Synthèse et résistance mécanique de couches de ZrO_2

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GdR ConCord 7 juil 2021

- **Context:** Mechanical strength of zirconia layers is important
  - to maintain the function of deposited layers
  - or to protect the metallic substrate from further oxidation

- **Objective:** Study of the mechanical strength of zirconia layers obtained from different conditions of growth

I . Film synthesis

II . Residual stresses within the layers

III . Multiple cracking tests

IV . Stress analysis at crack initiation

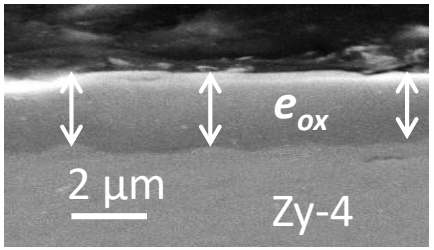
V . Conclusion

I . Film synthesis

Processes

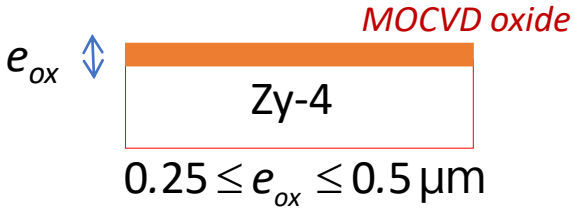
Substrate: plate (thickness 400 µm) recrystallized Zy-4

3 types of process for the zirconia film growth



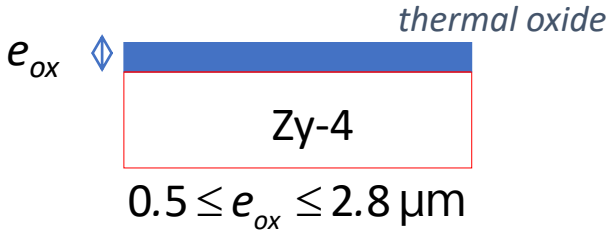
1) MOCVD

OM4: T_S= 400 °C **OM5:** T_S= 500 °C



2) Air oxidation

OX5: T_{ox}= 500 °C

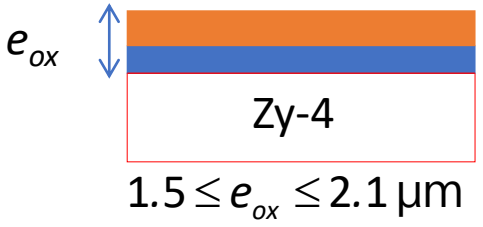


3) Mixed synthesis

2 steps: **A. Air oxidation** at 500°C 7h

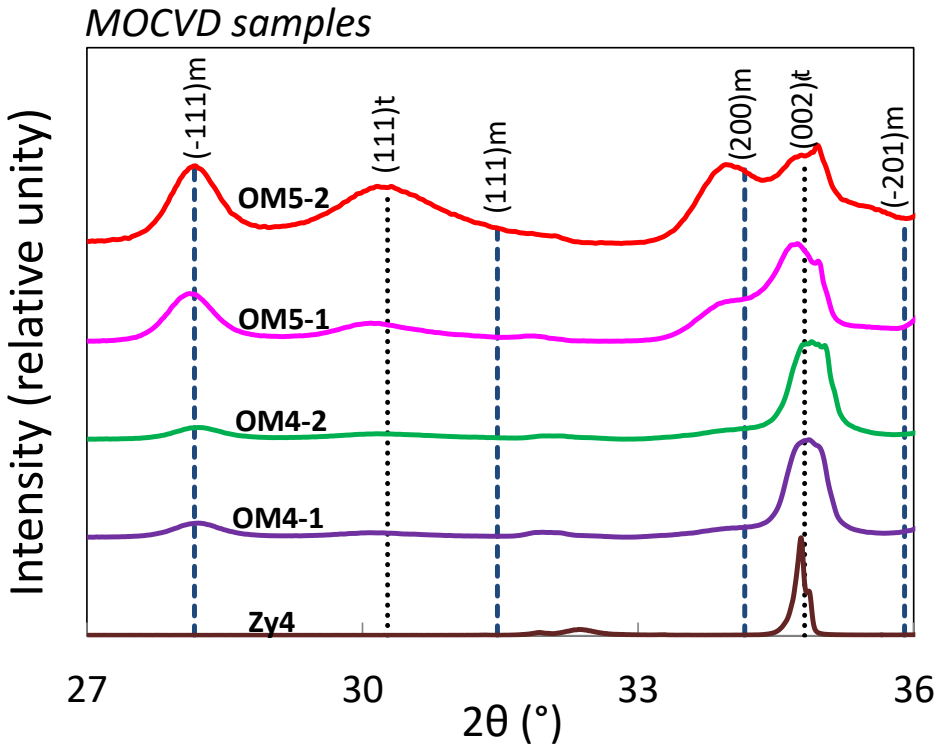
B. MOCVD at 400°C or at 500°C

X5M4 **X5M5**



Structures- microstructures

❖ Phase analysis of ZrO_2: GI-XRD (X'Pert PRO MRD de PANalytical)



❖ Volume fraction of ZrO_2t

[Garvie et Nicholson 1972]

