Oxide/Oxide Re-Crystallized Fiber Composites
For Use at ≥ 1400 °C

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O b j e c t i v e :

Materials for use in gas turbines at ≥ 1400 °C / ≥ 10,000 h

⇒ **(i)** ***FIBER* composites** (enabling damage tolerance → thermal shock stability)

(ii) ***OXIDES*** (because of limited thermodynamic stability of non-oxides > 1400 °C)

→ ***higher creep rates*** of polycrystals compared with optimized non-oxides

⇒ ***SINGLE crystalline* fibers.**

⇓

T e c h n o l o g i c a l Objectives for Processing:

(i) ***E N D L E S S* fibers** (for flexible, different processing approaches)

(ii) ***T H I N* fibers** (easily deformable, e.g. for winding)

(iii) available as *B U N D L E S* (~ 400 fibers/bundle → giving sufficient *volume*)

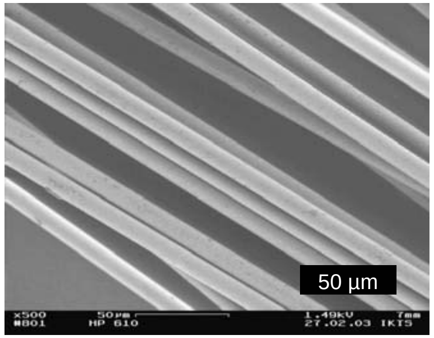
not available

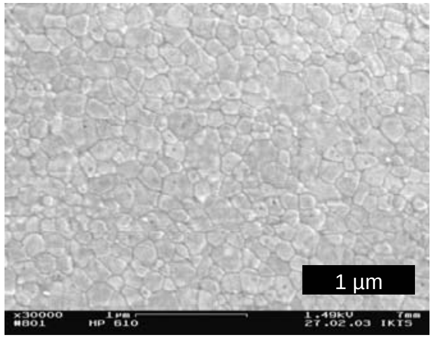
New Approach

New Approach

Use of commercial (= available, affordable !) polycrystalline oxide fibers

(example: Nextel 610 Al_2O_3)





→ **Processing**
(coating, shaping e.g. by winding**)**

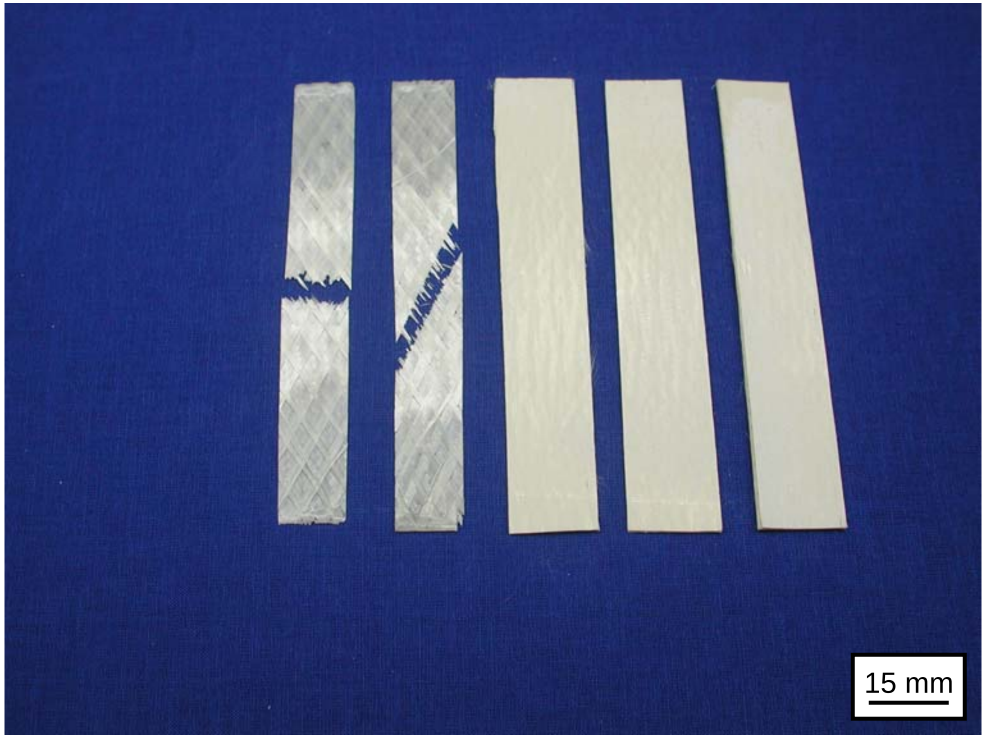
→ **Fiber – Re-Crystallization**
(annealing, e.g. 1750 °C / 1 h / Ar)

↓

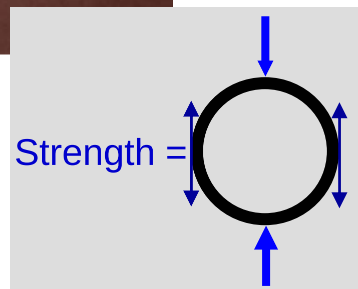
(optional: post – infiltration)

Strength & Damage tolerance at room temperature**:**

First tests of plane samples in tension



Tests of tubes (rings) in diametral compression:



Challenges:

(1) *Degree* of re-crystallization

- ❑ ***Requested** length* **of single-crystalline fiber-segments** ***for minimum creep*** **?**
- ❑ ***Possible** degree* **of re-crystallization ?**

(2) Re-crystallization with *minimum sinter-bridging*

(→ damage tolerance !)

