PIII: GG and Microst. Evolution

Outline:

Types of grain growth: Stationary vs. Nonstationary

- Liquid phase sintering (LPS)
  - Grain growth in a matrix (Ostwald ripening)
  - Effect of pores on microstructure development
  - Effect of interfacial energy anisotropy
- Solid state sintering (SSS)
  - Grain growth in a pure dense system
  - Effect of 2nd phase particles on grain growth
  - Effect of pores on microstructure development
  - Effect of solute segregation on boundary migration
  - Effect of boundary energy anisotropy

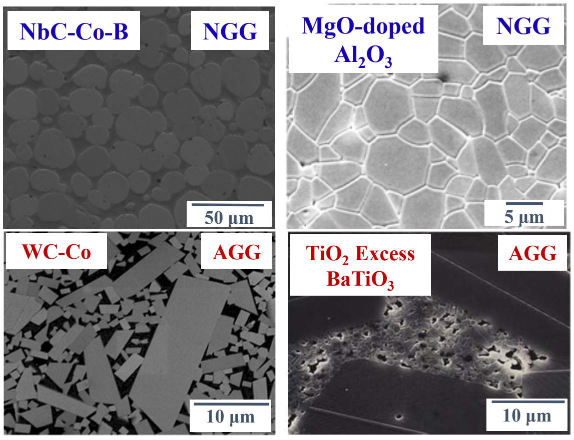
Mixed Mechanism Principle of Microstructural Evolution

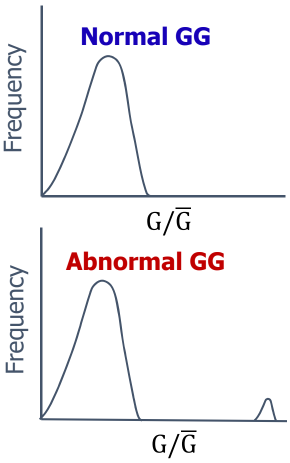
KAIST, S-J L. Kang

Grain Growth and Microstructure

Two Extreme Cases: Normal and Abnormal

Two phase system **Single phase system**





J. H. Lee, M.S. Thesis, (KAIST, 2005)
S. Y. Choi, Ph.D. Thesis, (KAIST, 2004)

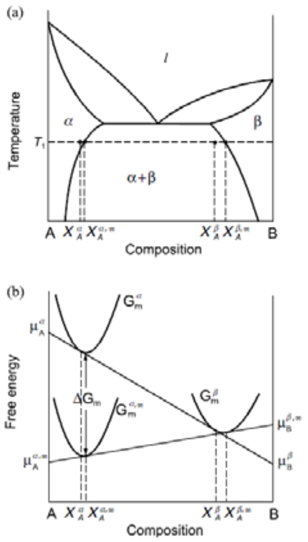
C. W. Park and D. Y. Yoon, *J. Am. Ceram. Soc.*, **83,** 2605 (2000).
D. Y. Yang and S.-J. L. Kang, *Int. J. Refract. H. Mater.*, **27**, 90 (2009)

KAIST, S-J L. Kang

Chap. Liquid Phase Sintering

Qn: Why grain growth takes place during sintering?

Driving Force



$$X_A^\beta = X_A^{\beta,\infty}\left(1+\frac{1-X_A^{\beta,\infty}}{X_A^{\alpha,\infty}-X_A^{\beta,\infty}}\frac{\gamma V^\alpha K}{RT}\right)$$

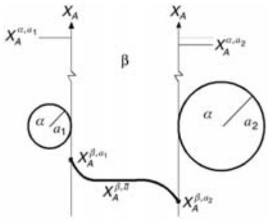


Figure 15.1. (a) Typical phase diagram showing limited solubility of $X_A^{\alpha,\infty}$ and $X_B^{\beta,\infty}$ at temperature T_1 and (b) schematic of the molar free energy versus composition at the temperature for α precipitates with a flat interface ($K = 0$) and with a finite radius of curvature ($K \neq 0$).

