P_{CO_2} ON CARBON TRANSFER



INFLUENCE OF P_{CO_2} ON CARBON TRANSFER



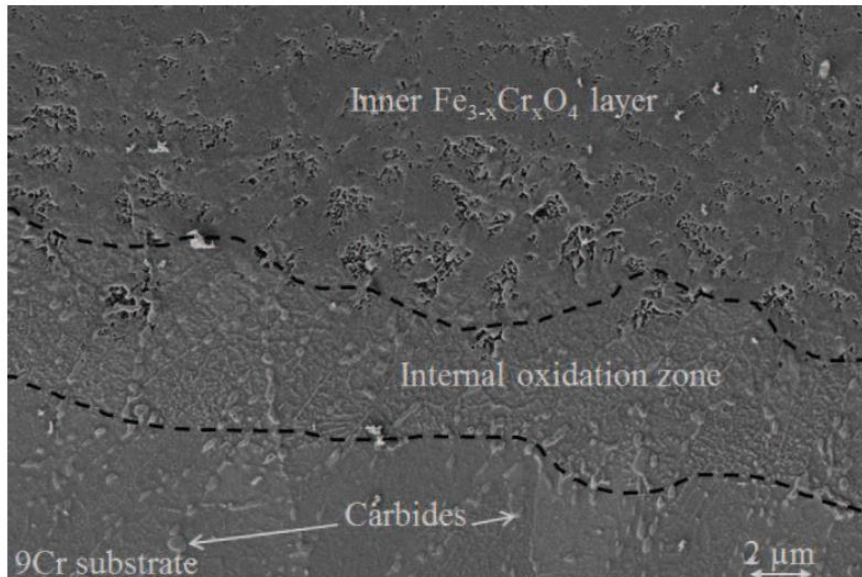
- %C at the O/M interface increases
- %C in the inner oxide scale increases