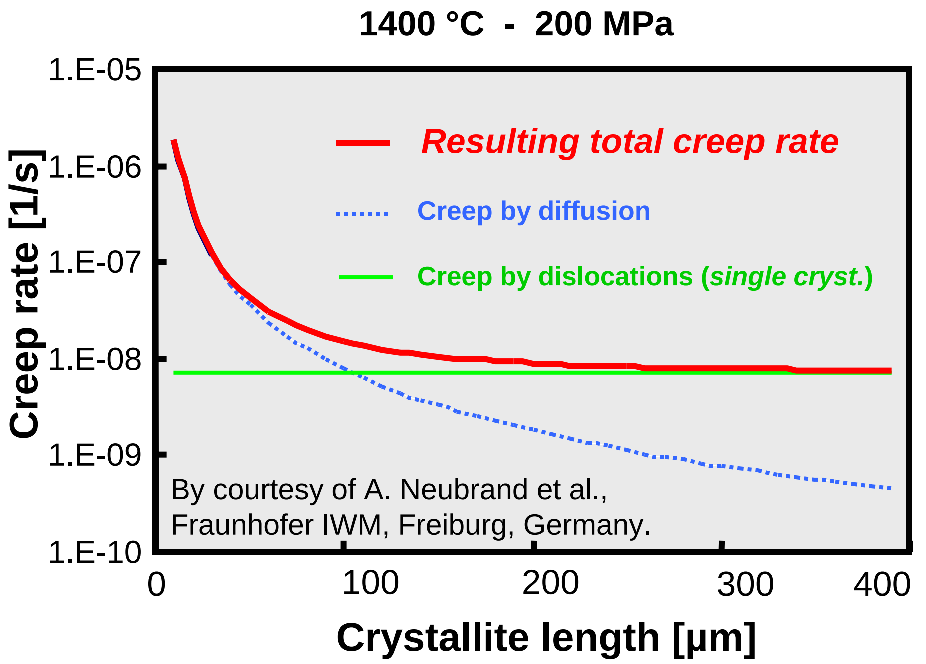
(3) Re-crystallization with *tailoring fiber/matrix binding*

(→ damage tolerance, total creep)

Challenges:

(1) *Degree* of re-crystallization

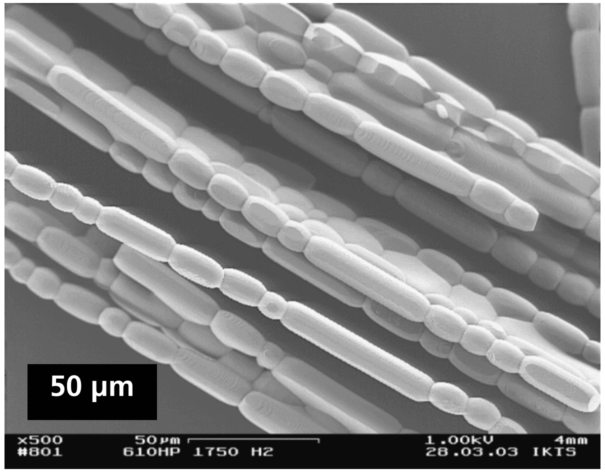
- ***Requested*** ***length*** **of single-crystalline fiber-segments** ***for minimum creep*** **?**



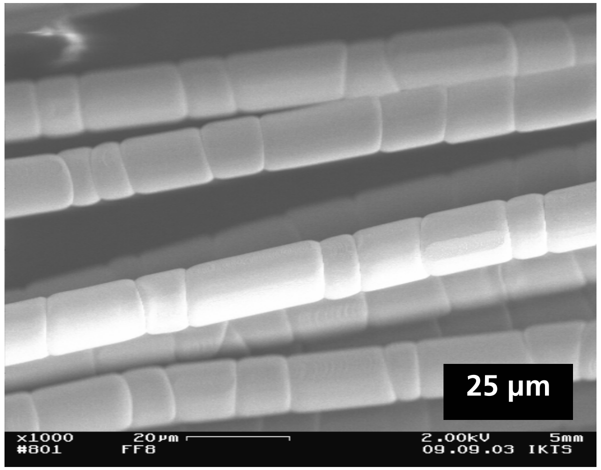
Challenges:

(1) *Degree* of re-crystallization

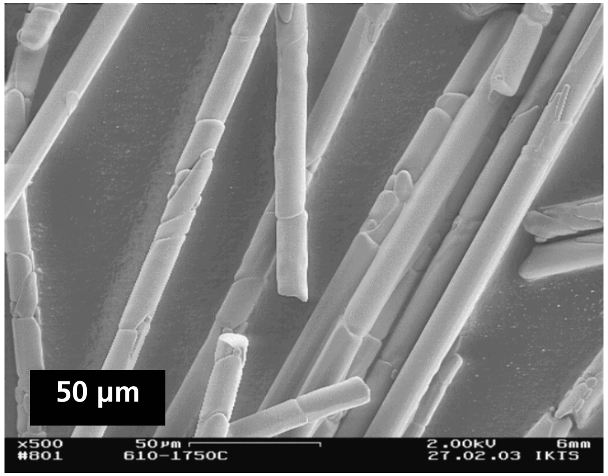
- ***Requested** length* of single-crystalline fiber-segments *for minimum creep* ?
- ***Possible** degree* of re-crystallization ?



dry H_2 / 1750 °C / 1 h



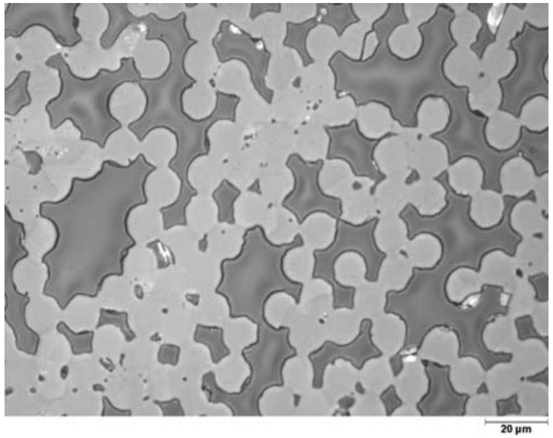
wet H_2 (dew pt 30 °C) / 1800 °C / 1 h



Ar / 1750 °C / 1 h

(2) Re-crystallization with *minimum sinter-bridging*

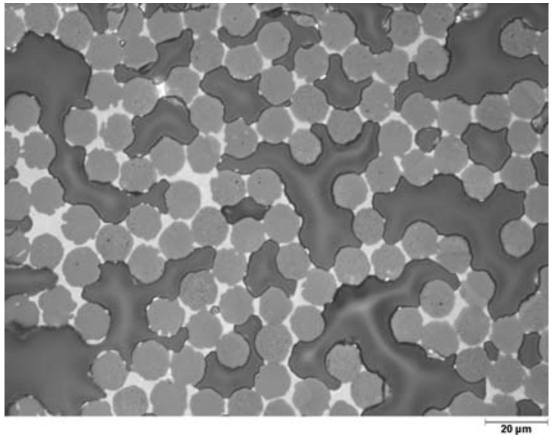
(→ damage tolerance !)



