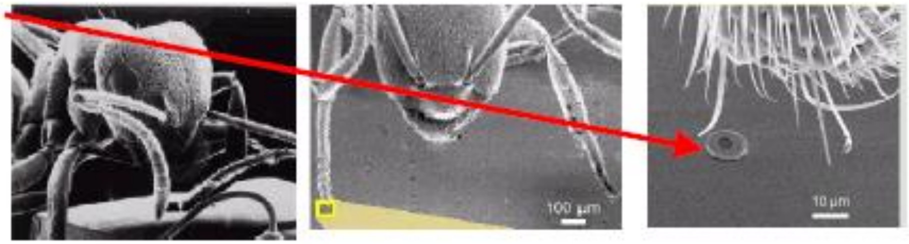
NANOMATERIALS AND NANOTECHNOLOGIES.

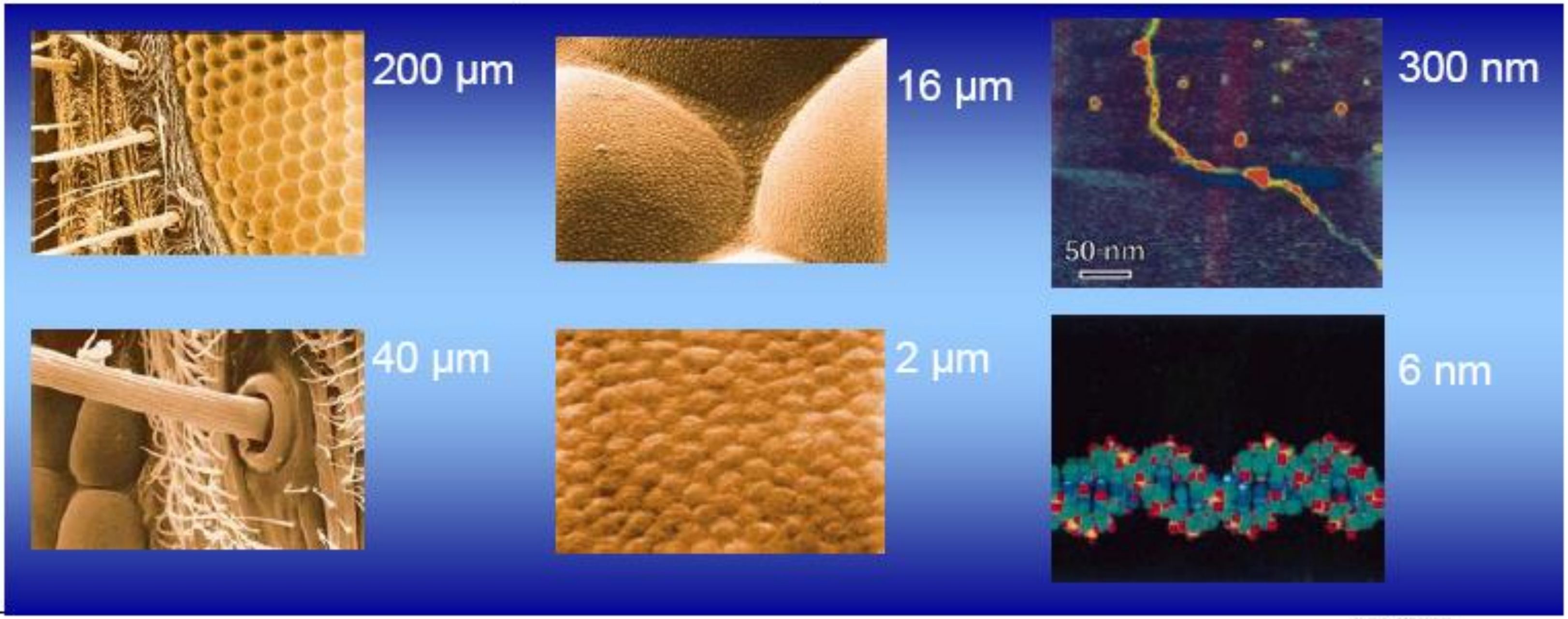
The journey into the nano-cosmos (1)

Ant and diode laser (VCSEL)



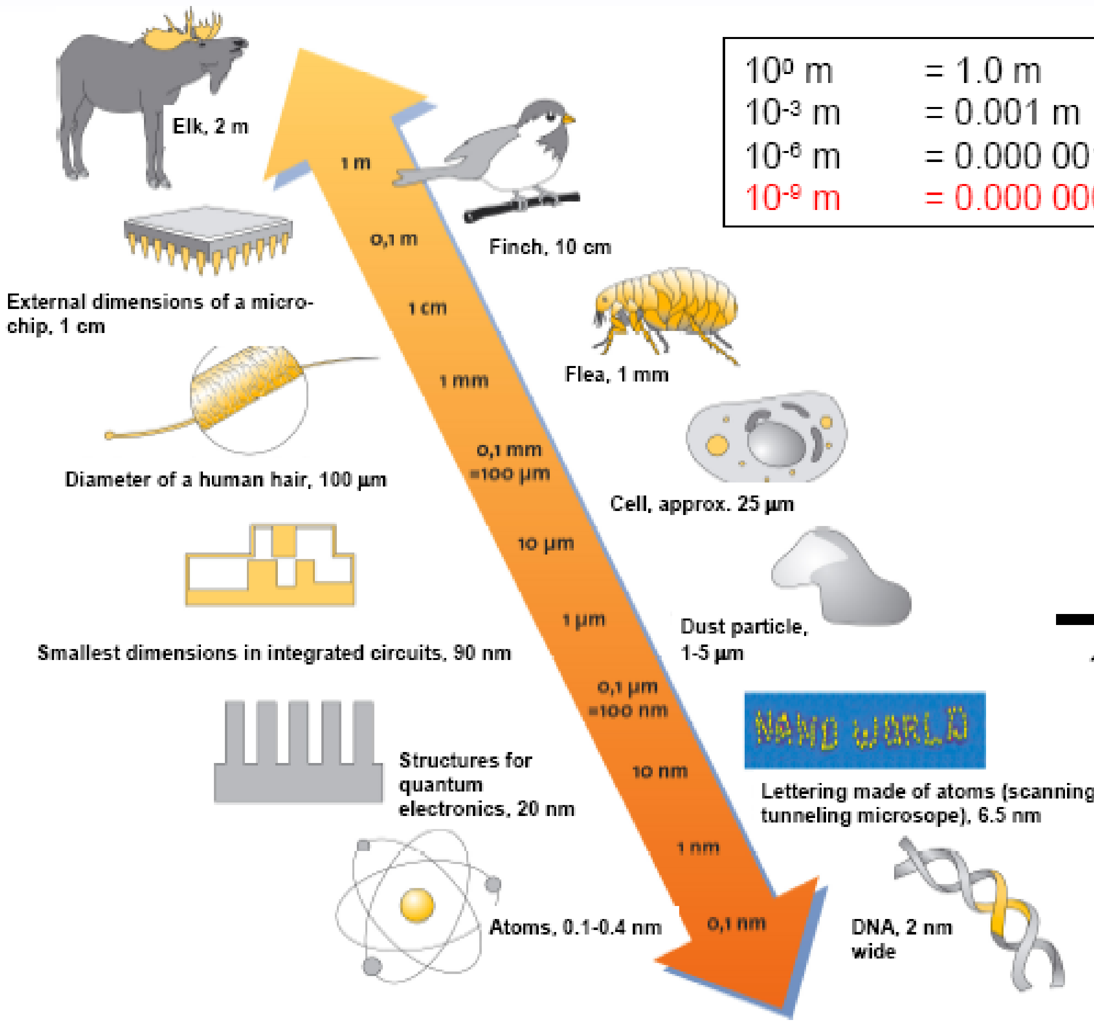
A fly's eye in the microcosm
(200 µm to 2 µm)

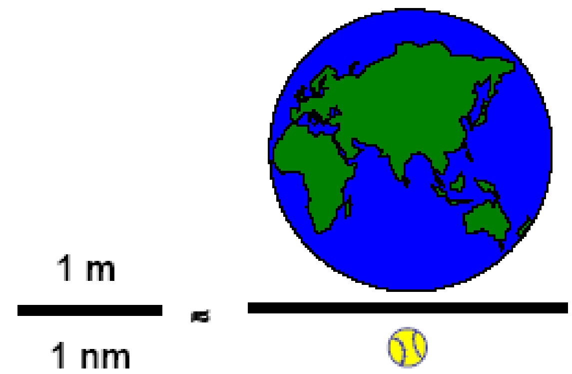
DNA in the nano-cosmos (300 nm to 6 nm)

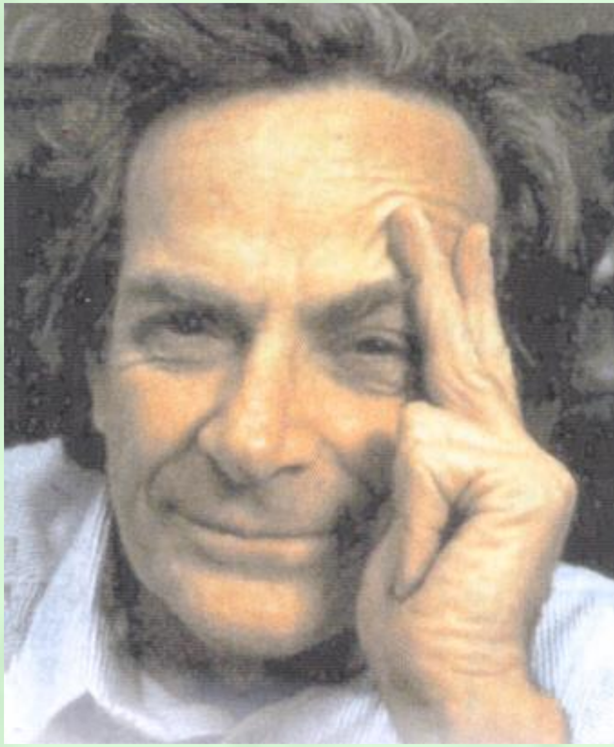
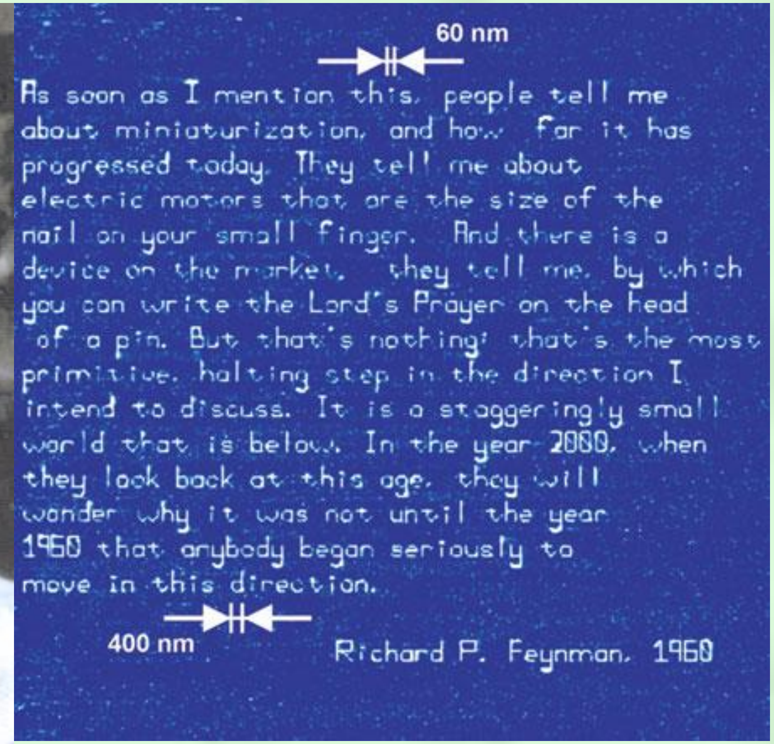


The journey into the nano-cosmos (2)
Size relationships

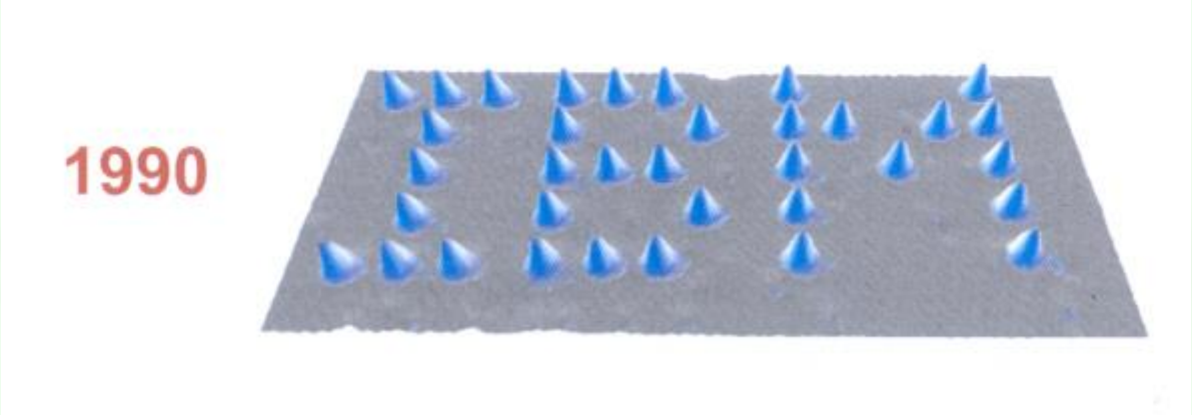
10^0 m	= 1.0 m	= 1 m	(1 metre)
10^{-3} m	= 0.001 m	= 1 mm	(1 millimetre)
10^{-6} m	= 0.000 001 m	= 1 µm	(1 micrometre)
10^{-9} m	= 0.000 000 001 m	= 1 nm	(1 nanometre)