$$f_t = \frac{A_{(111)t}}{A_{(\bar{1}11)m} + A_{(111)m} + A_{(111)t}}$$

$A_{(khl)}$ *peak area*

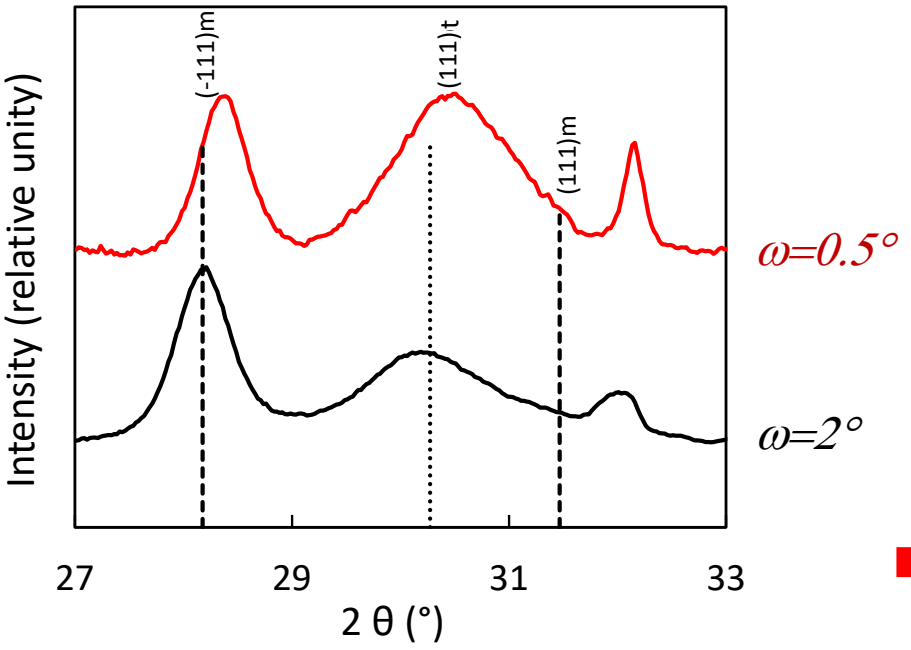
➡ monoclinic phase, **ZrO_2m** and tetragonal phase, **ZrO_2t**

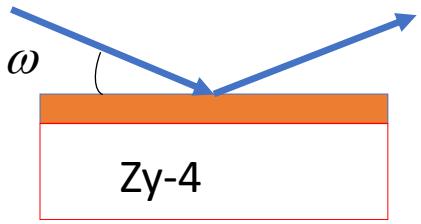
❖ Phase localization

In thermal growing ZrO_2 layers on the Zr alloys, there is a gradient of ZrO_2t with more ZrO_2t located at the metal-oxide interface
[Godlewski et al. 1994], [Petigny et al. 1998], [Polatidis et al. 2013]