at 1750 °C / 1 h / Ar

⇒ Need of mineral diffusion-blocking coatings

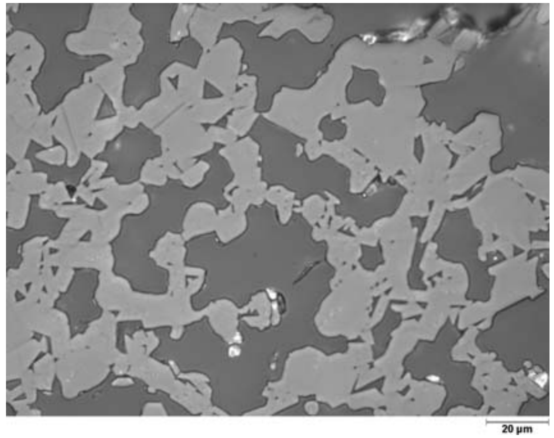
no coating,
carbon coating



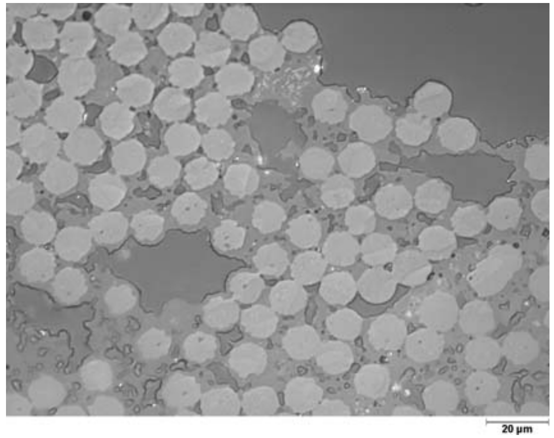
ZrO$_2$ coating

Mullite Coating from

→ *commercial* precursor (Siral, Condea)

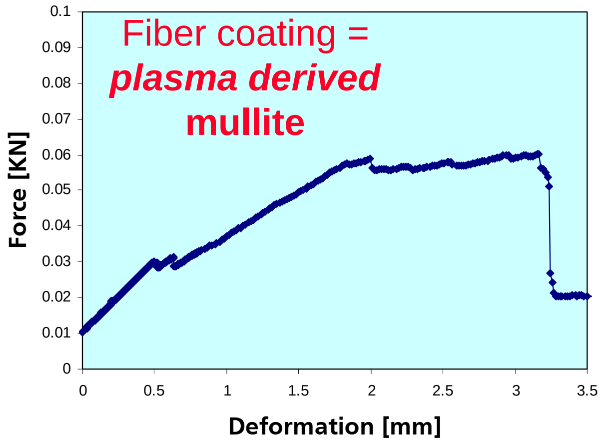


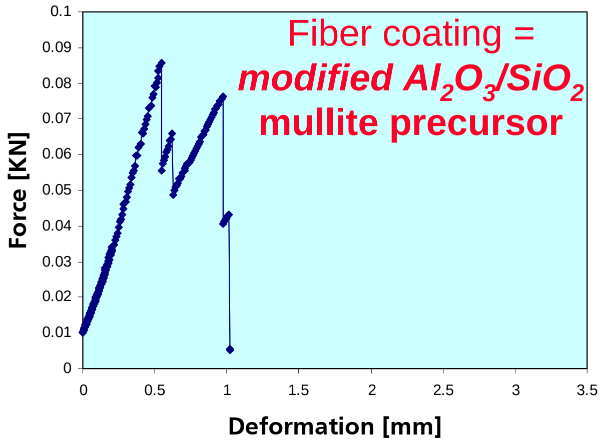
→ *modified Al_2O_3/SiO_2* precursor



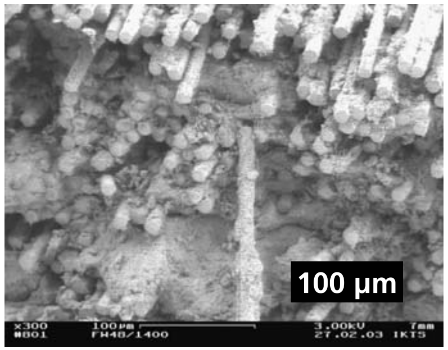
(3) Re-crystallization with *tailoring fiber/matrix binding*

(→ damage tolerance, total creep)

