Evolution of Solutions

Thermodynamics of Mechanical Alloying

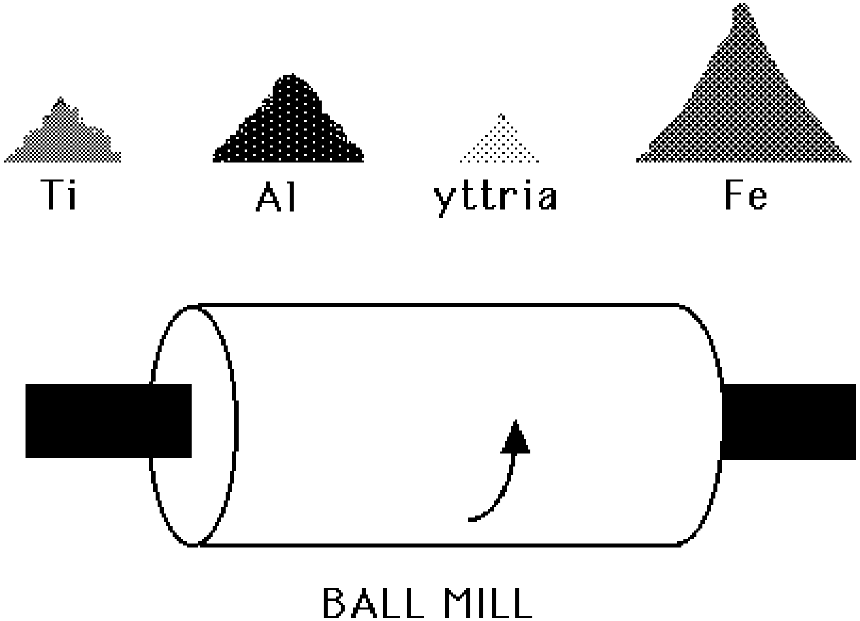
A. Badmos and H. K. D. H. Bhadeshia, Metall. & Mater. Trans. A, 18A (1997) 2189.

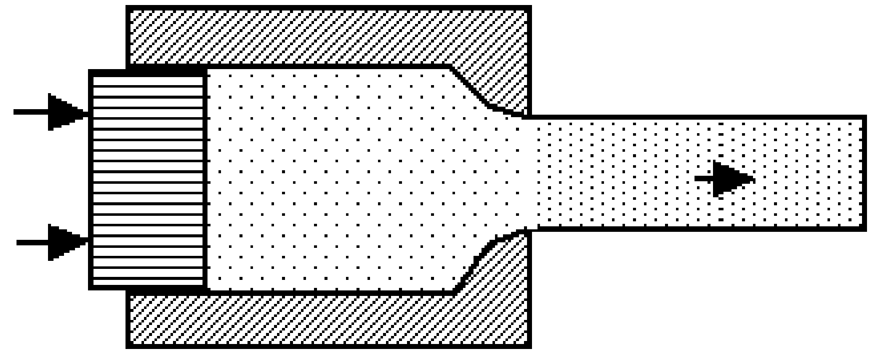
H. K. D. H. Bhadeshia,

Proceedings of the Royal Microscopical Society, 35 (2000) 95.

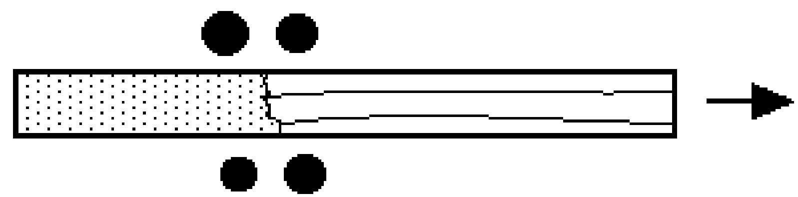
Materials Science and Technology, 16 (2000) 1404.

