Anisotropic kinetic of the kaolinite to mullite reaction sequence in multilayer ceramics

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Introduction

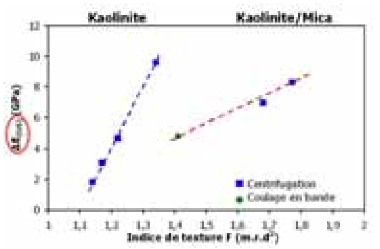
1000-1400°C

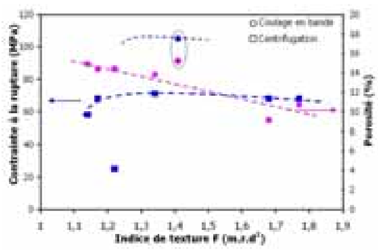
Silicate ceramics → Mullite

Fragile : - strength; - fracture toughness

Silicate ceramics with organized microstructure : Anisotropic growth of mullite

Ex : Kaolin – Mica ceramics

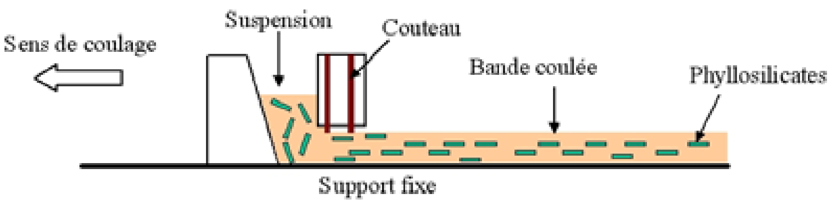




Role of texture index – shaping process – sintering

Powder compact of Kaolin – alumina or mullite fibers → layered material by tape casting

Tape Casting



Tape casting machine

Spreading a suspension containing powders, solvents, dispersants and plasticizers, on a flat surface.

Laminated tapes are organized powder compacts with controlled thickness, density and surface flatness

Thickness of green tapes : 500 µm

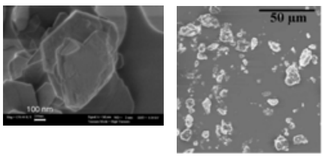
Cylindered samples (ϕ=30mm) : stacked (4-16 individual layers) at controlled temperature and pressure (T=60°C; p=50 bars)

Debinding at 900°C, 0.5°Cmn^{-1} - sintering at 1400°C during 2 hours.

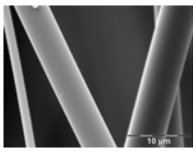
Experimental

Components

Kaolinite



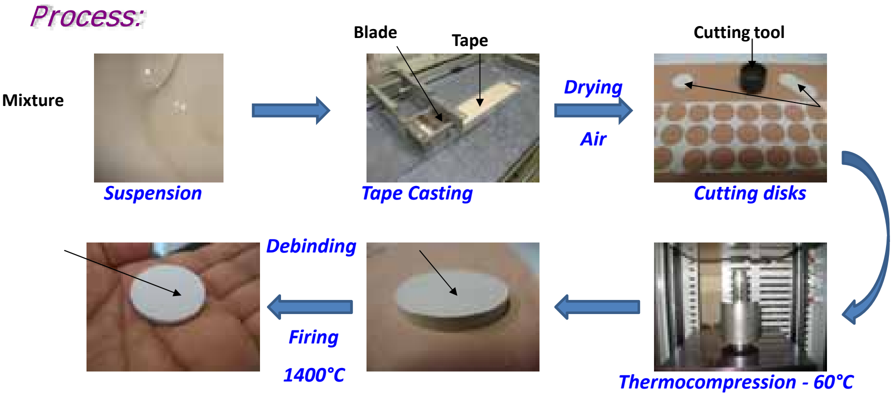
Alumina and mullite fibers



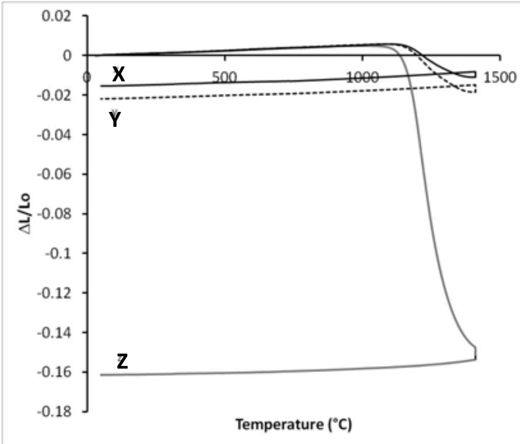
Diameter: 3-5 µm

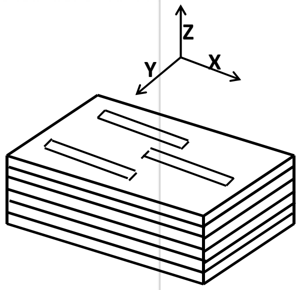
Length : 100-150 µm

Process:

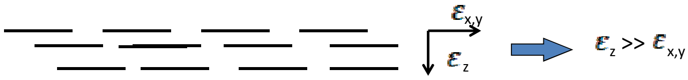


Sintering densification - Dilatometry

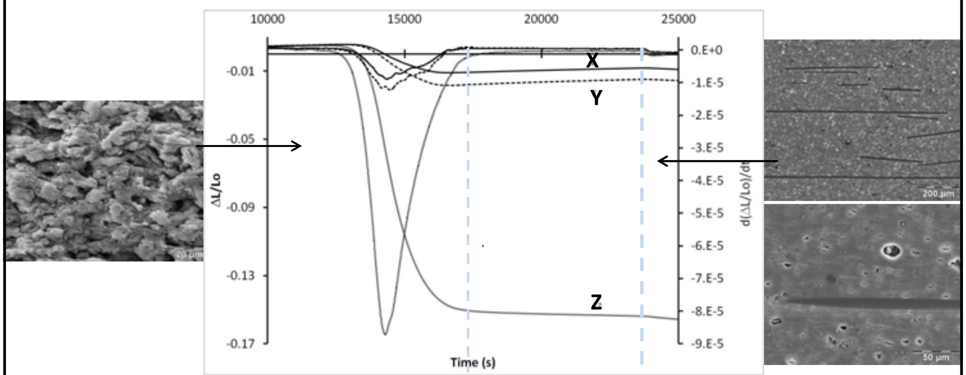




→ Anisotropy of densification (x;y)/z
→ (x;y) = kaolinite layers



Sintering densification - Dilatometry



3 main stages :

- 1080-1200°C → $\dot{\varepsilon}$ increases and $\dot{\varepsilon}_z >> \dot{\varepsilon}_{x,y}$

- 1200-1400°C → $\dot{\varepsilon}$ decreases : densification/mullite growth

-1400°C-0 à 2H → $\dot{\varepsilon}_{x,y}$ >0
$\dot{\varepsilon}_z$ <0 Mullite growth in a viscoplastic material

Activation Energy of Mullite Formation

Isotherm – rapid phenomenon in a very small temperature range

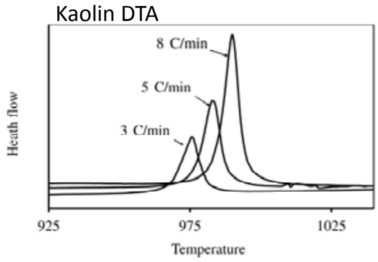
Kinetic theory: Jonhson-Mehl-Avrami

$Kt^n = -ln(1-x)$

with $K = k_o E^{(En/RT)}$

Ex. Kissinger : $\frac{d\ln(\beta/T_p^2)}{d(1/T_p)} = -\frac{E_n}{R}$

Kaolin DTA



At least 3 heating rates ≠ heating rates used for the material processing

Caracterization of : onset of recrystallization – small quantity of nano-mullite

3D information ≠ oriented microstructure

Activation Energy of Sintering

Isotherm thermal process ≠ cycle of sintering

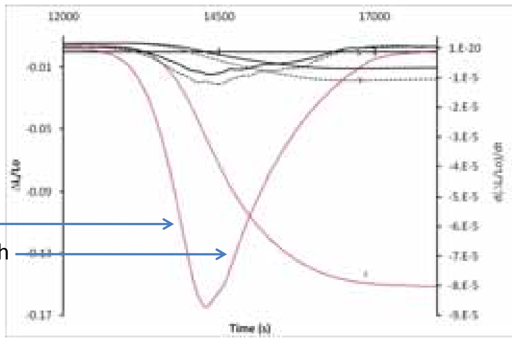
Usual description cannot be used

Perez-Maqueda :
Shrinkage rate - transport mechanisms

$$\frac{d(\Delta L/L_o)}{dt} = A_0 T^{-n} e^{-E_d/RT} \left(\frac{\Delta L}{L_o}\right)^{1-m/2}$$