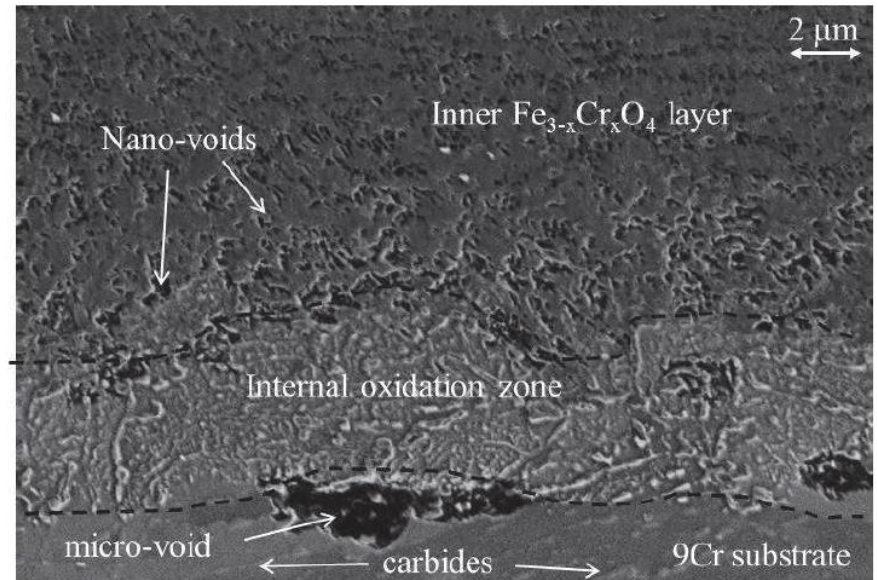
Carburisation rate increases

INFLUENCE OF CARBURISATION ON THE INNER OXIDE MICROSTRUCTURE

T91, **0.1 MPa**, 550 °C, 350 h



T91, **25 MPa**, 550 °C, 350 h



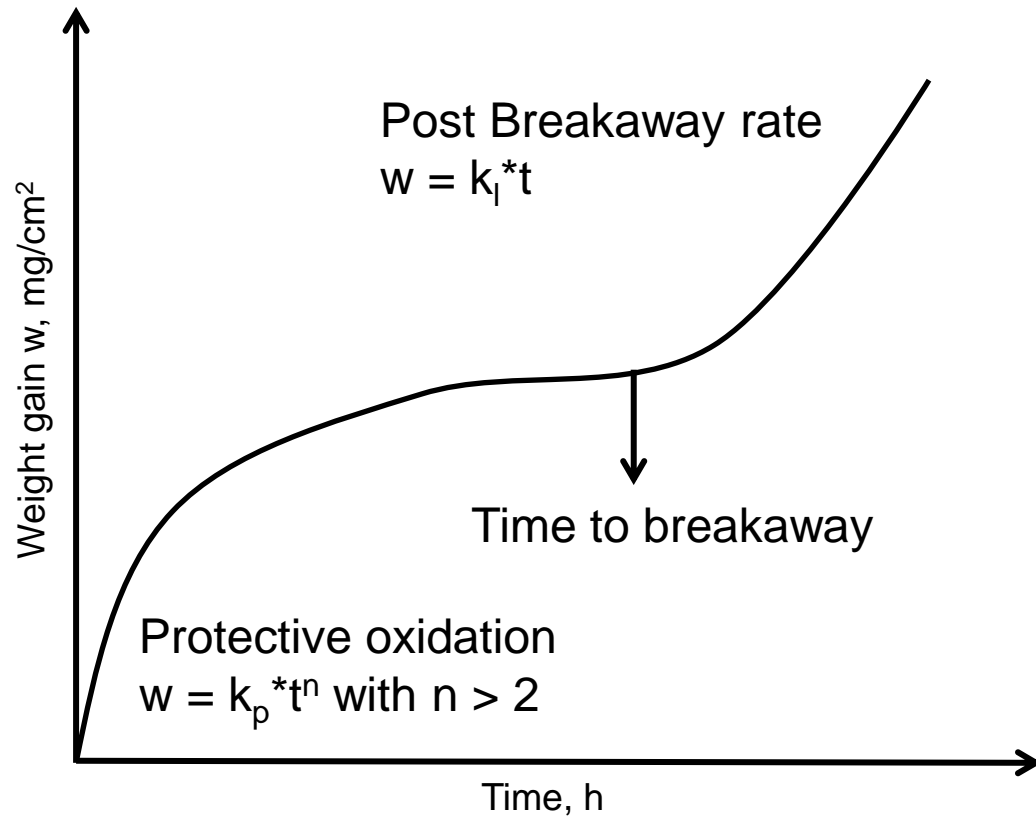
At high P_{CO_2} :

- 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 ?



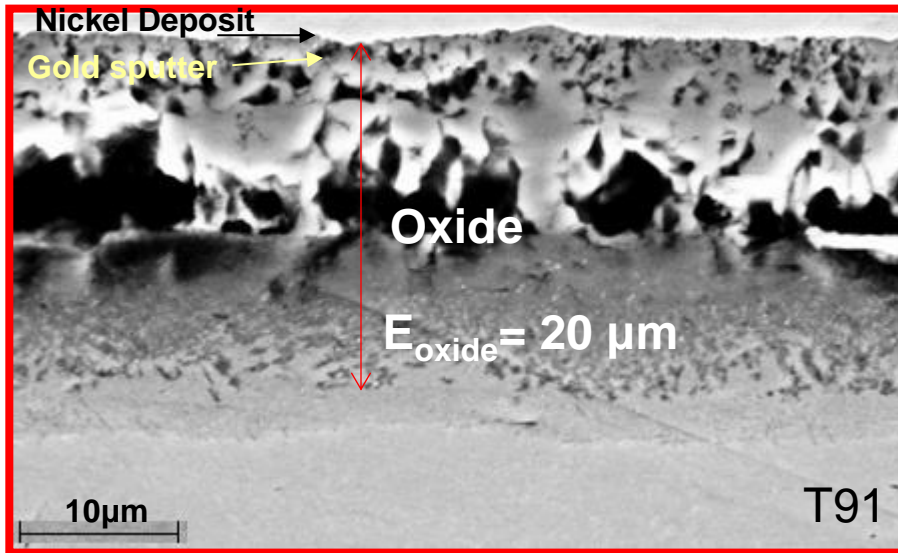
Feedbacks from CO_2 -cooled nuclear reactors*:

- Known for mild steels in S- CO_2 at $T > 350 \text{ }^\circ\text{C}$
- But already observed on 9Cr steel in CO_2 – 40 bar at 550°C (first in 1971)
- Favored at HP 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 CO_2* , British Nuclear Energy Society, Reading University (1974)

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

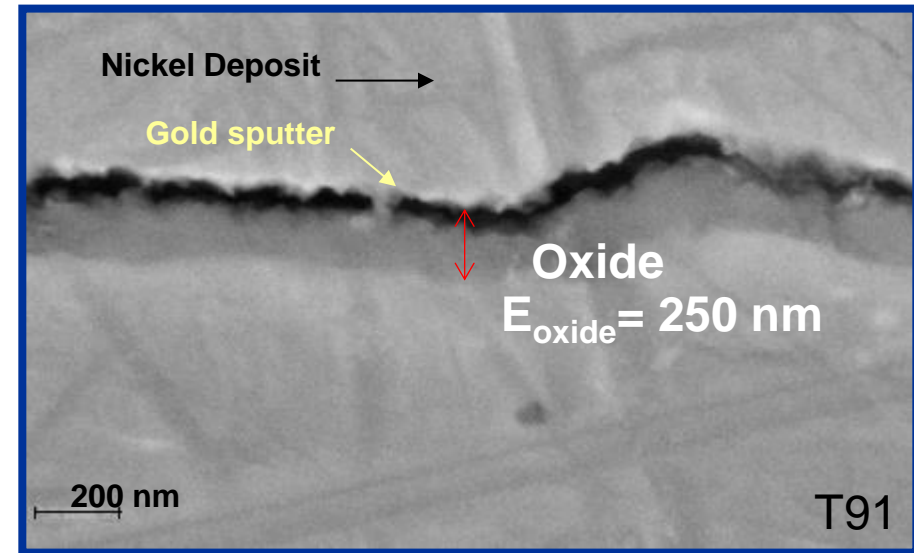
« Industrial » CO₂ purity (with O₂ ~ 100 μbar)



Fast growing iron rich duplex oxide scale

%Cr oxide ~ 9 at%

High CO₂ purity (with O₂ ~ 1 μbar)