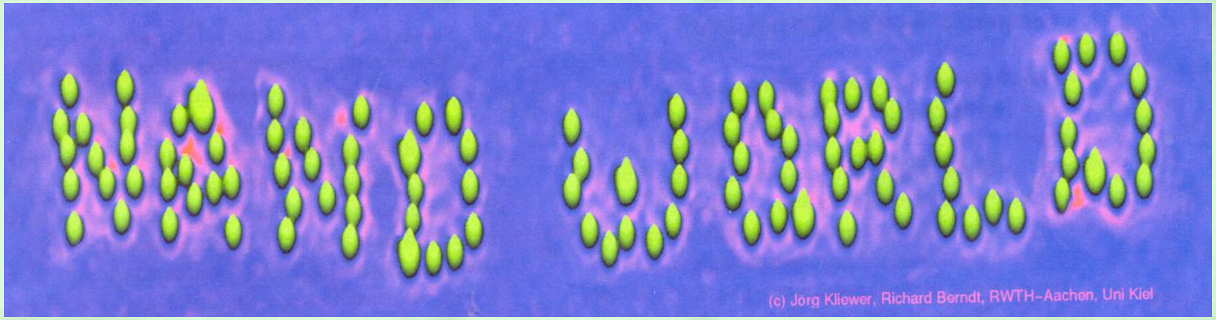


Richard Feynman: „There's plenty of room at the bottom”



Logo IBM (Donald Eigler i Erhard Schweizer)

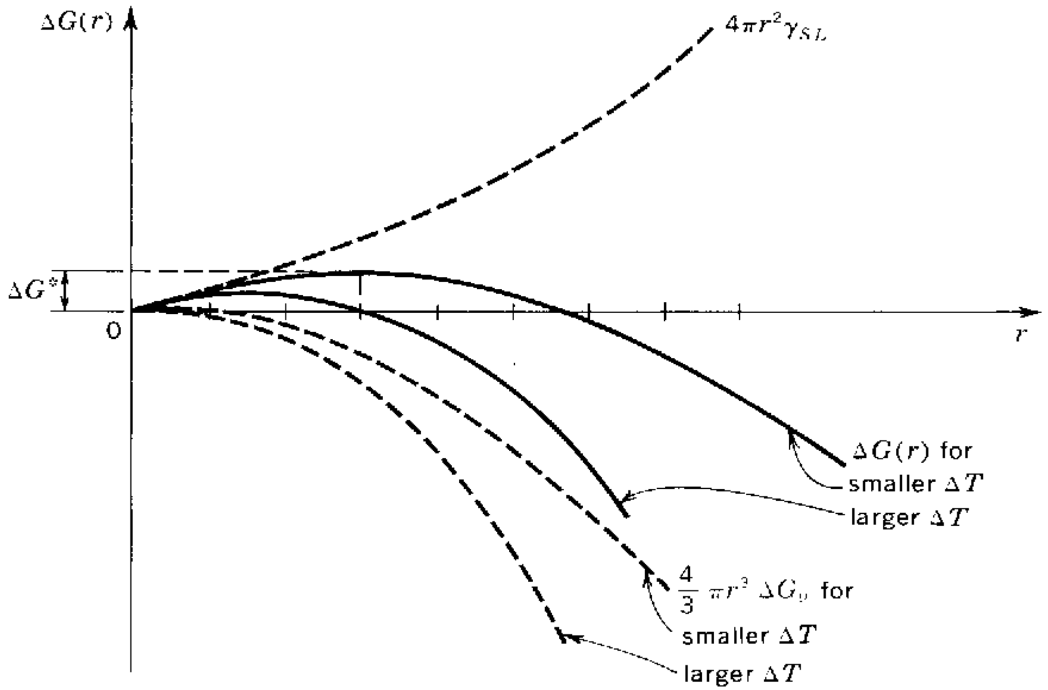


NANO WORLD

For nucleation, the critical size has always been of the order of nm!

$$\Delta G = \frac{4\pi}{3} r^3 \bullet \Delta G_V + 4\pi r^2 \bullet \gamma_{SL}$$

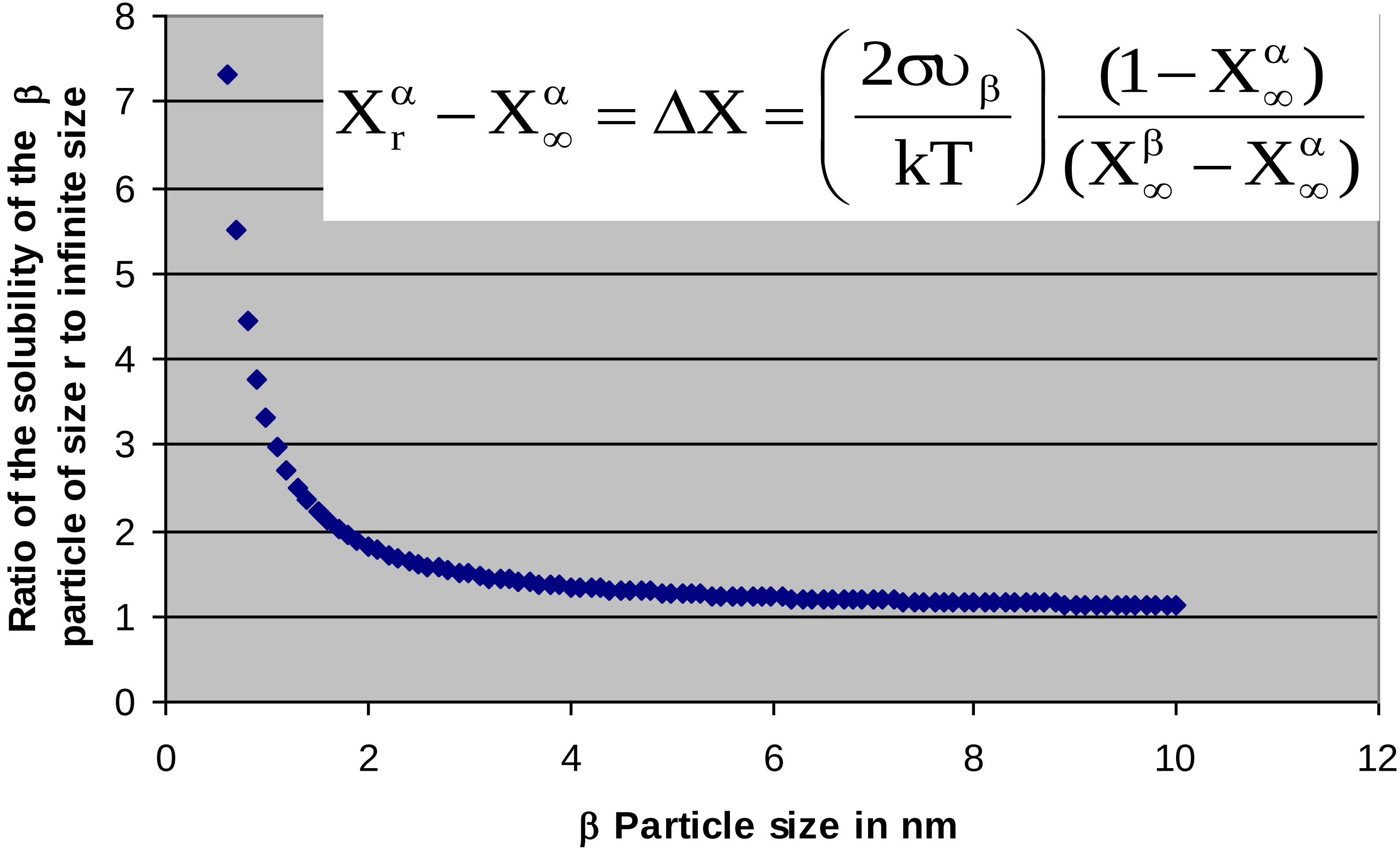
$$r^* = -\frac{2\gamma_{SL}}{\Delta G_V}$$



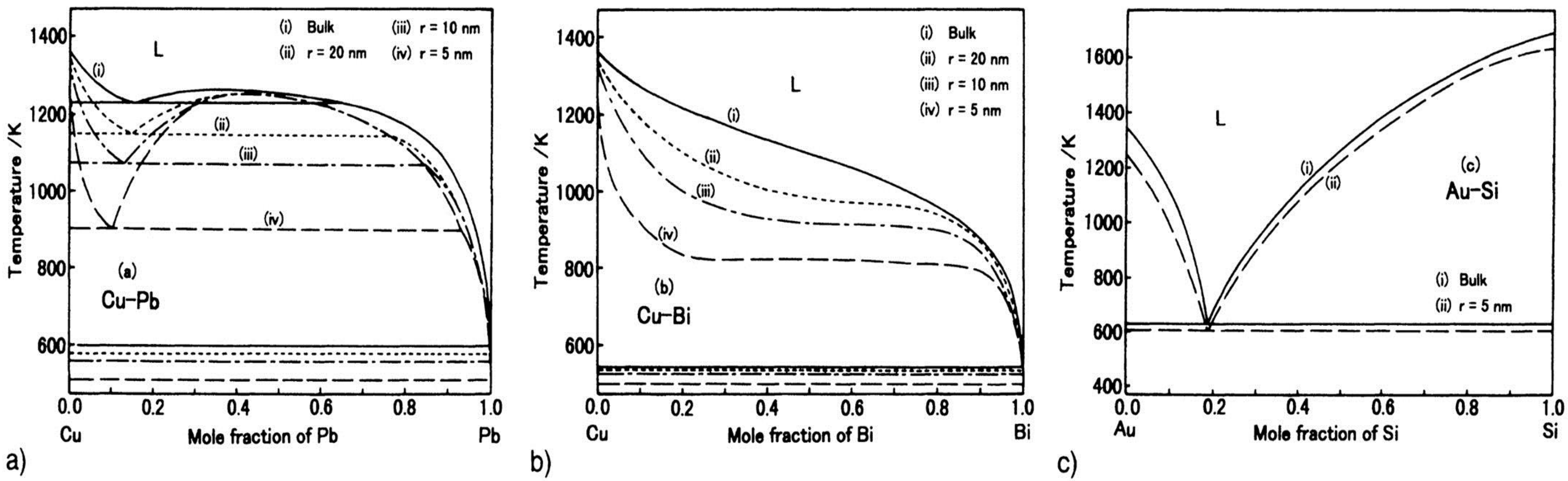
Plot of the free-energy terms making up $\Delta G(r)$ and of $\Delta G(r)$ for a small and large undercooling. The critical radius r^* is at the maximum in $\Delta G(r)$ and decreases as ΔT increases.

