

Corrosion behaviour of 9-12%Cr ferritic steels and 18-25%Cr austenitic steels in supercritical CO_2

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_2



F. ROUILLARD (CEA), T. FURUKAWA (JAEA)

B. DUPREY, G. MOINE

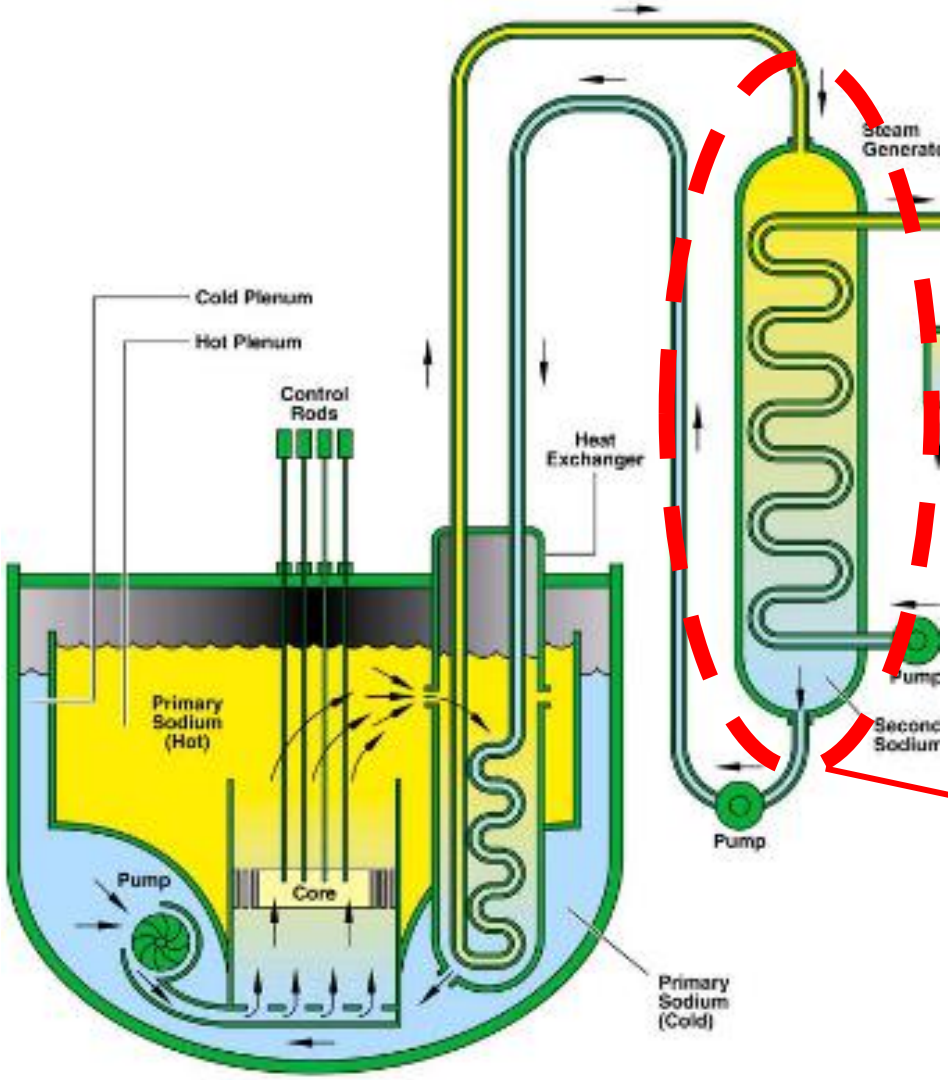
CEA/DEN/DANS/DPC/SCCME/LECNA (SACLAY)

JC RUIZ, P. VENDITTI

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

TMS2016
145th Annual Meeting & Exhibition

CONTEXT : S-CO_2 BRAYTON CYCLE COUPLED TO SFR



Advantages of S-CO_2 Brayton cycle :

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

International collaboration on S-CO_2 cycle coupled to Sodium Fast Reactor: France, USA, South Korea, Japan

T : 400 - 550 °C
P : 80 - 250 bar

CORROSION IN CO_2 ?
FEEDBACKS FROM FORMER CO_2-COOLED NUCLEAR REACTORS (60-80'S)

CO_2 + 1% vol CO + up to a few hundreds of vpm H_2O, H_2, CH_4
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

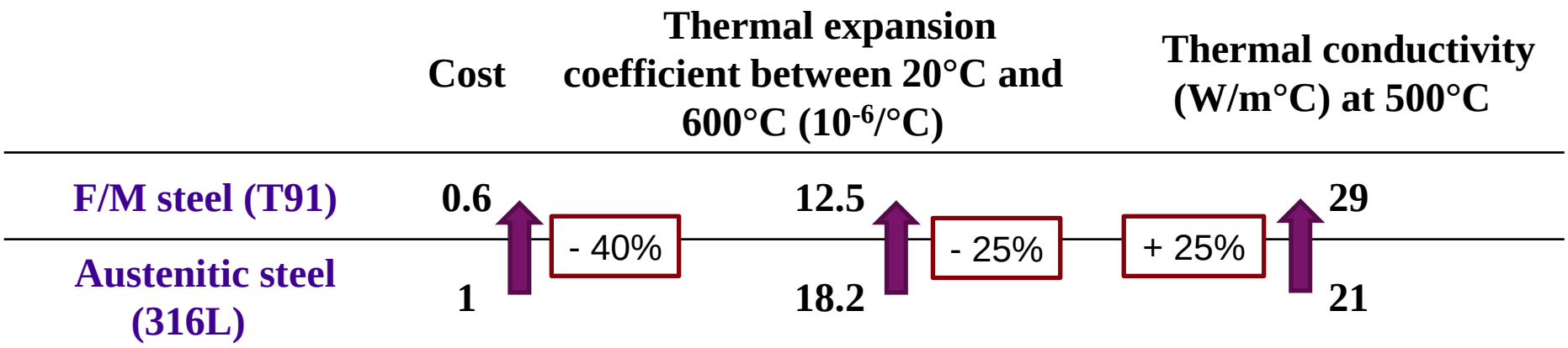
T max : strongly dependent on gas composition, steel composition, surface finish, …

[D.R. Holmes, R.B. Hill, and L.M. Wyatt, Corrosion of steels in CO_2, British Nuclear Energy Society, Reading University (1974)]

MATERIALS FOR APPLICATIONS UP TO 550 °C

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 ✚

CEA - JAEA COLLABORATION (2008-2014)

Objectives : Technical exchanges for comprehensive understanding of corrosion mechanisms in S-CO_2

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_2 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

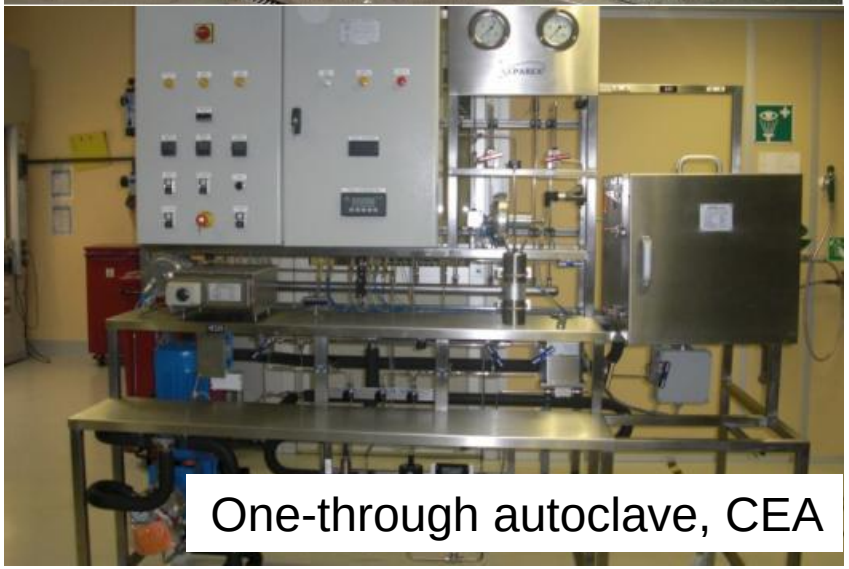
	Weigth %	%Cr	%Ni	%C	%Si	Other	Feedback
F-M steels	T91 (CEA)	9	0.2	0.1	0.3	Mo : 1%	SG in Fossil Power Plants
	VM12 (CEA)	11	0.4	0.1	0.3	W : 2% Co : 2%	New generation of 9-12Cr steel
	P122 (JAEA)	11	0.4	0.1	0.3	W : 2% Cu : 1%	New generation of 9-12Cr steel
Austenitic steels	316L (CEA)	17	11	0.02	0.6	Mo : 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_2



Loop, JAEA



One-through autoclave, CEA

Atmospheric pressure CO_2



CEA



Metallic coupons (25*15*1 mm)

« Industrial » CO_2 purity in JAEA and CEA tests (99,995%) :

- H_2O < 200 vpm
- O_2 < 50 vpm

CORROSION OF 9-12CR F/M STEELS

TODAY : WHAT WE THINK TO KNOW WITH A GOOD CONFIDENCE

F. ROUILLARD AND T. FURUKAWA, CORROSION SCIENCE JAN 2016

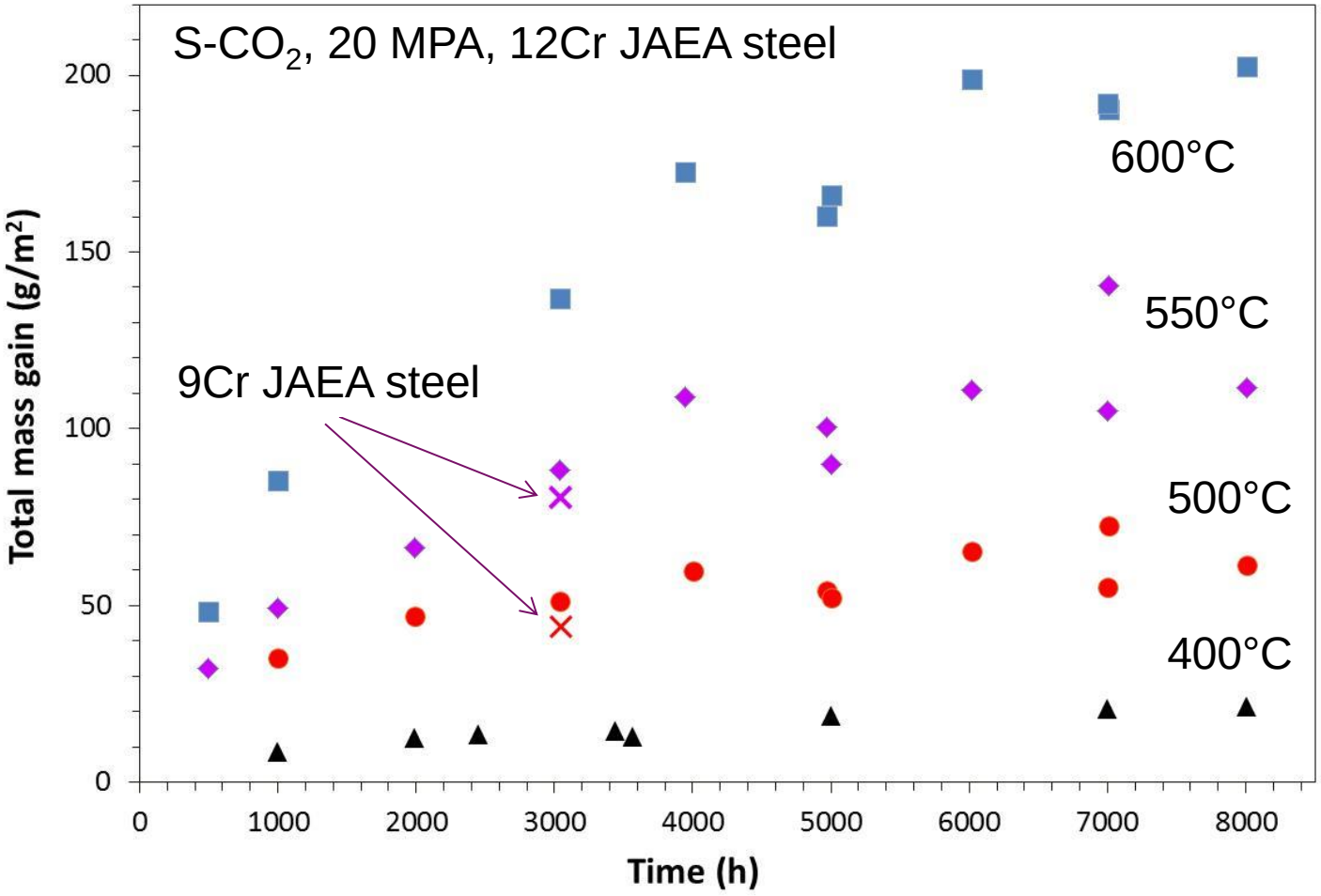
- The « short-term » corrosion kinetics of usual 9-12%Cr steels
  - ✓ Oxidation rate = f(T, P)
  - ✓ Carburisation rate = f(T, P)

Proposed corrosion model : « Available Space Model »