For MOCVD ZrO_2 layers (OM and X5M layers): GI-XRD with different angles ω

MOCVD sample

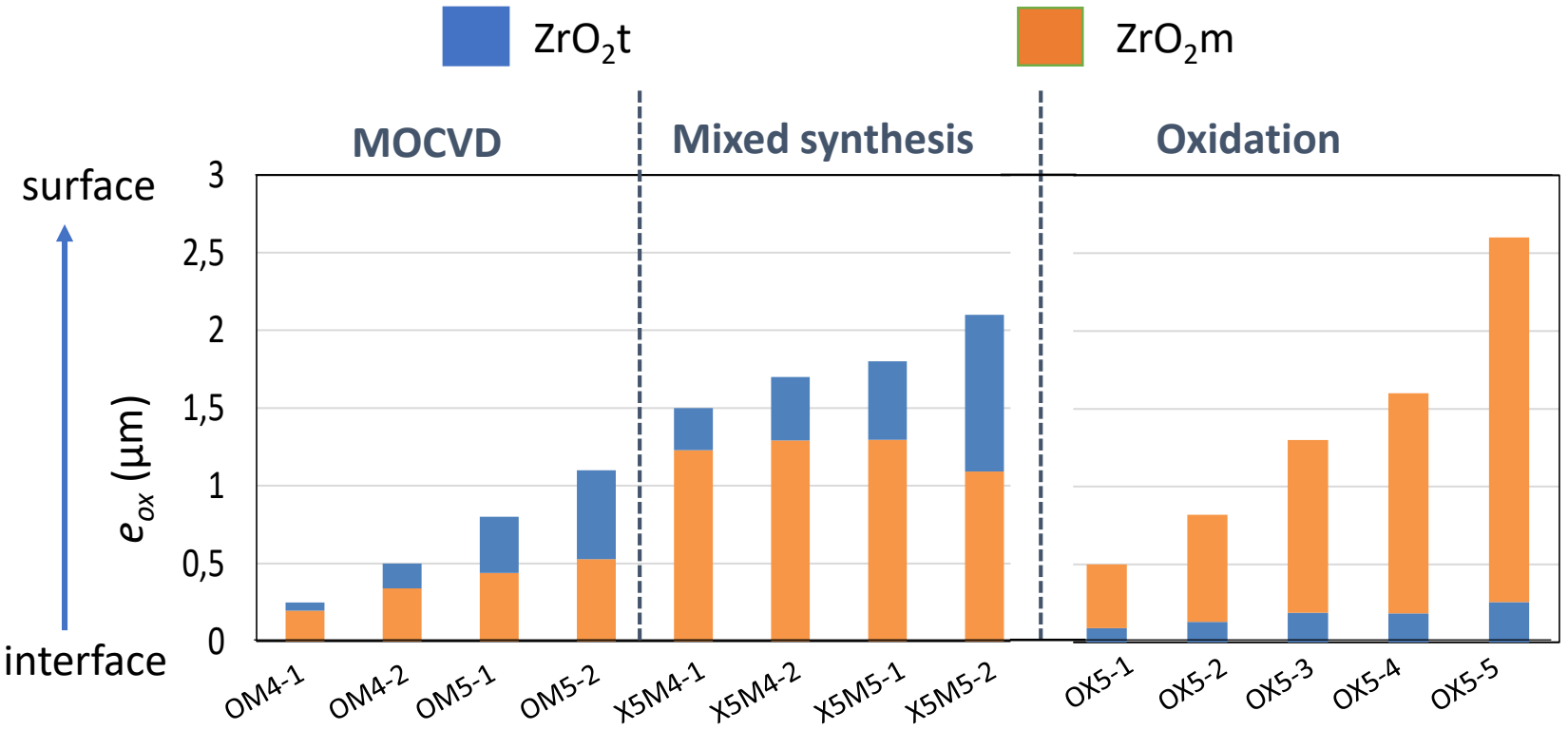




ZrO_2t is rather located at the surface of the layer

I . Film synthesis

Assuming that both phases are not mixed → **schemes of layer microstructures**



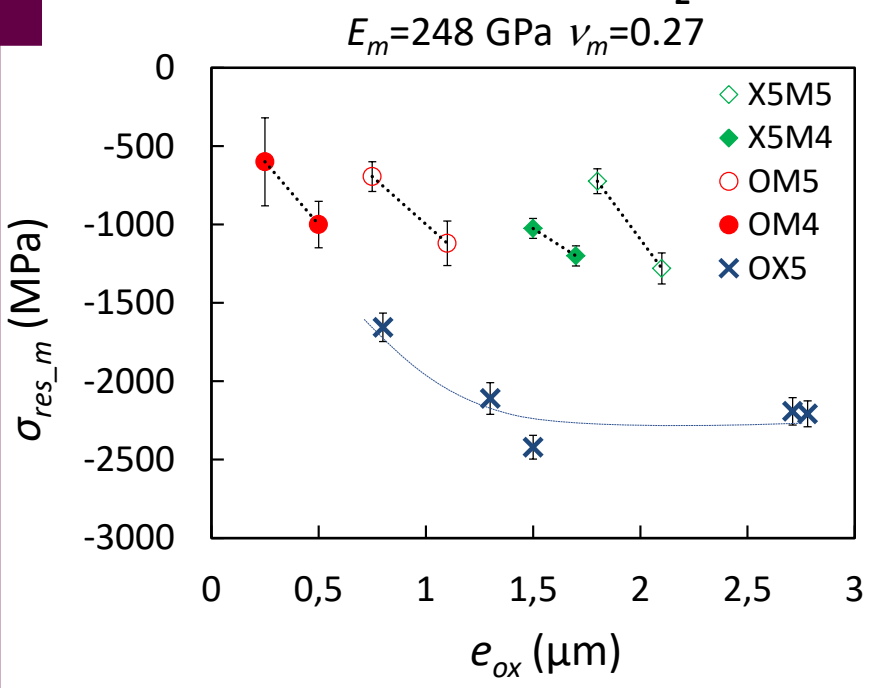
Layers of various thicknesses (0.25-2.8 µm) with different fractions of ZrO_2t mostly located at the metal-oxide interface or at the surface were obtained

II. Residual stresses

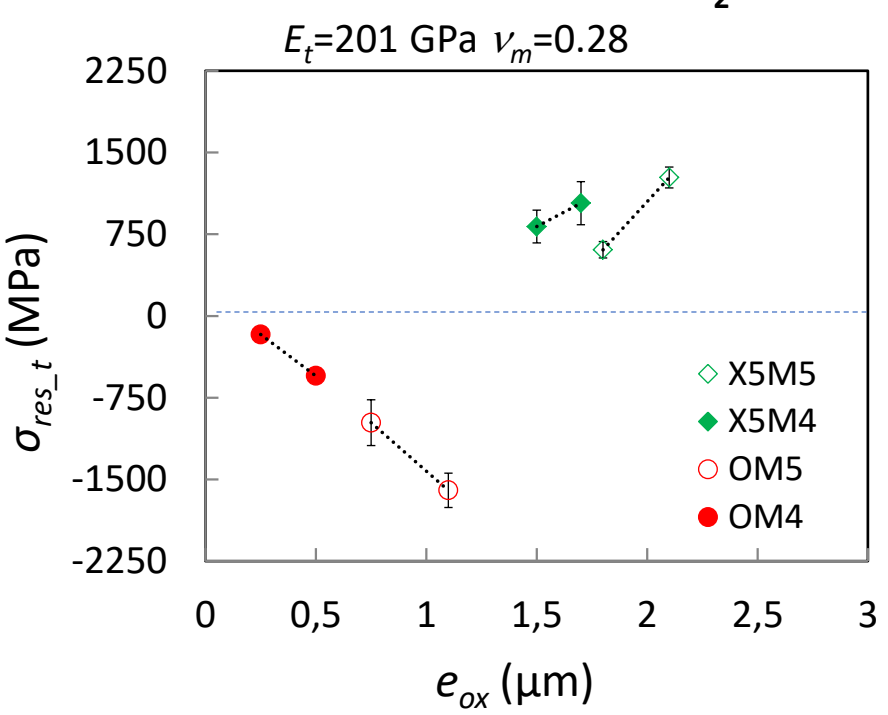
- **Method** $\sin^2\psi$ (X'Pert PRO MRD de PANalytical)

Hypothesis: isotropic layer

❖ **Residual stress in ZrO_2m**



❖ **Residual stress in ZrO_2t**



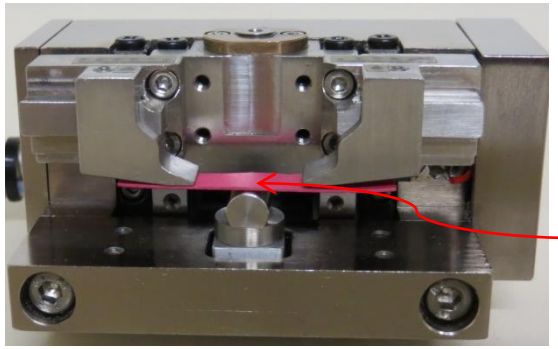
Compressive stresses in ZrO_2m

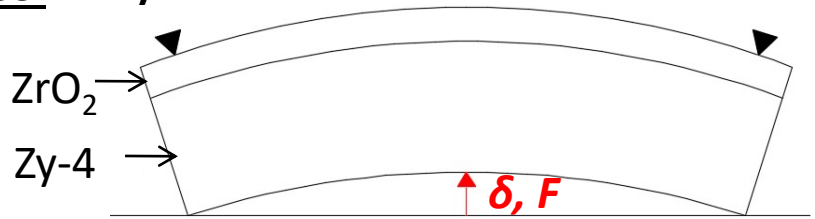
Compressive or tensile stresses in ZrO2t

Residual stresses varying with the layer thickness

Experimental method

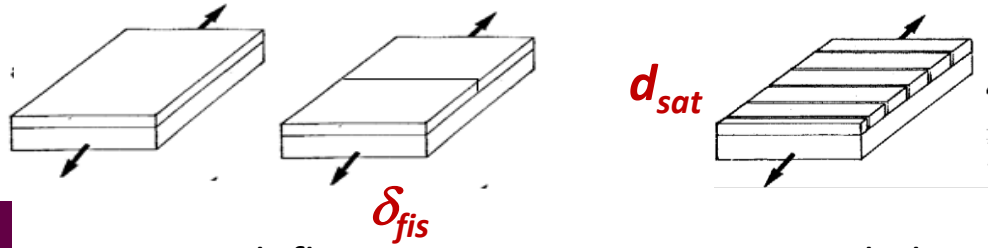
3-points bending test in SEM (MEB sigma ZEISS icmmo)