Shewmon, *Transformations in Metals*

Solubility of a β Particle as function of its size

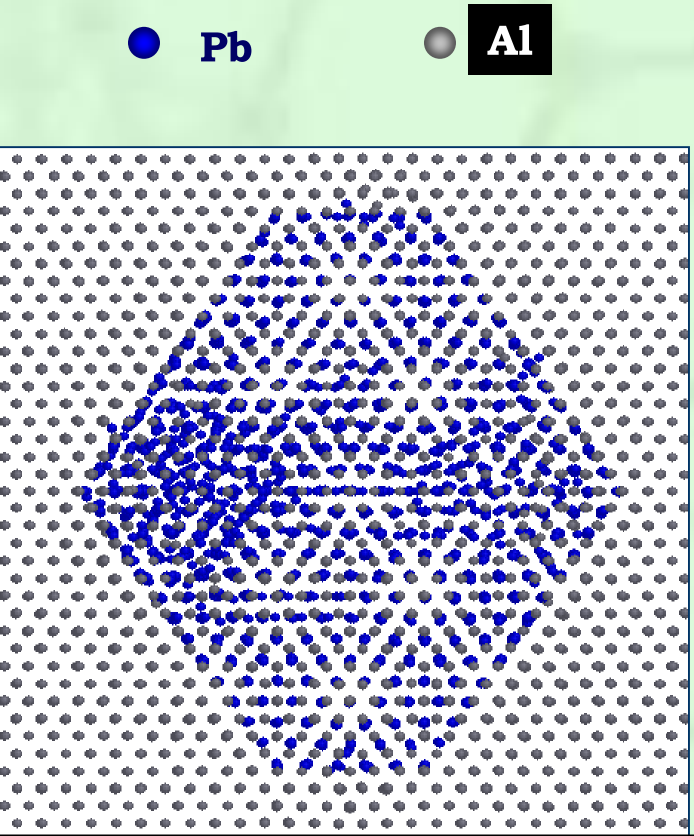


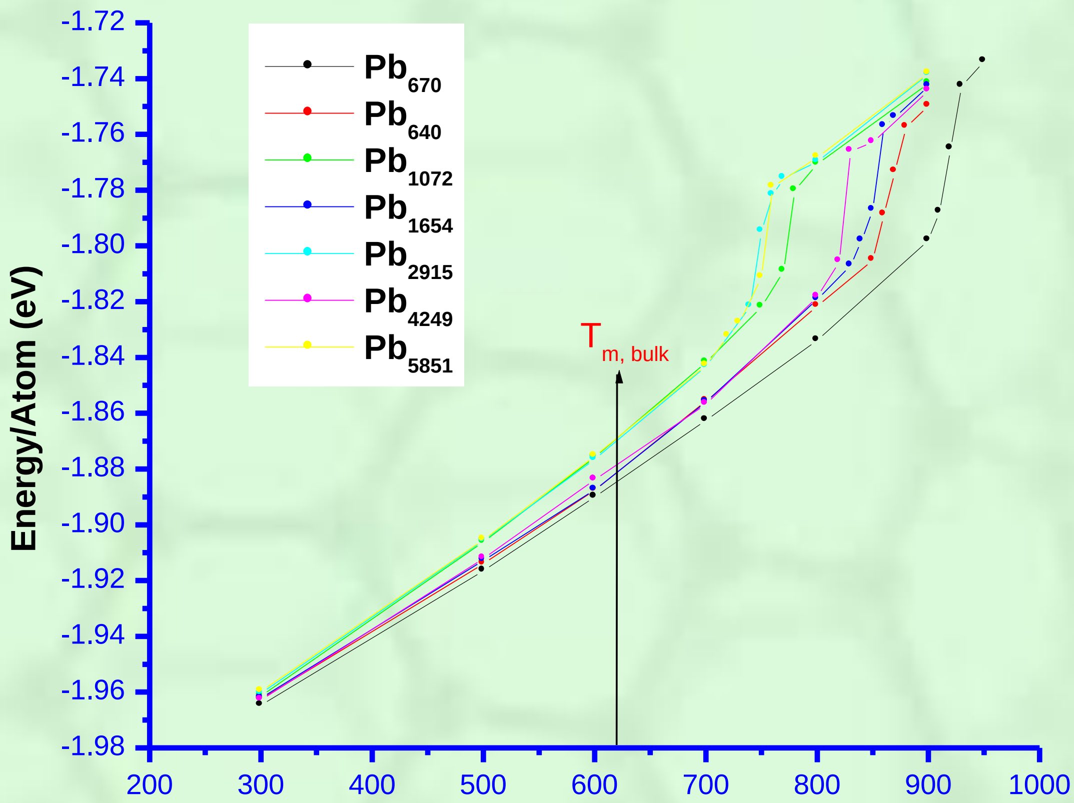
$$X_r^{\alpha} - X_{\infty}^{\alpha} = \Delta X = \left(\frac{2\sigma\upsilon_{\beta}}{kT}\right)\frac{(1 - X_{\infty}^{\alpha})}{(X_{\infty}^{\beta} - X_{\infty}^{\alpha})}$$



T. Tanaka, S. Hara: „Thermodynamic Evaluation of Binary Phase Diagrams of Small Particle Systems”, Z. Metallk. 92 (2001) 5, 467-472.

But…!



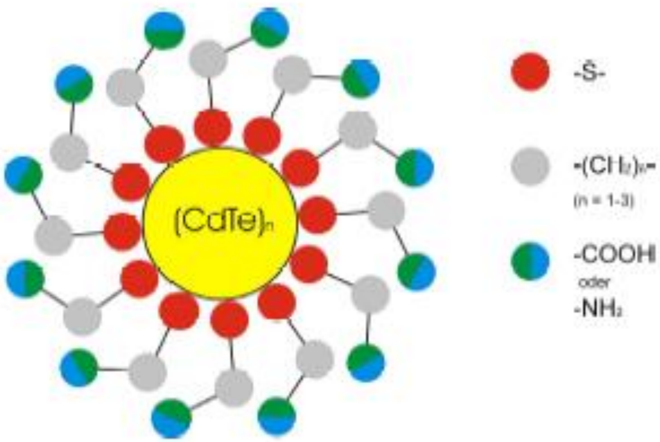


The melting of embedded Pb in Al occurs over a continuous range of temperatures. It is as though there is a two phase equilibrium between Pb(L) atoms at the surface and Pb(S) atoms in the interior. After Zhan Shi, Ph.D Thesis , CMU, 2004

Properties of different-sized nano-particles

Nano-particles are tiny crystals: the smaller they are, the more they behave **like a molecule**

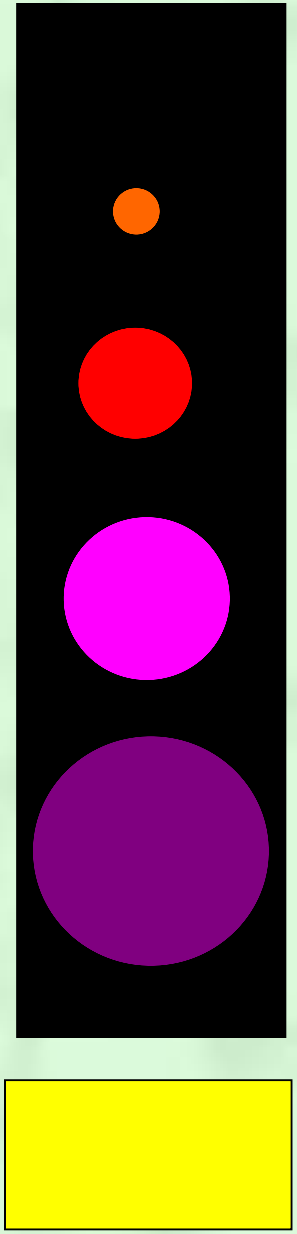
CdSe nano-particles in solution (1.5 - 4.0 nm)



Schematic of a CdTe nano-particle with stabilising shell

Fluorescence depending on the particle size

Paul Mulvaney, MRS Bulletin, Dec. 2001, p.1009



Au Atom: ~0,1 nm (1A), colorless

Au clasters: < 1nm, nonmetalic, orange

Au nanocrystallites: 3 - 30 nm, metalic, transparent / red

Au particles: 30 - 500 nm, metalic, transparent / turbid

crimson -> blue

Au bulk: golden color!

M. Faraday, Philos. Trans. R. Soc. London, 147 (1857) 145-181

Gold leaf can be beaten to thicknesses of 1/278000 of an inch (around 90 nm). Such films are continuous and green in transmission. Further thinning with KCN gives ruby red films.

Chemical means to finely divided gold. Also deflagration of gold wires to produce ruby red particles. Chemically indistinguishable from gold.

Paul Mulvaney,
MRS Bulletin,
Dec. 2001, p.1009

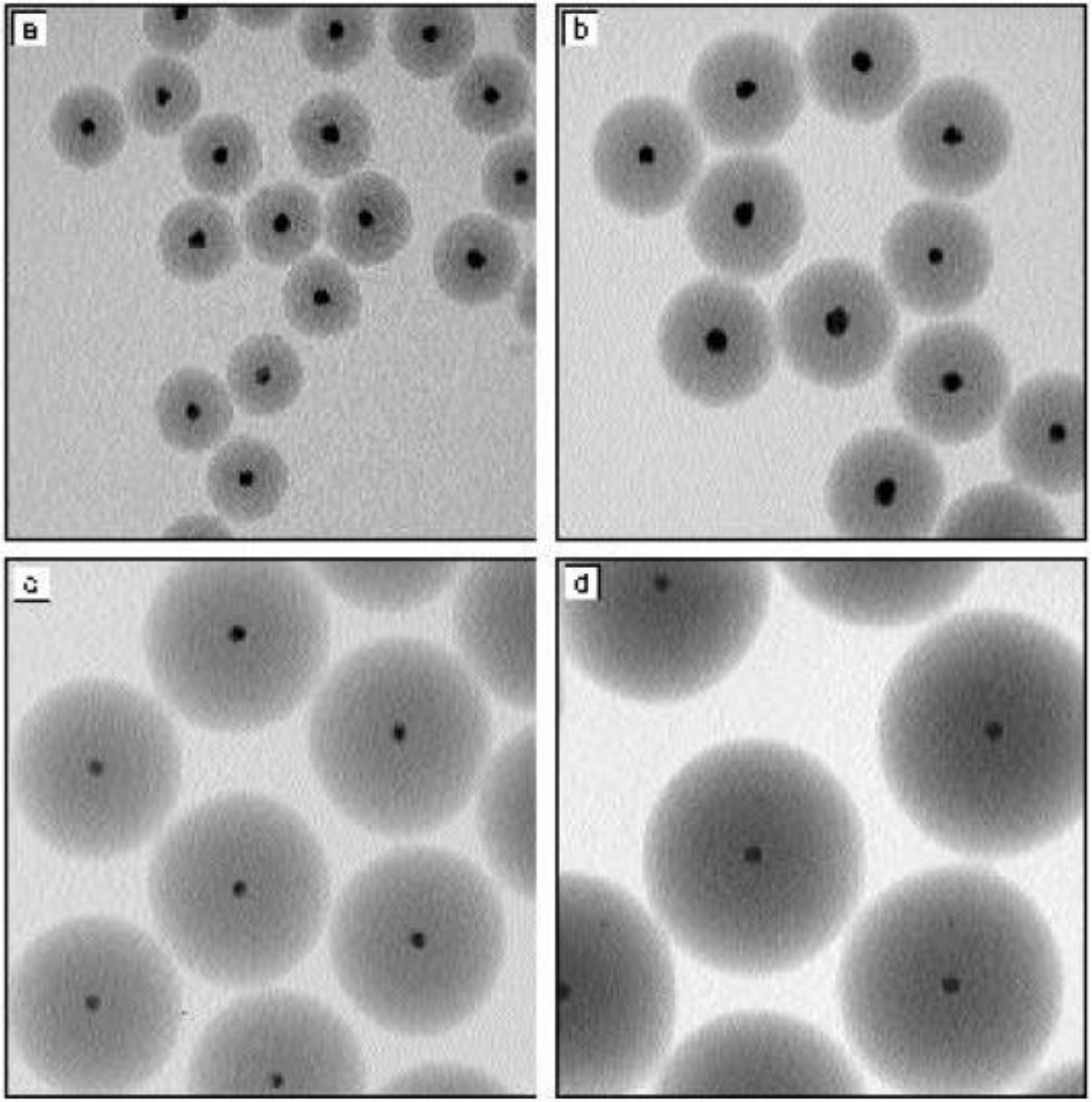


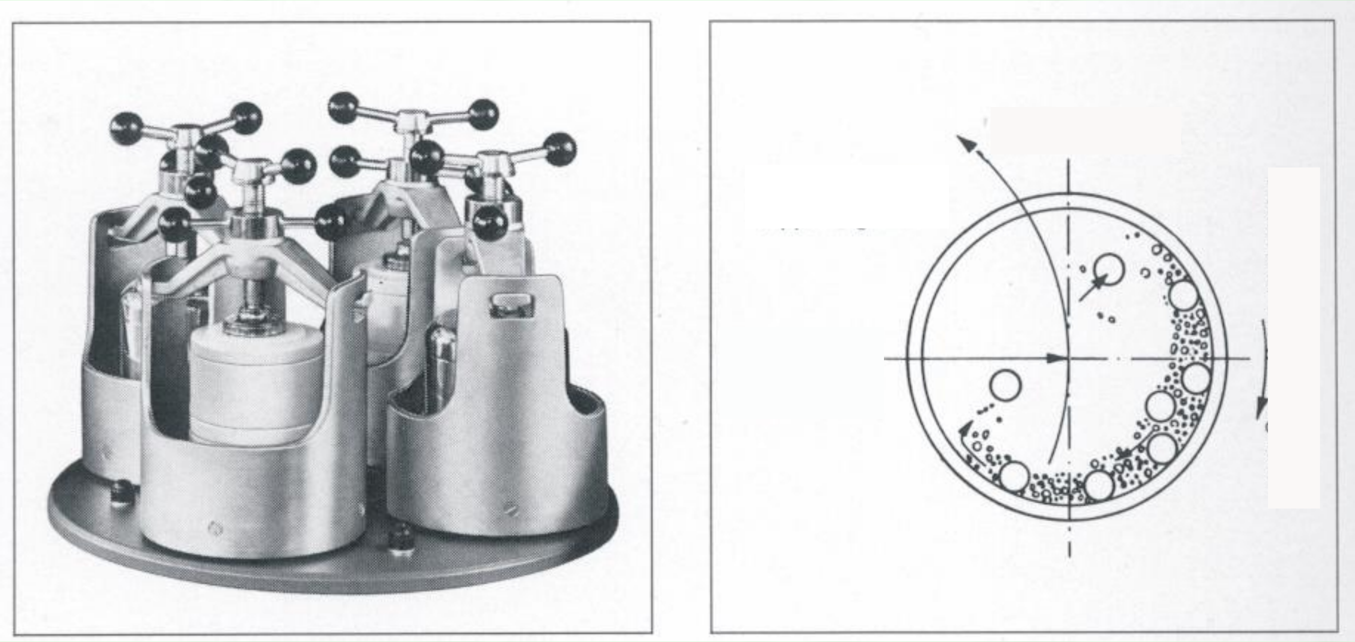
Figure4.(a)–(d) Electron micrographs of silica-coated 15-nm gold particles with various shell thicknesses.