≈ 1000-1200°C : Densification

≈ 1200°C : Densification + Mullite growth

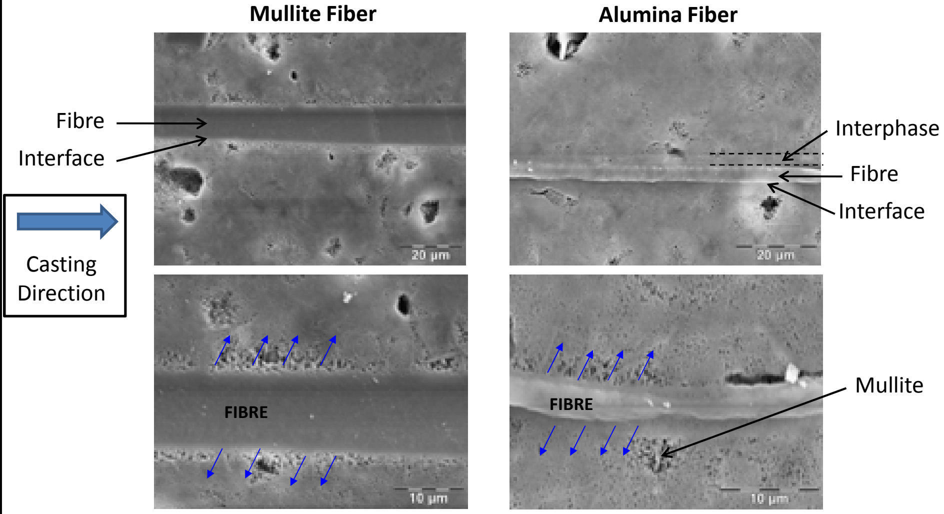


⇒Information in the early sintering

⇒ Unidirectional information

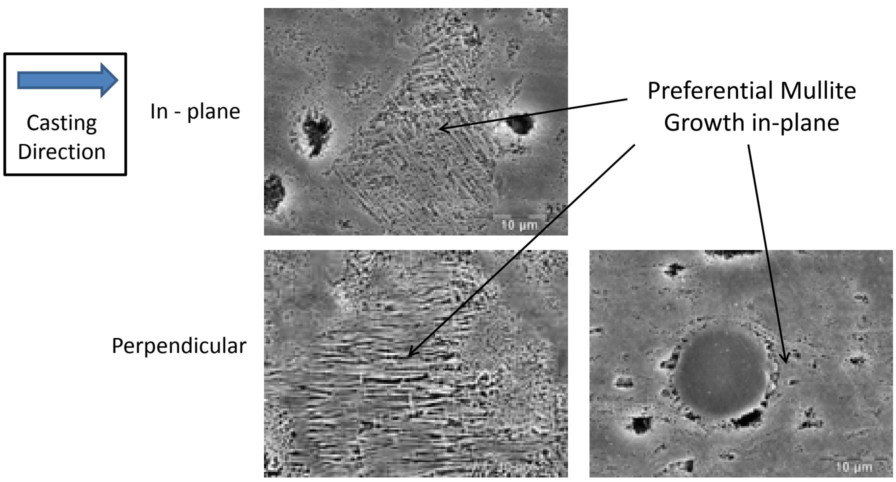
⇒ E_d of sintering ↑ when densification rate ↑

Fiber Role



→ **Strong interface-interphase Matrix-Fibers**
→ **Fibers : Template**

Layer Role



Anisotropic Mullite Growth

Mullite quantity at 1400°C

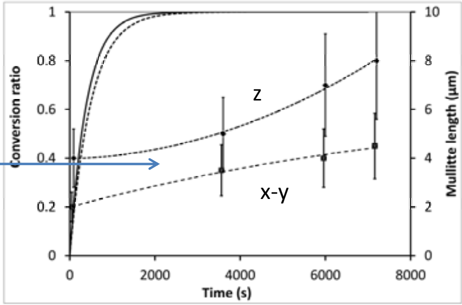
Reference kaolin KGa-1
high cristallinity $kt = 0.75[-\ln(1-x)^{1.33}]$

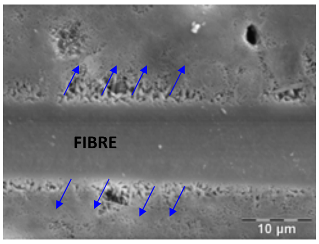
Reference kaolin KGa-2
Low cristallinity $kt = -\ln(1-x)$