Slow growing chromium rich oxide scale

%Cr oxide ~ 20 at%

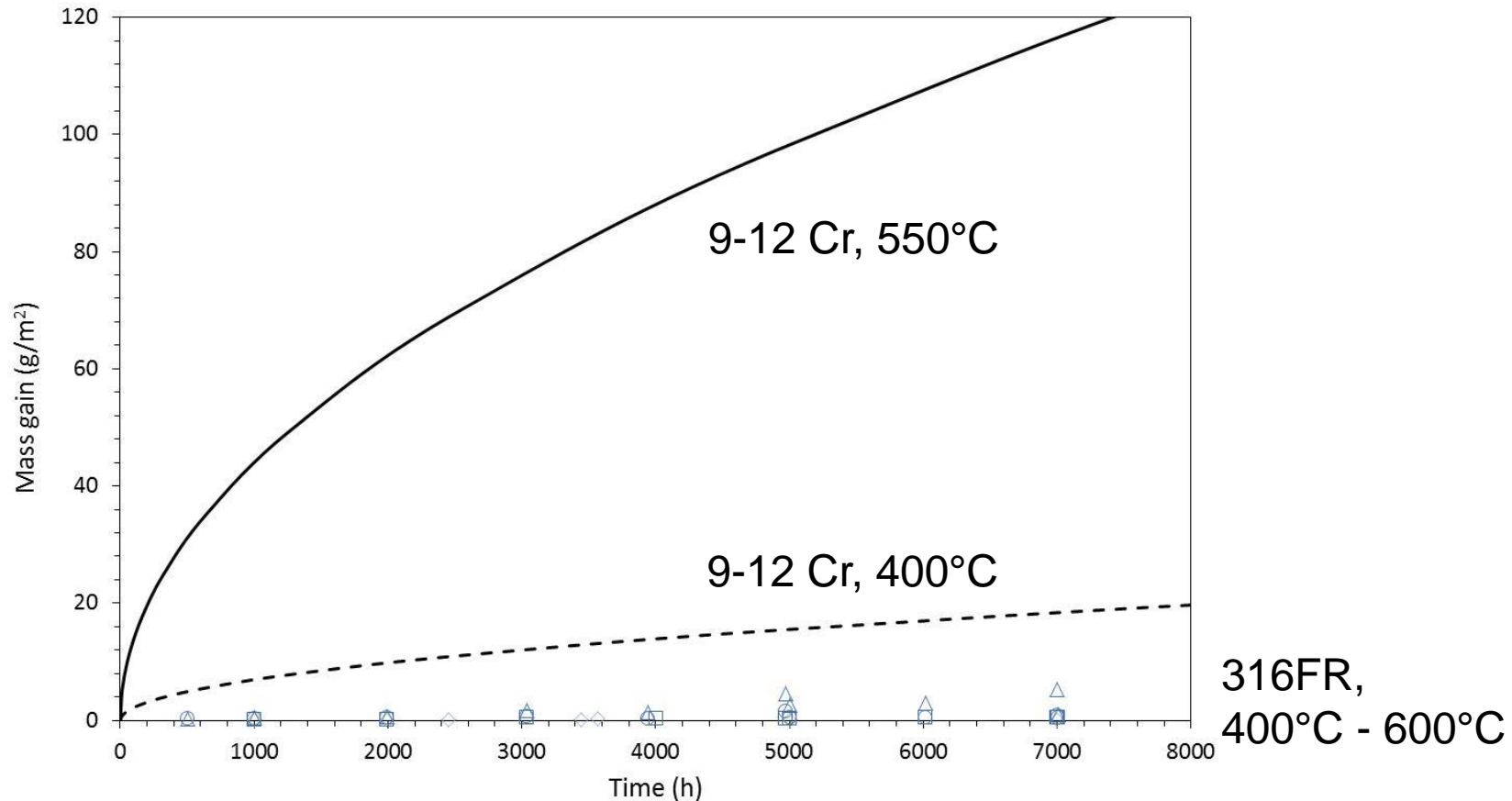
Still protective after 5000 h

Conclusions of PhD thesis (S. Bouhieda 2012) :

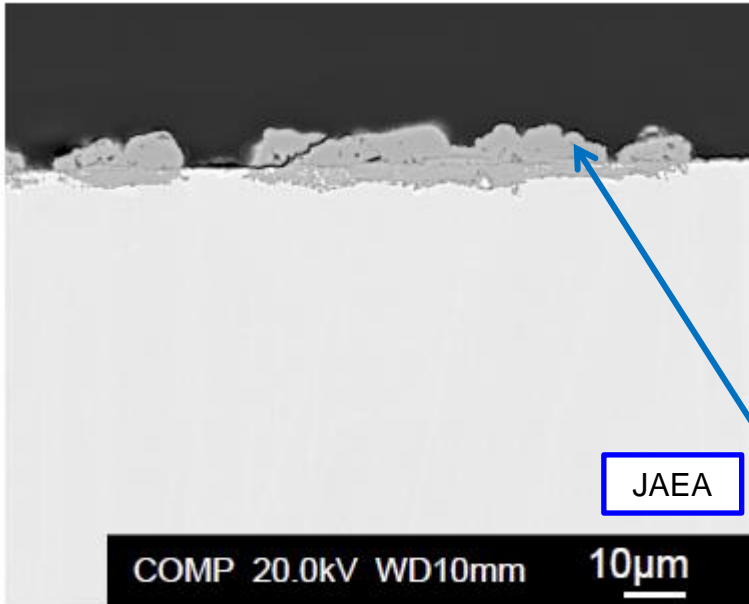
- O₂ impurities (μbar) react first during the thermal ramp
 - Its level in CO₂ impacts on the surface oxide composition (Cr enrichment)
- The surface finish (mainly roughness?) impacts on the critical O₂ partial pressure