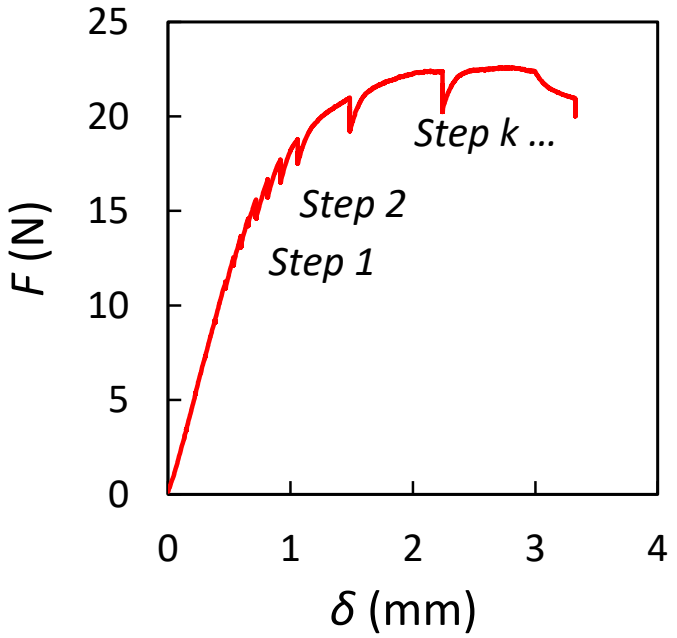
Interrupted test to observe the multiple cracking process of the layer

Step 1 **Initial step** **Final step**



deflexion at crack initiation

mean crack distance at saturation

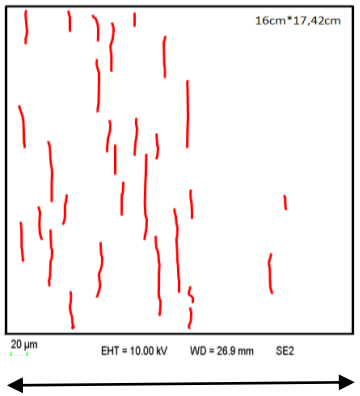


III. Multiple cracking tests

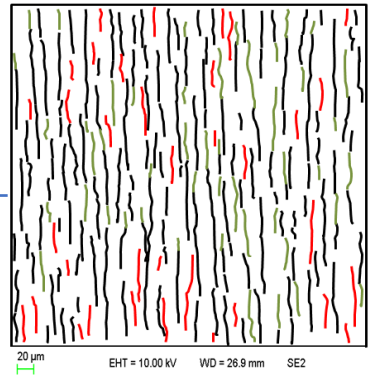
- **Results**

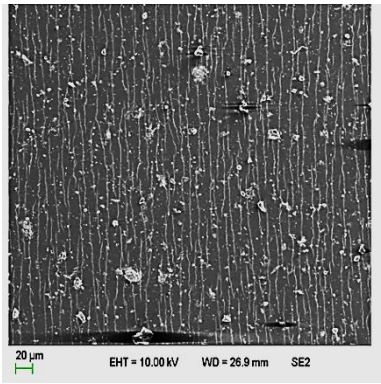
Initial Step | **Intermediate Step** | **Final Step**

