

Synthèse et résistance mécanique de couches de ZrO_2

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- **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**

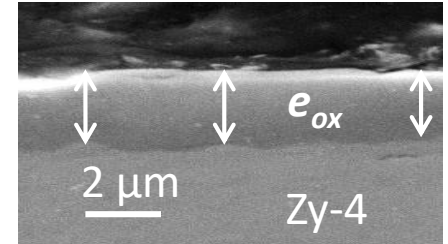
V . **Conclusion**

I. Film synthesis

Processes

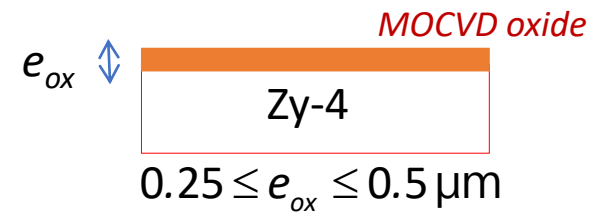
Substrate: plate (thickness 400 μm) recrystallized Zy-4

3 types of process for the zirconia film growth



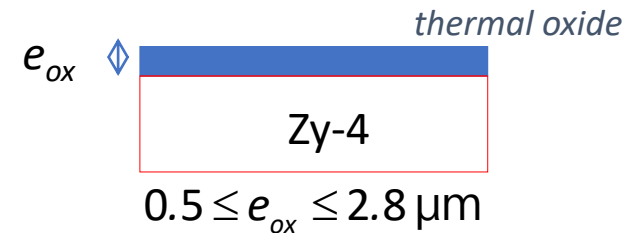
1) MOCVD

OM4: $T_s = 400\text{ }^\circ\text{C}$ **OM5:** $T_s = 500\text{ }^\circ\text{C}$



2) Air oxidation

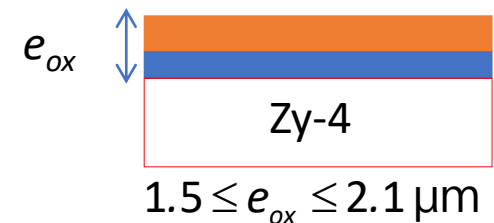
OX5: $T_{ox} = 500\text{ }^\circ\text{C}$



3) Mixed synthesis

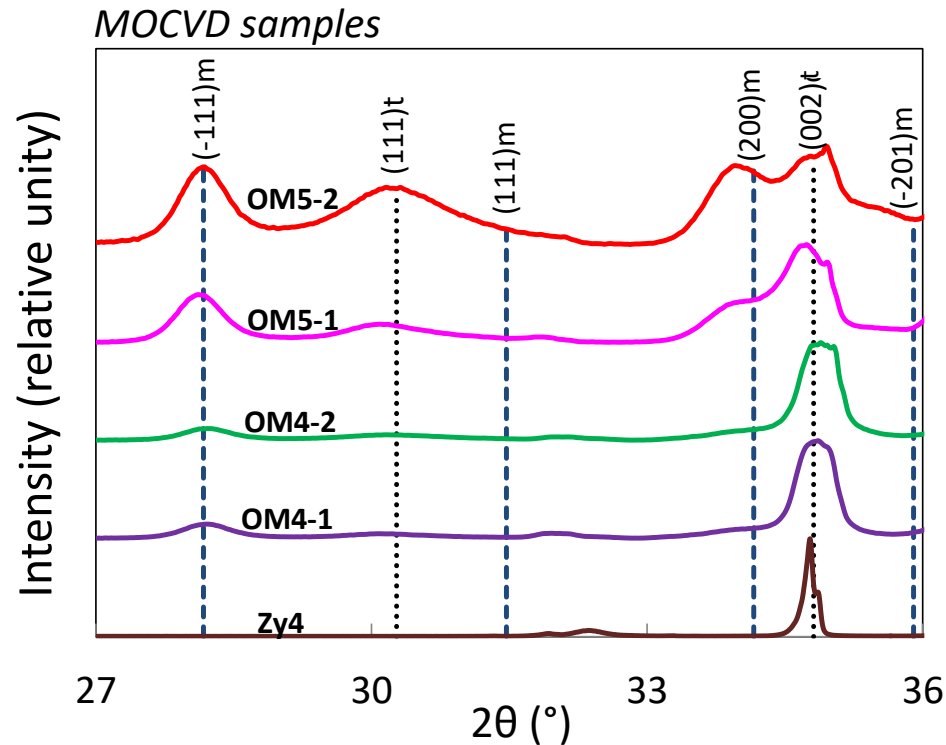
2 steps: **A. Air oxidation** at 500°C 7h

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

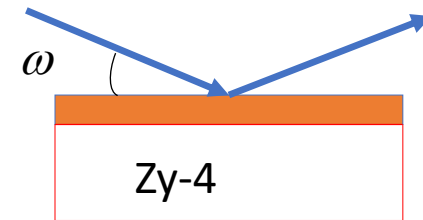
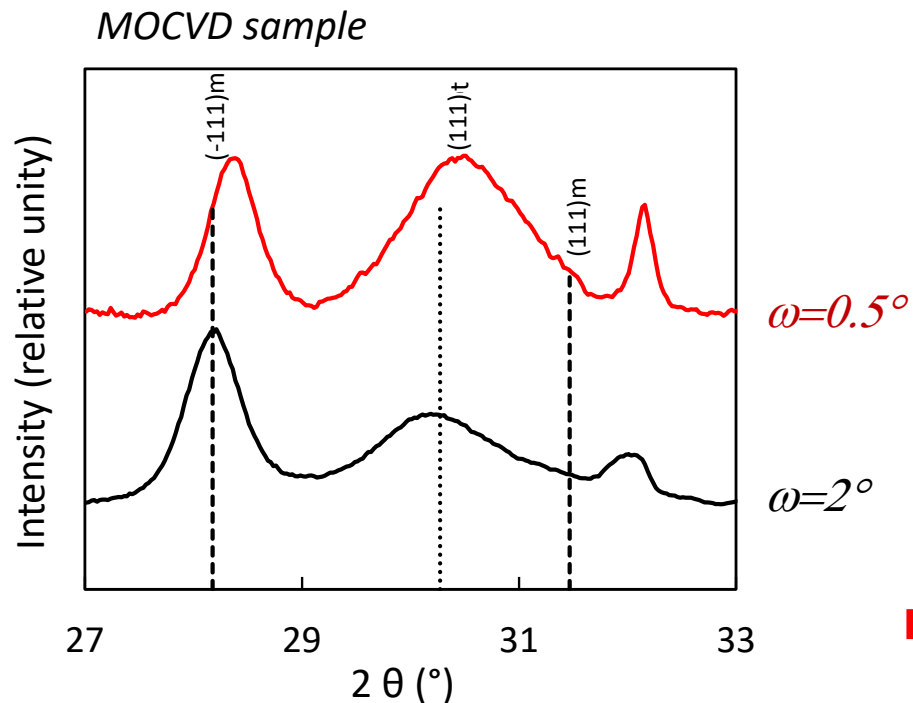
➔ monoclinic phase, ZrO_2m and tetragonal phase, ZrO_2t

