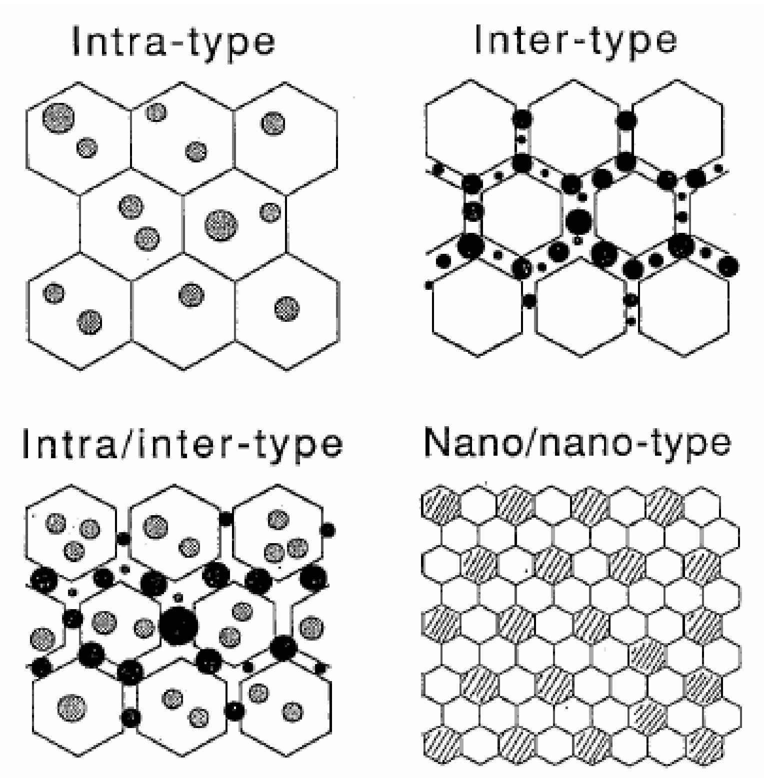
III.5 Ceramic Matrix Composites: Nanocomposites

Concept of nanocomposite:

- dispersion of nanometric particles (from 10 nm to less than 500 nm)
- inside or outside the matrix grains (at grain boundaries)

- need sourcing nanopowders
- adapt the process to control nanostructure

Niihara et Nakahira 1991



(2010) EU definition: from 1 to 100 nm

Alumina based nanocomposites (after annealing): matrix ~ 350 to 400 MPa – ~ 3.7 MPa√m

Year	Authors	Dispersion (% - type - nm)	Matrix GS (µm)	Strength (MPa)	Toughness ($MPam^{1/2}$)	Density
1991	**Niihara**	**5 – SiC – 40**		**1520**	**4.8**	
		- Si_3N_4		**850**	**4.7**	
1997	Zhu et al	15 – Si_3N_4 – 80	1.0	820	6.0	98.7
	Davidge et al	5 – SiC – 200	2.5	780	3.5	~100
	Bhaduri et al	10 – ZrO_2 – 25	0.04		8.4	98.0
1999	Anya et al	5 – SiC – 200	2.9	646	4.6	99.8
2001	Siegel et al	10 – MWCNT	0.50		4.2	~100
2002	Maensiri and Roberts	5 – SiC – 200	2.8	417	2.6	99.9
2005	Choi	3 – SiC – 80 ?	0.4 ?	760	5.06	
2006	Hae et al	5 – SiC – 20 20 – SiC – 20	0.2 ?	620 810	2.9 3.7	~100 ~100
2011	Lv et al	5 – SiC - 200	2,1	536	2.9	99.6

Even 20 years after, performances of Niihara's composites have not yet been achieved

Alumina based nanocomposites (after annealing): matrix ~ 350 to 400 MPa – ~ 3.7 MPa√m

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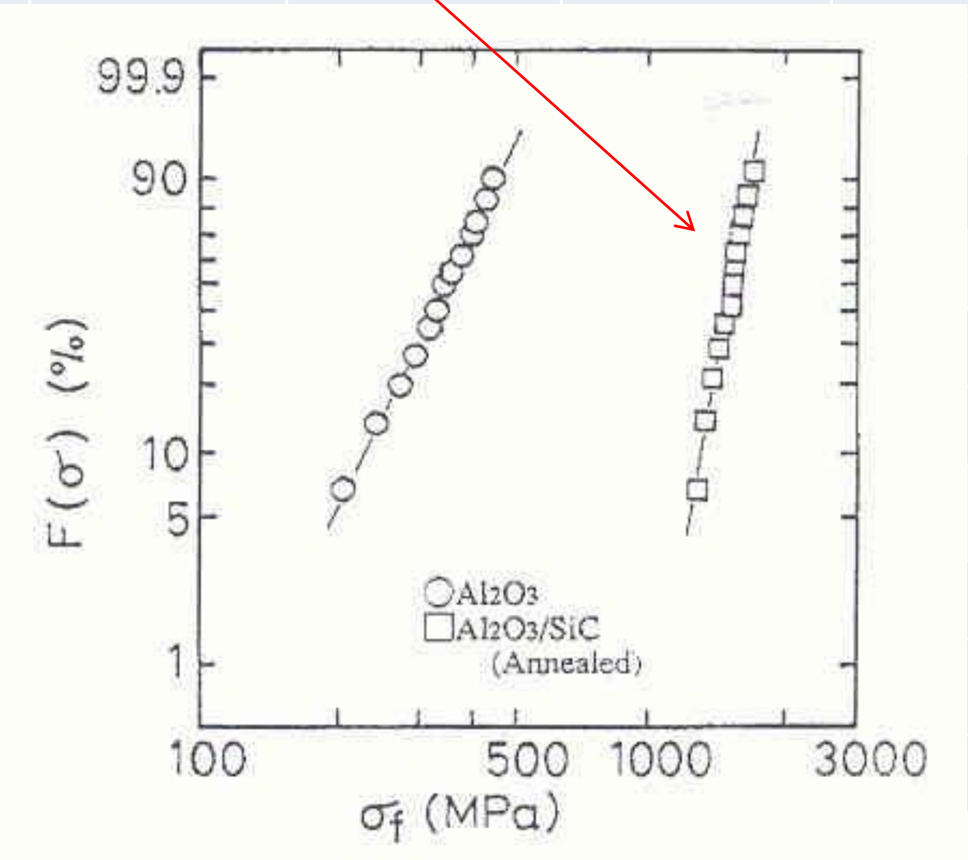
2001	Siegel et al	10 – MWCNT				
2002	Maensiri and Roberts	5 – SiC – 200				
2005	Choi	3 – SiC – 80 ?				
2006	Hae et al	5 – SiC – 20 20 – SiC – 20				
2011	Lv et al	5 – SiC - 200				



But reliability is highly improved !

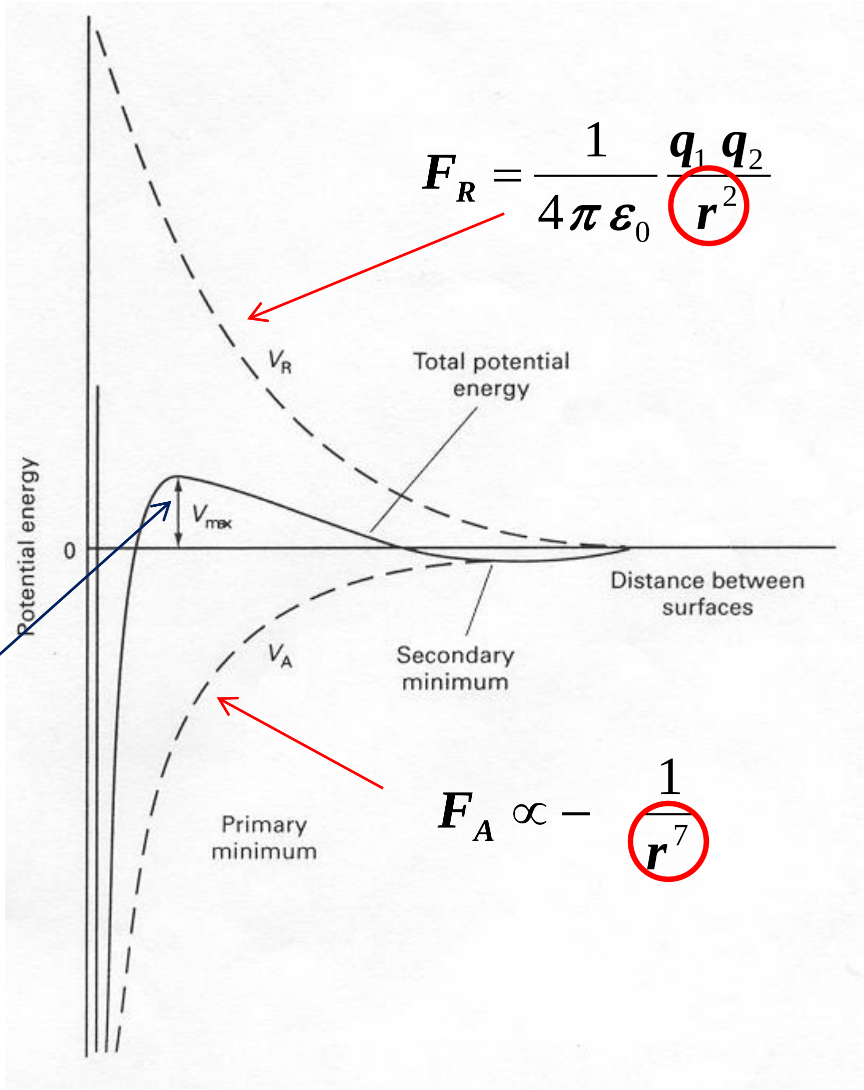
From micro- to nano- ceramic composites

Dispersion of nano- is difficult:

dispersion is the consequence of:
(DLVO theory)

- Vander Waals attraction forces
- electrostatic repulsion force
- steric shielding: function of the adsorbed species sizes

- a “potential barrier” impedes the particles to flocculate
- resulting level of repulsion depends also on particle size !