H. K. D. H. Bhadeshia & H. Harada, Applied Surface Science, 67 (1993) 328.

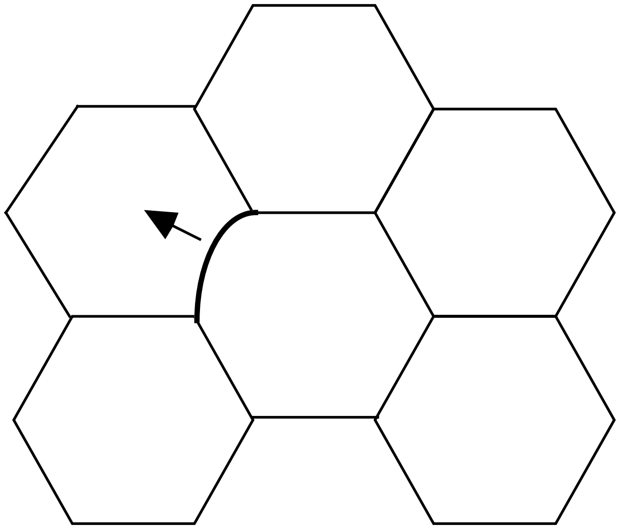




Mechanically Alloyed

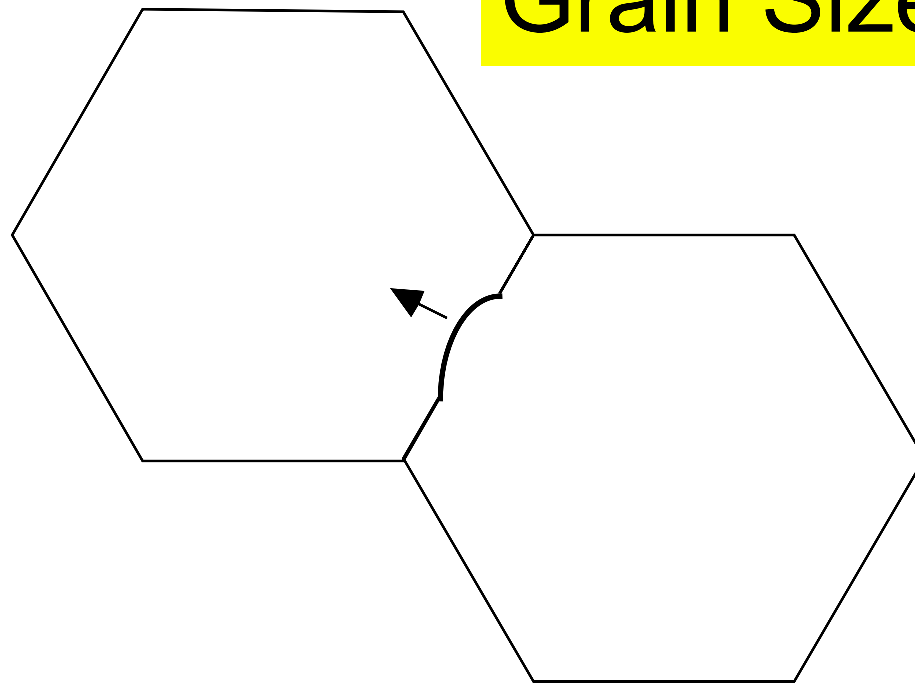


Oxide Dispersion Strengthened Metals

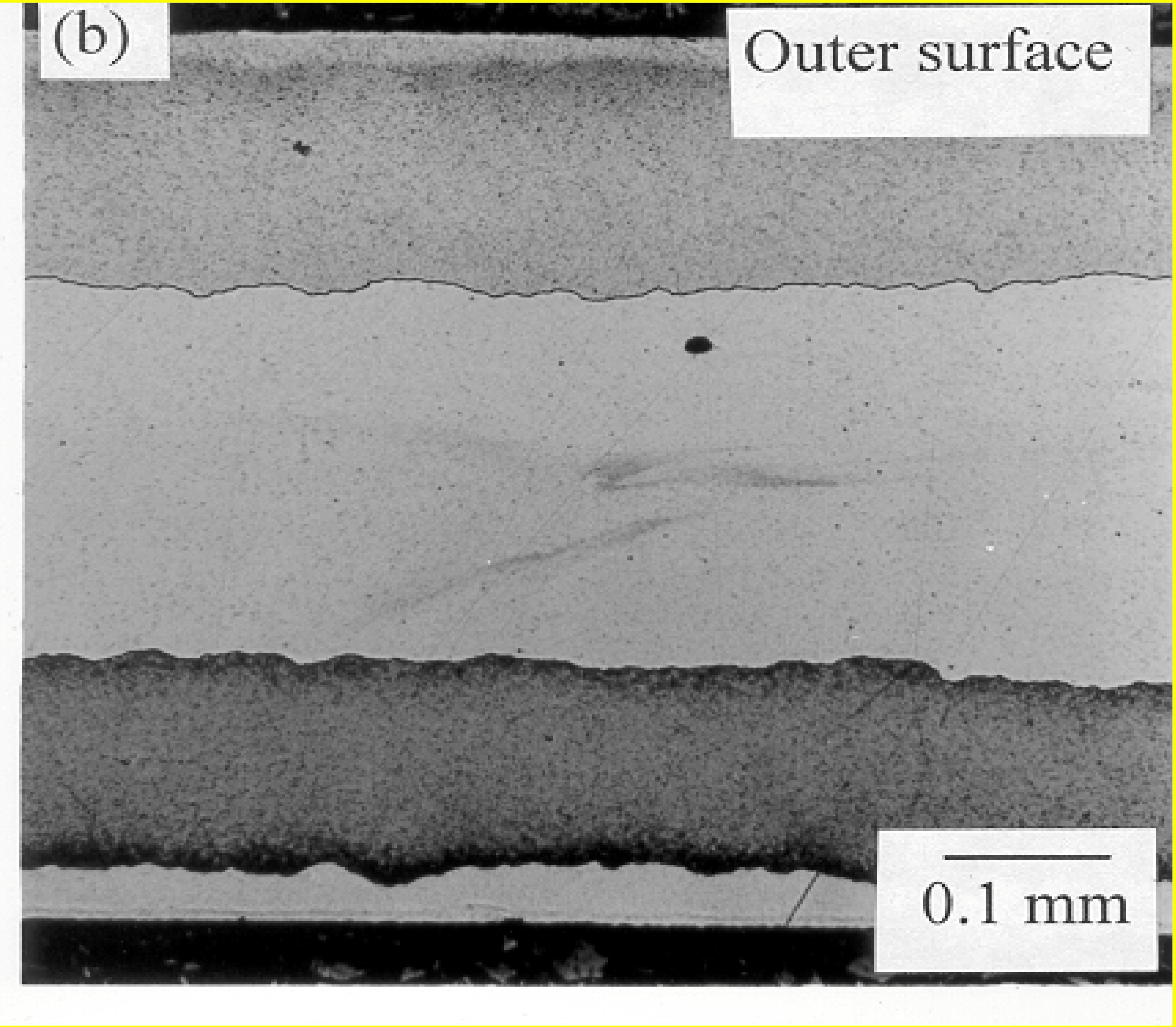


Sub Micron
Grain Size

Normal
Grain Size



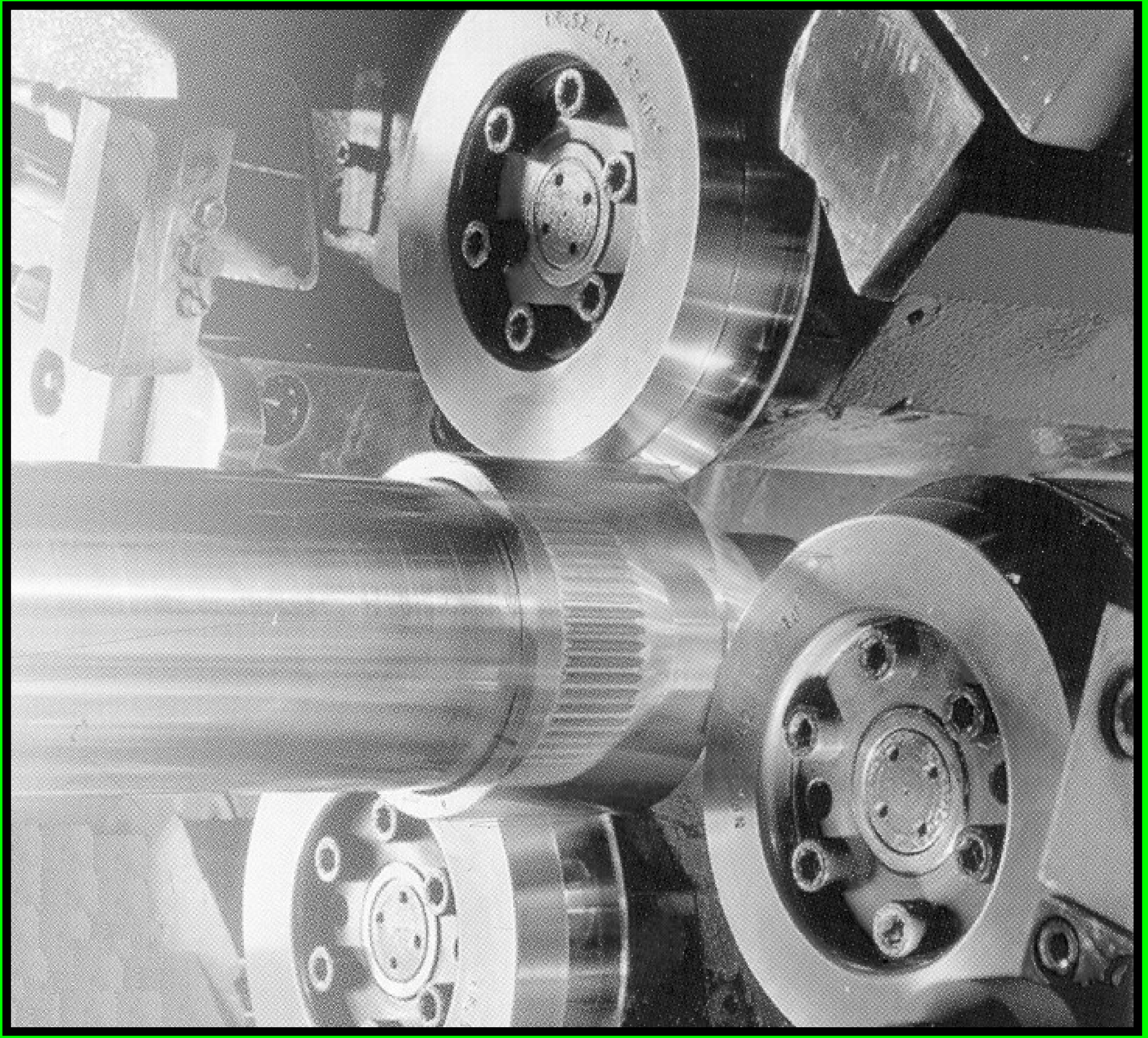
Grain junctions powerful pinning points for small grains, which are no longer topologically independent