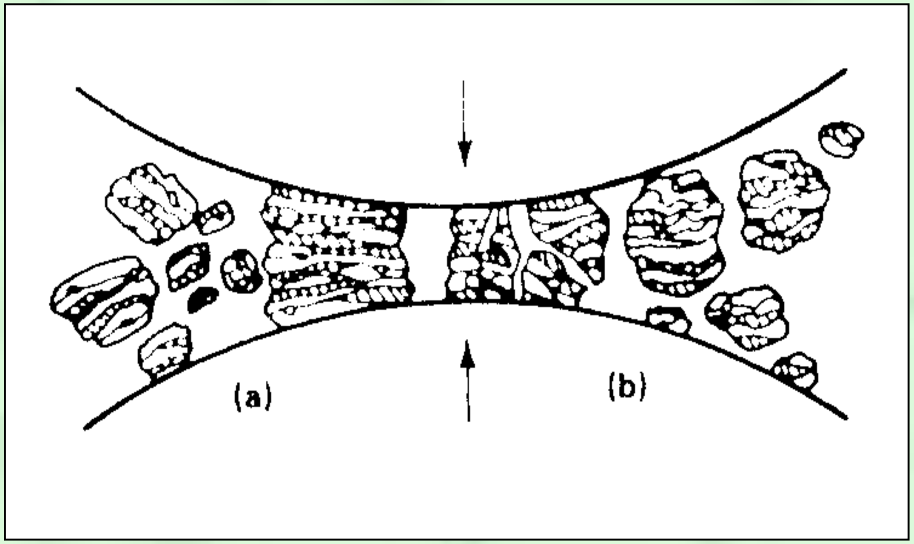
in the
limit of
very small
spacings
and
a gold volume
fraction 50%,
the film spectrum
is almost identical
to that
of the bulk
gold thin film

NANOMATYERIALS CAN BE PRODUCED USING TWO BASIC TECHNOLOGIES:

- **TOP - DOWN** CAN BE REALIZED BY:

- CRUSHING IN BALL MILLS.

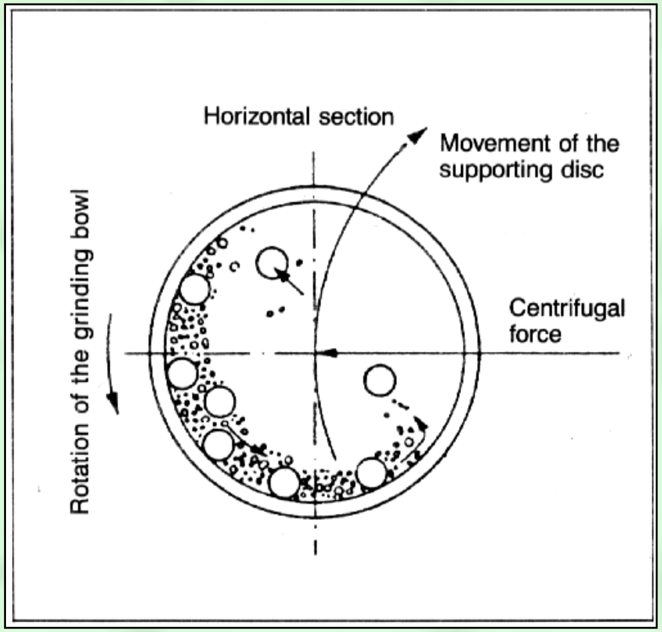




Scheme of mechanical alloying process

a) welding

b) fracturing

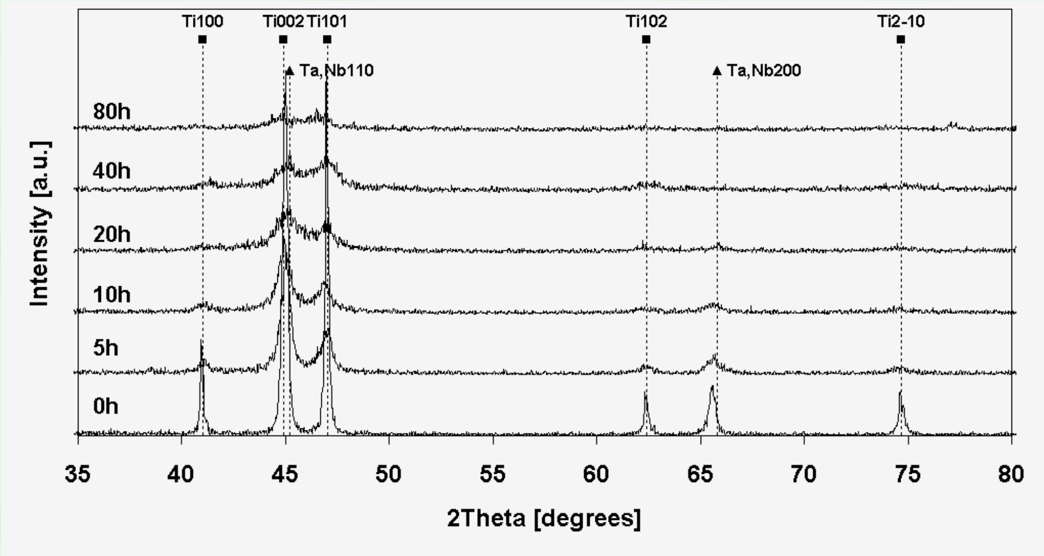


Planetary mill Fritsch Pulverisette P/4

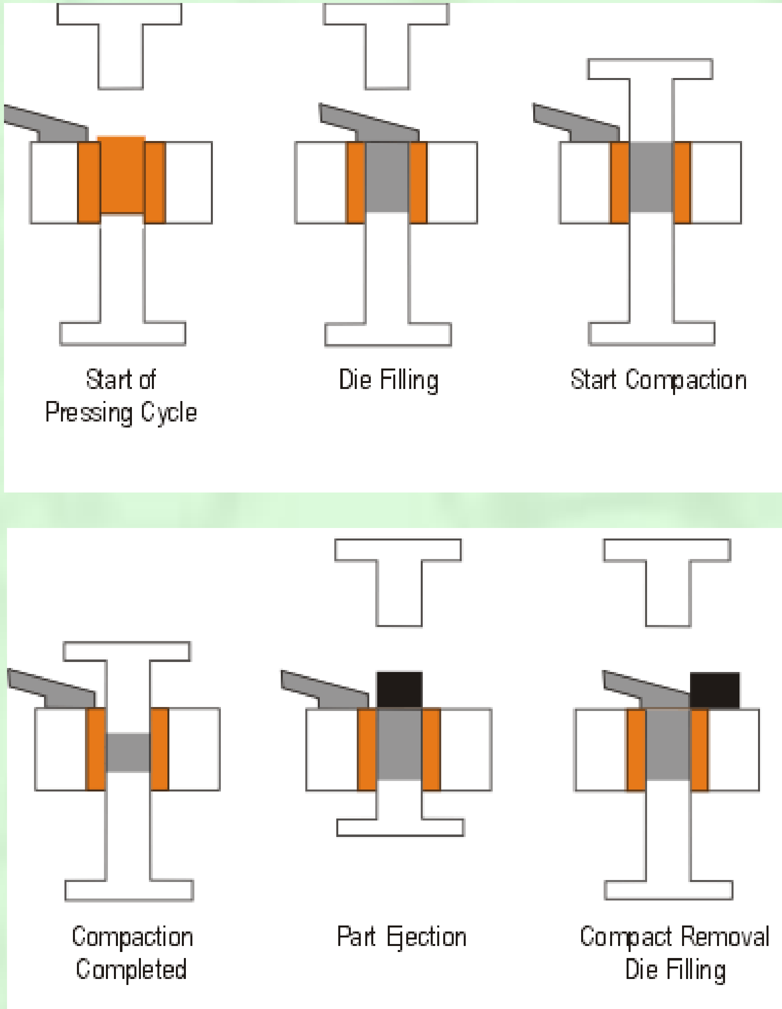
and scheme of ball movement during mechanical alloying process

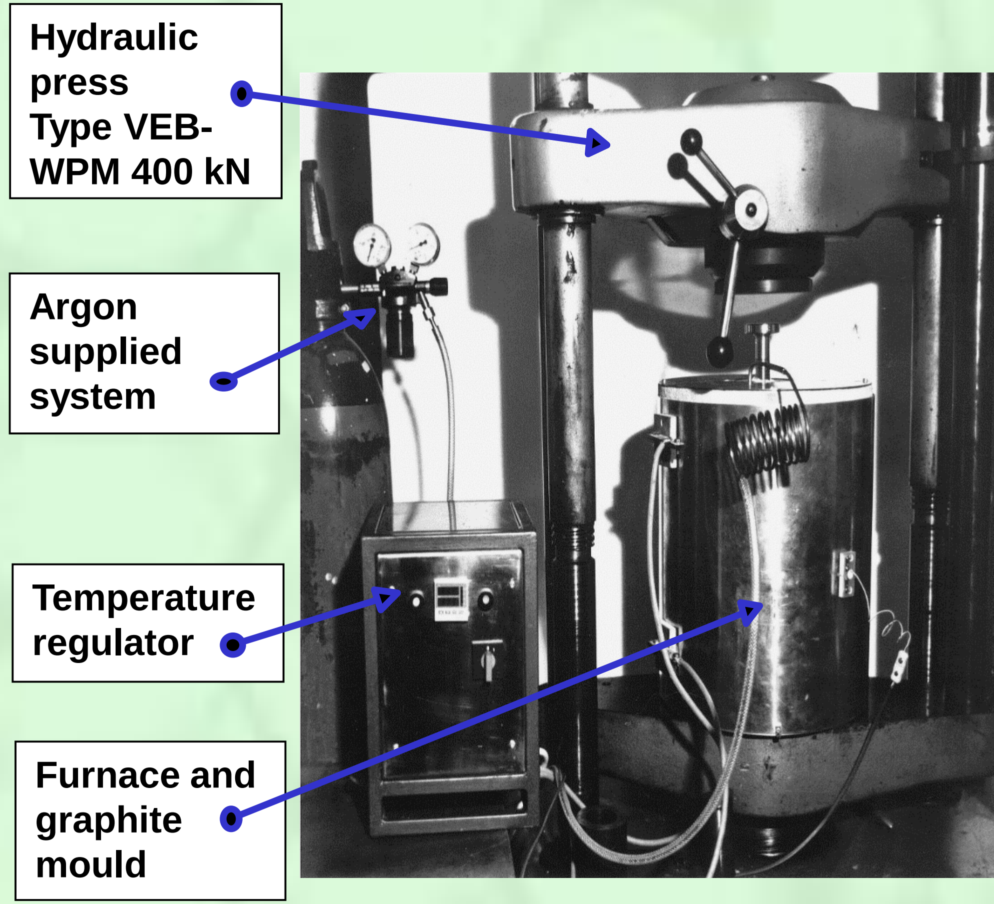
Table 2 Microhardness of Ti, TiNb and TiTaNb samples ball milled and uniaxially hot pressed

Sample	Ball milled powder μHV20	Uniaxially hot pressed μHV20
Ti	1029±149	1037±100
TiNb	822±40	773±69
TiTaNb	786±92	610±89



Set of diffraction pattern of Ti-10Ta-10Nb alloy after different milling time.