KAIST, S-J L. Kang

Lifshitz-Slyozov-Wagner (LSW) Theory

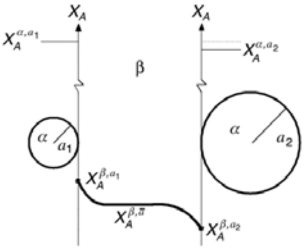
Basic Assumptions: (i) infinitely dispersed system (meaning?)
(ii) constant interface mobility (meaning?)

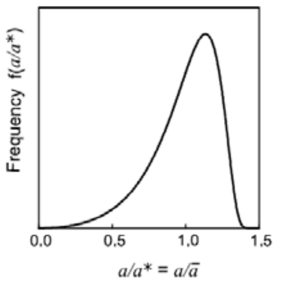
Diffusion-controlled GG (by LSW)

Interaction btw. average-sized grain and an individual grain

$$\frac{\mathrm{d}a}{\mathrm{d}t} = -\frac{D(C_a - C_{\bar a})}{a} \qquad \frac{\mathrm{d}a}{\mathrm{d}t} = \frac{2D\gamma C_\infty V_m}{RTa}\left(\frac{1}{\bar a}-\frac{1}{a}\right)$$

$$\bar a_t^3 - \bar a_0^3 = \frac{8}{9}\frac{D\gamma C_\infty V_m}{RT}t$$





Lifshitz and Slyozov, *J. Phys. Chem. Solids,* **19**, 35 (1961).
Wagner, *Z. Electrochem.,* **65**, 581 (1961).

KAIST, S-J L. Kang

Lifshitz-Slyozov-Wagner (LSW) Theory

Basic Assumptions: (i) infinitely dispersed system (meaning?)
(ii) constant interface mobility (meaning?)

Interface Reaction-controlled GG (by Wagner)

Interaction btw. average-sized grain and an individual grain

$$\frac{\mathrm{d}a}{\mathrm{d}t} = K(C_{\overline{a}} - C_a) = \frac{2K\gamma C_\infty V_m}{RT}\left(\frac{1}{\overline{a}} - \frac{1}{a}\right)$$

$$\overline{a_t}^2 - \overline{a_o}^2 = \frac{64}{81}\frac{K\gamma C_\infty V_m}{RT}t$$

(This Eq. is similar to that of NGG
for a single phase system)

Physically Wrong!

Wagner, *Z. Electrochem.*, **65**, 581 (1961).

KAIST, S-J L. Kang

Lifshitz-Slyozov-Wagner (LSW) Theory

Basic Assumptions: (i) infinitely dispersed system (meaning?)
(ii) constant interface mobility (meaning?)

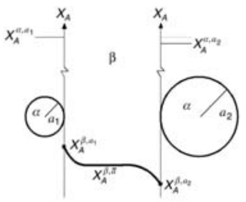
Diffusion-controlled GG (by LSW)

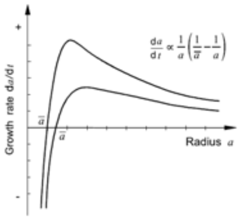
Interaction btw. average-sized grain and an individual grain

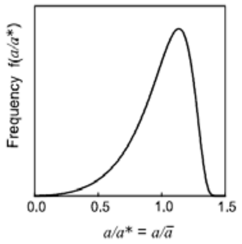
$$\frac{\mathrm{d}a}{\mathrm{d}t} = -\frac{D(C_a - C_{\overline{a}})}{a}$$

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{2D\gamma C_\infty V_m}{RTa}\left(\frac{1}{\overline{a}} - \frac{1}{a}\right)$$

$$\overline{a_t}^3 - \overline{a_0}^3 = \frac{8}{9}\frac{D\gamma C_\infty V_m}{RT}t$$