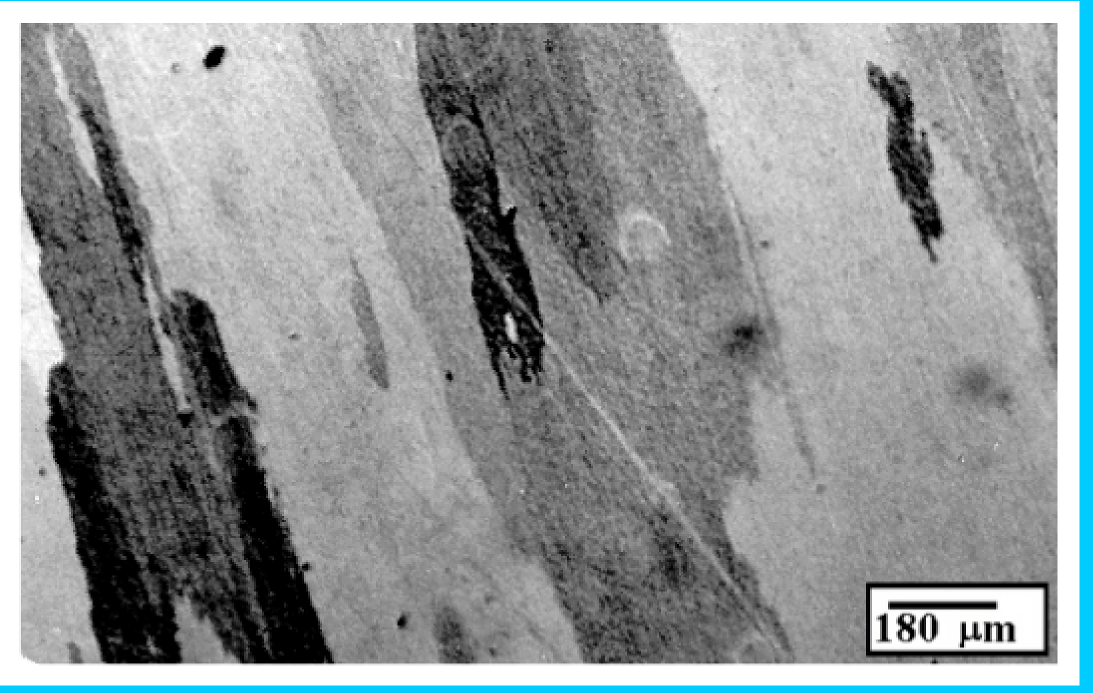
Fe-20Cr-5Al-0.5Ti-0.3 yttria wt%

90% reduction

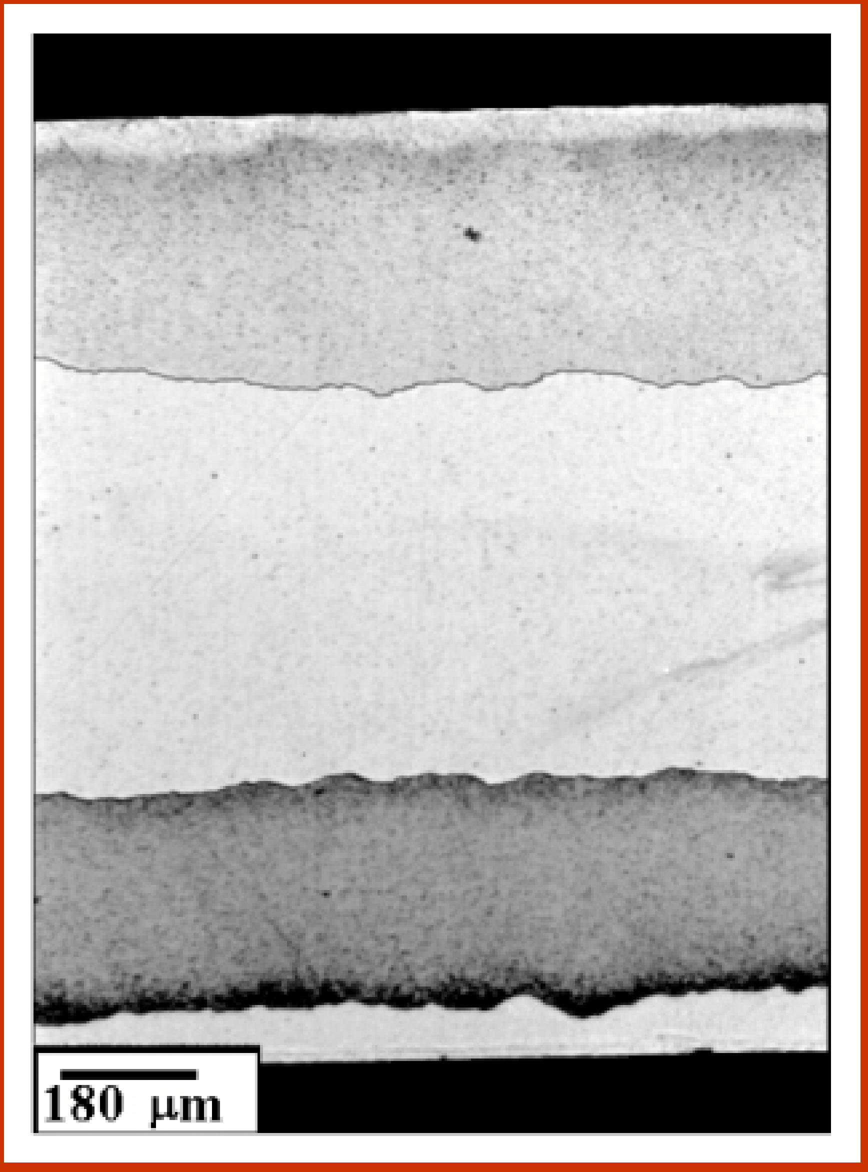
Capdevila & Bhadeshia, 2000



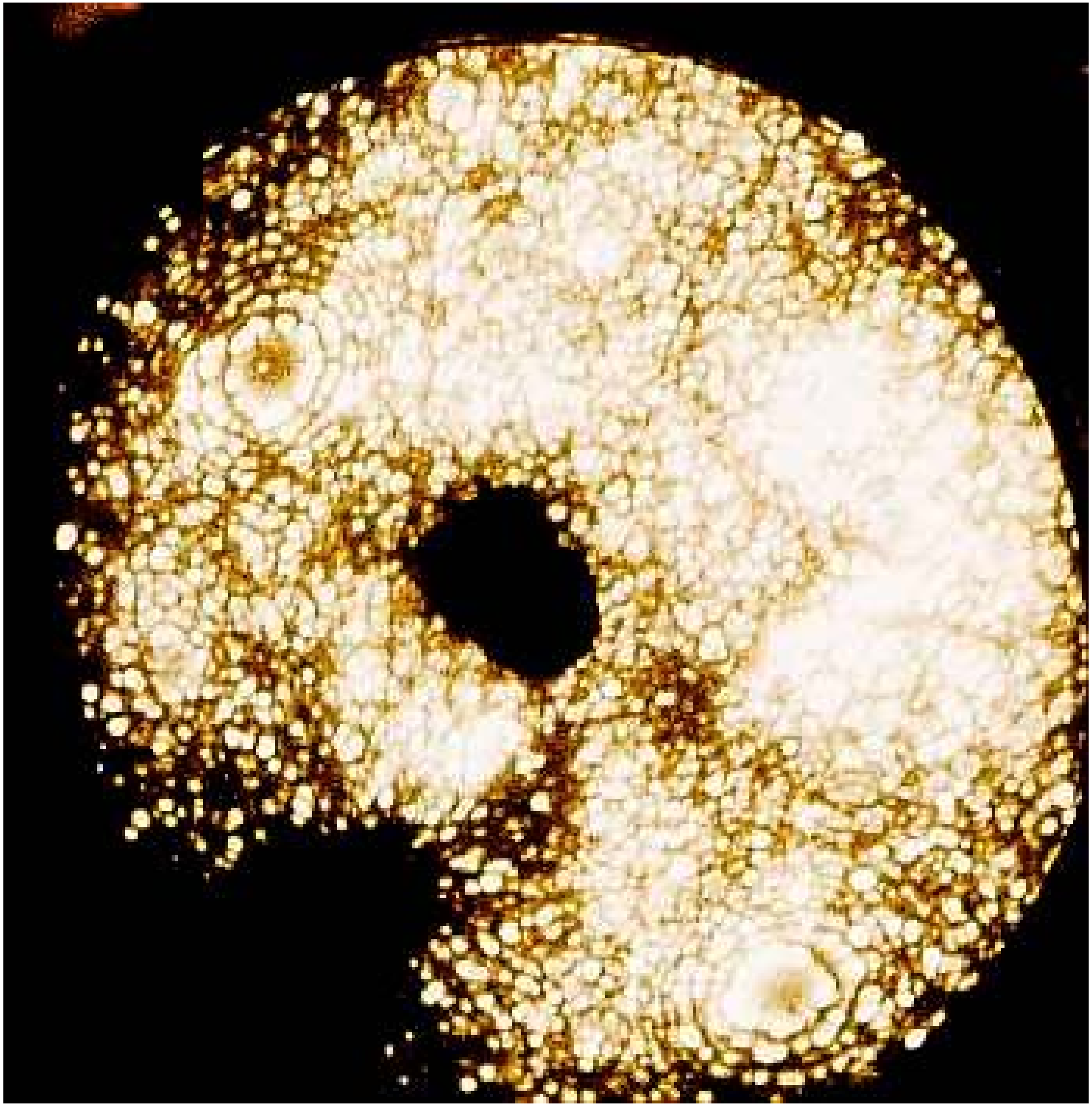
Helical grains



Capdevila & Bhadeshia, 2000

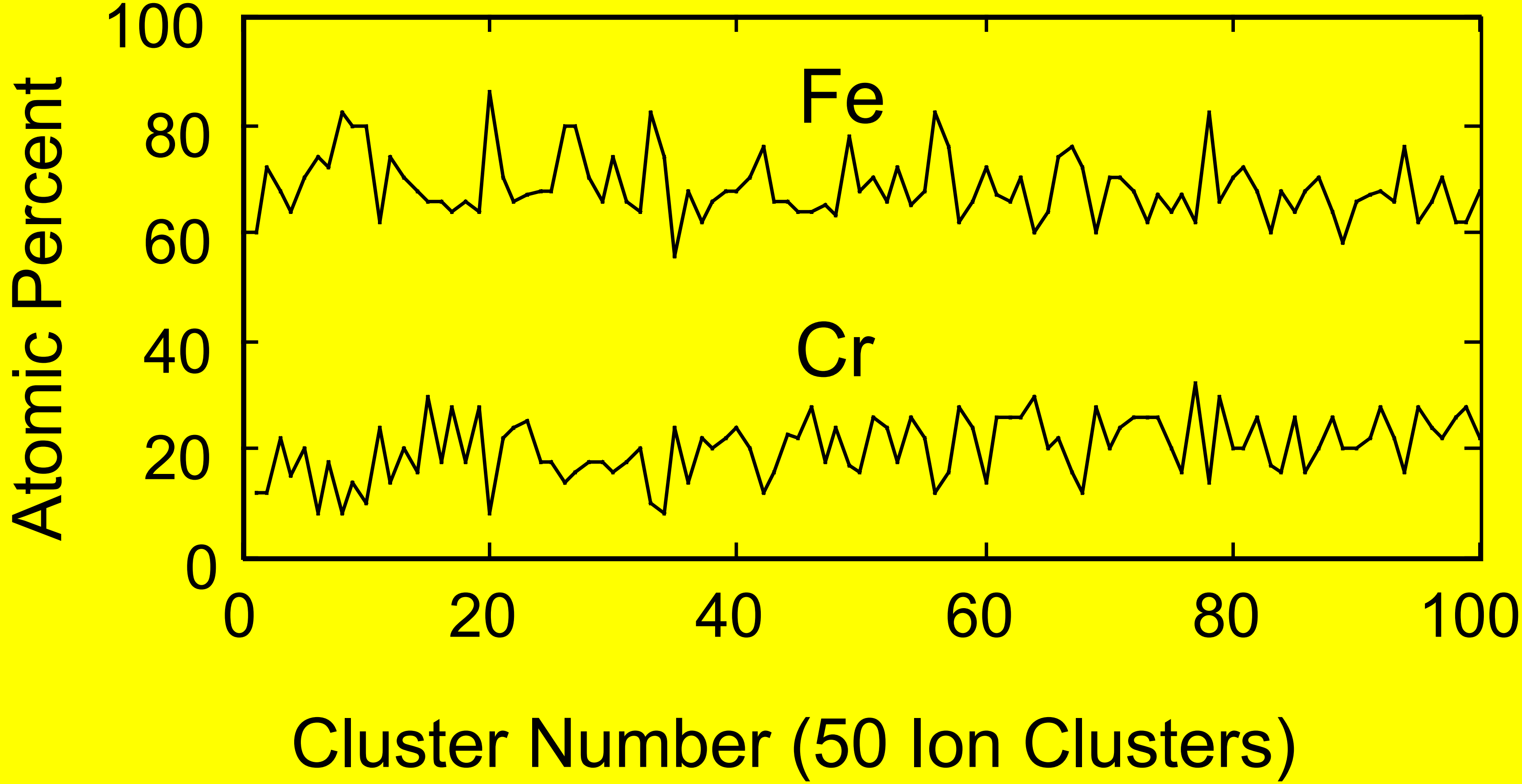


Capdevila & Bhadeshia, 2000



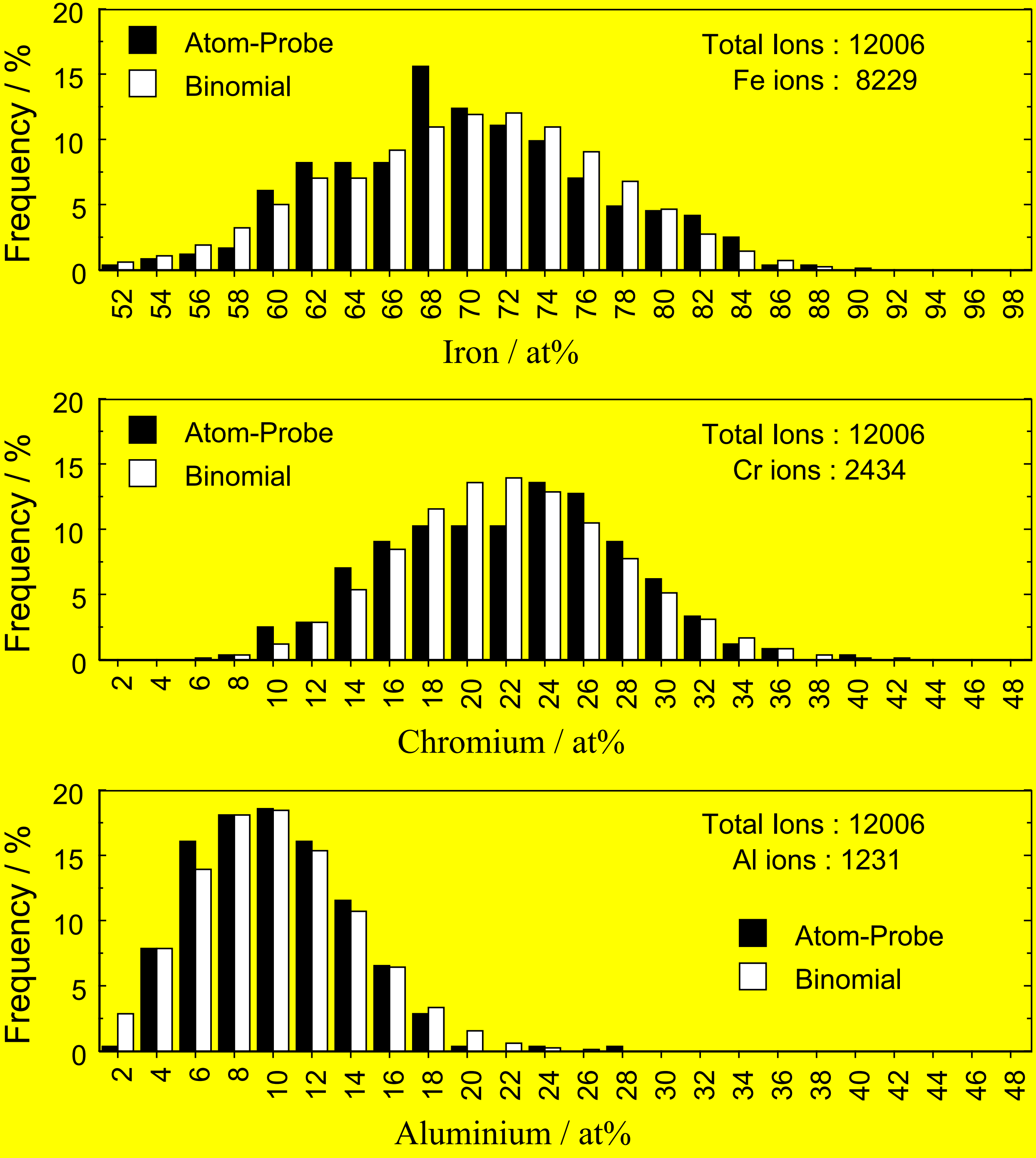
Atom probe image of MA957

MA956



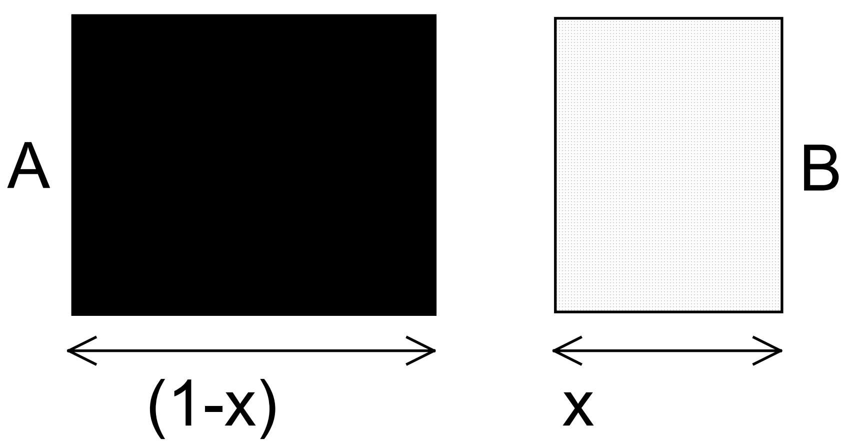