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

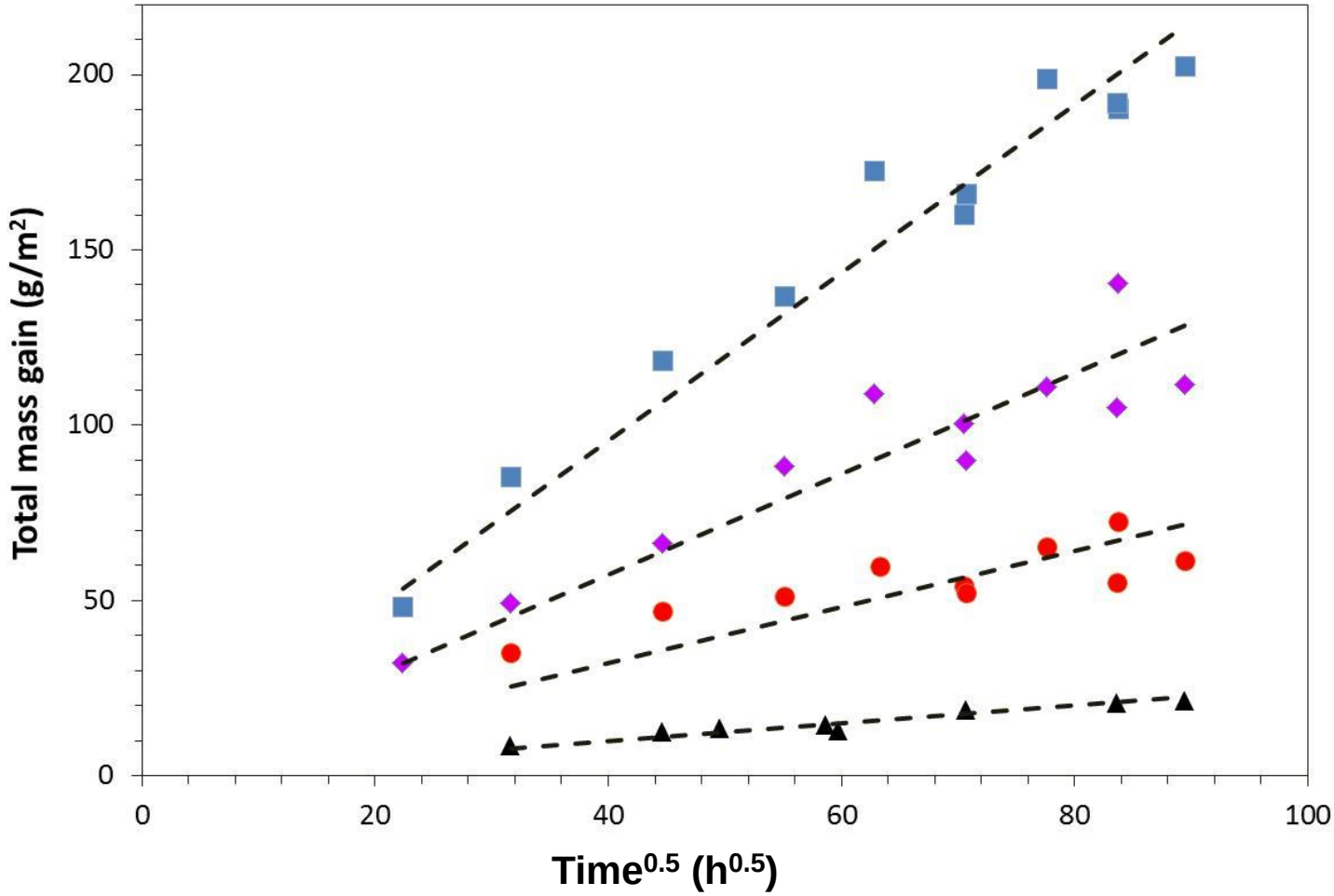
PhD thesis of S. Bouhieda (2009-2012)

CORROSION KINETICS OF 9-12CR JAEA STEELS



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

CORRODION KINETICS OF 9-12CR JAEA STEELS

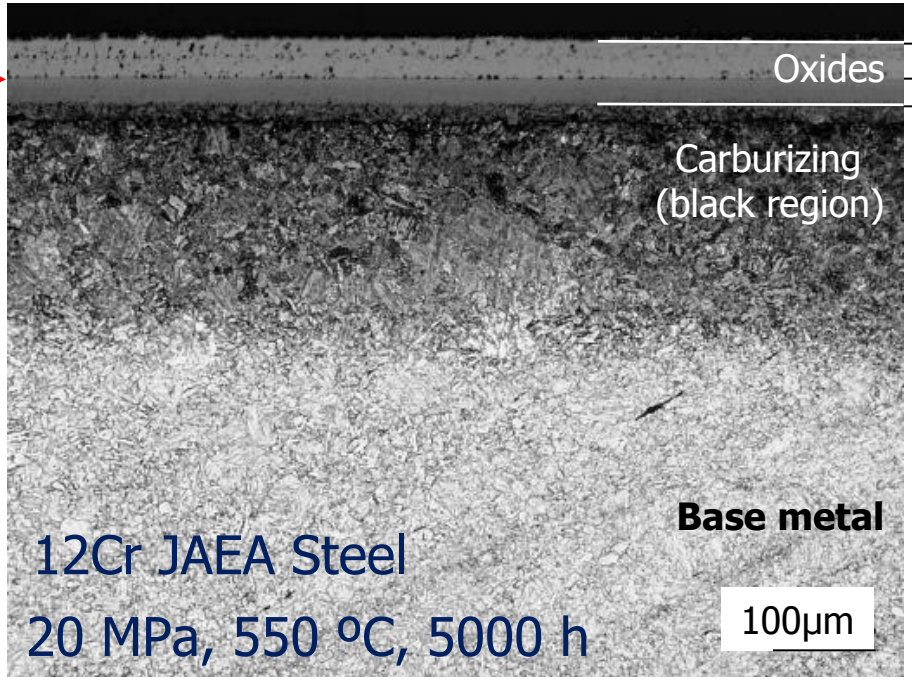


- ❑ Parabolic kinetics
- ❑ What does happen to the samples ?

CORRODED SURFACE UNDER CO_2

Mass gain = Oxidation AND Carburisation

Original surface of base metal



Outer layer: Fe_2O_3 and Fe_3O_4

Inner layer: $Fe(Fe_{1-X},Cr_X)_2O_4$

(by X-ray diffraction analyses)

Carburising region

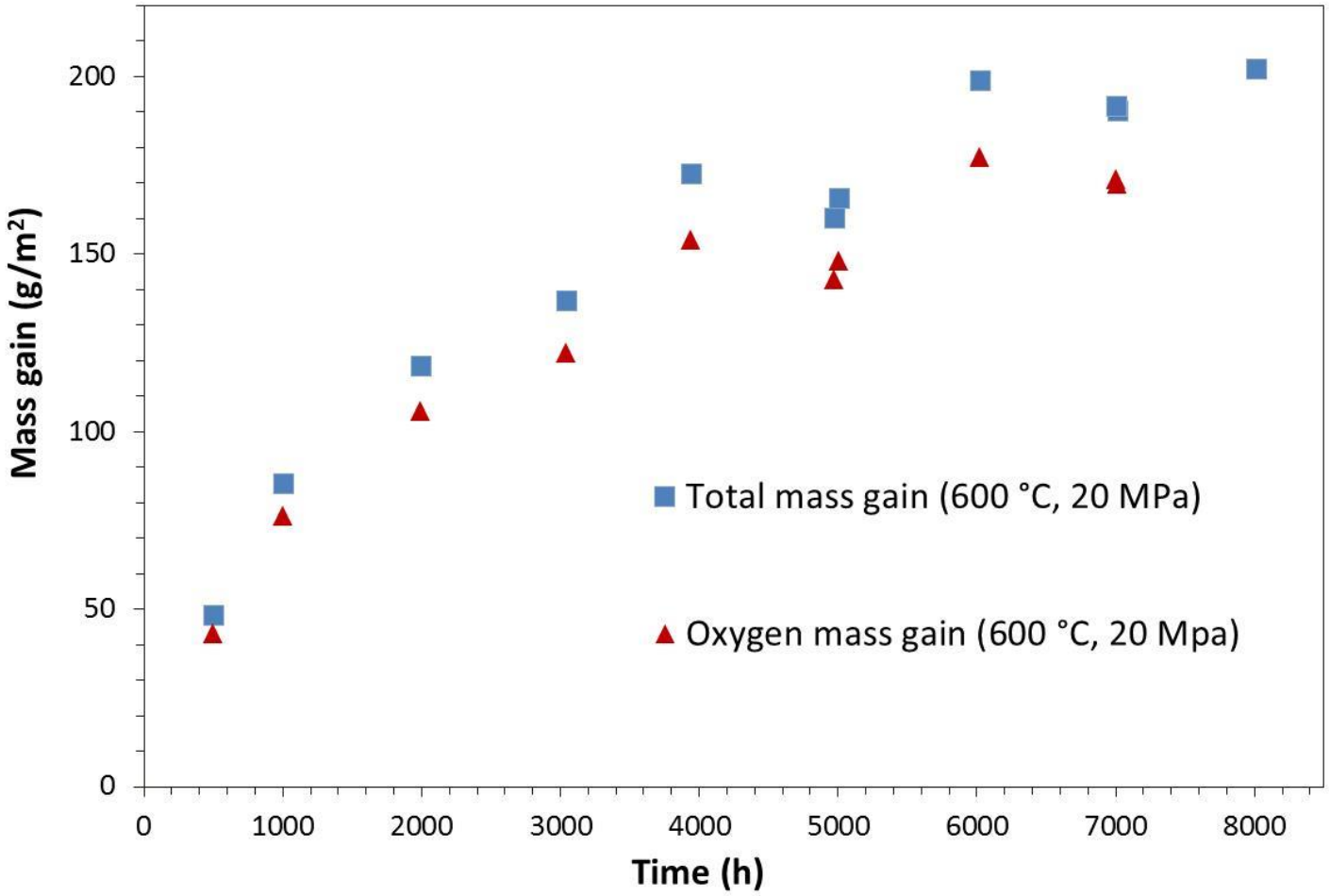
Loss of ductility

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_2

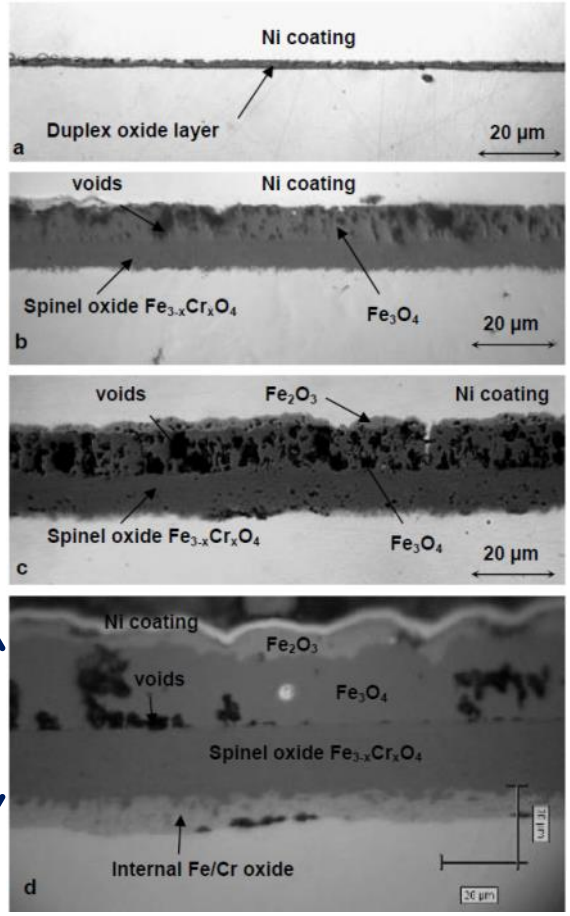
OXIDATION KINETICS



Parabolic oxidation rate = diffusion controlled

OXIDE FEATURES

9Cr CEA steel in CO_2, 550 °C, 0.1 MPa



1 h

110 h

322 h

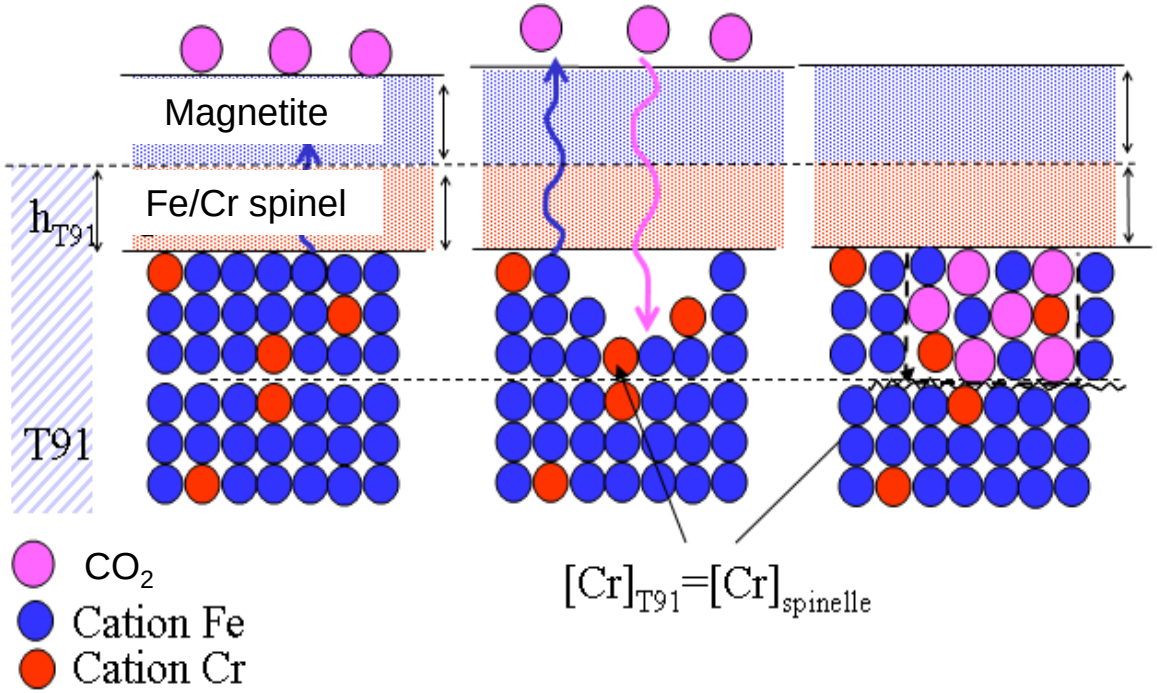
1000 h

~50 µm

Oxidation model ?