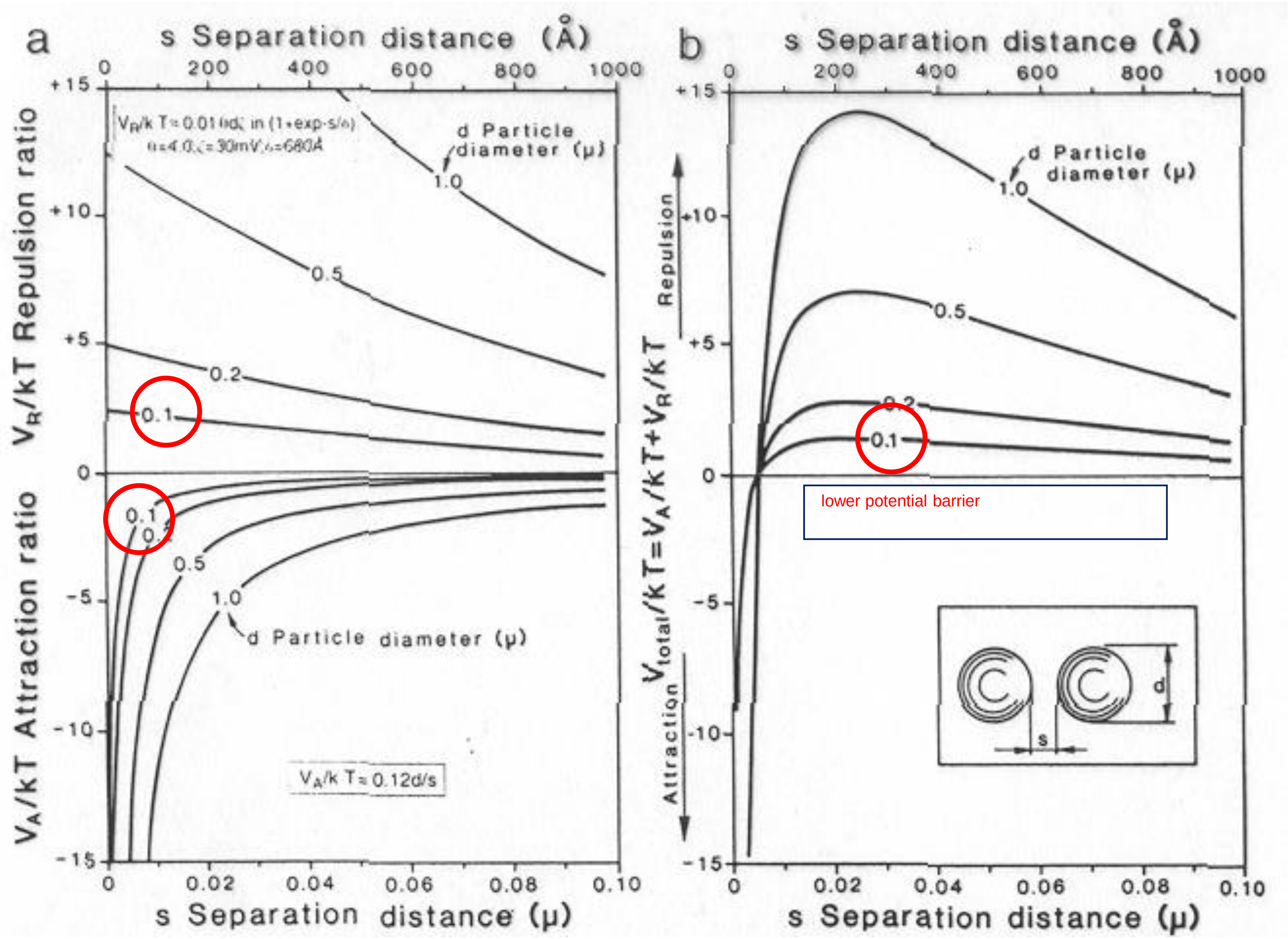


$$F_R = \frac{1}{4\pi\varepsilon_0}\frac{q_1 q_2}{r^2}$$

$$F_A \propto -\frac{1}{r^7}$$

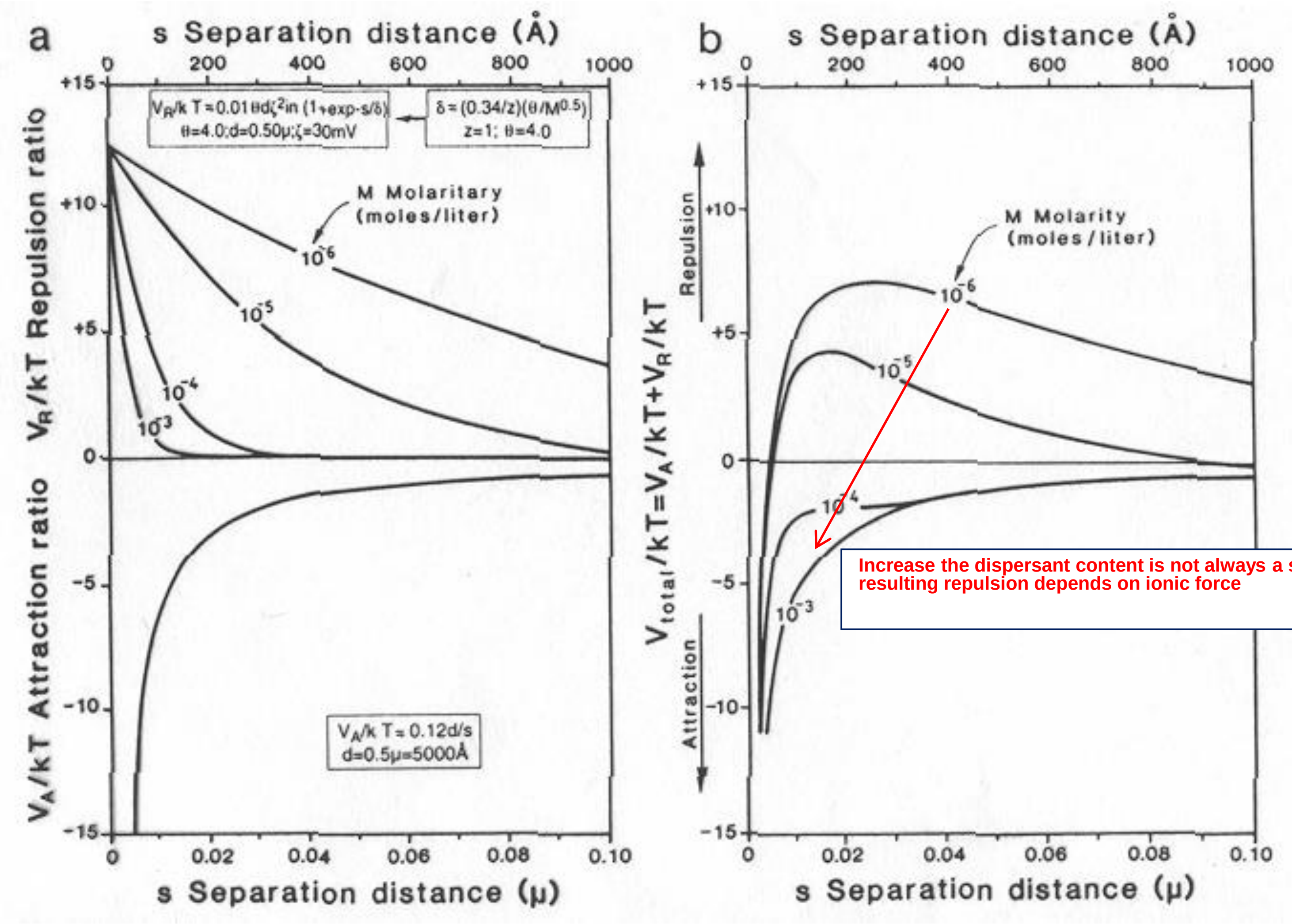
From macro- to nano- ceramic composites

Influence of particle size



lower potential barrier

From micro- to nano- ceramic composites



Increase the dispersant content is not always a solution: resulting repulsion depends on ionic force

