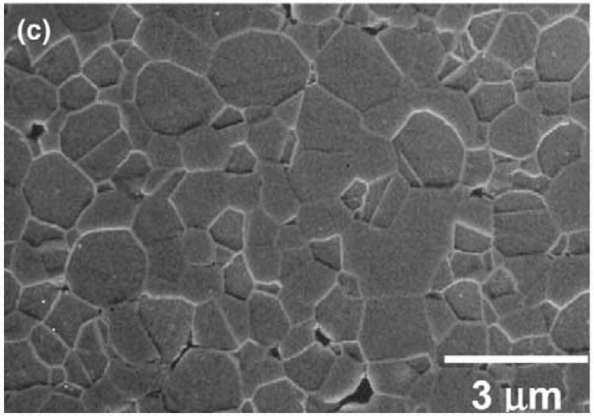
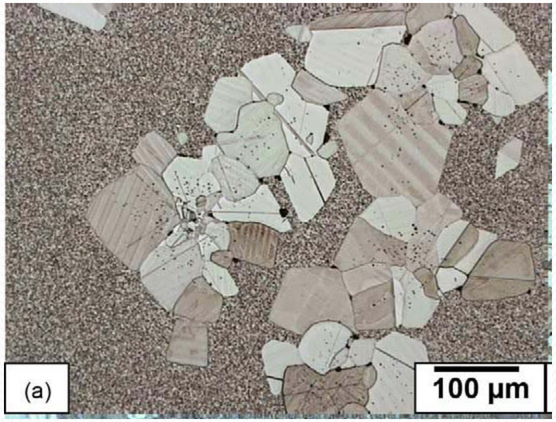
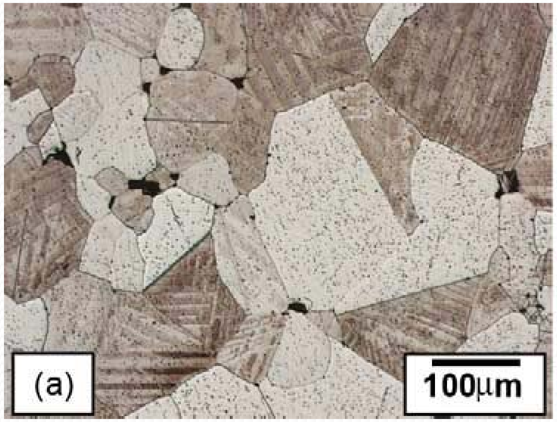
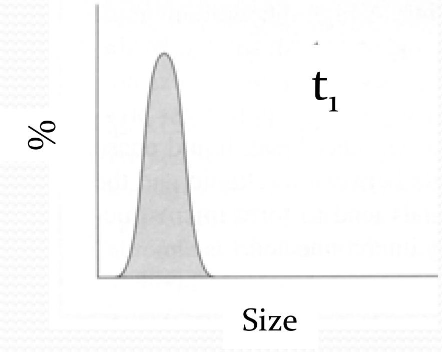
# Chapter 9 Abnormal Grain Growth

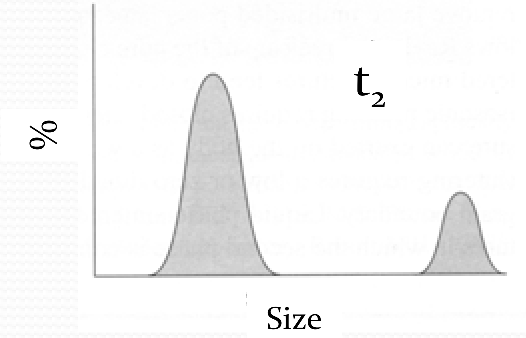
A microstructure where some grains grow very quickly in a matrix of fine grains which grow with a very slow growth rate.

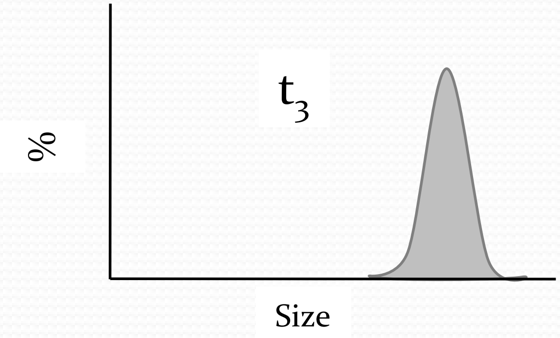












# How to define abnormal grain growth?

Several criteria have been established to define abnormal grain growth (AGG).

e.g. $\frac{\mathrm{d}\left(\frac{G}{\overline{G}}\right)}{\mathrm{d}t} > 0$ or $\frac{G}{\overline{G}} > 2$

$G$ = grain size of a specific grain

$\overline{G}$ = mean grain size

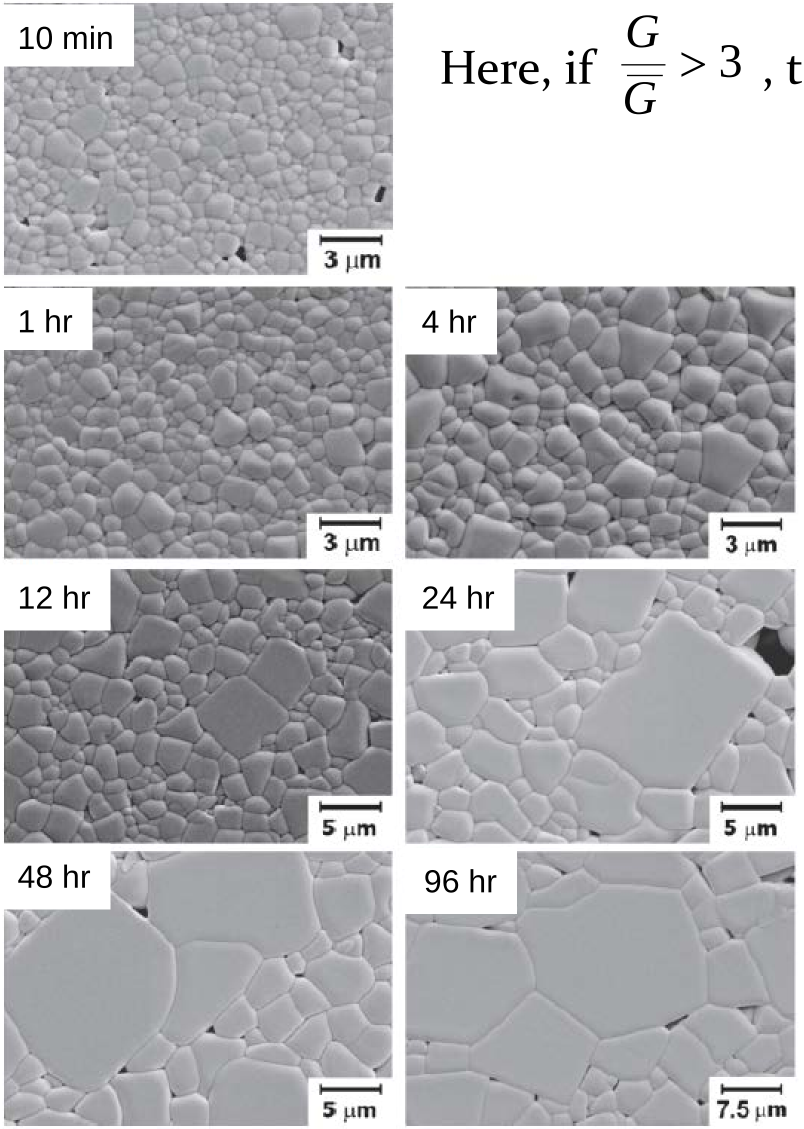
In practice, it is difficult to define AGG because of impingement of large grains.

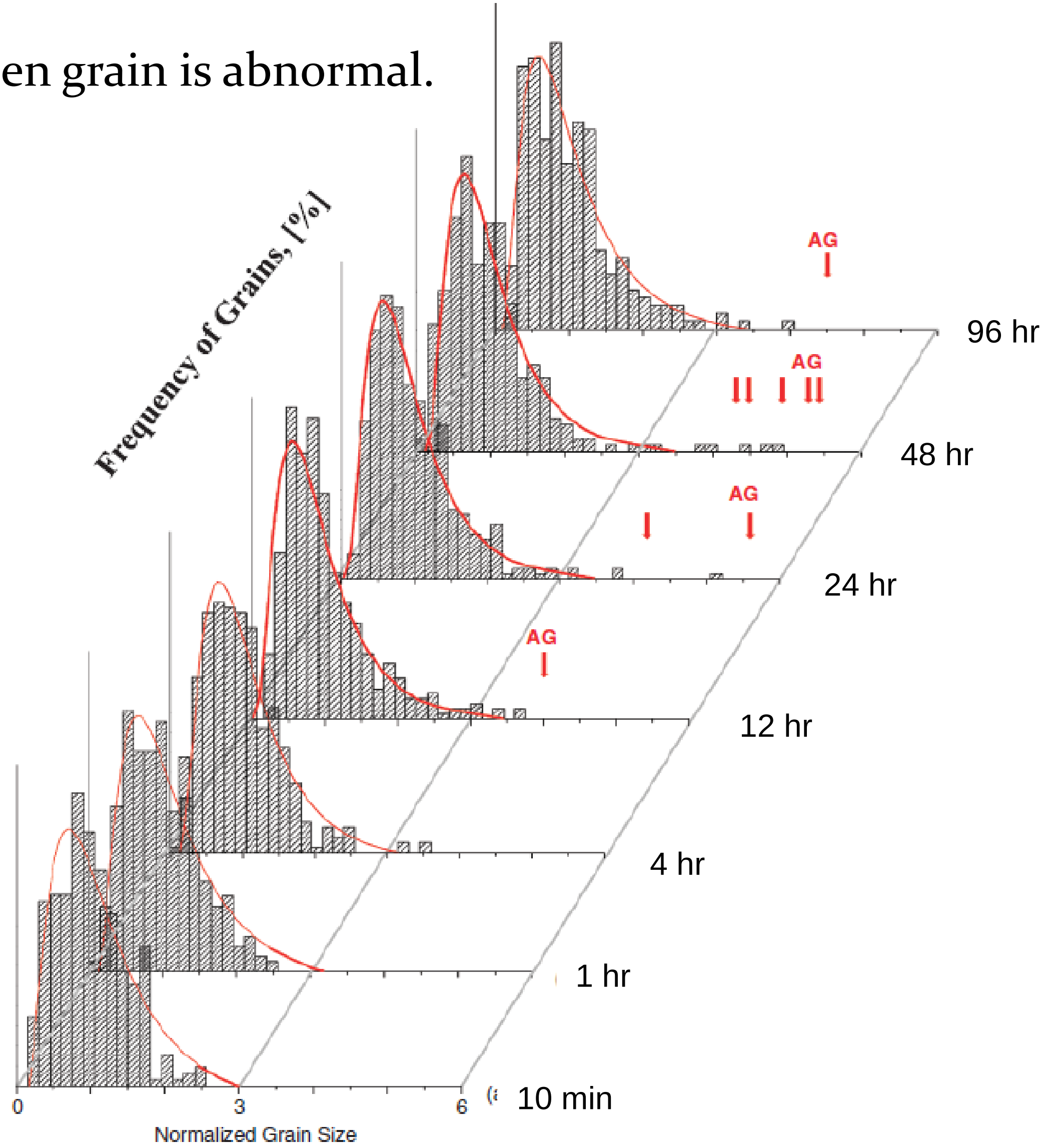
If the normalized size distribution $\frac{G}{\overline{G}}$ does not change much with time, growth is normal.