- **Duplex** oxide layer : Fe oxides (Fe_3O_4 + Fe_2O_3) and Fe/Cr oxide ($Fe_{2.3}Cr_{0.7}O_4$)
- The oxide/oxide interface = **original** metallic surface (gold markers)
- $[Cr]_{spinel}(mol/cm^3) \sim [Cr]_{substrate}(mol/cm^3)$ **Chromium does not diffuse and is oxidized in the substrate**.
- **Carbon** enrichment at the O/M interface (GDOES analysis)
- $Fe_{2.3}Cr_{0.7}O_4$ grows at the metal/oxide interface and Fe_3O_4 at the oxide/gas interface *(Taylor et al. OxMet. 1980 : Tracers experiment).*
- **Parabolic** growth rate

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

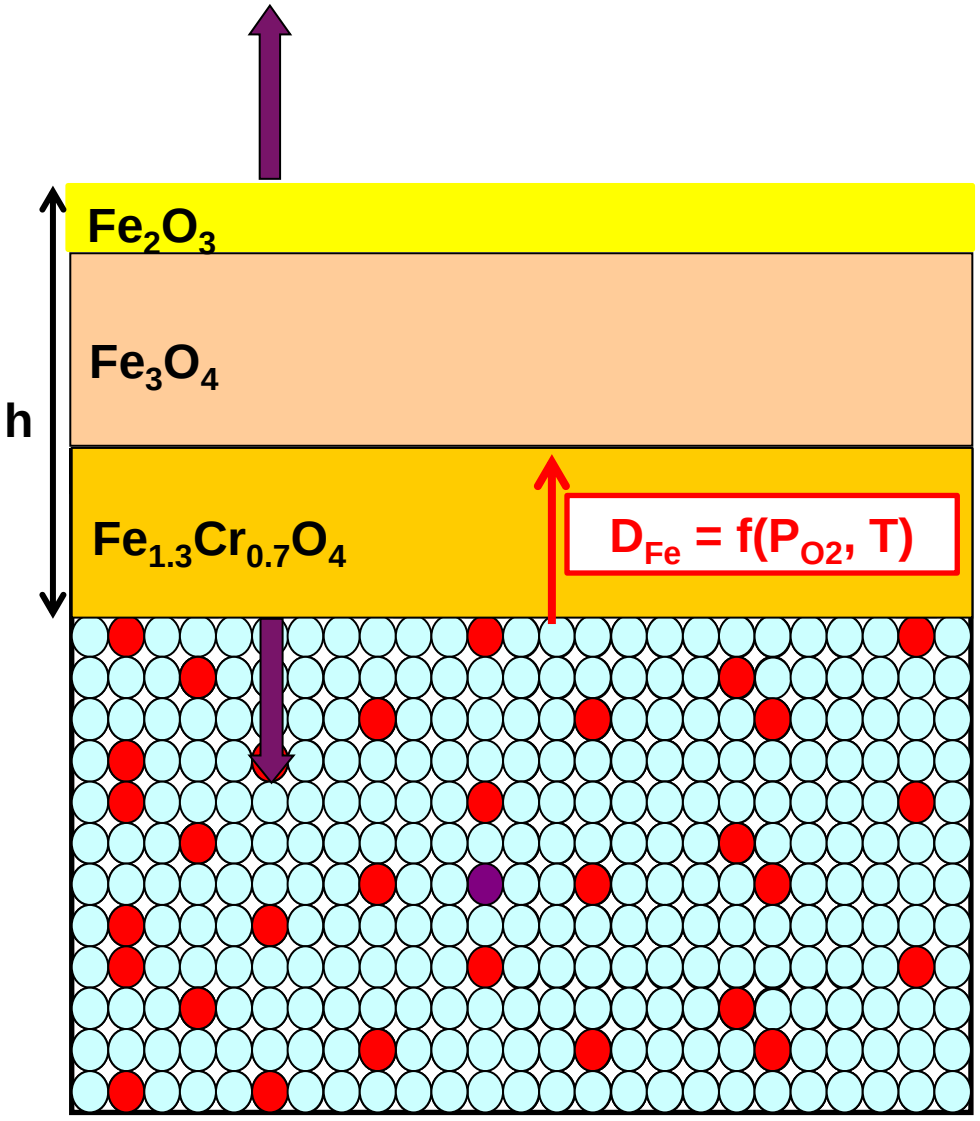


1. Outwards diffusion of Fe cations
   - ✓ Injection of vacancies at the O/M interface
   - ✓ **Formation of voids**
2. CO_2 diffusion to the O/M interface

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_{O2}^{ext}
- calculated from the gas phase composition (P_{CO2}/P_{CO} ratio)

or
- $= P_{O2}^{eq}$ for Fe_3O_4/Fe_2O_3 if Fe_2O_3 stable

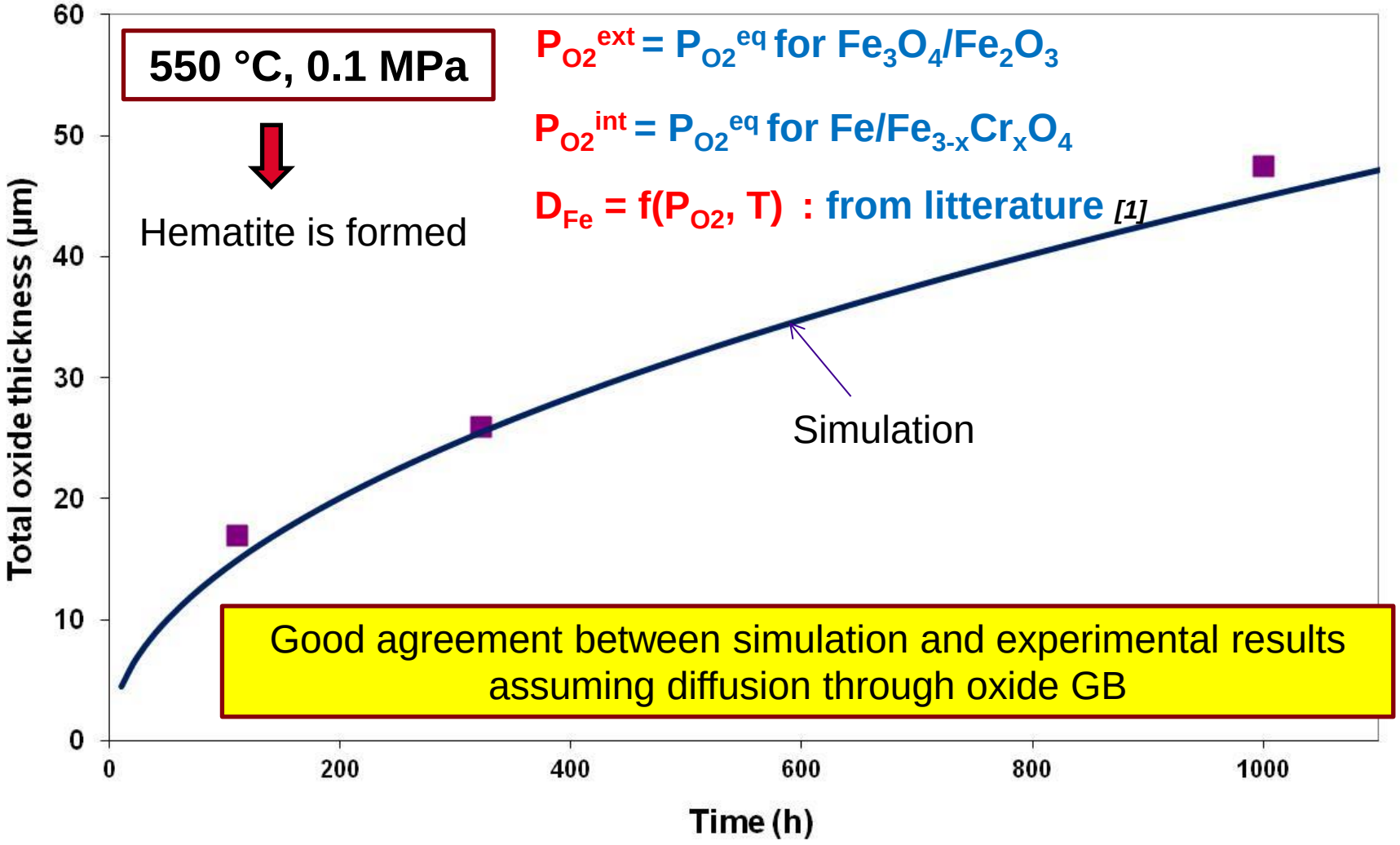
$P_{O2}^{int} = P_{O2}^{eq}$ for $Fe/Fe_{3-x}Cr_xO_4$

= Rate limiting oxide layer

$$h(t) = f(D_{Fe}, P_{O2}^{int}, P_{O2}^{ext})$$

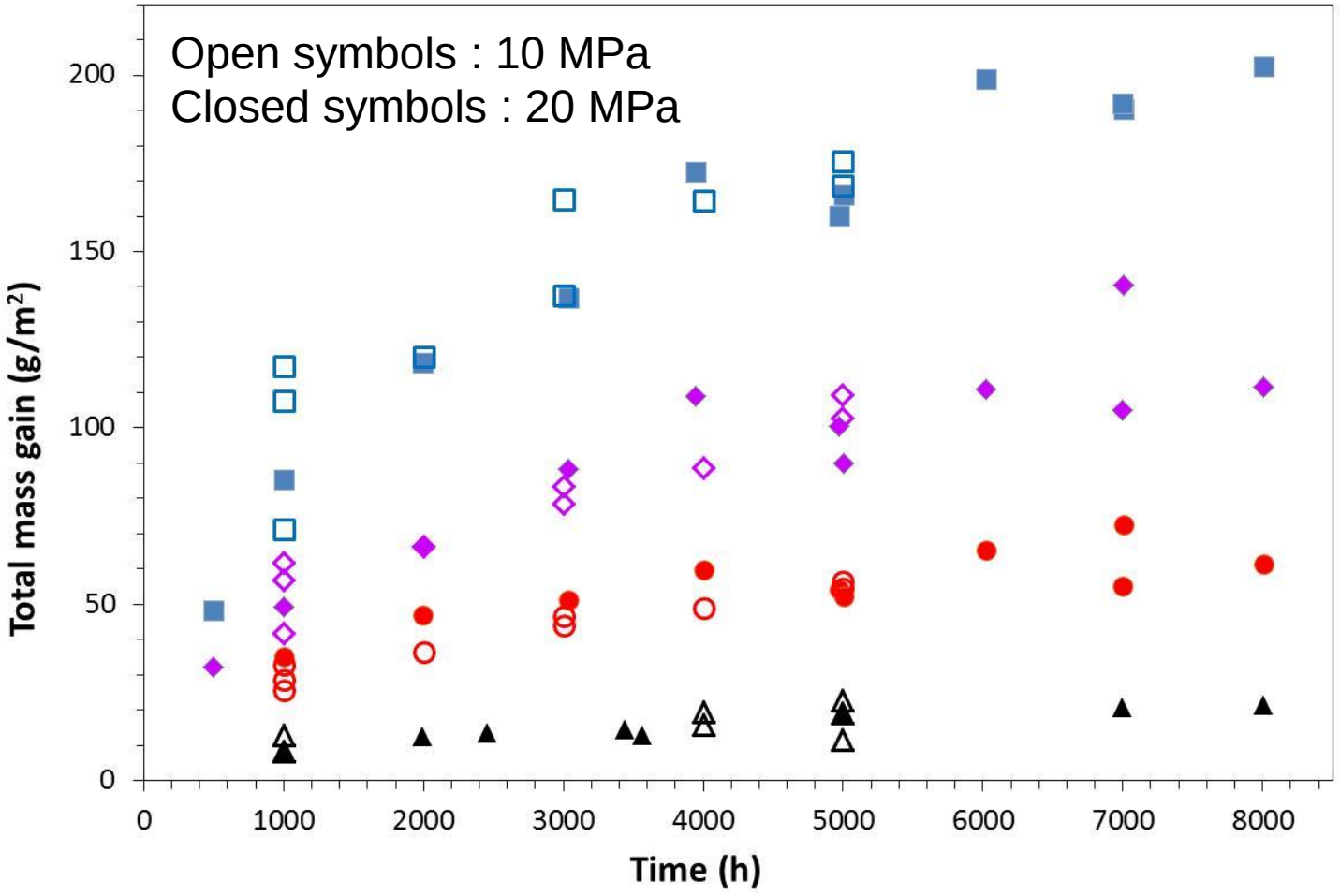
D_{Fe}, P_{O2}^{int}, P_{O2}^{ext} : input parameters (from literature review)

