

Study of corrosion mechanism of T91 at **intermediate** oxygen concentration : Comparison between Pb-Bi and gas phase reaction

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Outline



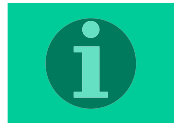
- State of the art
- Objectives
- Experimental
- Oxide morphology
- Comparison between different PO_2 and PH_2O in thermobalance
- Comparison between gas phase reaction and Pb-Bi
- Conclusion



State of the art



- Previous studies* on oxidation of a Fe-9Cr steel (T91) allowed the elaboration of an oxidation mechanism in the case of oxygen saturated Pb-Bi alloy at different temperatures.
- The simulation of the oxidation kinetics, considering the proposed mechanism, is in good agreement with the experimental points for all the tested temperatures and the ones of literature (470°C, 500°C, 550°C, 600°C, 620°C).
- However, when the dissolved oxygen content in the liquid alloy is lower than its solubility limit, the experimental kinetics is not in agreement with the simulated kinetics.



* L. Martinelli & al. works



Objectives



- Identify the corrosion mechanisms at oxygen under saturated concentrations
 - Points of similarity between Pb-Bi and gas phase reaction?
- Simulate this mechanism to obtain a predictive oxidation model (T and [O]) parameters which can vary in reactor



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Pb-Bi experiments

540°C

Static LBE

H₂/H₂O/Ar

In-situ measurement of [O]

PO₂ = 2.8 10⁻²⁵ atm

Gas phase reaction

540°C

Symmetric thermobalance

H₂/H₂O/Ar

In-situ measurement of [O]

PH₂O = 4.0×10⁻⁰⁴
1- PO₂ = 1.0×10⁻²⁶atm
2- PO₂ = 1.0×10⁻²⁴atm

PH₂O = 2.4×10⁻⁰² PO₂ = 1.4×10⁻²⁶ atm

PH₂O = 2.4×10⁻⁰²
1- PO₂ = 2.0×10⁻²² atm
2- PO₂ = 4.8×10⁻²⁴ atm
3- PO₂ = 5.9×10⁻²⁴ atm



Outline



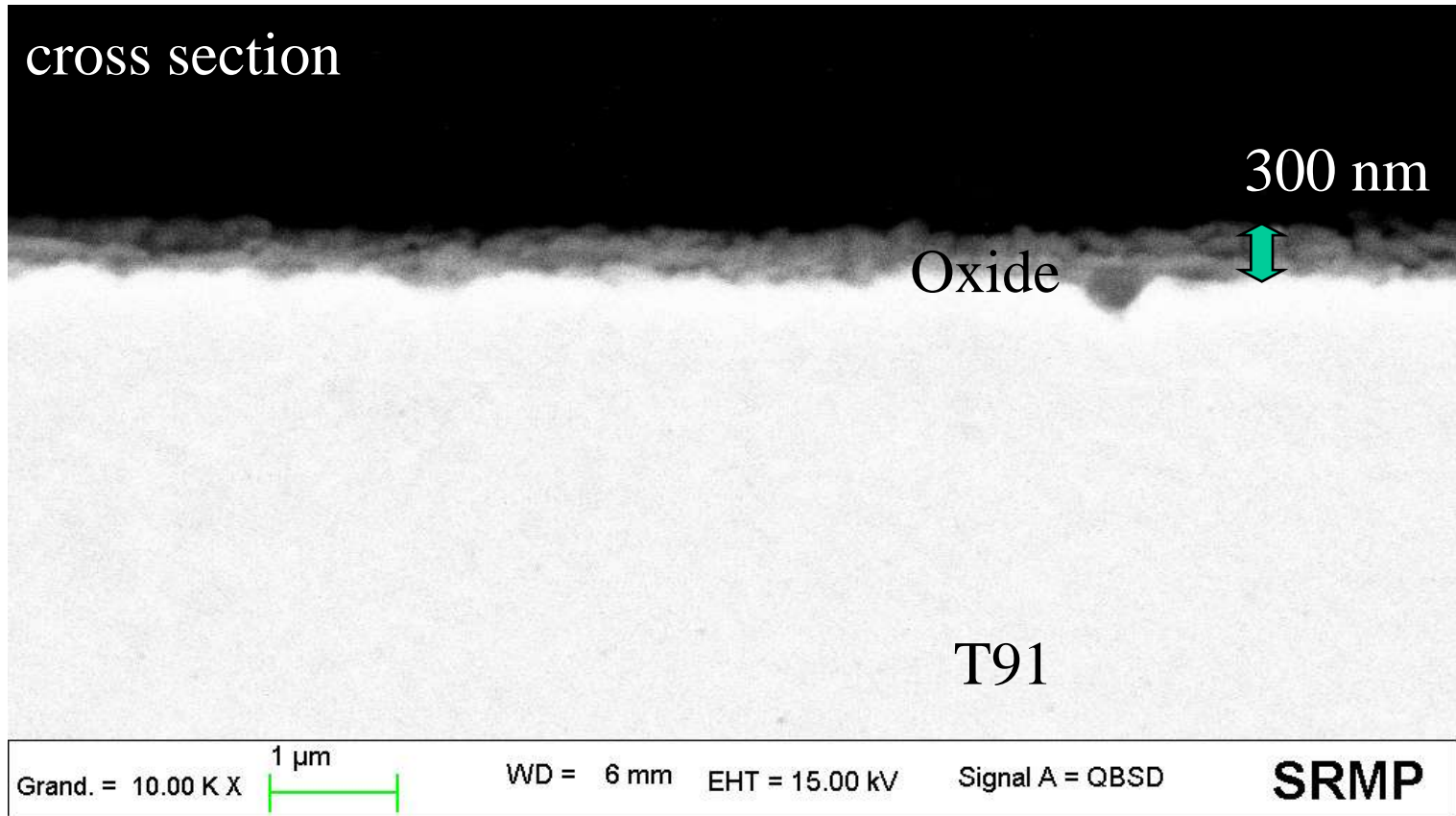
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T91, TB, 470h, $PO_2 = 1.10^{-24}$ atm, $PH_2O = 4.10^{-4}$ atm