If the normalized size distribution $\frac{G}{\overline{G}}$ becomes broad or bimodal with time, growth is abnormal.

# Example of AGG in $(Na_{0.5}Bi_{0.5})TiO_3$.

Here, if $\frac{G}{\overline{G}} > 3$ , then grain is abnormal.





K. S. Moon and S. J. L. Kang, J. Am. Ceram. Soc., **91** [10], 3191-96 (2008)

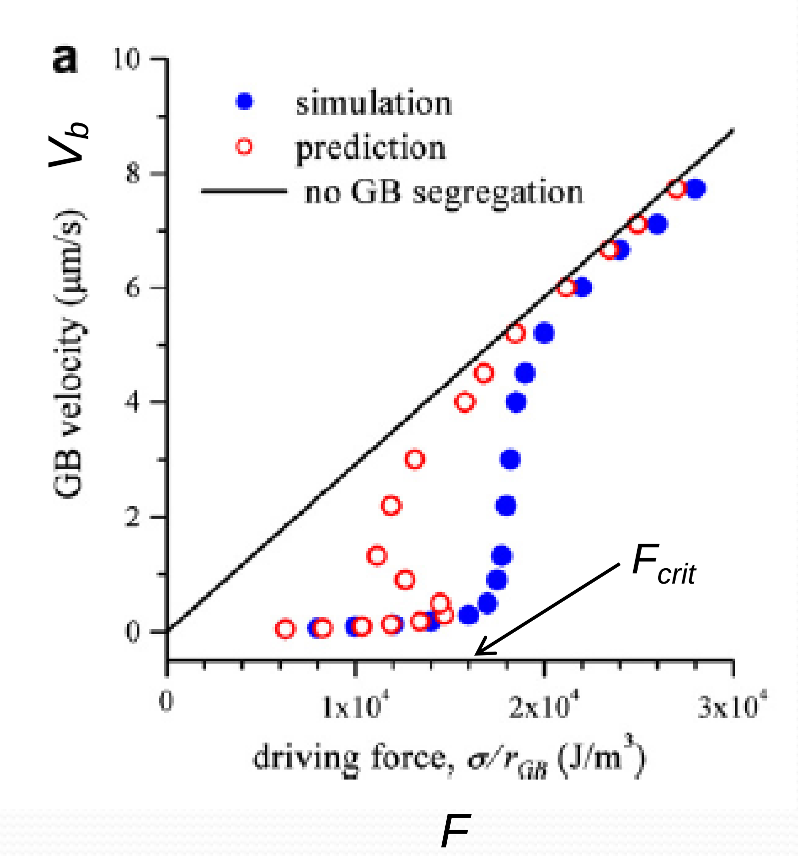
# Why does abnormal grain growth happen?

Several possible reasons:

1. non-uniform distribution of 2nd phase particles or solutes
2. materials with high anisotropy in interfacial energy (g.b. or solid / liquid)

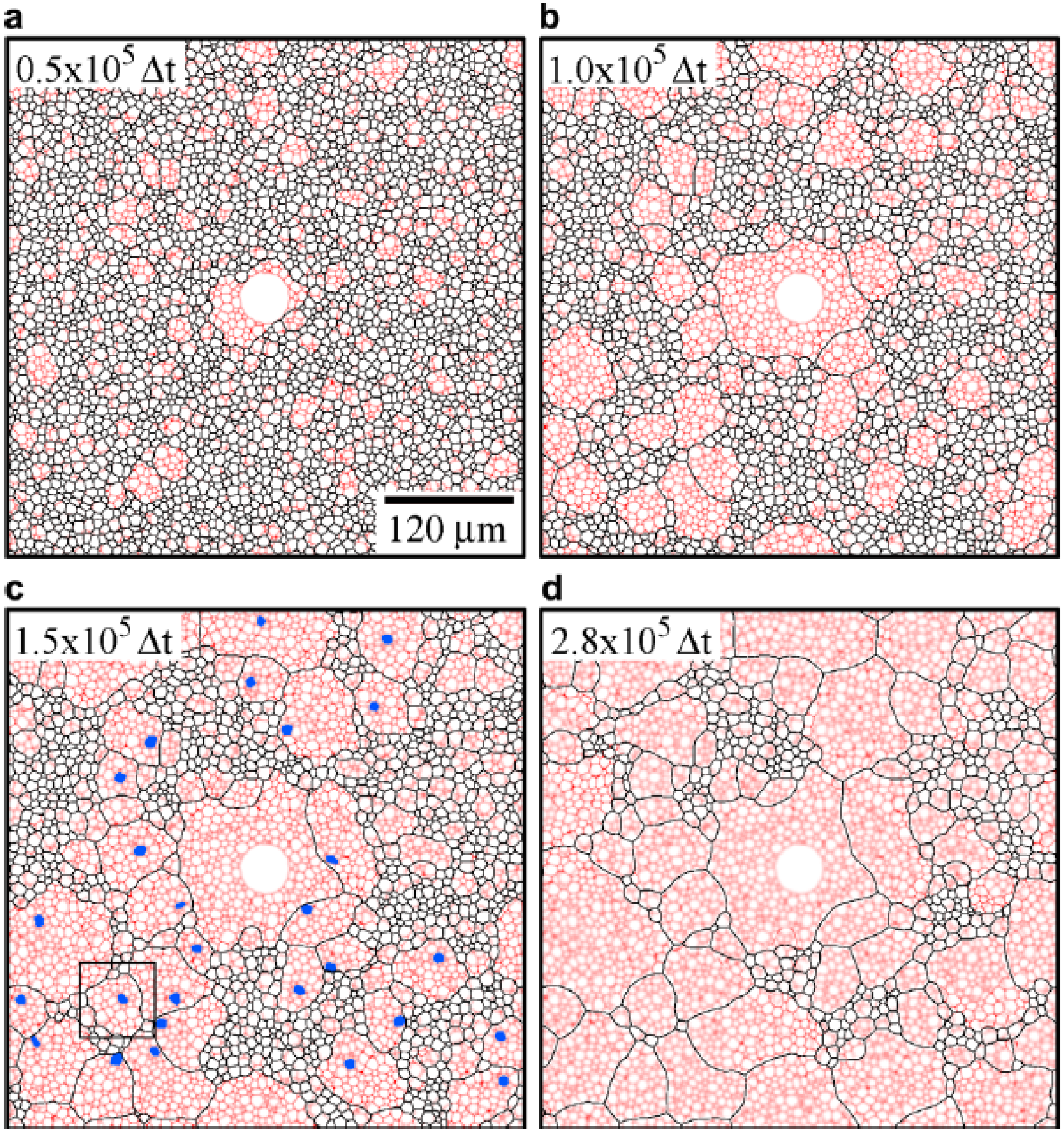
# Non-uniform distribution of 2nd phase particles or solutes

- 2nd phase / solute pins g.b. and reduces $V_b$.
- If driving force *F* is > critical driving force $F_{crit}$ , g.b. breaks away from 2nd phase / solute and $V_b$ increases rapidly.
- *F* depends on grain size.
- A few large grains can have large enough F to grow rapidly and form abnormal grains.



S. Y. Kim and Y. B. Park, *Acta Mater.*, **56**, 3739-3753 (2008)

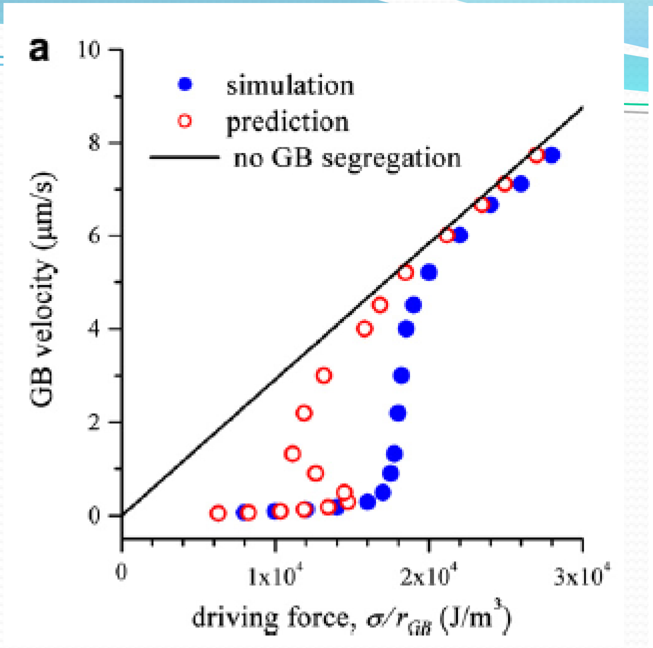
- Red: solute conc.
- Red lines: high solute conc. (original g.b.s)
- Black lines: g.b.s

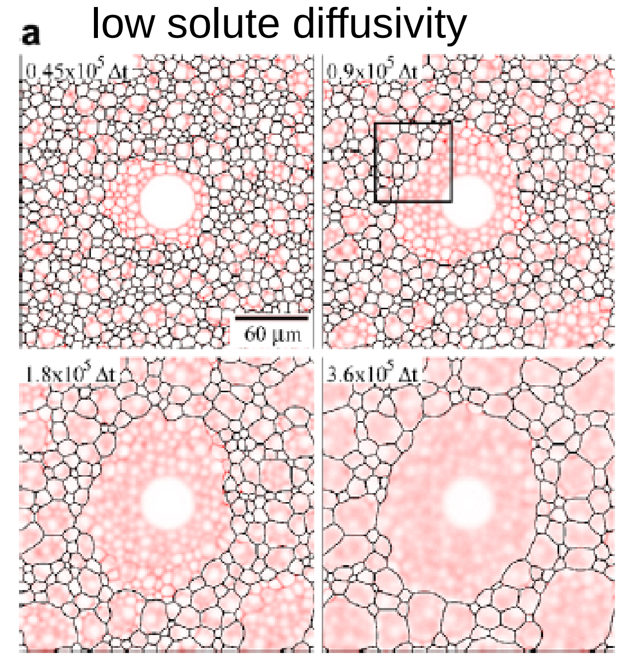


S. Y. Kim and Y. B. Park, *Acta Mater.*, **56**, 3739-3753 (2008)

Low solute diffusivity

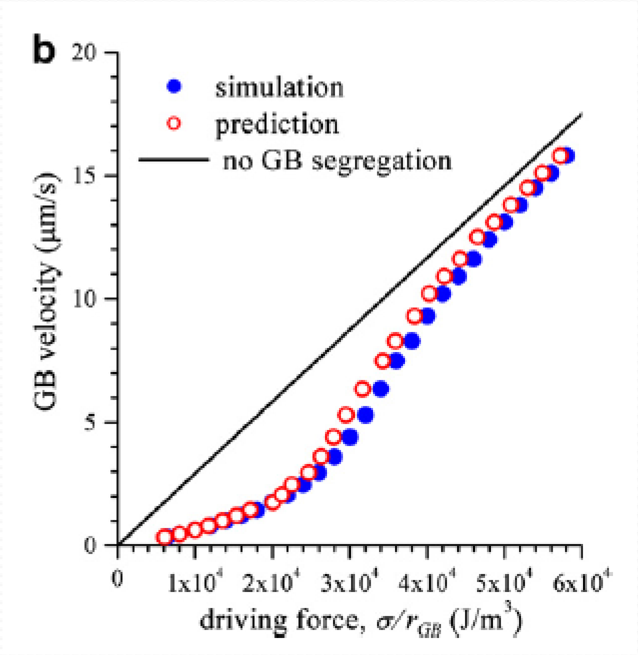
- solute drags g.b. at low *F*
- At $F > F_{crit}$, g.b. breaks away from solute and $V_b$ increases discontinuously
- AGG occurs