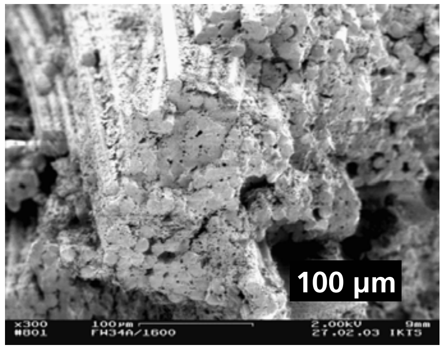




porosity = 35 % ←
E = 35 GPa
Strength = 179 ± 19 MPa



→„weak“ bonds after
sintering 1400…1500 °C / 2 h / air



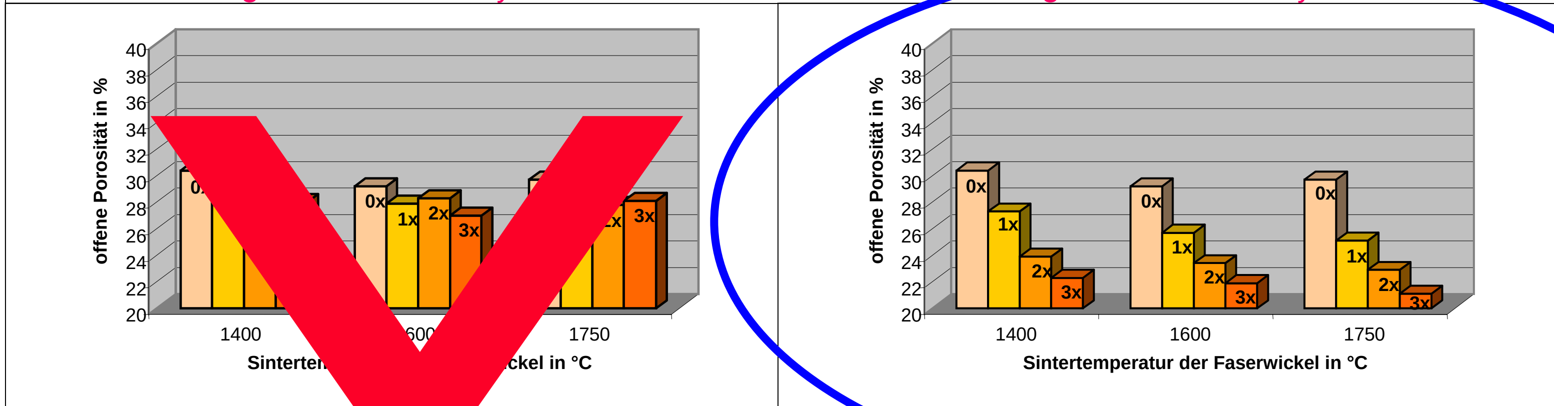
→ porosity = 22 %
E = 110 GPa
Strength = 149 ± 19 MPa

→ „strong“ bonds after
sintering 1600 °C / 2 h / air

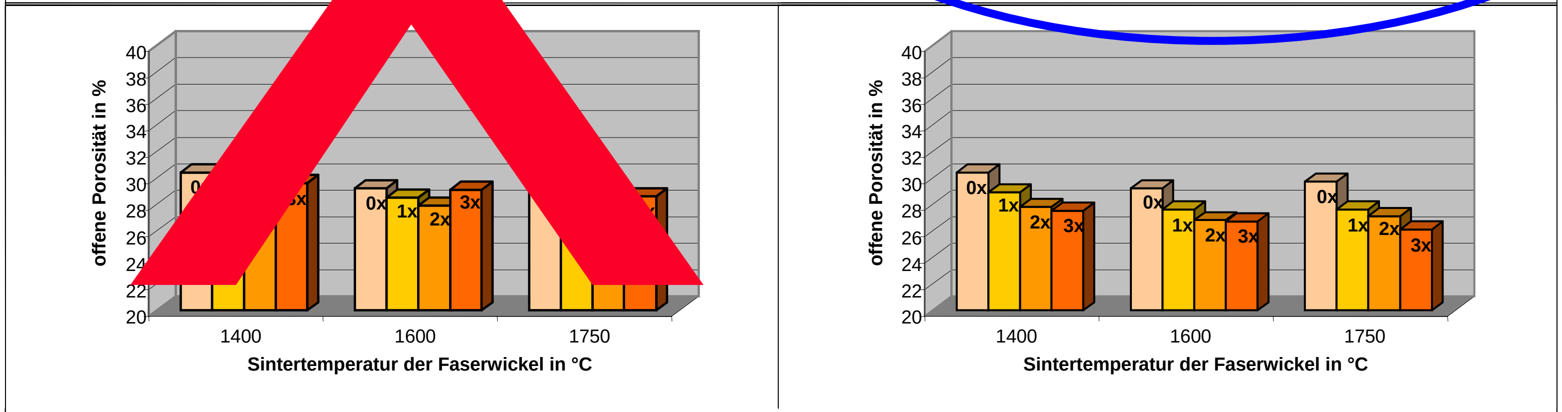
Optional: Post - Infiltration

Open porosity after infiltration + annealing at 1400, 1600 or 1750 °C

Solid loading of infiltration slurry = **10 wt. -%** | **Solid loading** of infiltration slurry = **30 wt. -%**



Infiltration with **0.2 µm Al_2O_3** powder slurry



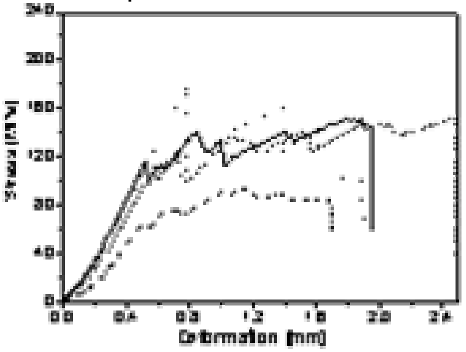
Infiltration with **1 µm Al_2O_3** powder slurry

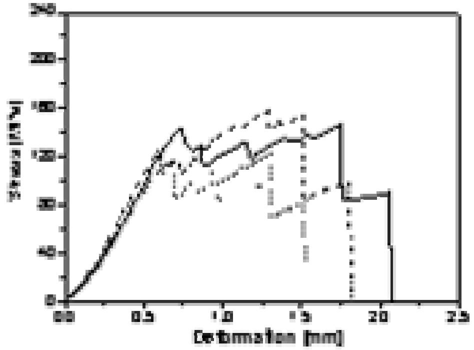
Manufacturing & testing of first tube demonstrators :

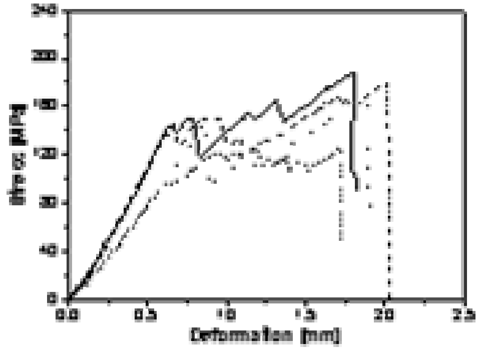
(→ damage tolerance at room temp., thermal shock resistance, creep resistance**)**

	Al_2O_3-fiber / mullite bond designed „**weak**“	designed „**strong**“	**Al_2O_3-fiber / zirconia bond** designed „**strong**“
[fibers]	= 56-61 vol.%	40-43 vol.-%	= 58-59 vol.%
total poros. ≈ / porosity	28 vol.-%	22-27 vol.-%	= 28-30 vol.-%

