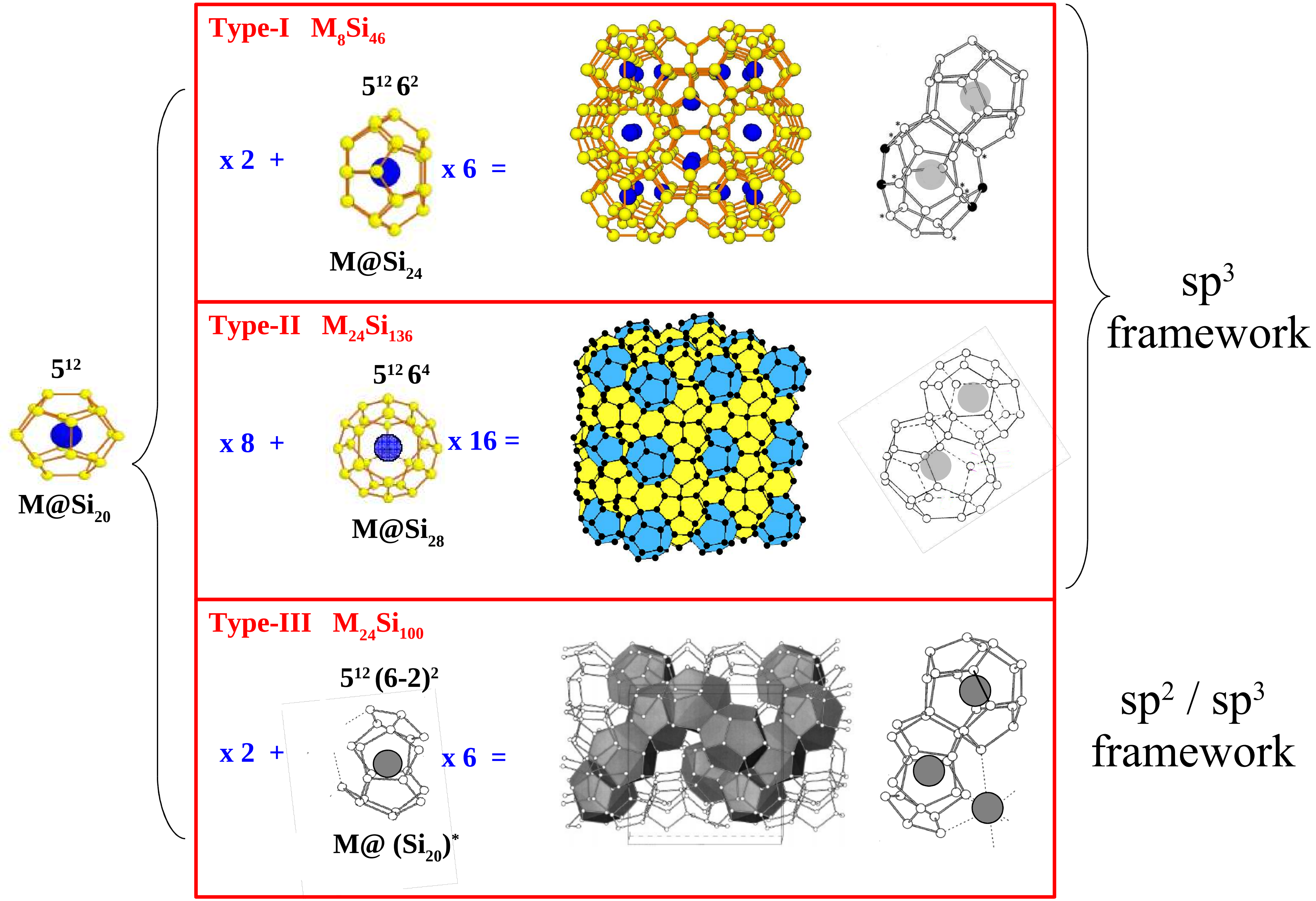
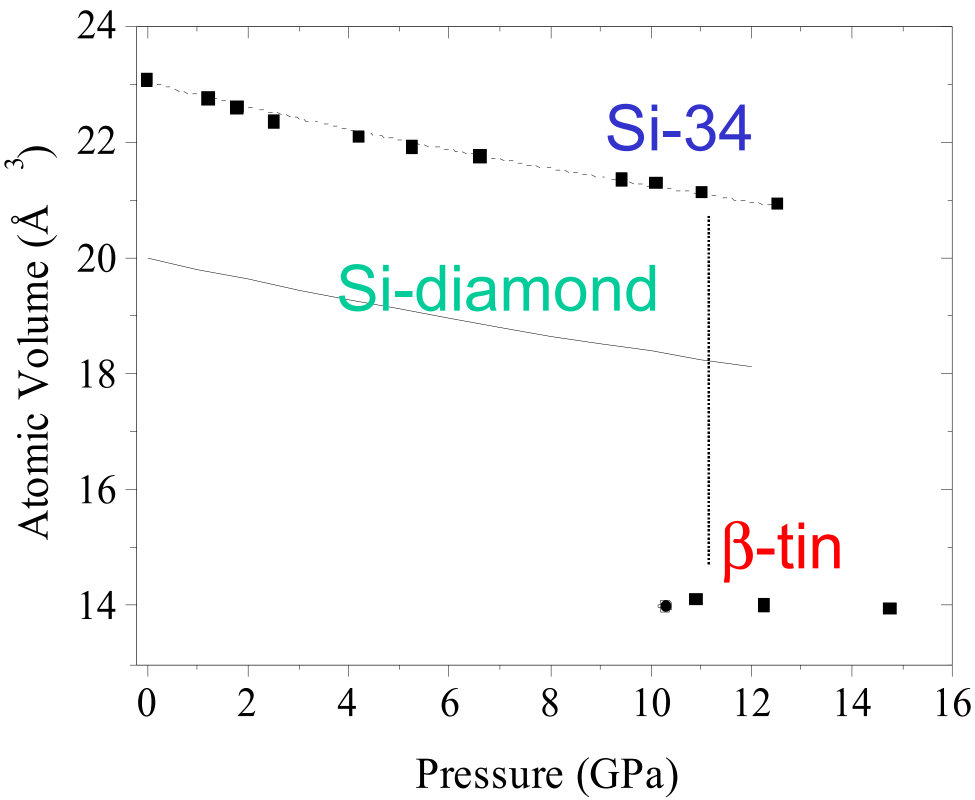
# Matériaux Nanostructurés homogènes

- Nanocristaux
- Cristaux de nanocages: fullerites et clathrates
- Assamblages de nanotubes

# Main clathrate structures



# Stability @ HP of empty clathrates




- Nanocages network stable → 11 GPa !
- $P_t$ ($Si_{136}$) ≈ $P_t$(Si-diamond)

- 1st order transition
- $\Delta V/V$=0.33 !
- for P > $P_t$ Si-diamond phase diagram

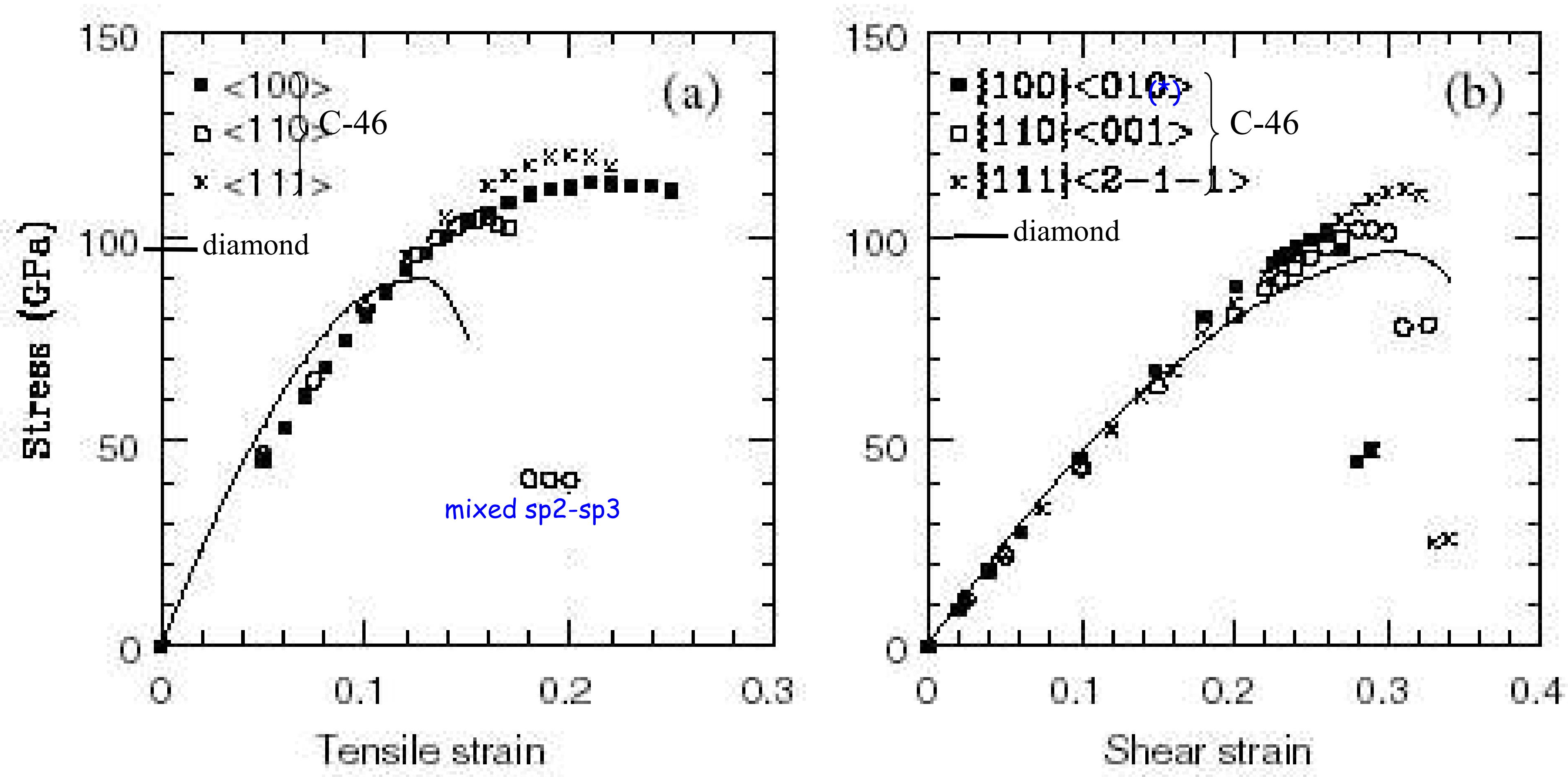
- $B_0(Si_{136})$ ≤ $B_0$(Si-diamant)
  = 90 GPa = 98 GPa

**Clathrates = low compressible & very stable !**

*A. San Miguel et al.,*
PRL 83 (1999), PRB 65 (2002).

# Carbon clathrates : harder than diamond ?

**Ideal strength :** *maximum stress that a single crystal can sustain before yielding to a plastic deformation*



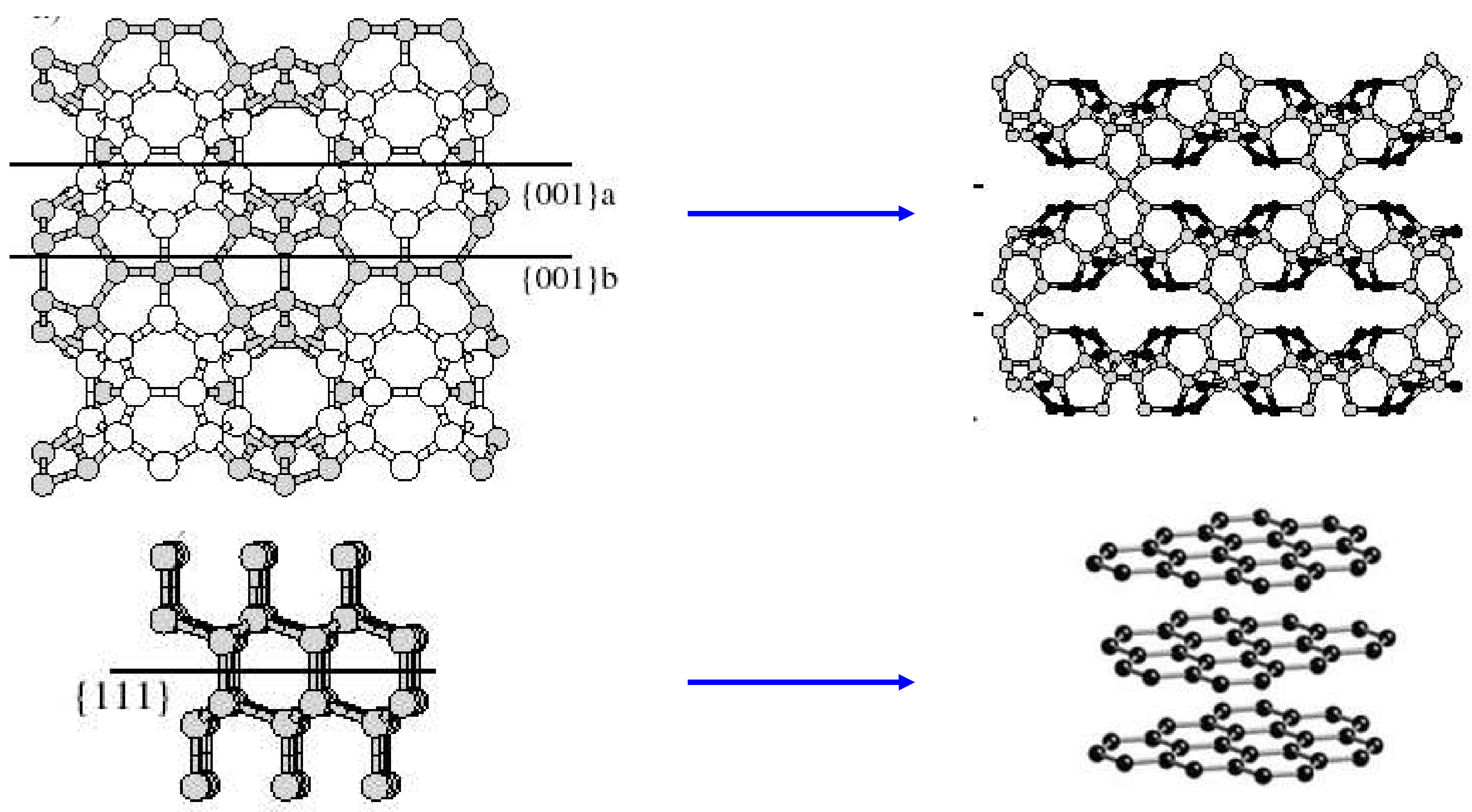

ab initio LDA-DFT Siesta

(*) Shearing the {100} slip plane along the <010> direction

X. Blase, P. Gillet, A. San Miguel and P. Mélinon, Phys. Rev. Lett. **92** (2004)

# Carbon clathrate/diamond stability

The clathrate cage structure frustrates the existance of easy slip planes and Diamond/graphite instability




Diamond (111) easy slip plane : - Clivage plane ; - Unstability towards graphite

# Cohesion of Si intercalated clathrates

| | $B_o$ exp. (GPa) | $B_o$ calc. (GPa) | $B_o$calc –$B_o$(Si-2) (%) |
|---|---|---|---|
| $Xe_8$Si-46 | N.S. | 85 | 12 |
| Si-46 | N.S. | 87 | 10 |
| Si-34 | 90±5 | 87.5 | 9.5 |
| $Ba_8$Si-46 | 93 ±5 | - | - |
| $I_8$Si-46 | 95±5 | 91 | 6 |
| $Te_8$Si-46 | N.S. | 95 | 2 |
| $Sn_8$Si-46 | N.S. | 96 | 1 |
| Si-2 diamond) | 97.88 | 97 | 0 |