Chou & Bhadeshia, 1994

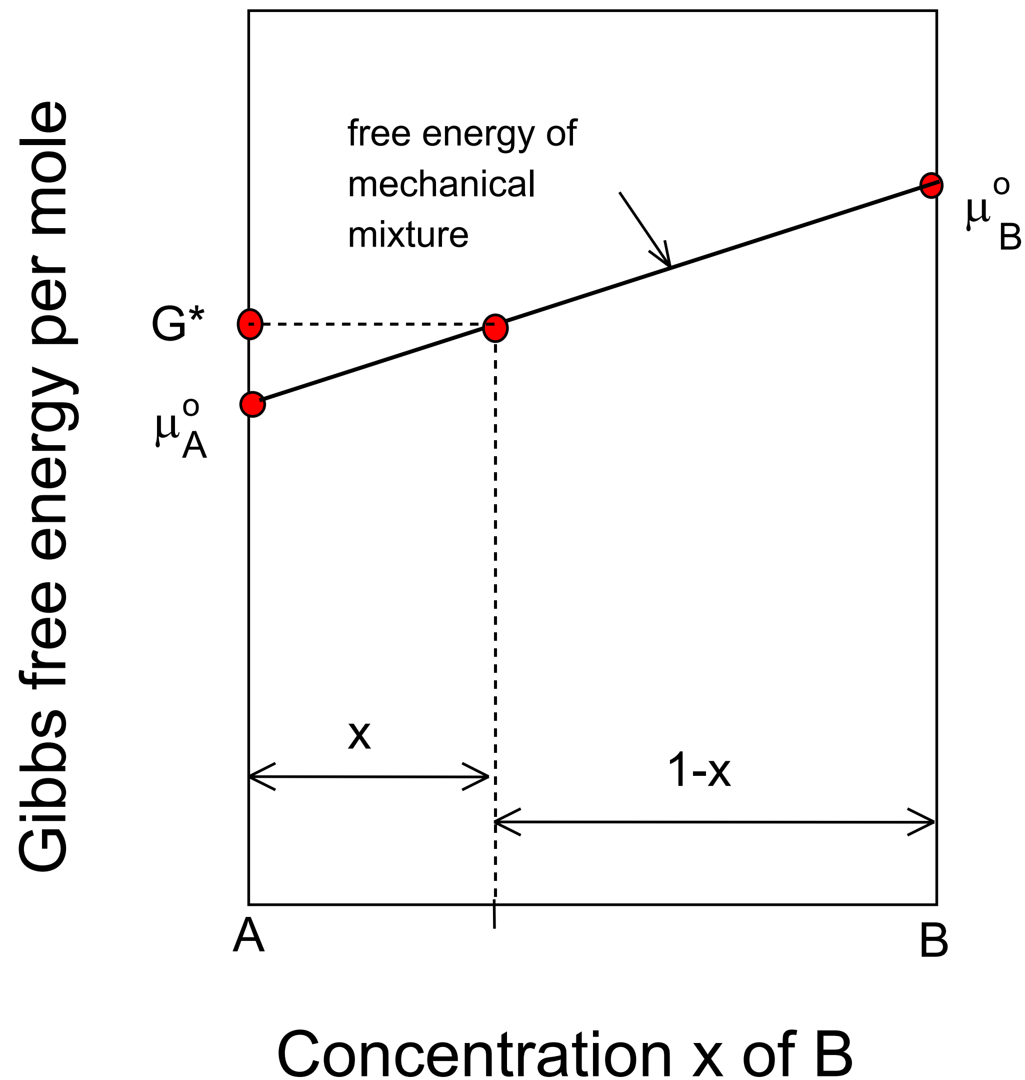
MA956



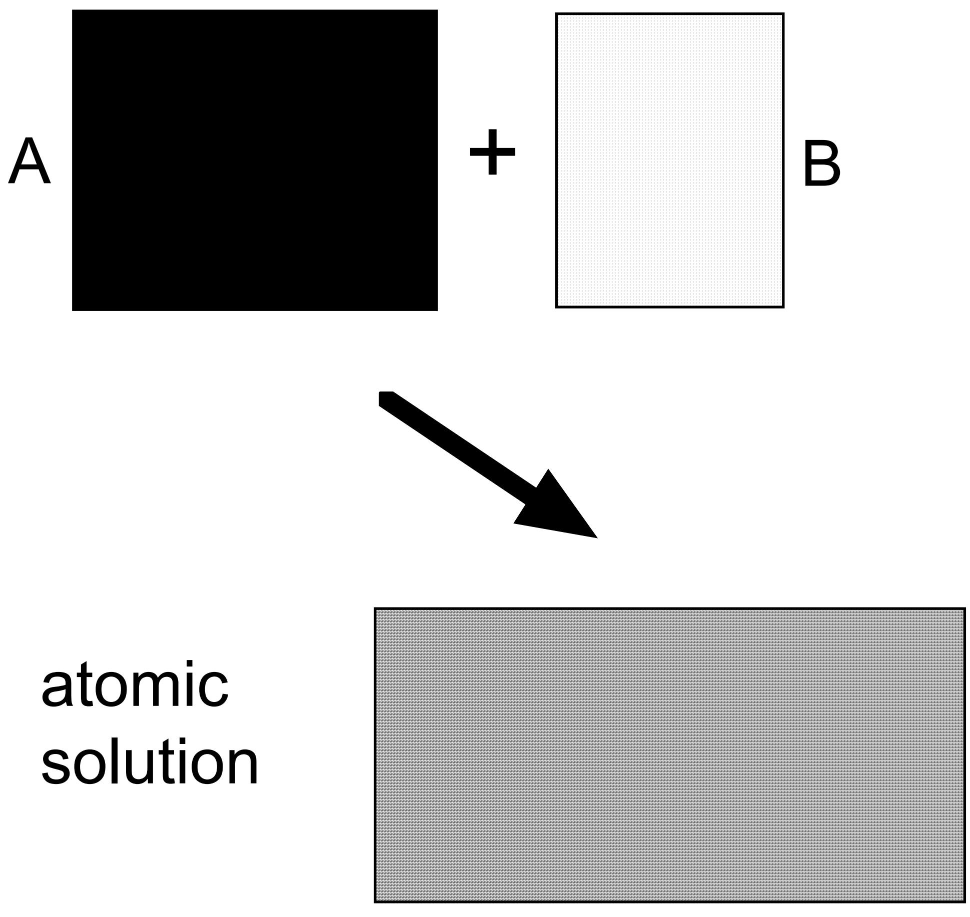
Chou & Bhadeshia, 1994

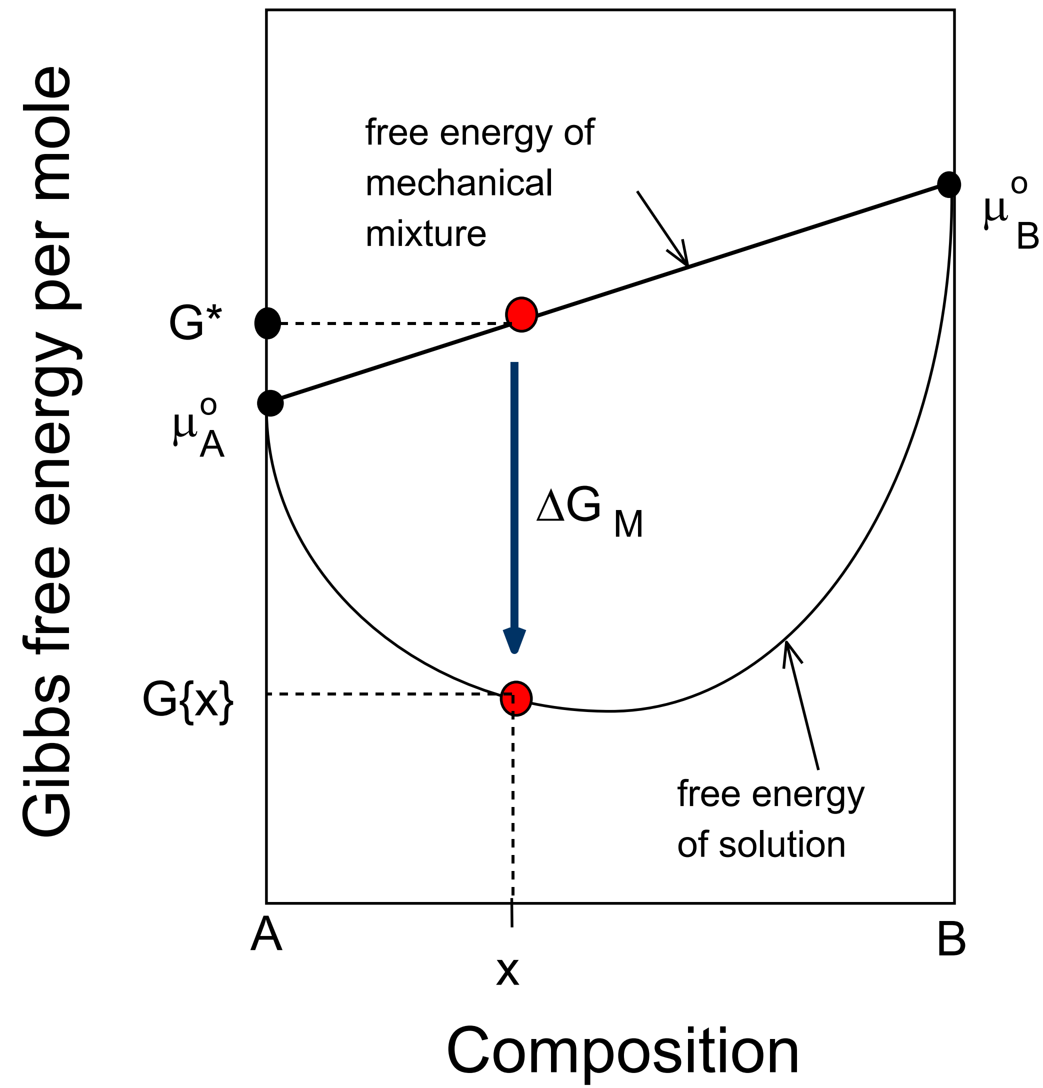
Mechanical Mixture



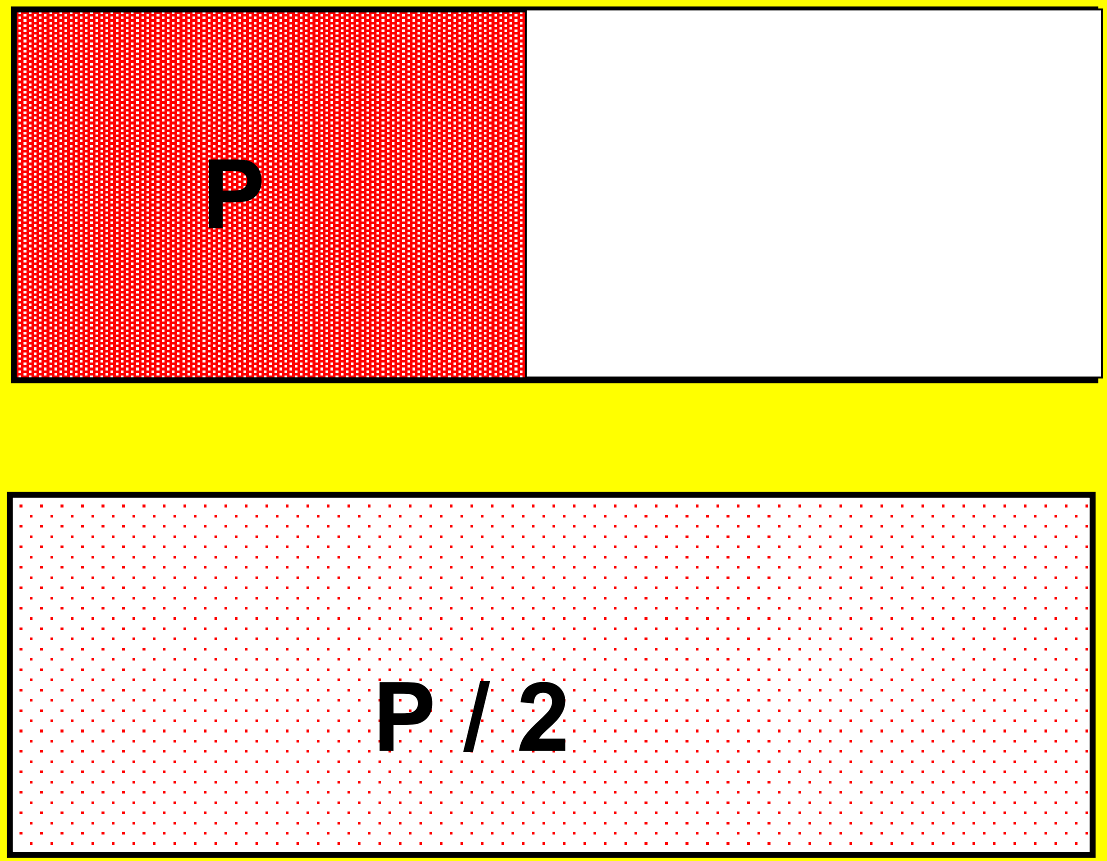


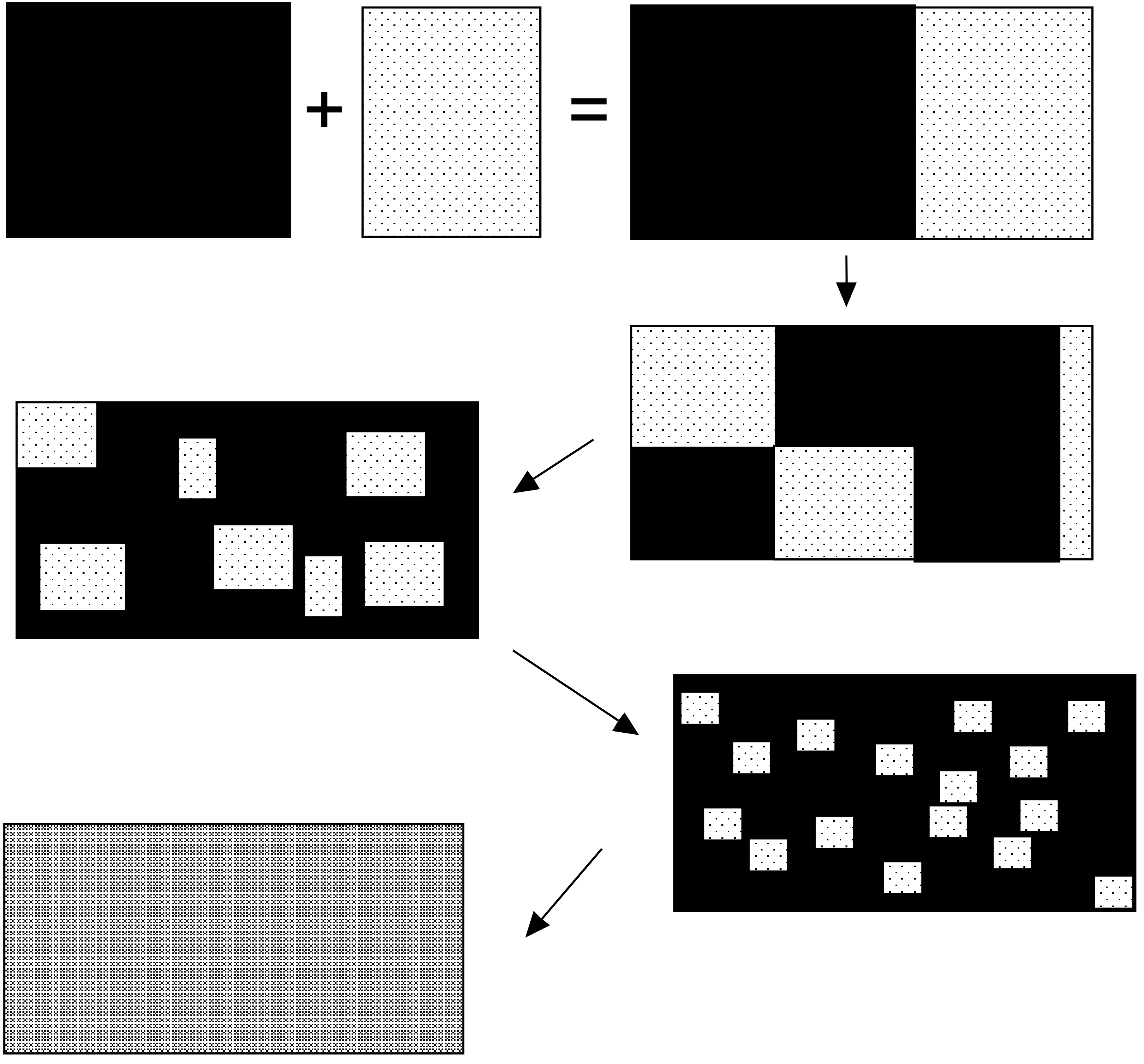
Solution


A
+
B
atomic
solution


Gibbs free energy per mole
free energy of
mechanical
mixture
μ^o_B
G*
μ^o_A
ΔG_M
G{x}
free energy
of solution
A
x
B
Composition