cea

cross section

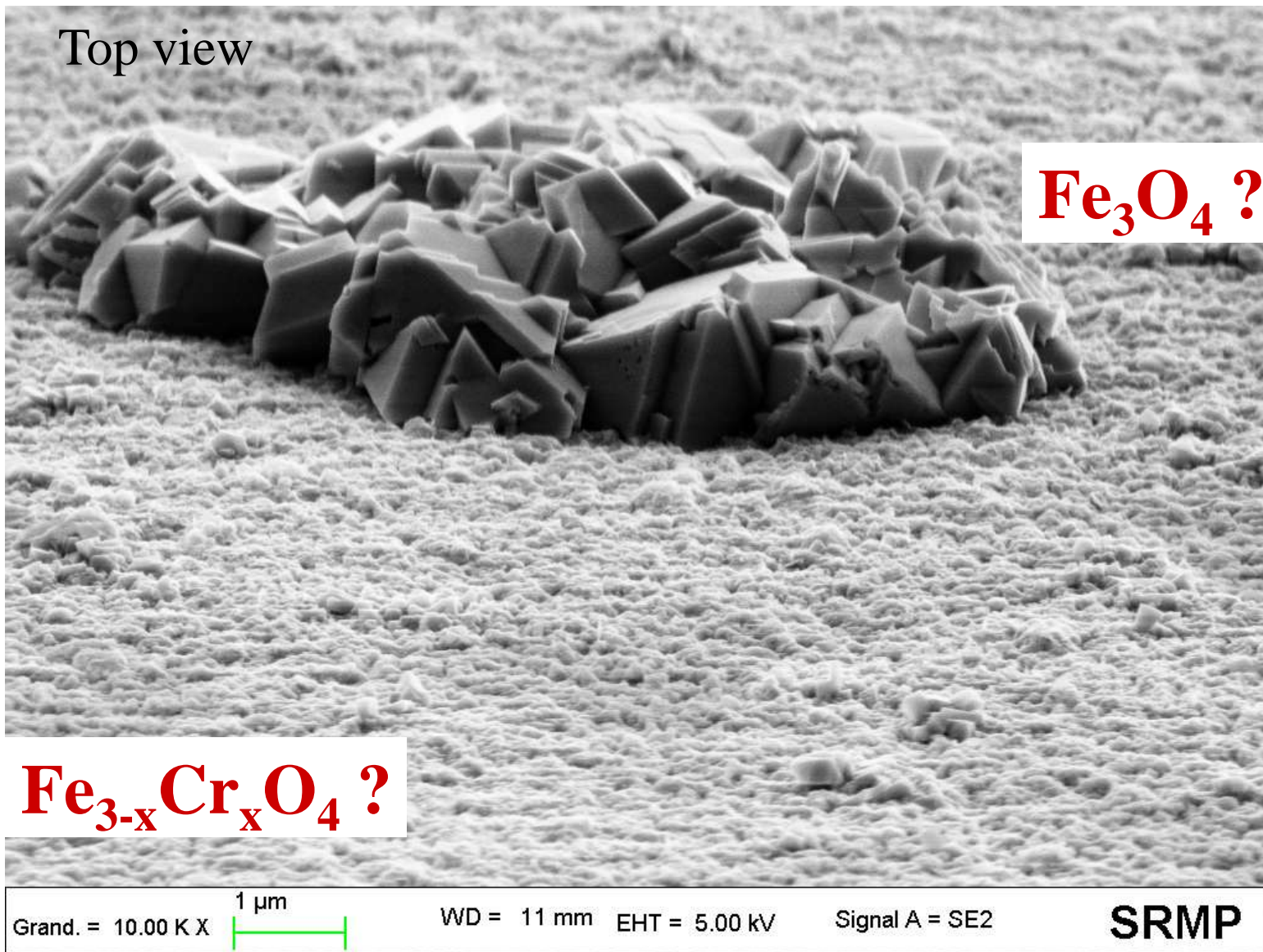


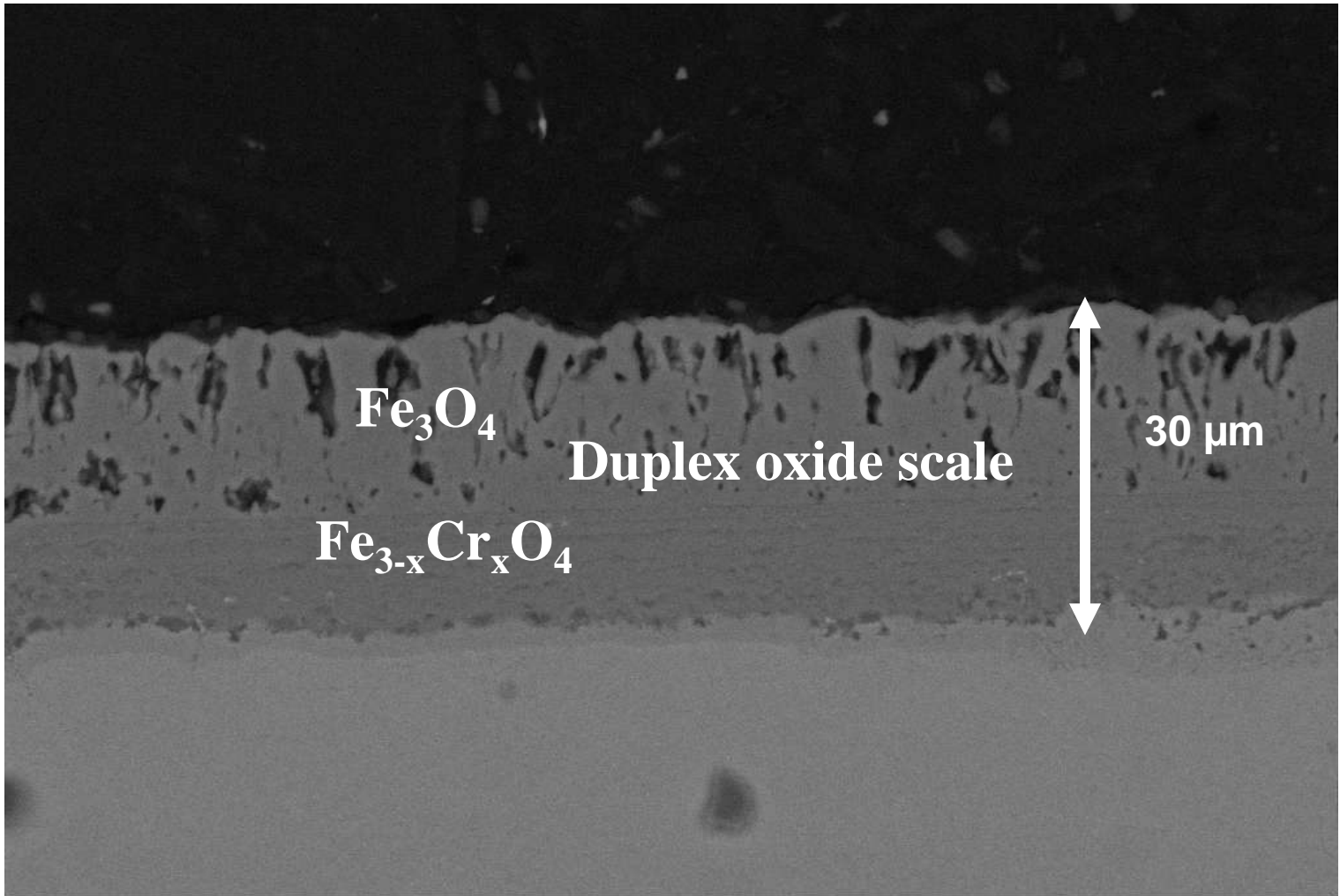
Very thin oxide layer ~ 300nm

T91, TB, 470h, $PO_2 = 1.10^{-24}$ atm, ($PH_2O = 4.10^{-4}$ atm)