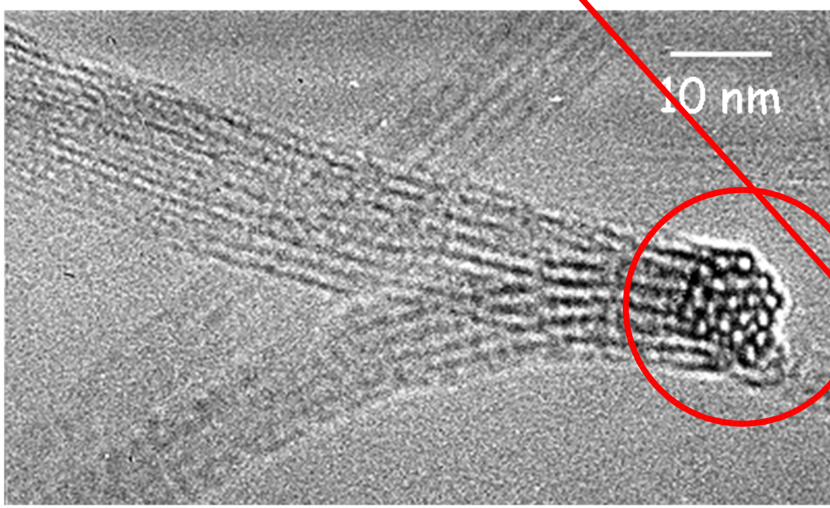
✓ Intercalation can improve cohesivity

A. San Miguel, P. Mélinon, X. Blase et al., Phys. Rev. B. **65** (2002)

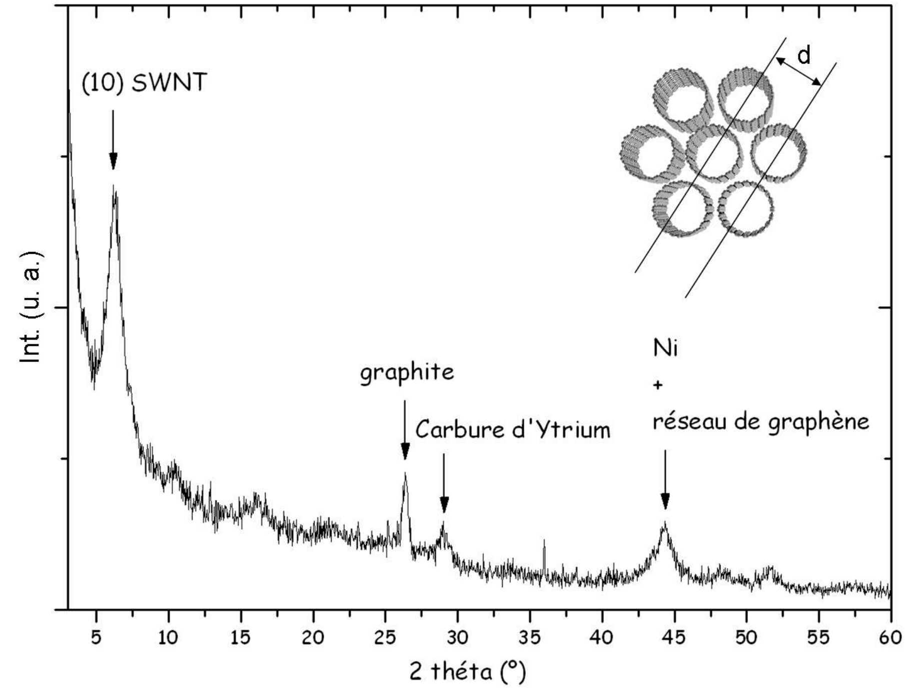
# Nanotubes assemblés

# Les nanotubes de carbone monoparois
# Structure et propriétés

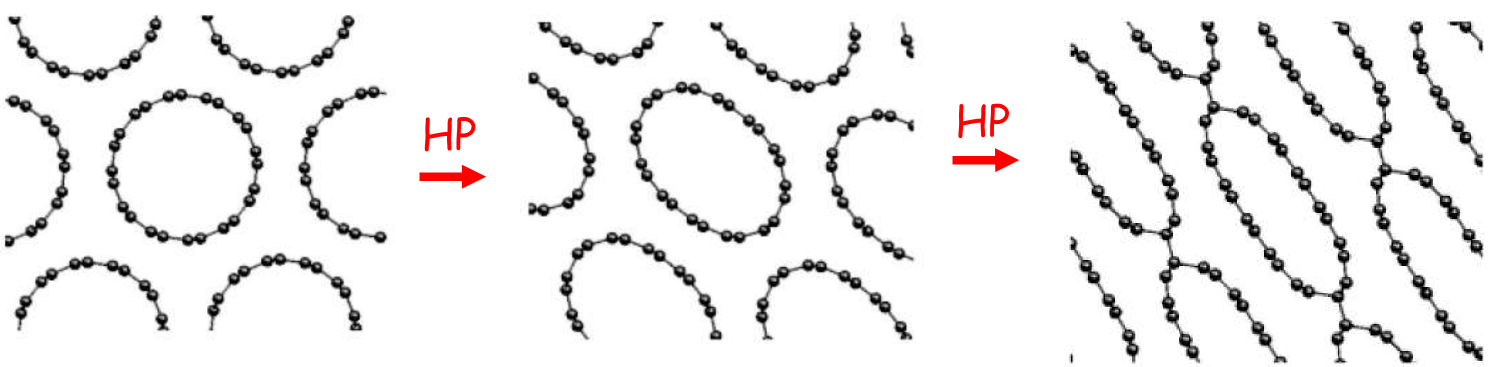
Organisation en fagots




C. Journet et al., Nature (1997)



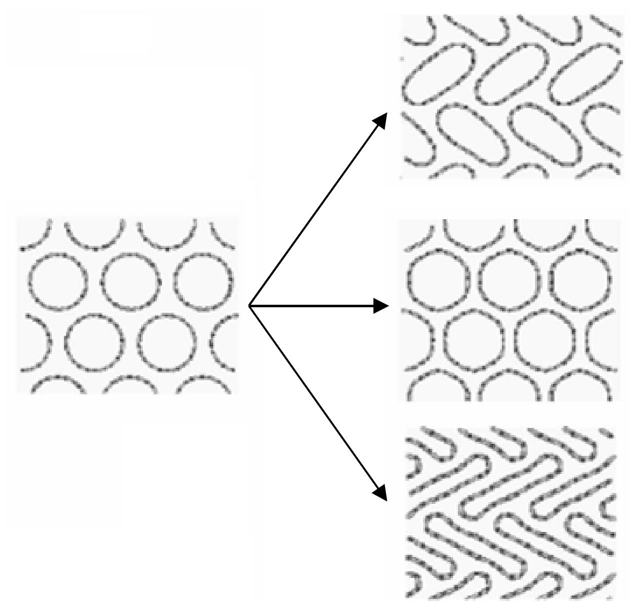

Diffraction de rayons X des fagots des nanotubes de carbone




Reich et al., phys. Stat. Sol. (b) (2003)

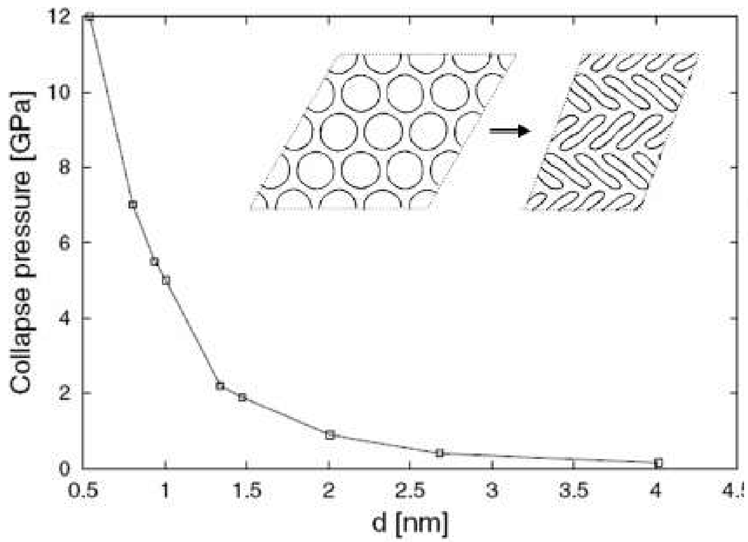
# Les nanotubes de carbone sous pression

<u>Changement de section</u>



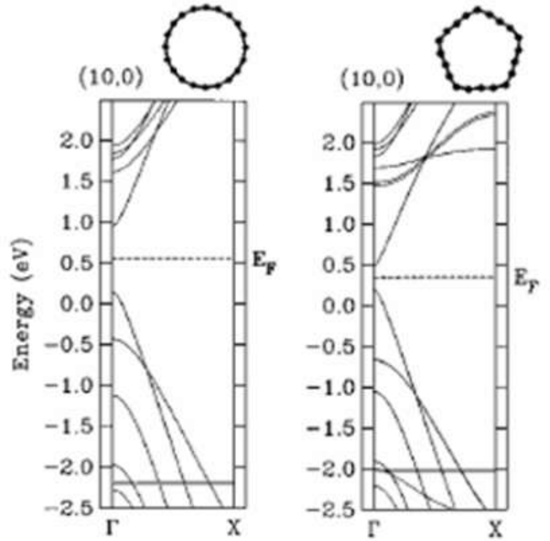
S.P. Chan et al. (2003)

<u>Pression de transition</u>



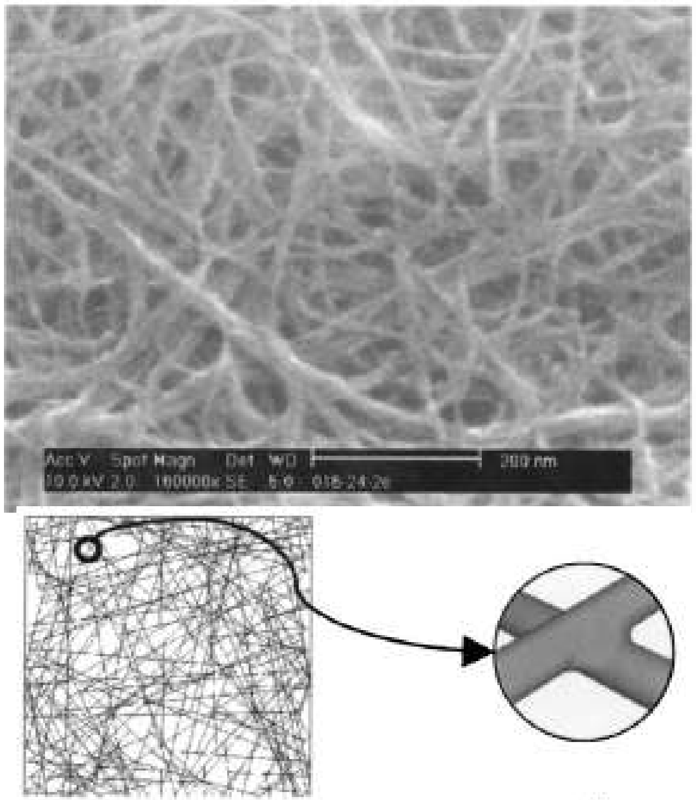

Elliot et al. (2004)

<u>Évolution des propriétés électroniques</u>

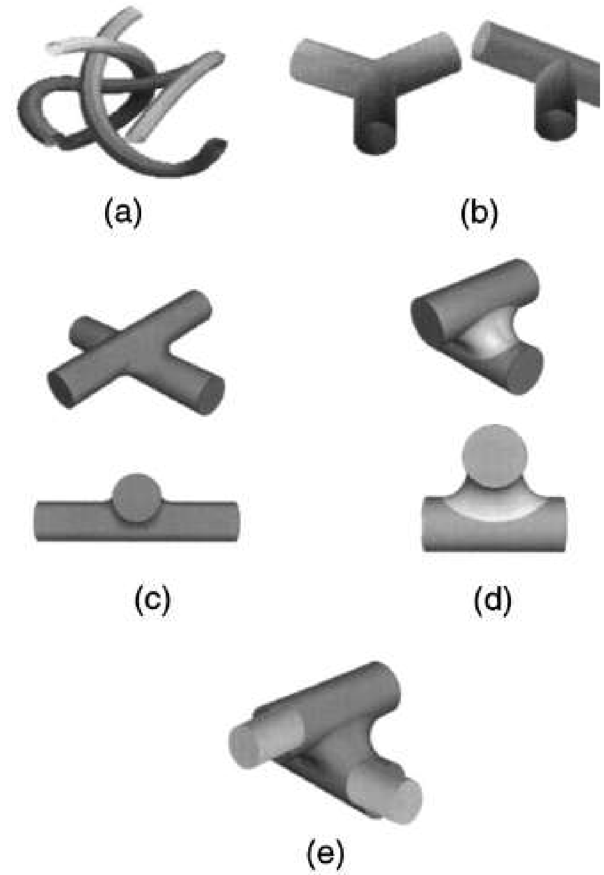



Charlier et al. (1996)

# Sheets of nanotubes (buckypaper)




SEM image (left) and modelization (right) of a buckypaper




Various observed morphologies of joints in nanotube mats,

Measured Young's moduli in produced nanotube sheets have been reported up to 60 GPa, but also with very low values (2 to 4 GPa).

The critical parameters are the mean number of crossings per fiber, the mean segment length, and bonding between tubes.

L. Berhan et al., J. Appl. Phys., 95, 15 (2004)

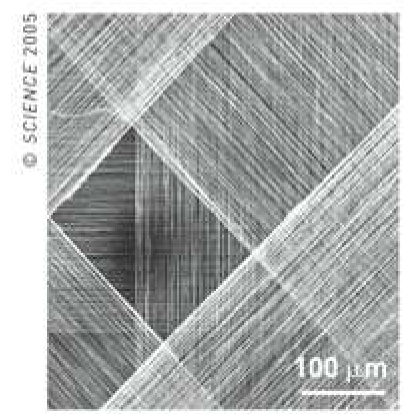
# Industrial elaboration of NT Sheets

Researchers at the University of Texas at Dallas, US, and Commonwealth Scientific and Industrial Research Organization (CSIRO) Textile and Fibre Technology, Australia have drawn multiwalled carbon nanotubes into transparent sheets that are **5 cm wide and 1 m long and about 15 microns thickness.**

**-Sheets made from CVD grown oriented MWNT**

**- Production rate : 7 meters per minute!**

- Electronically conducting with a density of 0.0015 g/cm3
- Sheets could be densified (through surface-tension effects by inmersion in methanol) up to 0.5 g/cm3.
- An array of 8 sheets had a strength comparable to milar or capton.




Four sheets cross-oriented to provide the same strength in all directions

M. Zhang et al. Science (2005) 309, 1215

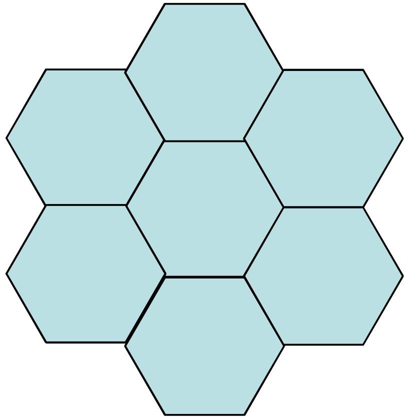
# Heterogeneous Nanomaterials: Nanocomposites

**Composites**: A combination of two or more simple materials to yield another material with better properties.

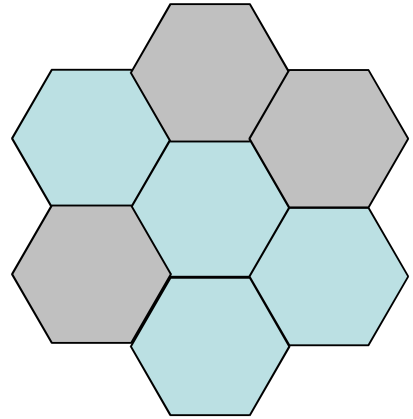
From the point of view of applications we can consider 3 main classes:

- **Particle composites** (sinthered ceramics)
- **Fiber composites** (kevlar, safety glass)
- **Sandwich composites** (glass protection layers)

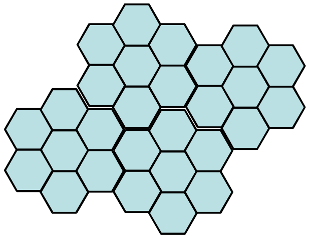
# Particle composites : Ceramic or metallic nanocomposites types



Monolythic ceramic

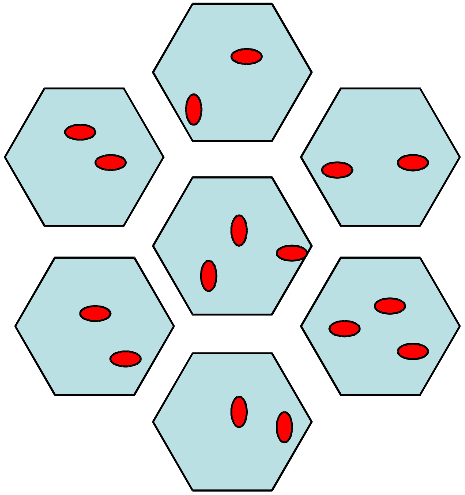


Microcomposite

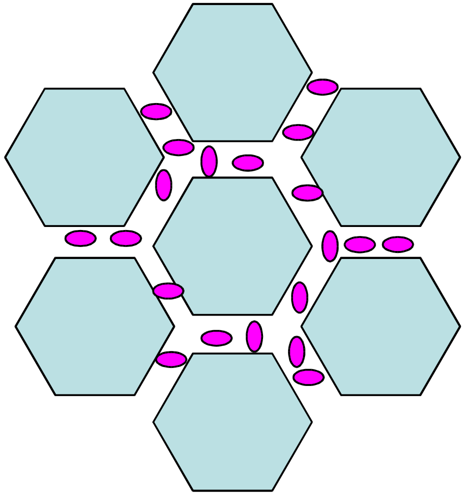


Monolythic nanoceramic

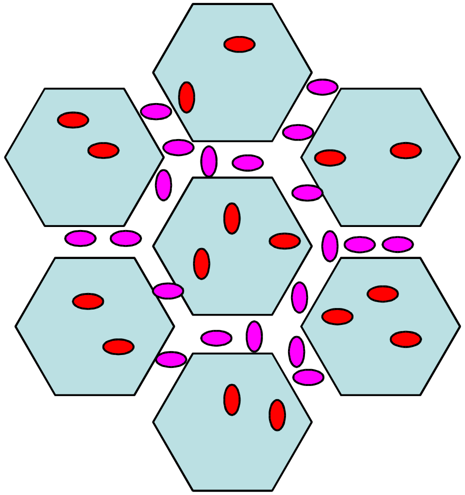
## Nanocomposites



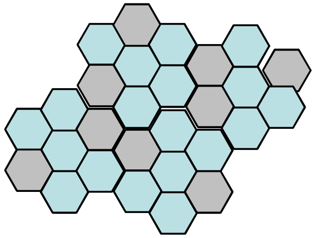
Intra-type



Inter-type



Intra/Inter-type



nano/nano-type

# Advantages of nanocomposites

• **Intra**granular dispersion: generate and ***fix dislocations*** during processing, annealing, cooling.