e_{ox} = 1.1 µm
OM5

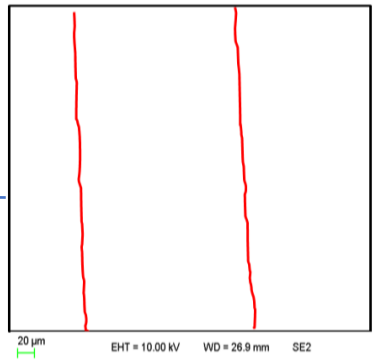


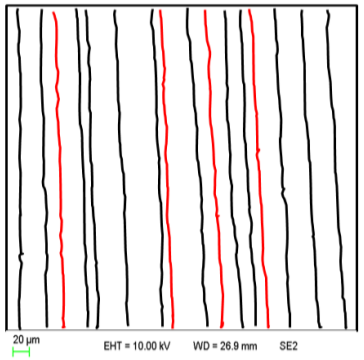
416 µm

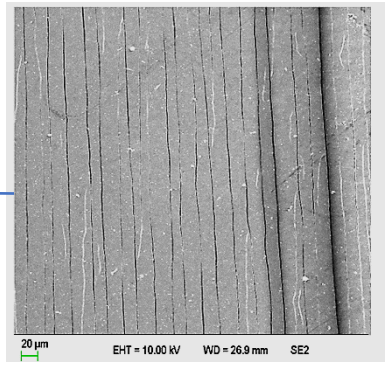




e_{ox} = 2.1 µm
X5M5



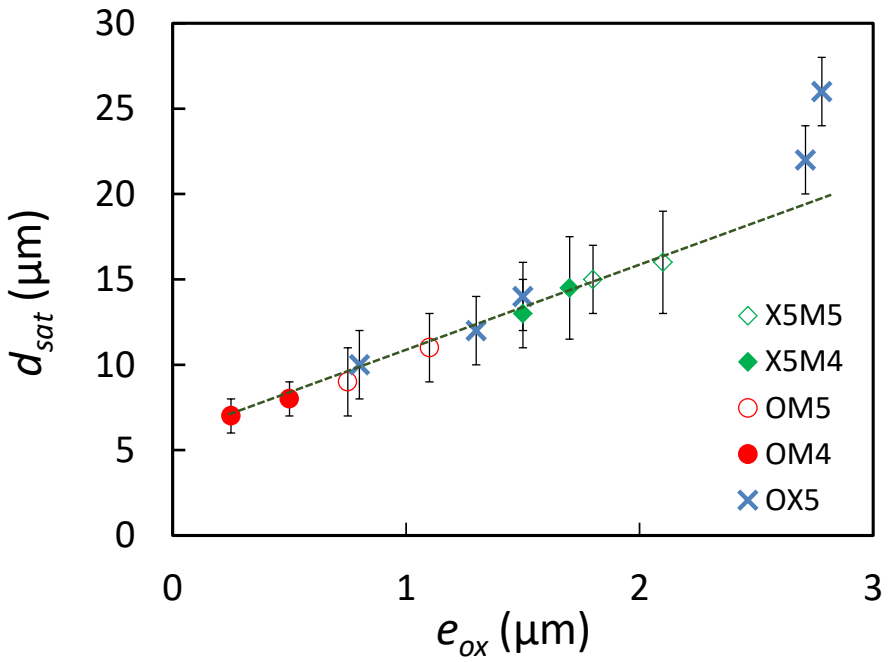




The thicker the layer, more straight and uniform are the cracks

III. Multiple cracking tests

❖ **Crack distance at saturation d_{sat}**



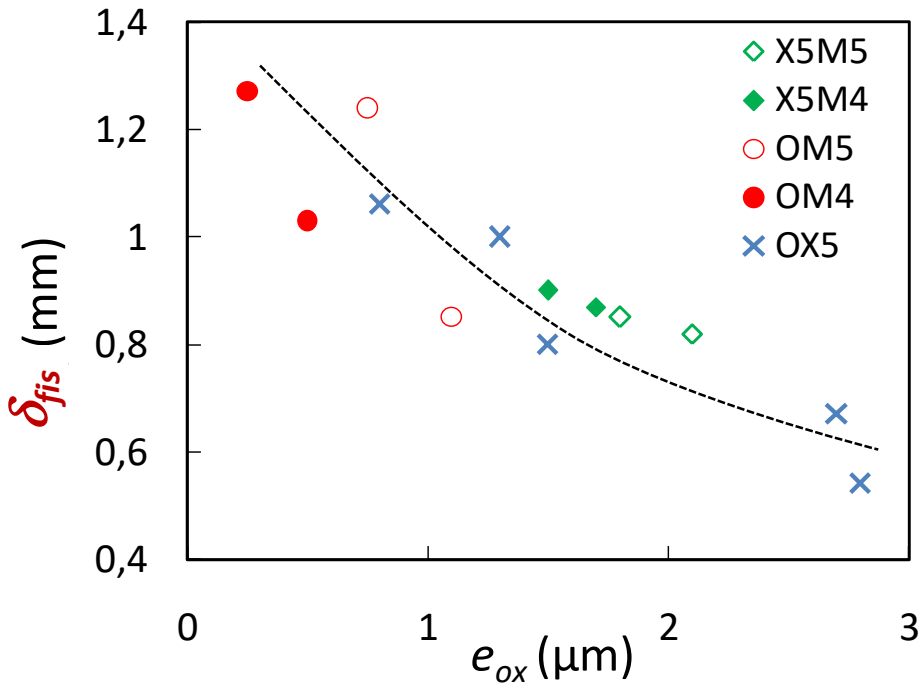
Linear variation of d_{sat} for $0.25 \leq e_{ox} < 2$ µm

[Ganne et al. 2002] [Bernard et al. 2007] [Nagl et al. 1993] …

➡ d_{sat} does not depend: - neither on the structure/microstructure
- nor on the residual stresses

III. Multiple cracking tests

❖ **Deflection at crack initiation δ_i**



δ_i decreases as the thickness of the layer increases for all the processes

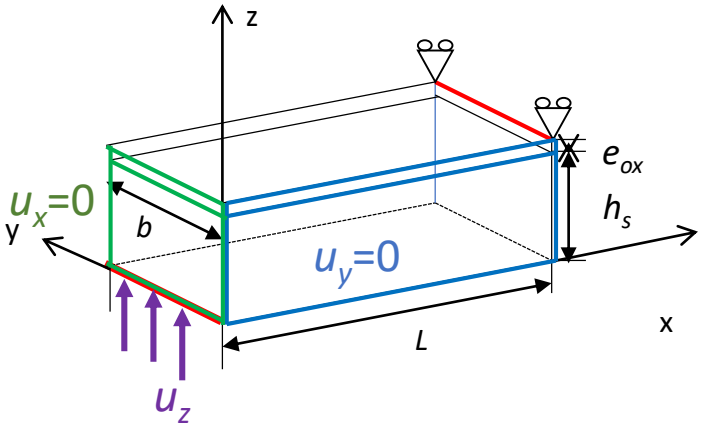
➡ δ_{fis} does not depend neither on the structure nor on the residual stresses ?!

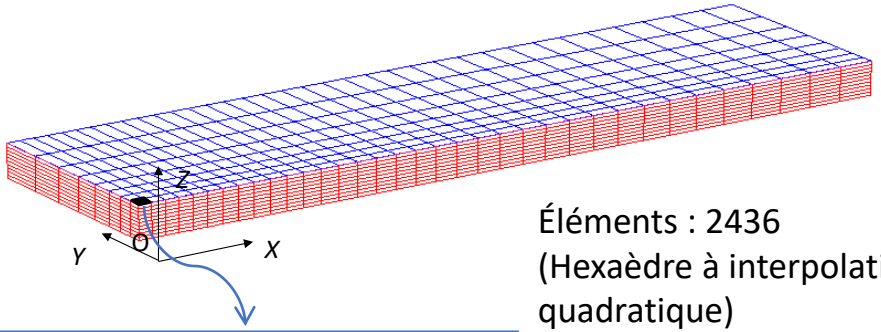
In order to obtain a local variable => mechanical analysis of the 3 points bending test

- **Modelling of 3 points bending test (cast3M)**

❖ **Numerical model : 3D**

- Symmetry => ¼ specimen





Gage volume
(150 x 150 x e_{ox} µm³)
Damage mechanisms observation

Éléments : 2436
(Hexaèdre à interpolation quadratique)
4 éléments dans l'épaisseur de la couche

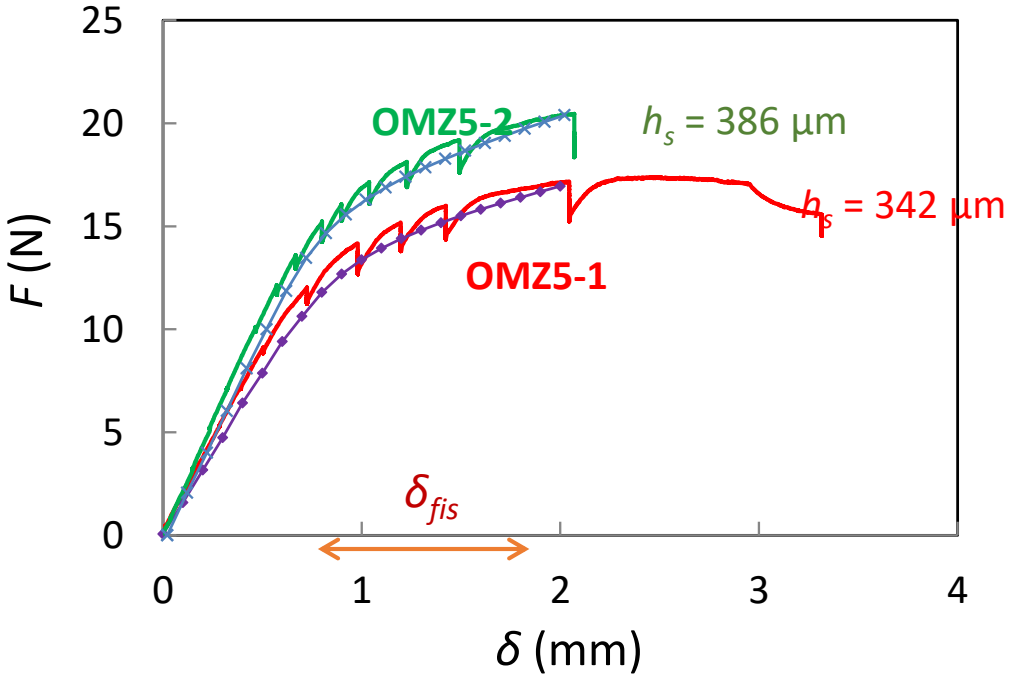
Substrat (Zy4) : - élasticité linéaire isotrope
- critère de von Mises avec écrouissage isotrope