OXIDE GROWTH MODELING AND SIMULATION



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

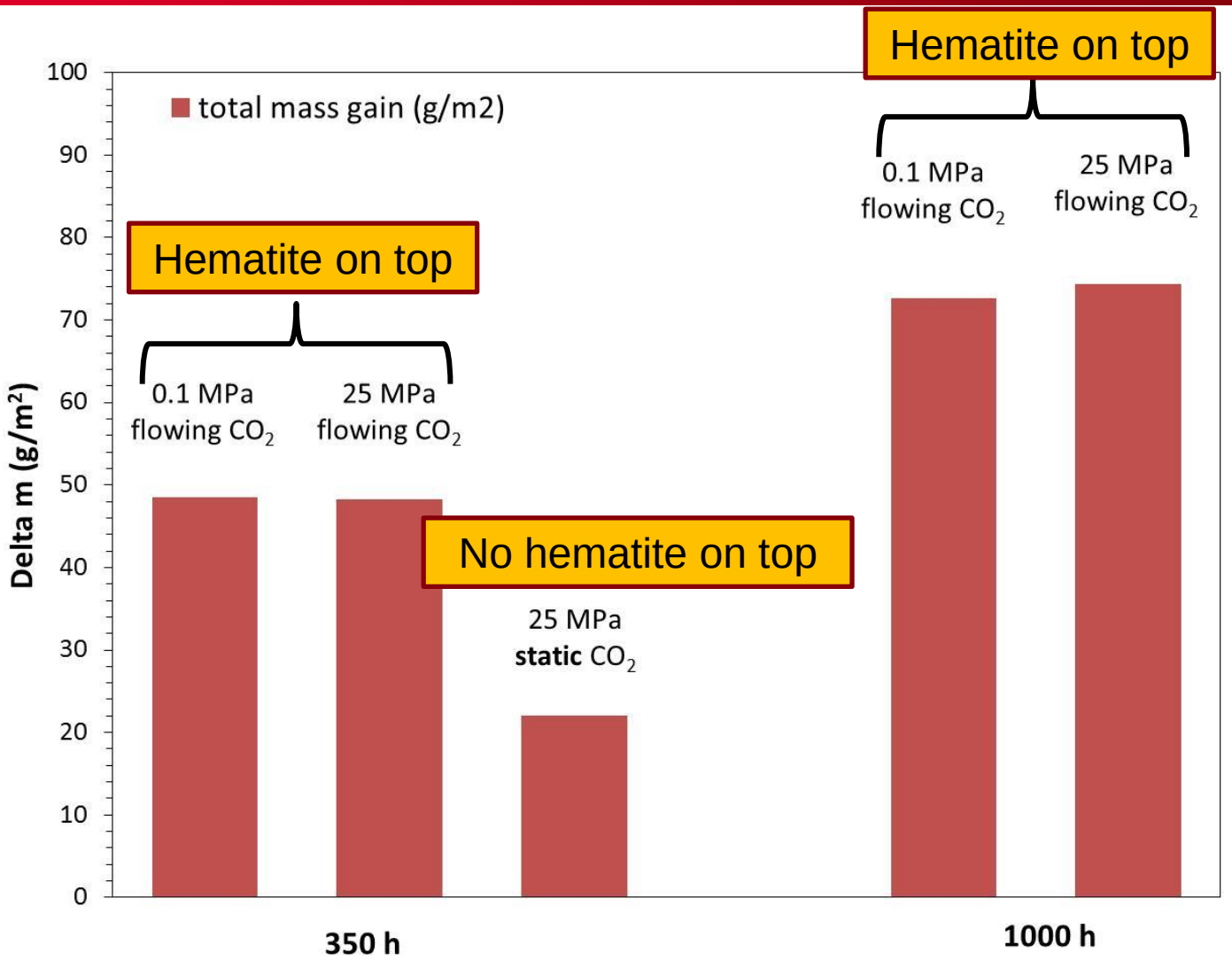
EFFECT OF P_{CO2} ON OXIDATION



No detectable effect of P_{CO2} between 10 and 20 MPa

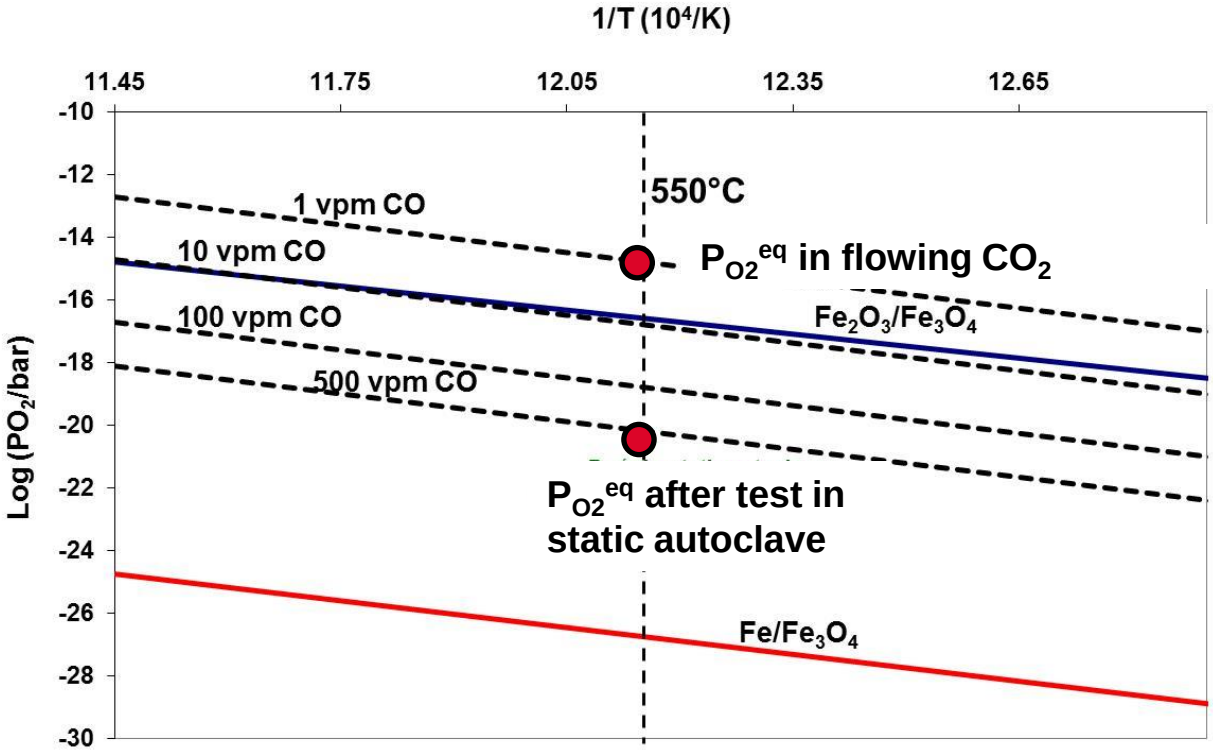
With higher P_{CO2} difference : 0.1 MPa and 25 MPa ?

EFFECT OF P_{CO2} ON OXIDATION



The oxidation rate does not depend on P_{CO2}: the external driving force for oxide growth P_{O2}^{ext} is « buffered » by the presence of hematite

FORMATION OF FE_2O_3 ?



The formation of Fe_2O_3 is controlled by the P_{CO2}/P_{CO} ratio in the gas phase :

$$CO_2(g) = CO(g) + 0.5O_2(g)$$

$$P_{o_2}^{ext} = \left(\frac{K * P_{CO_2}}{P_{CO}} \right)^2$$

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

$$xM + yCO_2(g) = M_xO_y + yCO(g)$$

As a consequence, the driving force for oxidation **P_{CO2}/P_{CO} is driven by any CO accumulation** encoutered along the flow :

- Depends on the hydrodynamics encoutered 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_2

QUESTIONS ?

What is the carburisation kinetics ?
Is there any effect of P_{CO2} ?

Could we model the carburisation propagation into the steel ?

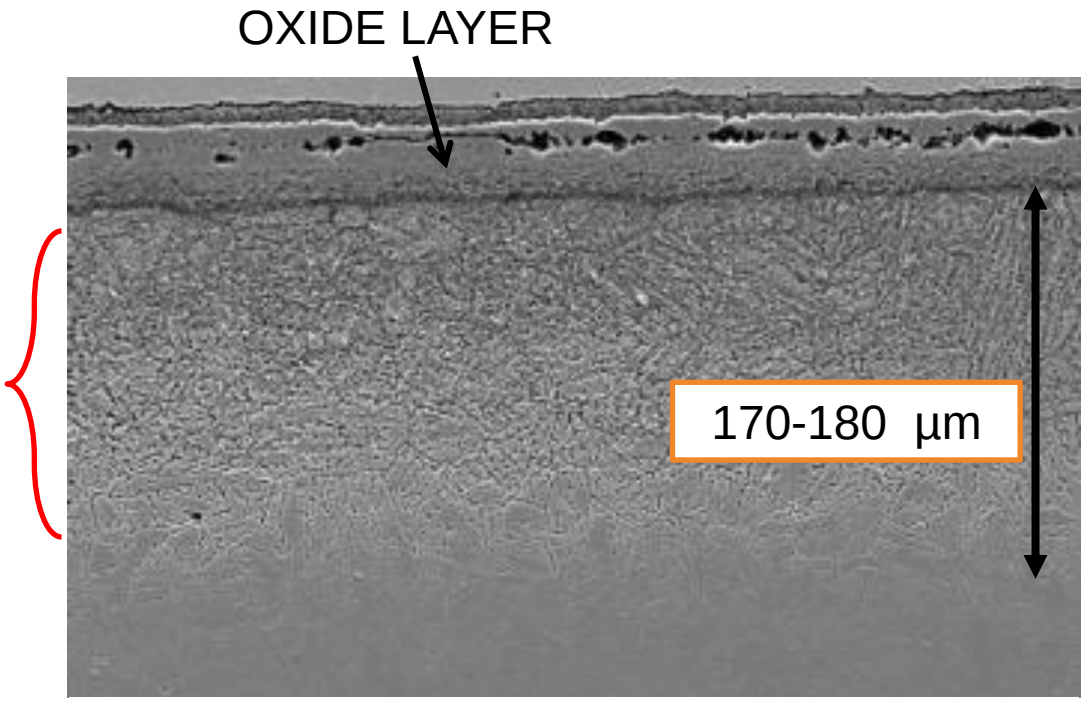
Why does the steel carburise ?

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

CARBURISATION MICROSTRUCTURE

CARBURISED ZONE :

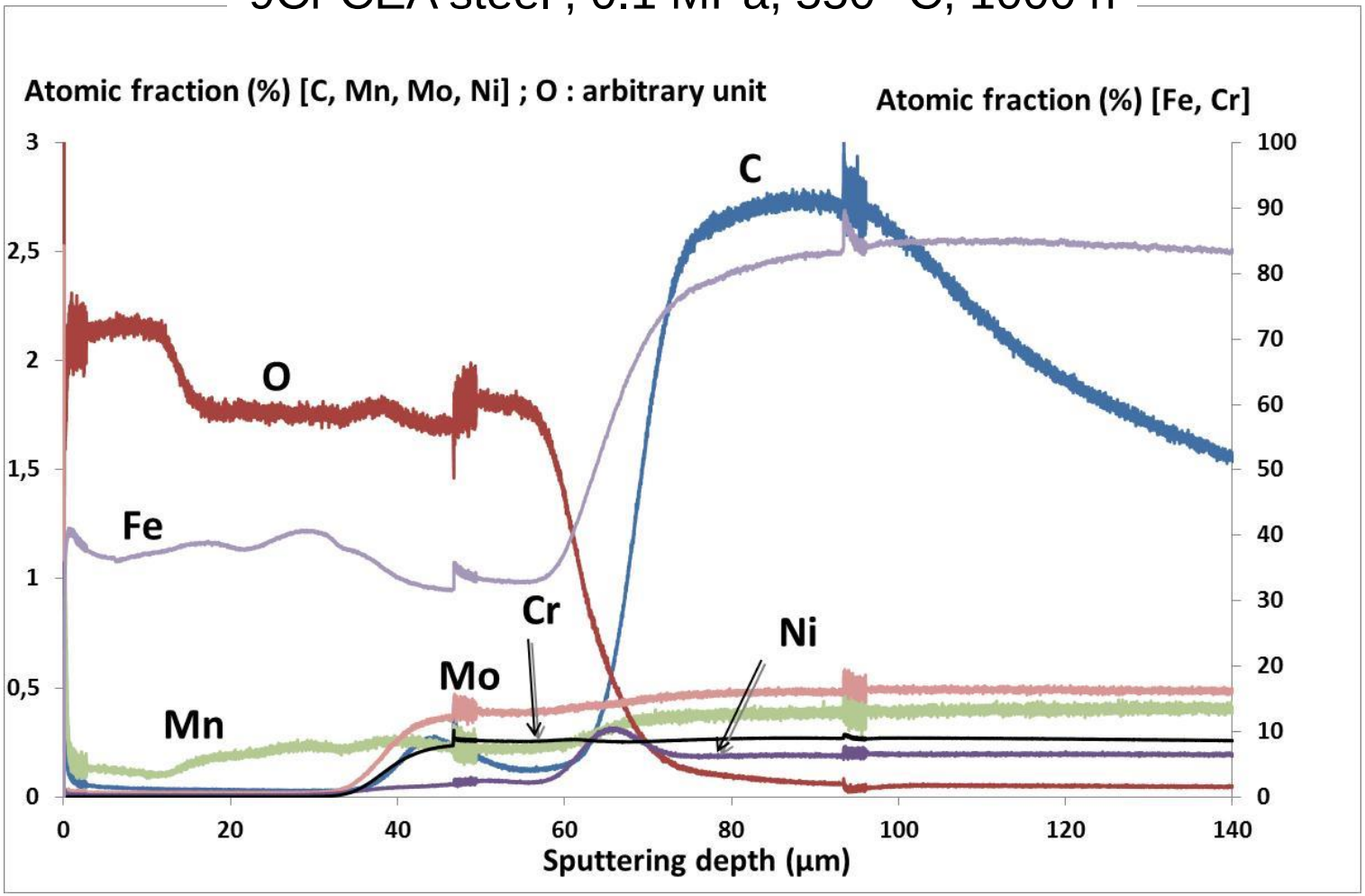
On martensitic laths and old primary austenitic GB