• **Inter**granular nanodispersion: must have **a *role in the grain bundary*** structures in oxides (Al2O3 or MgO) and nonoxyde (Si3N4, SiC) ceramics, which improve their high-temperature mechanical properties (the creep region).

In general, dispersion of soft materials into a hard ceramic generally decreases its mechanical properties (eg. Hardness).

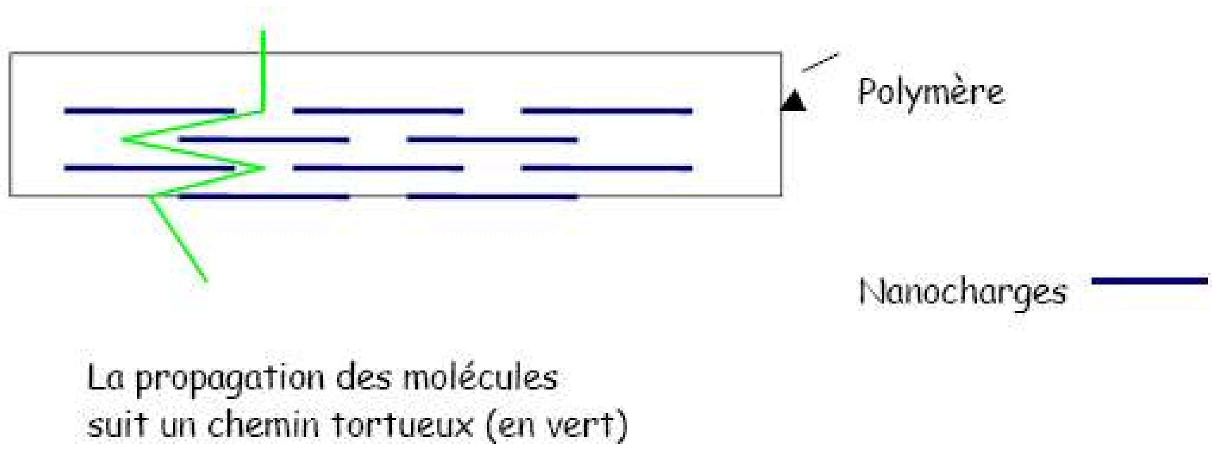
However, in nanocomposites, soft materials added to several kinds of ceramics can improve their mechanical properties.
**Example**: adding h-BN to silicon nitride (Si3N4) ceramic can enhance its fracture stregt at room anat very high temperature up to 1500 C.

# Sandwich nanocomposites: application to food conservation

La présence de nanoparticules de taille nanométrique dans le polymère :

- augmente les propriétés mécaniques et thermiques
- certaines nanoparticules, comme l'argile,permettent d'accroître la résistance au feu
- améliorent les propriétés barrières
- elles permettent également l'absorption des UV.

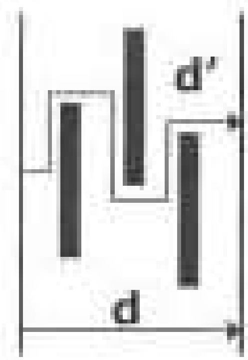
et tout ça sans augmenter la densité du polymère de base et sans réduire ses propriétés optiques ni sa recyclabilité.



# Sandwich nanocomposites: application to food conservation

**Tortuosité $\tau$**

$$\tau = d' / d = 1 + \Phi_s \, L / 2w$$




**Dimension des plaquettes**
- **L longueur**
- **w épaisseur**

**Fraction volumique de plaquettes $\Phi_s$**

**Effet de la tortuosité sur la perméabilité**

$$P_s / P_p = 1 - \Phi_s / \tau$$

**$P_s$ nanocomposite**
**$P_p$ polymère**

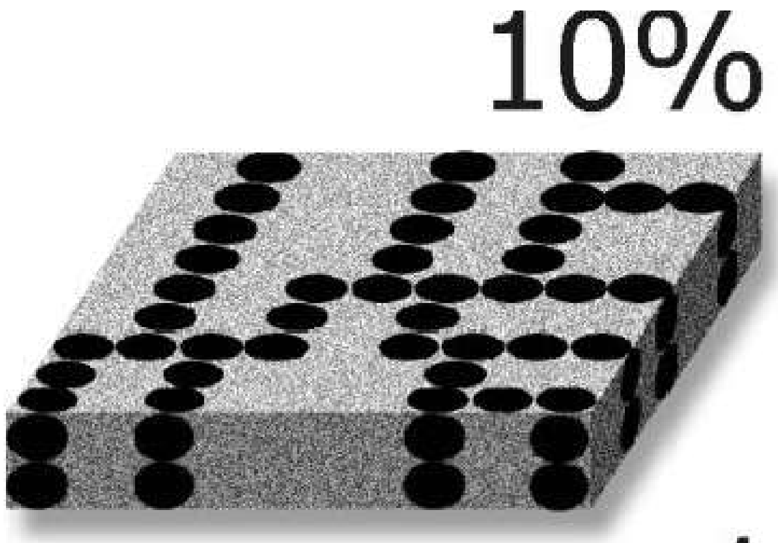
*Durethan® BASF Co.* Développé avec Nanocor, amélioration de la barrière O2 de 50 %.

*Nanocomposites PA-6* : *Aegis® Honeywell Co. Et Capron XA-3071® Honeywell Co.*

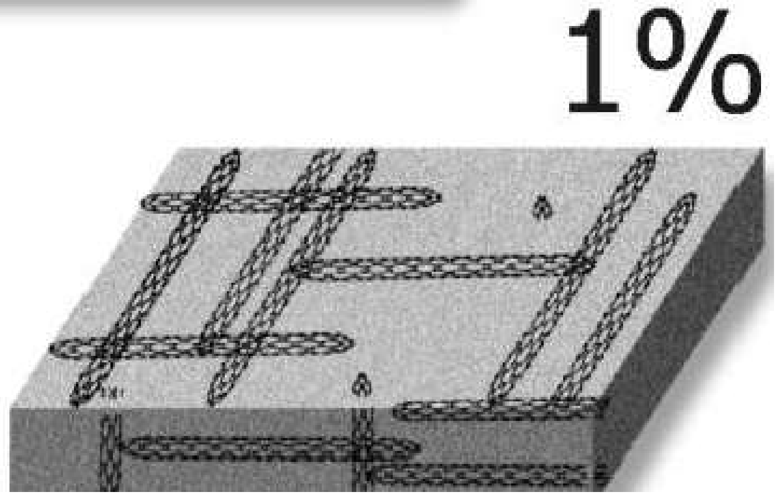
*Imperm® Mitsubishi Gas Chemical/Nanocor Co.* (Remplacement de la couche EVOH dans les flacons Ketchup). Le polymère utilisé est le Nylon MXD6 associé à des nanocharges. La résine semi-cristalline est une très bonne barrière aux gaz. Elle est même exceptionnelle à forte humidité. Grâce aux nanocharges, la conversion de MXD6 est un succès, faisant de ce matériau une barrière supérieure à celle de l'EVOH, la plus commune des barrières.

# Fiber composites : CNT / polymer composites

- Current technology
  - carbon black
  - 10 – 15 wt% loading
  - loss of mechanical properties



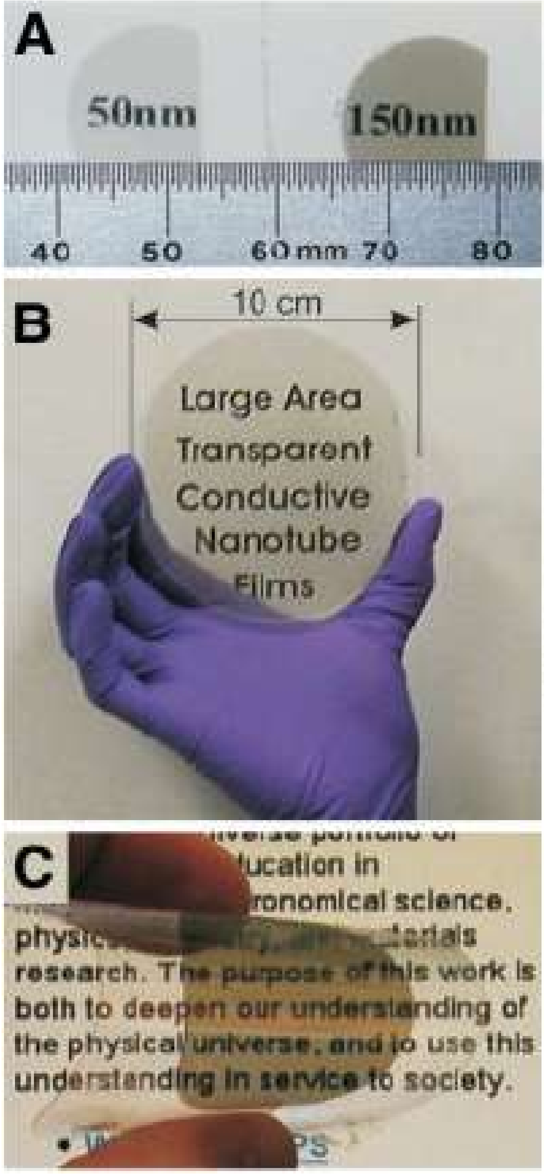

- CNT composites
  - 0.1 – 1 wt% loading
  - low percolation treshold



# Fiber composites : CNT / polymer composites

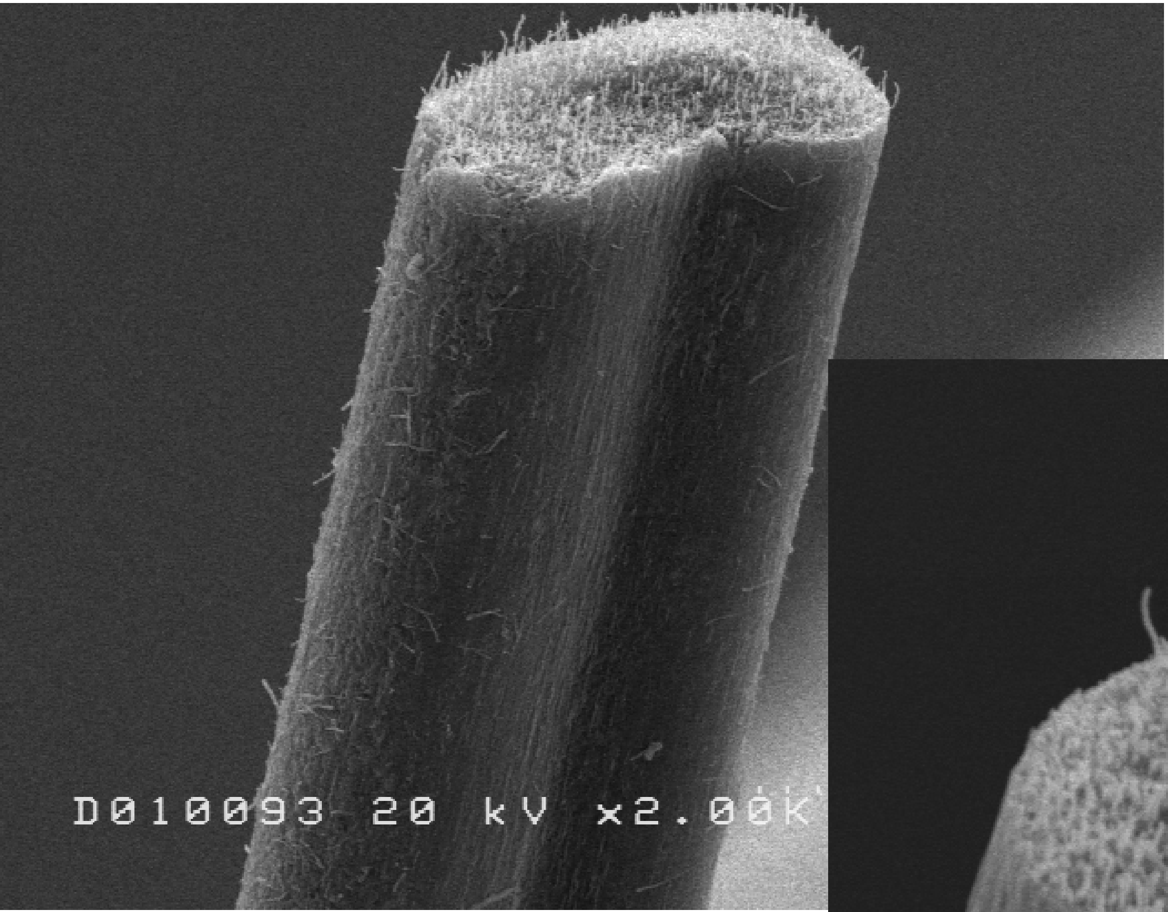
• Transparent electrical conductor

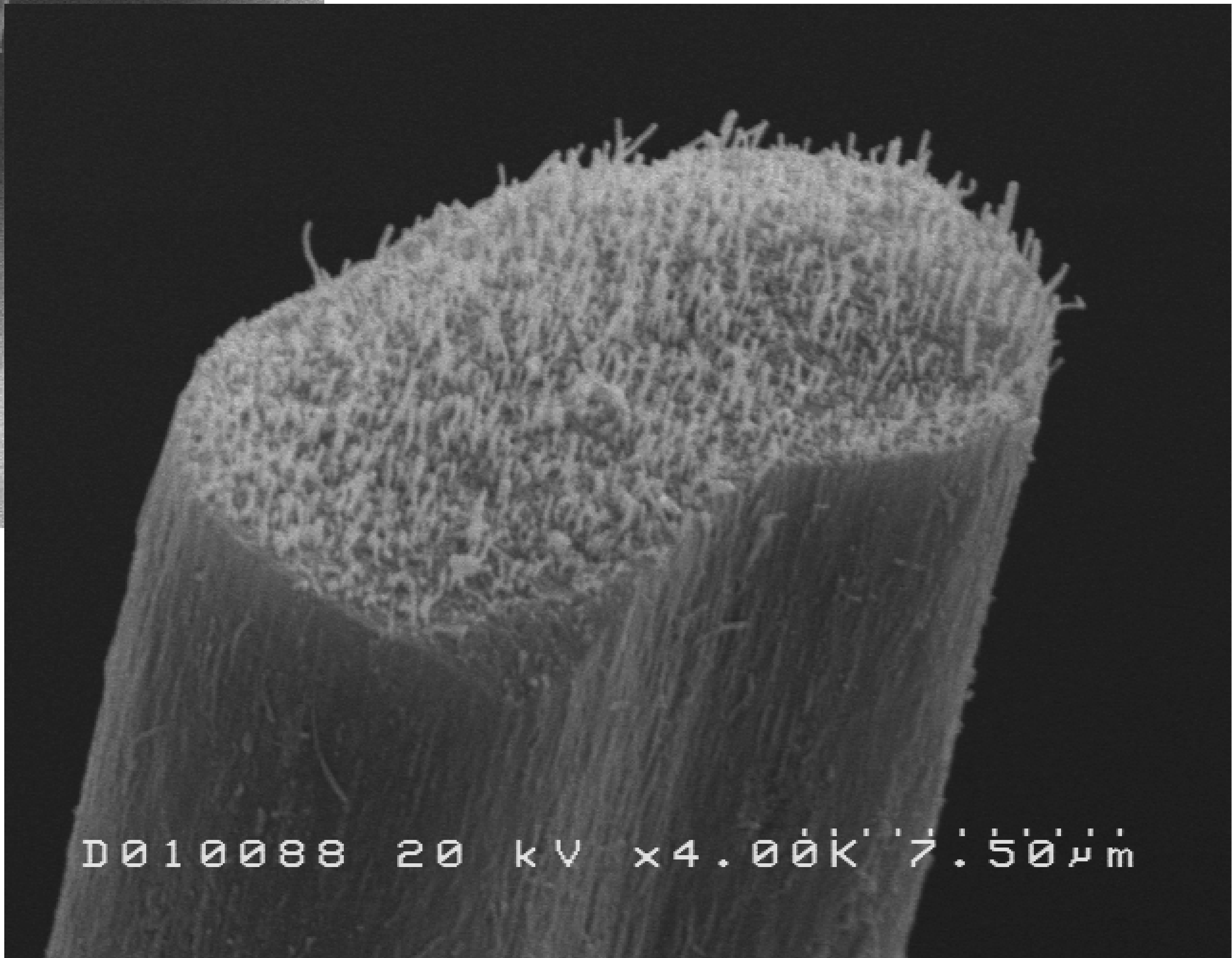
- Thickness: 50 – 150 nm
- High flexibility



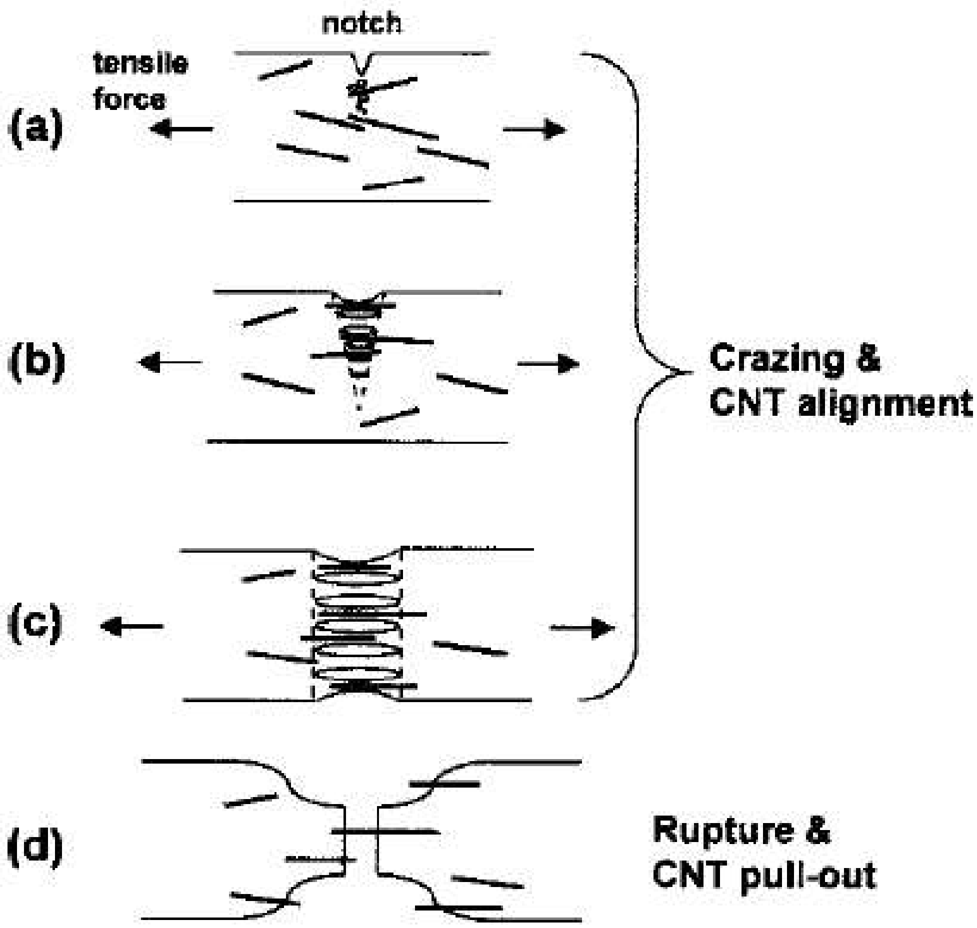

Wu *et al*. Science **305** (2004) 1273.