❖ Phase localization

In thermal growing ZrO_2 layers on the Zr alloys, there is a gradient of ZrO_2 t with more ZrO_2 t located at the metal-oxide interface

[Godlewski et al. 1994], [Petigny et al. 1998], [Polatidis et al. 2013]

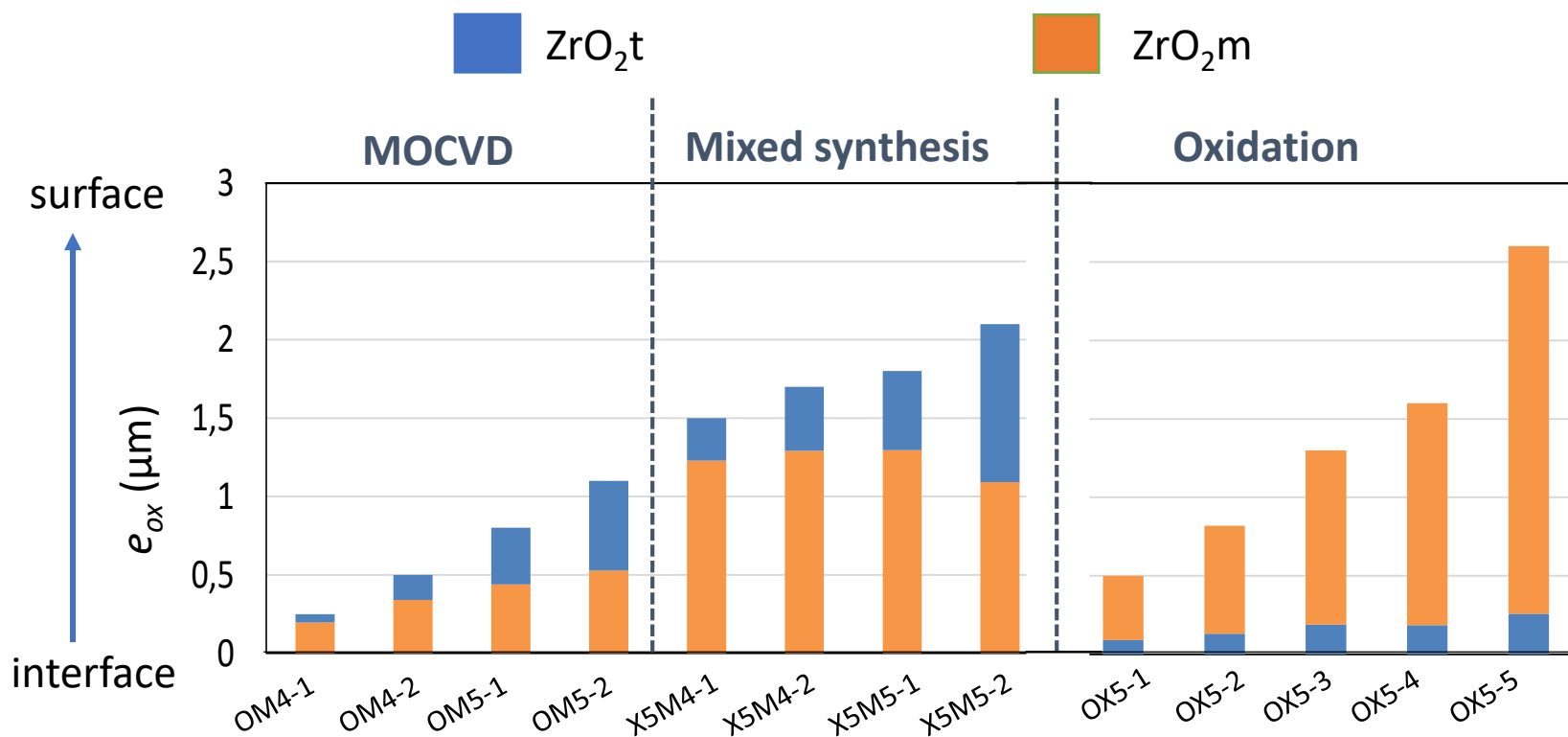
For MOCVD ZrO_2 layers (OM and X5M layers): GI-XRD with different angles ω