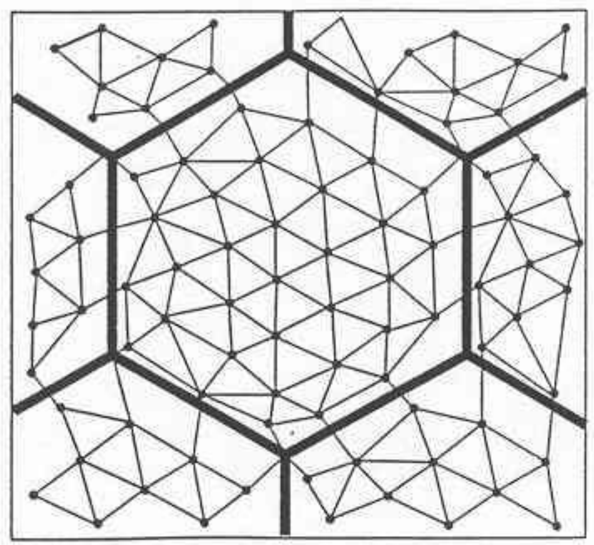
Strengthening mechanisms (nano-)

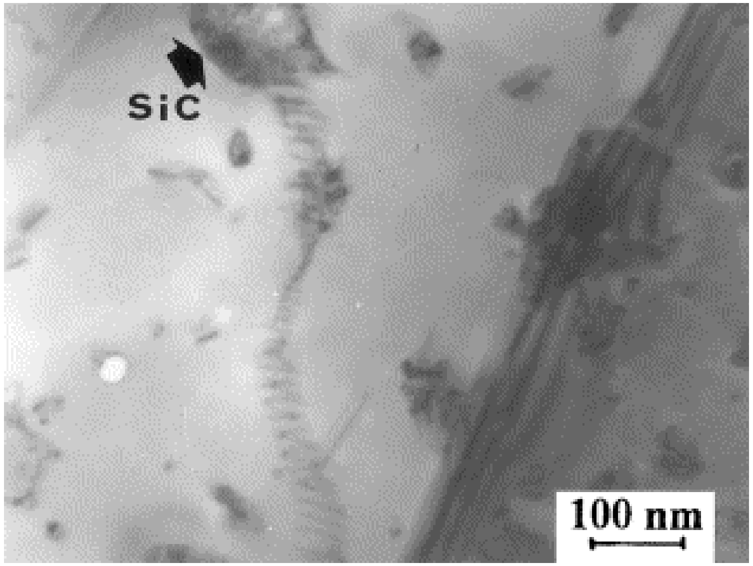
Still controversial:

a number of possible mechanisms have been proposed

- **Niihara** (91): - Nano-sized dispersions restrain the grain growth

-Thermal mismatch between matrix and dispersoids → tensile stresses in the matrix → dislocation movements → dislocation pin and pile up by nanoparticles → subgrain boundaries within the matrix → refinement of matrix induces strengthening





Strengthening mechanisms (nano-)

Many authors **did not agree** with Niihara proposal:

- calculated tensile stresses ($\Delta\alpha$) too low to form substructure, but strengthening is due to matrix grain refinement (Fang 97)
- strengthening effect is still present at high temperature (Deng 98)
- flaws healing (Wu 98 ; Anya 98 – 2000)

Other proposals:

- near surface compressive stress strengthening (Wu 2008)
- dislocation network strengthening (Zhang 2007)
- strengthening via reduction in process defect size (Sternitzke 97)
- calculation of internal stress fields during cooling ($\Delta\alpha$) → reduction of flaw size → crack penetrates into the matrix grain (Pezzoti et al 2001 – 02)

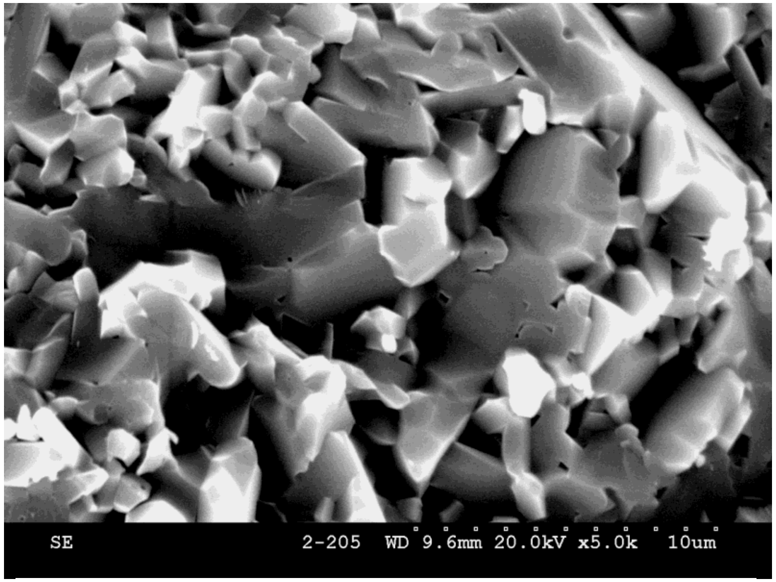
Stresses were calculated:

- ~147 MPa (Lv, Zhang 2010)
- > 1 GPa (Choi 2005)

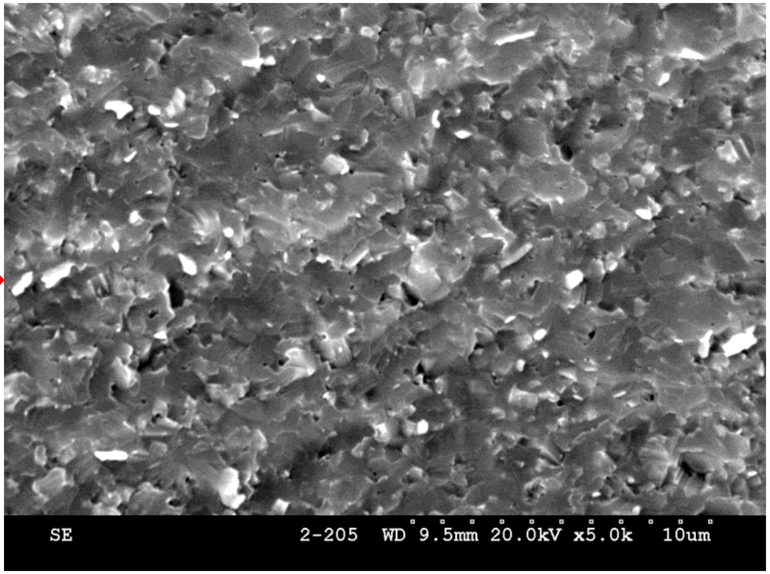
Strengthening mechanisms (nano-)

However, all authors **agree** on:

- residual stresses relaxation is much more difficult in nanocomposites
- the rupture mode changes from inter- to trans-granular



pure alumina fracture face



same alumina + 1 vol% SiC fracture face

Strengthening mechanisms (nano-)

Other proposals:

Grain boundary strengthening through:

- pinning effect (**Deng 98-Anya 97-Ohji 99**)
- inter-granular fracture energy > trans-granular fracture energy **(Jiao 97)**
- crack deflection by SiC particles **(Honglai-Tan 98)**
- compression of the grain boundaries **(Pezzotti 2001)**

Dislocation network blocked by SiC movement impedes the movement of new dislocations **(Anya 2000)**

Strengthening mechanisms (nano-)

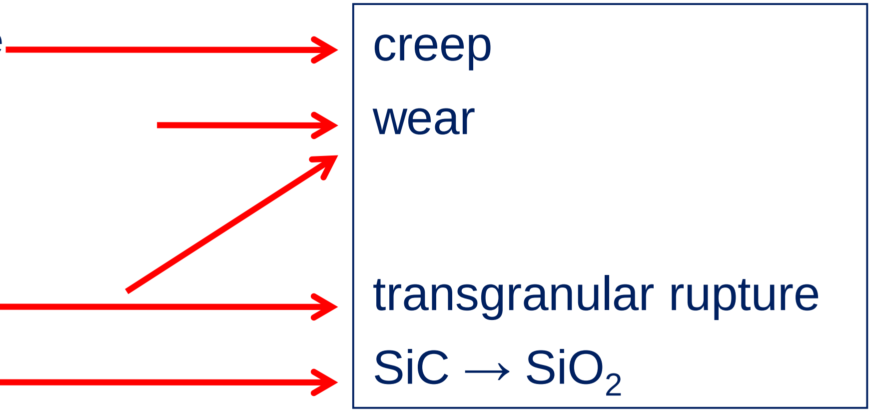
Combination of effects ? (example of Al_2O_3 – SiC)

Intergranular nanoparticles:

- Pinning of grain boundaries
- Refinement of matrix microstructure

Intragranular nanoparticles:

- Dislocations
- Flaw healing

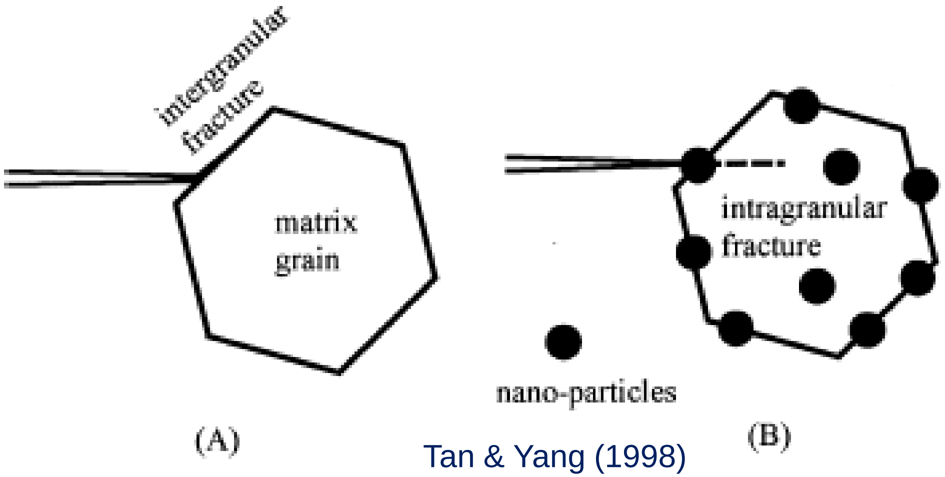


creep

wear

transgranular rupture

SiC → SiO_2



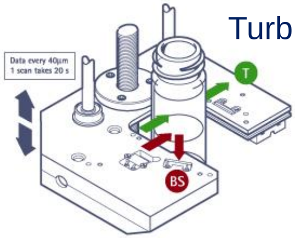
Tan & Yang (1998)

Lab processing of ceramic nanocomposites

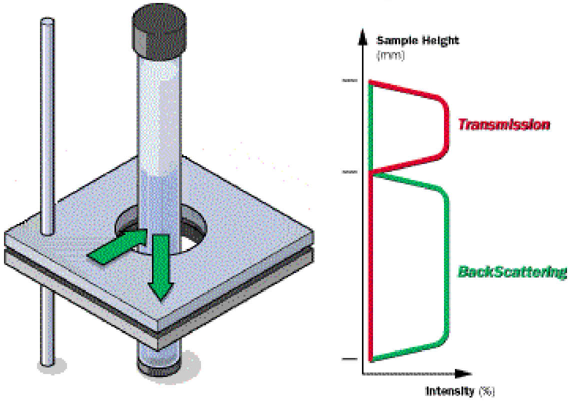
ζ potential measurement - adjustment (acoustic method)

nano-mill

Turbiscan



ceramic beads (from 50 to 300 µm)



Example: Al_2O_3-SiC nanocomposites

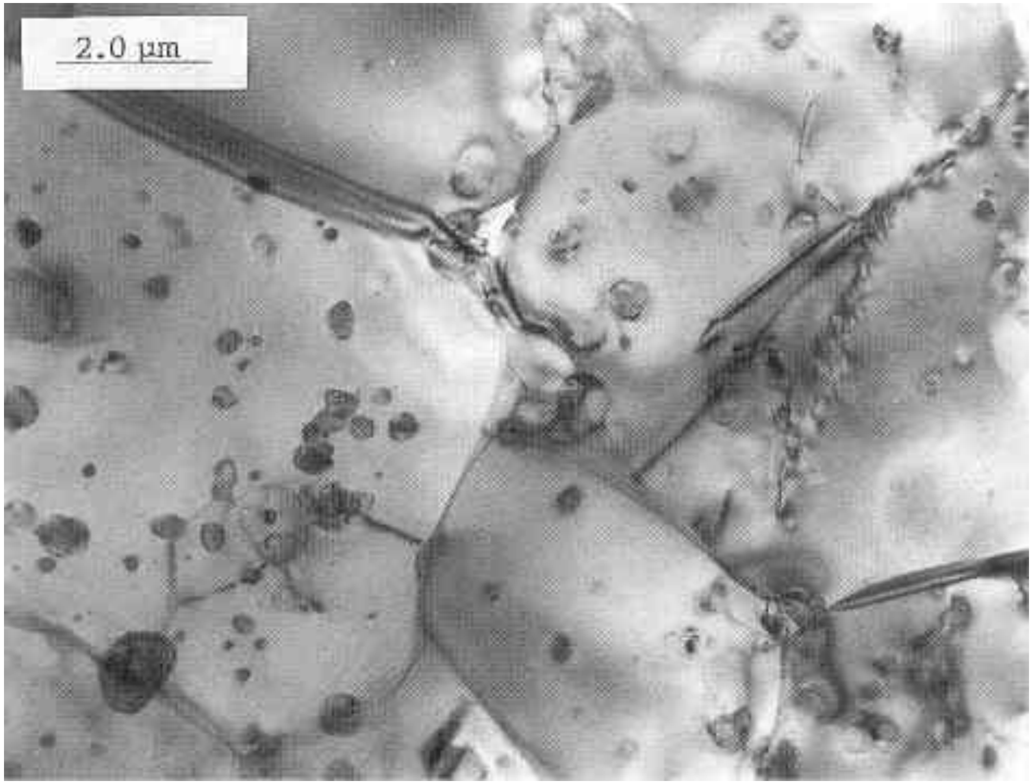
Some examples of enhanced behaviours:

Typical microstructure (TEM)

Al_2O_3 – SiC nano 40nm (7.5 wt%)

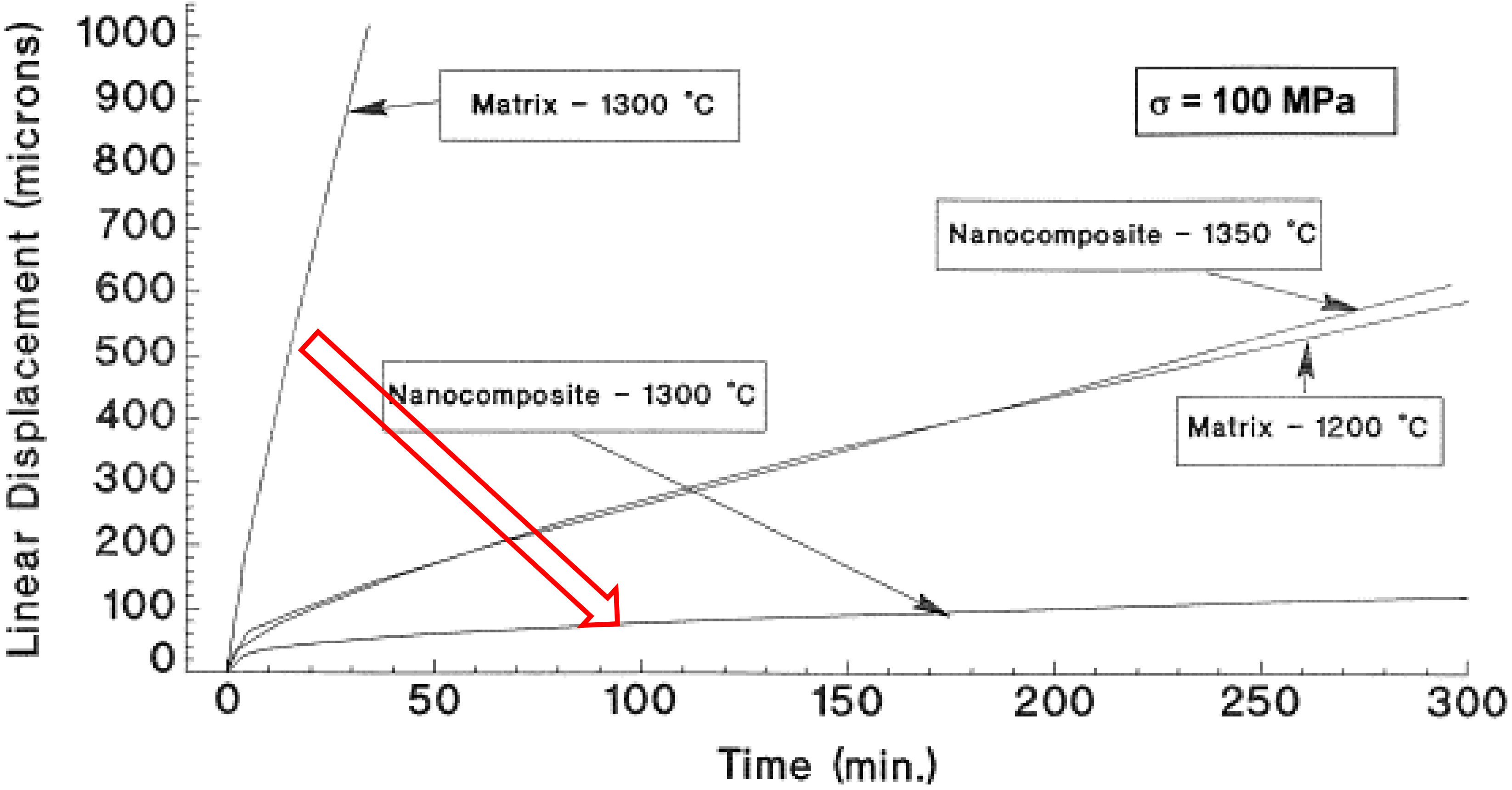
Hot Pressing

σ_F up to ~ 1000 MPa



Example: Al_2O_3-SiC nanocomposites

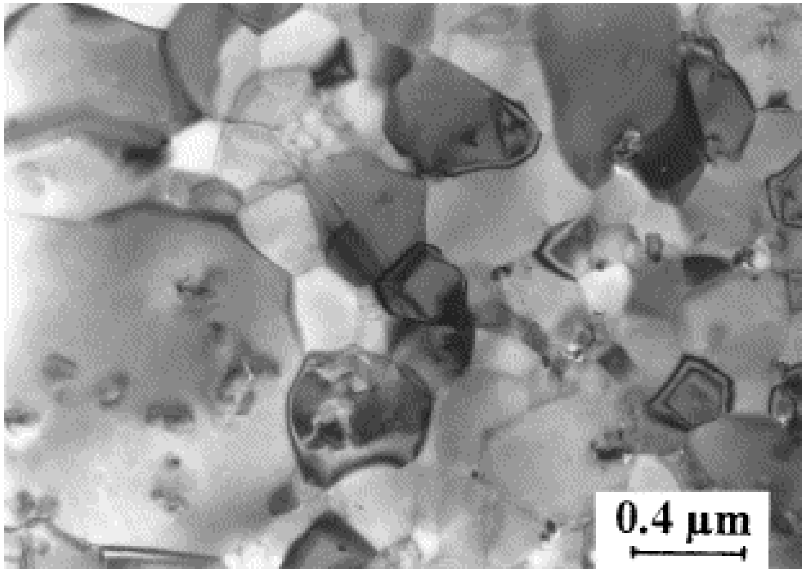
Creep resistance (flexural tests)