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

MASS GAIN KINETICS OF 316 AUSTENITIC STEEL

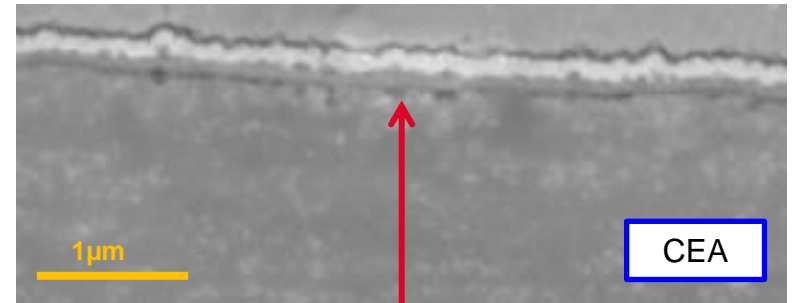


- Very low mass gain : mass gain (316FR) < 100*mass gain (9-12Cr)
- No detectable effect of total pressure
- Larger mass gain is detectable after 5000 h at T = 600°C



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)

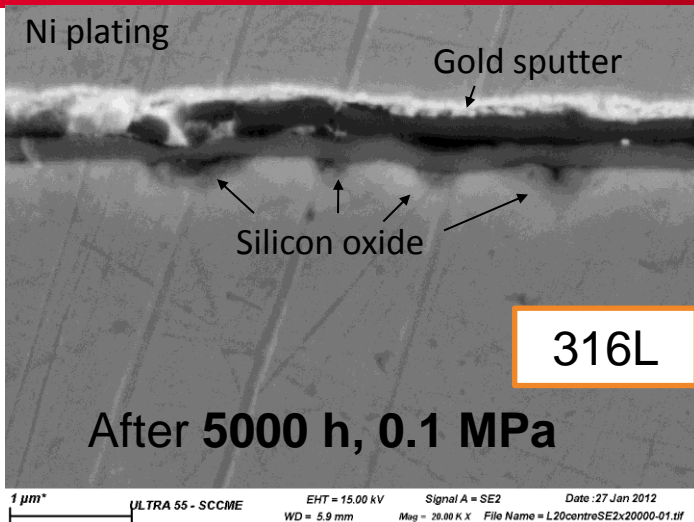
The « short-term » resistance of Cr rich austenitic steels is evaluated by its ability to form thin Cr rich oxide scale

8 µm thick

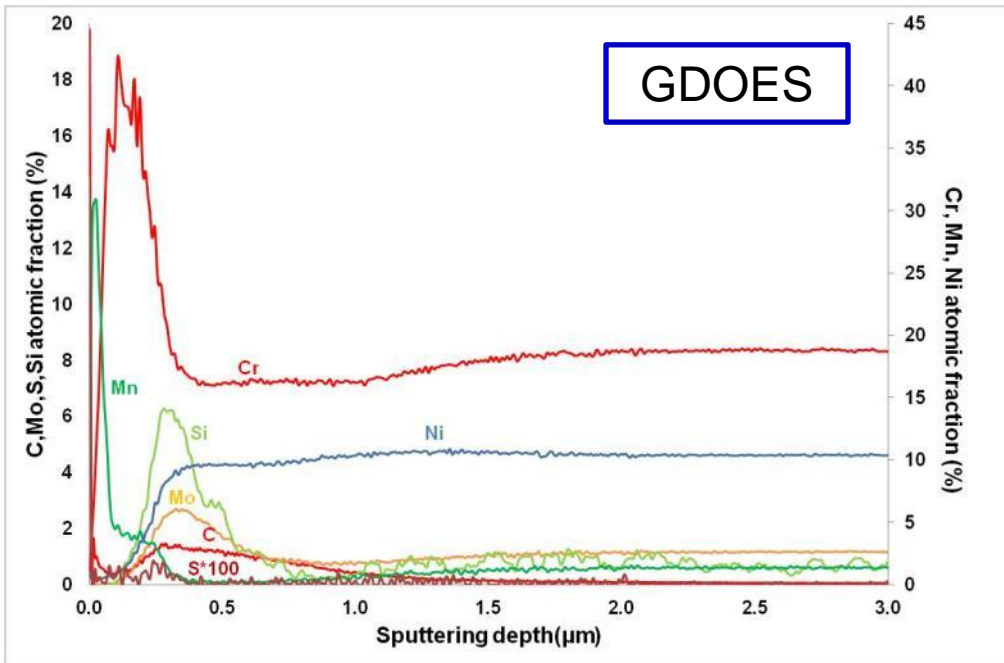
316L, 550 °C, 25 MPa, 1000 h

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)