Interface Reaction-controlled GG (by Wagner)

$$\frac{\mathrm{d}a}{\mathrm{d}t} = K(C_{\overline{a}} - C_a) = \frac{2K\gamma C_\infty V_m}{RT}\left(\frac{1}{\overline{a}} - \frac{1}{a}\right)$$

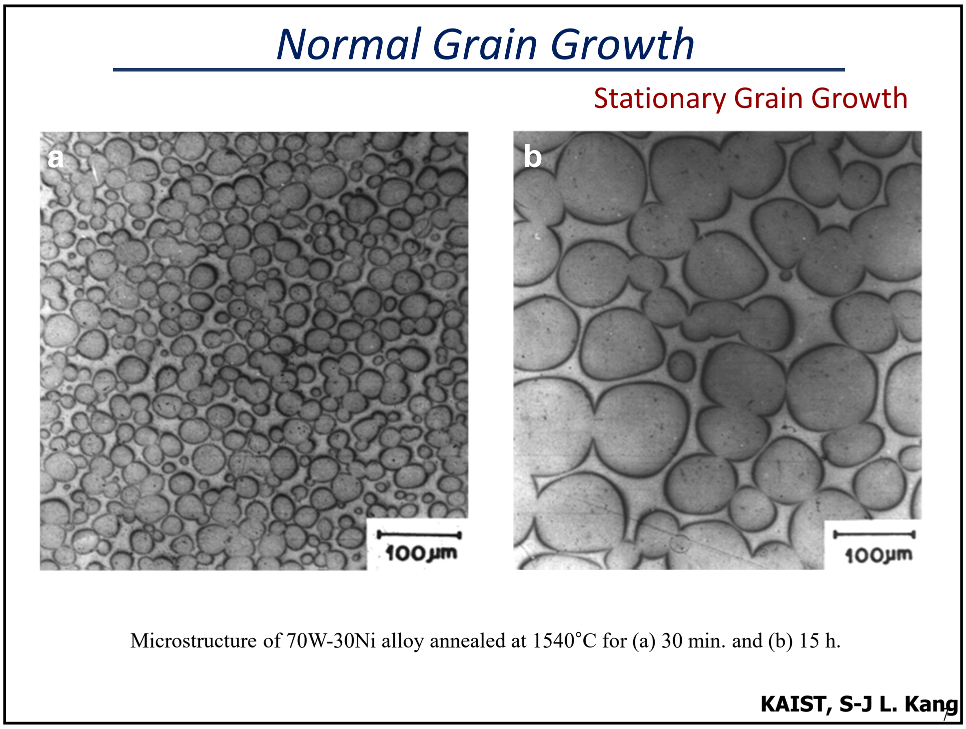
Physically Wrong!

$$\overline{a_t}^2 - \overline{a_o}^2 = \frac{64}{81}\frac{K\gamma C_\infty V_m}{RT}t$$

(This Eq. is similar to that of NGG
for a single phase system)

Lifshitz and Slyozov, *J. Phys. Chem. Solids,* **19**, 35 (1961).
Wagner, *Z. Electrochem.*, **65**, 581 (1961).