Entropy





For a random mixture, number of configurations given by:

$$\frac{\left(N_a([1-x]/m_A + x/m_B)\right)!}{(N_a[1-x]/m_A)!\ (N_a x/m_B)!}$$

m_A = number of atoms per particle of A

m_B = number of atoms per particle of B

N_a = Avogadros number

Boltzmann

$$S = k \ln\{w\}$$

$$\frac{\Delta S_M}{kN_a} = \frac{(1-x)m_B + xm_A}{m_A m_B} \times$$

$$\ln\left\{N_a \frac{(1-x)m_B + xm_A}{m_A m_B}\right\}$$

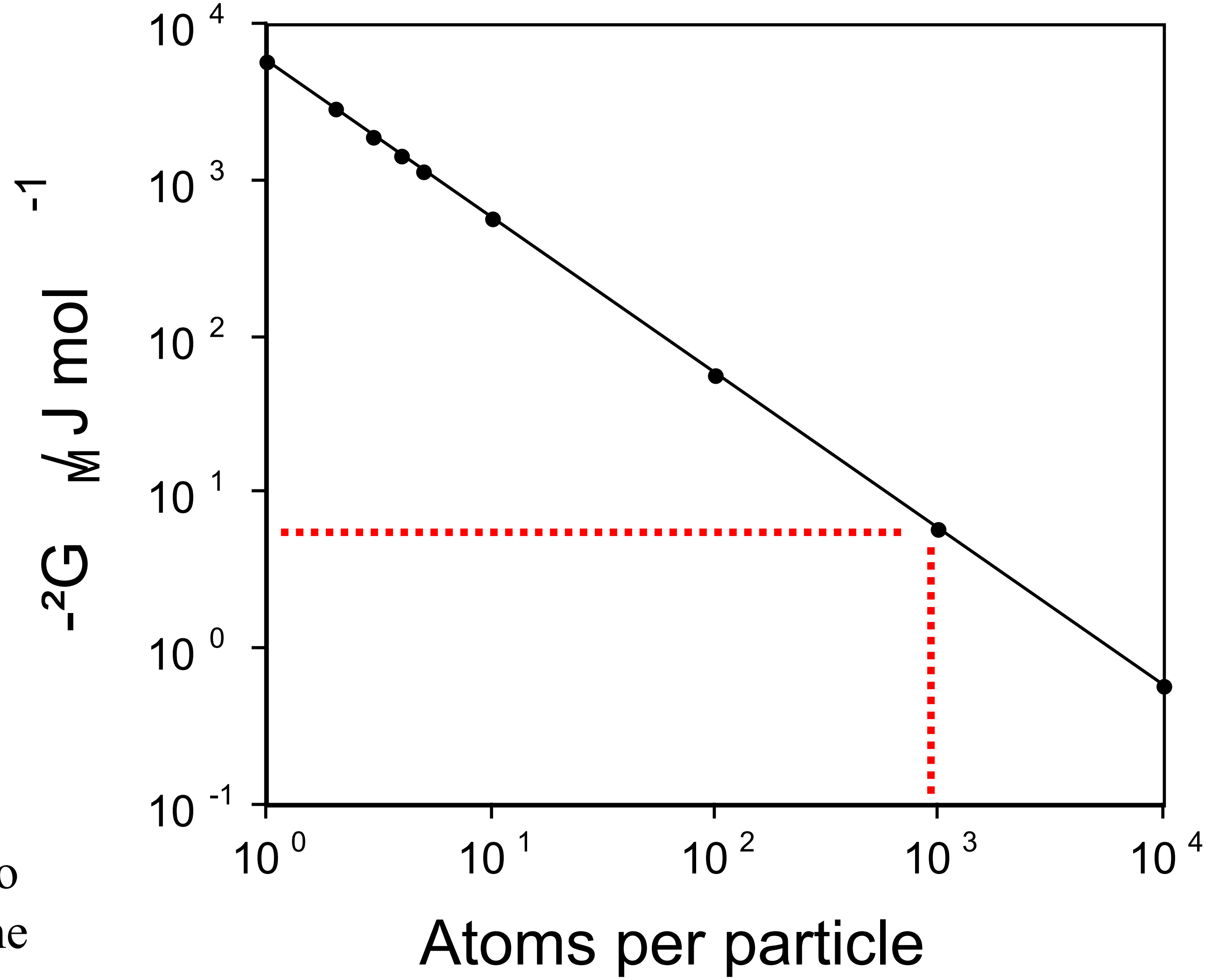
$$- \frac{1-x}{m_A} \ln\left\{\frac{N_a(1-x)}{m_A}\right\}$$

$$- \frac{x}{m_B} \ln\left\{\frac{N_a x}{m_B}\right\}$$

Classical theory for entropy of mixing

$$-\frac{\Delta S_M}{kN_a} = (1-x)\ln\{1-x\} + x\ln\{x\}$$

Solution-like behaviour when particles about **1000 atoms** in size

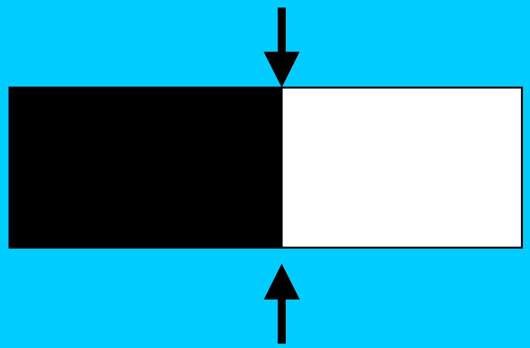


Free energy of mixing due to configurational entropy alone

Enthalpy

$$\Delta H_M \simeq N_a z(1-x)x\omega$$

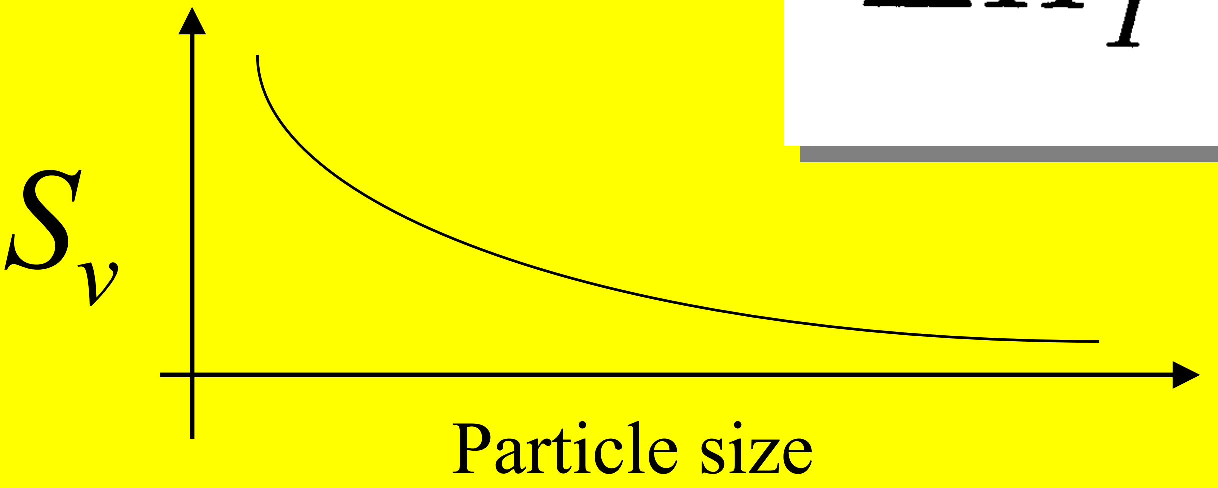
$$\omega = \epsilon_{AA} + \epsilon_{BB} - 2\epsilon_{AB}$$