ZrO_2 t 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

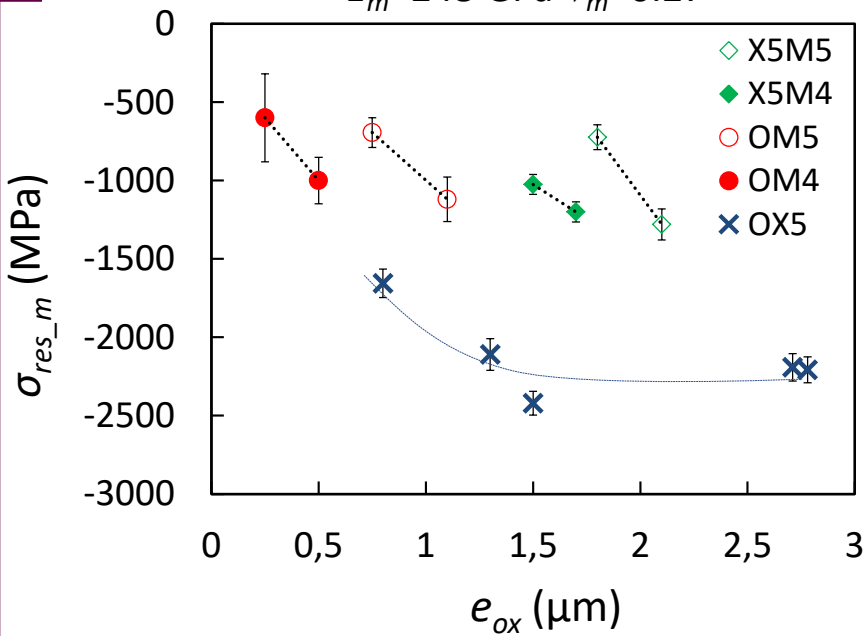
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- Method $\sin^2\psi$ (X'Pert PRO MRD de PANalytical)

Hypothesis: isotropic layer

❖ Residual stress in ZrO_2m

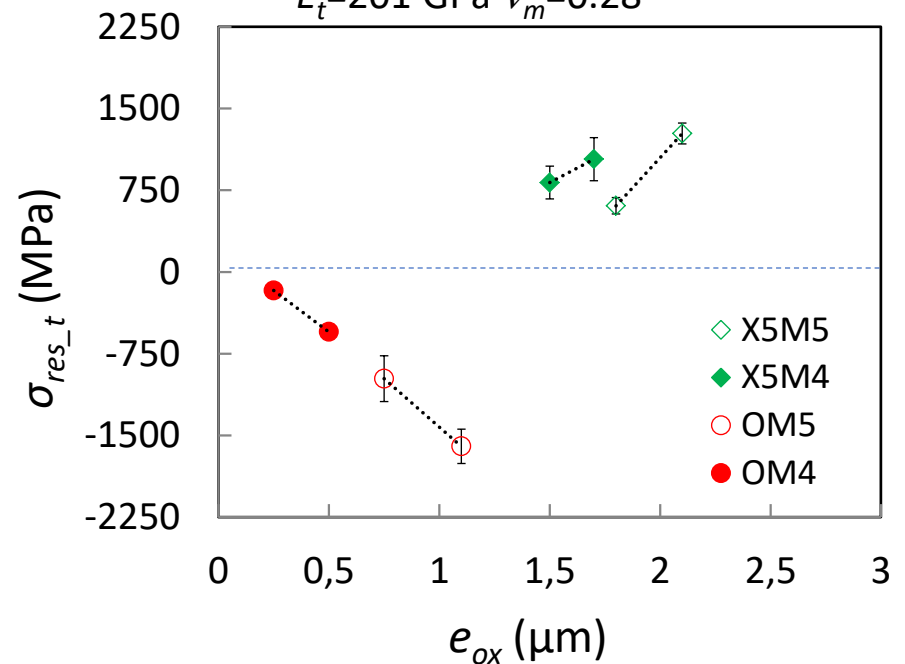
$E_m=248$ GPa $\nu_m=0.27$



Compressive stresses in ZrO_2m

❖ Residual stress in ZrO_2t

$E_t=201$ GPa $\nu_m=0.28$



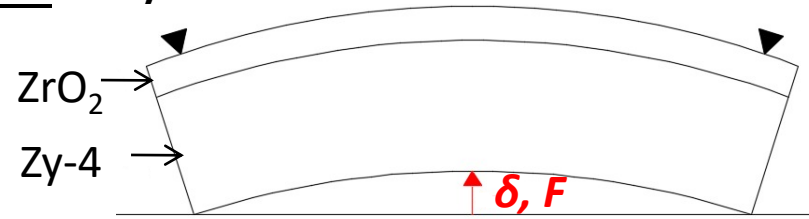
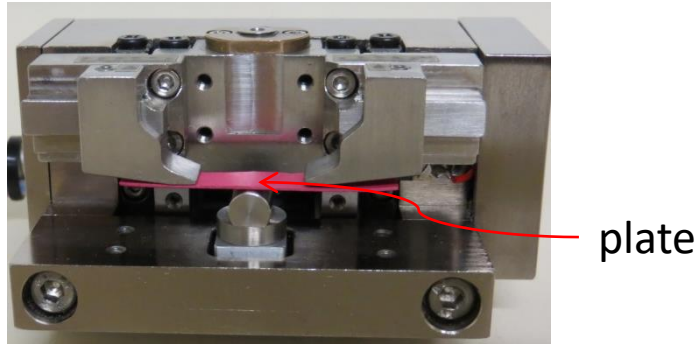
Compressive or tensile stresses in ZrO_2t

