### 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.





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







Concentration x of B

### Solution







### Entropy













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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

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

 $\frac{\Delta S_M}{\Delta M} = \frac{(1-x)m_B + xm_A}{X} \times \frac{M}{2} + \frac{M}$  $kN_a$  $m_A m_B$  $\ln \left\{ N_a \frac{(1-x)m_B + xm_A}{m_A m_B} \right\}$  $\frac{1-x}{m_A} \ln \left\{ \frac{N_a(1-x)}{m_A} \right\}$  $\frac{x}{m_B} \ln \left\{ \frac{N_a x}{m_B} \right\}$ 

## 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

Particle size

 $S_{V} = \frac{1}{2} \sum_{i} n_{i} 6(m_{i} \Phi_{i})^{\frac{2}{3}} / \sum_{i} \frac{N_{a} x_{i}}{m_{i}} V_{i}$  $\Delta H_I = V_m S_V \sigma$ 

Solution formation impossible!





**Single barrier** to solution formation when components attract

Badmos and Bhadeshia, 1997



**Double barrier** to solution formation when components immiscible

Atoms per particle

Badmos and Bhadeshia, 1997

### Barrier to solution formation



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Badmos and Bhadeshia, 1997







Badmos and Bhadeshia, 1997



Gibbs free energy per mole

Paradox at concentration extremities vanishes in the discrete model of concentration





Atom probe image of *Scifer*,

5.5 GPa steel wire





#### Scifer, 5.5 GPa with ductility!





Kobe Steel

### Mechanical tempering



Amorphous phase formation during mechanical alloying of Cu and Cd powders

....contribution from Cu/ $\delta$  interfaces, and accompanying increase in free energy, provide additional driving force for amorphisation....

Zhang & Massalski

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