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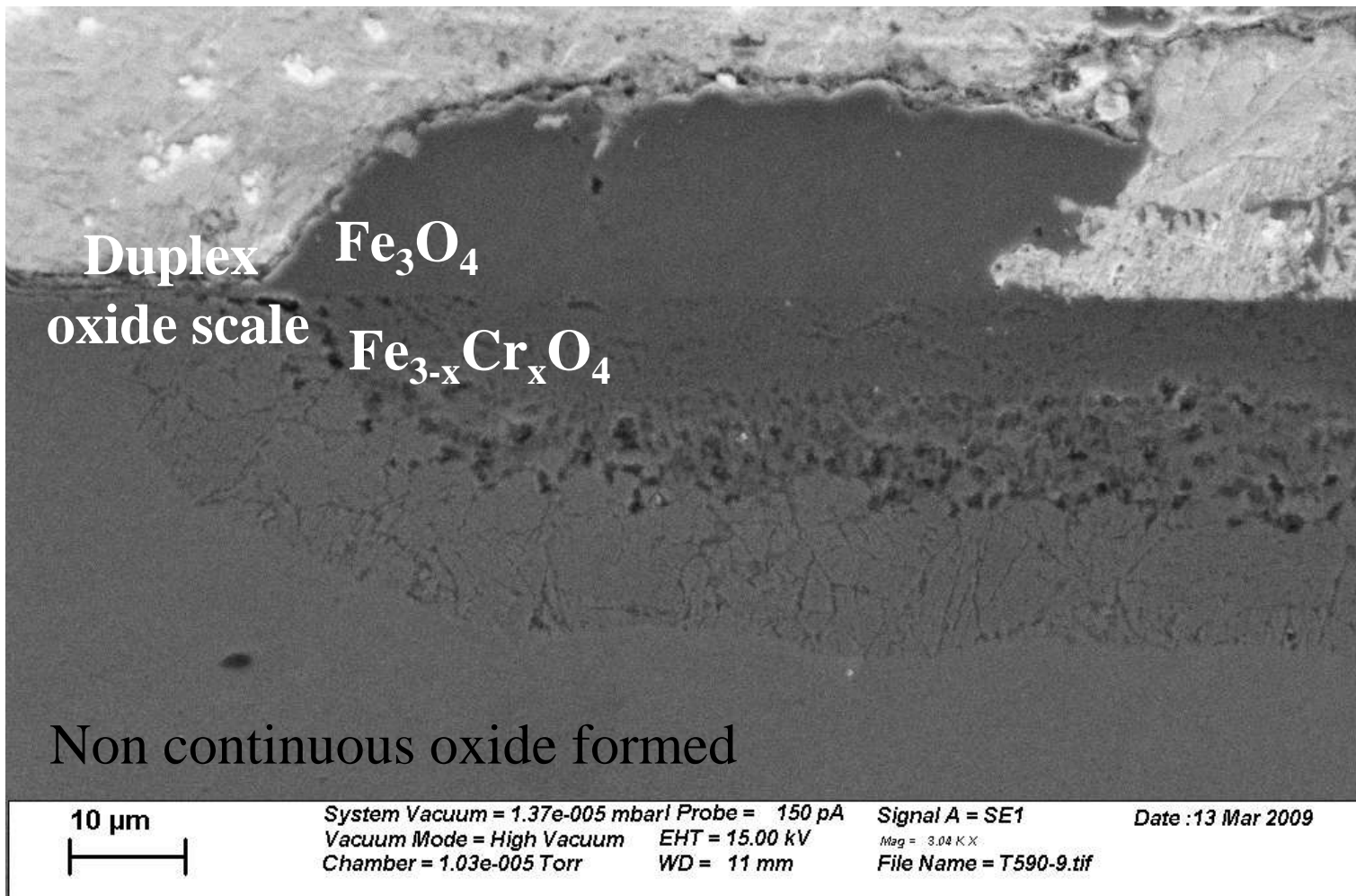
Top view





10µm* System Vacuum = 6.18e-007 Torr I Probe = 150 pA Signal A = QBSD Date :3 Sep 2008
Vacuum Mode = High Vacuum EHT = 20.00 kV Mag = 1.04 KX
Chamber = 4.70e-003 mBar WD = 15 mm File Name = T609_22.tif





By microprobe analysis : $x = 0.6 \rightarrow \text{Fe}_{2.4}\text{Cr}_{0.6}\text{O}_4$