Residual stresses varying with the layer thickness

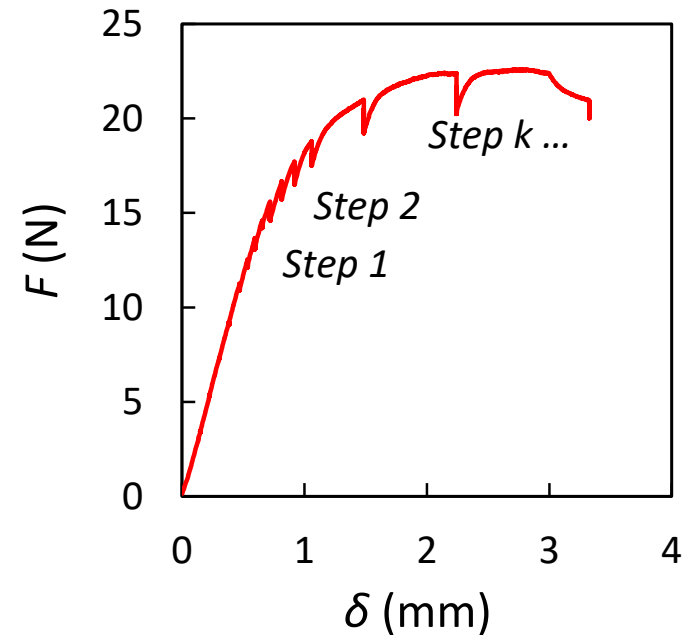
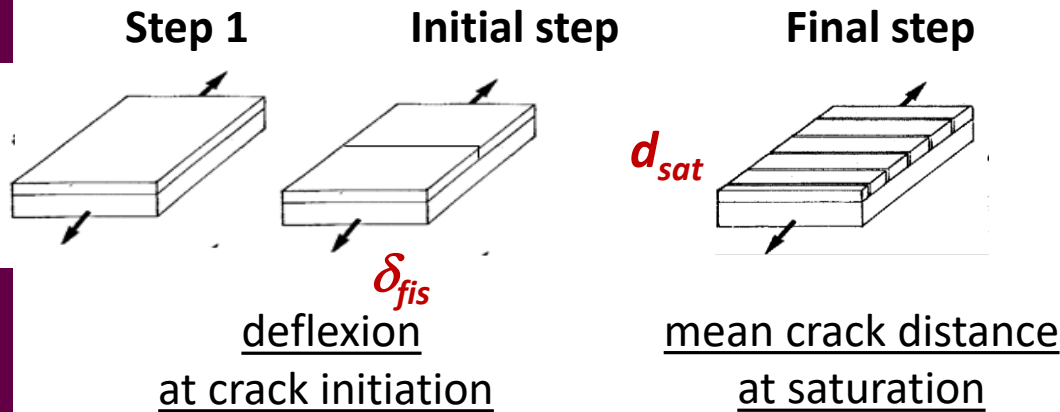
III. Multiple cracking tests