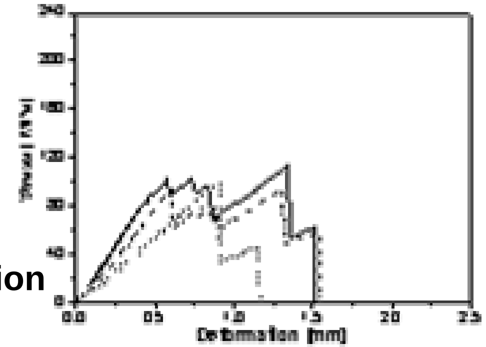
Reference (fine-crystall. Al_2O_3 fibers ↔ sintered 1400-1600 °C)

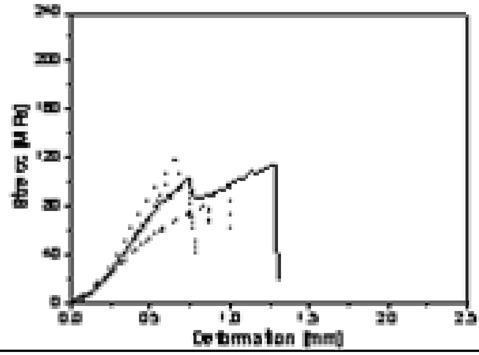


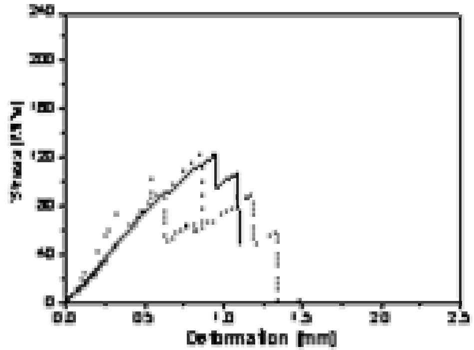




Fiber Re-crystallization 1750 °C







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Damage tolerance at room temperature:

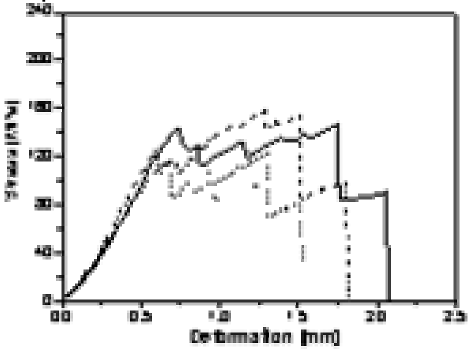
Present results vs. State of the art

Present results

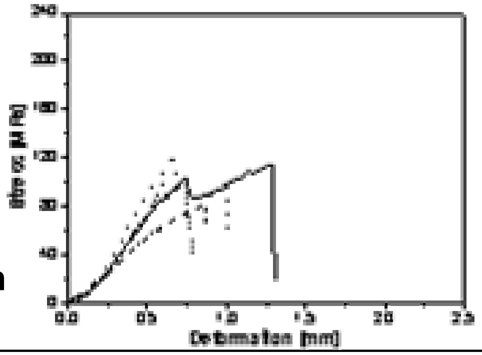
e.g. Al_2O_3-fiber
+ mullite matrix (→ „**strong**“ **bond**)

[fibers] = 40-43 vol.-%
total poros. ≈ 22-27 vol.-%

Reference
(fine-crystall. Al_2O_3 fibers ↔ sintered 1400-1600 °C)



Fiber Re-crystallization 1750 °C

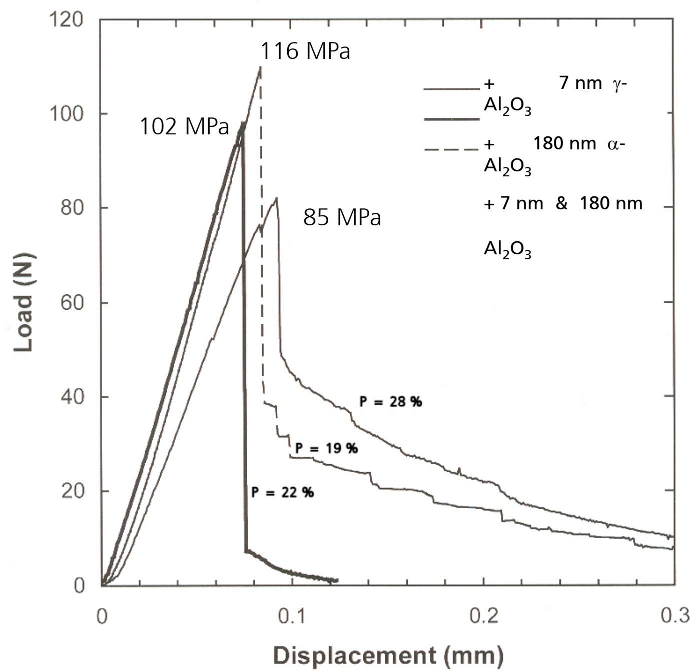


State of the art

e.g. Lee & Yano [2004]**: satin woven Al_2O_3-fiber cloth**
La-monazite interface + Al_2O_3 matrix (→ „**weak**“**bond**)

[fibers] = (high, no information about amount of infiltrated matrix)
porosity = 22-28 vol.-%

P.Y. Lee, T. Yano / Journal of the European Ceramic Society 24 (2004) 3359–3365



Composite hot-pressed at 1225 °C

Testing of first tube demonstrators :