KAIST, S-J L. Kang

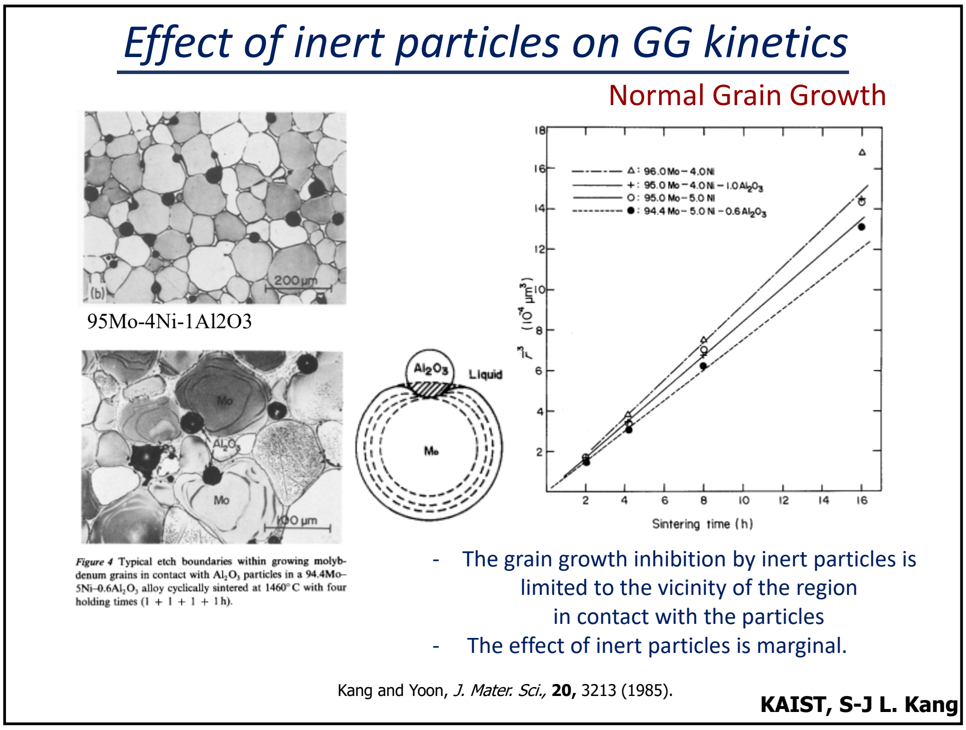


Normal Grain Growth

Stationary Grain Growth

Microstructure of 70W-30Ni alloy annealed at 1540°C for (a) 30 min. and (b) 15 h.

KAIST, S-J L. Kang



Effect of inert particles on GG kinetics

Normal Grain Growth

95Mo-4Ni-1Al2O3

Figure 4 Typical etch boundaries within growing molybdenum grains in contact with Al_2O_3 particles in a 94.4Mo–5Ni–0.6Al_2O_3 alloy cyclically sintered at 1460° C with four holding times (1 + 1 + 1 + 1 h).

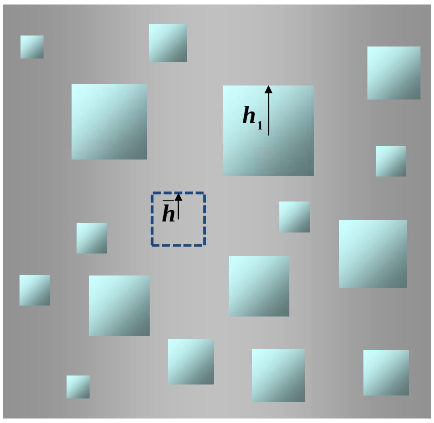
- The grain growth inhibition by inert particles is limited to the vicinity of the region in contact with the particles
- The effect of inert particles is marginal.

Kang and Yoon, *J. Mater. Sci.,* **20,** 3213 (1985).