Experimental method

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

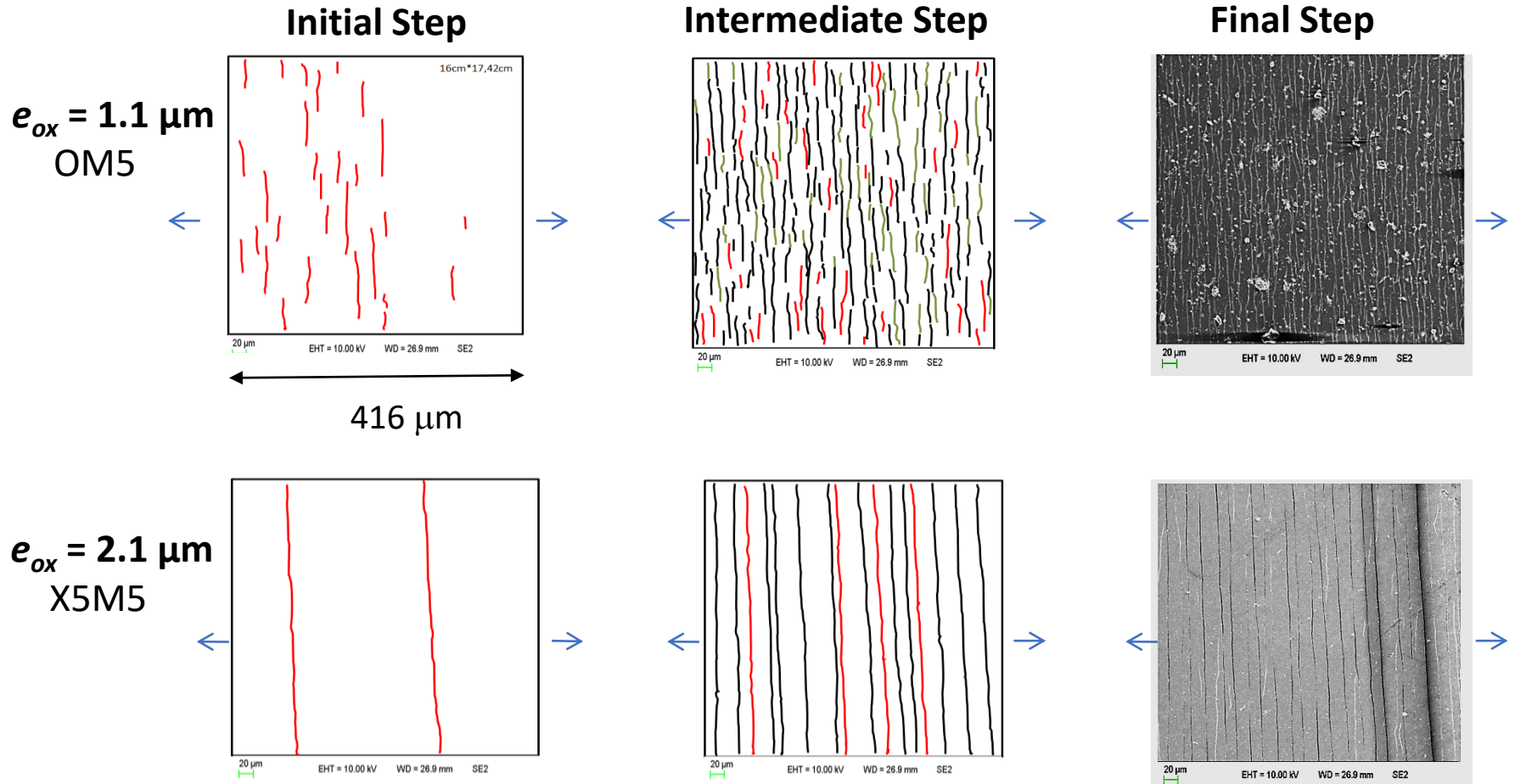


Interrupted test to observe the multiple cracking process of the layer



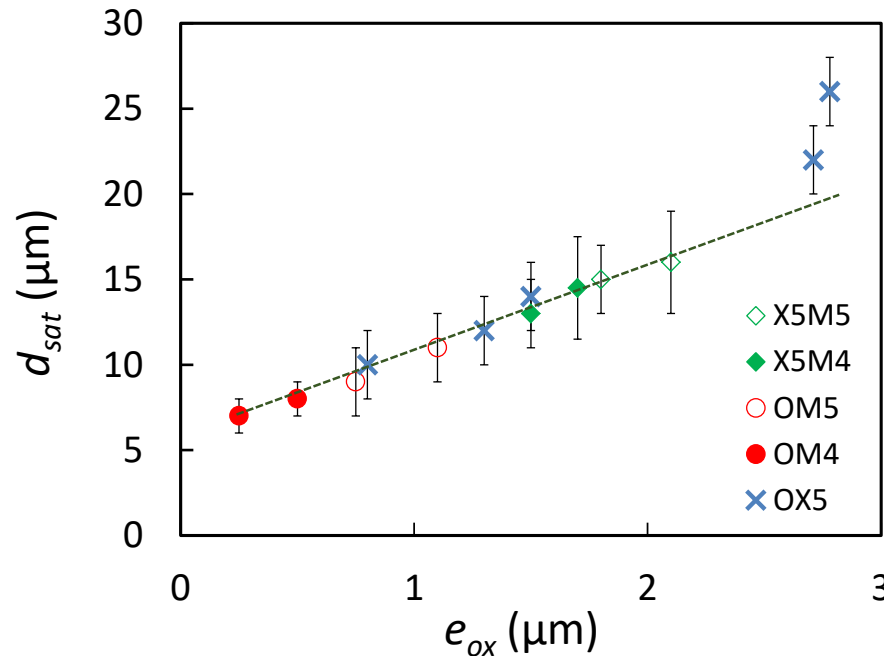
III. Multiple cracking tests

Results



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

❖ Crack distance at saturation d_{sat}



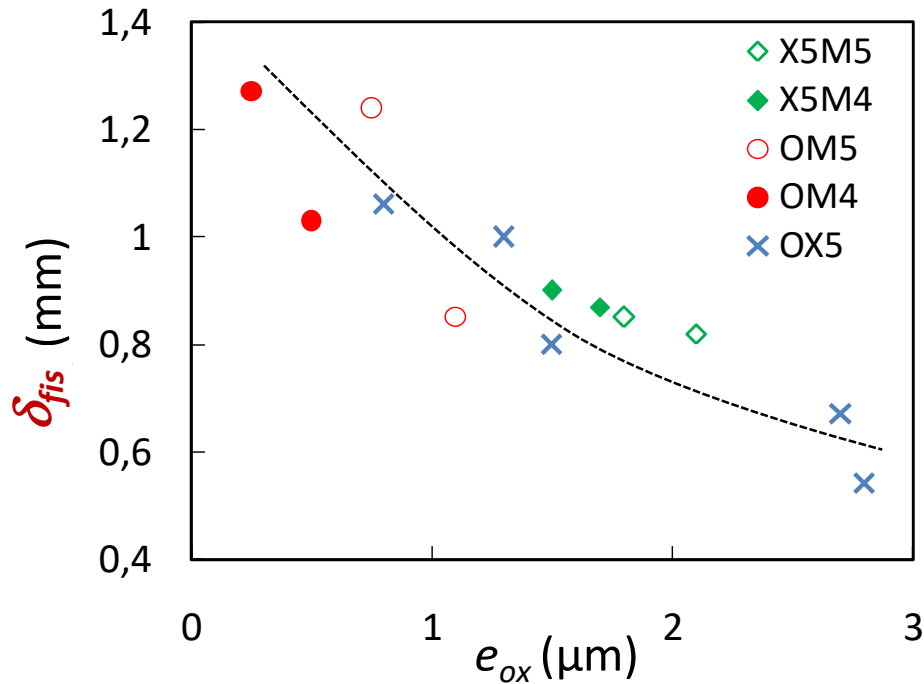
Linear variation of d_{sat} for $0.25 \leq e_{ox} < 2 \mu\text{m}$

[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

❖ 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

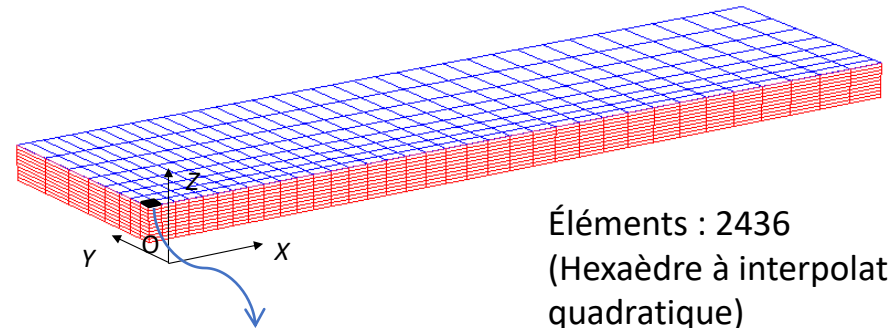
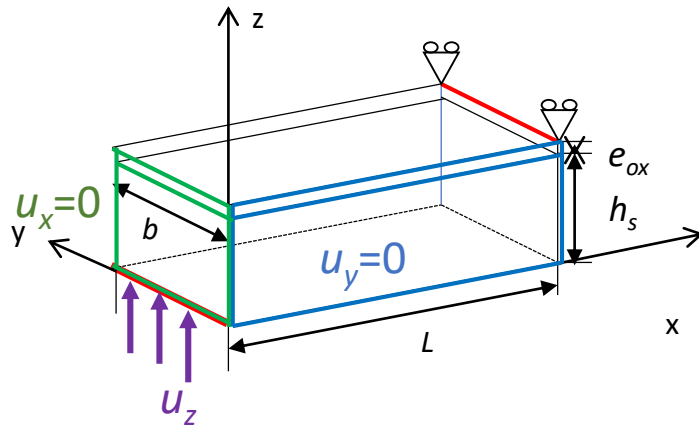
IV . Stress analysis at crack initiation