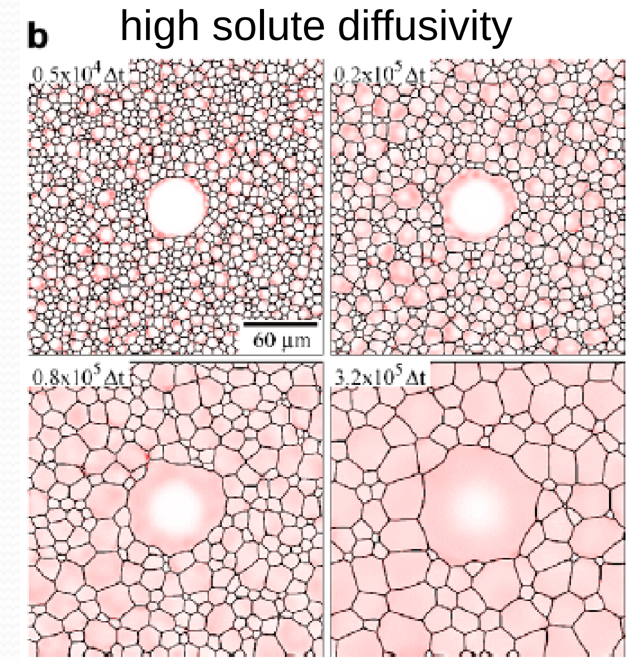




High solute diffusivity

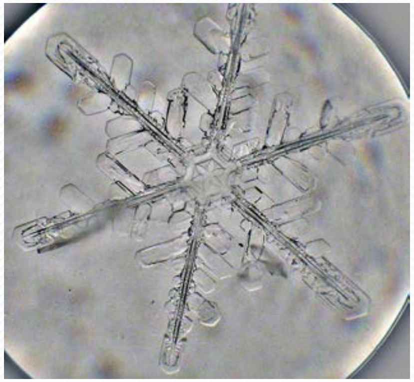
- solute drags g.b. at all values of *F*
- No discontinuous increase in $V_b$
- Normal growth occurs





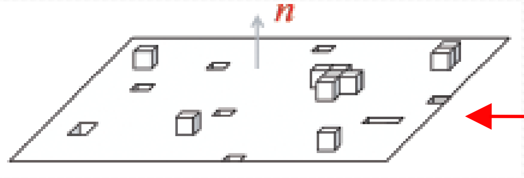
# Materials with high anisotropy in interfacial energy

- $\gamma$ changes with surface orientation
- $\gamma$ is anisotropic
- faceted shape
- facets are crystallographic planes with lowest values of $\gamma$.

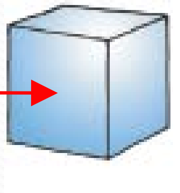


- $\gamma$ does not change with surface orientation
- $\gamma$ is isotropic
- spherical (rough) shape

# Types of surface

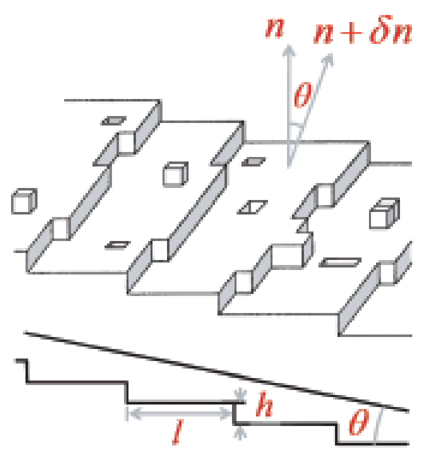


singular



lowest values of $\gamma_{sv}$

At T > 0K, vacancies and adatoms form

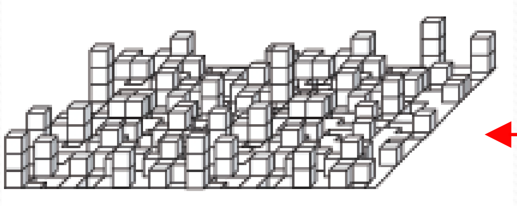


vicinal / stepped

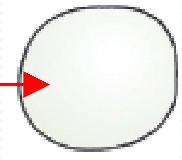
singular plane that is tilted a few °

steps and terraces

steps have excess energy $\varepsilon$



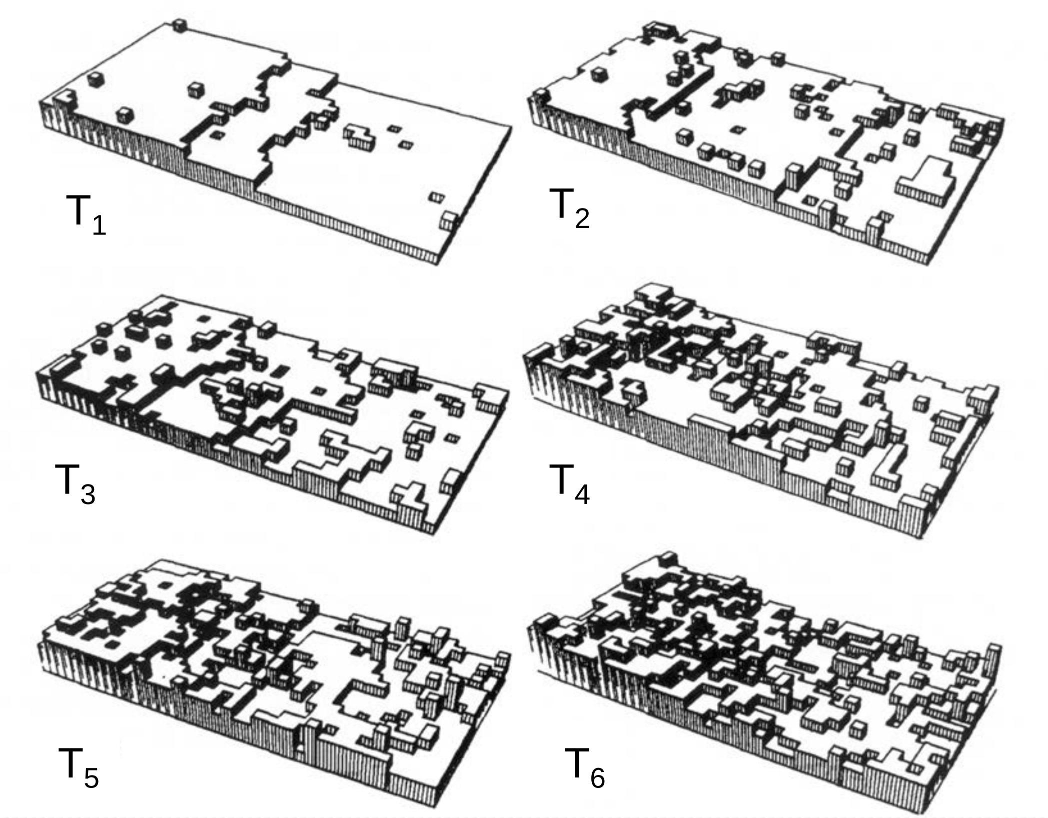
rough



$\gamma_{sv}$ is same at all orientations

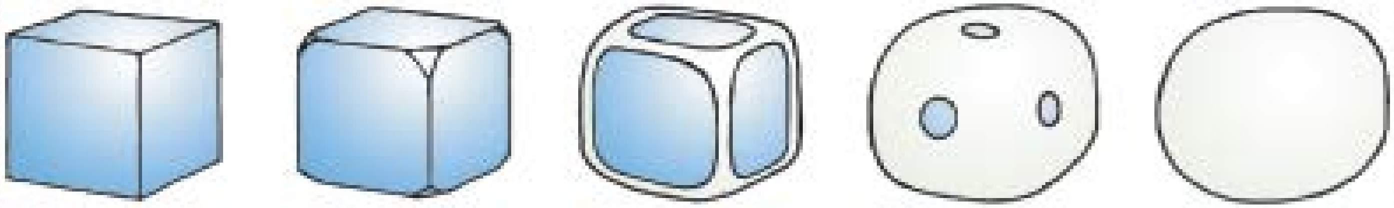
All crystals are faceted at T = 0K

As T ↑, crystal faces become rough



$T_1<T_2<T_3<T_4<T_5<T_6$

decreasing anisotropy →



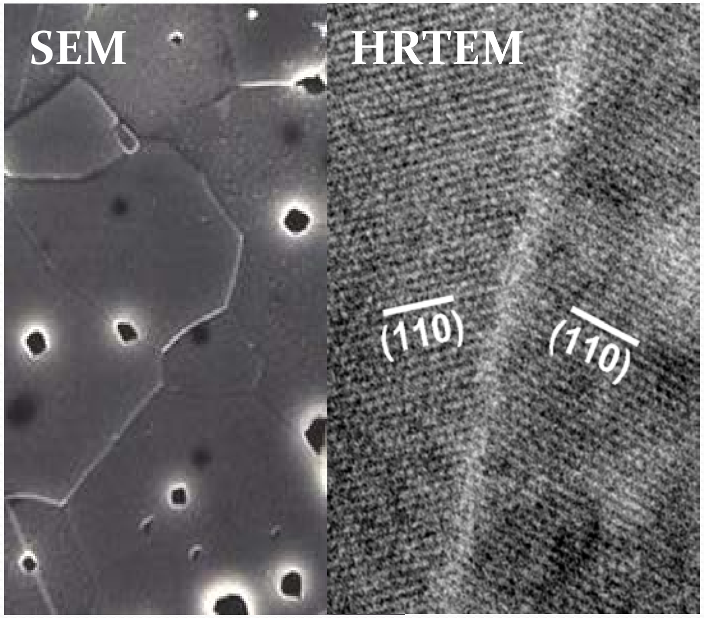
$T$ = 0K

increasing $T$ →

$T \approx T_{melting}$

## Isotropic $\gamma_{gb} / \gamma_{sl}$

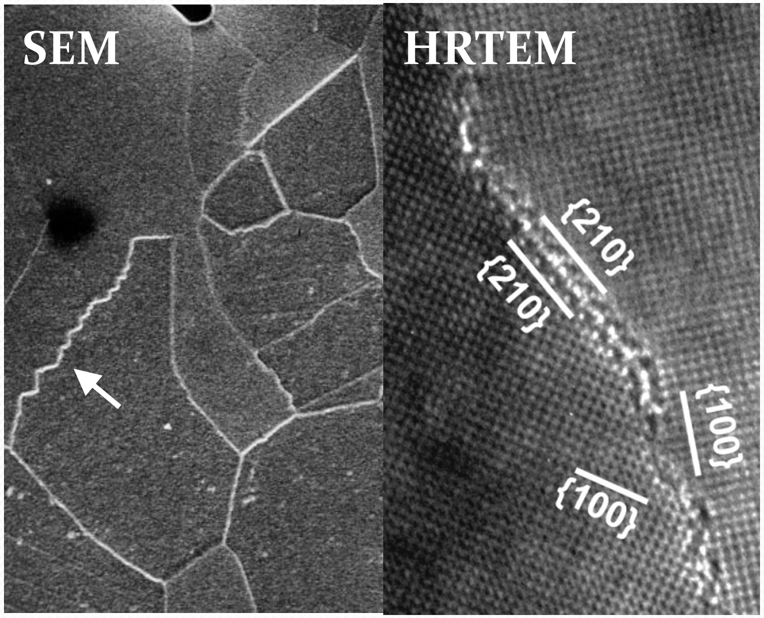
### Disordered (rough) grain boundaries



G.b. curved on microscopic scale
$M_b$ is constant [not function of *F*]