$$R_z(p) = 350 + 205\left(1 - \exp\left(-26p\right)\right) \text{ en MPa}$$

Couches (ZrO_2m et ZrO_2q) : élastique linéaire isotrope $\begin{cases} E = 225 \text{ GPa} \\ \nu = 0{,}275 \end{cases}$

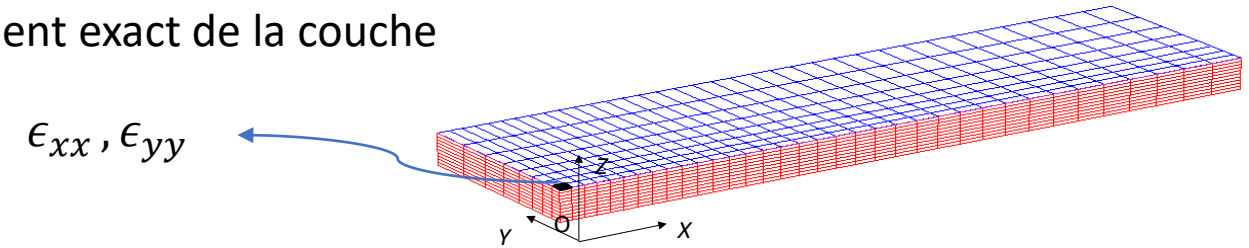
❑ Résultats

❖ Comparaison des courbes globales avec le calcul par EF



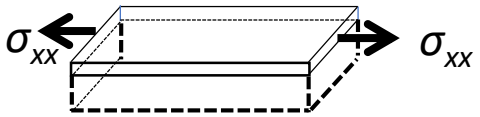
❖ Evaluation des grandeurs locales dans les phases de la couche de ZrO_2

Hypothèse : la cinématique est correctement modélisée quelle que soit le comportement exact de la couche



❖ **Contrainte de rupture des phases de ZrO_2**

Rupture en mode ouverture, contrainte critique σ_{xx}



$$\sigma_{xx} \rightarrow \sigma$$

Contrainte **subie par chaque phase** à l'amorçage de fissures $\boldsymbol{\sigma_R}$

$$\sigma_{R_i} = \sigma_{res_i} + \sigma_{fis_i} \quad i = t,m$$

ZrO_2**t** et ZrO_2**m**

σ_{res_i} : valeur mesurée par DRX dans la phase *i*

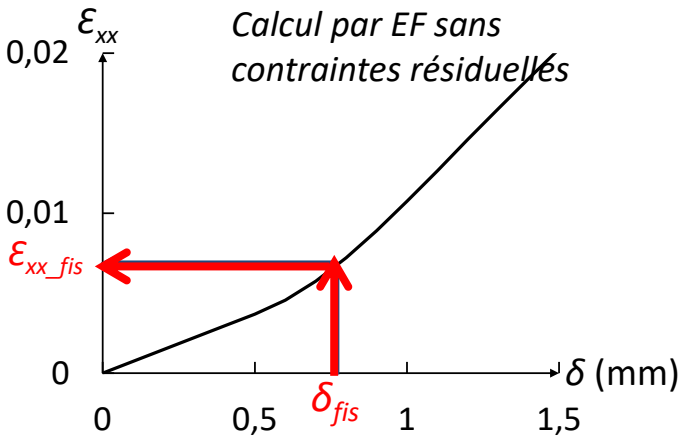
σ_{fis_i} : contrainte **induite** par la déflexion à l'amorçage des fissures

Sollicitation du volume de jauge :

$$\sigma_{fis_i} = \frac{E_i}{1-\nu_i^2}\left(\varepsilon_{xx_fis} + \nu_i \varepsilon_{yy_fis}\right) \quad i= t,m$$

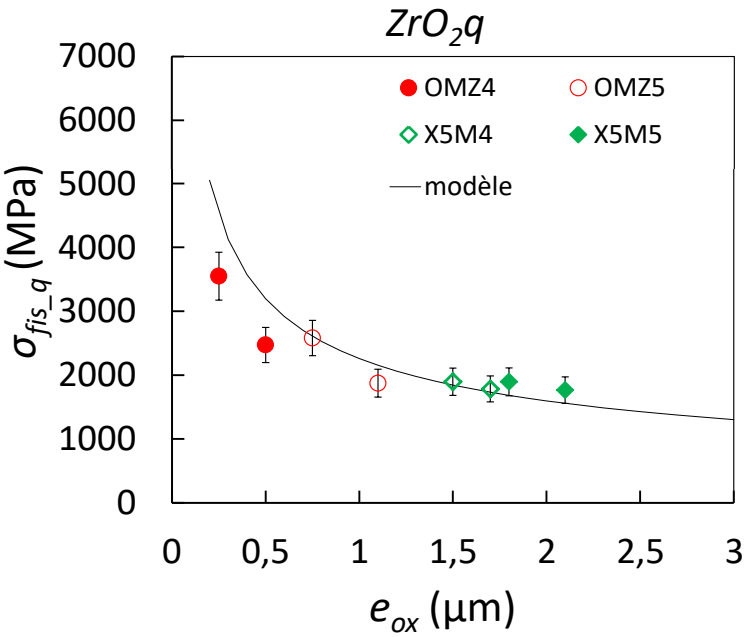
E_i, ν_i : caractéristiques d'élasticité de la phase *i*