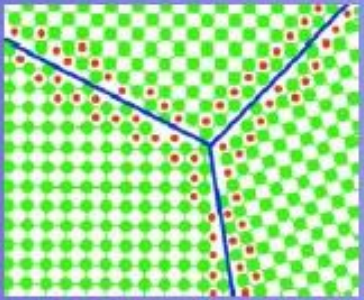
Scheme of the applied uni-axial hot pressing

Photograph of the applied hot pressing device

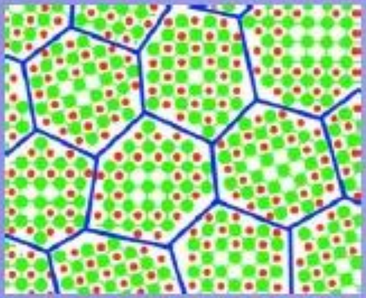
✓Nano-Powders

- ➕ Enhanced diffusion and kinetics through grain boundaries
- ➕ Low desorption temperature
- ➖ Surface contamination
- ➖ Commercially non usable technique and environmental risks

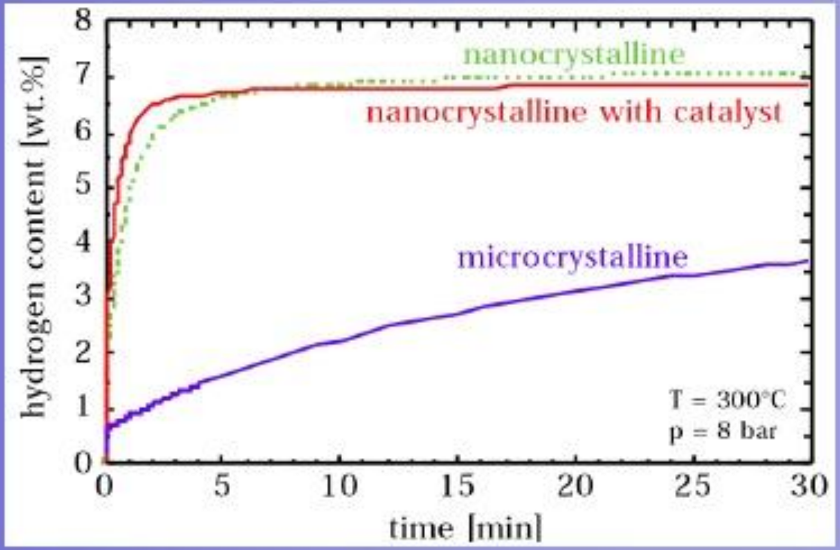
⇒ Bulk NMs



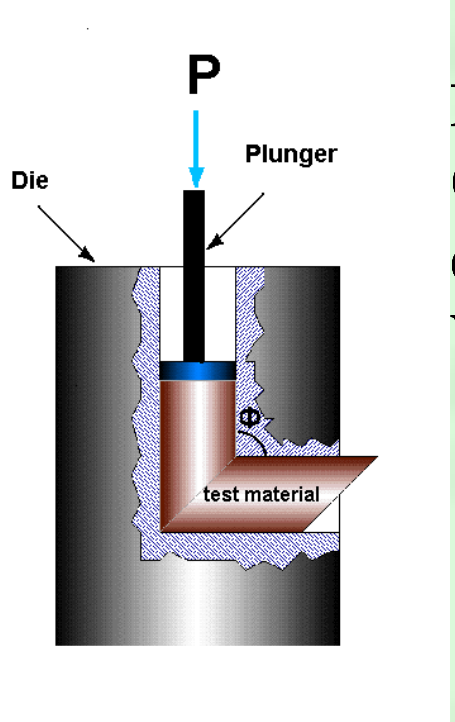
Coarse grained structure



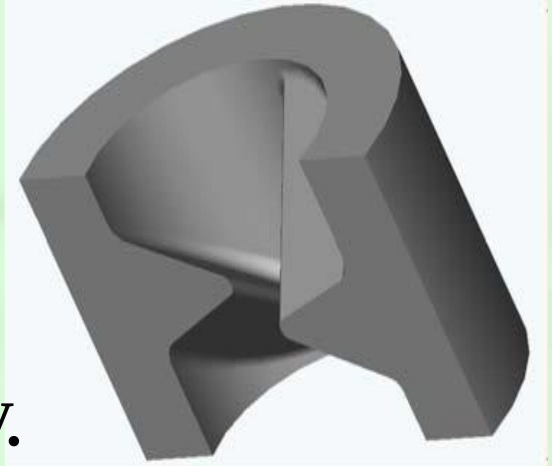
Nanocrystals



T.Klassen, et al., Z. Metallkd., **94**, 610 (2003)

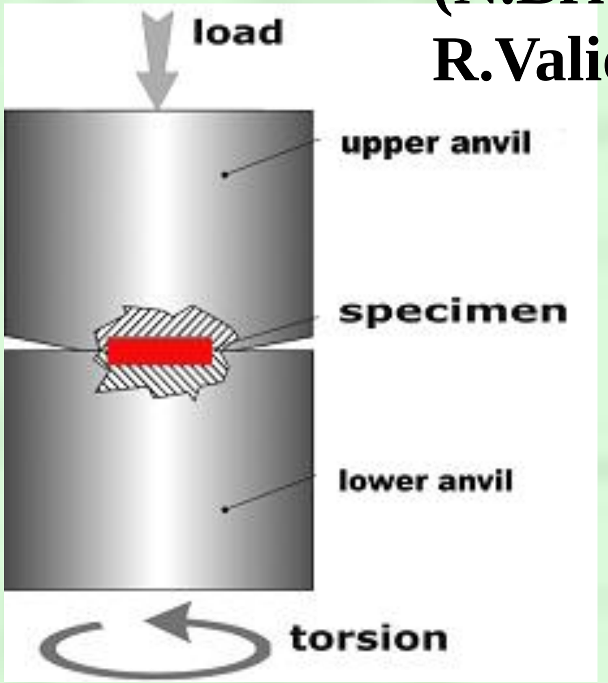


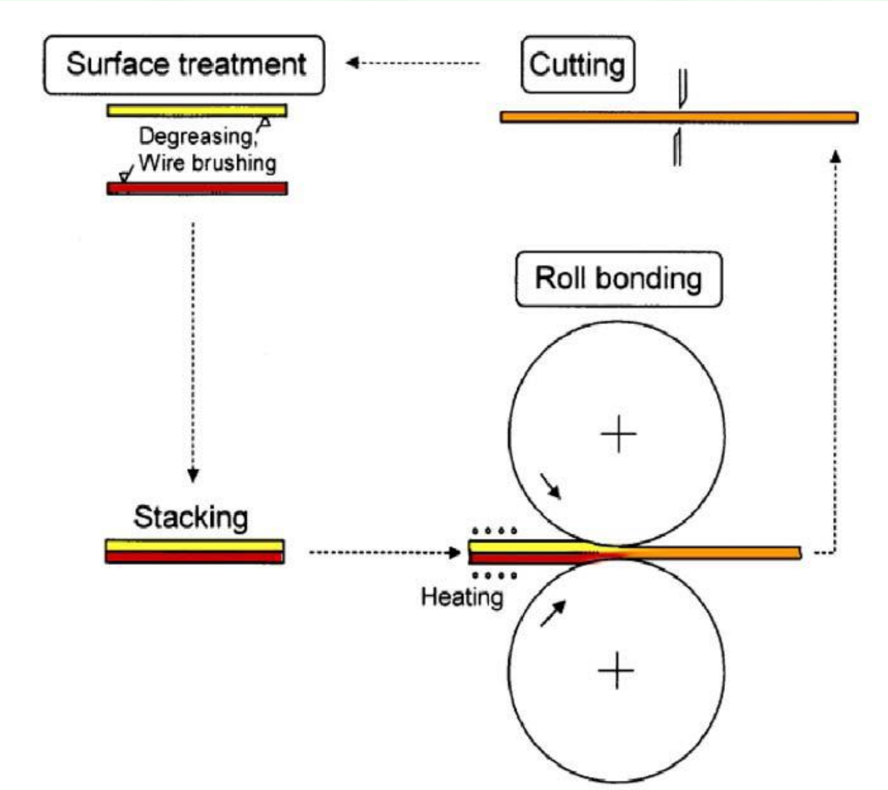
Equal ChannelAngularPressing (V. Segal, R. Valiev)



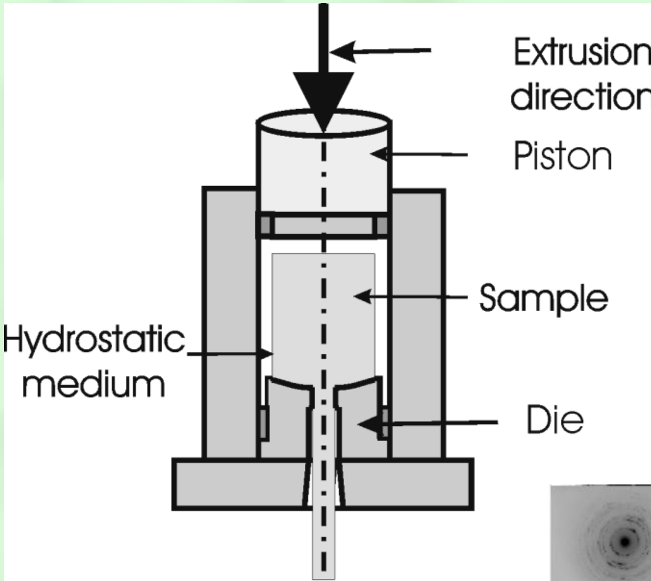
Torsional Extrusion(V. Varyukhin)

High Pressure Torsion (N.Bridgman, R.Valiev)



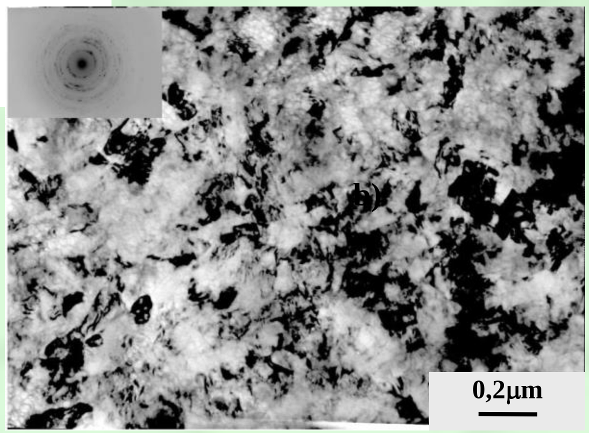


Accum. Roll Bonding (N. Tsuji)

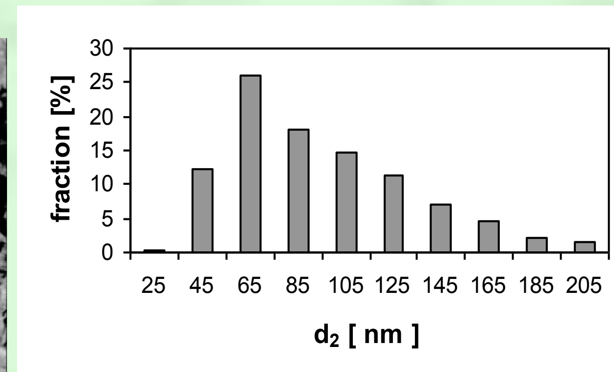


Scheme of the hydrostatic extrusion processing

a)



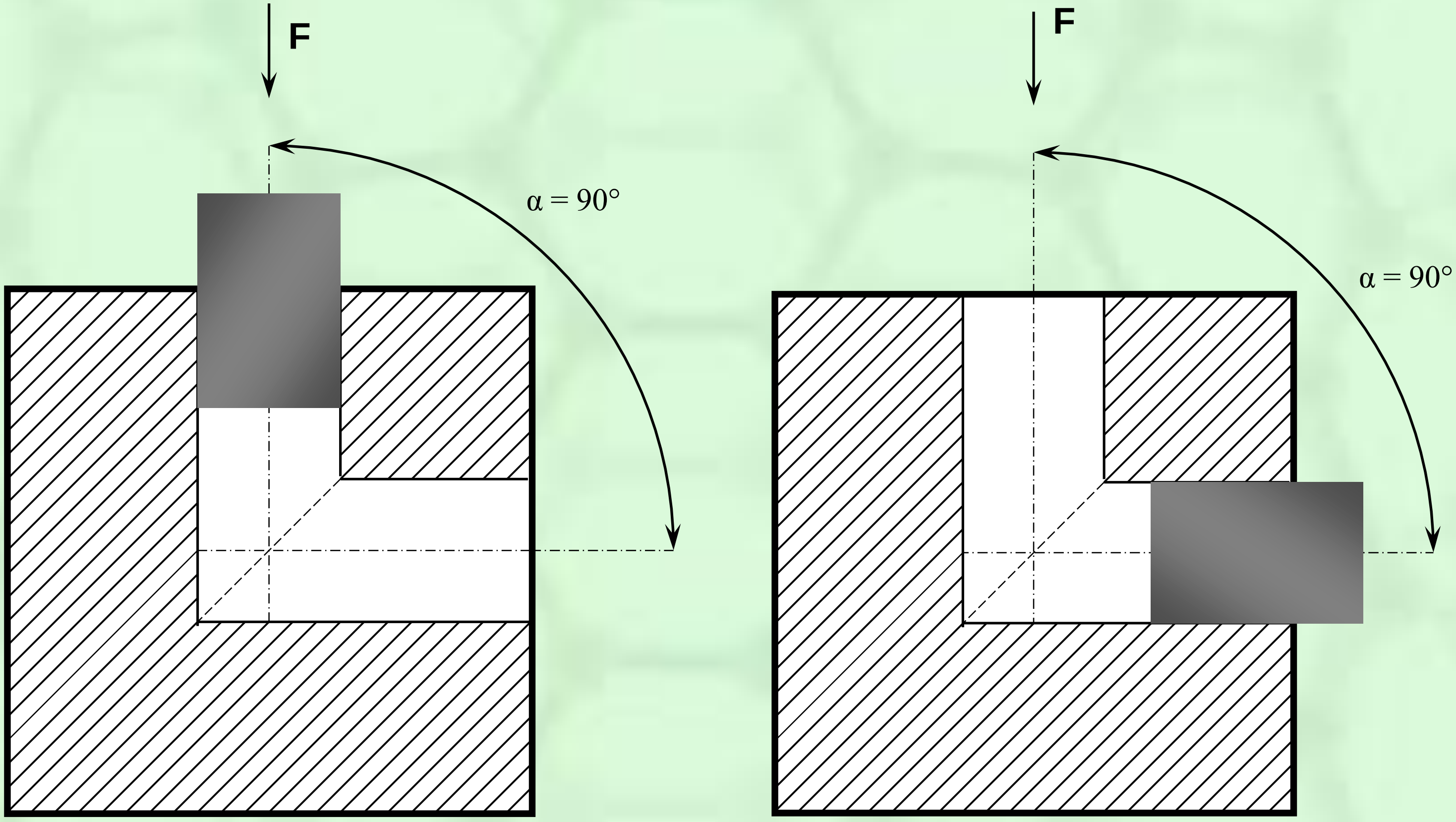
b)