KAIST, S-J L. Kang

Fundamentals of Grain Growth in a Matrix

Ostwald ripening: Result of growth/dissolution of individual grains



Interaction of an individual grain with a critical sized grain

$$\Delta g \propto \left(\frac{1}{\bar{h}} - \frac{1}{h_1}\right)\gamma_{sl}$$

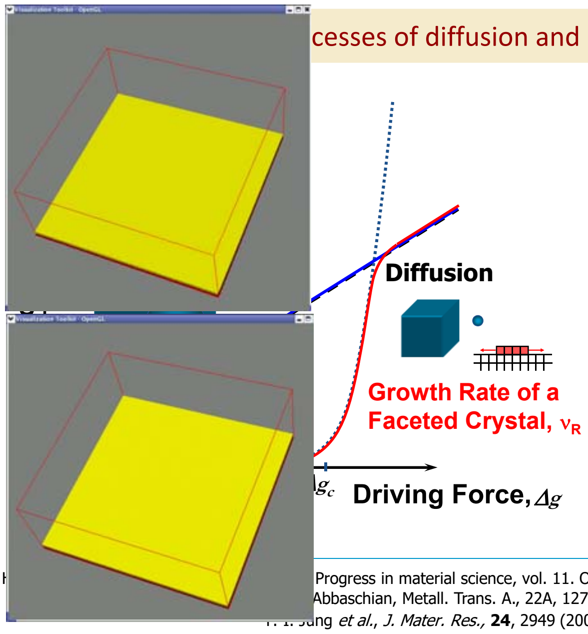
(Difference in Capillary Pressure)

Growth and dissolution of single crystal grains in a liquid matrix

KAIST, S-J L. Kang

Crystal Growth in a Matrix

cesses of diffusion and interface reaction



Effective Rate

$$v = \frac{v_D v_R}{v_D + v_R}$$

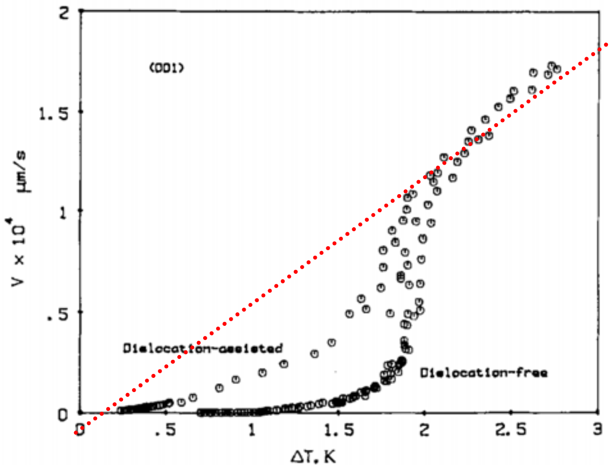
H Progress in material science, vol. 11. Oxford, UK: Pergamon Press; 1963. p. 77.
Abbaschian, Metall. Trans. A., 22A, 1271 (1991).
ng *et al.*, *J. Mater. Res.*, **24**, 2949 (2009).

KAIST, S-J L. Kang

Nonlinear Migration of Faceted Sol./Liq. Interface

Experimental Observation

(001) Ga Single Crystal

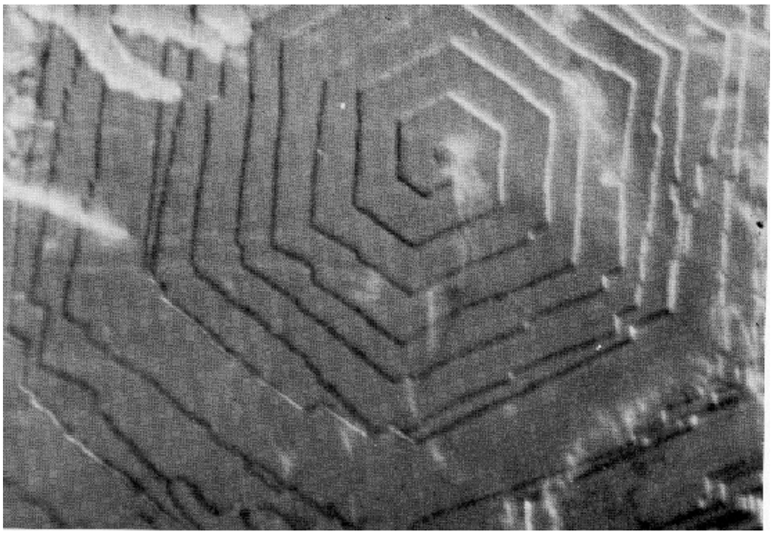


S.D. Peteves and R. Abbaschian, *Metall. Trans. A*, **22** **[6]**, 1259 (1991).