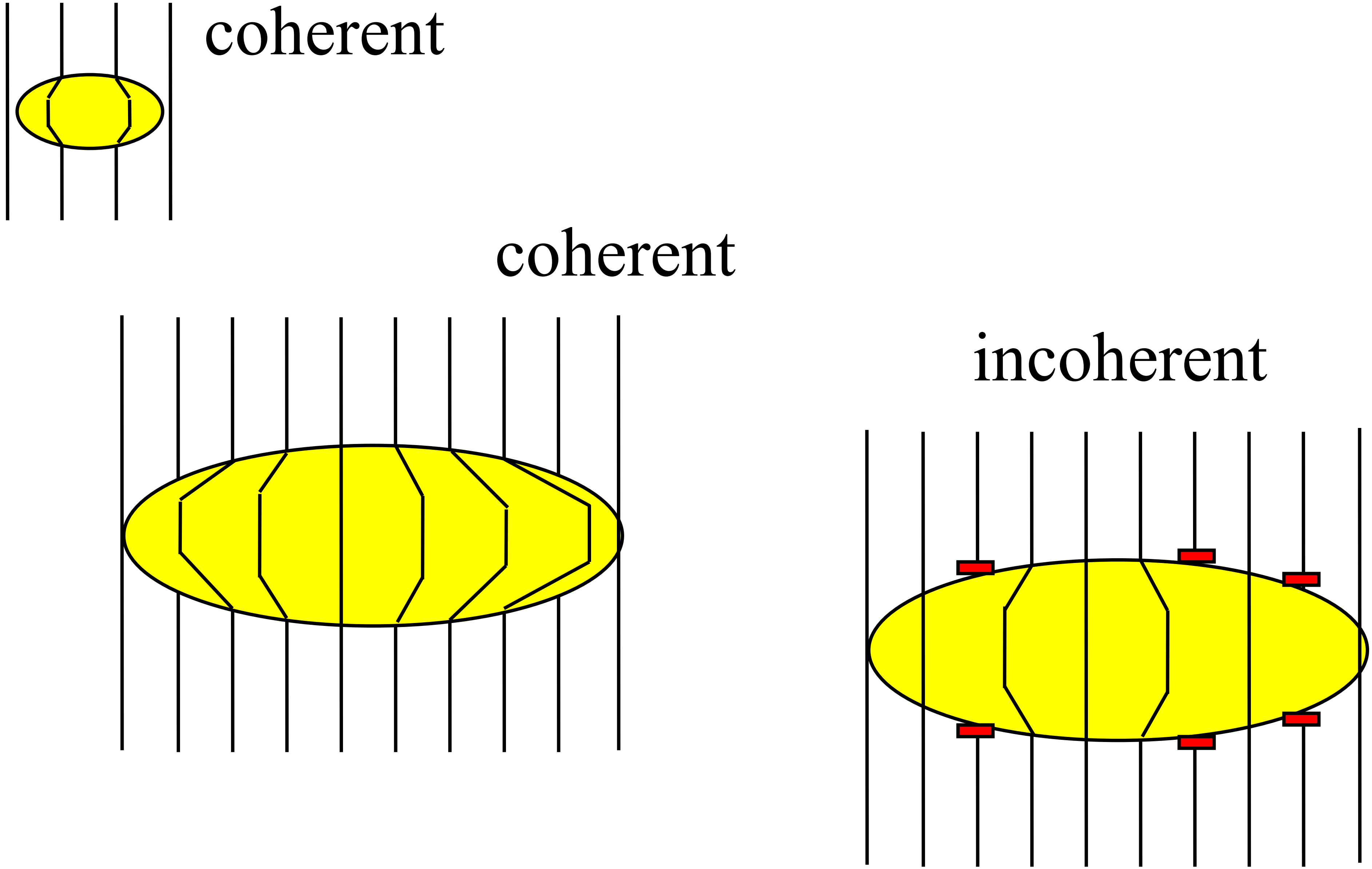
Surface per unit volume

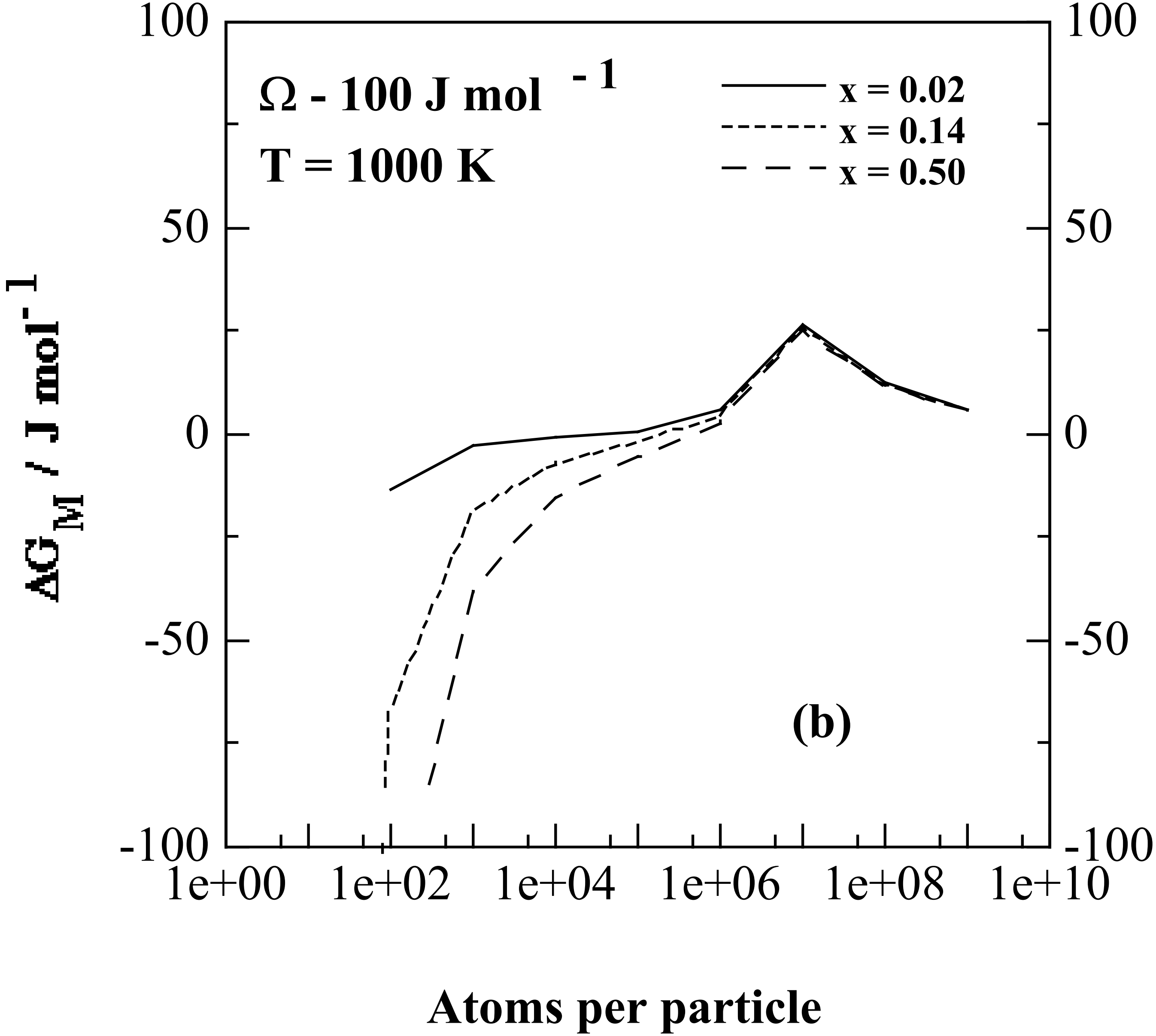
$$S_V = \frac{1}{2}\sum_i n_i 6(m_i \Phi_i)^{\frac{2}{3}} \bigg/ \sum_i \frac{N_a x_i}{m_i} V_i$$

$$\Delta H_I = V_m S_V \sigma$$



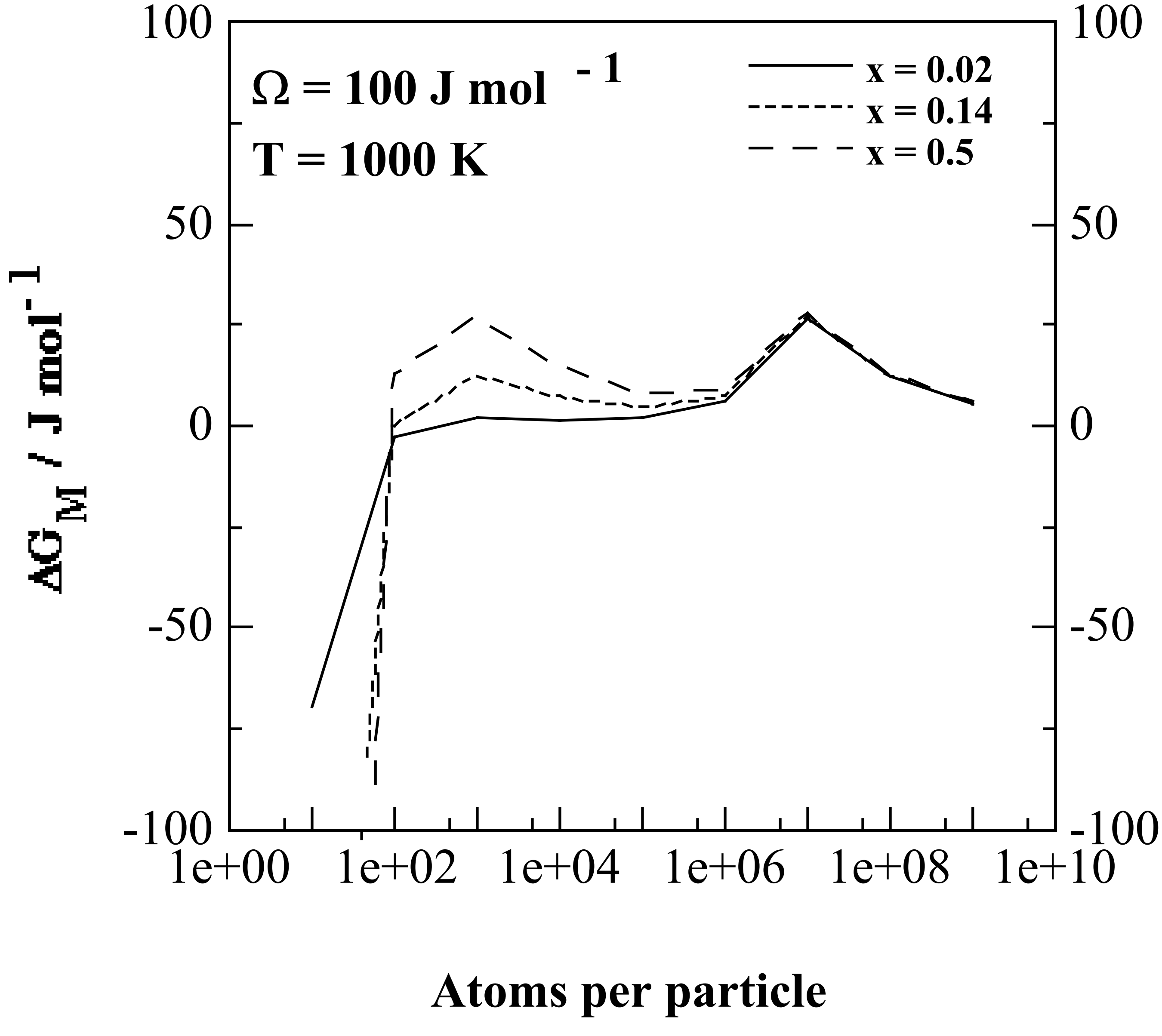
Solution formation impossible!