Oxide morphology related to environment



LBE experiments

Up to 3000 hrs

- Heterogeneous oxidation (localized)
- A dissolution on some samples after 750 hrs
- Duplex oxide scale : Fe_3O_4 and spinel $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$ ($0.6 < x < 0.7$)

Gas phase reaction

Up to 750 hrs

- Heterogeneous oxidation if low PH_2O
- Homogeneous oxidation with duplex oxide scale if high oxidant concentration (H_2O and O_2)
- No dissolution observed
- Duplex oxide scale : Fe_3O_4 and spinel $\text{Fe}_{3-x}\text{Cr}_x\text{O}_4$ ($0.6 < x < 0.7$)

Same oxide scale morphology and nature leads to consider a similar oxidation mechanism



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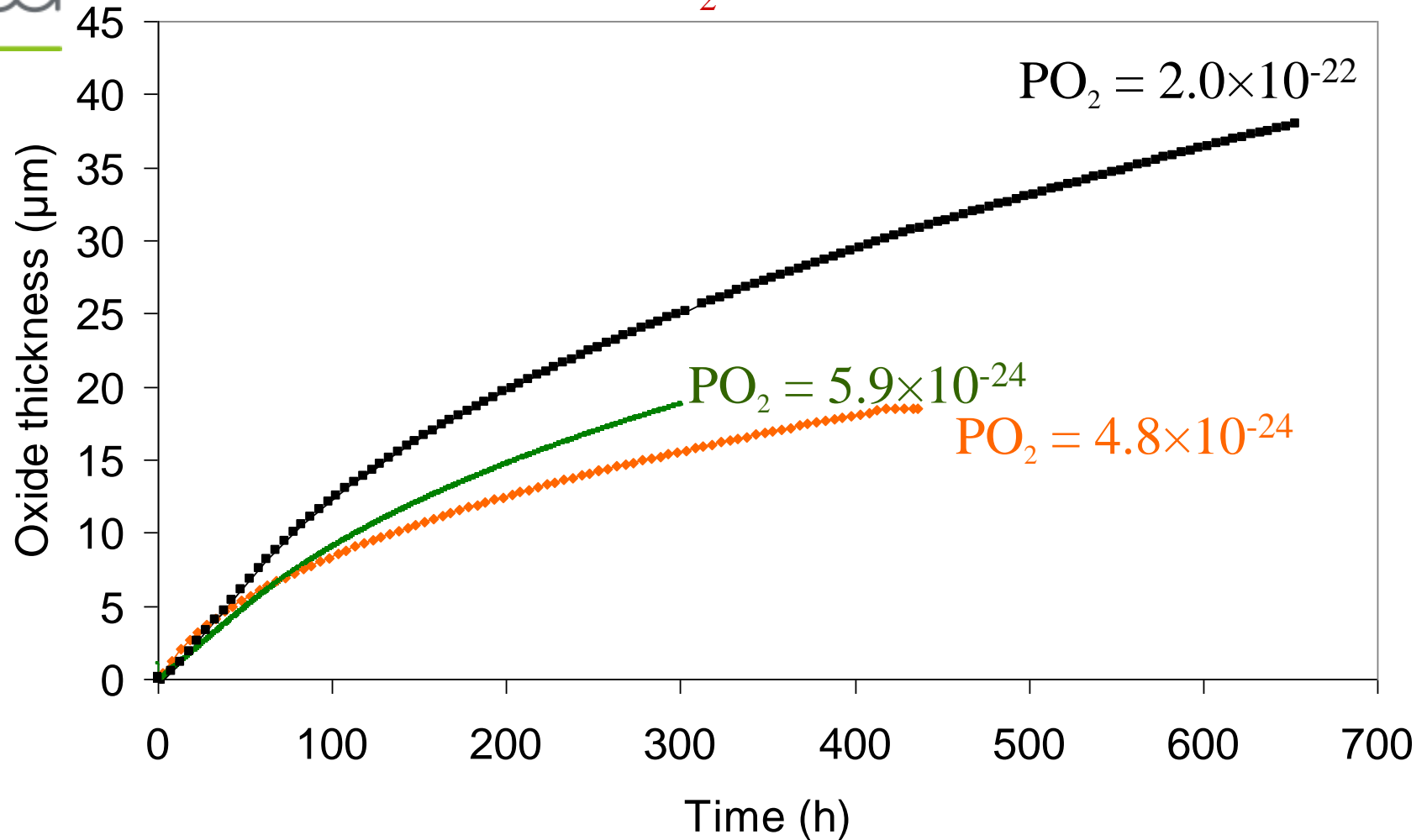