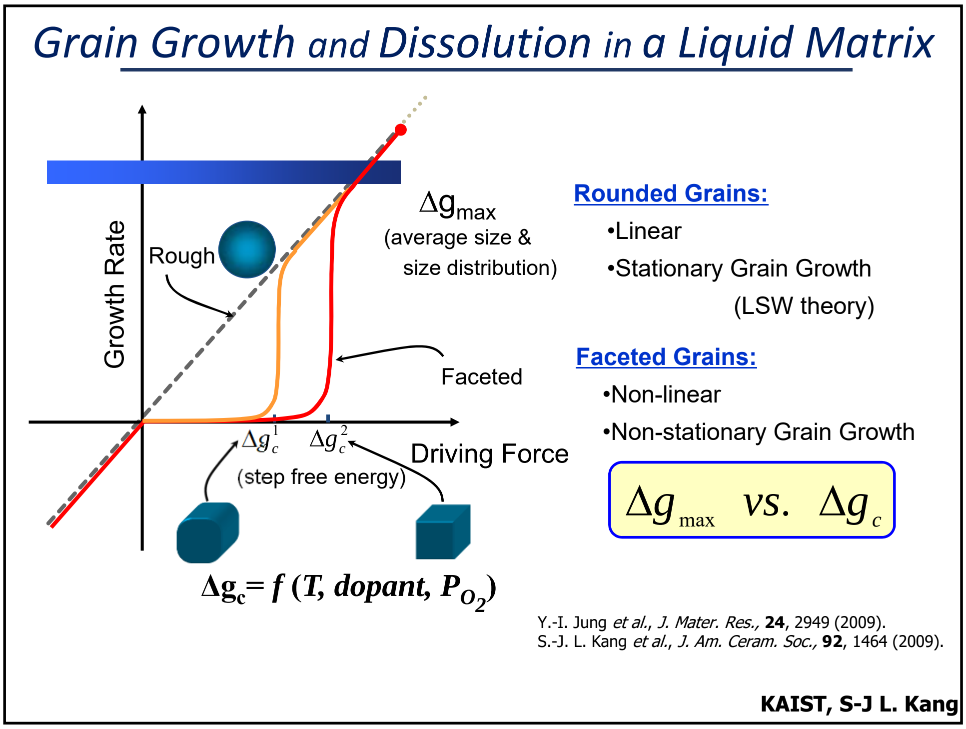
KAIST, S-J L. Kang

Defect-assisted Growth of a Crystal in a Matrix

Growth spiral on CdI crystals growing from water solution (by Jackson)



KAIST, S-J L. Kang



Grain Growth and Dissolution in a Liquid Matrix

Rounded Grains:
- Linear
- Stationary Grain Growth (LSW theory)