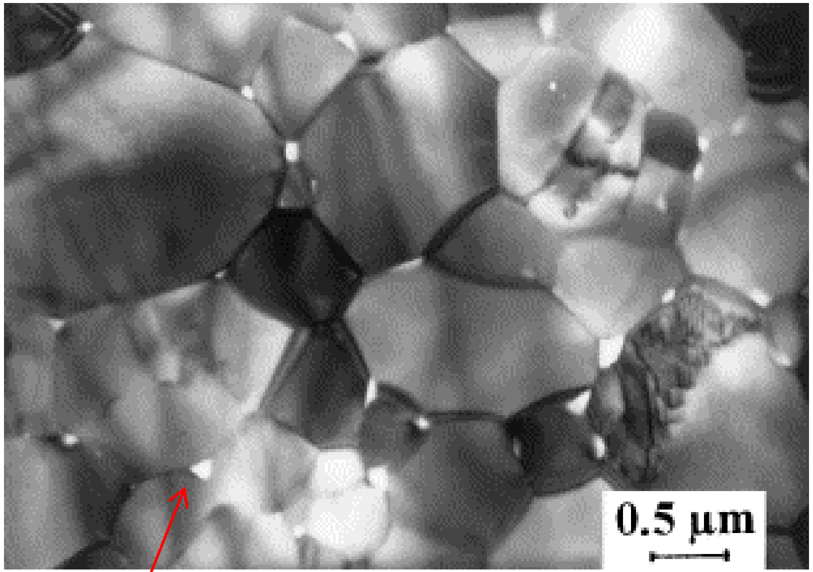
Example: Al_2O_3-SiC nanocomposites

Creep resistance (flexural tests)

nanocomposite



matrix

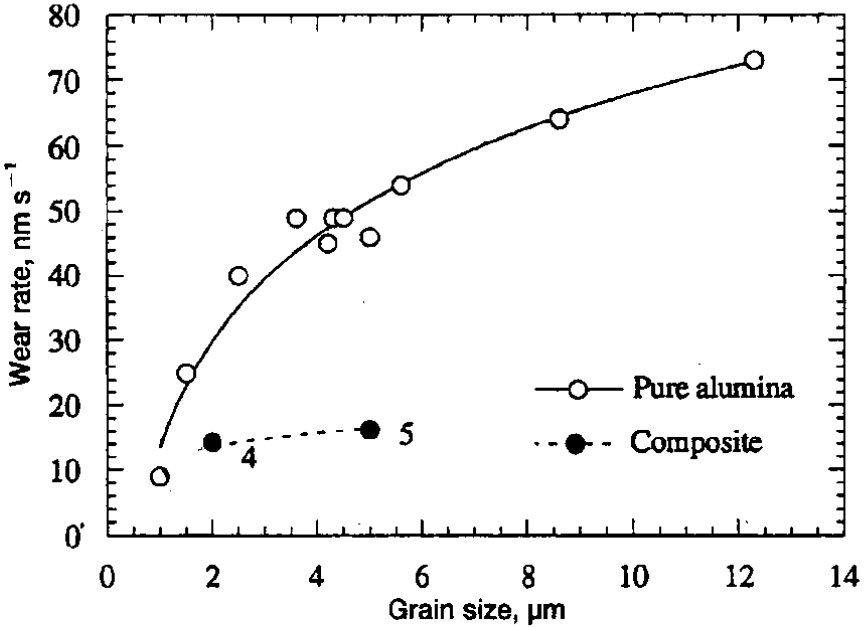


For a same test temperature, a lot of cavitations can be seen in the matrix

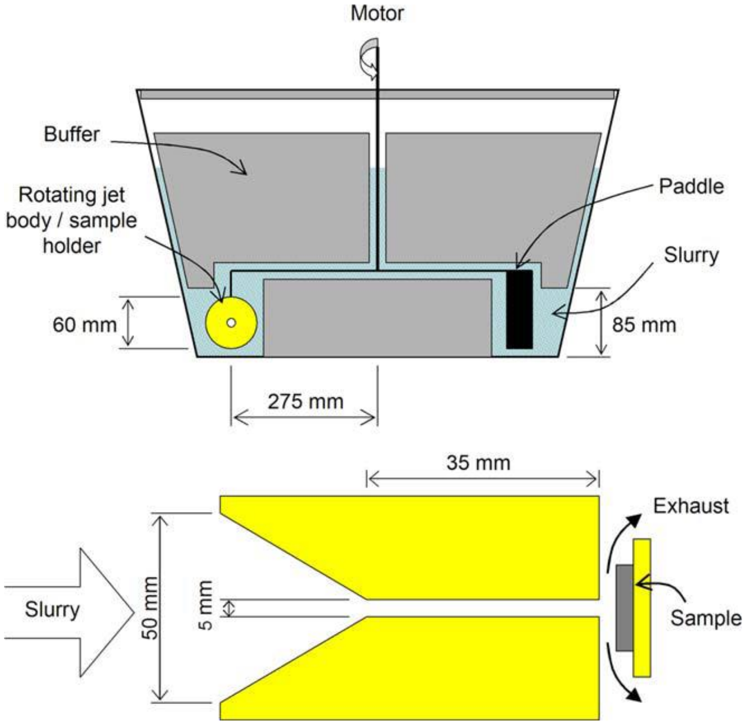
Example: Al_2O_3-SiC nanocomposites

Wear resistance (erosion)

- It has to be noted that wear increases with matrix grain size
- But SiC addition limits also the grain growth



Tests on same materials carried out at Oxford University



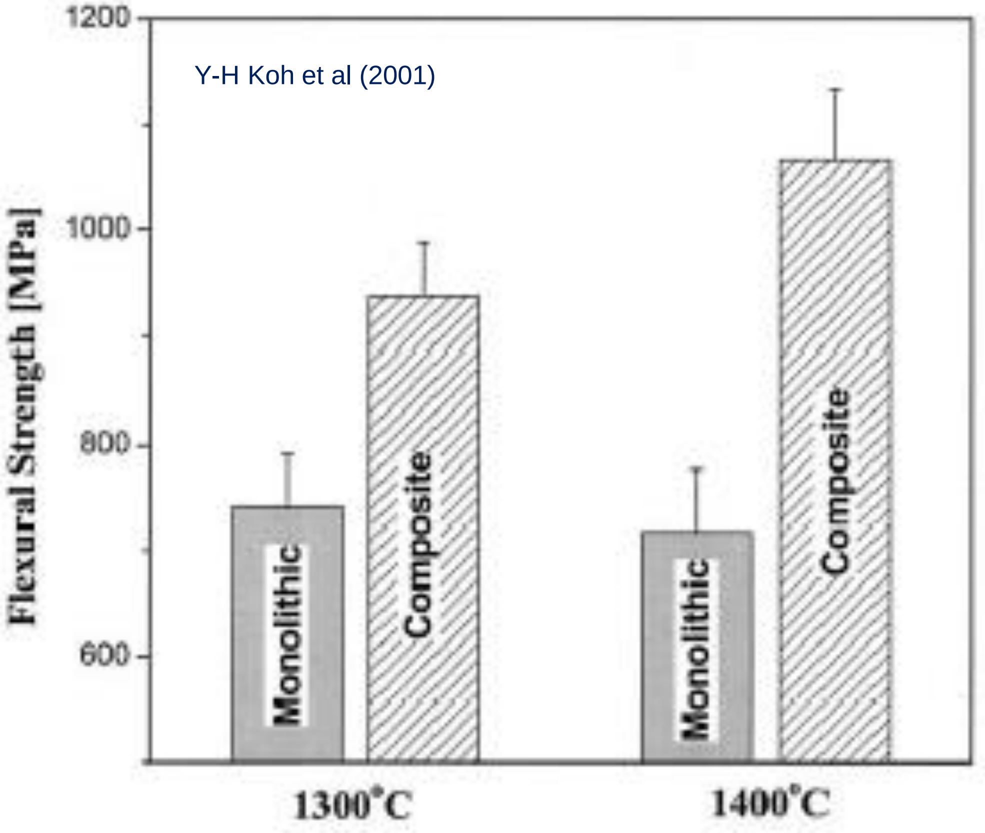
Courtesy R. Todd

Example: Al_2O_3-SiC nanocomposites

Corrosion resistance

oxidation tests in air
during 100 h

+ 40 % σ_F

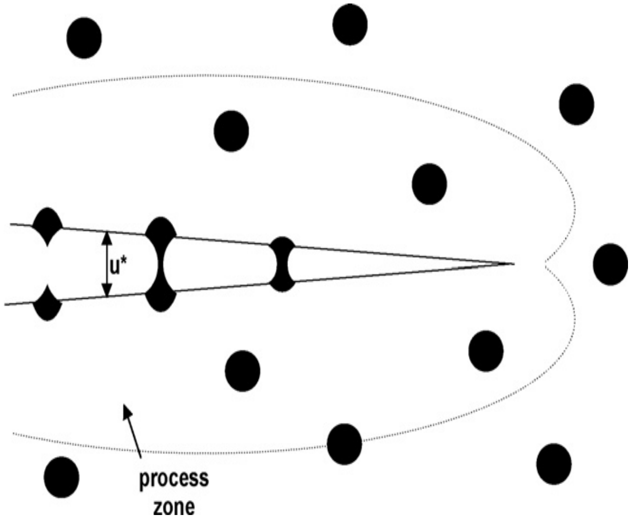


Y-H Koh et al (2001)