Thermobalance experiments : 540°C, H₂O/H₂/Ar



Same $P_{H_2O} = 2.4 \times 10^{-02}$ atm

$P_{O_2} = 2.0 \times 10^{-22}$



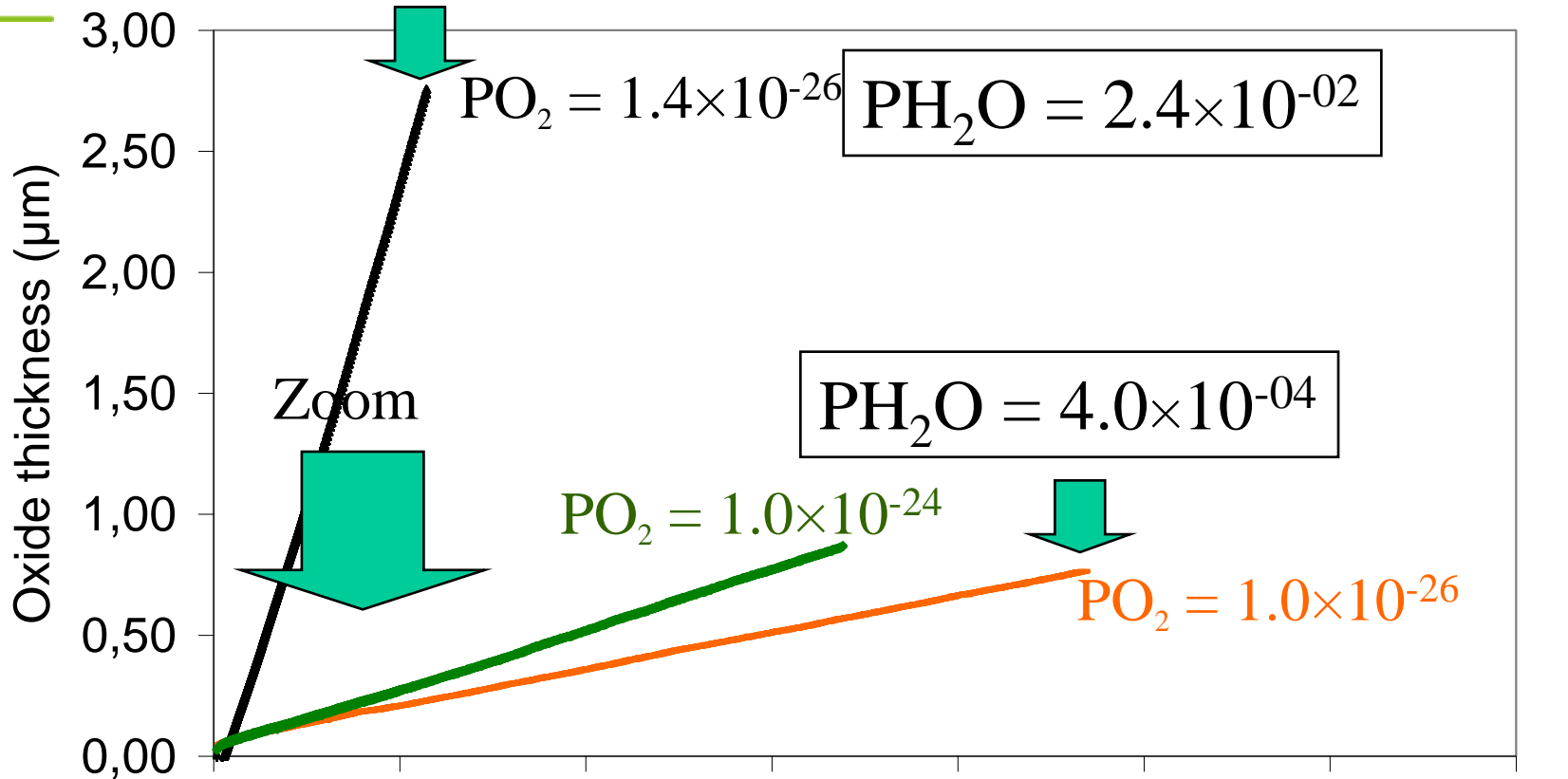
Parabolic law fits the exp points: diffusion control mechanism