E (d_2) = 87 [nm]
SD (d_2) = 42,9 [nm]

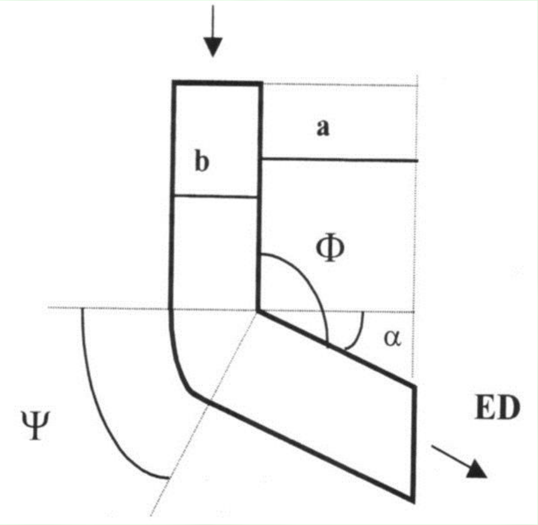
TEM micrograph (a) and grain size distribution (b) of Ti after hydrostatic extrusion (d2- equivalent diameter of grain size, E(d2)- mean equivalent diameter of grain size, SD(d2)-standard deviation, Cv(d2)-variation coefficient

(EQUAL–CHANNEL ANGULAR PRESSING)



(EQUAL–CHANNEL ANGULAR PRESSING)

$$\varepsilon_N = N * [2 * ctg(\phi/2 + \psi/2) + \psi * \sin^{-1}(\phi/2 + \psi/2)] / \sqrt{3}$$



$$\Phi = 90^o + \alpha$$

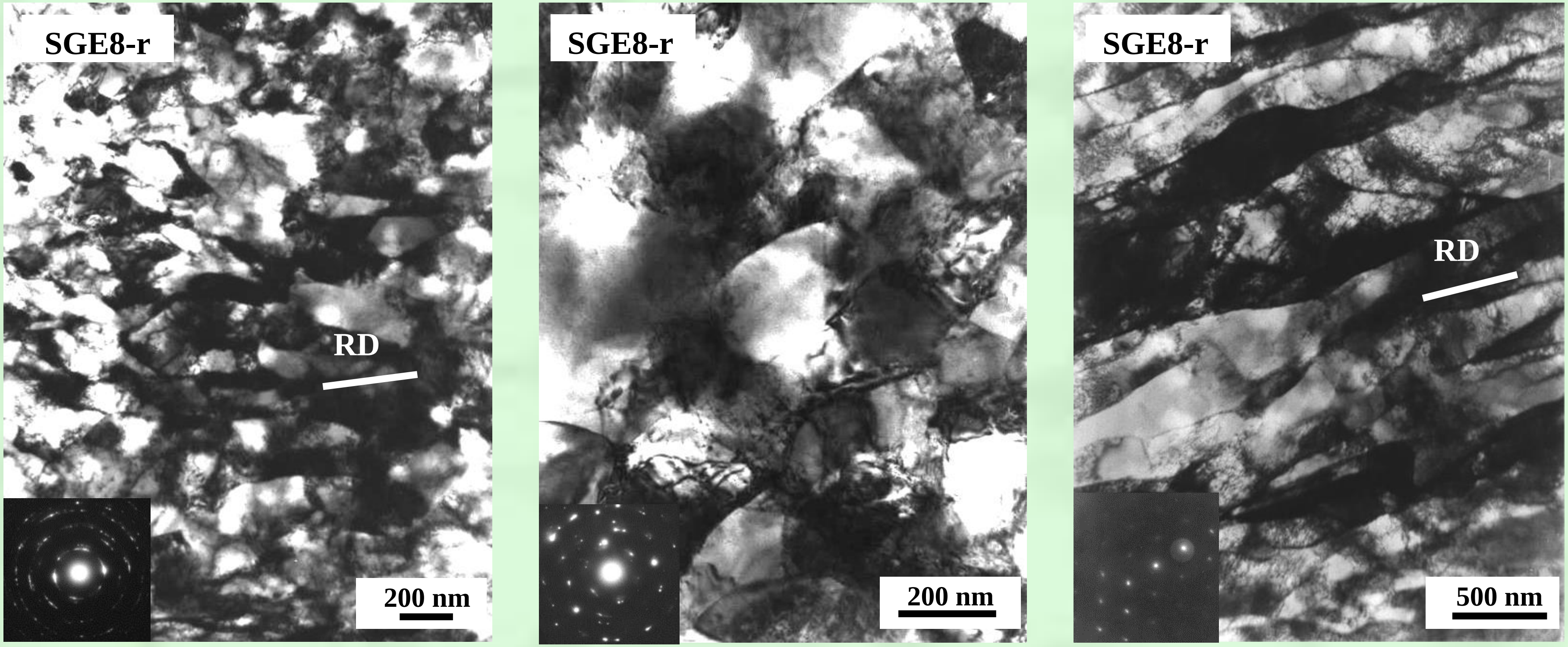
$$\Psi = 90^o - \alpha$$

$$\alpha = 0$$

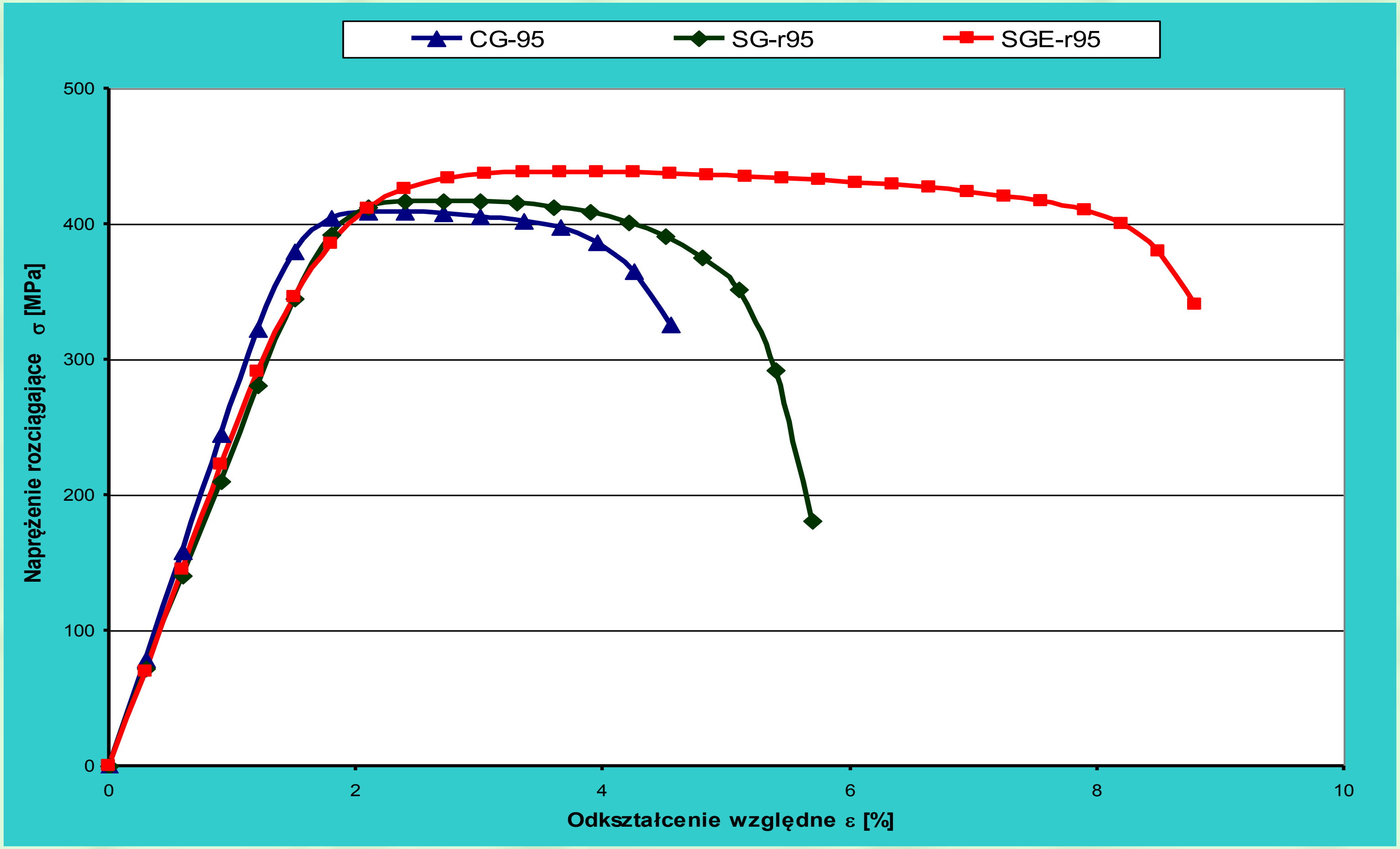
$$\varepsilon_N = N * 0,9069$$

J. Kuśnierz Microstructure and texture evoling under Equal Channel Angular (eca) processing Archives of Metallurgy Vol. 46 2001