## Anisotropic $\gamma_{gb} / \gamma_{sl}$

### Ordered (faceted) grain boundaries

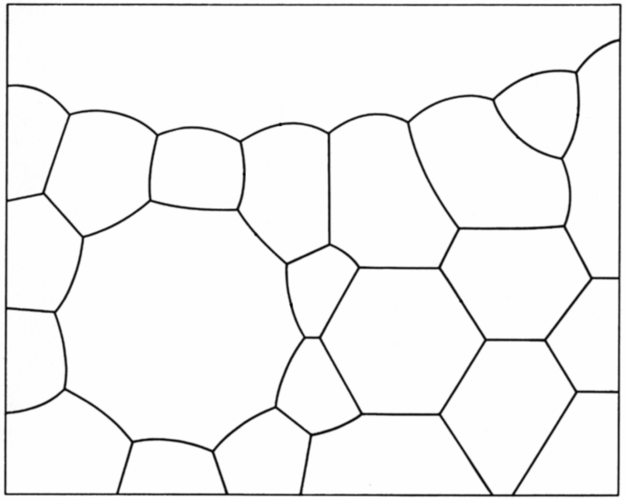


G.b. faceted on microscopic scale
$M_b$ is variable [function of *F*]

# Driving force for grain growth

Driving force $\propto$ g.b. curvature

$$\Delta G = \sigma_{gb} V_m \left( \frac{1}{\bar{r}} - \frac{1}{r} \right)$$



$\Delta G$ = driving force

$\sigma_{gb}$ = grain boundary energy

$V_m$ = molar volume

$\bar{\mathbf{r}}$ = mean grain radius

$\mathbf{r}$ = grain radius

Each grain has it's own values of r and $\Delta G$

Largest grain has $\Delta G = \Delta G_{max}$

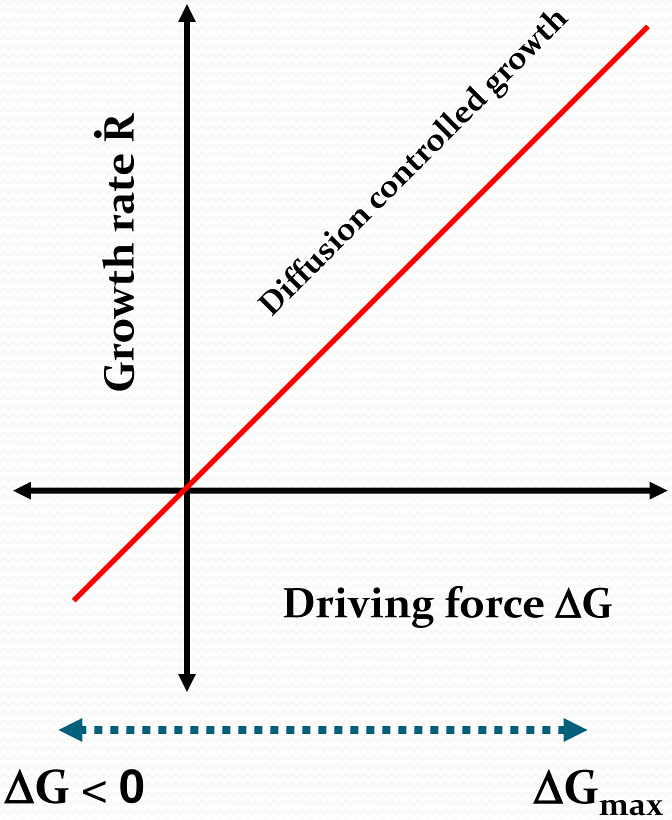
Grains with $\Delta G > 0$ can grow

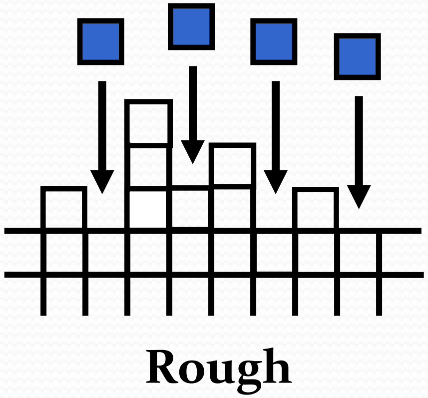
Grains with $\Delta G = 0$ will not grow or shrink

Grains with $\Delta G < 0$ will shrink

N.b. $\Delta G$ has same meaning as *F*

# Grain growth behaviour of disordered (rough) boundaries





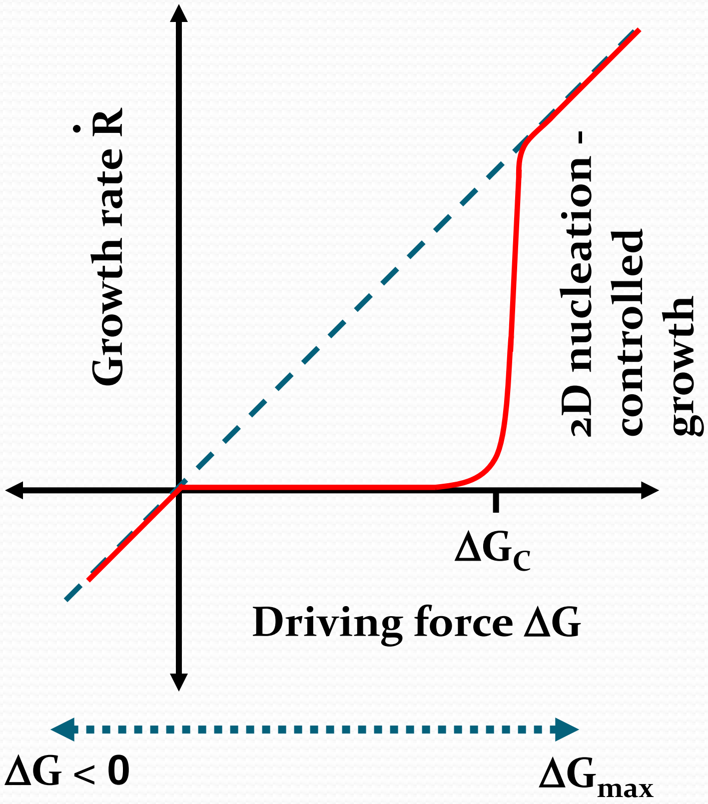
**For diffusion controlled growth:**

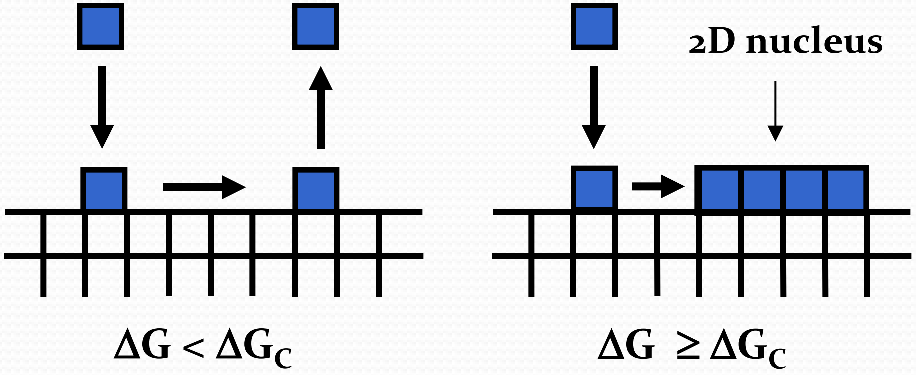
$$\boxed{\dot{R} = \frac{D_b \mathbf{V}_m \Delta G}{\delta R T}}$$

$D_b$ = grain boundary diffusivity
$V_m$ = molar volume
$\delta$ = boundary thickness
$R$ = gas constant
$T$ = absolute temp

Normal grain growth takes place.

# Grain growth behaviour of ordered (faceted) boundaries





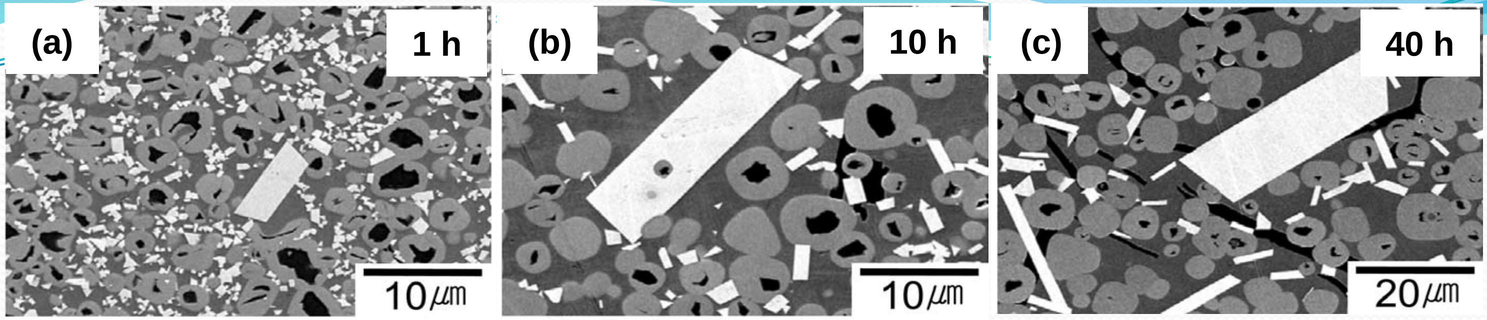
**For 2D nucleation controlled growth:**

$$\boxed{\dot{R} \cong v_{st}\, exp\left(\frac{-\pi V_m \varepsilon^2}{6h\Delta G kT}\right)}$$

$\nu_{st}$ = step velocity
$V_m$ = molar volume
$\varepsilon$ = edge free energy of 2D nucleus
h = step height

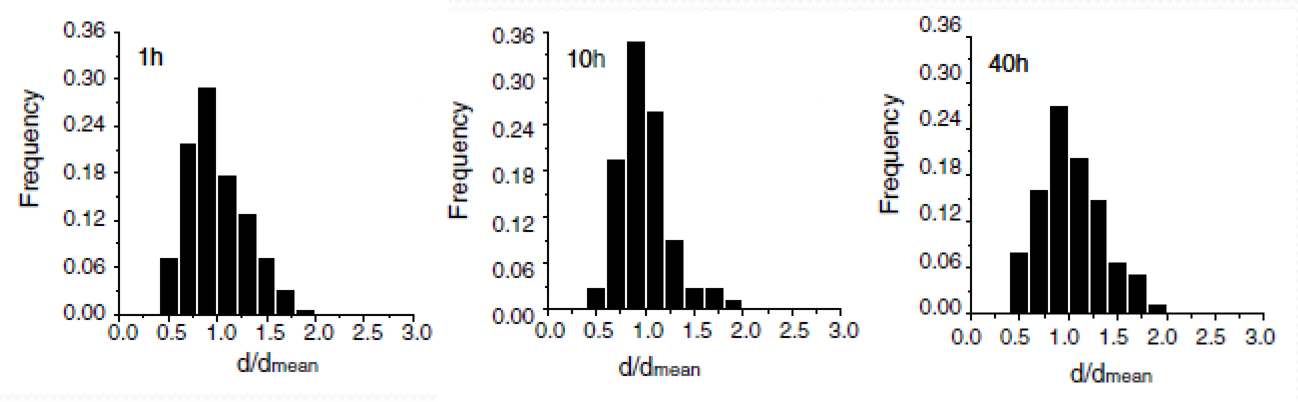
At $\Delta G > \Delta G_C$, growth is diffusion controlled.

Abnormal grain growth can take place.