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

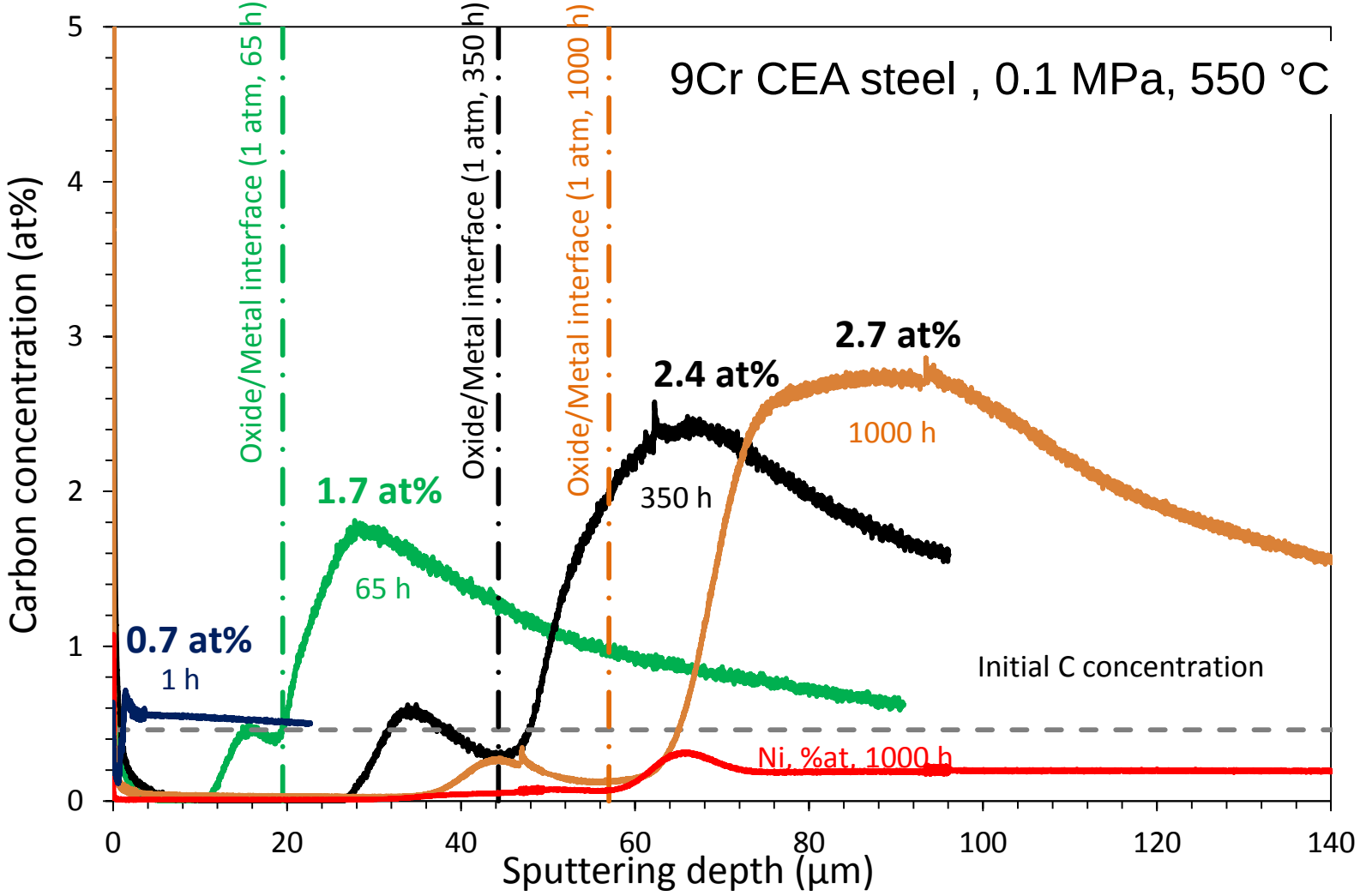
CARBON PROFILE BY GDOES

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_2 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 :