crystallisation of the amorphous phase

Example: Al_2O_3-metal nanocomposites

ductile nanosized particles addition ?



Al_2O_3 – metal particles :
Ni, Cu, Co, Fe, Cr, Mo, Nb...

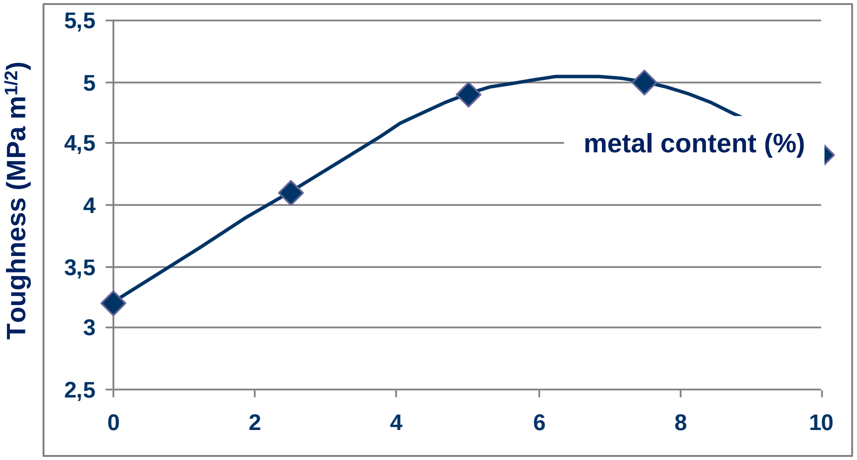
Processing

liquid precursors (nitrates...)

+ alumina powder,

calcination under reducing atmosphere

sintering



Al_2O_3 / Ni

Example: Al_2O_3-metal nanocomposites

Literature data

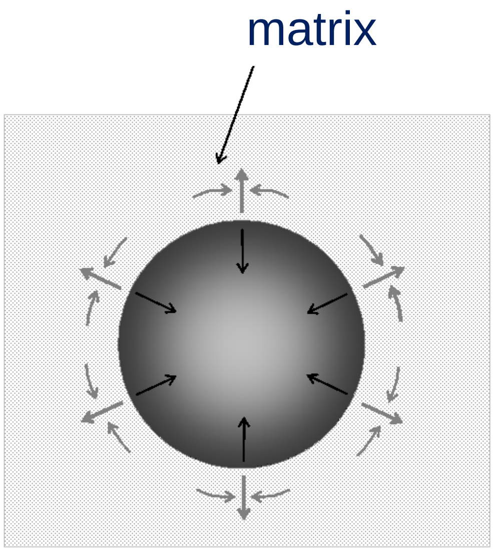
			σ_F MPa	K_{IC} MPa√m
1995	Sekino	5% W	528 → 645	3.2 → 3.8
1996	Sekino	5% Ni	683 →1090	3.5 → 3.5
1999	Chen	5% Ni	390 → 526	3.6 → 4.2
2001	Oh	5%Cu	536 → 953	3.6 → 4.8
2002	Ji	5% Cr	475 → 736	3.6 → 4.8
2003	Li	5% Ni	420 → 530	3.3 → 5.2

- many reported works consider high (5 to 20 %) metal particles additions

- a recent paper shows only 0.69 % Mo give rise to an large increase of strength (from 320 to over 700 MPa) and toughness (from 4.0 to 6.3 MPa√m)
- even for so limited additions, fracture changes from inter- to transgranular mode

Example: Al_2O_3-metal nanocomposites

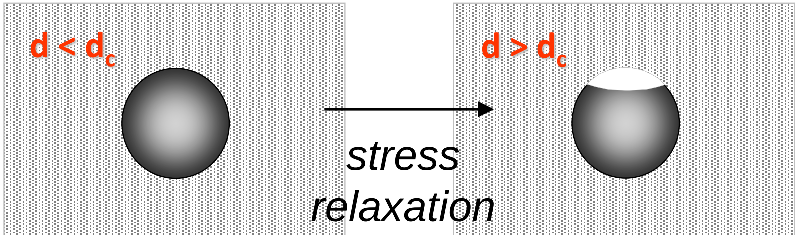
Matrix : Al_2O_3 $\alpha = 8{,}6\ 10^{-6}\ K^{-1}$

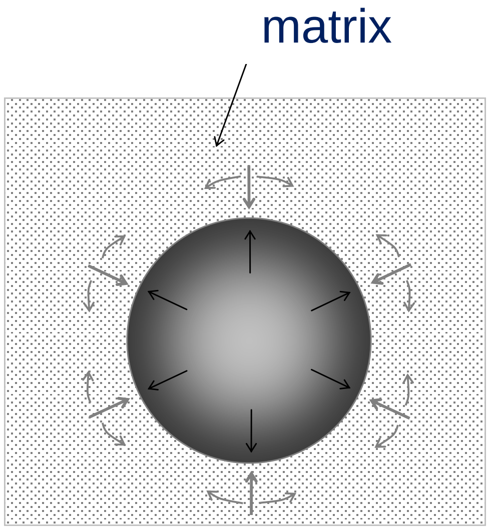


$$\Delta\alpha = \alpha_m - \alpha_p < 0$$

(nickel, iron, cobalt)

$\alpha_{Ni} = 13\ 10^{-6}\ K^{-1}$ $\alpha_{Fe\ and\ Co} = 12\ 10^{-6}\ K^{-1}$

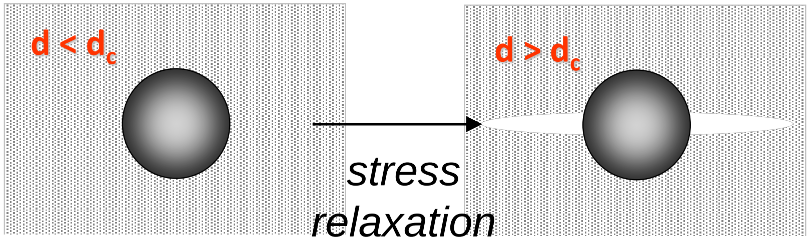




$$\Delta\alpha = \alpha_m - \alpha_p > 0$$

(molybdenum, chromium)