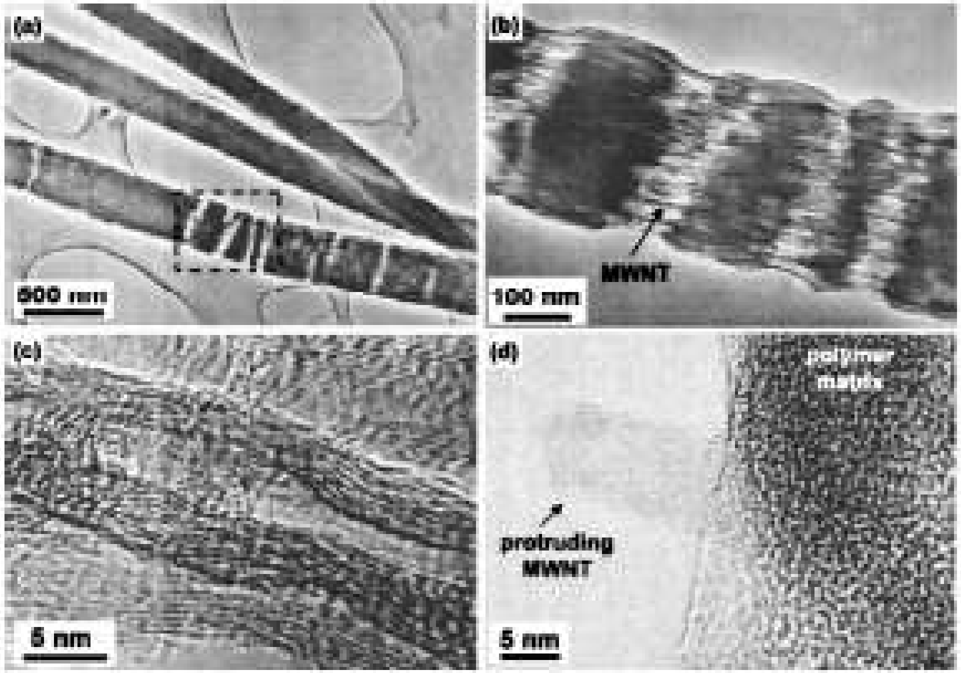
# 20 wt% MWNT/Carbon Fiber



# Fiber reinforcement in carbon nanotube composites




carbon nanotube–polyacrylonitrile composite fibers

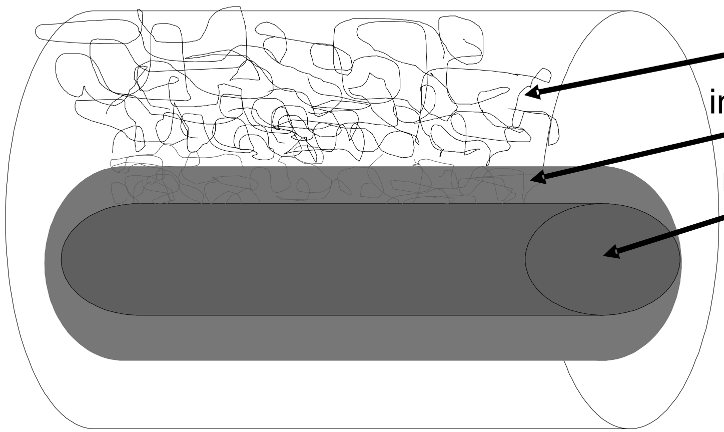
CNTs reinforce the fiber by pull-out and bridging mechanism

H. Ye et al., Appl. Phys. Lett.,
Vol. 85, 1775 (2004)

# Issues at the Interface

Interfacial region, or interaction zone, can have different properties than the bulk polymer:

- chain mobility,
- entanglement density,
- crosslink density
- geometrical conformation



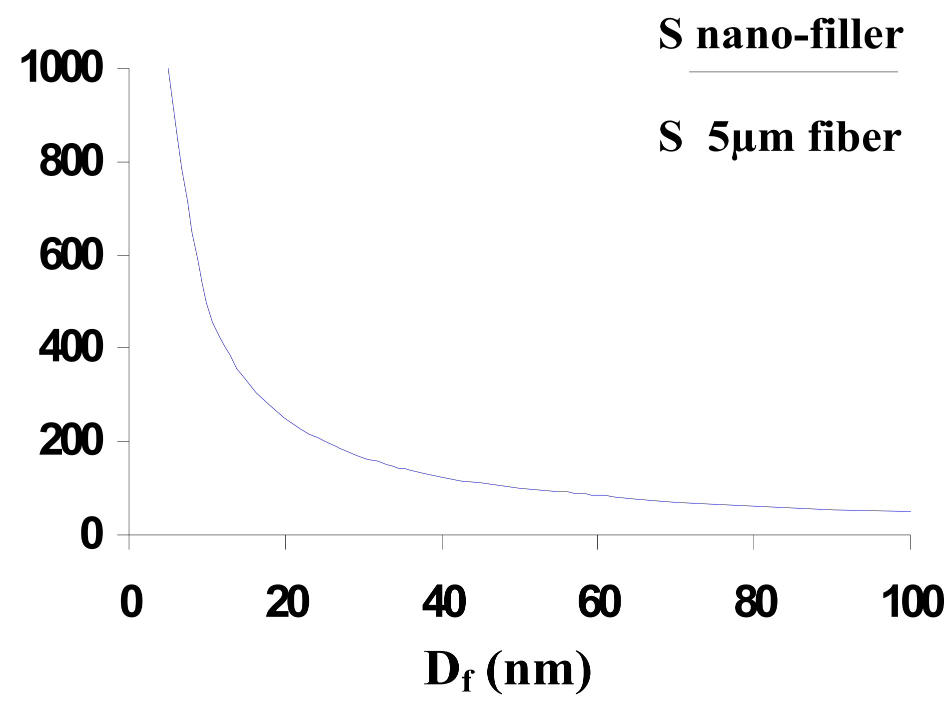

Unique reinforcement mechanism

- diameter is of the same size scale as the radius of gyration
- can lead to different modes of interactions with the polymer.
- possible wrapping of polymer chains around carbon

# MWNT/Matrix Interface

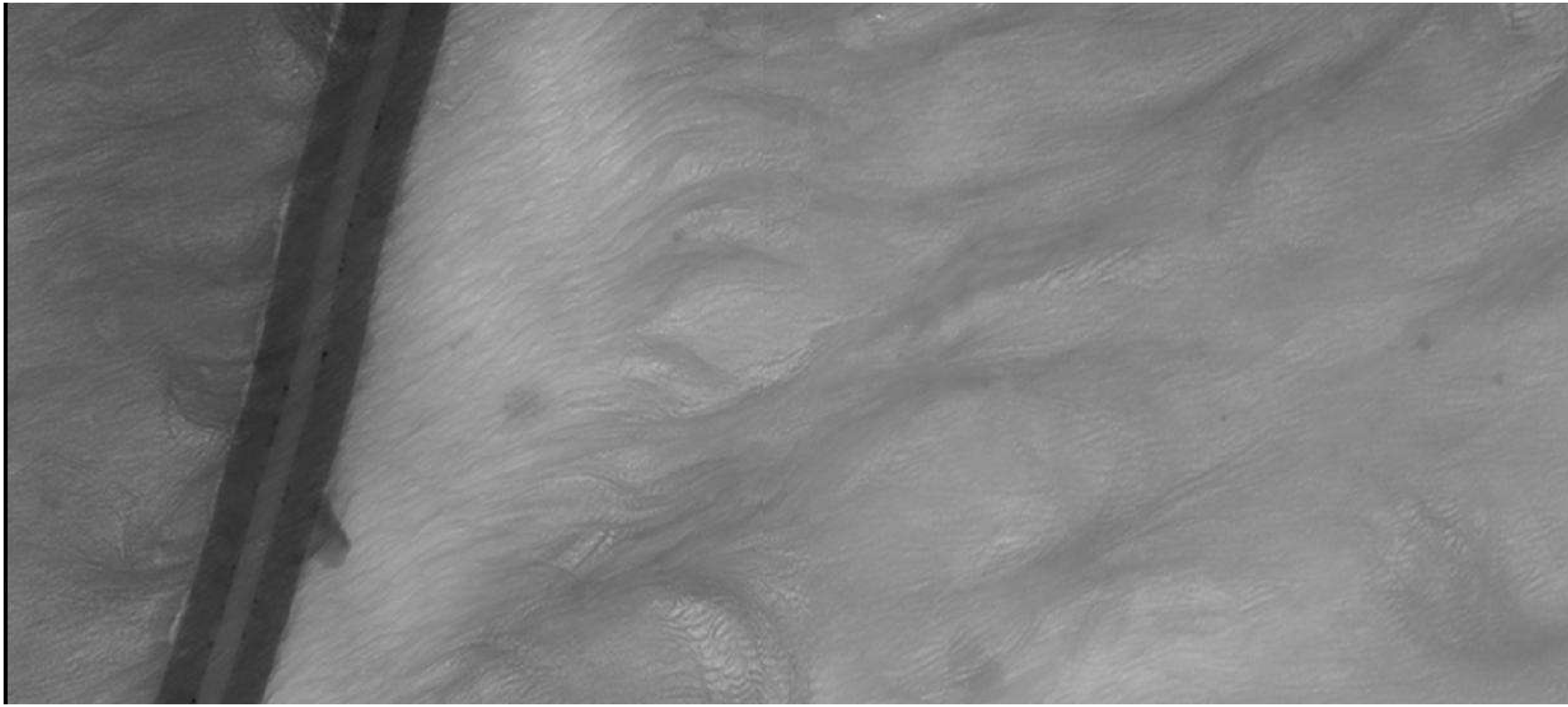
- The volume of matrix that can be affected by the nanotube surface is significantly higher than that for traditional composites due to the high specific surface area.

- 30nm diameter nanotubes have about 150 times more surface area than 5 µm fibers for the same filler volume fraction




Ding, W., et al., *Direct observation of polymer sheathing in carbon nanotube-polycarbonate composites.* Nano Letters, 2003. **3**(11): p. 1593-1597.

# Interphase Region



200 nm

- Nanotube effecting crystallization of PP
- Sandler et al, J MacroMol Science B, B42(3&4), pp 479-488,2003

# Polymer Nanocomposites

• **Particle dispersion**: fillera ggregation leads to better mechanical properties

• **Polymer-filler intercations**: more important in the rubbery plateau (T> Tg) rigidifying the structure

• **Filler-Filler interactions**: filler networks plays an important rôle in the reinforcement of nanocomposites at T>Tg.
Debate on the contribution of Two main effects :

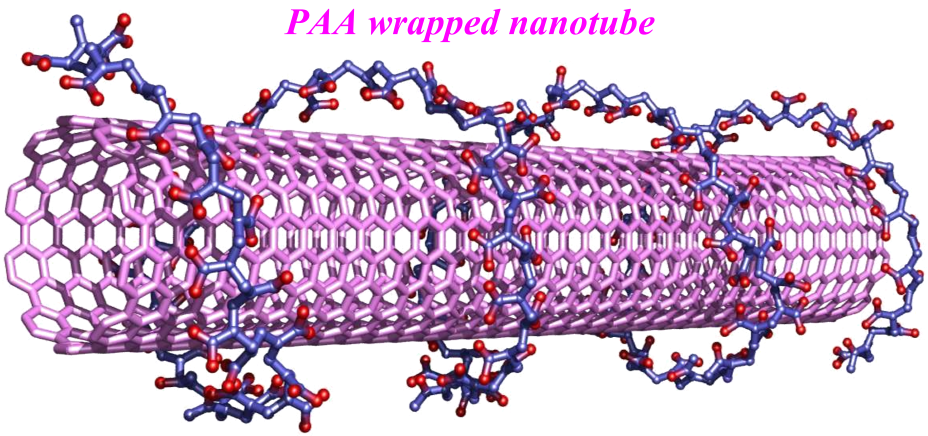
- formation of a flexible filler network
- immobillized polymer interphase

.

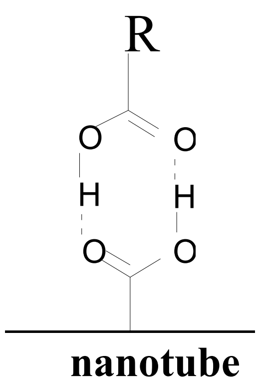
# Polymer-filler interactions: Two Approaches for Surface Modification of MWNTS

- Non-covalent attachment of molecules
  - van der Waals forces: polymer chain wrapping
  - Alters the MWNT surface to be compatible with the bulk polymer
  - Advantage: perfect structure of MWNT is unaltered
    - mechanical properties will not be reduced.
  - Disadvantage: forces between wrapping molecule / MWNT maybe weak
    - the efficiency of the load transfer might be low.
- Covalent bonding of functional groups to walls and caps
  - Advantage: May improve the efficiency of load transfer
    - Specific to a given system – crosslinking possibilities
  - Disadvantage: might introduce defects on the walls of the MWNT
    - These defects will lower the strength of the reinforcing component.

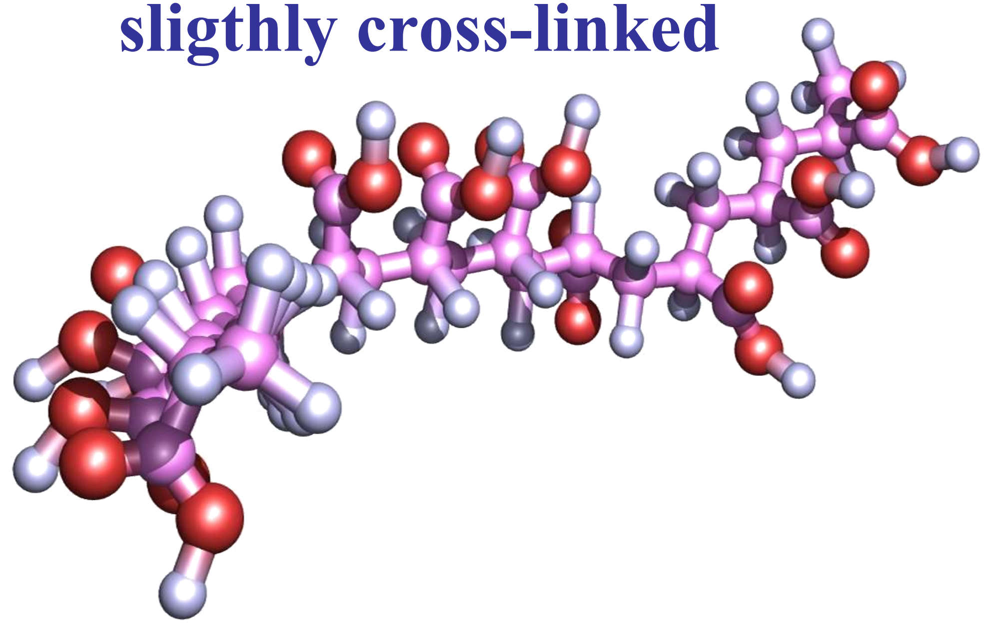
# Example of polymer-filler interactions:




**hydrogen bonds between the oxidized nanotubes and the PAA**



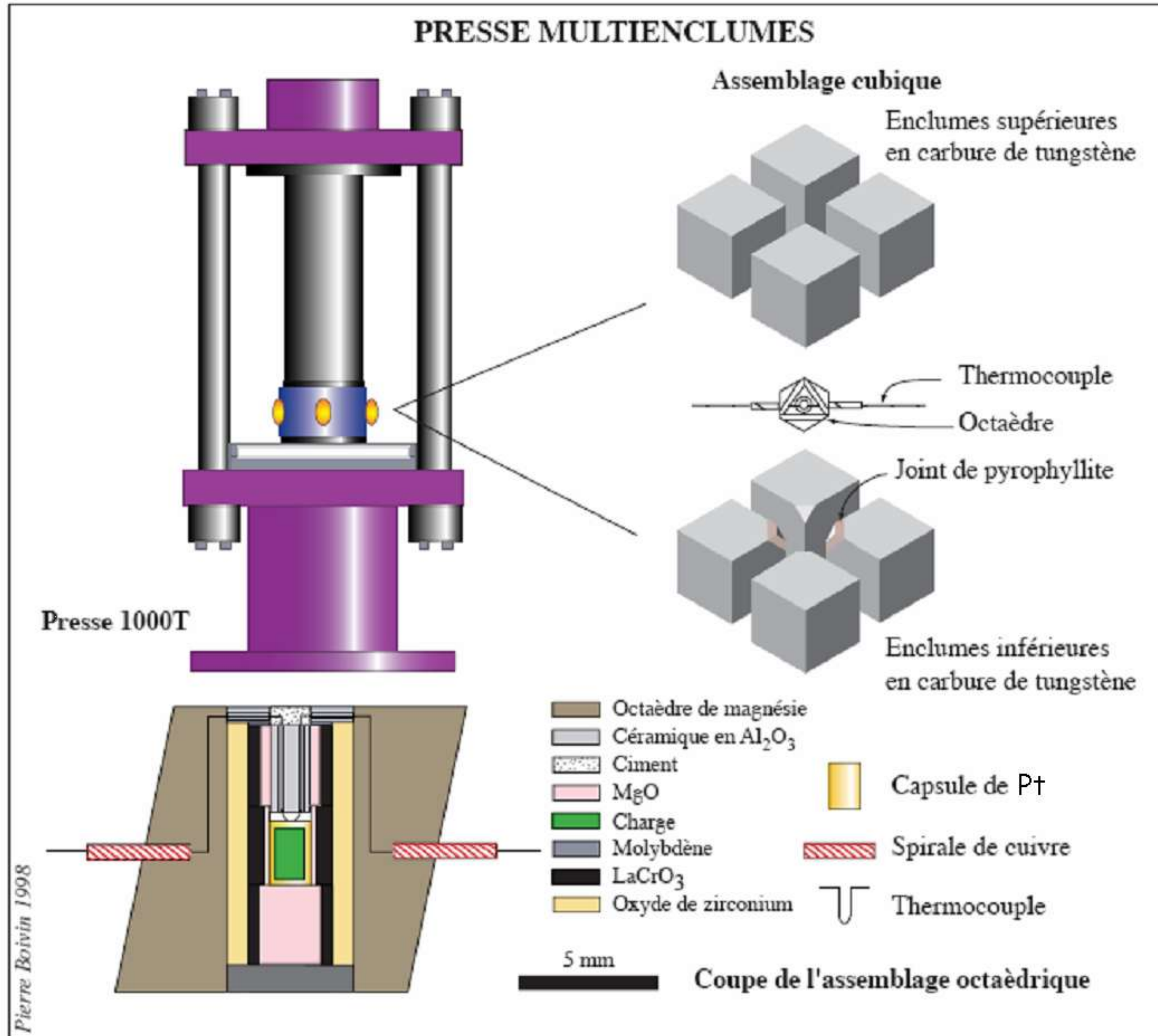

**PAA = poly acrylic acide partly potssium salt sligthly cross-linked**



# Mechanical methods
# for nanomaterials elaboration

- High pressure and high temperature methods
- Severe Plastic Deformation methods

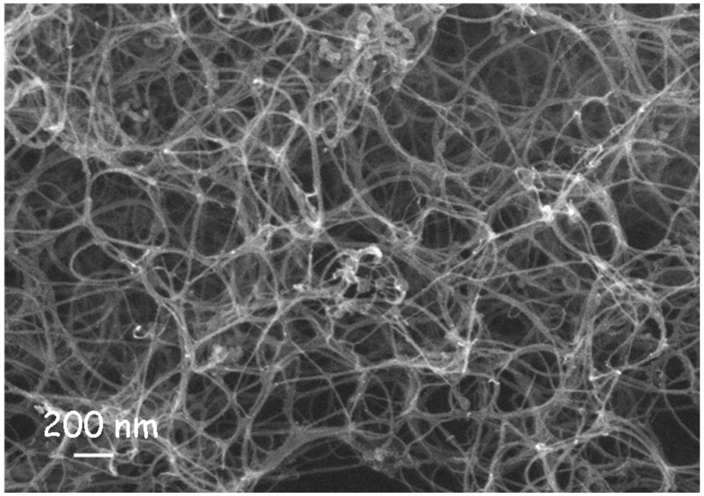
# Synthèse de phases carbonées à partir de nanotubes de carbone




<u>Gamme de pression</u>: 0-20 GPa
<u>Gamme de température</u>: 0-2000°C

# Synthèse de phases carbonées à partir de nanotubes de carbone

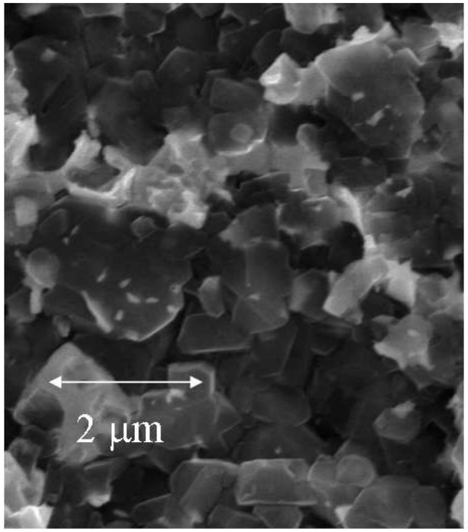
Conditions de synthèse: 14.5 GPa, 1500°C




Nanotubes vierges (Nanoledge©)

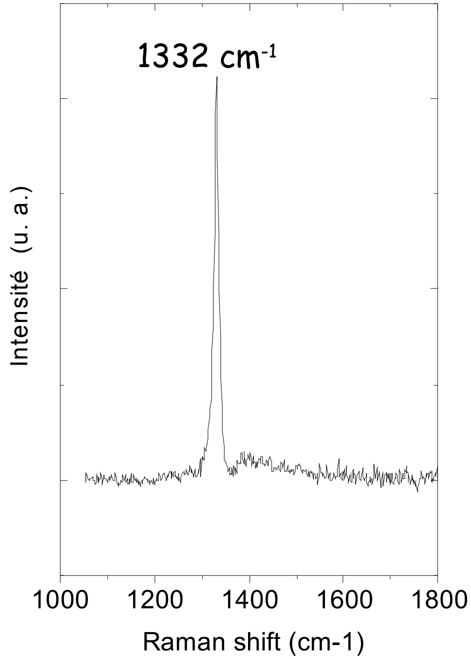
→ Synthèse HP-HT

MEB



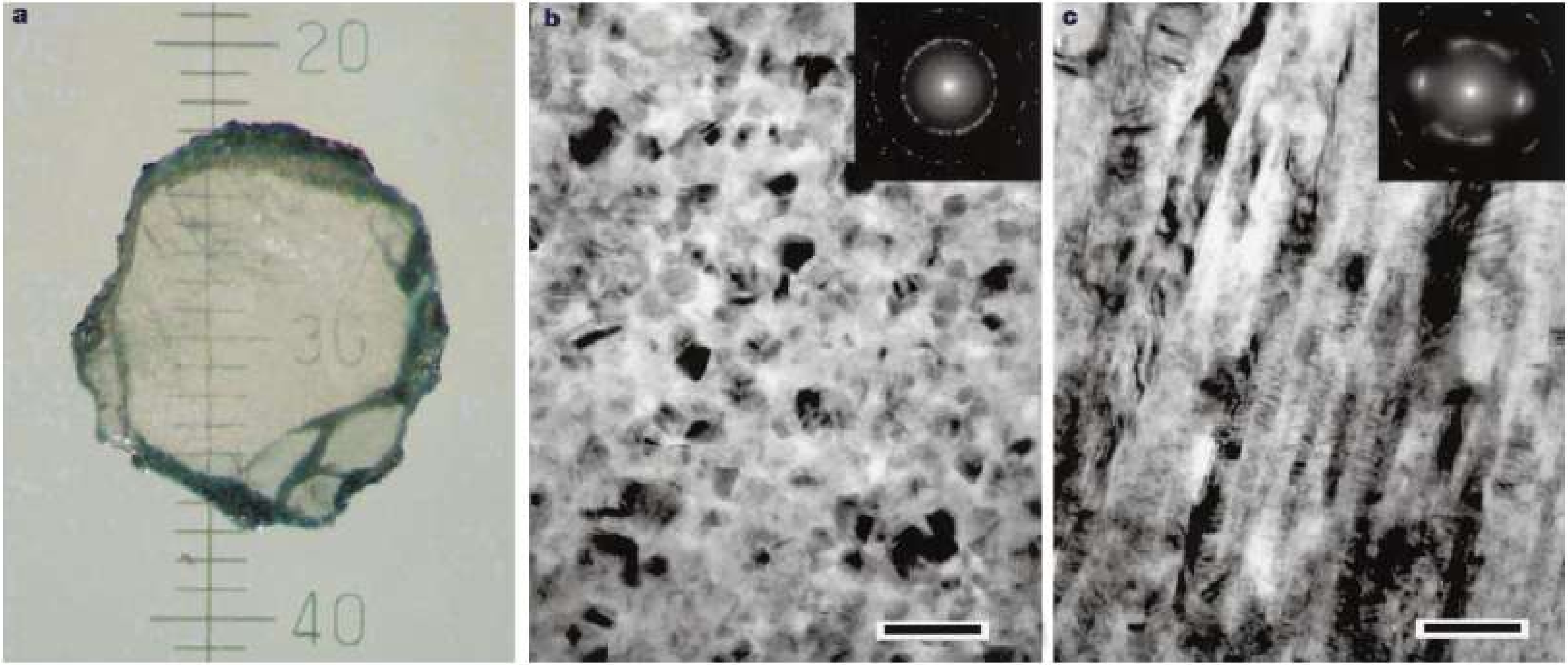

microcristallites

Spectre Raman




Synthèse de diamant

Diamant nanocristallin obtenu par transformation du graphite à P=12-25 GPa et T=2300-2500 C.




Dureté de Knop du diamant monocristallin : 60-120 GPa

Dureté de Knop du diamant nanocristallin : 110-140 GPa !!

T. Irifune et al. Nature (2003)

# Nanostructured superhard carbon phase obtained under high pressure with shear deformation from single-wall nanotubes HiPco

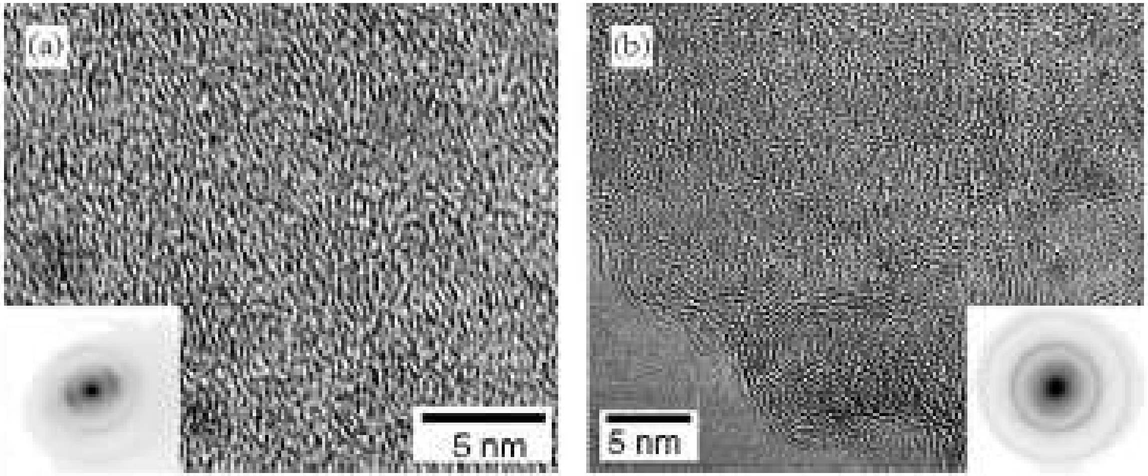



Fig. 7. HREM images and SAED patterns (insets) of some particles (a, b) of superhard phase.