coherent
coherent
incoherent



Single barrier to solution formation when components attract

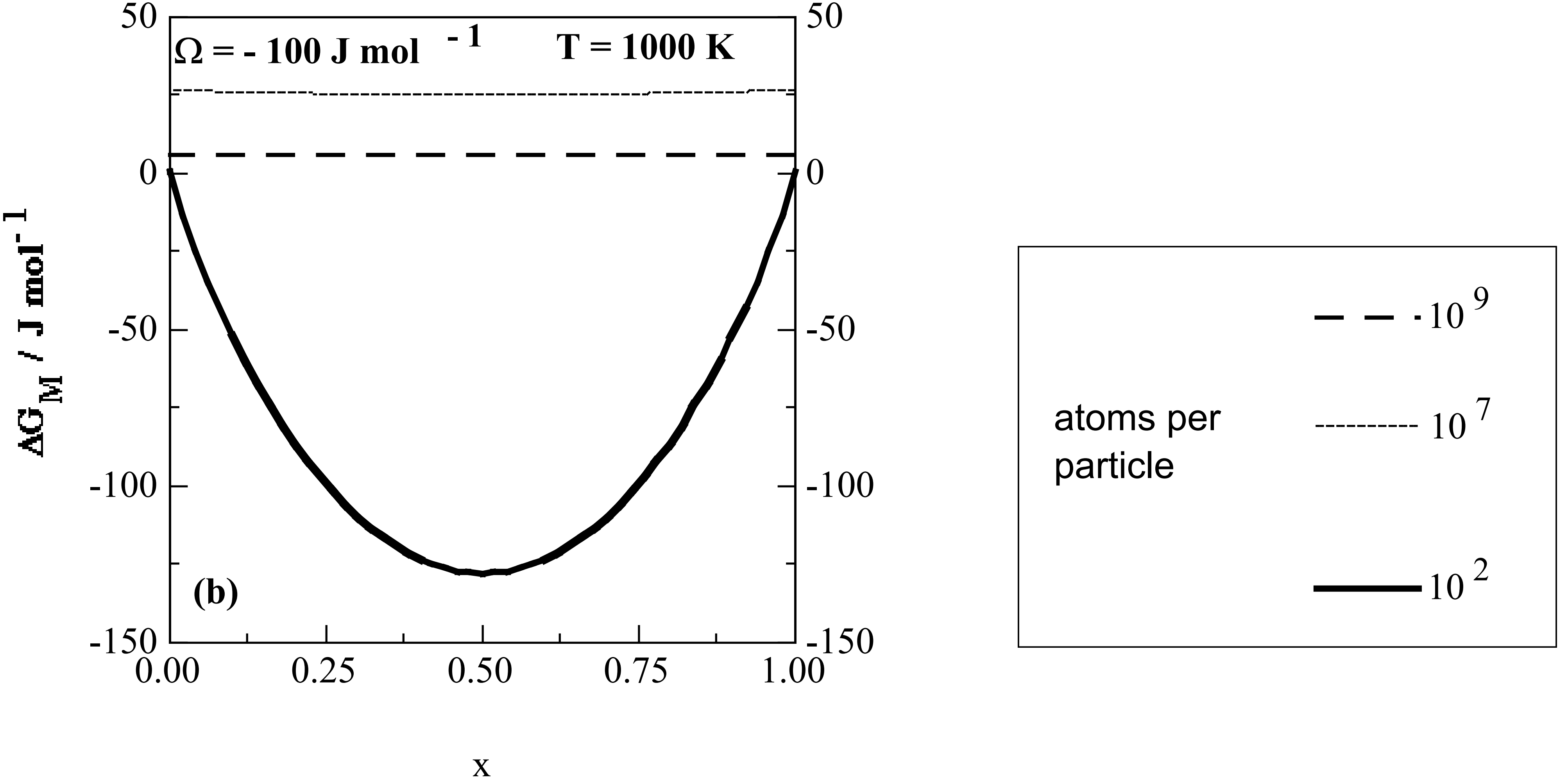
Badmos and Bhadeshia, 1997



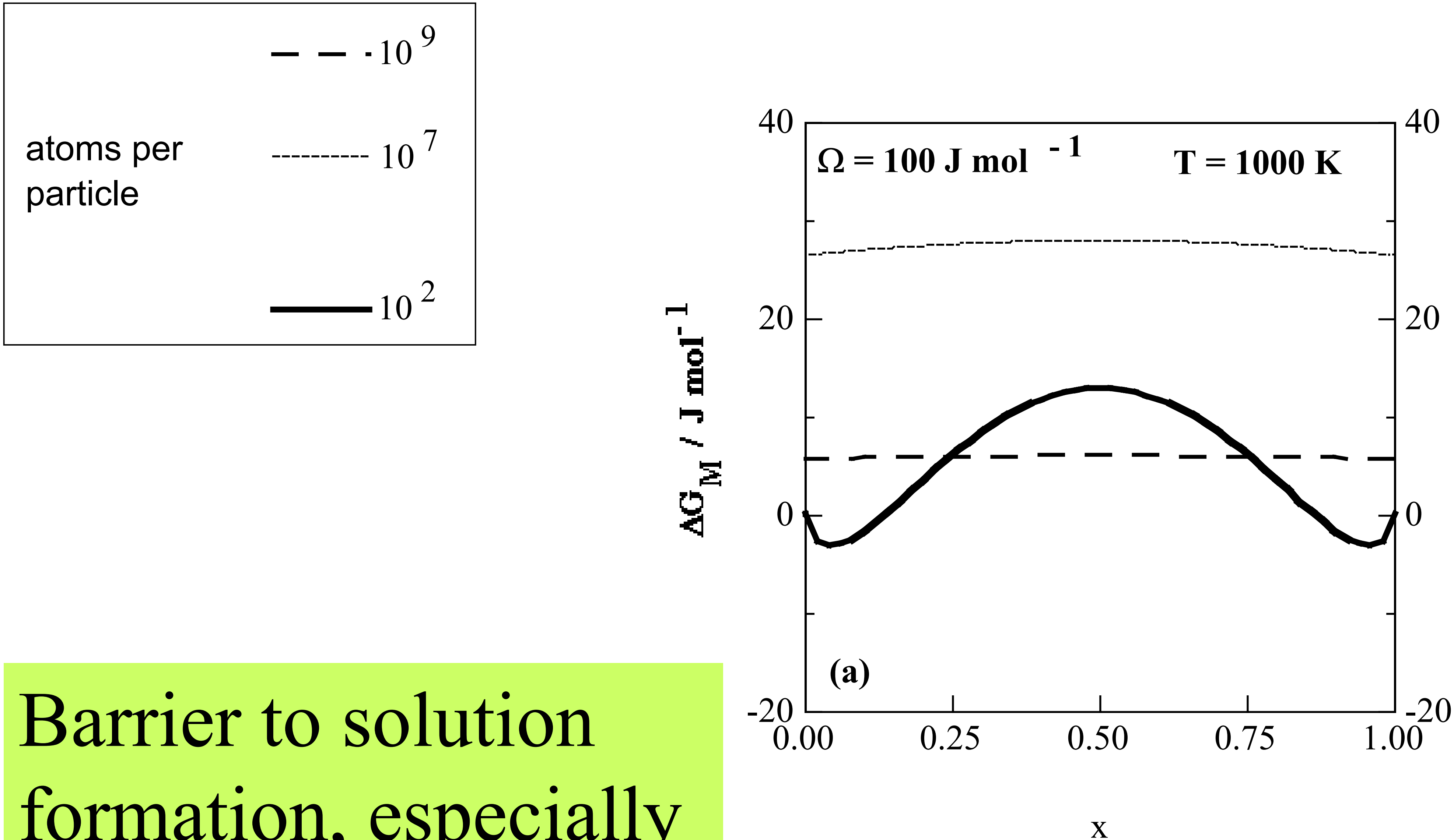
Double barrier to solution formation when components immiscible

Badmos and Bhadeshia, 1997

Barrier to solution formation

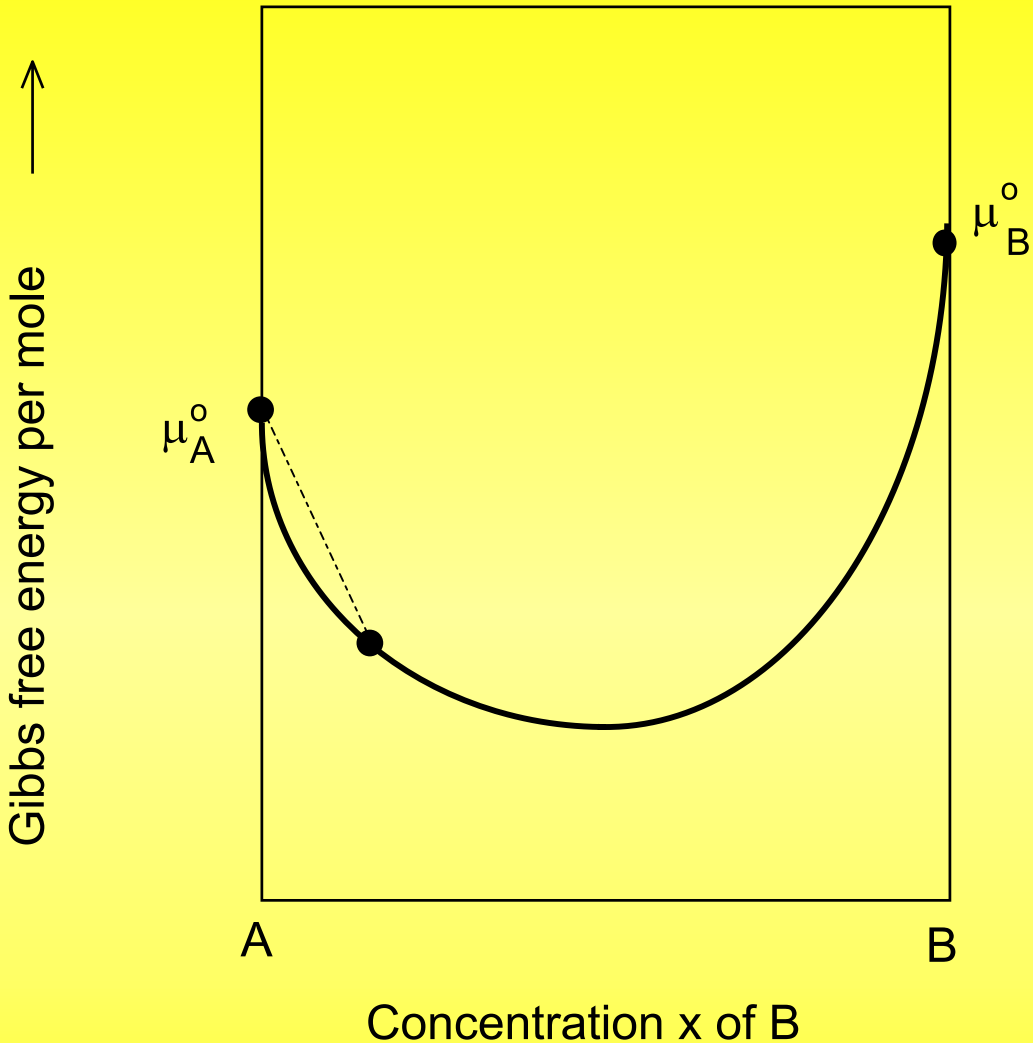


Badmos and Bhadeshia, 1997

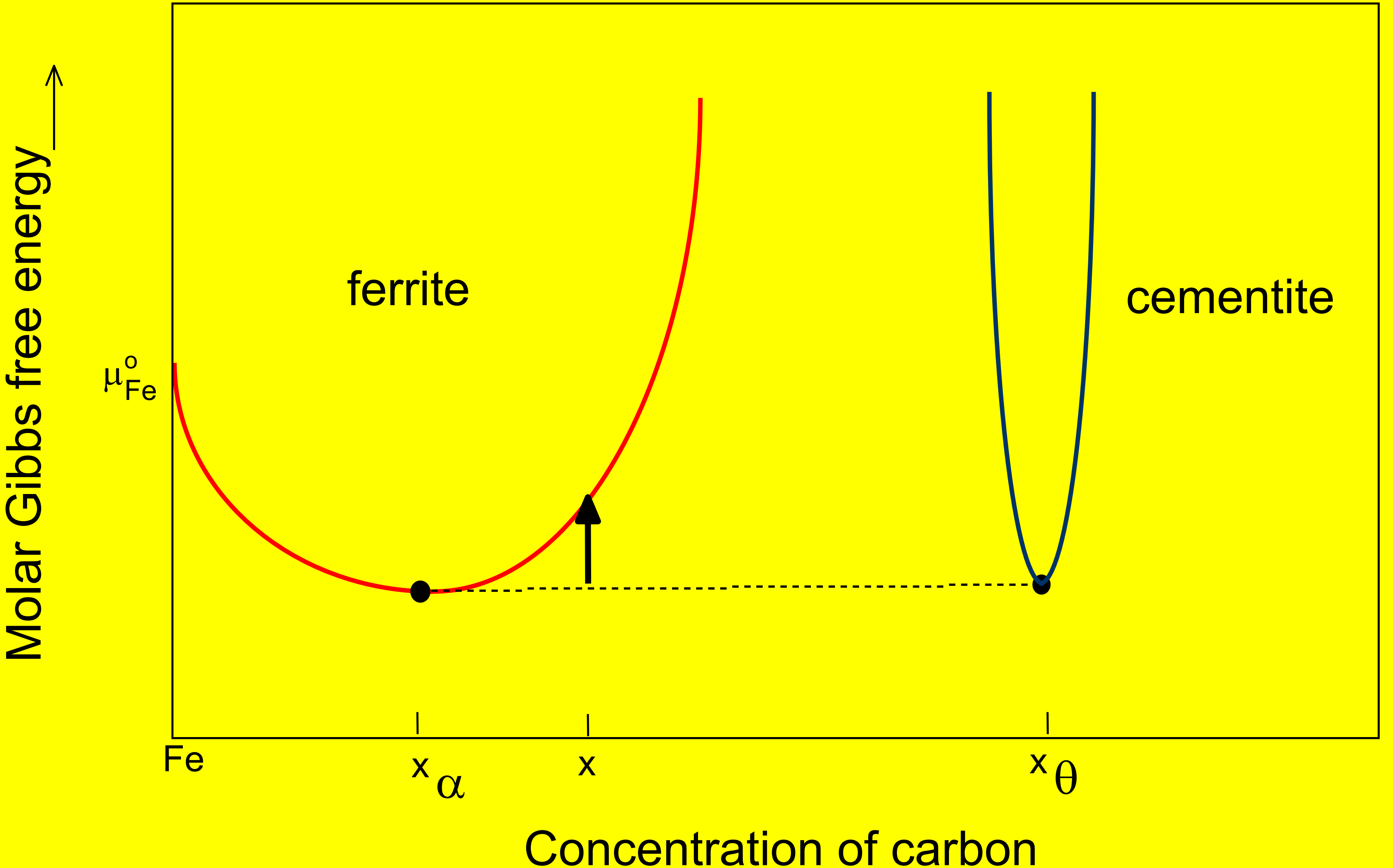


Barrier to solution formation, especially in rich solutions

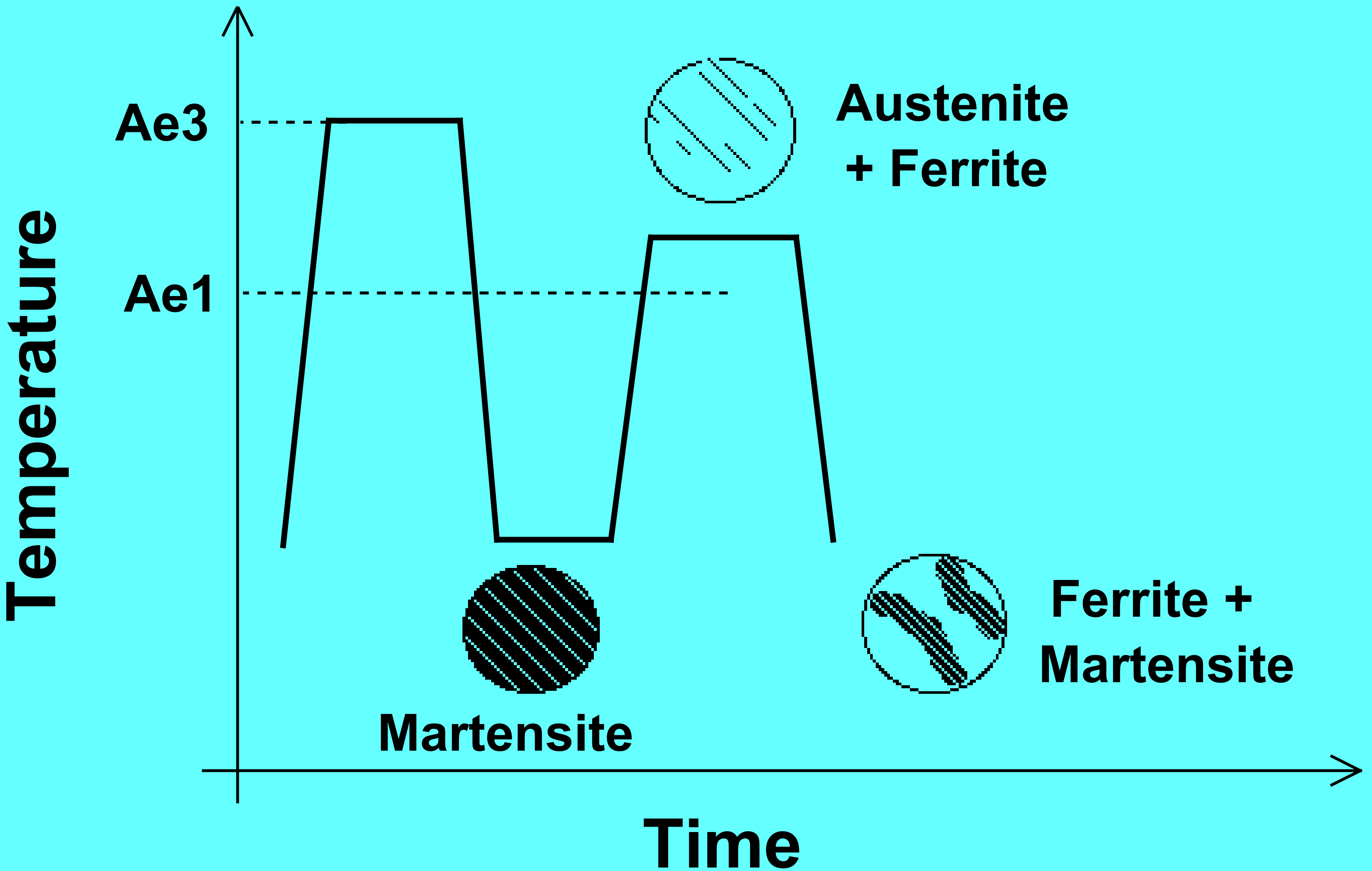
Badmos and Bhadeshia, 1997



Paradox at concentration extremities vanishes in the discrete model of concentration