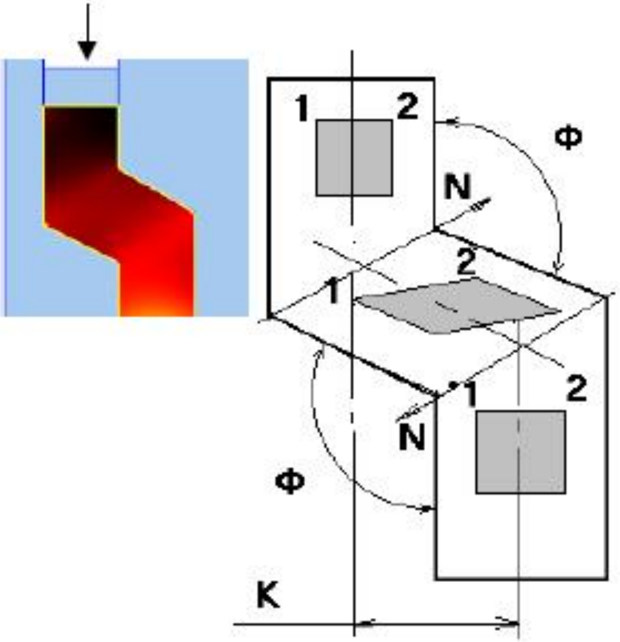
TEM MICROSTRUCTURES

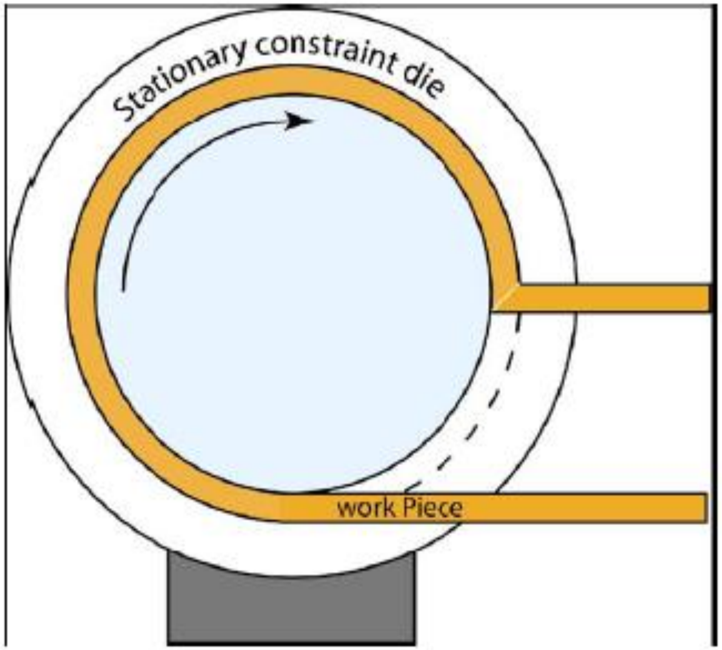


Mechanical properties tensile strength



New modifications of ECA pressing

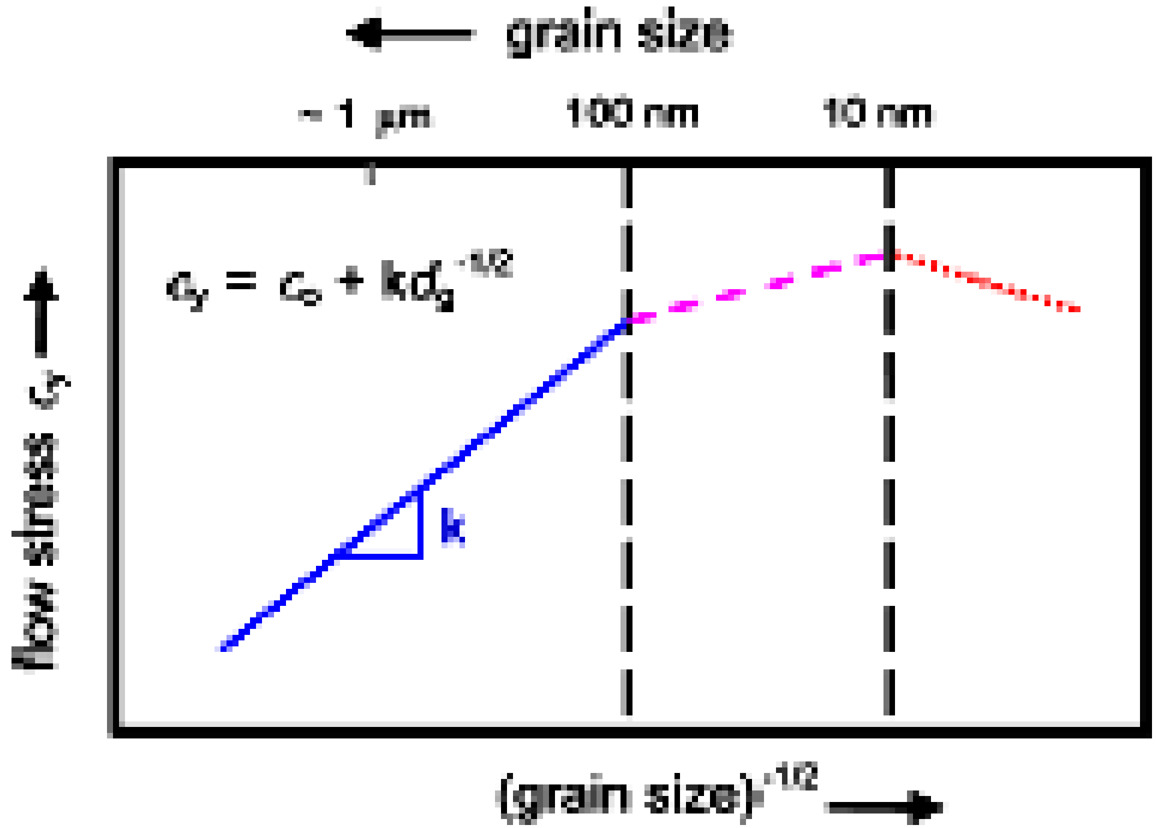




ECAP with parallel channels

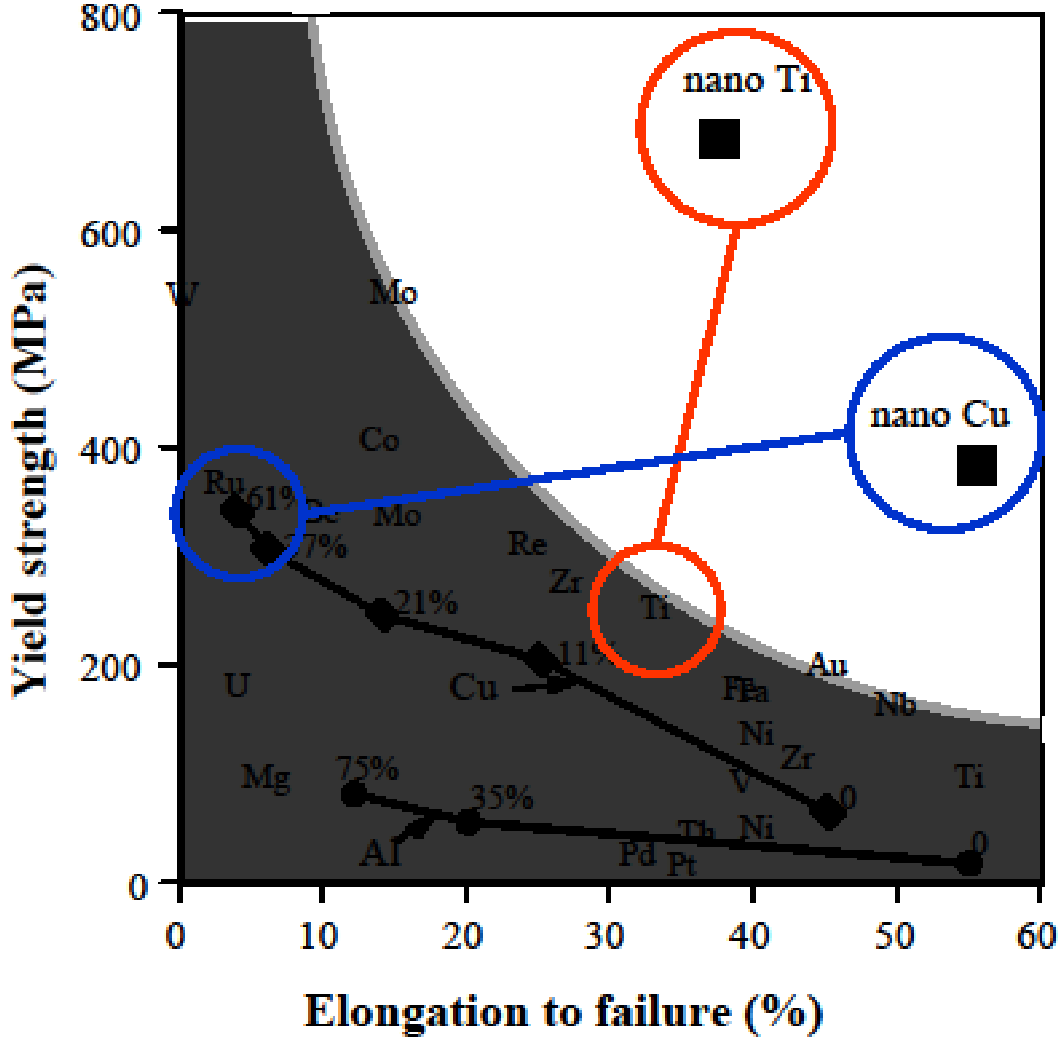
ECAP-Conform

RZ Valiev and TG Langdon, **Progr. Mater.Sci.,2006**



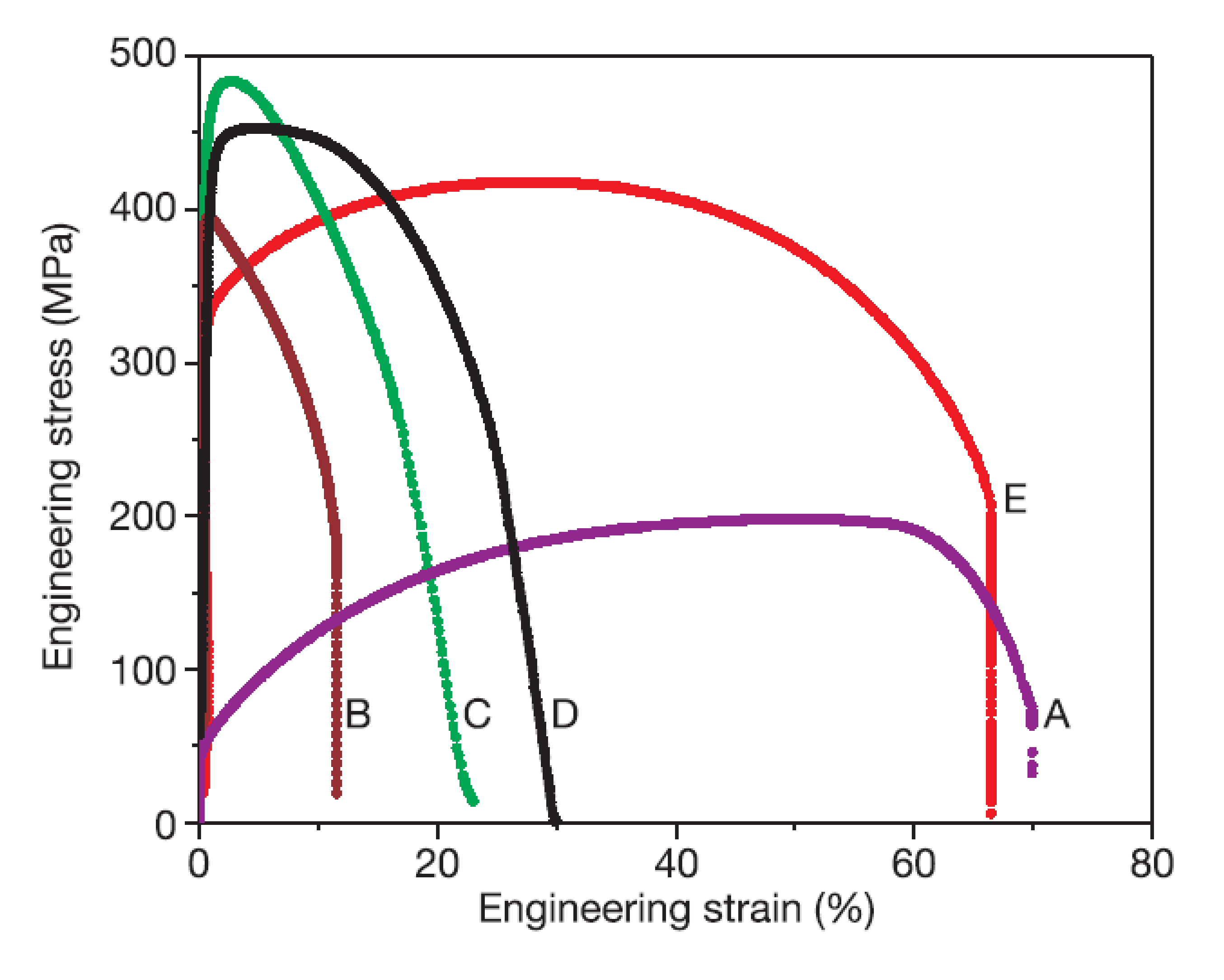
Yiekld stress as a function of grain size (-1/2) in micro and nano range for alloys and metals (after Kumar Acta mat. 2003 str.5747