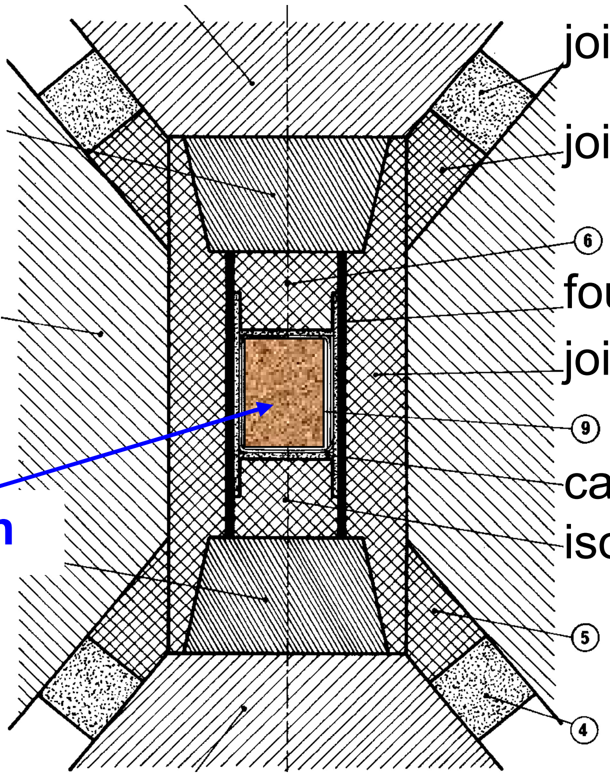
H = 58±6 GPa
comparable à c-BN

V.D. Blank et al. , Physica B 2006

Shear diamond anvil cell

# II
# Synthèse HP-HT des clathrates de silicium

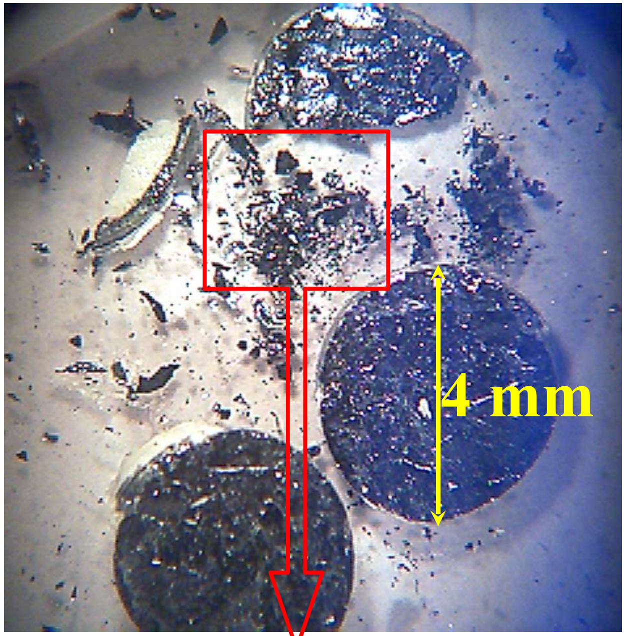
# Si-clathrates synthesis

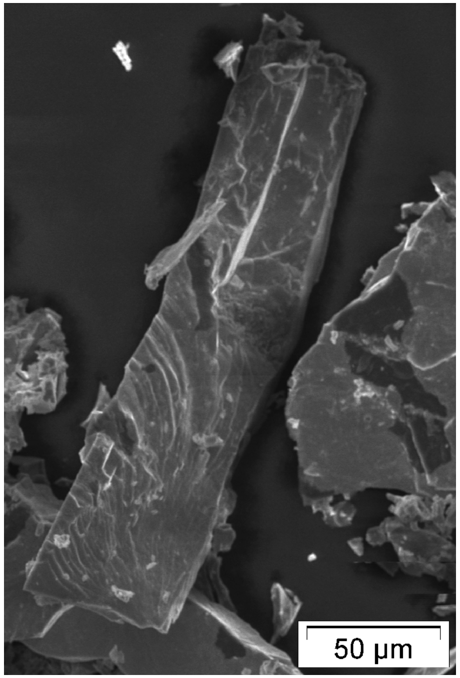



$P_{max}$ = 5 GPa

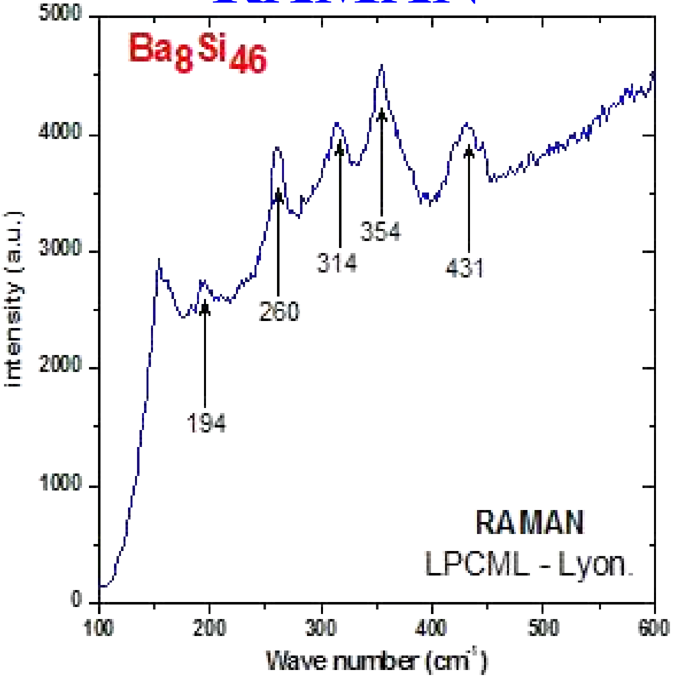
$T_{max}$ = 1500°C

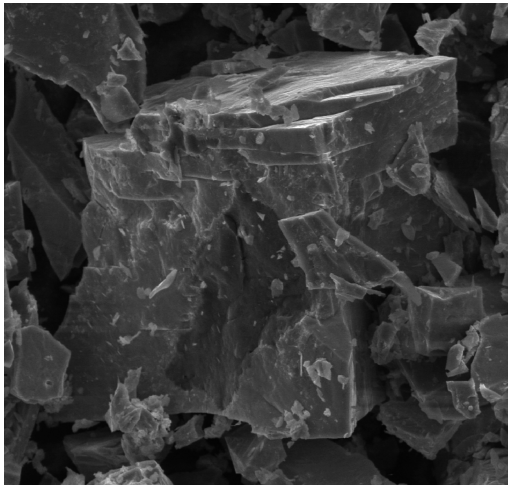
# $Ba_8Si_{46}$ (HP-HT) : crystals

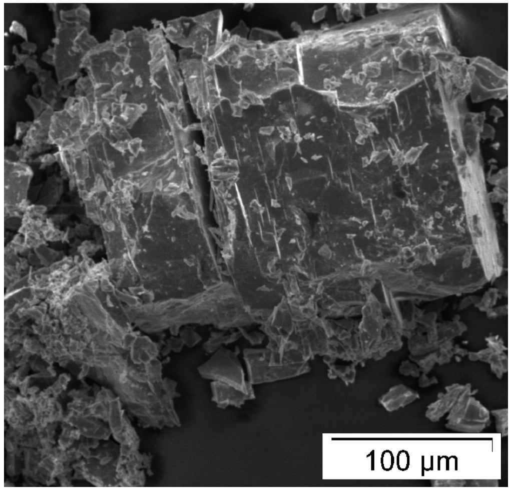



## RAMAN

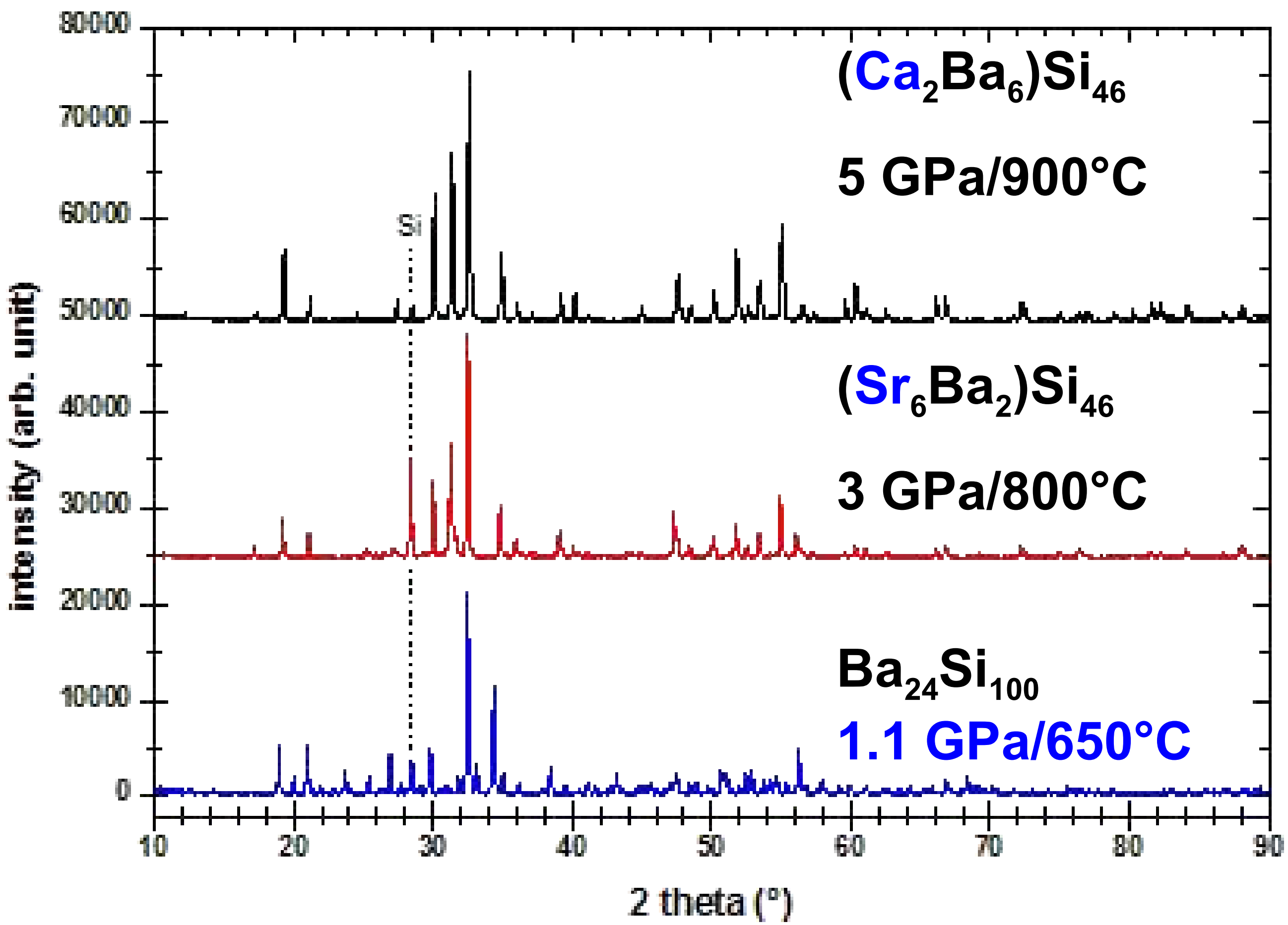


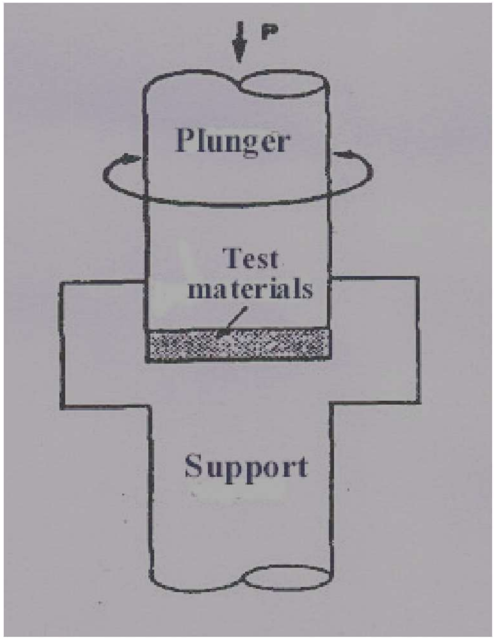


# Clathrates synthétisés à Lyon

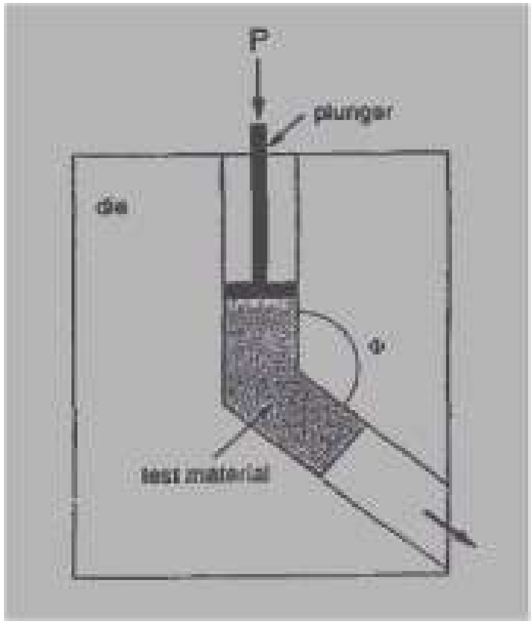
- $Ba_8Si_{46}$
- $M_xBa_{8-x}Si_{46}$ avec M=Sr,Ca
- $Ba_{24}Si_{100}$
- $Te_8(Si_{38}Te_8)$



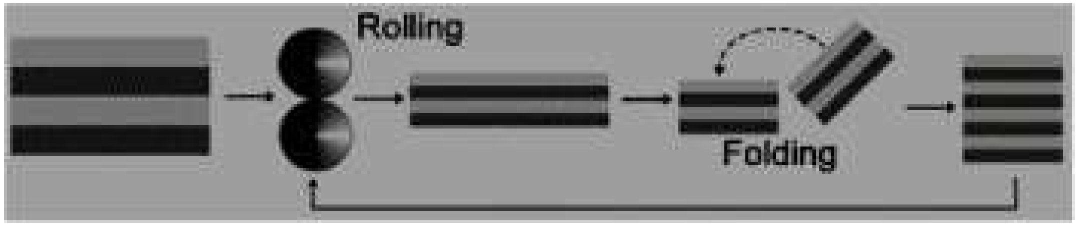
# Experimental techniques for Mechanically driven phase transformation



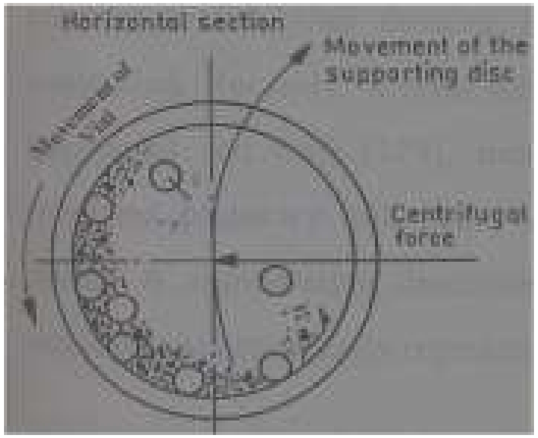

Angular torsion




Equal channel angular extrusion



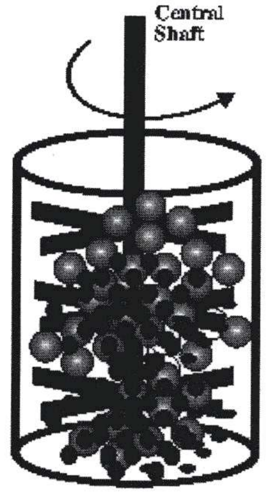

Pack
rolling



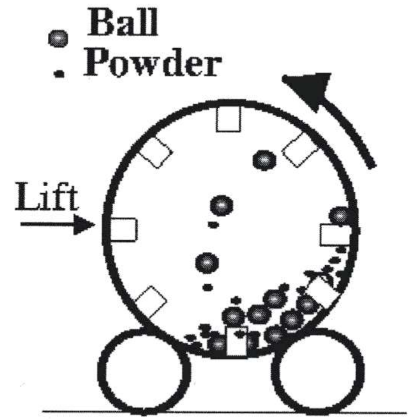

Mechanical milling

# Milling Machines

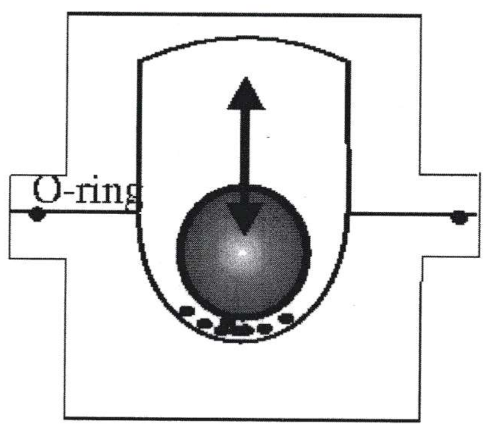
Milling Machines

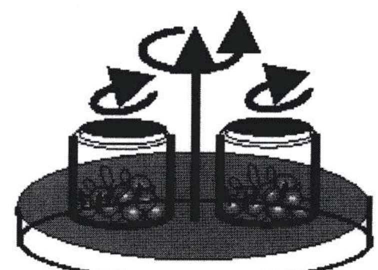

Attritor-type Mill



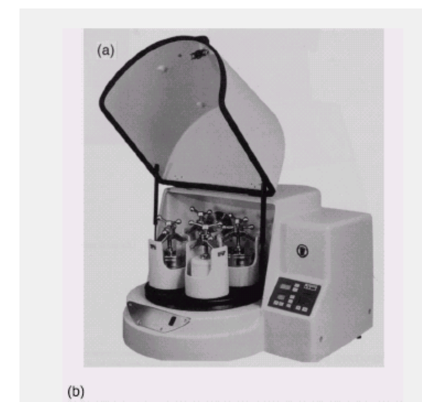

Horizontal Ball Mill

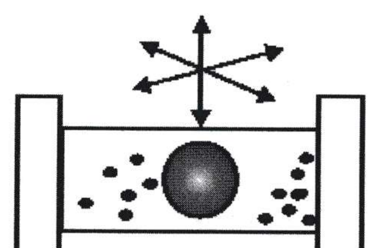



Vibratory Mill



Planetary Mill



Spex Mill (3D vibrations)

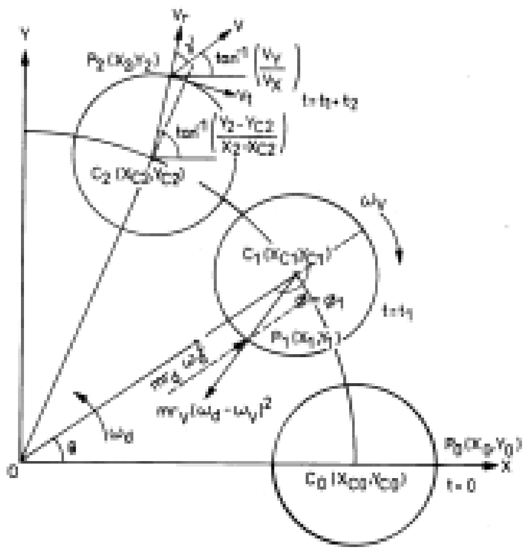
# Severe Plastic Deformation methods

Some precautions need to be taken :

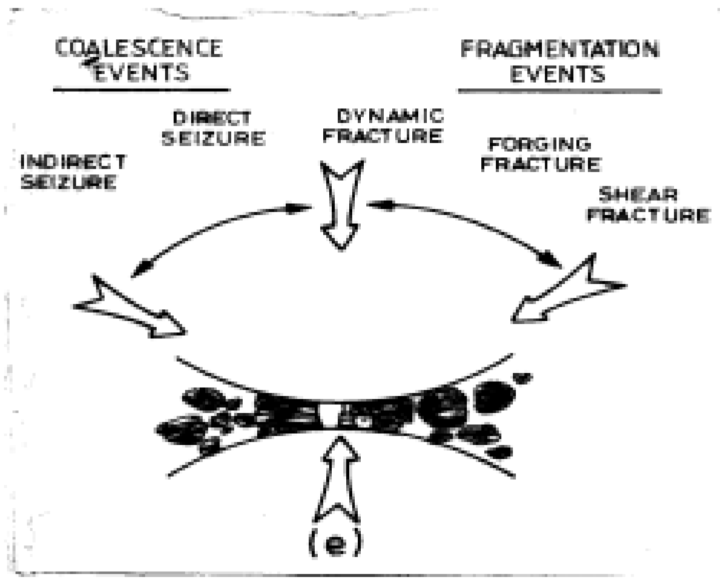
- Work under inert atmosphere

- Control of temparature. This leads to some standby to avoid too much heating

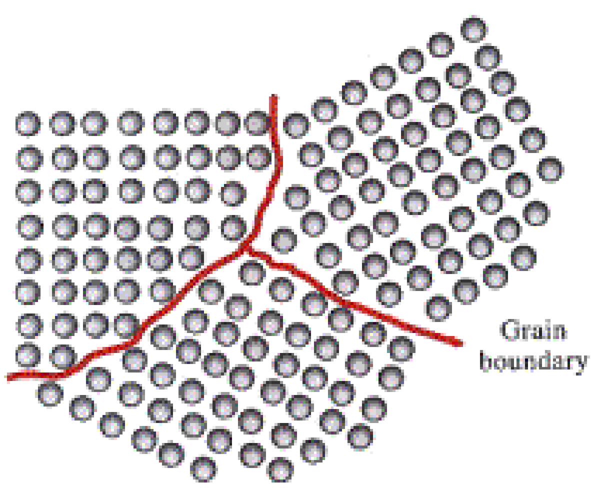
# Grain refinement by mechanical milling