Thermal shock resistance at ΔT = - 350 K

Example: Al_2O_3-fiber / mullite bond

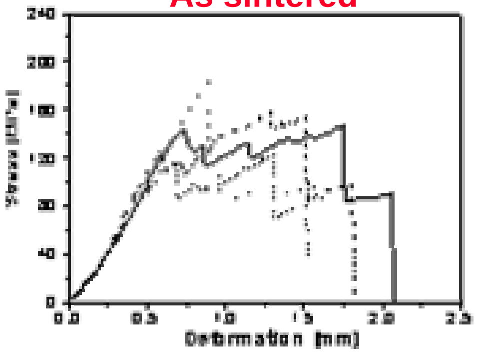
designed „**strong**“

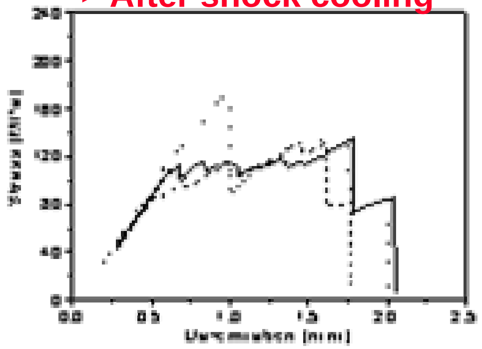
[fibers] = 40-43 vol.-%

total poros. ≈ 22-27 vol.-%

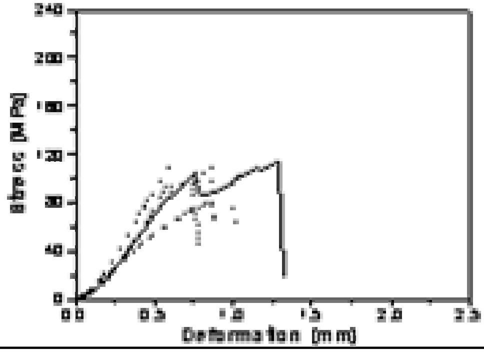
As sintered → **After shock cooling**

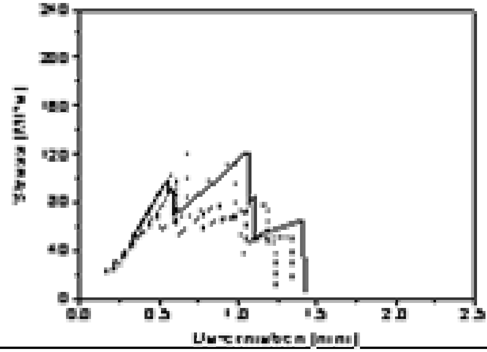
Reference
(fine-crystall. Al_2O_3 fibers ↔ sintered 1400-1600 °C)





Fiber Re-crystallization 1750 °C

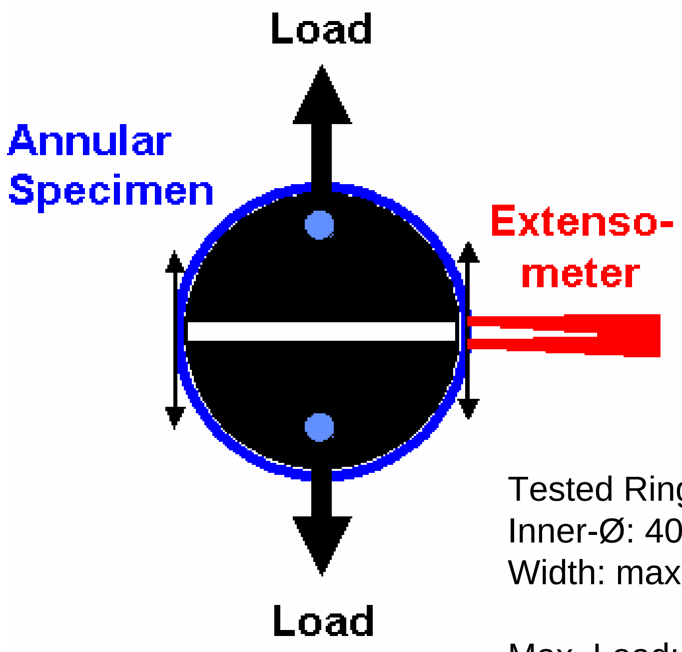




Testing of first tube demonstrators :

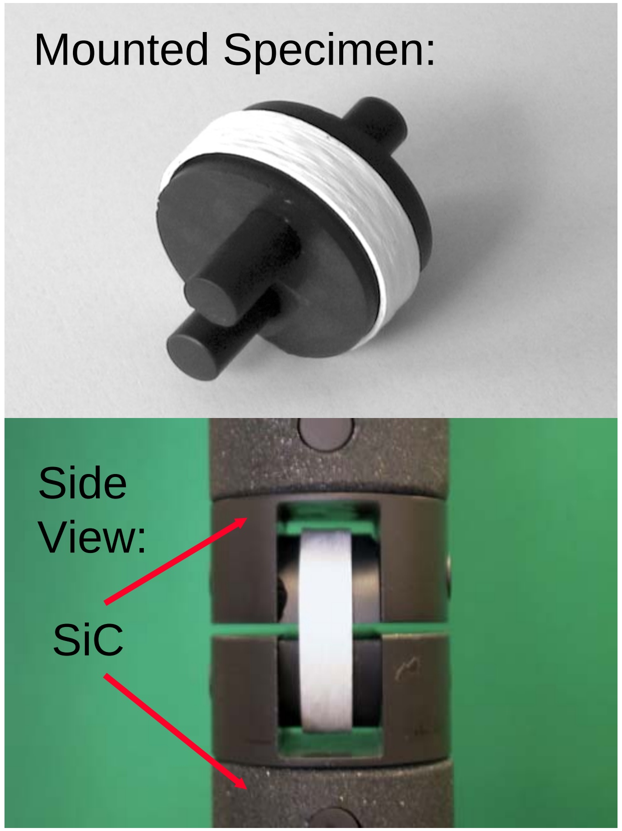
Creep Testing at ≥ 1300 °C

Testing Approach at IWM Freiburg :



Tested Ring:
Inner-Ø: 40 mm
Width: max. 20 mm

Max. Load: 6 kN



First creep tests at 1300°C:

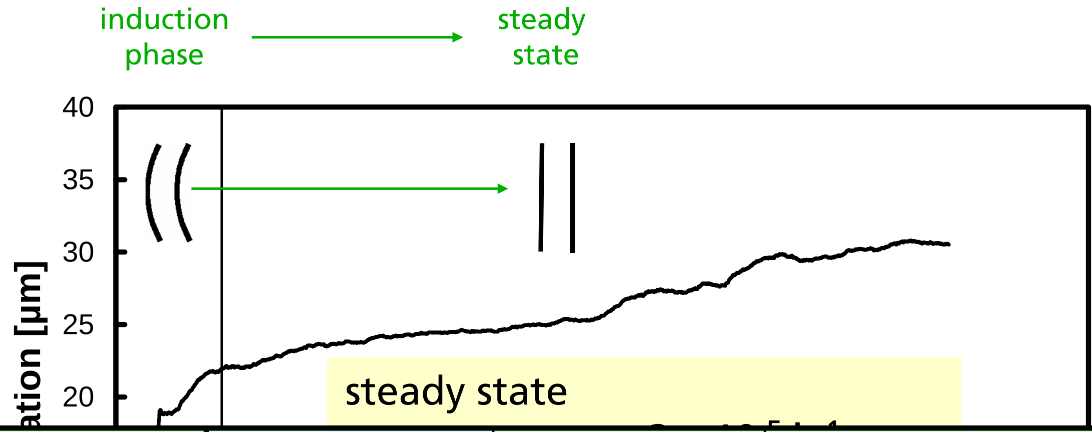
(applied stress 9 MPa)

(1) Induction Phase:
Stretching of Ring segment
(Creep rate not constant)

(2) Steady State:

Example: Al_2O_3-fiber / mullite bond
designed „**strong**"
[fibers] = 40-43 vol.-%
total poros. ≈ 22-27 vol.-%

„Reference" sample = sintered 1600 °C
(no re-crysrallization annealing)



	Dense Mullite Ceramics (grain sizes 2-5 µm)	***Reference* composite** (*no recrystallization, sintered 1600 °C*)	***Re-crystallized* at 1750 °C Al_2O_3-fiber + mullite matrix composite**
1300 °C / 10 MPa		**$3 \cdot 10^{-5}$ h^{-1}**	
1400 °C / 10 MPa	~ $5 \cdot 10^{-4}$ h^{-1}	**$3 \cdot 10^{-4}$ h^{-1}**	**0.8 ... $2 \cdot 10^{-4}$ h^{-1}**
1550 °C / 20 MPa	~ $2.5 \cdot 10^{-2}$ h^{-1}	?	?

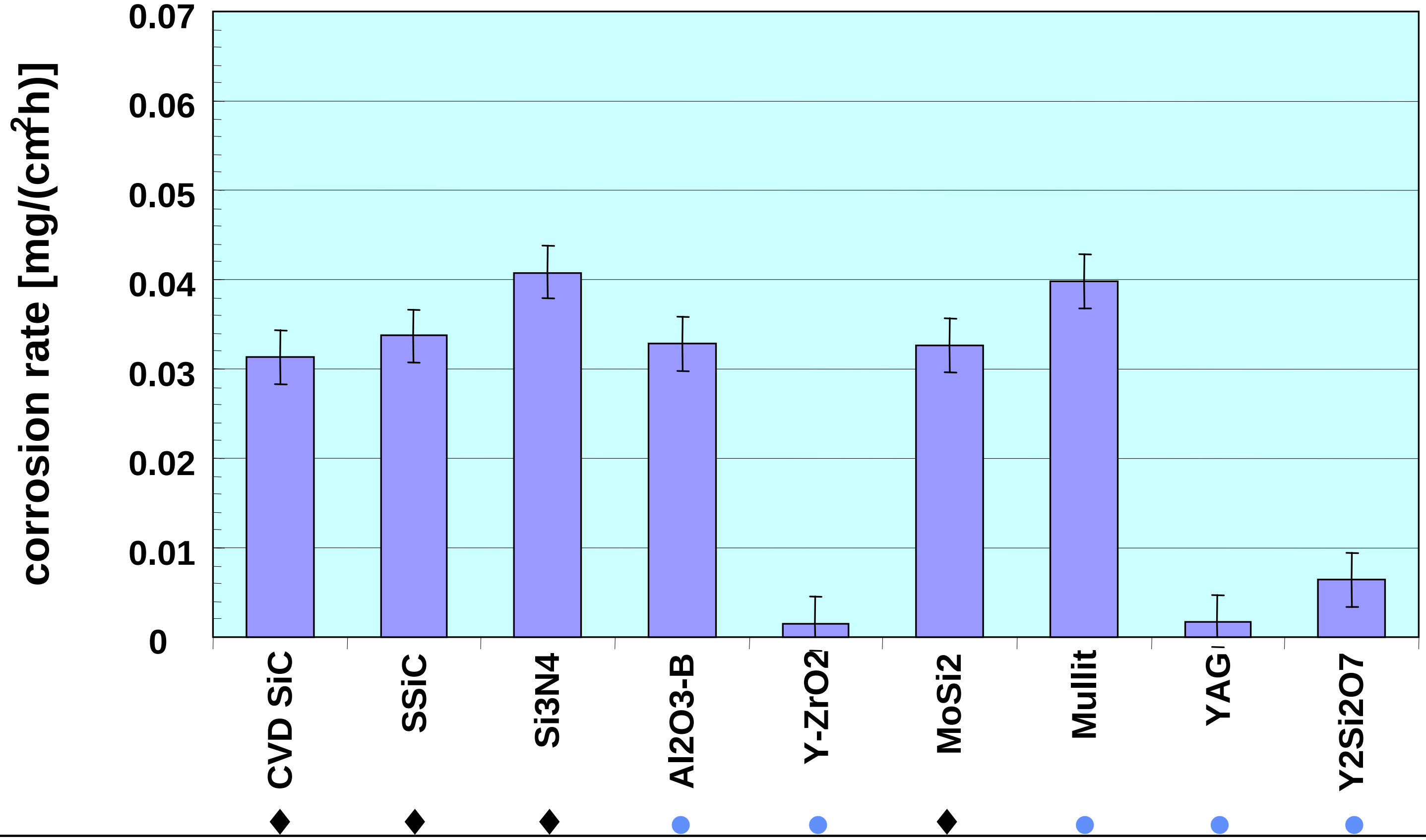
Si_3N_4/SiC ≈ 10^{-6} h^{-1}

Saphir ≈ 10^{-8} ... 10^{-9} h^{-1}

Comparison of Hot Gas Corrosion of different Ceramics

(♦ Non-Oxides - ● Oxides)