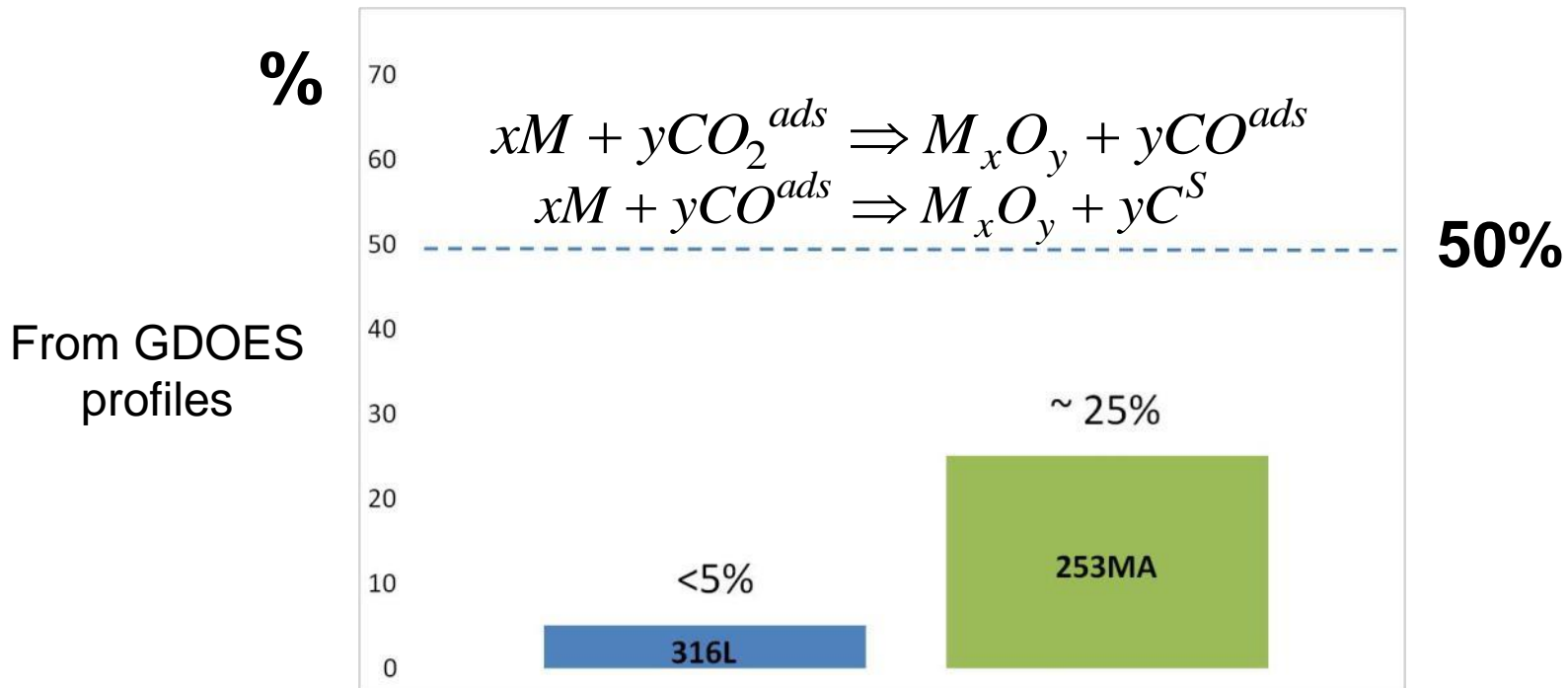


- ✓ **Substrate :**
 - **C** enrichment below the oxide layer and diffusion profile