⇒Delayed mullite growth (> 890°C)

⇒ Continuous anisotropic mullite growth

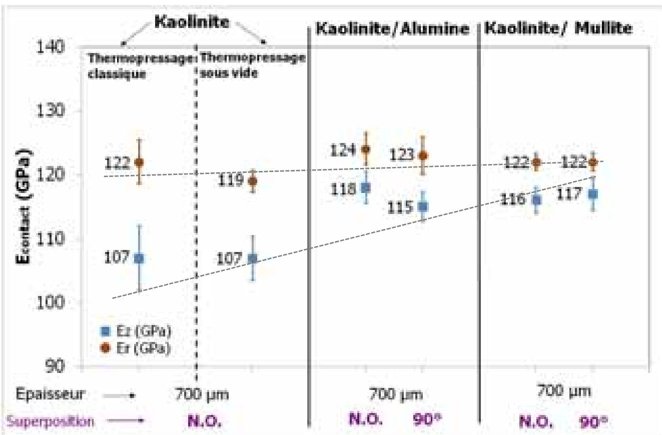
⇒ Swelling along x-y at 1400C

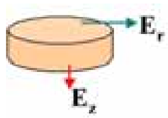


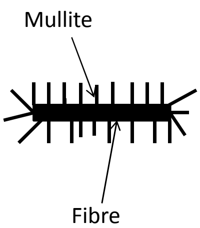


Layered material – kaolinite relicts
Fibers composition

Young Modulus by U.S. Echography – Process Parameters



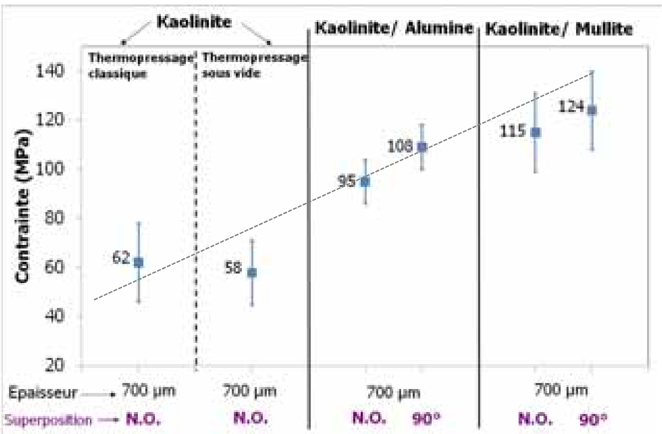


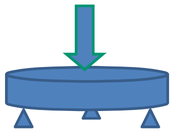


→ $E_r > E_z$: *c* axe of mullite (Intrinsic $E_c \approx 282$ Gpa)
→ 3-5 Vol % of fibers : ↑≈ 20% E_r and ~ E_z

→~ Vacum Thermocompression – Interlayer porosity
→~ Layers Mutual Orientation

Strength – Process Parameters





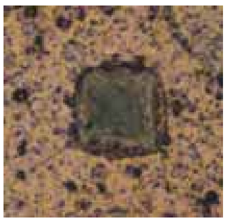
→ 3 Vol % of fibers : ↑ ≈ 50% of σ_r
→ Mullite fibers / Alumina fibers

→~ Layers Mutual Orientation ↑ ≈ 10% of σ_r
→~ Vacum Thermocompression – Interlayer porosity

Thoughness by Vickers Indentation – Process Parameters

Crack size vs Load on layer surface

$$K_{ICP} = 0.0319 \frac{P}{al^{1/2}}$$



Results

	Common Porcelain	Dense Alumina	Multilayer Kaolin
Toughness	0,8 ± 0,05	4,2 ± 0,2	2,5 ± 0,3

≈ ×3

	Kaolin+Alumina N.O. Multilayers	Kaolin+Alumina O. Multilayers	Kaolin+Mullite O. Multilayers	Kaolin+Mullite O. Multilayers
Toughness	5,8 ± 0,3	6,4 ± 0,1	6,1 ± 0,2	6,5 ± 0,2

Conclusion

Organized Microstructure → *Mechanical properties*

-Powder compact – process

-Oriented layers of phyllosilicates

-Fibers in-plane

-Fibers –Matrix interface - interphase

-Mullite Nucleation in-plane

-Mullite Growth – Oriented layers and fiber role

+ 20% of Young Modulus with + 3Vol% fibers

+50% Flexural strength

- x3 Toughness