Evidence of the oxidation dependence on PH_2O



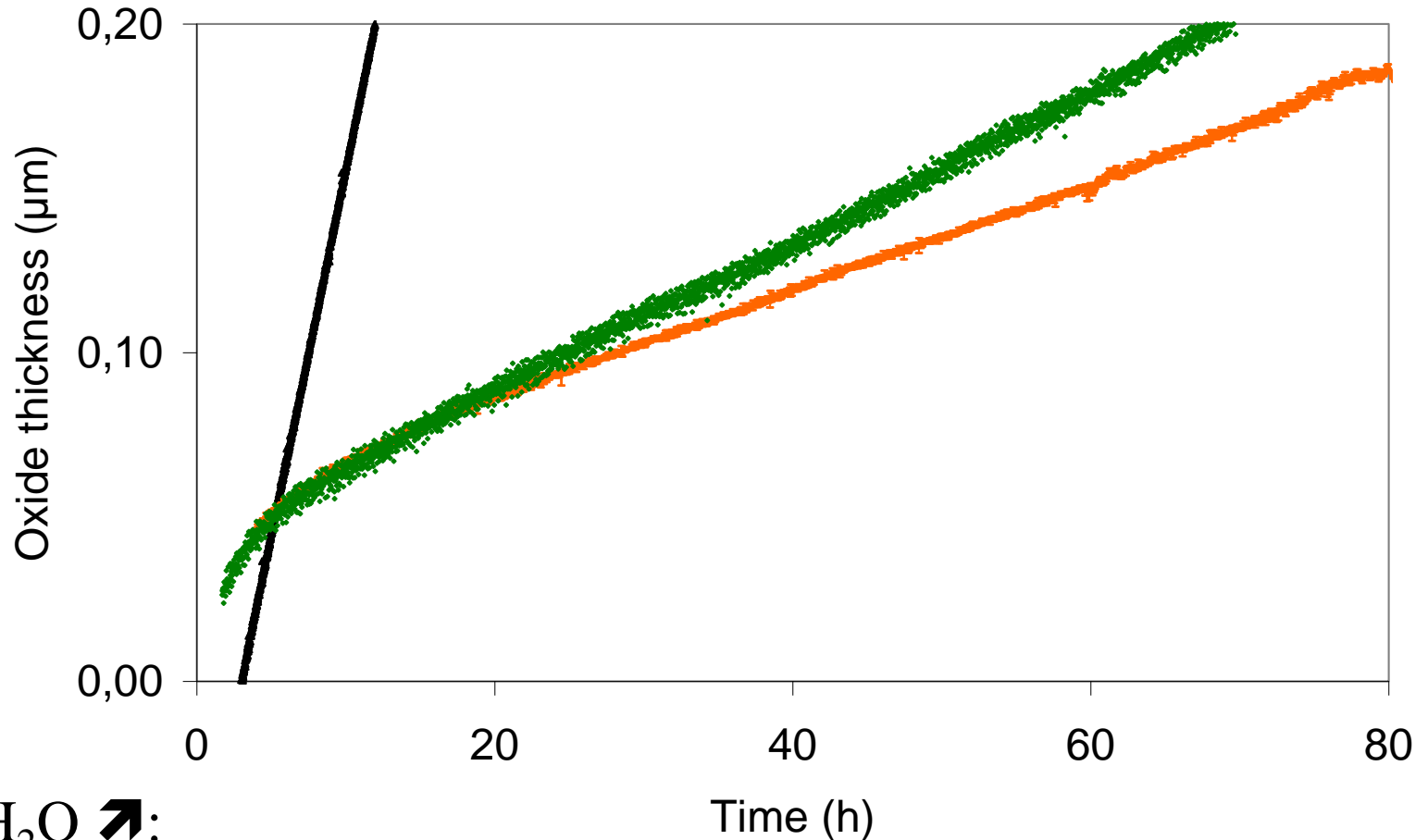
Same PO_2



Linear law fits the exp points (globally):
At same PO_2 : if $\text{PH}_2\text{O} \nearrow$ the kinetic \nearrow