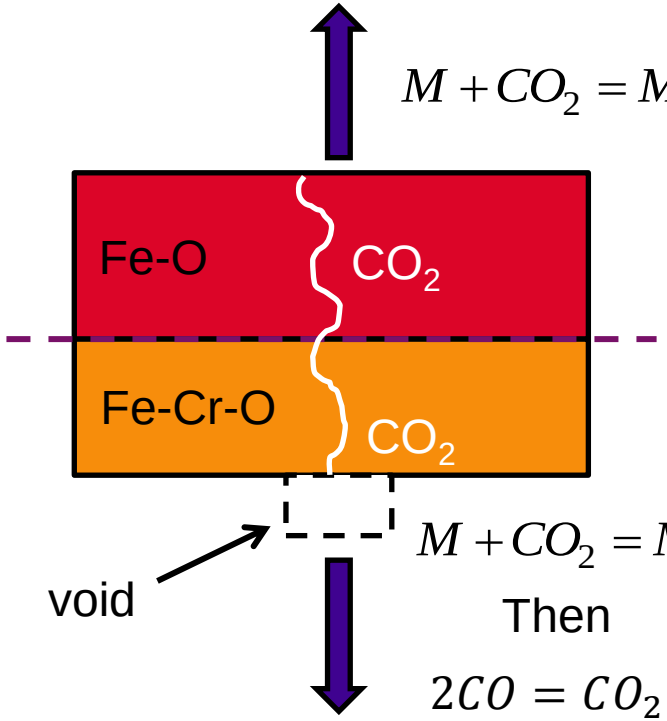
$$v_c = \alpha(C^{eq} - C^s)$$

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



$$M + CO_2 = MO + \underset{\cup}{CO}$$

→ Released in the gas flow

Initial 9-12Cr metallic surface

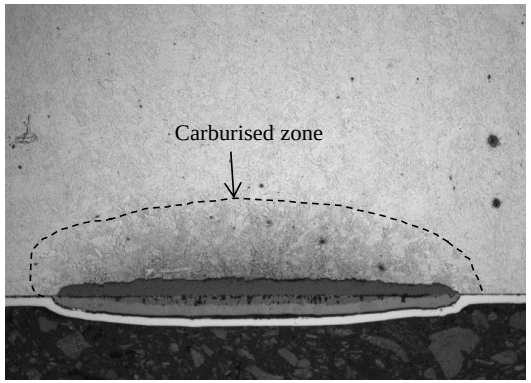
$$M + CO_2 = MO + \underset{\cup}{CO}$$

Then

$$2CO = CO_2 + C$$ Boudouard reaction

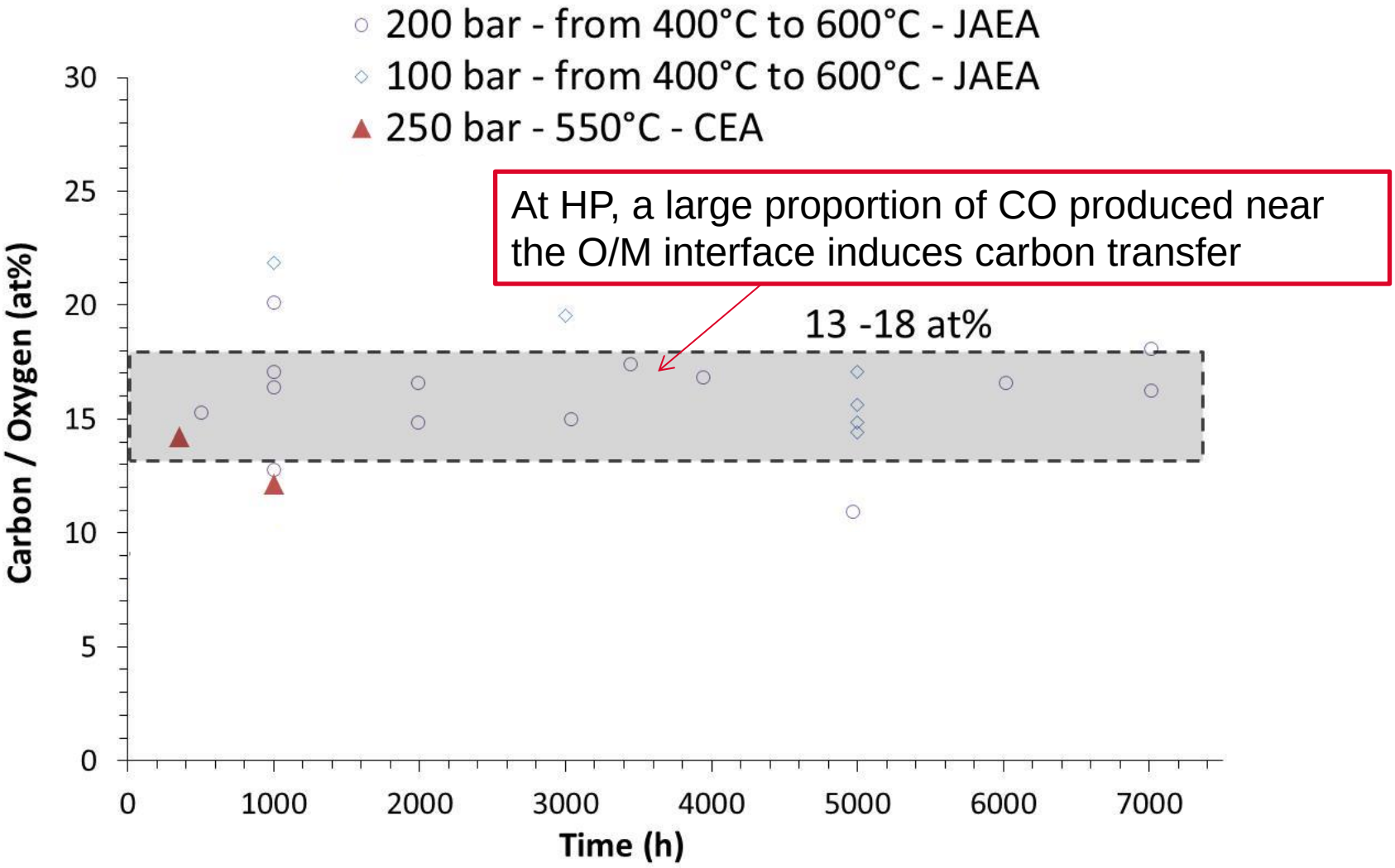
Or

$$Cr + CO = Cr[O] + C$$ Reaction with Cr



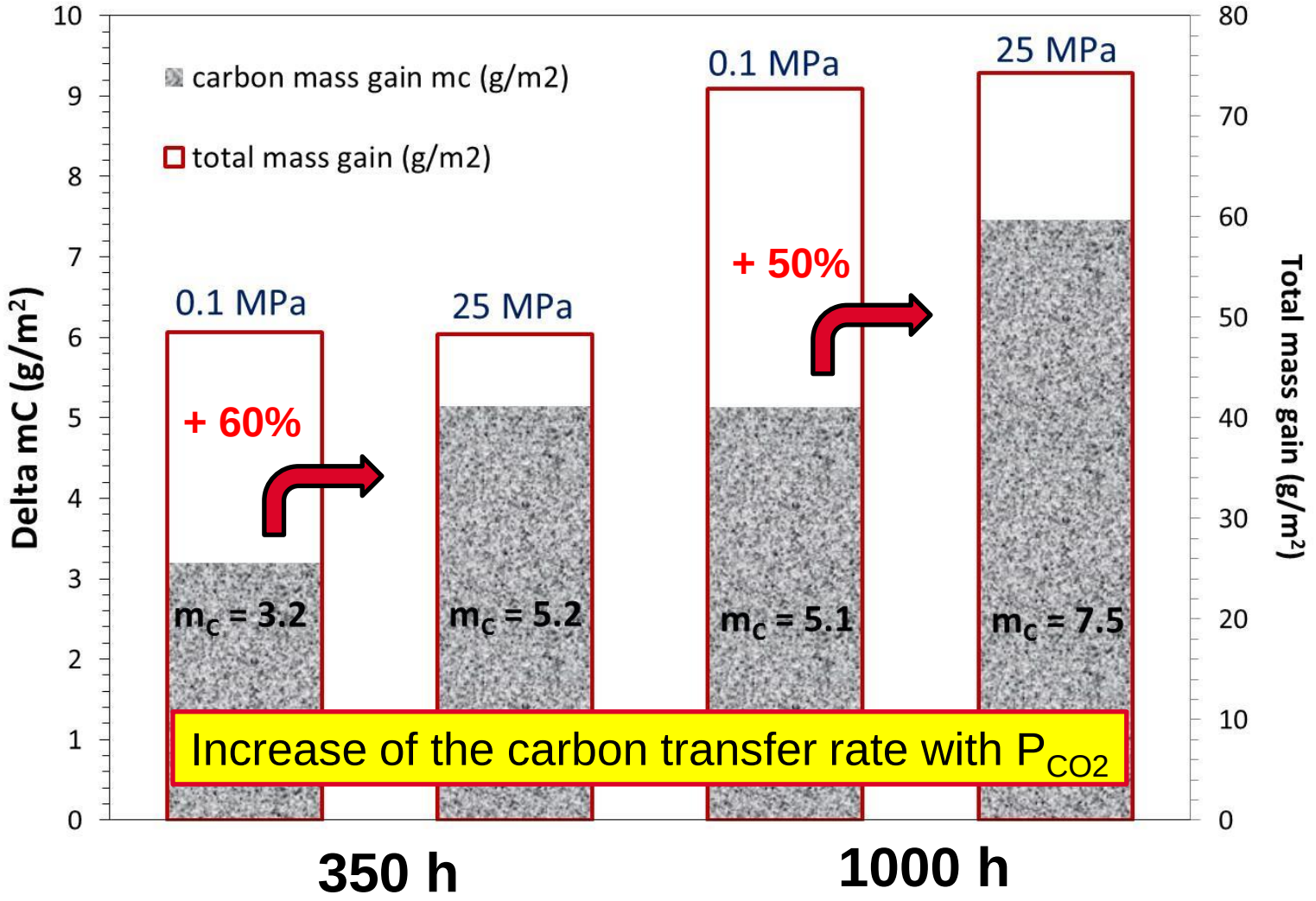
If all CO molecules carburise then %C/%O = 20 at%

CARBON TRANSFER

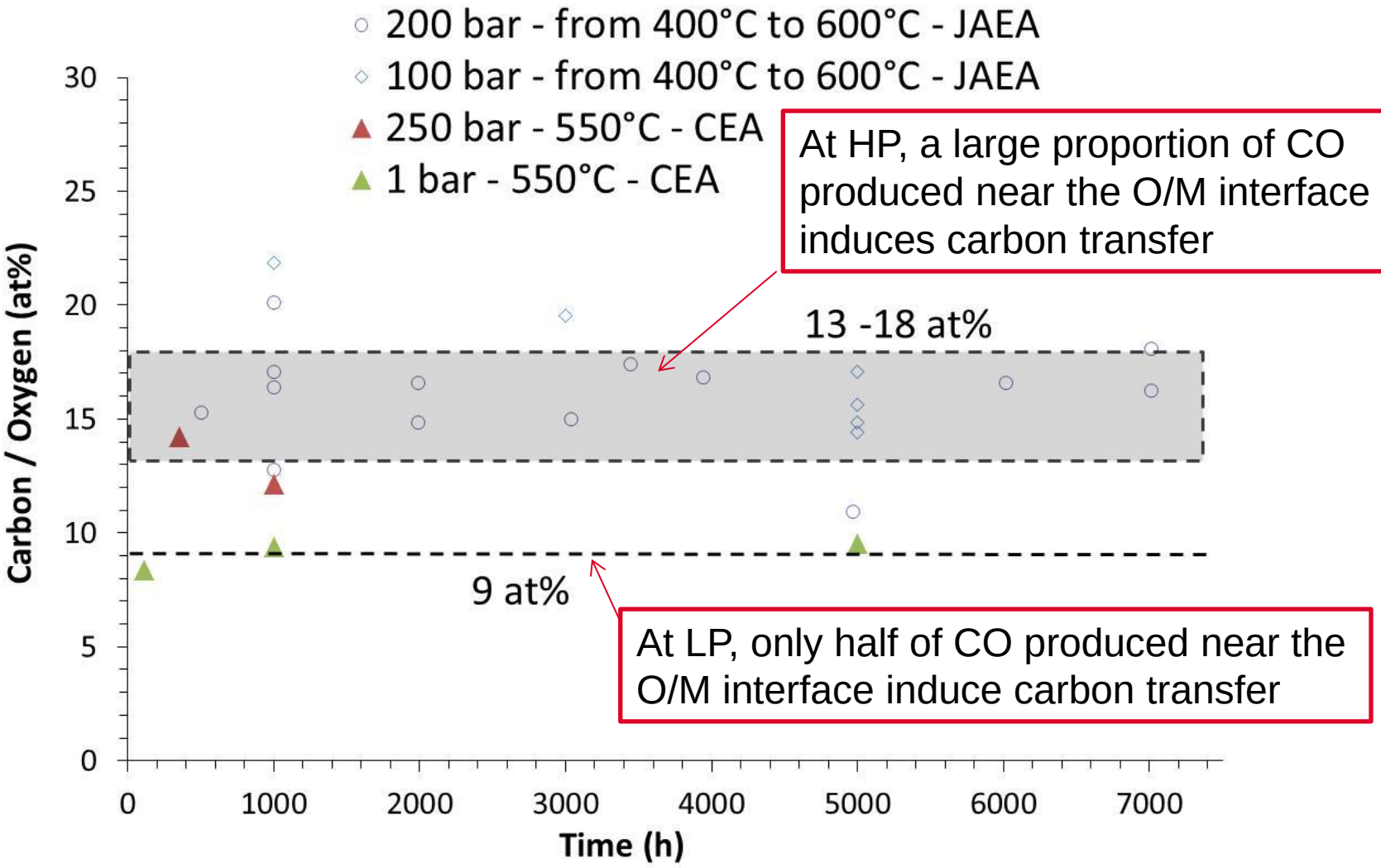


INFLUENCE OF P_{CO2} ON CARBON TRANSFER

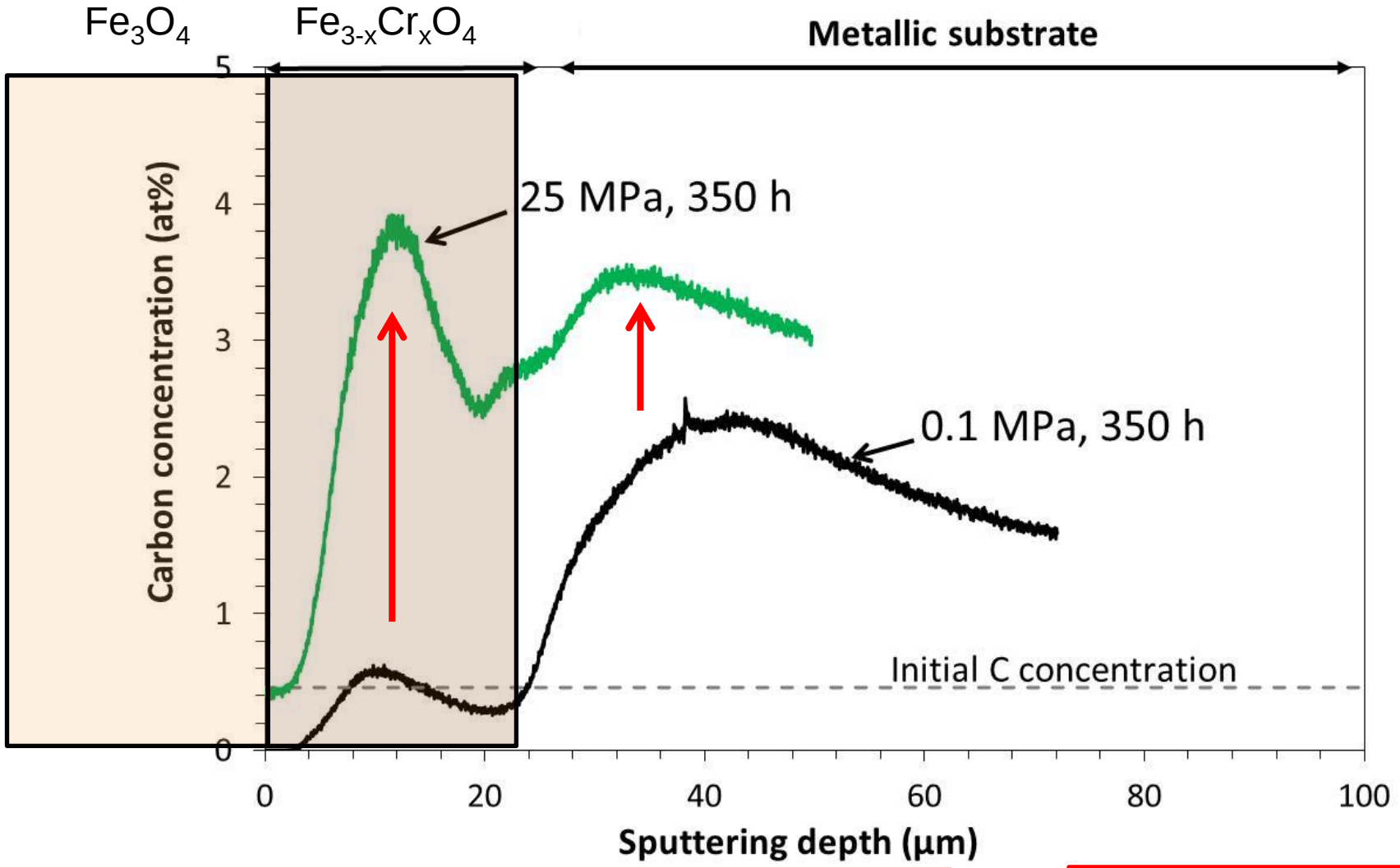
❑ No « detectable » influence of P_{CO2} between 10 and 20 MPa …
… but higher carbon transfer rate detectable when increasing from 0.1 to 25 MPa