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■ Modelling of 3 points bending test (cast3M)

❖ Numerical model : 3D

- Symmetry => ¼ specimen



Gage volume
($150 \times 150 \times e_{ox} \mu\text{m}^3$)
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

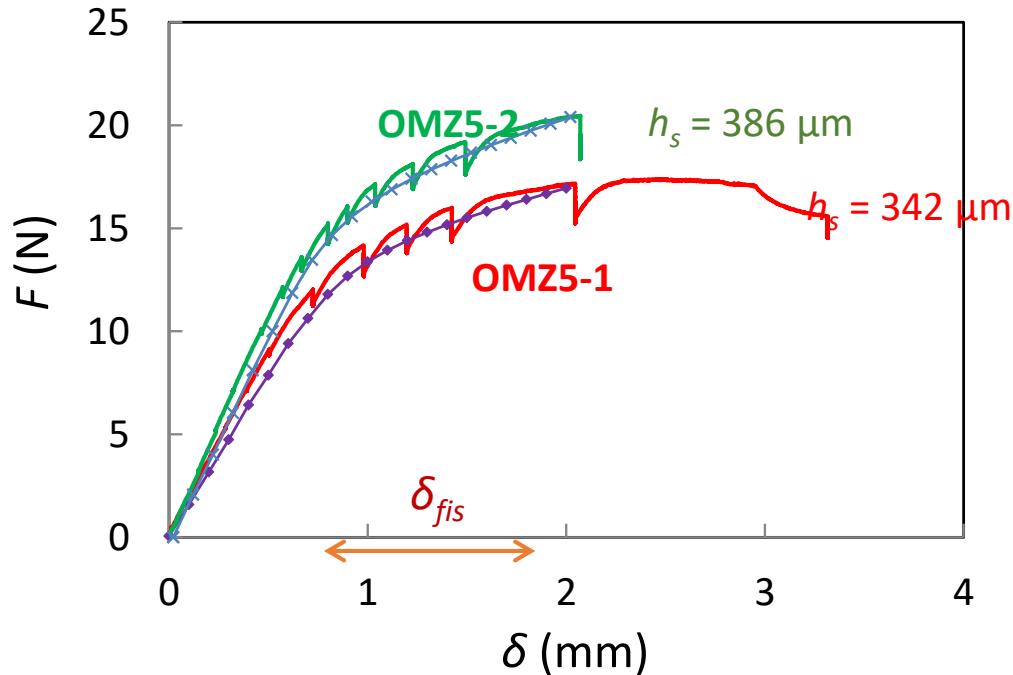
$$R_z(\rho) = 350 + 205(1 - \exp(-26\rho)) \text{ en MPa}$$

Couches (ZrO_2m et ZrO_2q) : élastique linéaire isotrope

$$\left\{ \begin{array}{l} E = 225 \text{ GPa} \\ \nu = 0,275 \end{array} \right.$$

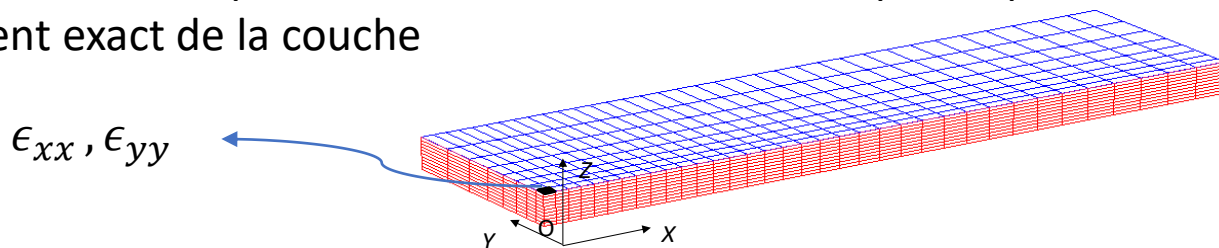
❑ Résultats

❖ 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



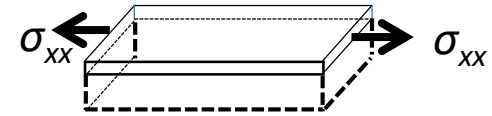
IV . Stress analysis at crack initiation

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❖ 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 σ_R

$$\sigma_{R_i} = \sigma_{res_i} + \sigma_{fis_i} \quad i = t, m \quad ZrO_2t \text{ et } ZrO_2m$$

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

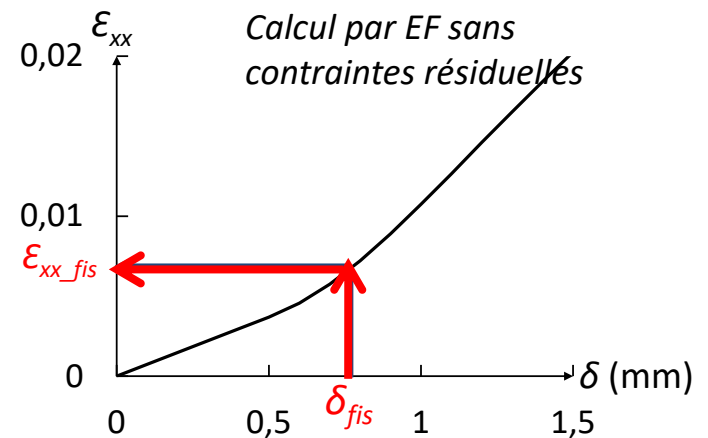
σ_{fis_i} : contrainte **induite** par la déflexion à l'amorçage des fissures

Sollicitation du volume de jauge :