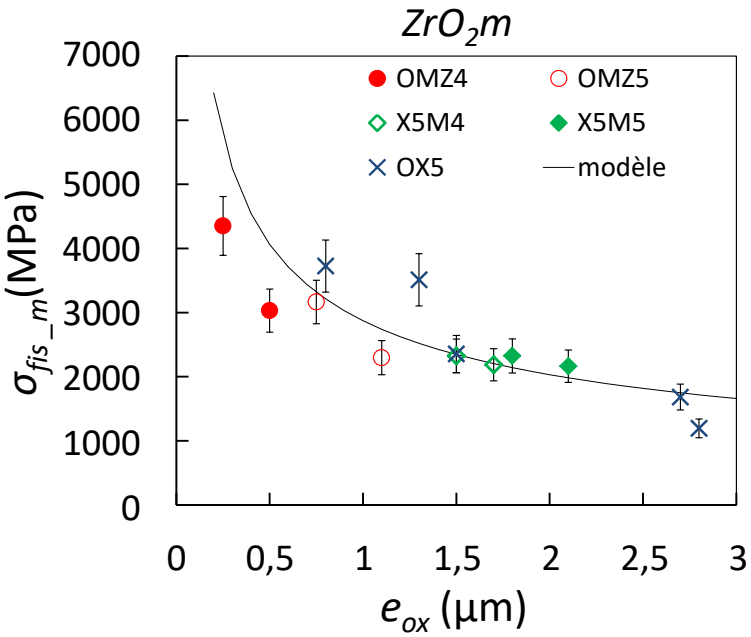
ε_{xx_fis} : ε_{xx} à l'apparition des premières fissures dans le volume de jauge due à la déflexion



Analyse

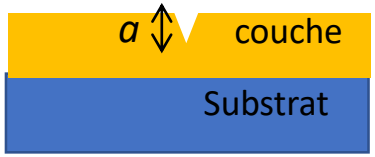
Contrainte induite par la déflexion à l'amorçage de fissures σ_{fis}





$$\sigma_{fis} = \frac{K_{IC}}{Y\sqrt{\pi a}} \qquad a = \alpha e_{ox}$$

[Nagl et al. 1993]



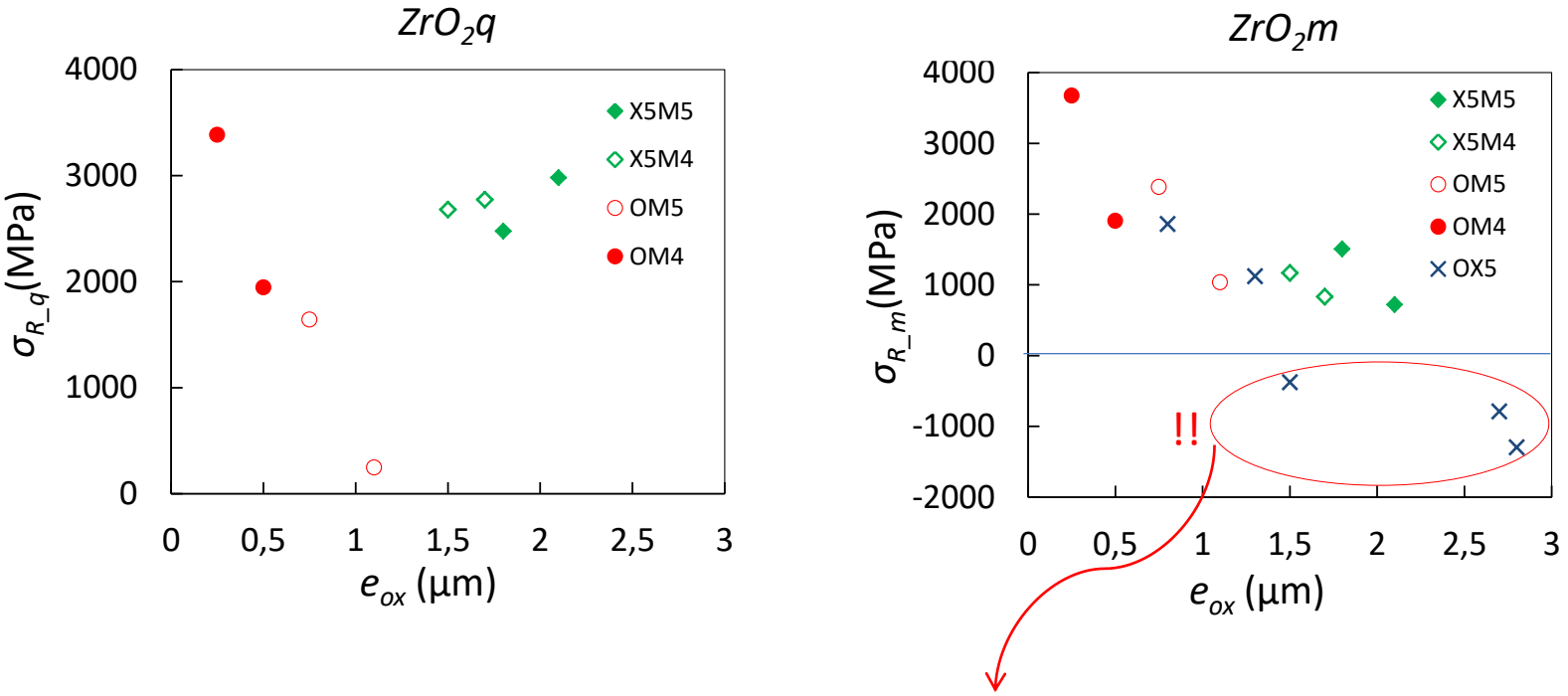
	K_{IC} (MPa.m$^{1/2}$)	Y	α
ZrO_2m	1,2	1,12	0,06
ZrO_2q	1,2	1,12	0,08

➡ Rupture de la couche amorcée par un défaut type fissure, de taille proportionnelle à l'épaisseur de la couche ?

IV . Stress analysis at crack initiation

➢ **Contrainte <u>subie</u> par la couche à l'amorçage de fissures (avec σ_R)**

$\sigma_{R_i} = \sigma_{res_i} + \sigma_{fis_i}$ $i = q,m$ σ_{res_i} : contrainte résiduelle dans la phase *i*



σ_R négative : impossible en mode ouverture de fissure

⟹ Incertitudes sur δ_{fis} ?
Hypothèse de contraintes résiduelles homogènes dans la couche ?