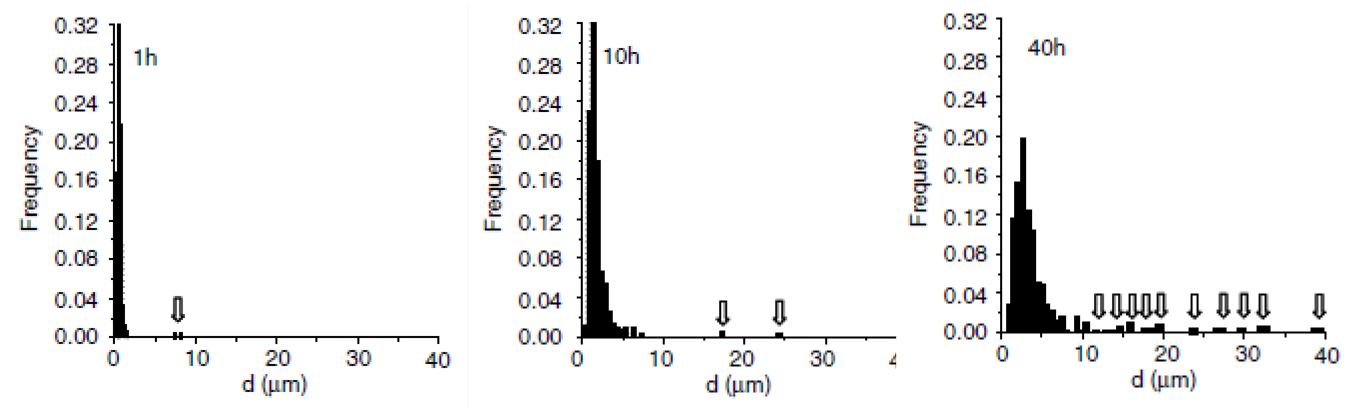


Microstructures of 70(25TiC–75WC)–30Co (wt%) samples sintered at 1450°C for: (a) 1 hour; (b) 10 hours and (c) 40 hours (mean WC starting powder size = 0.5µm). The rounded grains are (Ti,W)C and the faceted grains are WC

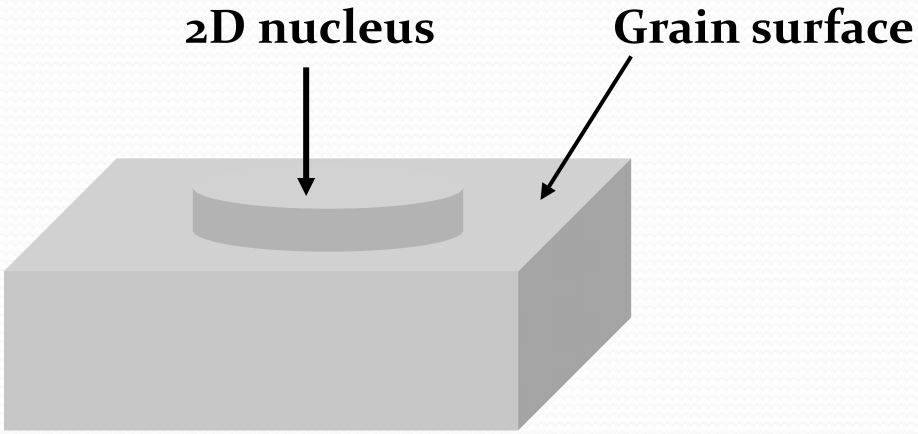
(Ti,W)C
(rough interfaces) –
normal grain growth



WC (faceted
interfaces) –
abnormal grain
growth

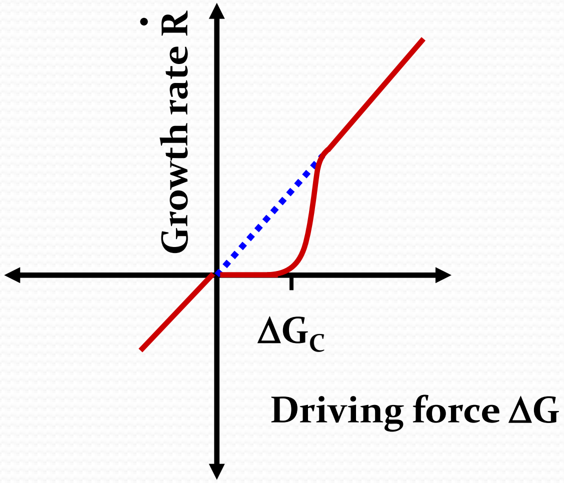


# Critical driving force



$$\Delta G_C = \frac{V_m \varepsilon^2}{3hRT}$$

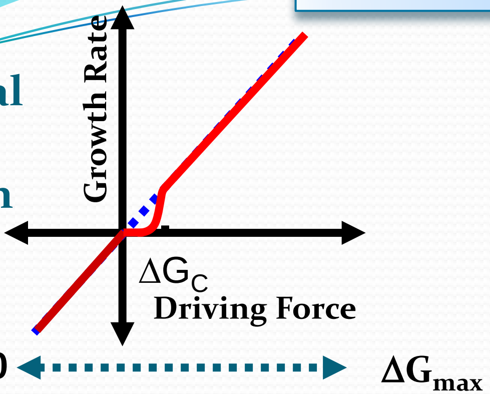
$\Delta G_C$ = critical driving force
$V_m$ = molar volume
$\varepsilon$ = step /edge free energy
h = step height



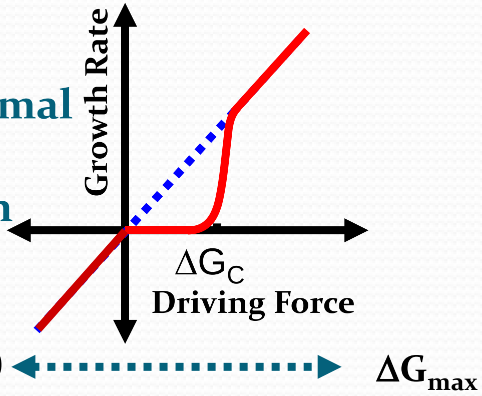
**ε varies with temperature, atmosphere and dopant.**