Advanced mechanical properties by SPD



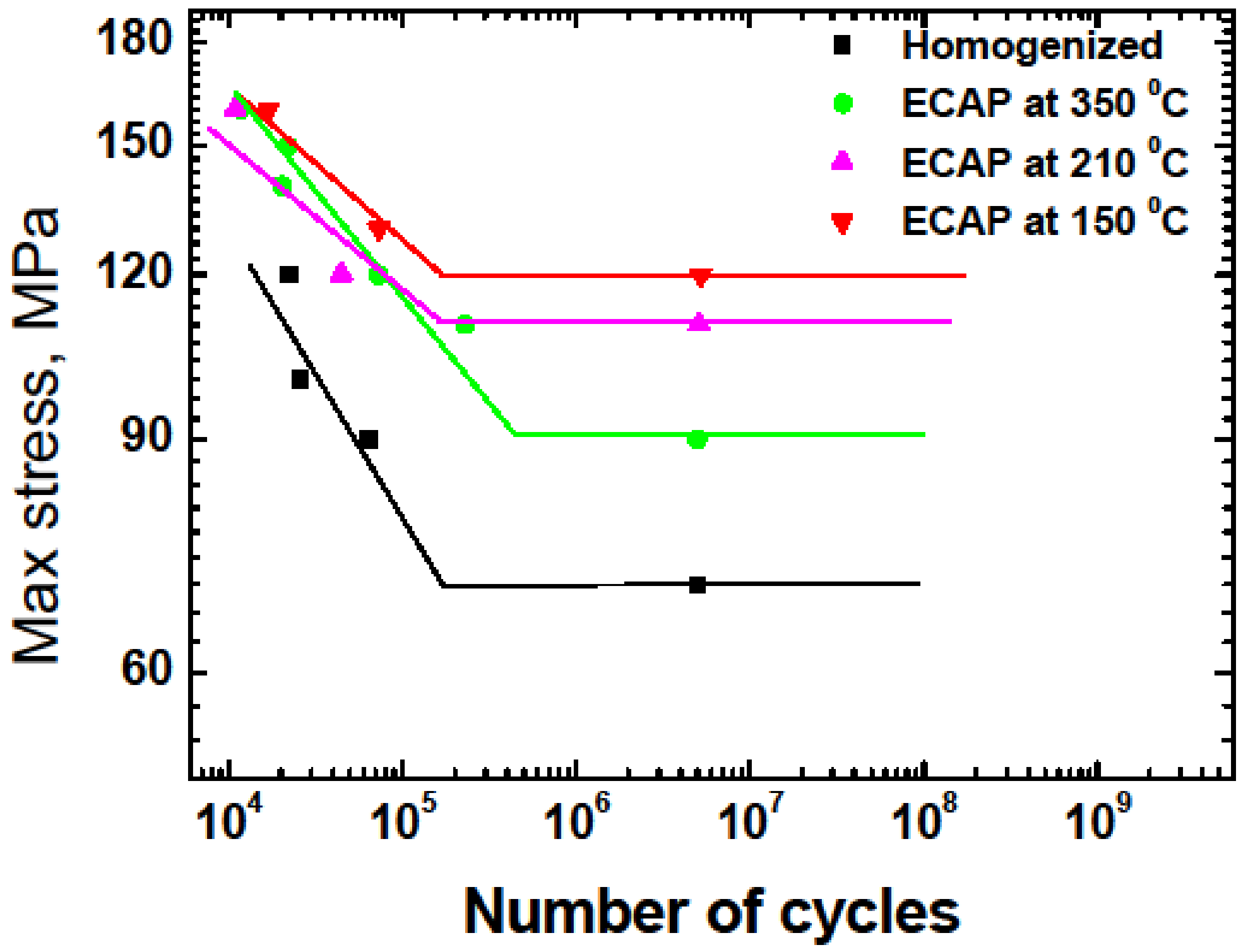
R.Z.Valiev et al., J. Mater. Res. 17, 5-8 (2002)

Cu99,9 9



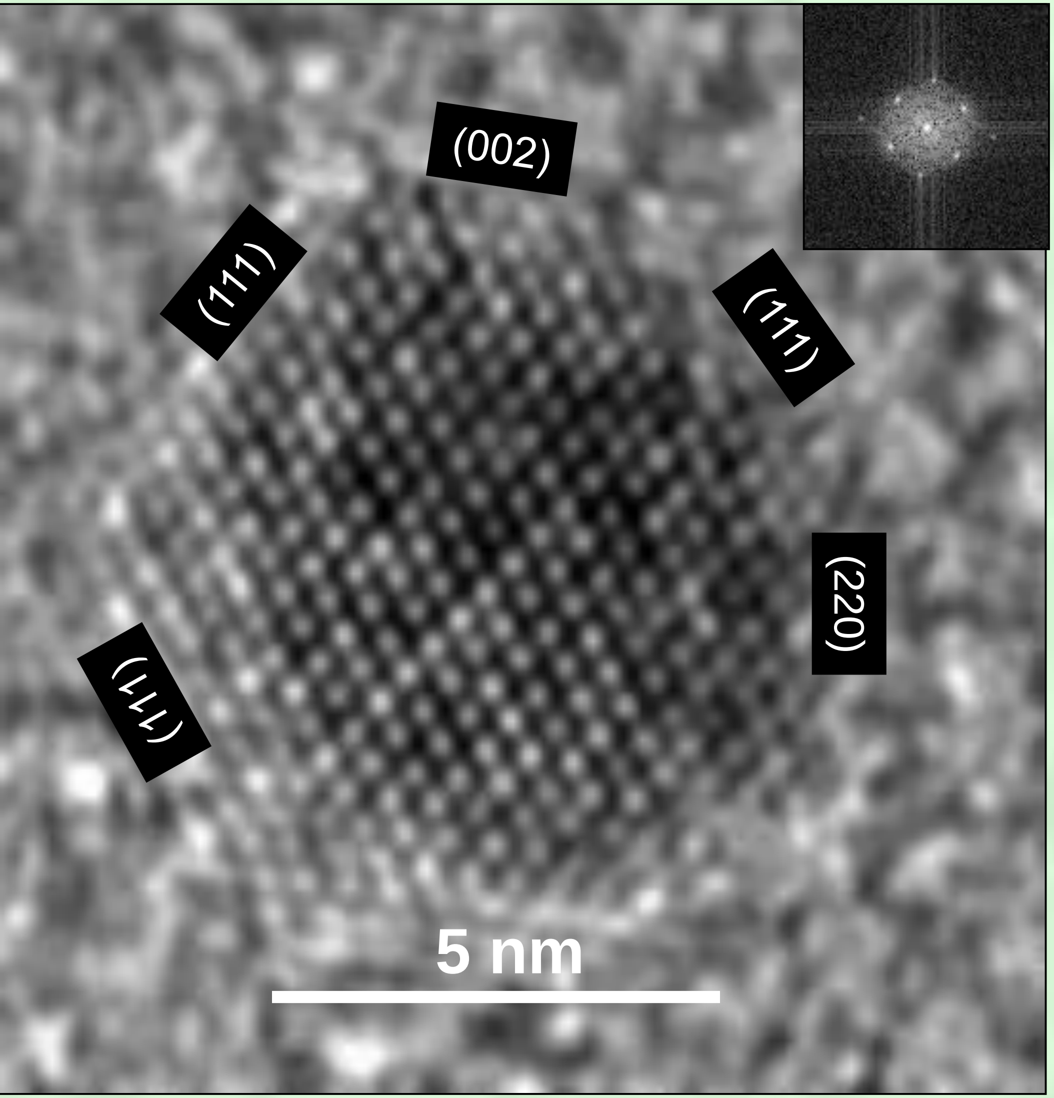
High Strength ***and High Ductility of SPD Nanomaterials*** **Y.Wang, M.Chen, F.Zhou, En Ma, Nature 419, 912-915 (2002**

Enhanced Fatigue Strength in ECAPed Mg-Al AM 60 alloy

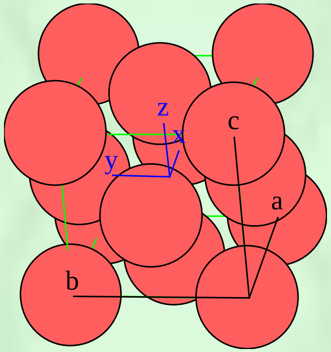


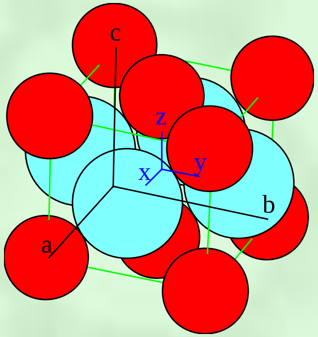
O. Kulyasova (USATU) et al., M. Zehetbauer et al. (Univ. Vienna) (2008)

FePt Nanoparticles

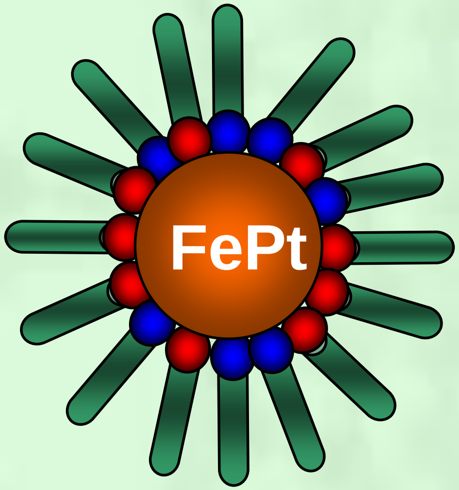


fcc disordered





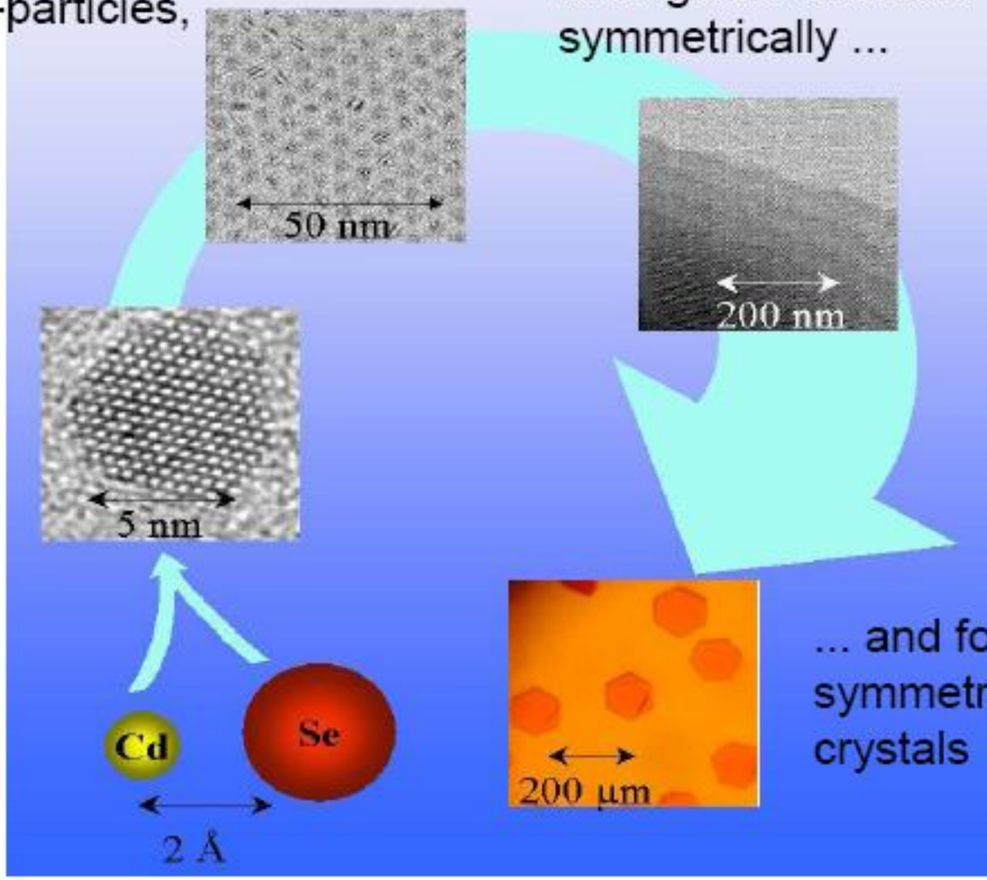
$L1_0$



Surface structures of nano-particles: from the atom to the super-crystal

Cd and Se atoms form nano-particles, ...

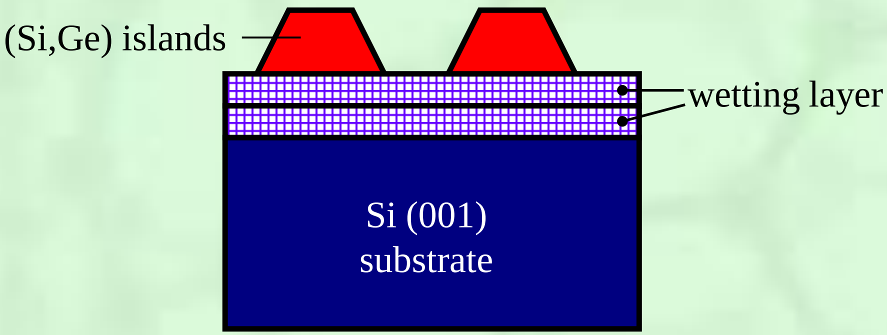
... the nano-particles arrange themselves symmetrically ...



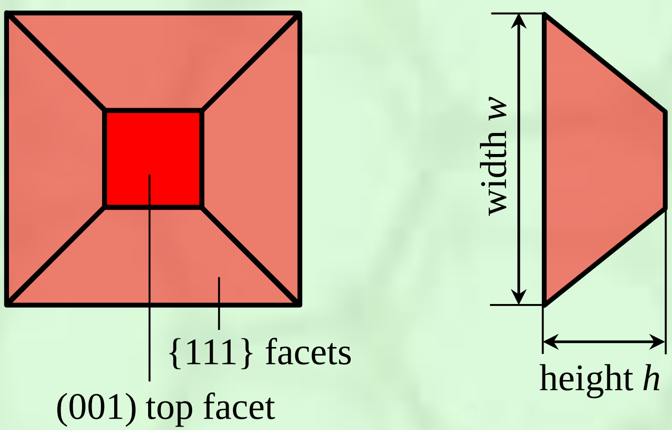
... and form symmetrical crystals

Motivation

Shape and geometry



Stranski-Krastanov growth *(Self-organized growth)*



Aspect ratio: $\boxed{A_r = w / h}$

experimental: $A_r \approx 2.0$

Topography by AFM