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

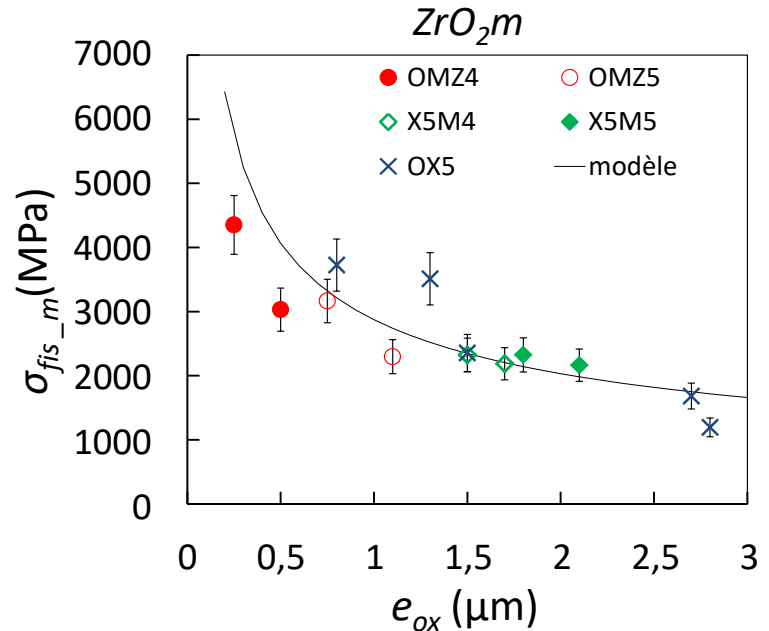
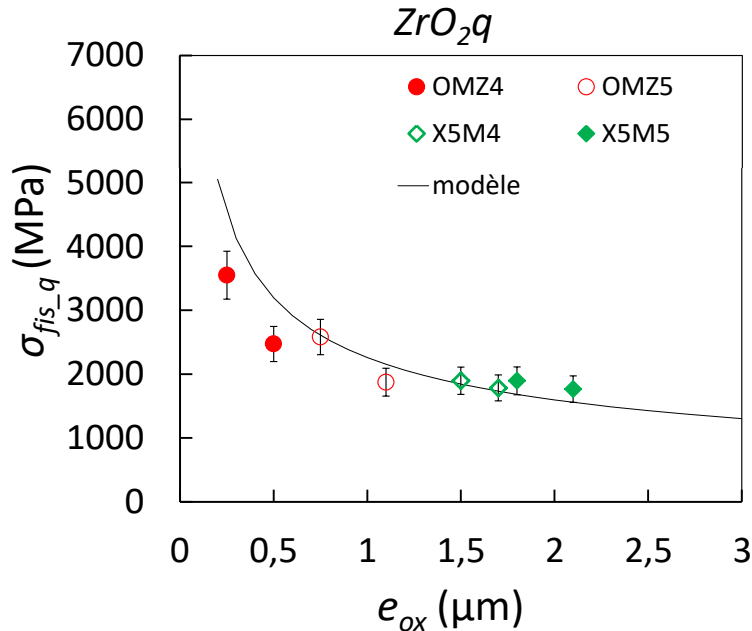
E_i, ν_i : caractéristiques d'élasticité de la phase i

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}



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

[Nagl et al. 1993]

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

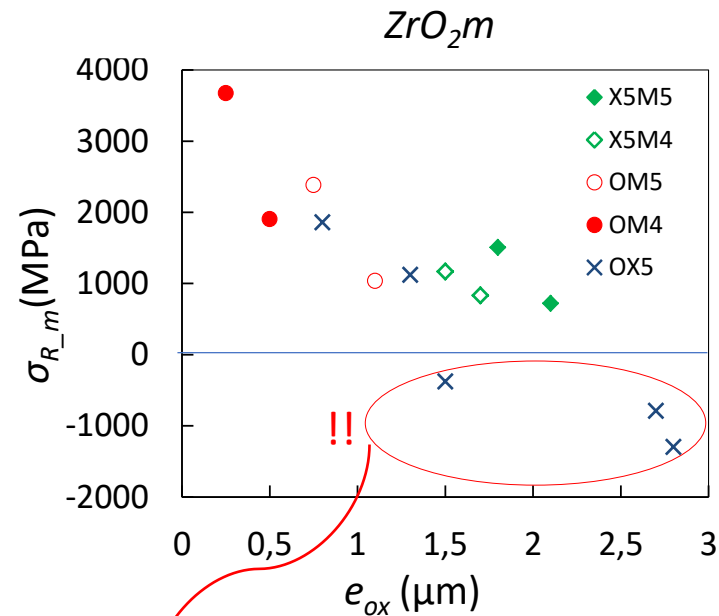
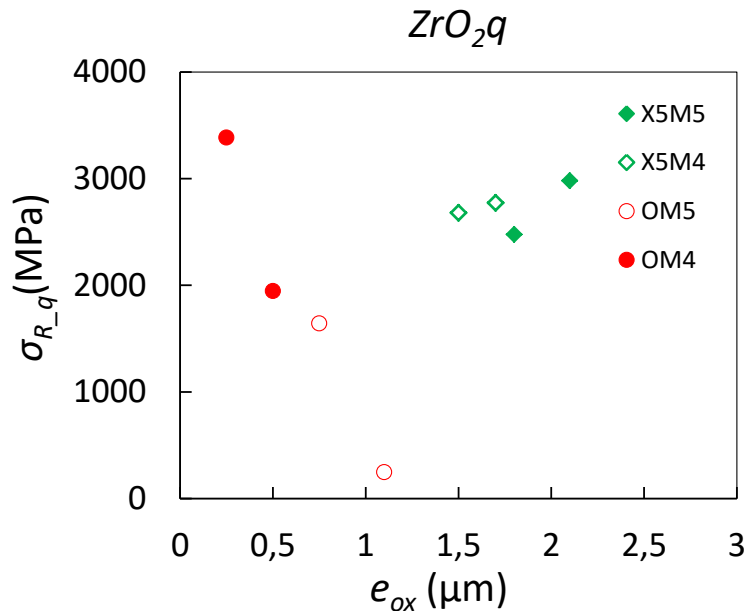
	K_{IC} (MPa.m ^{1/2})	γ	α
ZrO ₂ m	1,2	1,12	0,06
ZrO ₂ q	1,2	1,12	0,08

IV . Stress analysis at crack initiation

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➤ Contrainte subie par la couche à l'amorçage de fissures (avec σ_R)

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



σ_R négative : impossible en mode ouverture de fissure

➡ Incertitudes sur δ_{fis} ?