INFLUENCE OF P_{CO2} ON CARBON TRANSFER



INFLUENCE OF P_{CO2} ON CARBON TRANSFER

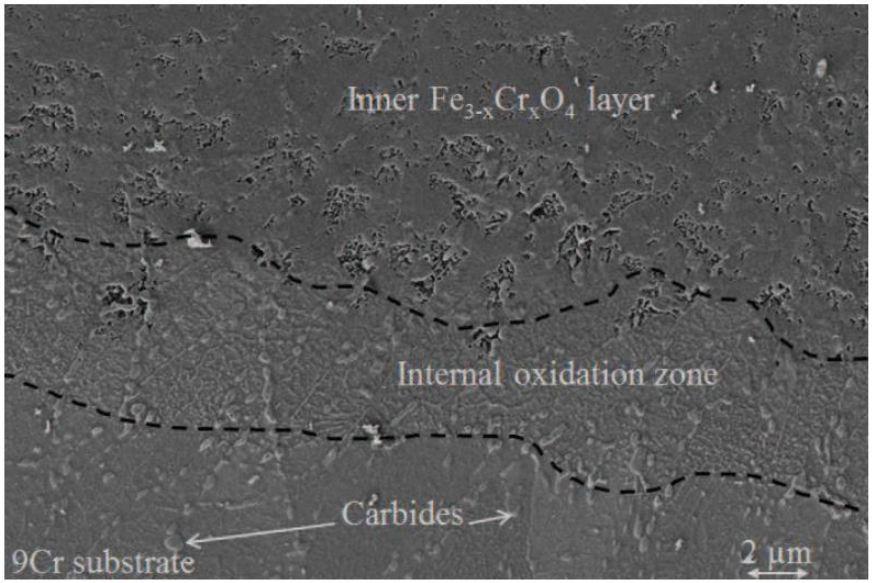


- %C at the O/M interface increases
- %C in the inner oxide scale increases

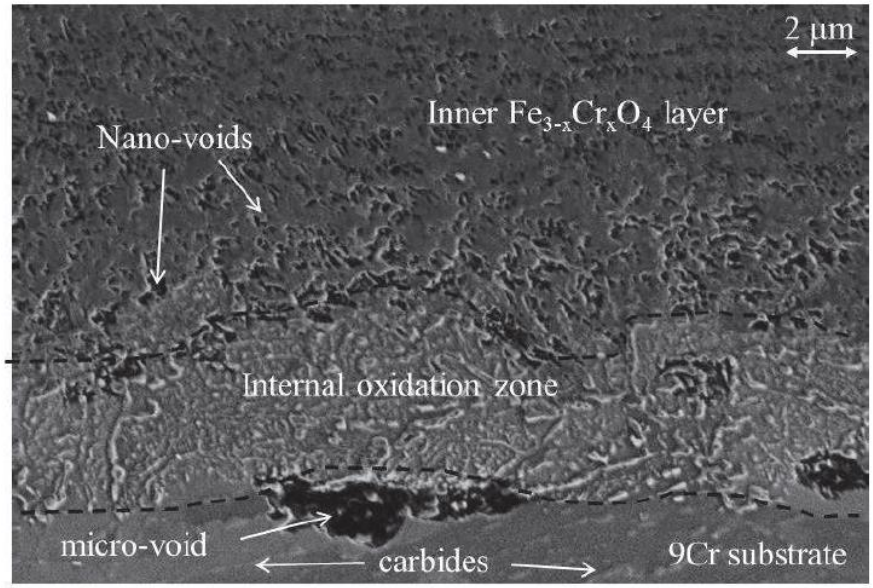
→ Carburisation rate increases

INFLUENCE OF CARBURISATION ON THE INNER OXIDE MICROSTRUCTURE

T91, **0.1 MPa**, 550 °C, 350 h



T91, **25 MPa**, 550 °C, 350 h



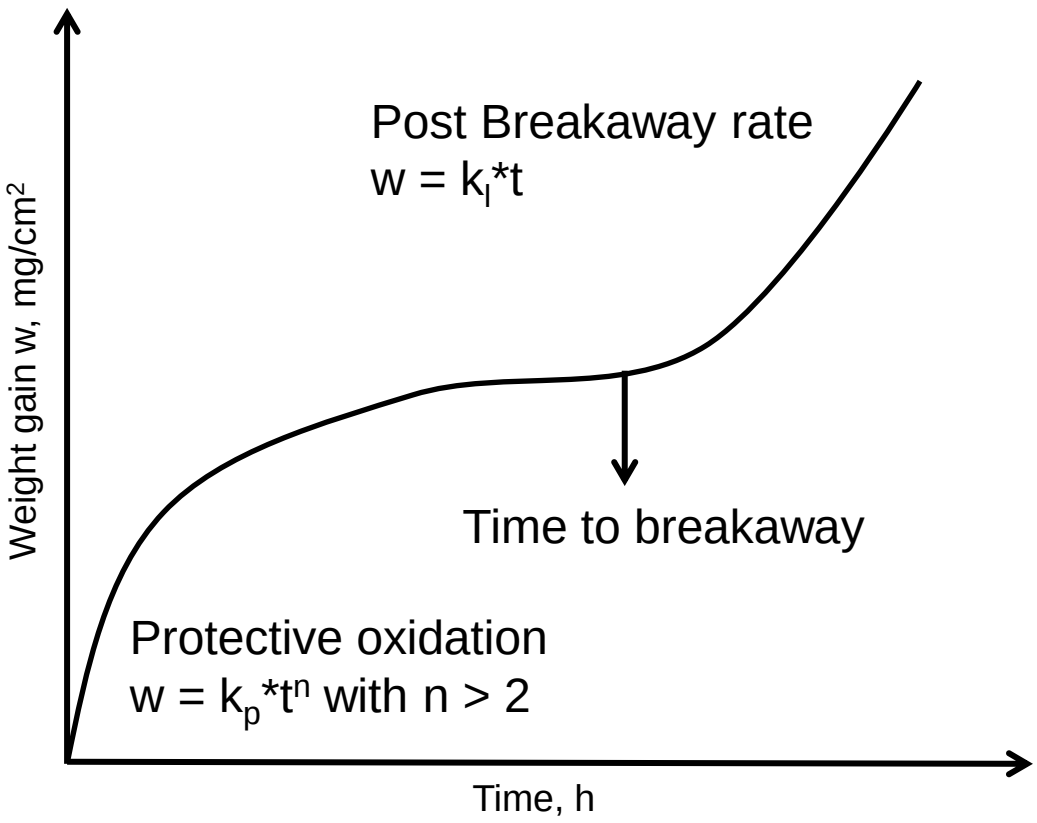
At high P_{CO2} :

- ❑ 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*:

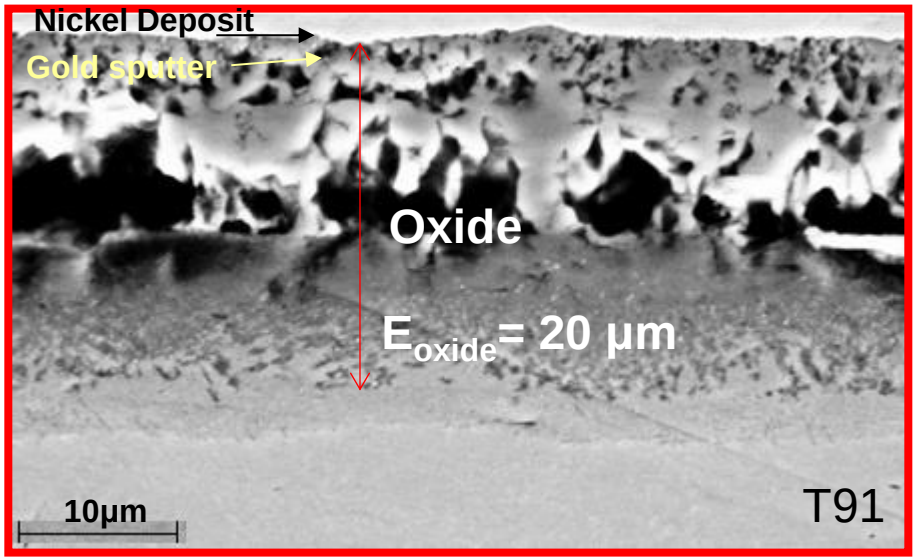
- Known for mild steels in S-CO_2 at T > 350 °C
- But already observed on 9Cr steel in CO_2 – 40 bar at 550°C (first in 1971)
- Favored at HP CO_2 with high water vapour content (>0.1%) and low Si content

**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 ?

INFLUENCE OF CO_2 PURITY ON THE SURFACE OXIDE COMPOSITION

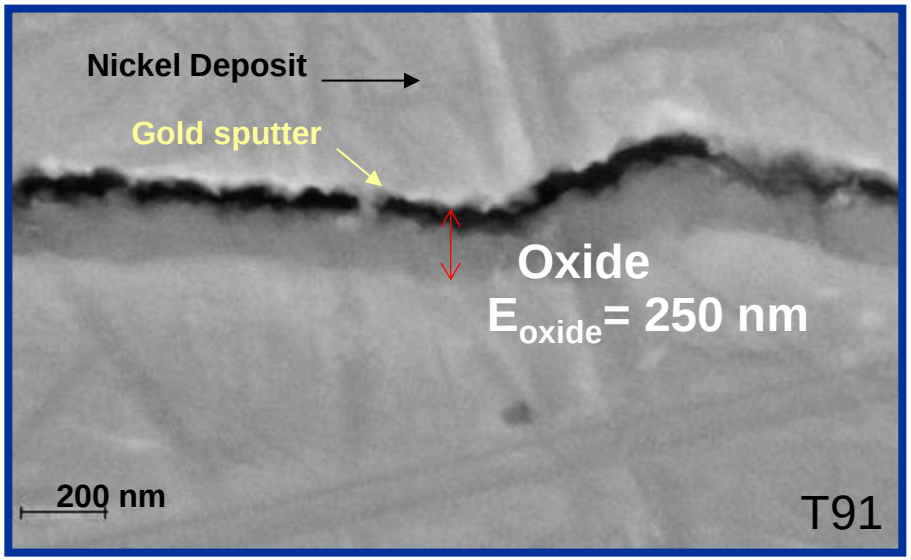
« Industrial » CO_2 purity (with O_2 ~ 100 µbar)



Fast growing iron rich duplex oxide scale

%Cr oxide ~ 9 at%

High CO_2 purity (with O_2 ~ 1 µbar)



Slow growing chromium rich oxide scale

%Cr oxide ~ 20 at%

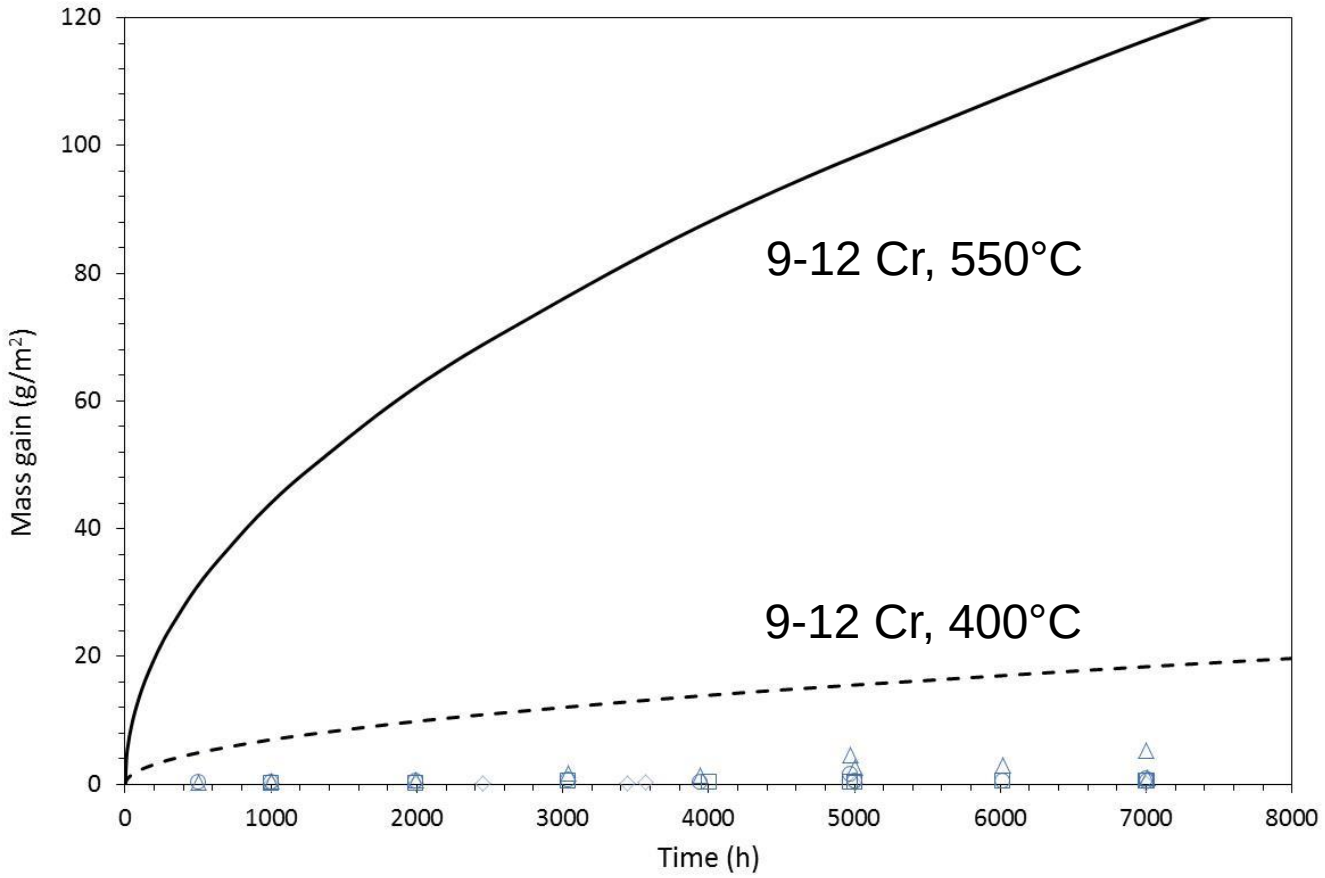
Still protective after 5000 h

Conclusions of PhD thesis (S. Bouhieda 2012) :

- O_2 impurities (µbar) react first during the thermal ramp
- Its level in CO_2 impacts on the surface oxide composition (Cr enrichment)
- The surface finish (mainly roughness?) impacts on the critical O_2 partial pressure