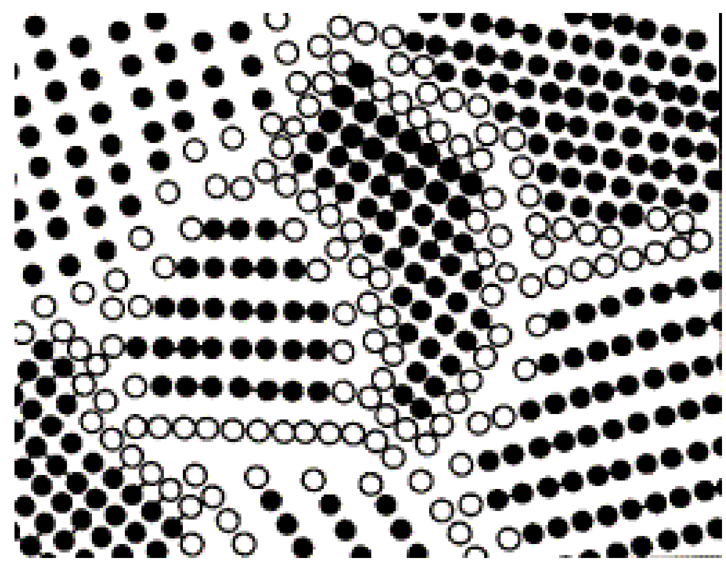
Mechanics of a planetary ball mill




Microstructure formation by ball milling

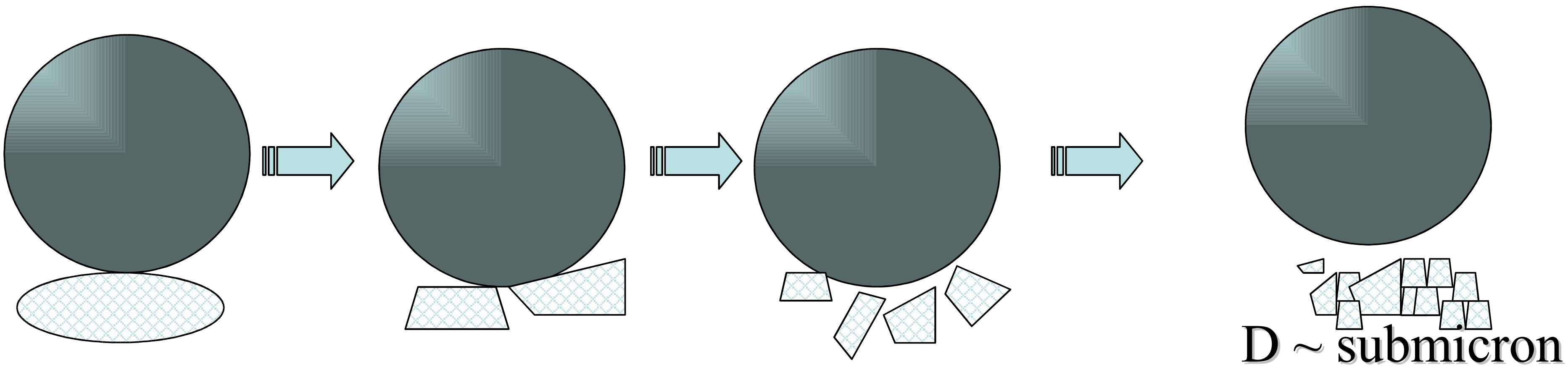



Microcrystalline structure



Nanocrystalline structure

# Particle Size Limitation for Mechanical Grinding



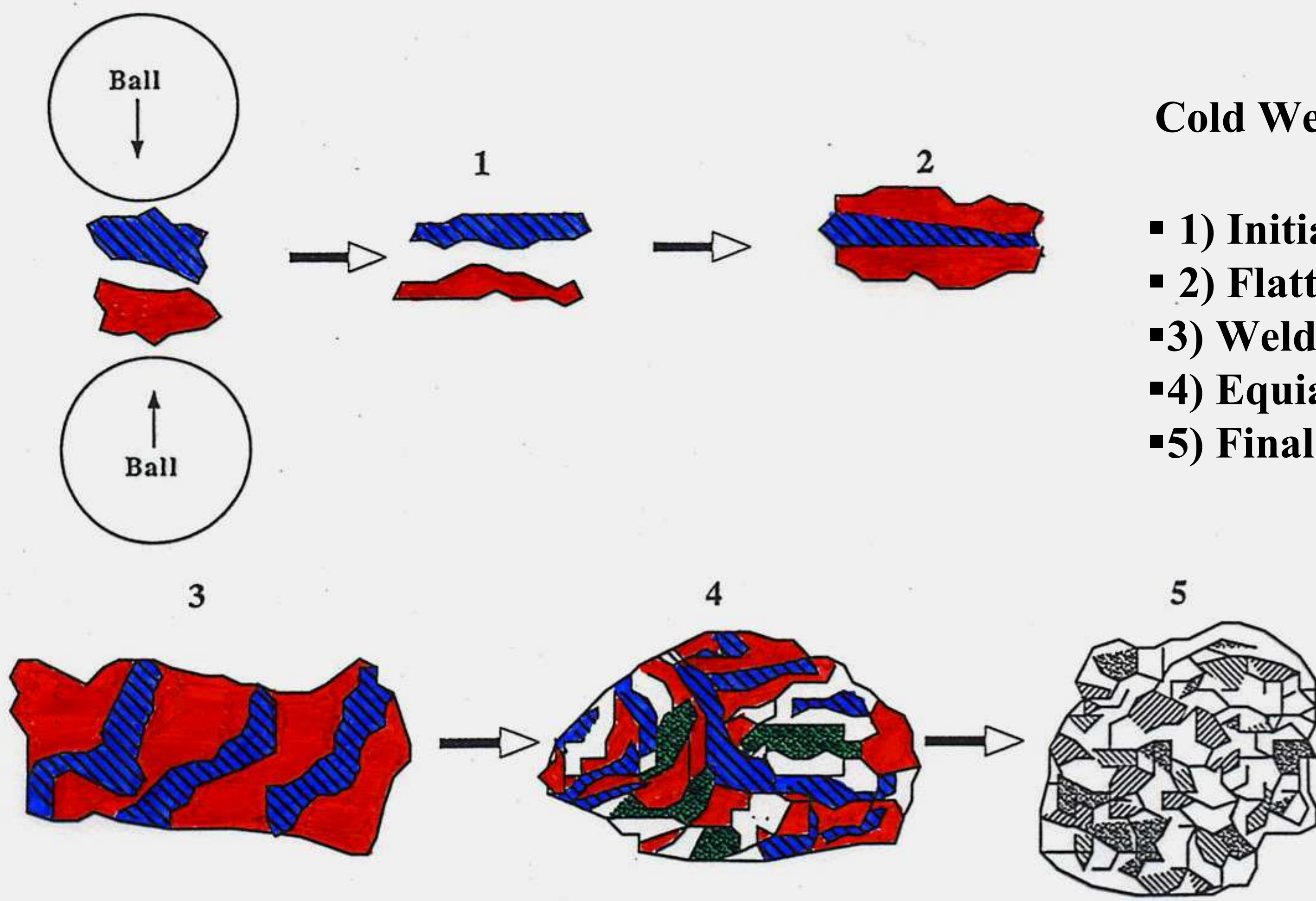

Two reasons:

1. When D < 50 nm, most single particle becomes a monocrystal;
   Breaking a monocrystal requires too much energy.

2. Welding of small particles into coarse clusters occurs.

# POWDER EVOLUTION STAGES DURING MECHANOSYNTHESIS

## Powder Evolution Stages during Mechanosynthesis



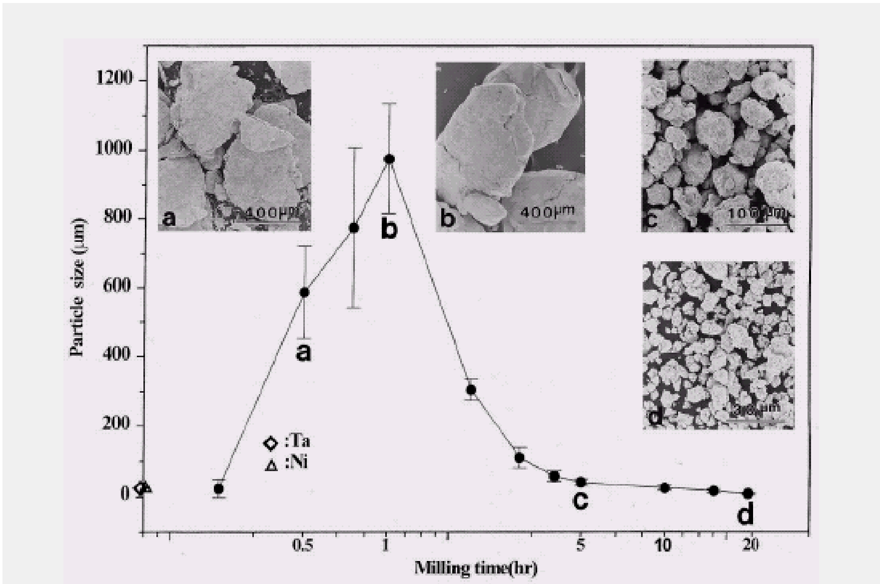

**Cold Welding & Fracturing**

- 1) Initial Powder
- 2) Flattening
- 3) Welding
- 4) Equiaxial Particles
- 5) Final State (Stationary)

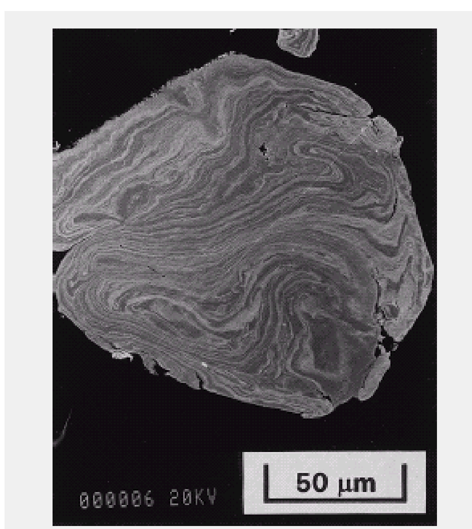
**Cold Welding & Fracturing :**

# Macroscopic Evolution

◀ Mechanical Alloying

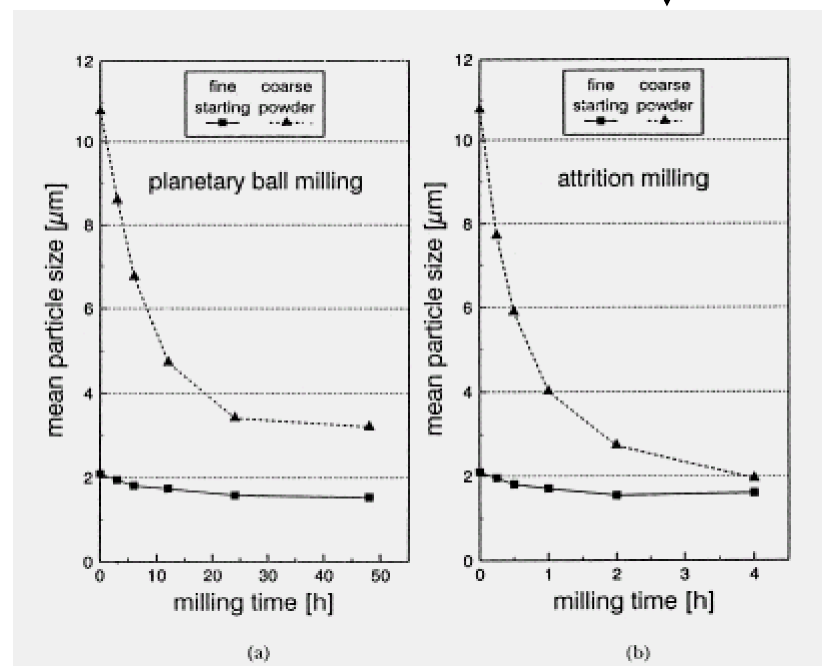



Narrow particle size distribution caused by tendency of small particles to weld together and large particles to fracture under steady-state conditions.



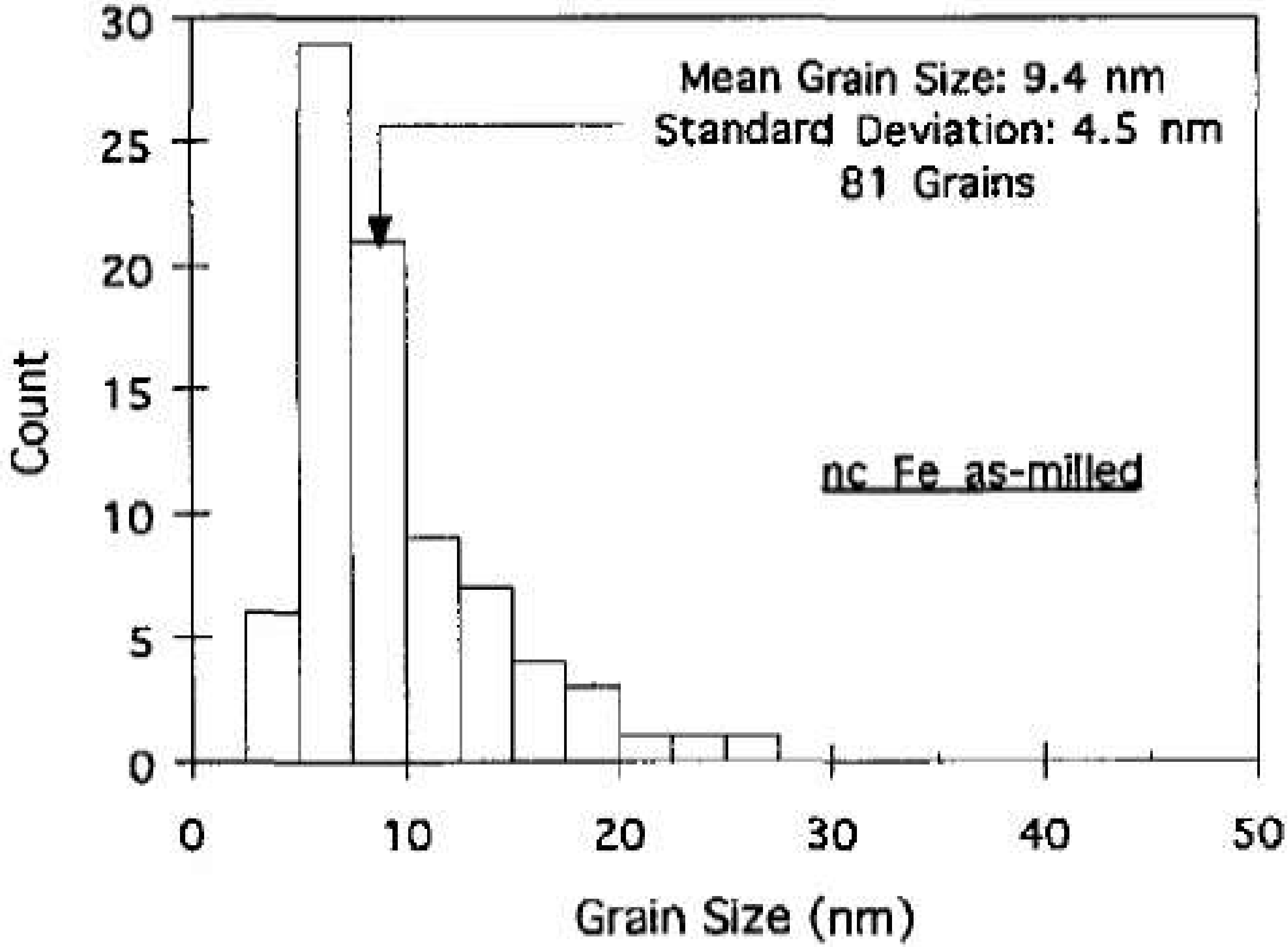

Scanning electron micrograph depicting the convoluted lamellar structure obtained during milling of a ductile±ductile component system (Ag - Cu).

Ball Milling ▼



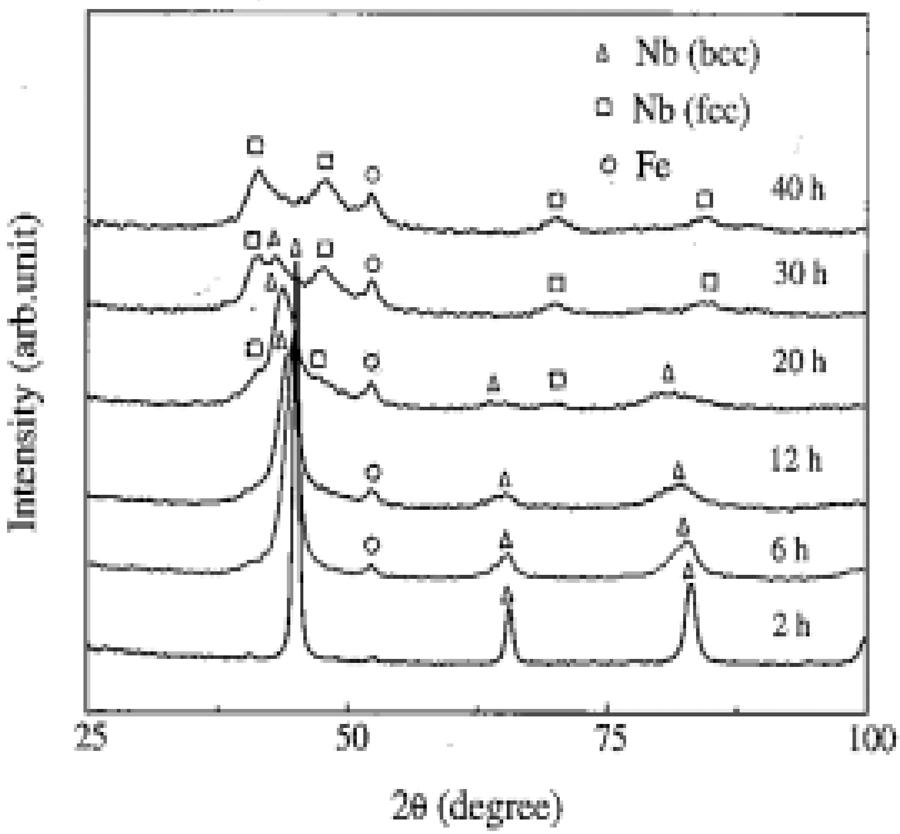

TiB2 Powder
Time to reach similar particle sizes during milling (a) planetary ball mill and (b) attritor.