# Effect of step free energy on grain growth

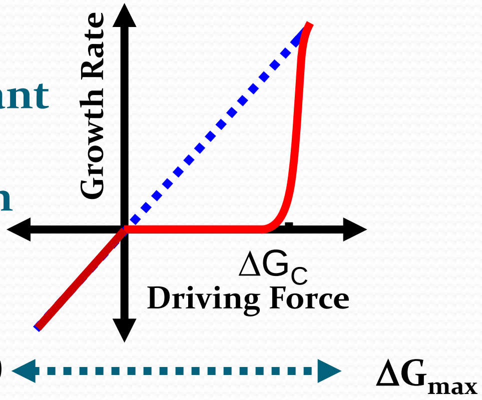
**NGG**
**Normal grain growth**

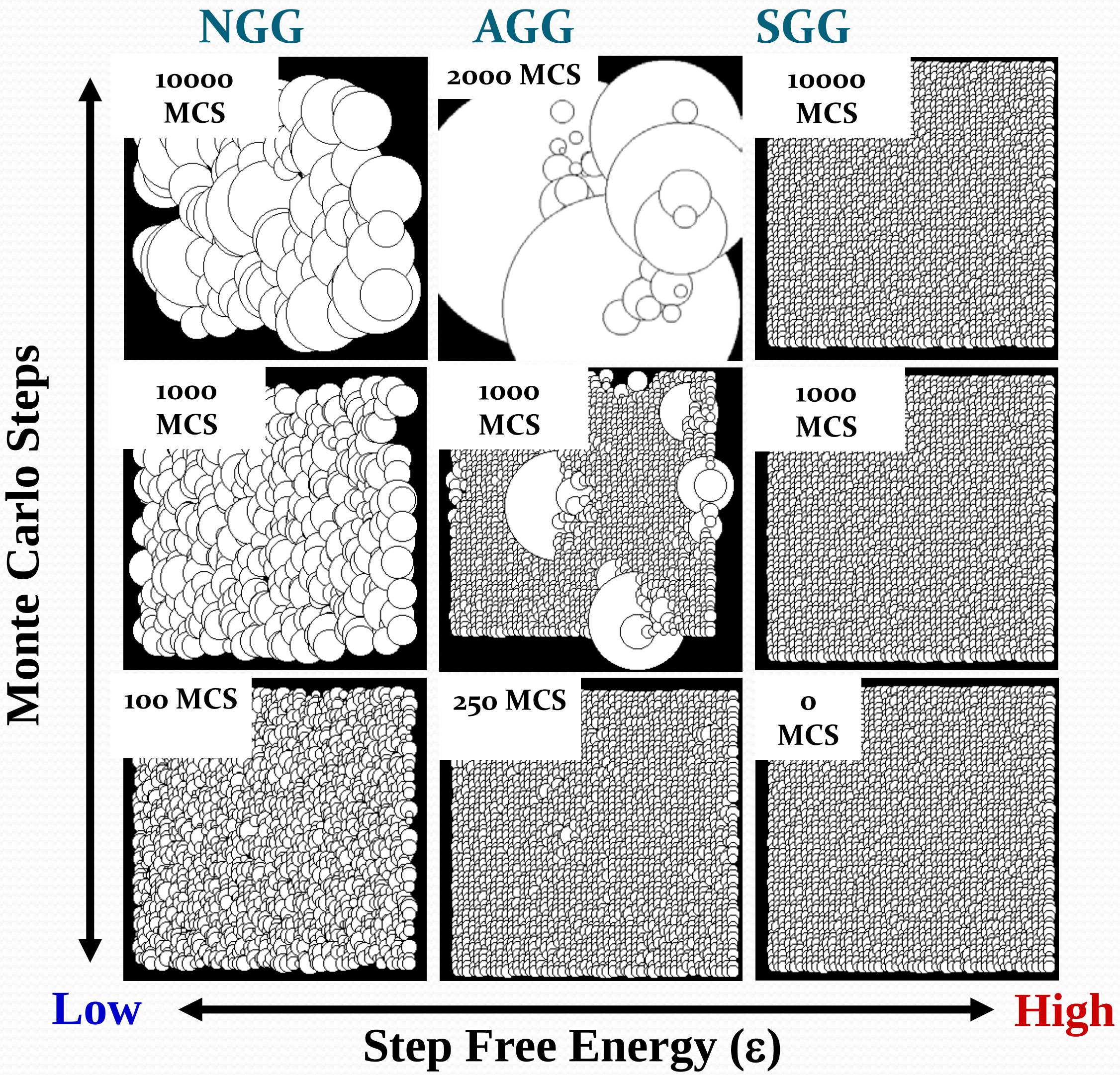


**AGG**
**Abnormal grain growth**



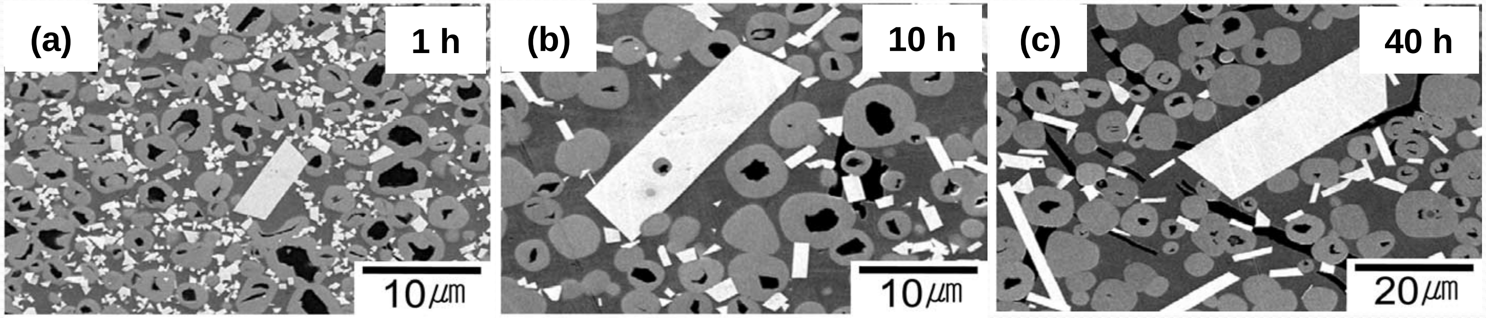
**SGG**
**Stagnant grain growth**



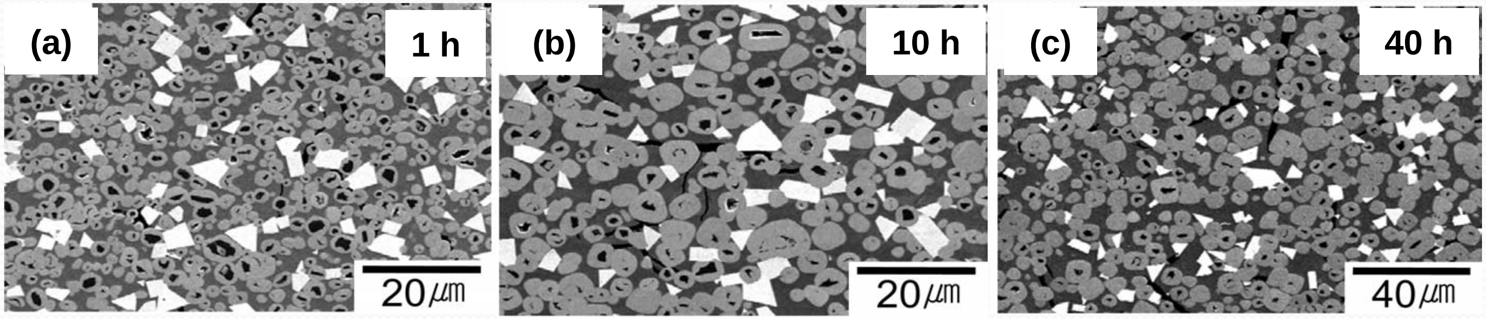


Suk-Joong L. Kang, Sintering :Densification, Grain Growth and Microstructure, Elsevier, 2005.

# Effect of mean grain size on grain growth

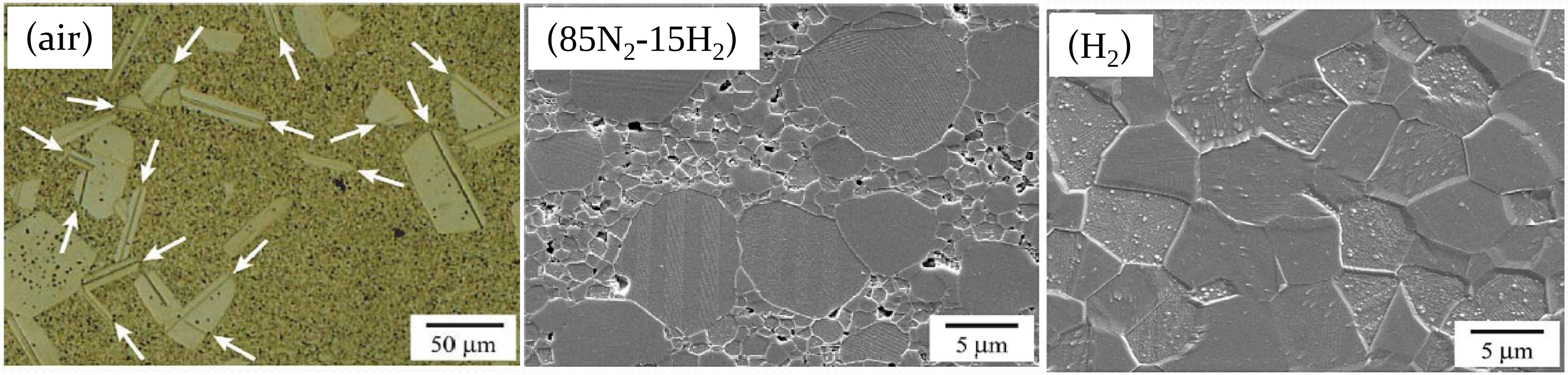


Microstructures of 70(25TiC–75WC)–30Co (wt%) samples sintered at 1450°C for: (a) 1 hour; (b) 10 hours and (c) 40 hours (mean WC starting powder size = 0.5µm). The rounded grains are (Ti,W)C and the faceted grains are WC

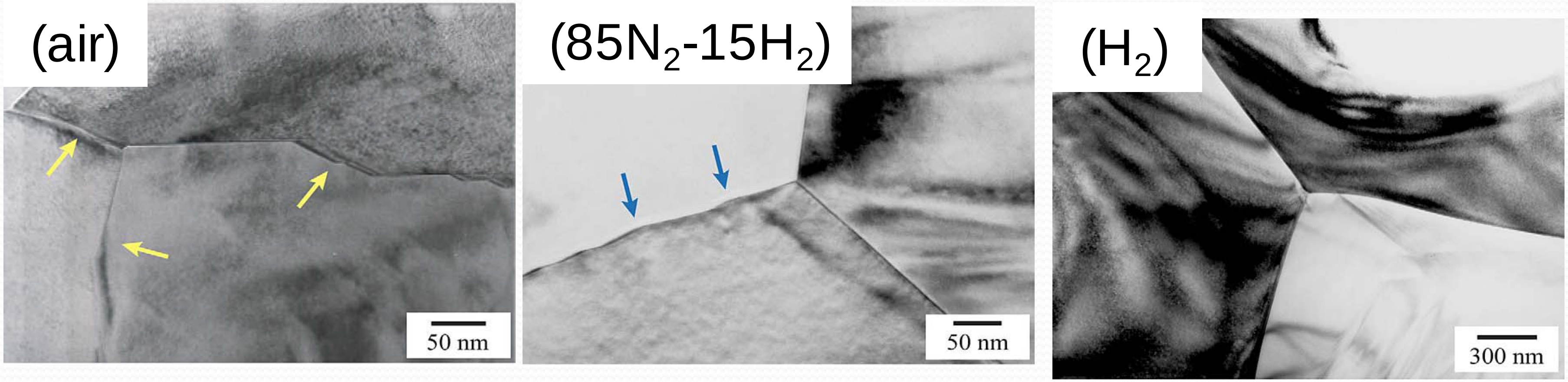


Microstructures of 70(25TiC–75WC)–30Co (wt%) samples sintered at 1450°C for: (a) 1 hour; (b) 10 hours and (c) 40 hours (mean WC starting powder size = 4.1µm).

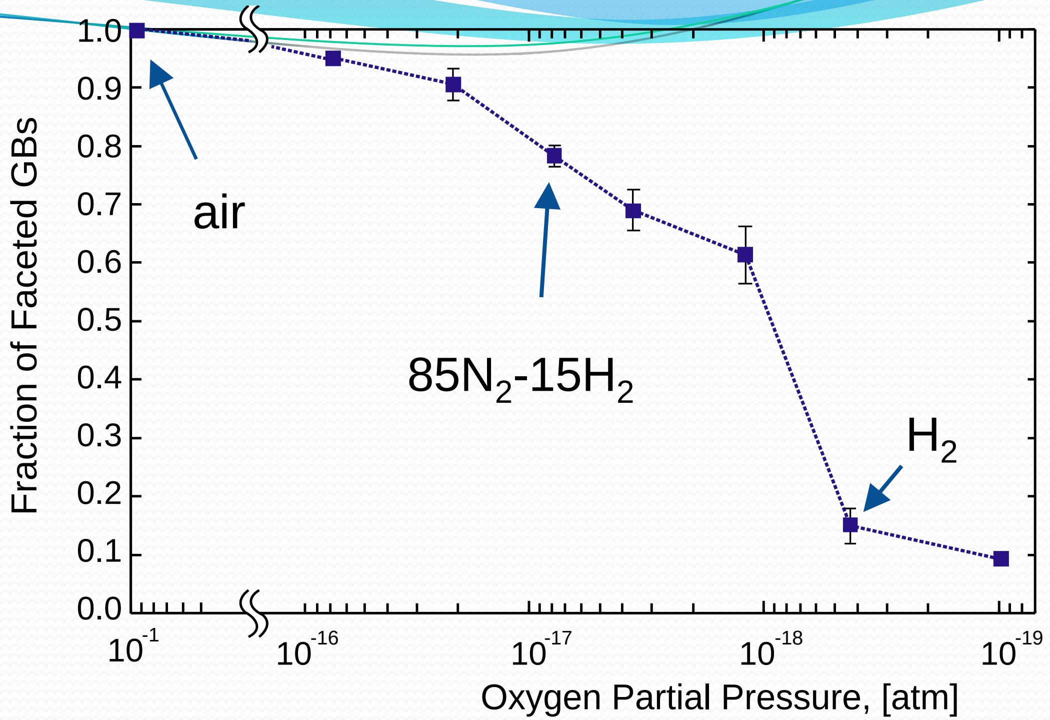
# Effect of sintering atmosphere on grain growth

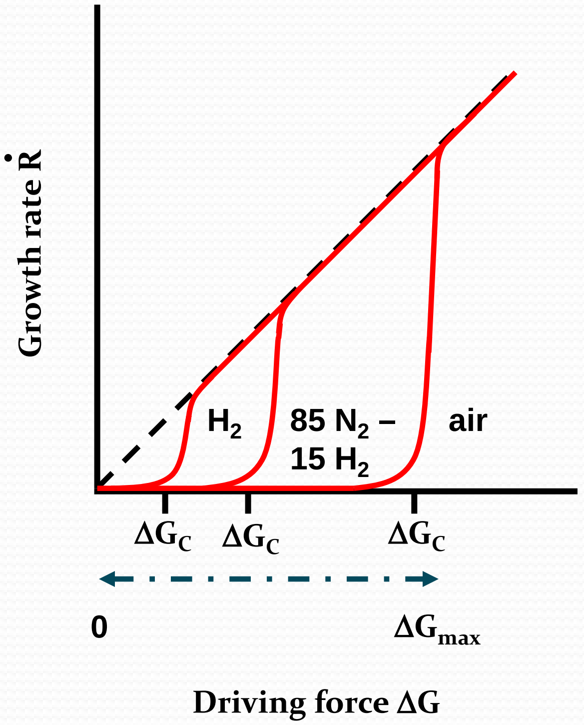


BaTiO$_3$ ceramics sintered at 1250°C for 24 h

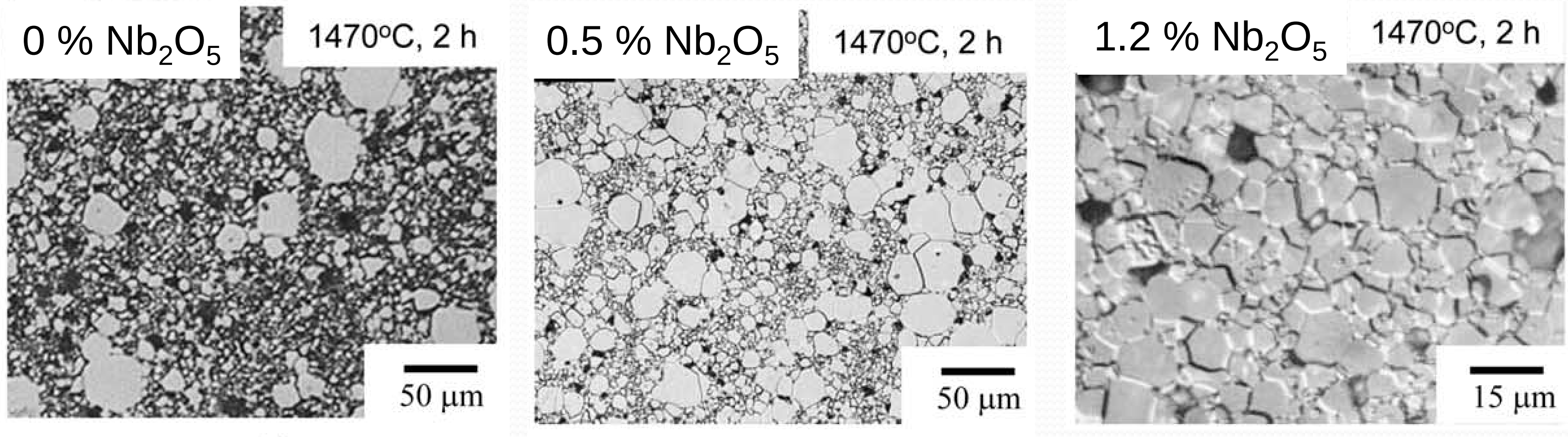


- Sintering in reducing atmosphere causes $[V_O^{\bullet\bullet}]$ increase.
- Increase in $[V_O^{\bullet\bullet}]$ causes increase in entropy.
- Increase in entropy causes decrease in $\varepsilon$ and $\Delta G_C$