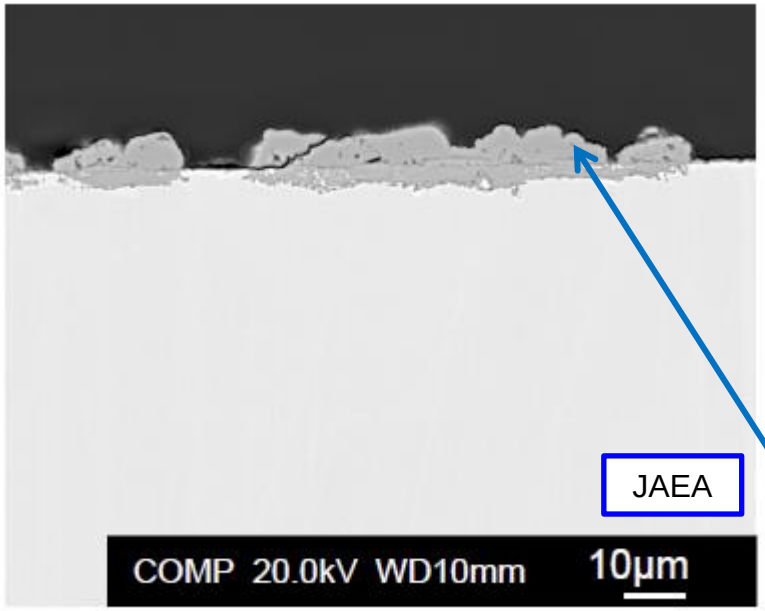
CORROSION MECHANISM OF 17-21CR AUSTENITIC STEELS

MASS GAIN KINETICS OF 316 AUSTENITIC STEEL



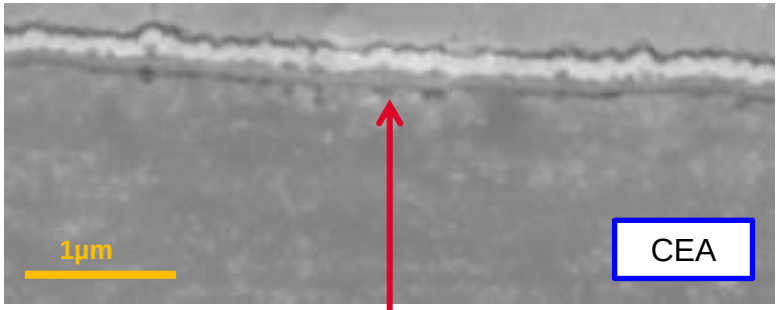
- Very low mass gain : mass gain (316FR) < 100*mass gain (9-12Cr)
- No detectable effect of total pressure
- Larger mass gain is detectable after 5000 h at T = 600°C

OXIDE SCALE



316FR, 600 °C, 20 MPa, 4000 h

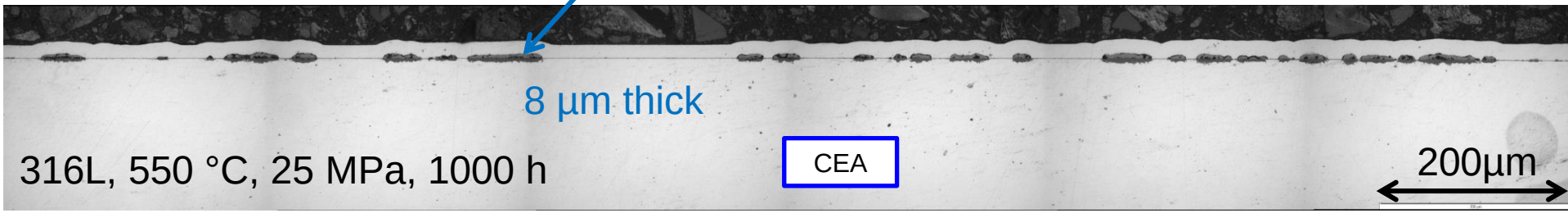
316L – 0.1 MPa – 550°C – 1000 h



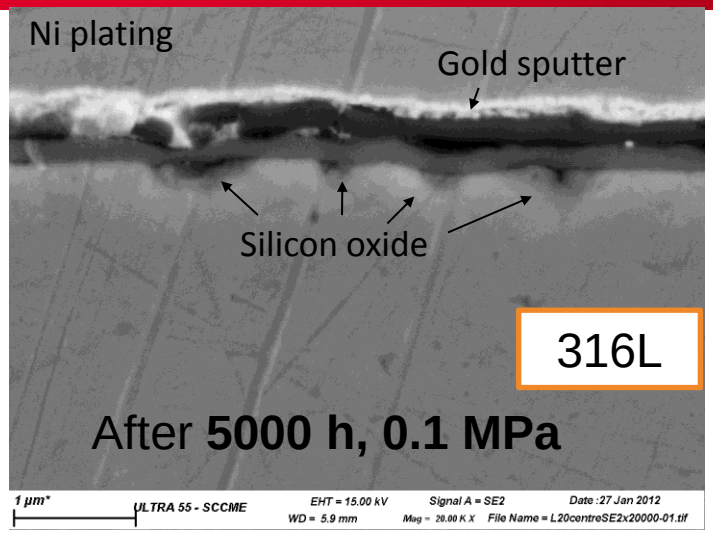
< 200 nm

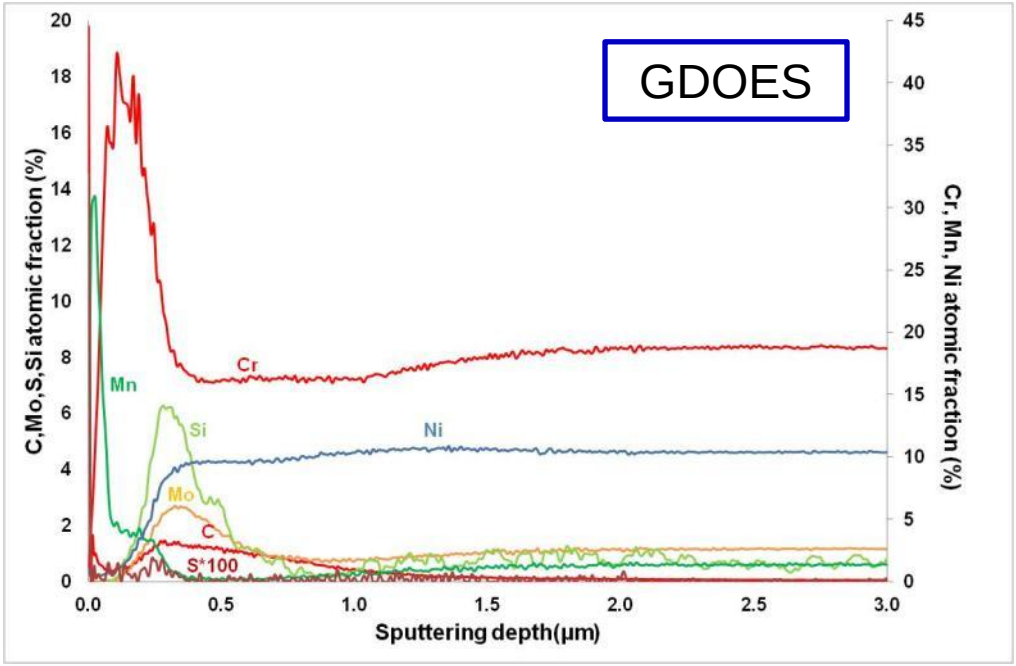
Formation of thin « protective » Cr rich oxide scale and thick nodules of duplex oxide scale (as on 9-12Cr steel but higher %Cr)

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



DETAILS ON THE THIN CR RICH OXIDE SCALE





✓ **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 :**

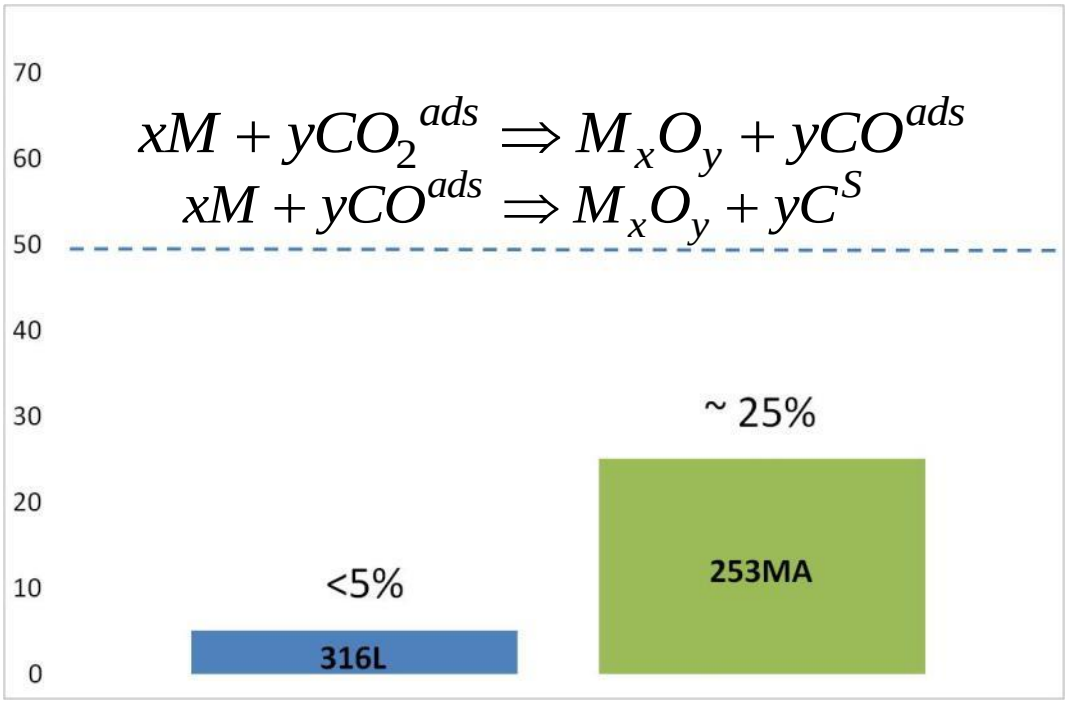
- **C** enrichment below the oxide layer and diffusion profile

INFLUENCE OF STEEL GRADE ON CARBON TRANSFER

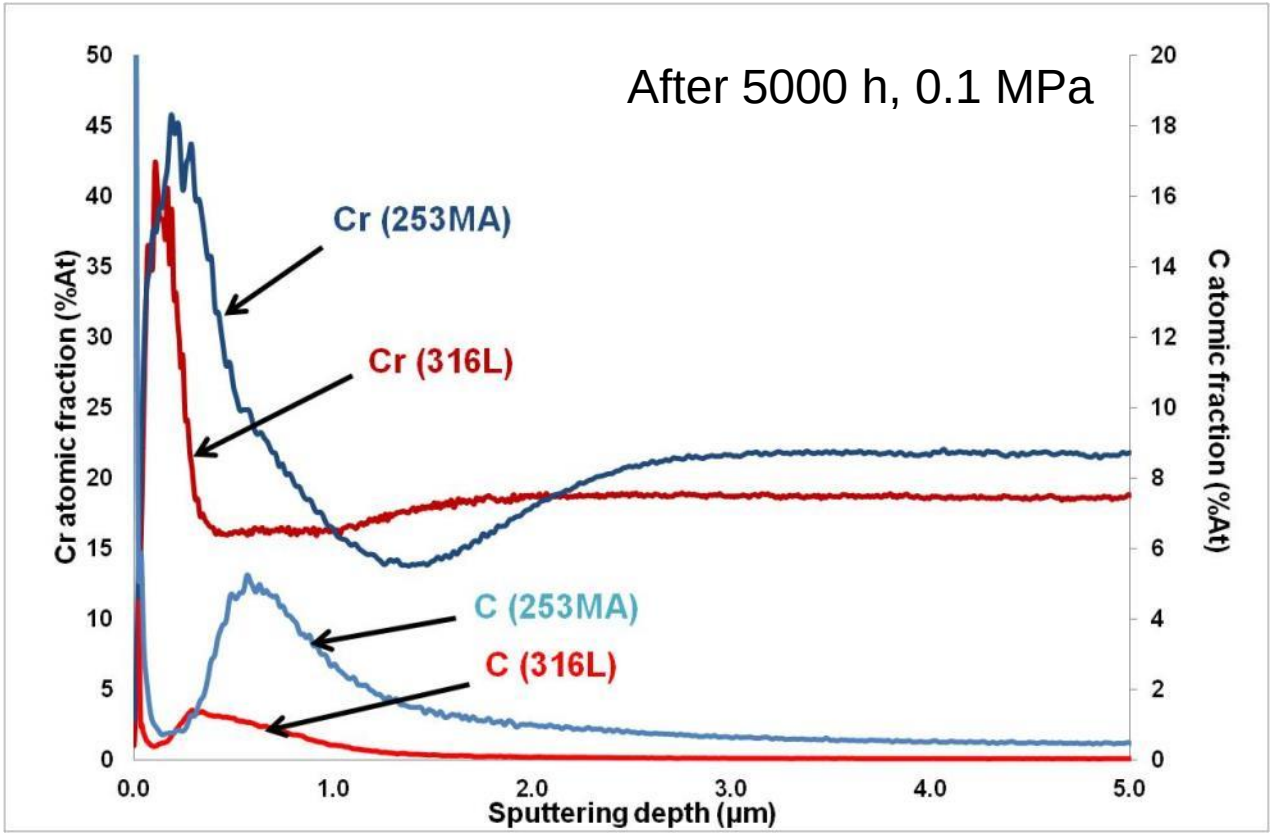
At%	%Cr	%Ni	Other
316L	19%	10%	/
253MA	22%	10%	Si : 3%, Ce

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

From GDOES profiles



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

$$xM + yCO_2^{ads} \Rightarrow M_xO_y + yCO^{ads}$$

Carburisation Or **Desorption**

$$xM + yCO^{ads} \Rightarrow M_xO_y + yC^S \qquad CO^{ads} \Rightarrow CO(g)$$

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 ?

SUMMARY

9Cr F/M Steels

➢**Thick duplex oxide scale**
[Fe-oxides + Fe/Cr oxide]
➢Fast parabolic growth rate
Driving force = P_{O2}^{eq} Fe_3O_4/Fe_2O_3

➢**Strong Carburisation rate**
[via Boudouard reaction ?]
Carbon transfer rate increases with P_{CO2}

Is Breakaway Oxidation possible ??
One should look for it …

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 ?



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

THANK YOU FOR YOUR ATTENTION