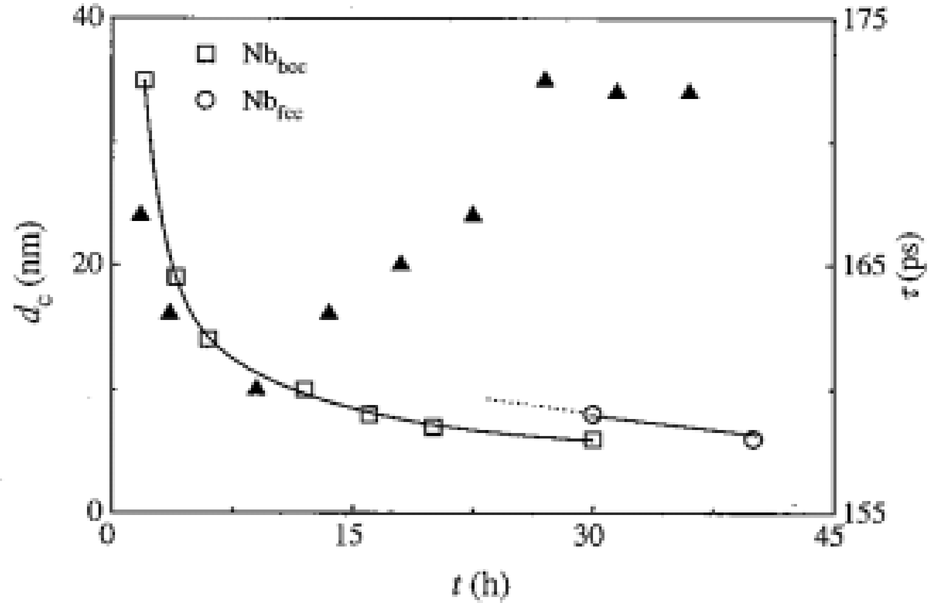
**Grain size distribution in nc Fe after milling for 24 h.**
**(from TEM dark – field images)**




**T.R. Malow, C.C. Koch**
**Acta Mater., 45(5) (1997) 2177 - 2186**

# Polymorphic transformation in Nb by mechanical milling

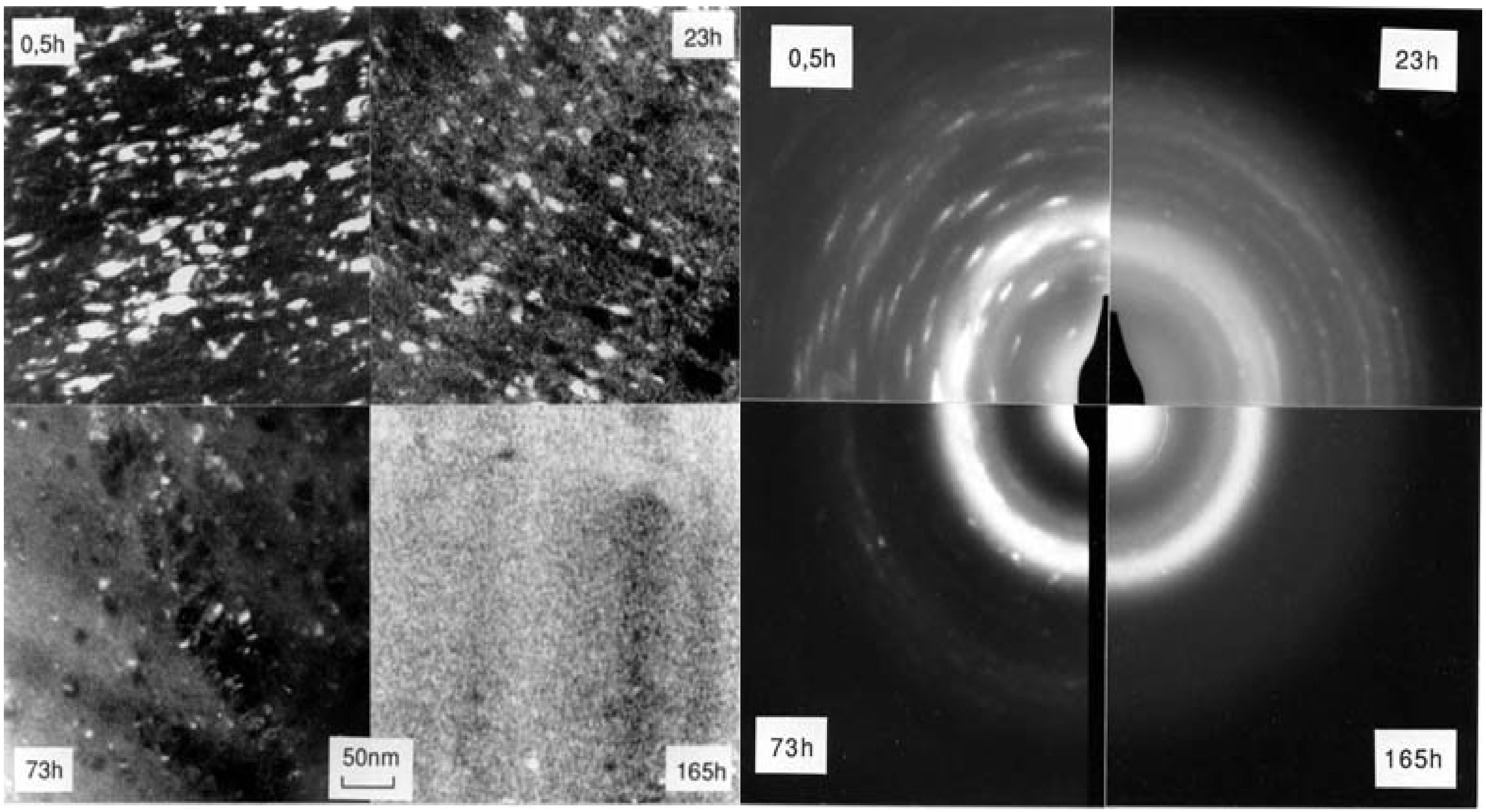


Amorphization by extended mechanical milling

# Extended Milling → Amorphization

Ni-Zr alloys




Chen et al, Phys. Rev. B 48,1993, 14

# Industrial Developments (MechanoChemistry)

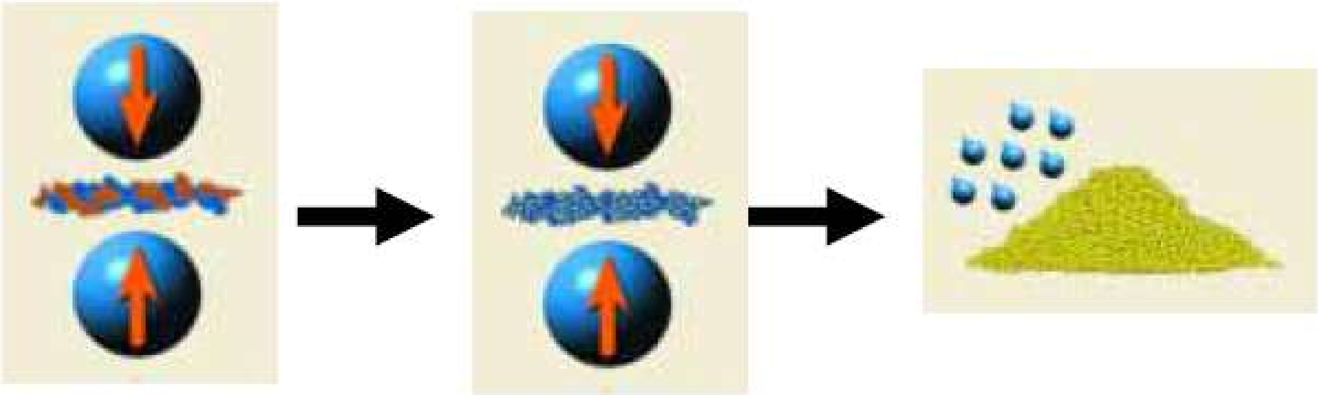
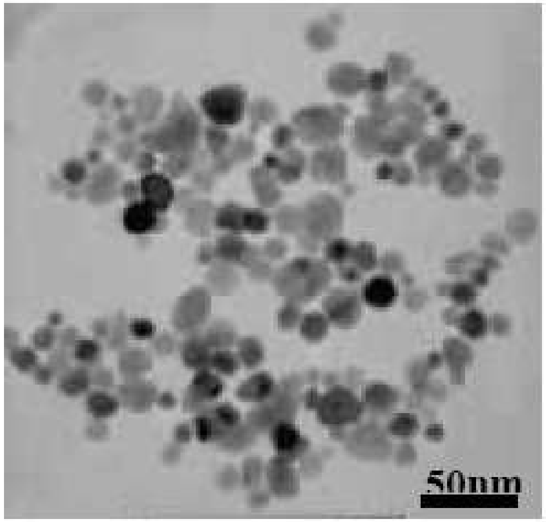


Figure 12. Schematic of the MCP™ Process

The MCP™ process is distinguished by its ability to form equiaxed nanoparticles, with a very narrow size distribution and low levels of agglomeration, as can be seen in Figure 13 below.



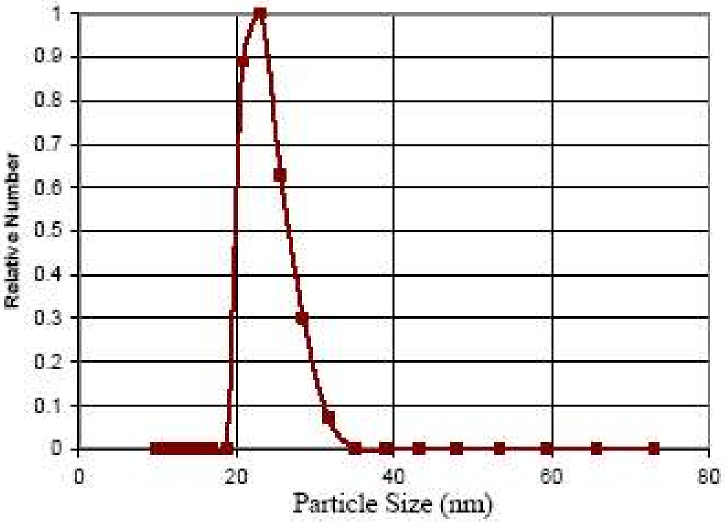




Figure 13. TEM Micrograph and PCS curve of MCP 25nm zinc oxide nanopowder

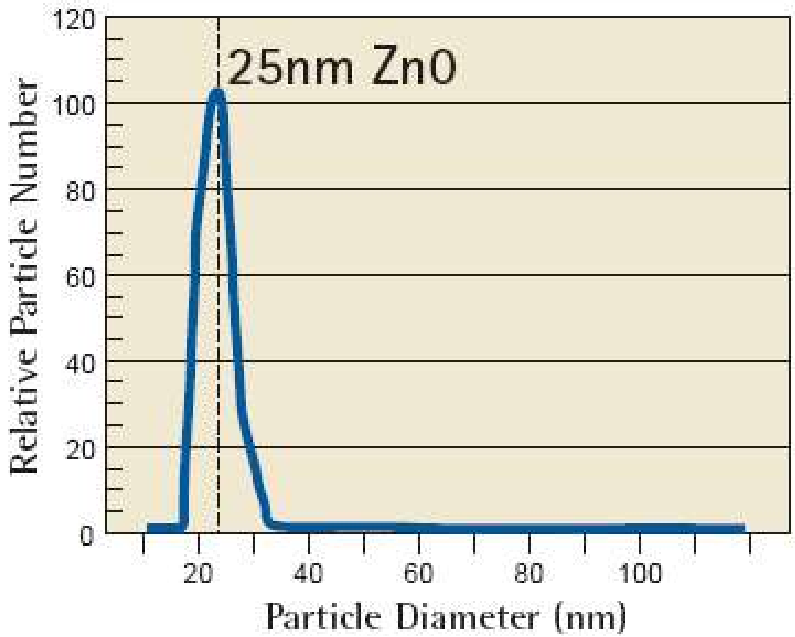
zinclear

# The Nanofine Zinc Oxide for Cosmetic Clarity and Broad Spectrum UV Protection

Advanced Powder Technology Pty Ltd *Manufacturer of the World's Finest Powders*

# Discrete Nanosized ZnO Particles

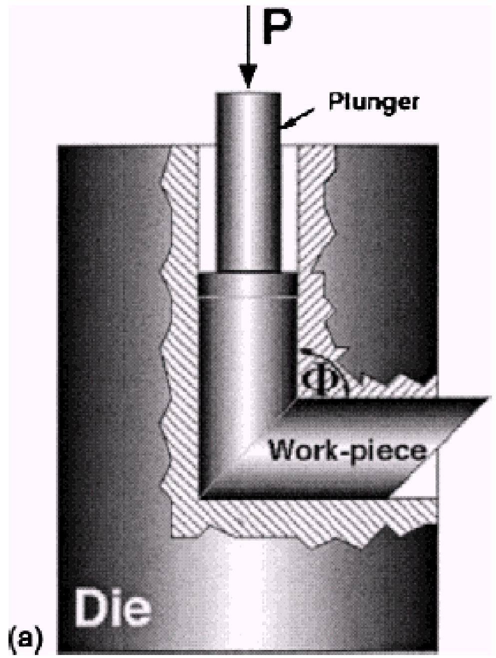
The superior properties of *ZinClear*™ derives from our patented MCP™ technology.

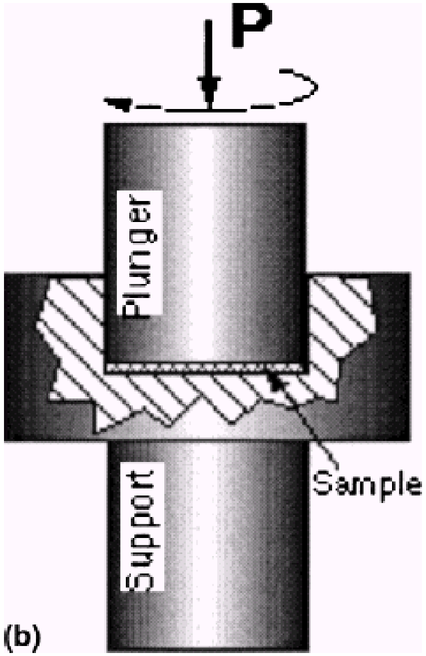


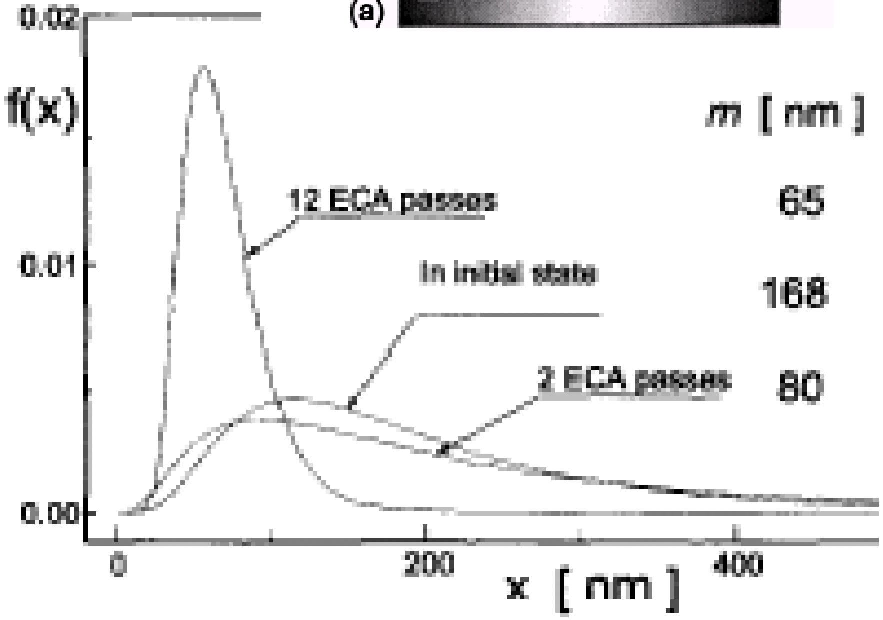

## The MCP™ process produces nanoparticles with a narrow size distribution.

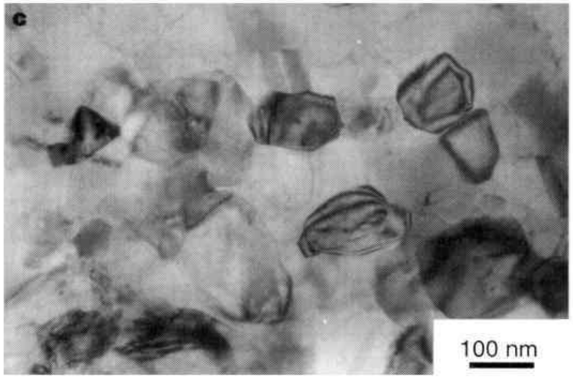
Particle size distribution of *ZinClear*™ measured using photon correlation spectroscopy (PCS)[1]. The mean particle diameter is 24nm with a standard deviation of 4nm.

# SPD Processing
# Severe Plastic Deformation





R.Z. Valiev et al. - J. Mater. Res., Vol. 17, No. 1, Jan 2002
Iwahashi Y, Horita Z, Nemoto M, Langdon TG. Acta Mater, 46 (1998) 1589
Ruslan Z. Valiev, Igor V. Alexandrov Ann. Chim. Sci. Mat., 2002, 27 (3), 3-14

FIN