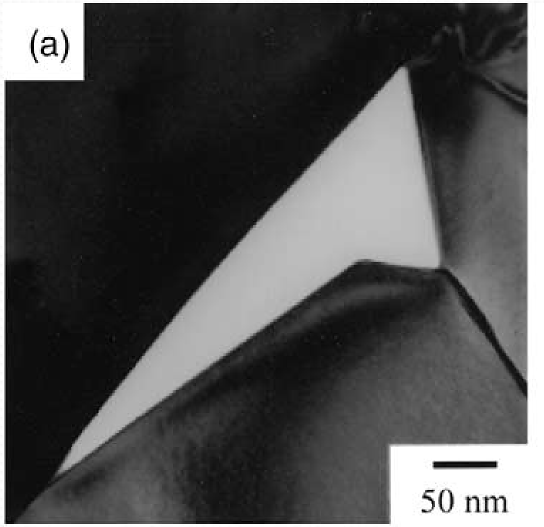




# Effect of dopants on grain growth

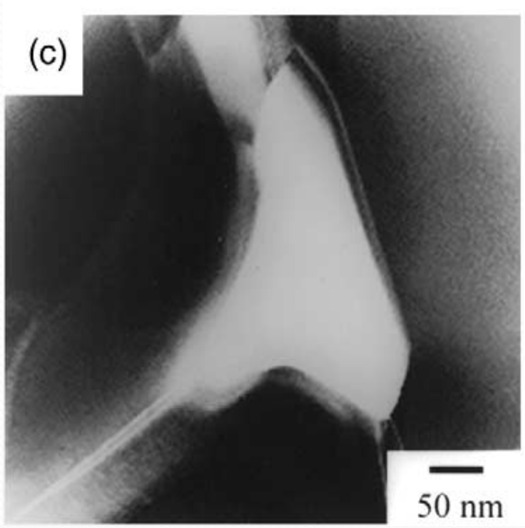


$SrTiO_3$ doped with $Nb_2O_5$ and sintered in air

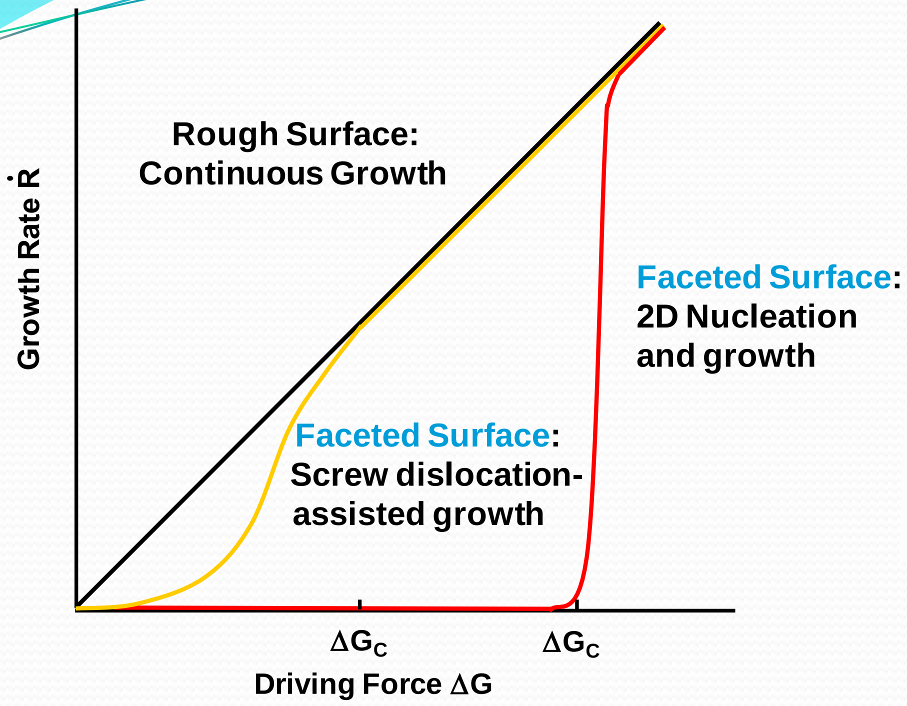


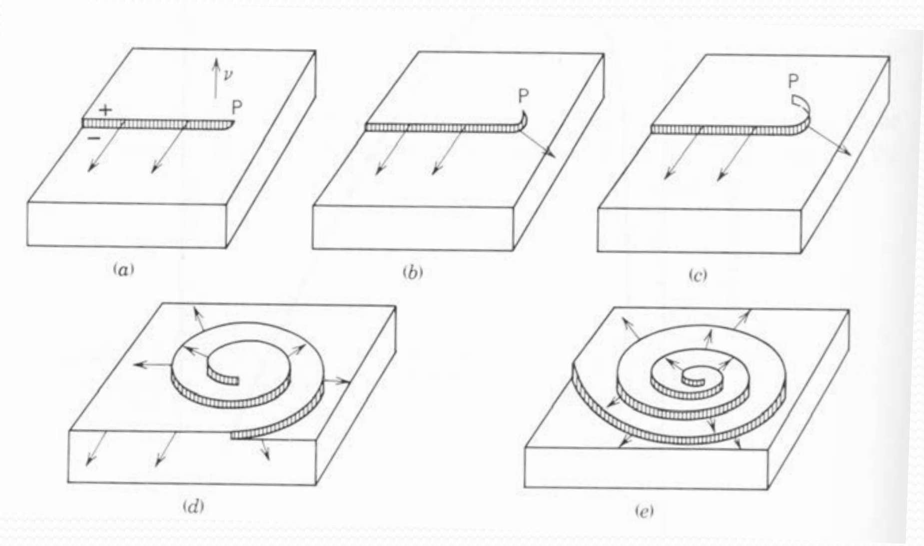
$2Nb \rightarrow 2Nb_{Ti}^{\bullet} + V_{Sr}''$

Similar effect to $V_O^{\bullet\bullet}$



# Effect of surface defects on grain growth





Screw dislocation

$$\boxed{\dot{R} = A\frac{(\Delta G)^2}{\varepsilon}\tanh\left(\frac{\varepsilon}{\Delta G}\right)}$$

A = constant

ε = step free energy

# Abnormal Grain Growth in $Al_2O_3$

$Al_2O_3$

MgO doped $Al_2O_3$

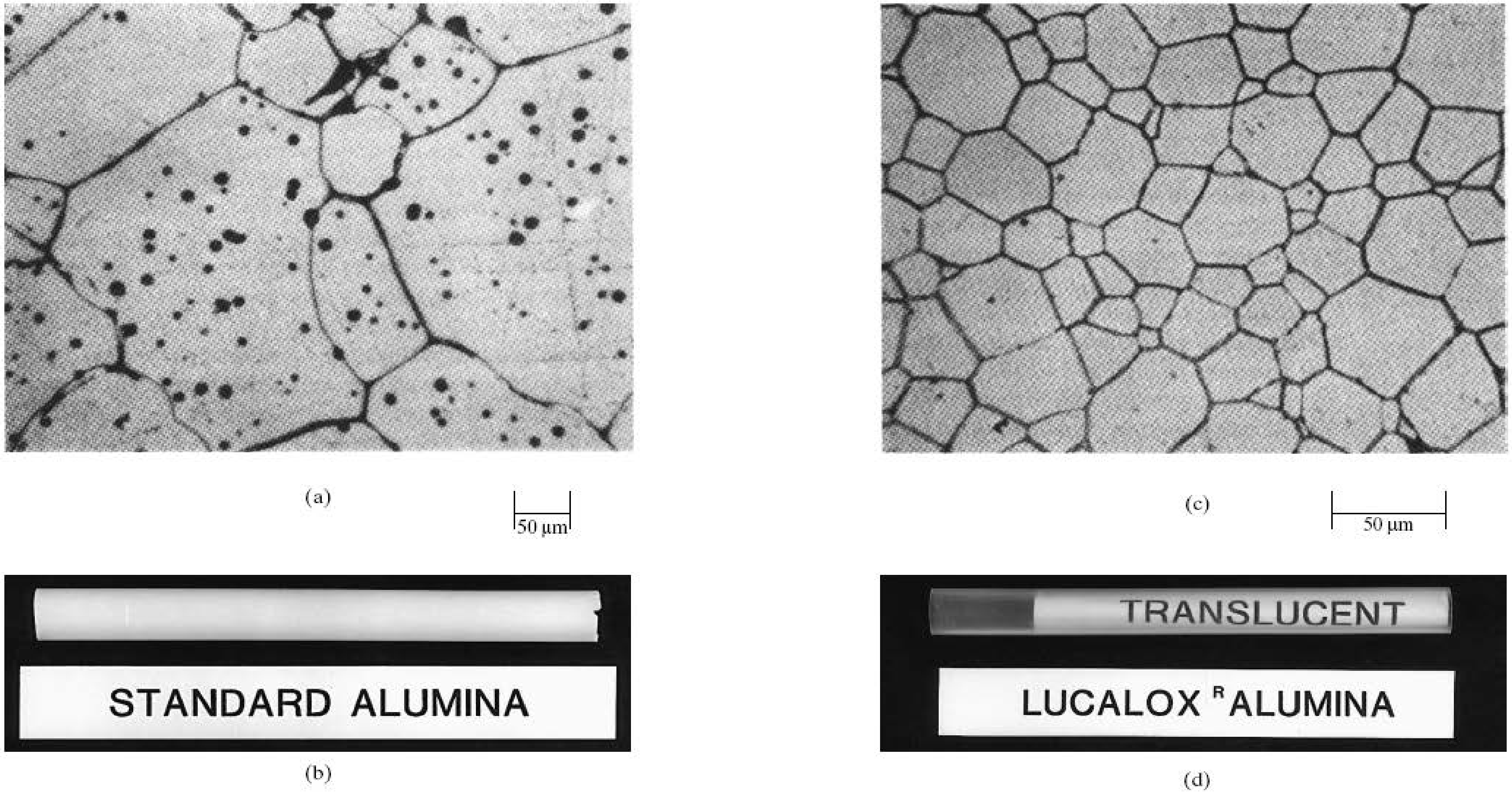
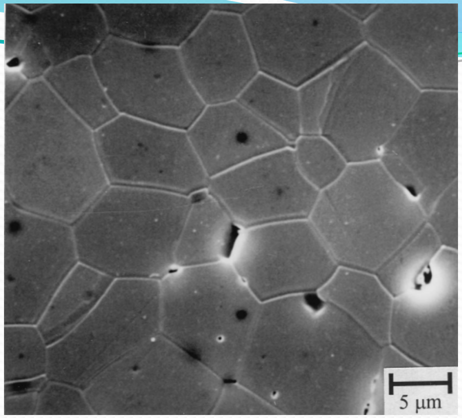
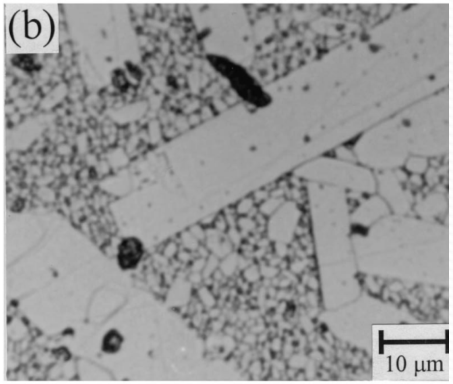