$\alpha_{Mo} = 5\ 10^{-6}\ K^{-1}$ $\alpha_{Cr} = 6.2\ 10^{-6}\ K^{-1}$

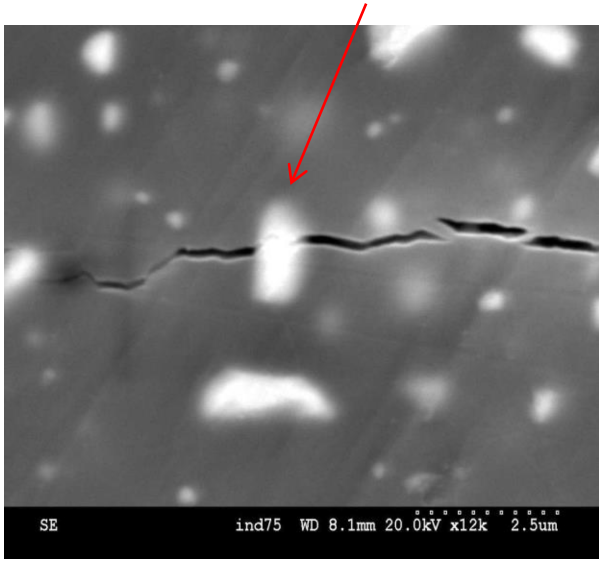


From micro- to nano- ceramic composites

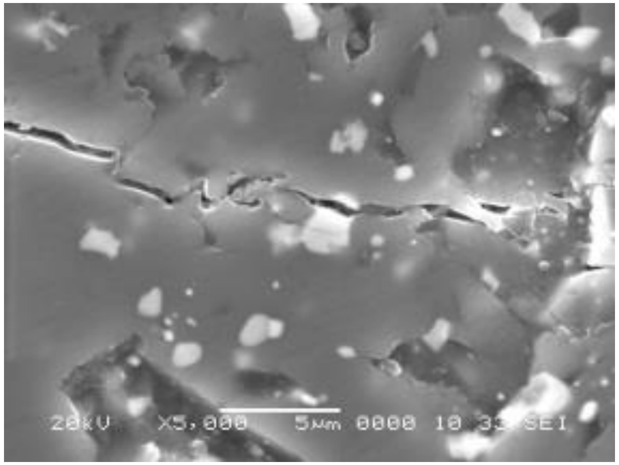
Lab data

Al_2O_3 - Ni

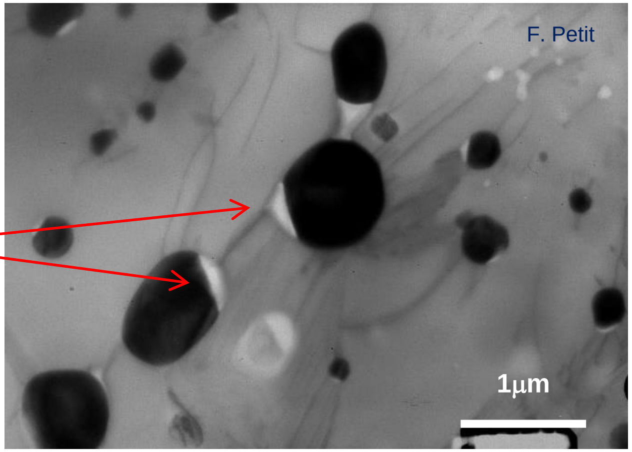
bridging by a ductile particle



Mo



micro-cracking Al_2O_3 - Ni


F. Petit

From micro- to nano- ceramic composites

Compared to microcomposites:

- increase of strength (up to 100%)
- creep resistance
- wear behaviour improvement
- high reliability
- high temperature resistance

....

BUT no increase of toughness
lack of reproducibility!
processing difficult to control

Despites this, today applications:

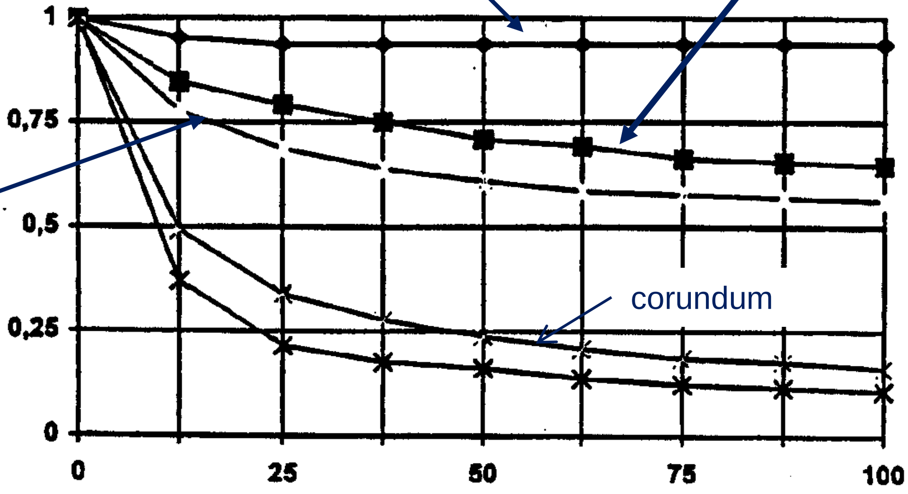
Towards applications

Wheel grinding nanocomposite grains

Treibacher Schleifmittel – UVHC patent

mixing of SiC particles slurry into a boehmite sol

gelling → calcination → milling → sintering



grinding wheel wear resistance

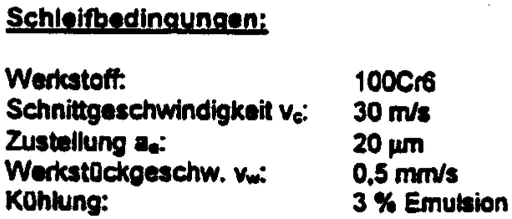
cBN

nanocomposite
Al_2O_3 – 5 wt% SiC

fine Al_2O_3
sol-gel

corundum

C. Kermel



Schleifbedingungen:

Werkstoff:	100Cr6
Schnittgeschwindigkeit v_c:	30 m/s
Zustellung a_e:	20 µm
Werkstückgeschw. v_w:	0,5 mm/s
Kühlung:	3 % Emulsion

Towards applications

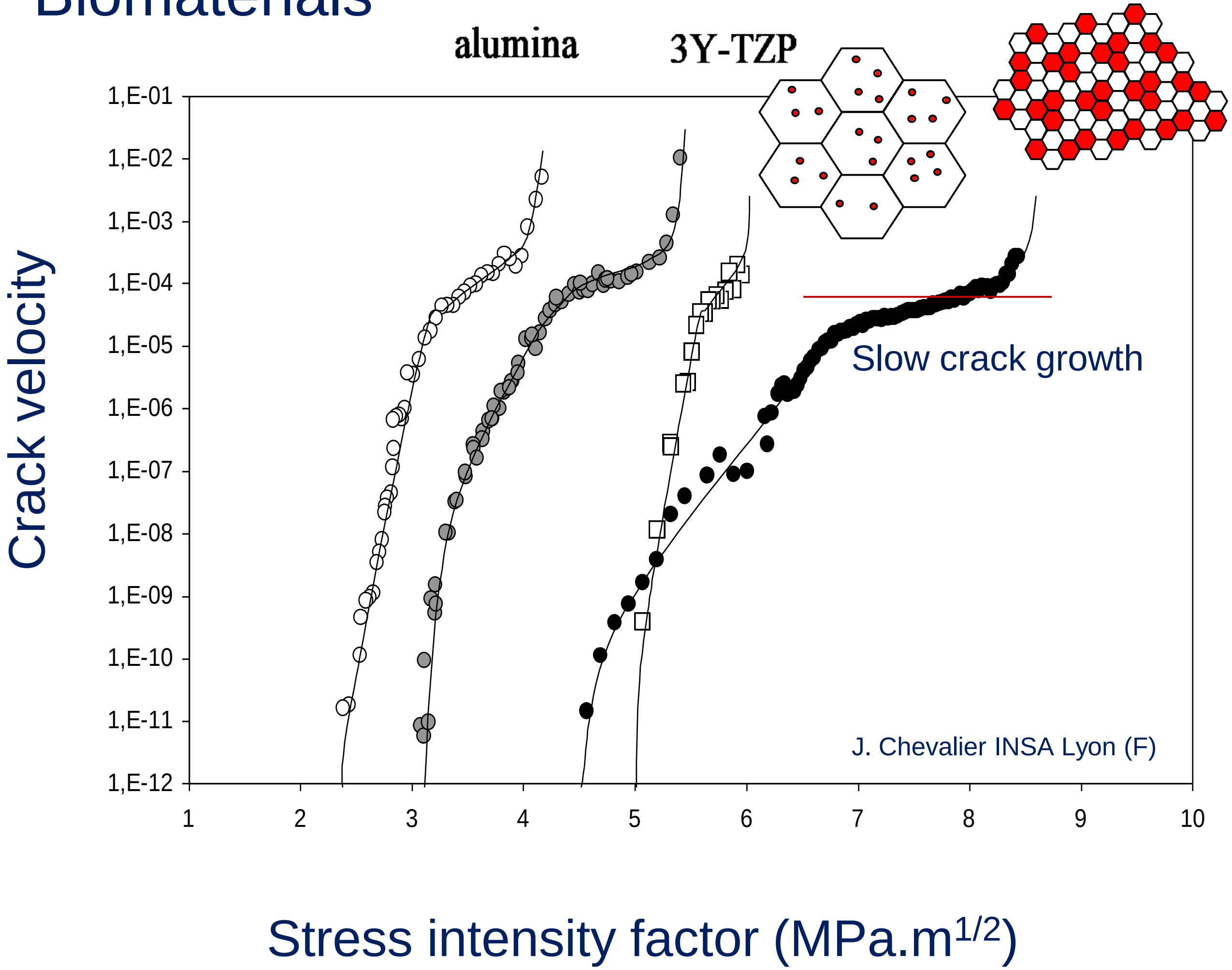
Biomaterials


Biomaterials Biolox® delta Ceramtec

- alumina – alumina friction pair is the most couple used today
- Y-TZP could decompose in wet atmosphere
- alumina – zirconia composites and close control of the micro- nanostructure allow to imagine new applications

Towards applications

Biomaterials



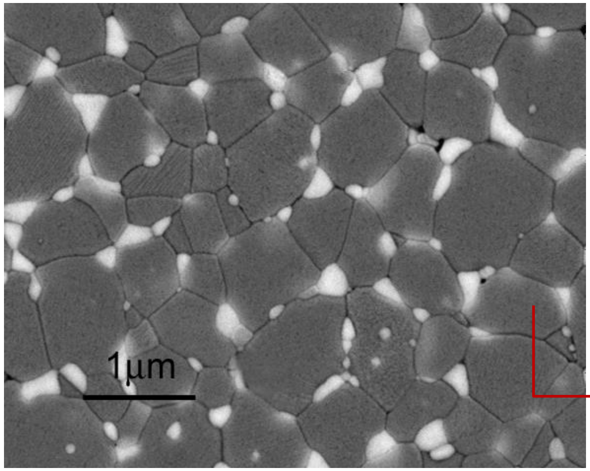
Towards applications

Biomaterials

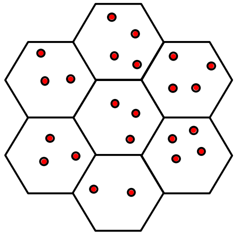
The process allows to limit the grain size