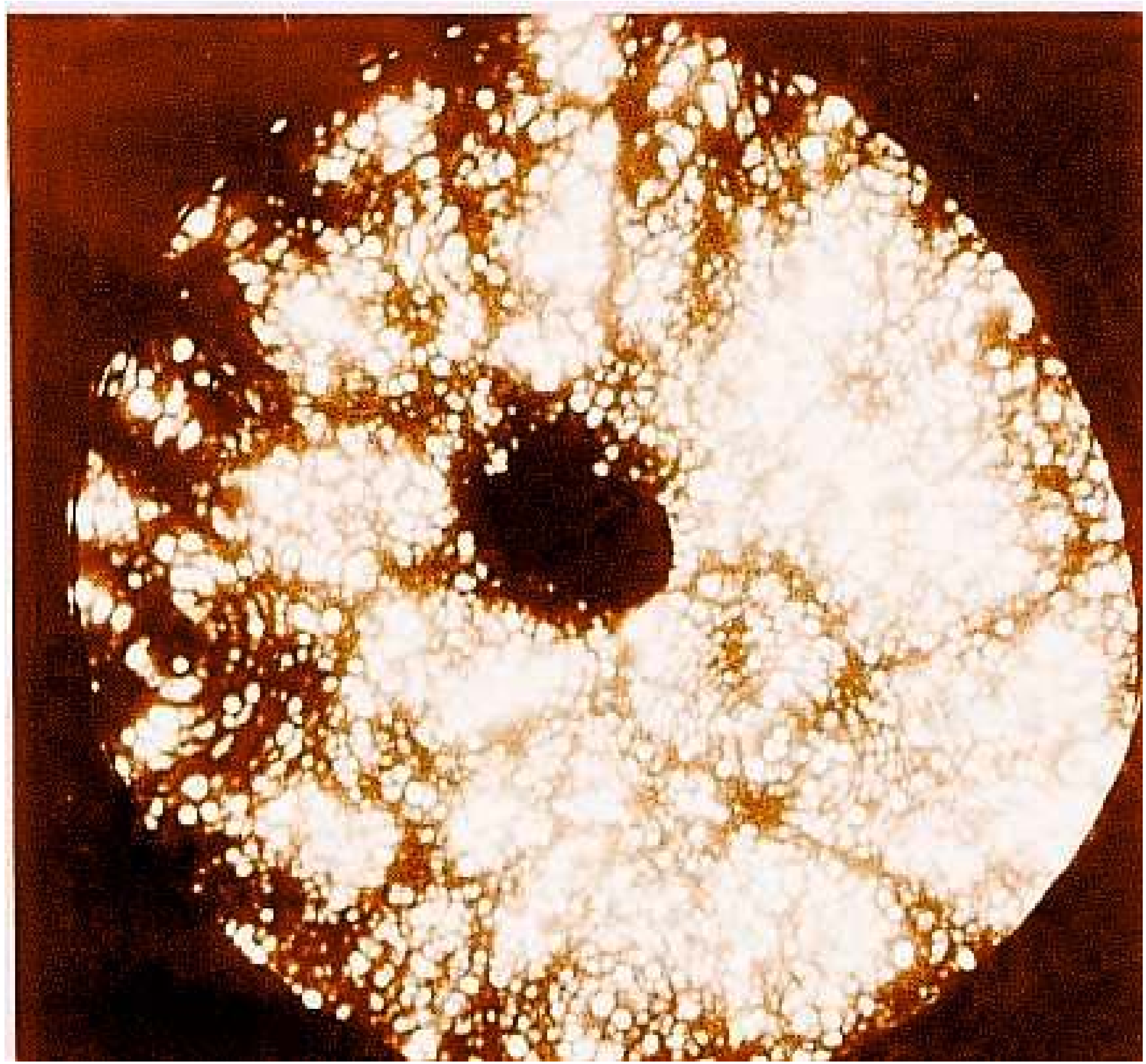
Molar Gibbs free energy
ferrite
cementite
μ^{o}_{Fe}
Fe
x_{α}
x
x_{θ}
Concentration of carbon


Ae3
Ae1
Temperature
Austenite
+ Ferrite
Martensite
Ferrite +
Martensite
Time

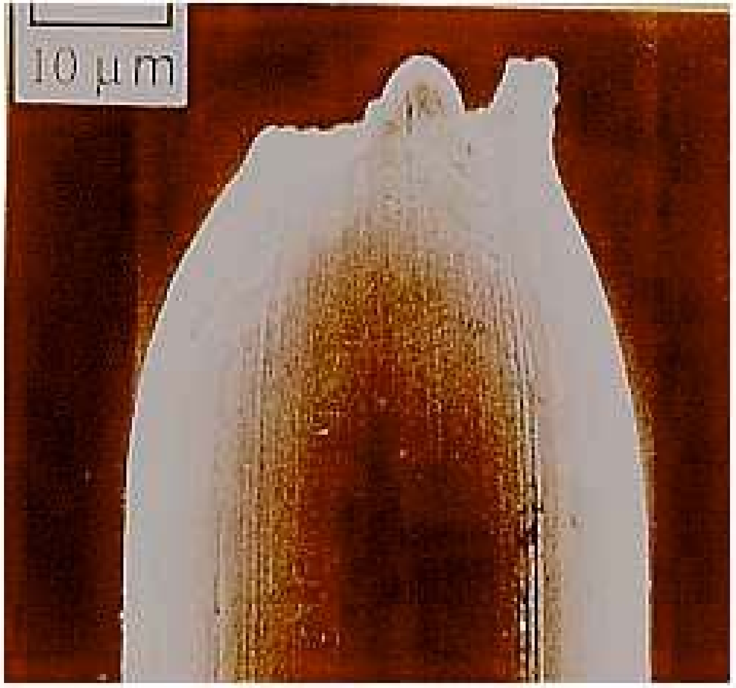
Atom probe image of *Scifer*,

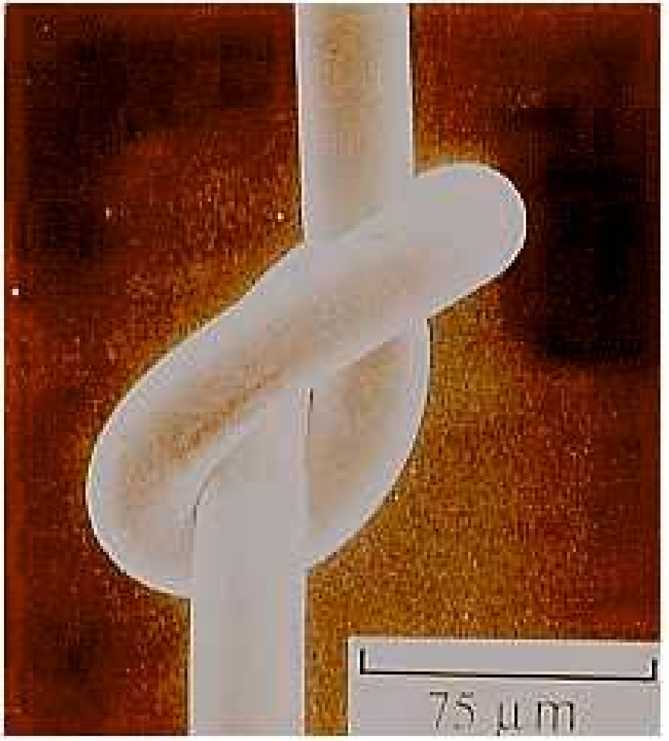
5.5 GPa steel wire

Bhadeshia and Harada, 1993



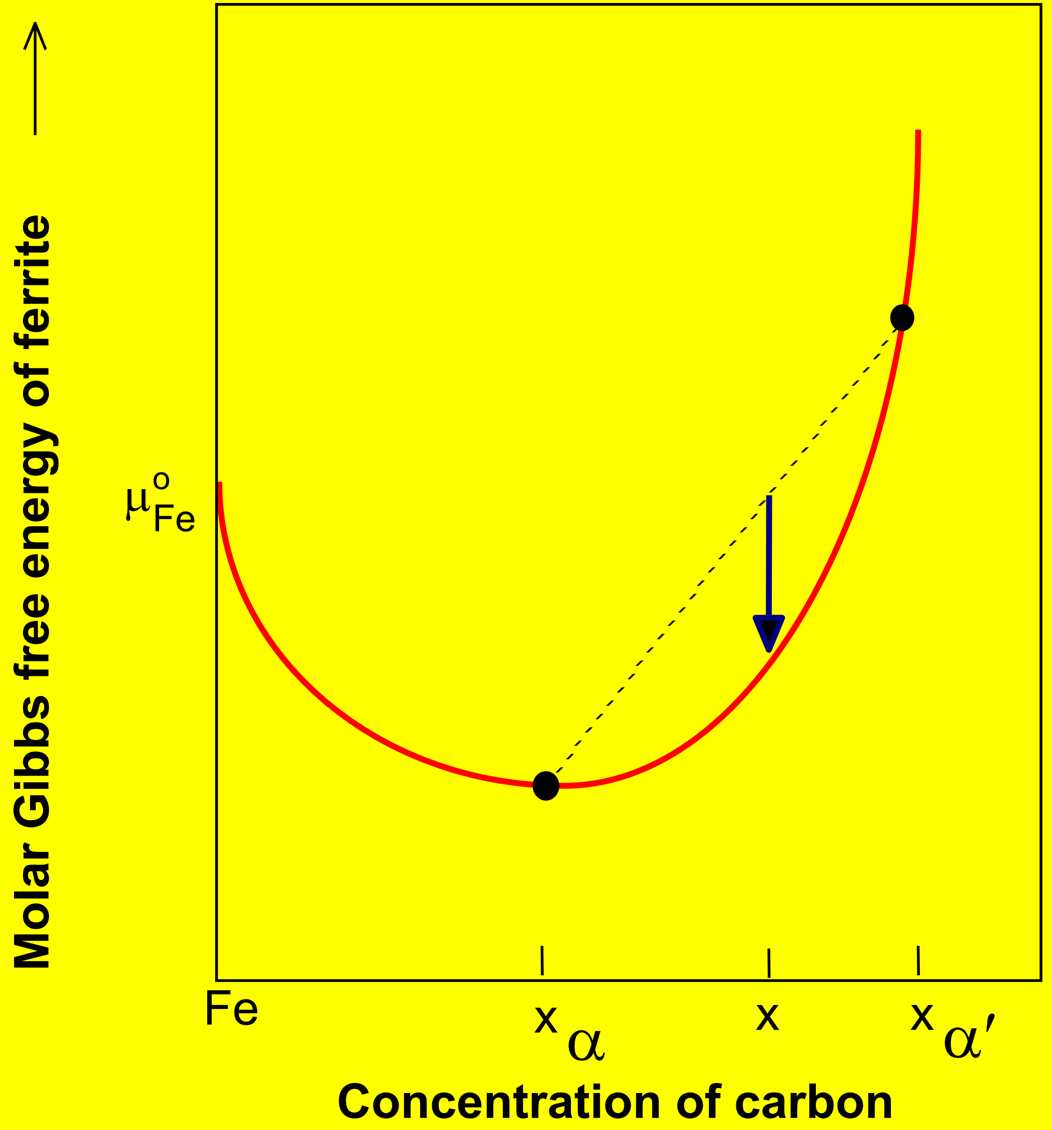
Scifer, 5.5 GPa with ductility!





Kobe Steel

Mechanical tempering



Amorphous phase formation during mechanical alloying of Cu and Cd powders

….contribution from Cu/δ interfaces, and accompanying increase in free energy, provide additional driving force for amorphisation….

Zhang & Massalski

Metall. & Mater. Trans. 29A (1998) 2425