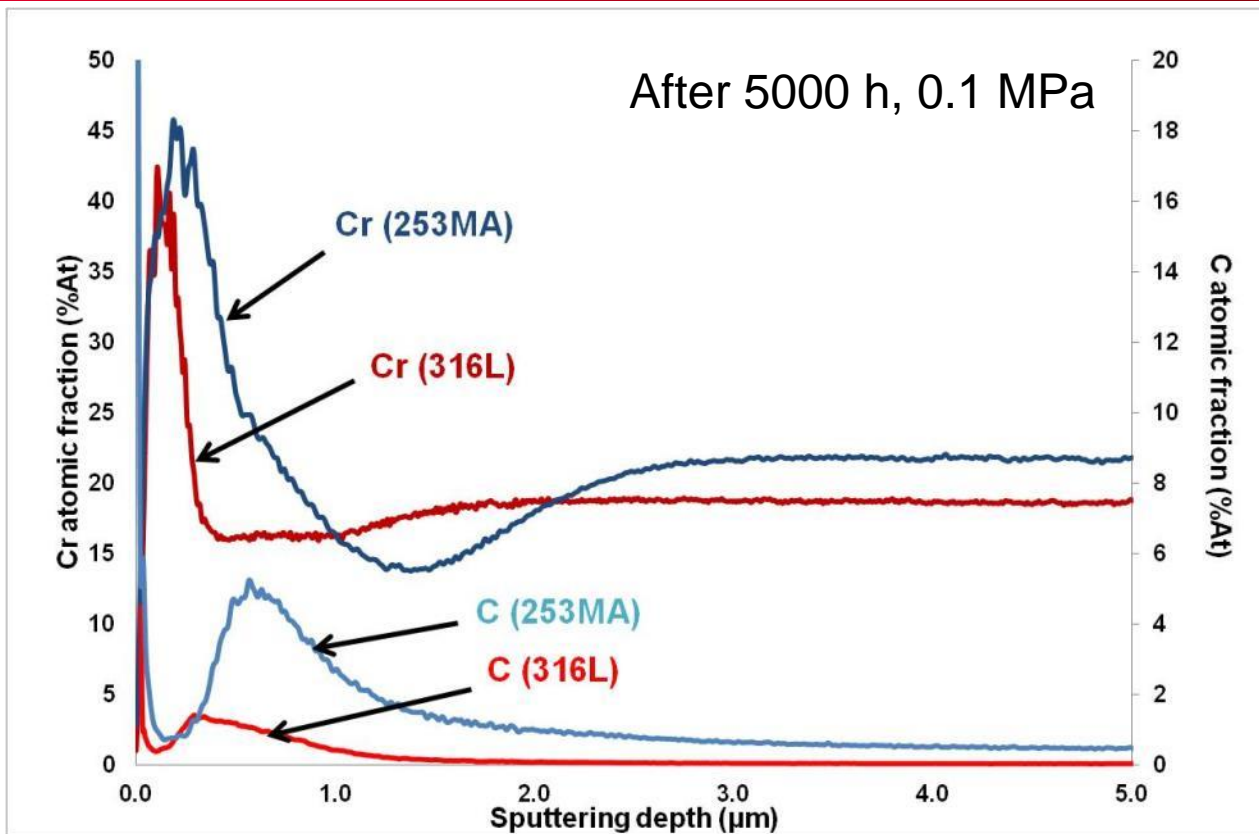
INFLUENCE OF STEEL GRADE ON CARBON TRANSFER

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

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



INFLUENCE OF STEEL GRADE ON CARBON TRANSFER

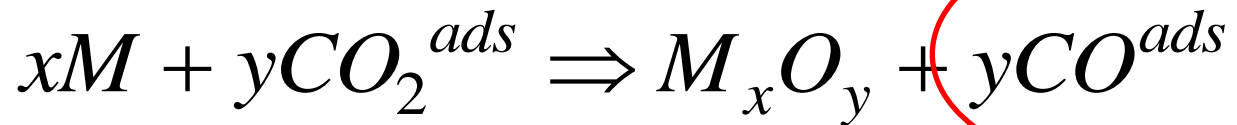


ThermoCalc

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 ?

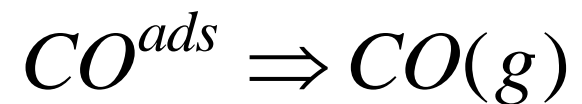
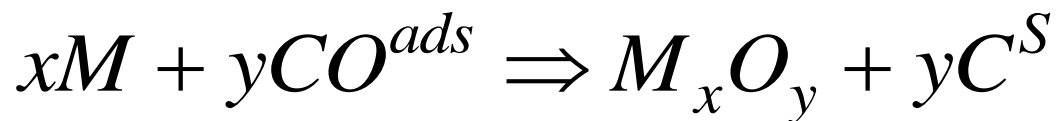
Oxidation



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**