V. Conclusion

- **Using 3 growing layer processes**, different ZrO_2 layers were obtained in the same layer thickness range (0.5 - 3 mm):
  - **Different structural states :** volume fraction of ZrO_2t varying between 10% and 55%
  - **Different mechanical states** with residual stresses depending on layer thickness

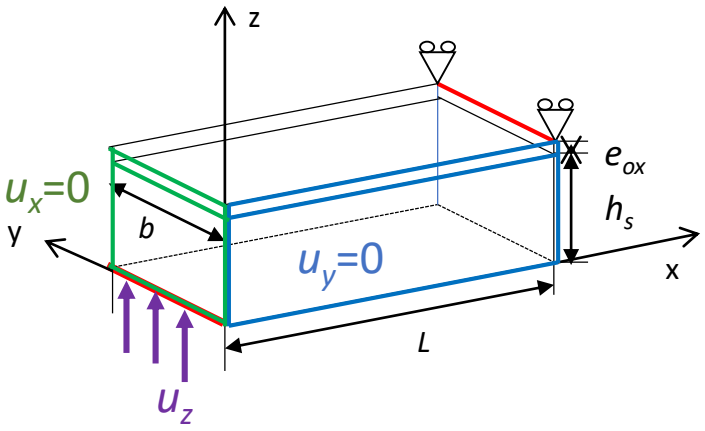
- **Using bending tests in a SEM**, multiple cracking process was observed:
  - **Morphology of the** cracks depends on the thickness layer: more straight and longer for thicker layer
  - **Strength of layer** difficult to obtain from crack initiation information
  - **Crack distance at saturation** independent on the phase composition, and on the residual stresses

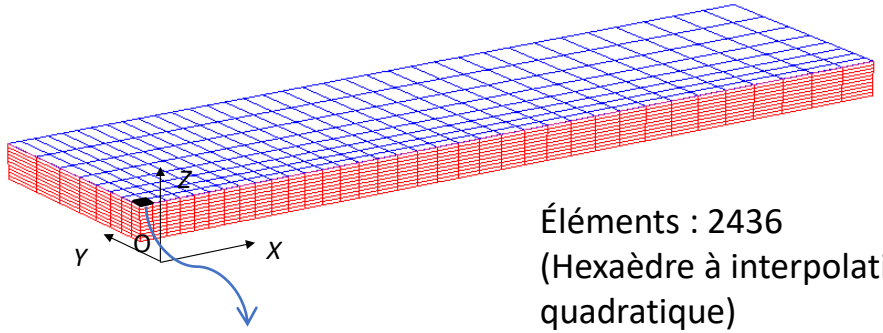
Thank you for your attention

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  ❖ **Numerical model : 3D**

  - Symmetry => ¼ specimen





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(150 x 150 x e_{ox} µm^3)
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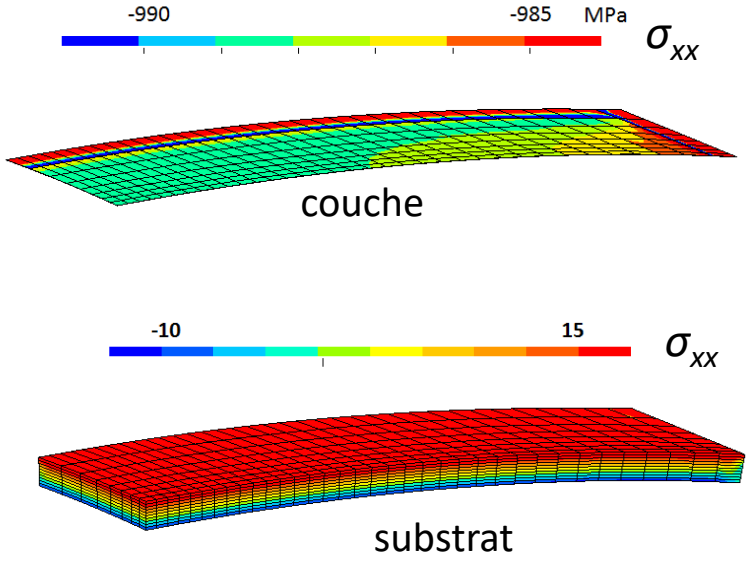
Simulation of residual stress σ_{res}^{ox} :

« thermal loading » in order to achieve the value measured by XRD:

$$\left(\alpha_s - \alpha_{ox}\right)\Delta T = \frac{(1-\nu_{ox})}{E_{ox}}\sigma_{res}^{ox}$$

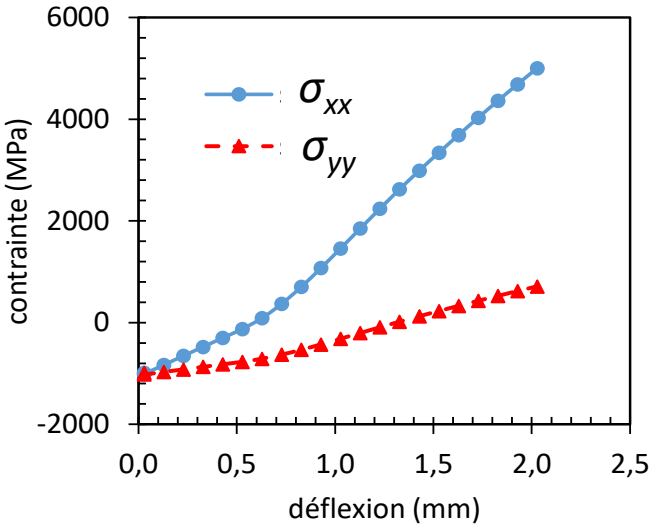
➢ Isovaleurs σ_{xx} et contraintes dans la couche

e_{ox} = 2 µm
h_s = 368 µm



(déformée x 30) σ_{res} = -1 GPa

Contraintes dans la couche (volume de jauge)



→Flexion : sollicitation biaxiale sur le volume de jauge

Courbure → gradient de contrainte dans l'épaisseur :

* 0,4 MPa/µm pour σ_{res} = -988 MPa
* 12 MPa/µm pour δ = 1 mm (σ_{xx} = 1500 MPa)

➡ Contraintes homogènes dans la couche