Evidence of the oxidation dependence on PH_2O

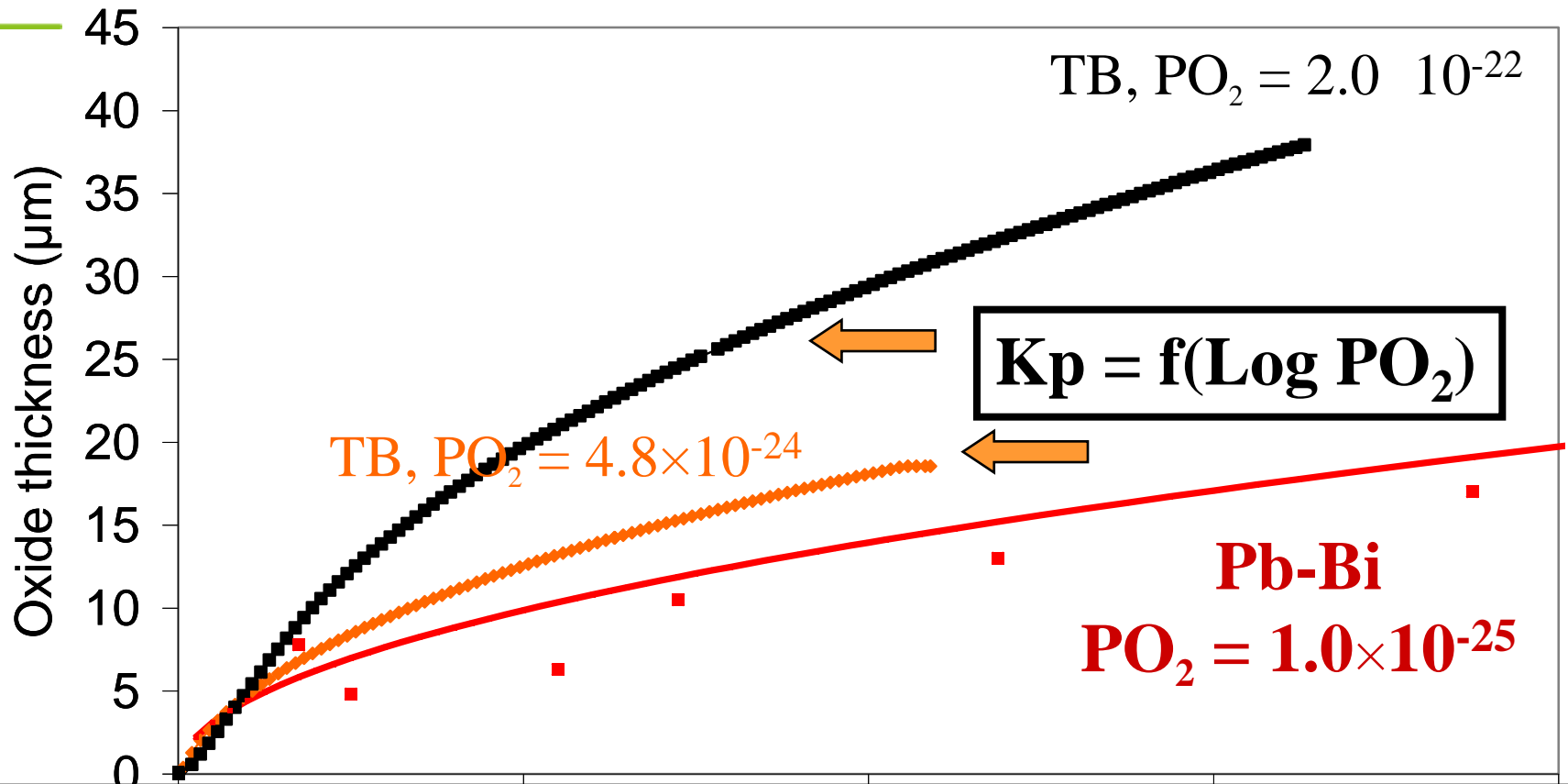


PH_2O ↗:

- the kinetic ↗
- and the mechanism changes from diffusion (at first instance) to surface reaction)



Strong point: similarity between the environments



By extrapolation of K_p at this $\text{PO}_2(\text{TB})$: Simulated oxide thickness is very similar to experimental points obtained in LBE



Role of H_2O in the mechanism



- $\text{PH}_2\text{O} : 4.0 \cdot 10^{-4} \text{ atm} \rightarrow$ Surface reaction, Kr
- $\text{PH}_2\text{O} : 2.4 \times 10^{-2} \text{ atm}$ but $\text{PO}_2 : 1 \times 10^{-26} \text{ atm} \rightarrow$ Surface reaction, Kr
- $\text{PH}_2\text{O} : 2.4 \times 10^{-2} \text{ atm}$ and $\text{PO}_2 > 1 \times 10^{-25} \text{ atm} \rightarrow$ Diffusion, Kp

A threshold oxidant concentration (H_2O and O_2) is needed to control the oxidation by diffusion (kp) instead of surface reaction (kr)

Important role of H_2O to start the oxidation :
first step of the mechanism seems to be the adsorption/dissociation of H_2O on the surface

Study of the role of H_2O in the germination process in progress



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Conclusions and perspectives



- For oxidation process :
 - The oxidation kinetic in both the environments (Pb-Bi and gase phase reaction) is quite similar
 - LBE and gaseous media play the same role as an oxidizing molecules supplier
- However, corrosion in LBE is more complicated (there is oxidation + dissolution)
 - A non-uniform corrosion observed on LBE oxidized samples
 - A dissolution attack from 750 hrs
- For oxidation mechanism (for LBE and gaseous media):
 - $[H_2O]$ seems to control the first instants of oxidation reaction
 - Once the PH_2O sufficient to obtain parabolic law, the oxidation kinetic is limited by PO_2

Establish a mechanism related to germination and growth in the aim of modelling anisotropic growth of nodules



*Thank you for your
attention*