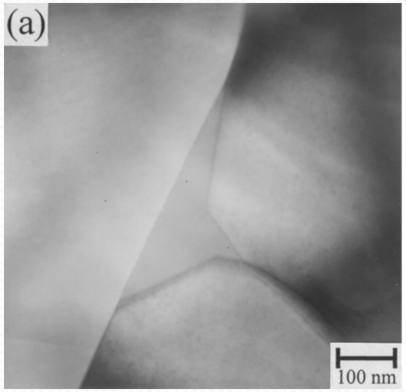
**Figure 1-20** *Porous microstructure in polycrystalline* $Al_2O_3$ *(a) leads to an opaque material (b). Nearly pore-free microstructure in poly crystalline* $Al_2O_3$ *(c) leads to a translucent material (d). (Courtesy of C. E. Scott, General Electric Company)*

In pure $Al_2O_3$, g.b.s are disordered and no AGG occurs.

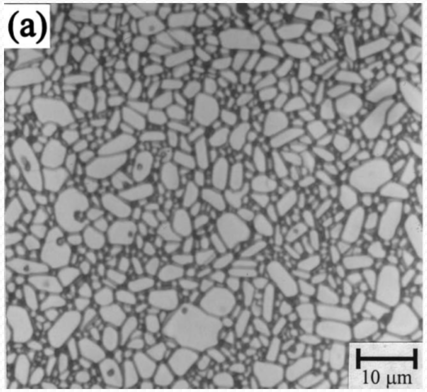


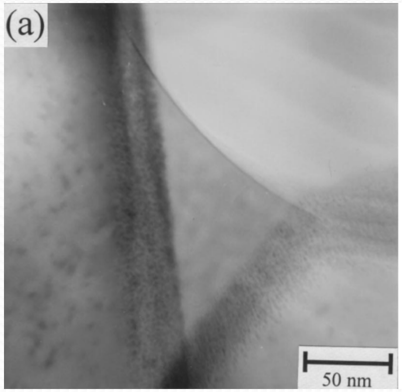
If impurities (CaO, $SiO_2$) are present, g.b.s become ordered and AGG occurs.





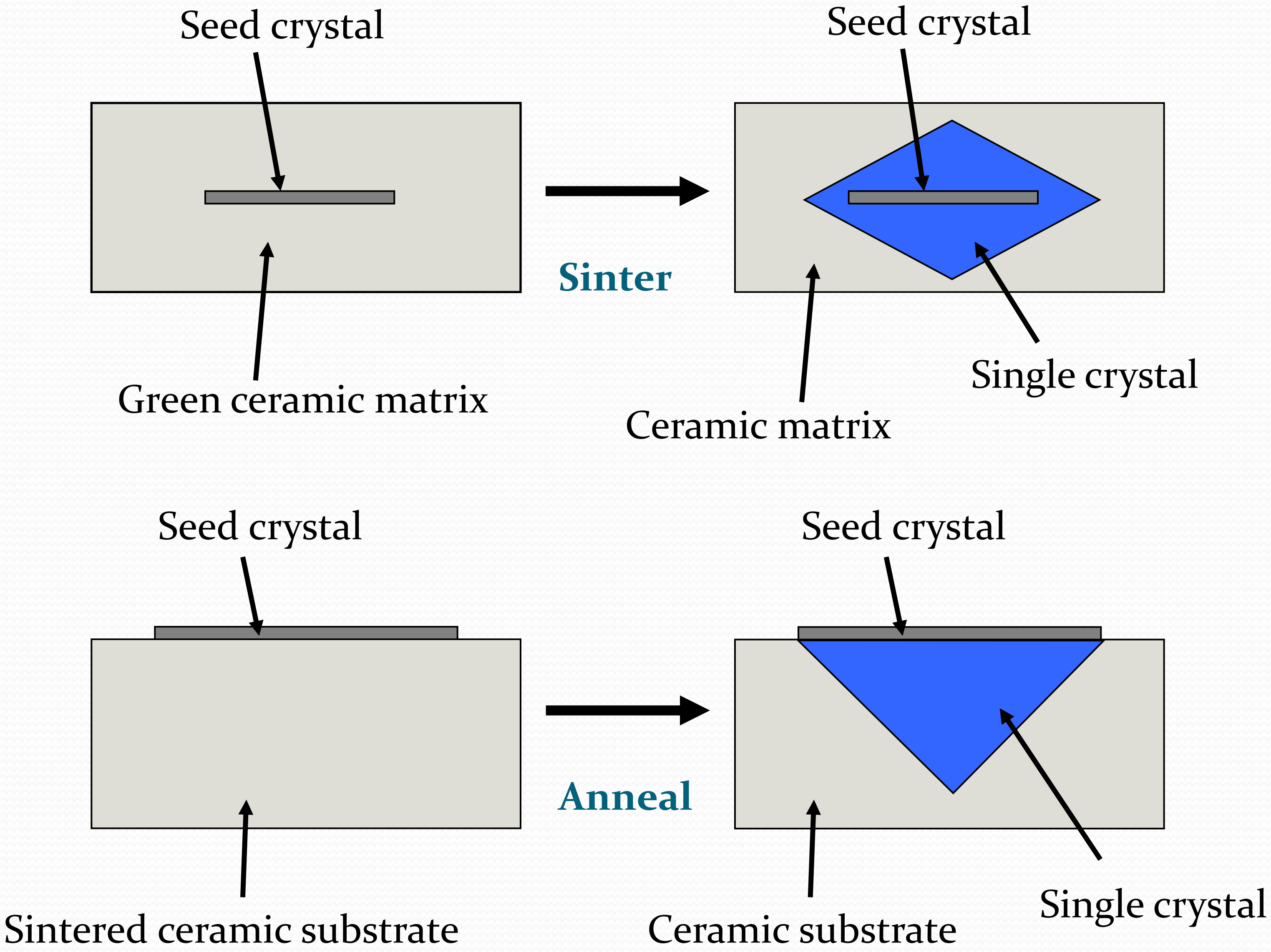
Addition of MgO lowers $\varepsilon$ and $\Delta G$, causing change from AGG to normal growth.





C. W. Park and D. Y. Yoon, *J. Am. Ceram. Soc.* **85** [6] 1585-93 (2002)

# Solid State Single Crystal Growth (SSCG)



Seed crystal

Green ceramic matrix

**Sinter**

Seed crystal

Single crystal

Ceramic matrix

Seed crystal

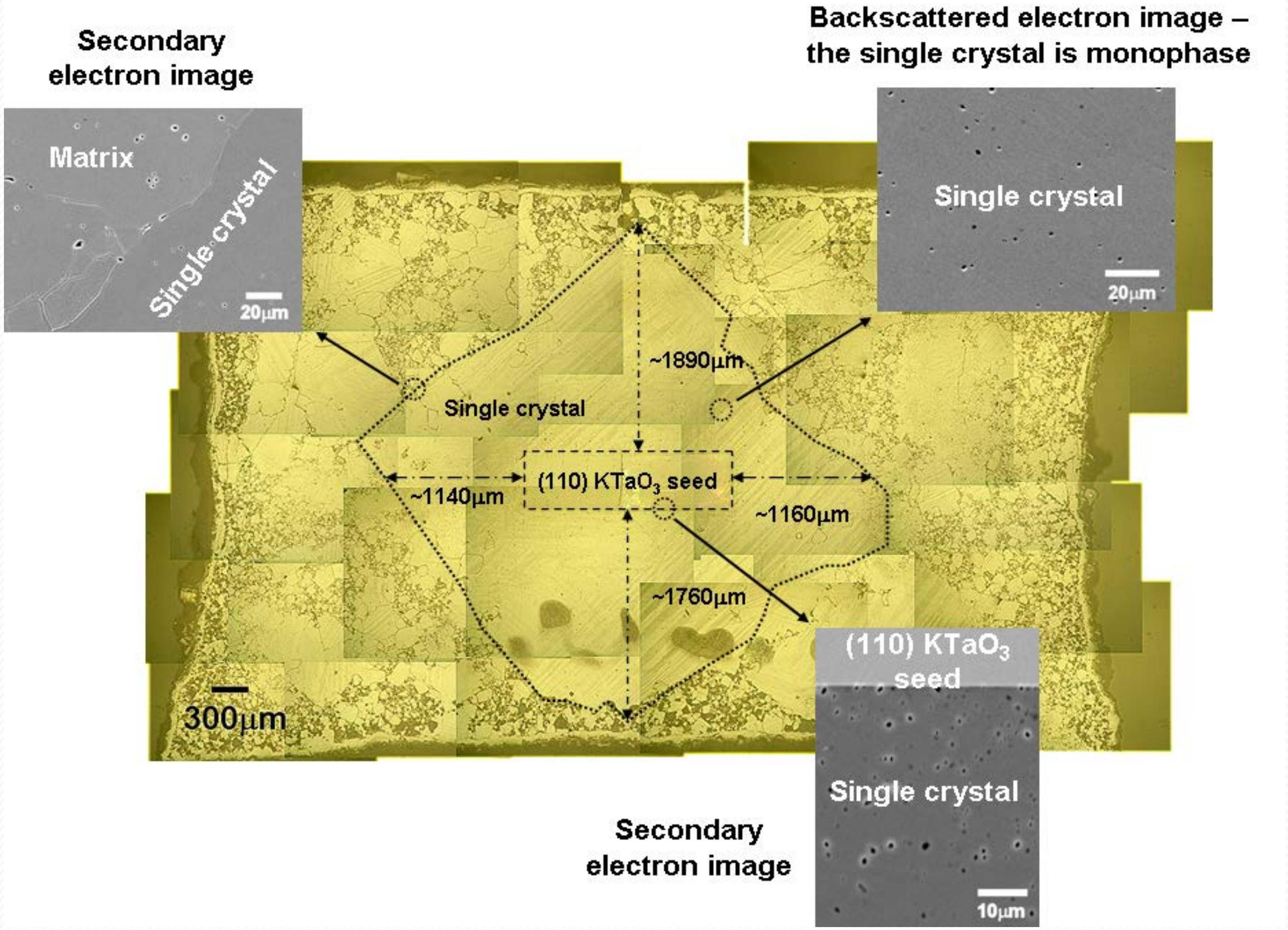
Sintered ceramic substrate

**Anneal**

Seed crystal

Single crystal

Ceramic substrate



Single crystal of $(K_{0.5}Na_{0.5})NbO_3$ grown in a hot press at 1100°C and 50 MPa for 100 hours