Hypothèse de contraintes résiduelles homogènes dans la couche ?

- **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_2 varying between 10% and 55%
 - ❖ **Different mechanical states** with residual stresses depending on layer thickness

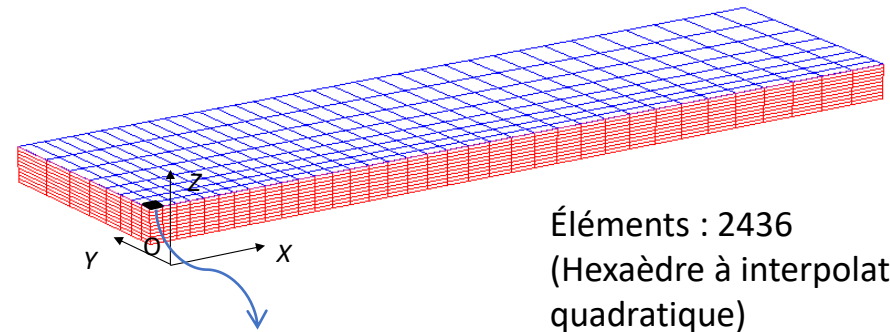
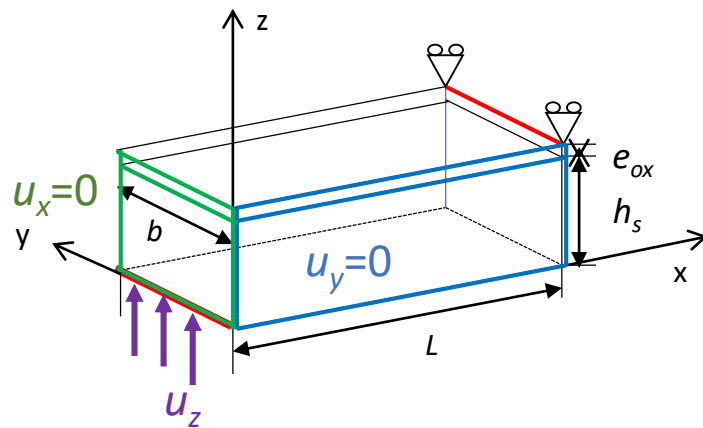
- **Using bending tests in a SEM**, multiple cracking process was observed:
 - ❖ **Morphology of the cracks** depends on the thickness layer: more straight and longer for thicker layer
 - ❖ **Strength of layer** difficult to obtain from crack initiation information
 - ❖ **Crack distance at saturation**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

Thank you for your attention

■ Modelling of 3 points bending test (cast3M)

❖ Numerical model : 3D

- Symmetry => ¼ specimen



Gage volume
($150 \times 150 \times e_{ox} \mu\text{m}^3$)
Damage mechanisms
observation

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

Simulation of residual stress σ_{res}^{ox} :

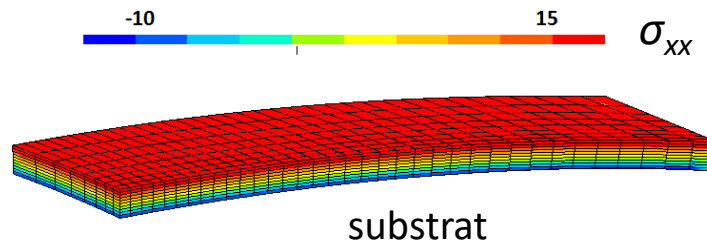
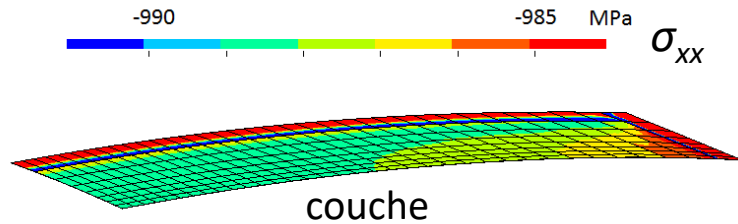
« thermal loading » in order to achieve the value measured by XRD:

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

➤ Isovaleurs σ_{xx} et contraintes dans la couche

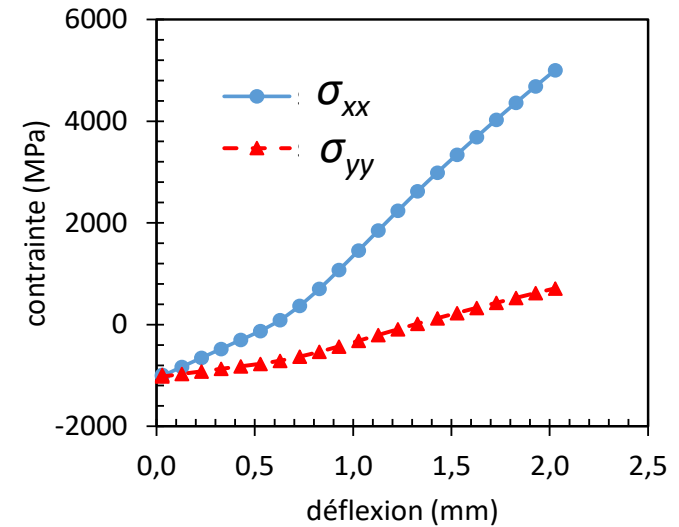
$$e_{ox} = 2 \mu\text{m}$$

$$h_s = 368 \mu\text{m}$$



(déformée x 30) $\sigma_{res} = -1 \text{ GPa}$

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 $\sigma_{res} = -988 \text{ MPa}$
- * 12 MPa/ μm pour $\delta = 1 \text{ mm}$ ($\sigma_{xx} = 1500 \text{ MPa}$)

➔ **Contraintes homogènes dans la couche**