at 1450 °C / air + 27 % H_2O / velocity of flow 100 m/s



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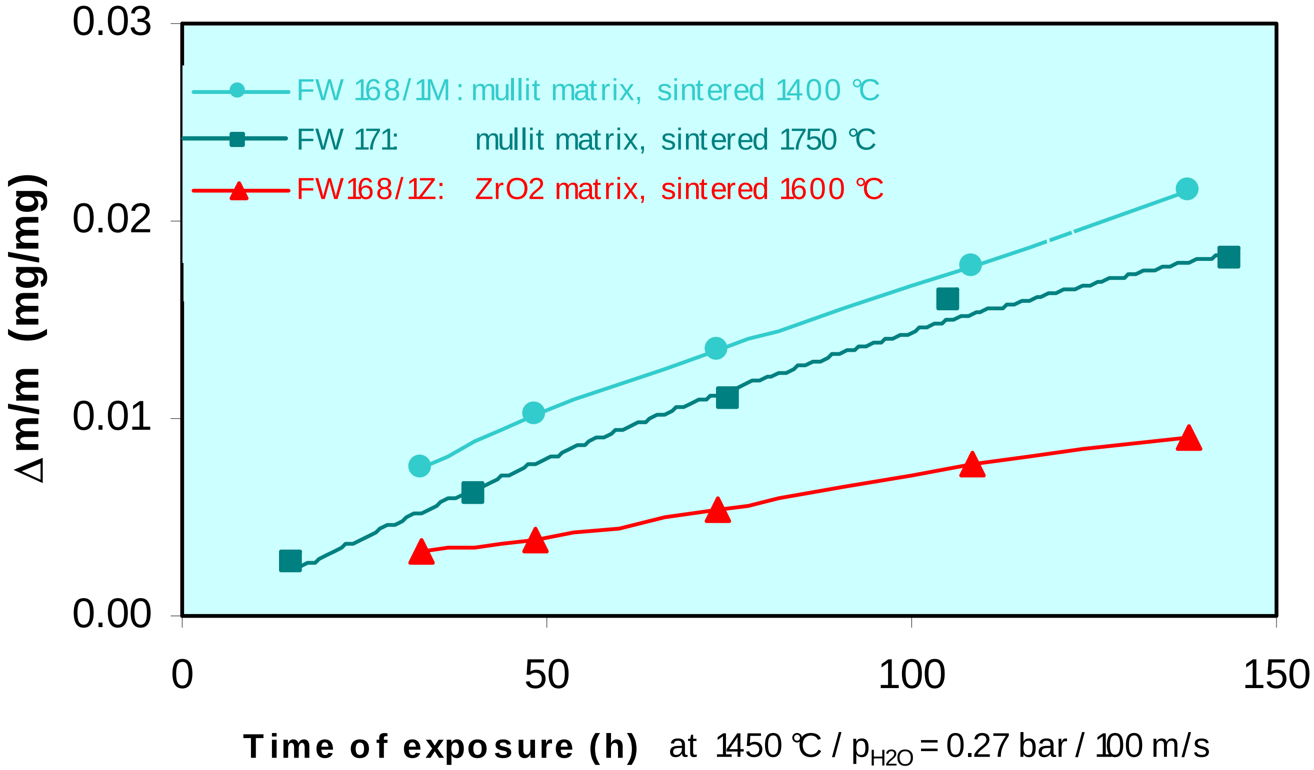
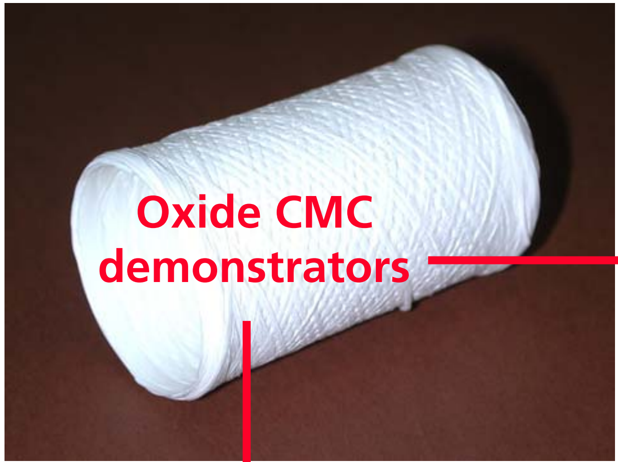
First use of hot-corrosion results for fiber OCMC:

Reduced hot-gas corrosion by matrix substitution

Mullit matrix
↓
ZrO_2 matrix



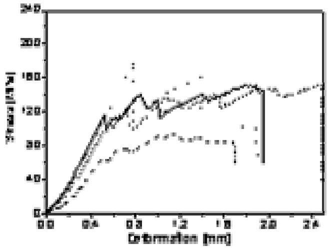
C o n c l u s i o n s

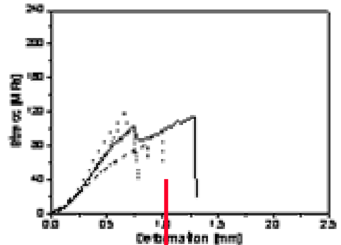


can be developed **by a new approach:**

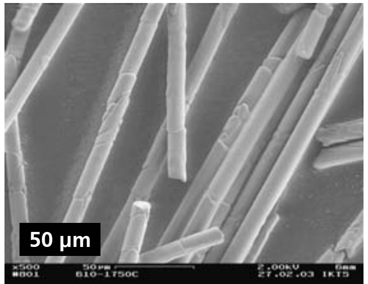
from *poly*crystalline (= processable)
commercial (= available)
fiber bundles
by (e.g.) **winding + subsequent re-crystallization**

<u>with</u>
„weak“ or **„axially strong“**
fiber/matrix bonds





with single crystalline segments ~ 100 µm



designed to match **creep resistance of single crystalline fibers at T ≥ 1400 °C**

and exhibit a strength ~ 100 MPa
+ promising damage tolerant thermal shock resistance:

ΔT = - 350 °C