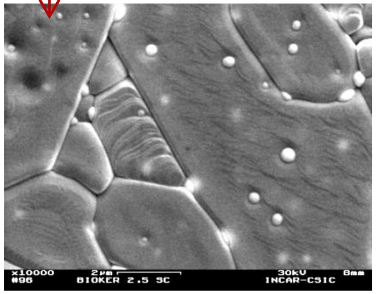
J. Chevalier INSA Lyon (F)
with Politecnico Torino

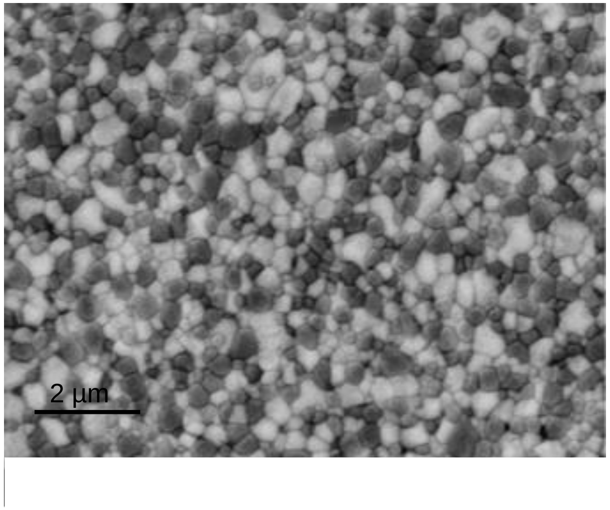
alumina-zirconia nano-composites



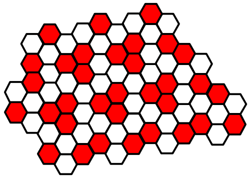
micro – nano



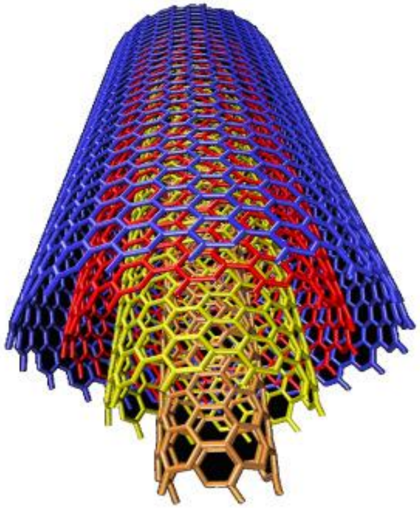




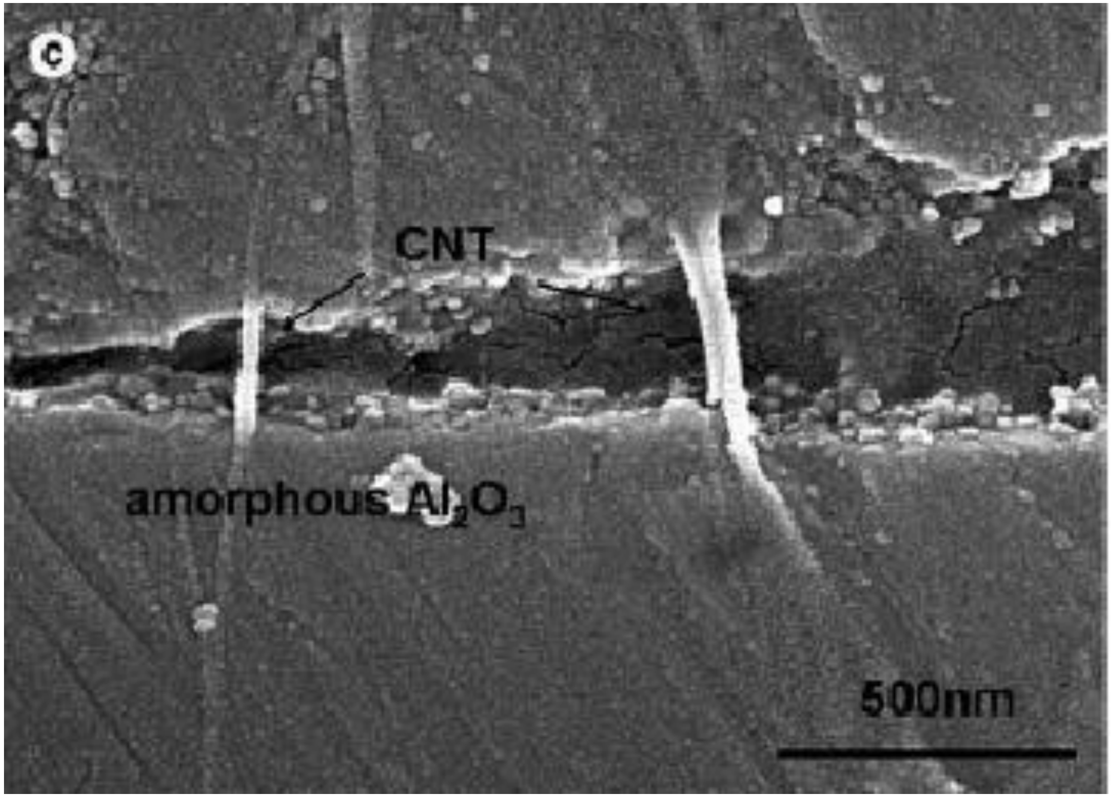
nano – nano



And the future?



crack bridging in alumina matrix by multiwall CNT

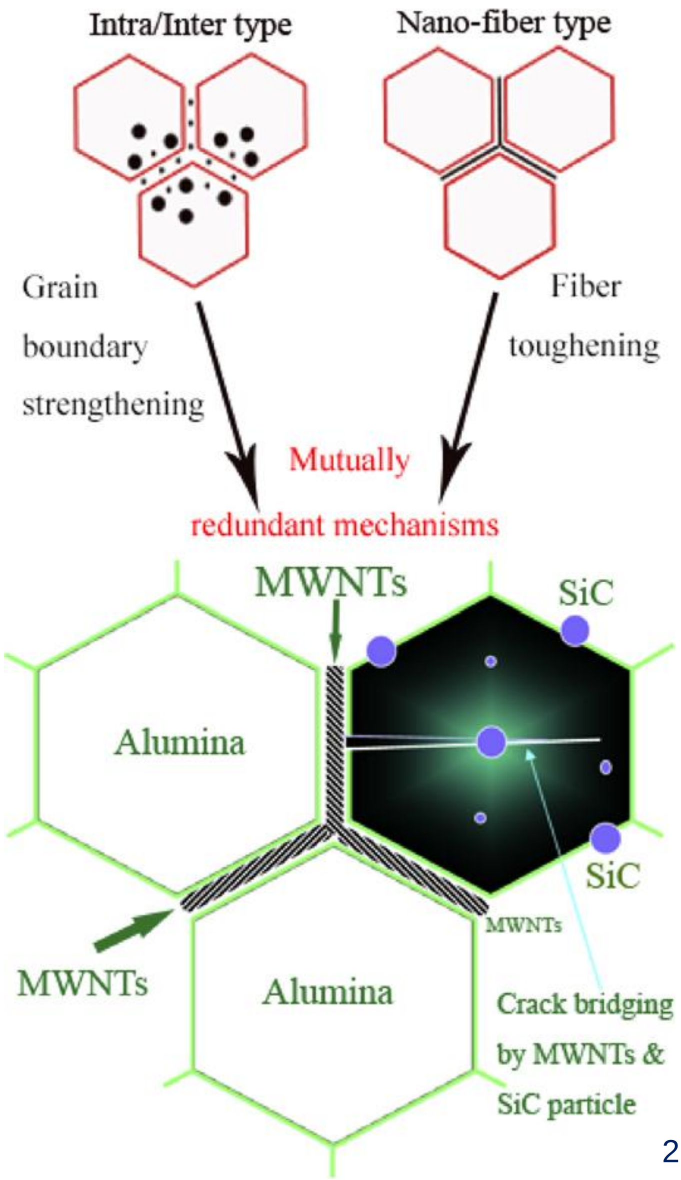


And the future?

New hybrid nanocomposites?

	K_{IC} (MPa√m)	**σ_F (MPa)**	**H_V (GPa)**
Al_2O_3	3.1	340	17.0
1% SiC	4.0	550	16.5
1% SiC, 5% MWNT	6.4	480	16.3
1% SiC, 7% MWNT	6.9	470	16.0
1% SiC , 10% MWNT	5.6	450	14.5

Ahmad, Pan 2008



Conclusion

Positive points:

- Increase of wear resistance
- Increase of creep resistance
- Either better strength or better toughness
- Possibility to use classical process (cost effective)
- Very limited additive content (low cost increase)

Negative points:

- It is difficult to optimise both strength and toughness
- Reproducibility!