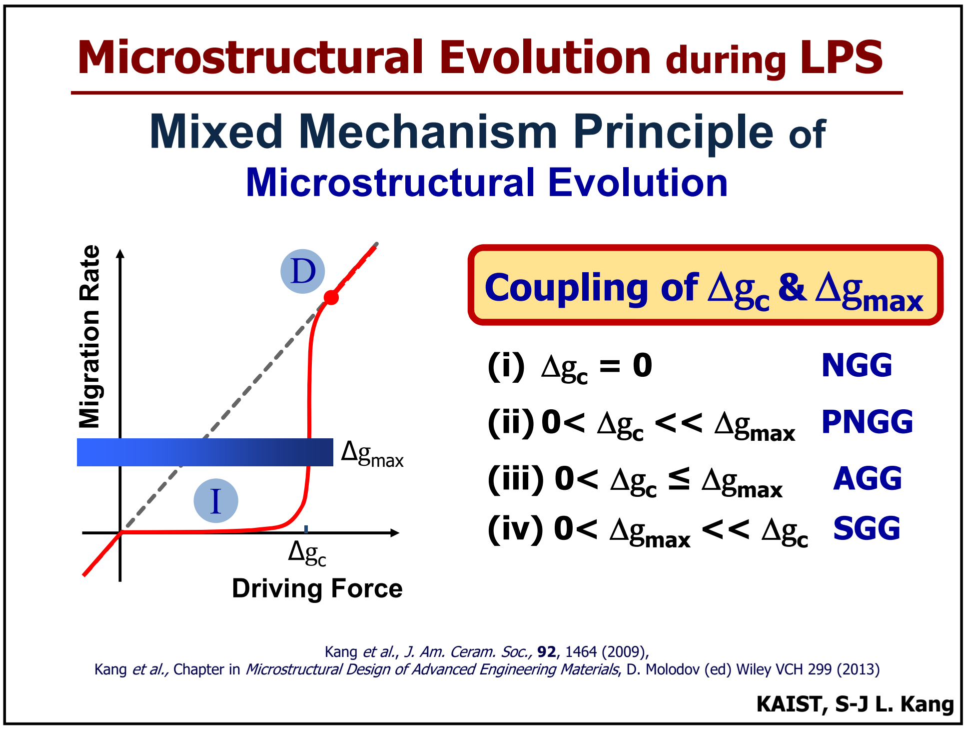
Faceted Grains:
- Non-linear
- Non-stationary Grain Growth

Δg_{max} vs. Δg_c

$\Delta g_c = f\,(T, dopant, P_{O_2})$

Y.-I. Jung *et al., J. Mater. Res.*, **24**, 2949 (2009).
S.-J. L. Kang *et al., J. Am. Ceram. Soc.*, **92**, 1464 (2009).

KAIST, S-J L. Kang



Microstructural Evolution during LPS

Mixed Mechanism Principle of Microstructural Evolution

Coupling of Δg_c & Δg_{max}

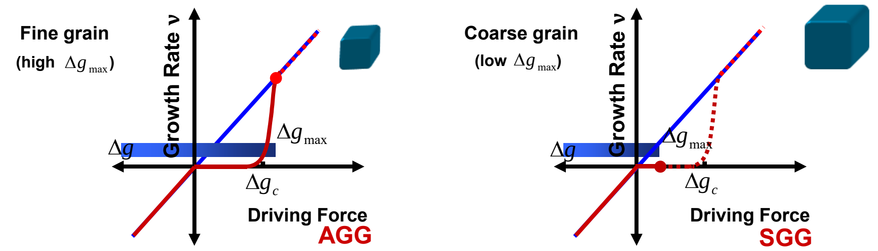
(i) $\Delta g_c = 0$	**NGG**
(ii) $0 < \Delta g_c << \Delta g_{max}$	**PNGG**
(iii) $0 < \Delta g_c \leq \Delta g_{max}$	**AGG**
(iv) $0 < \Delta g_{max} << \Delta g_c$	**SGG**

Kang *et al., J. Am. Ceram. Soc.*, **92**, 1464 (2009),
Kang *et al.*, Chapter in *Microstructural Design of Advanced Engineering Materials*, D. Molodov (ed) Wiley VCH 299 (2013)

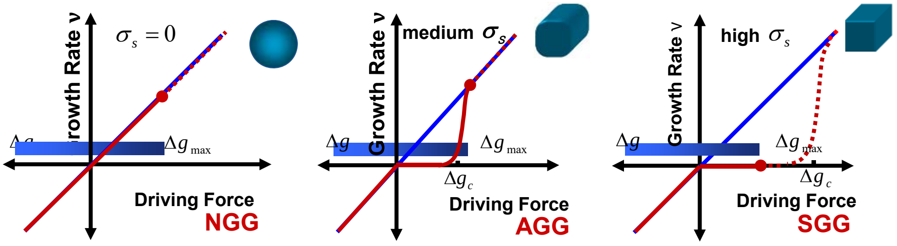
KAIST, S-J L. Kang

Thought Experiments

I. Effect of Δg_{max} (Initial Particle Size)



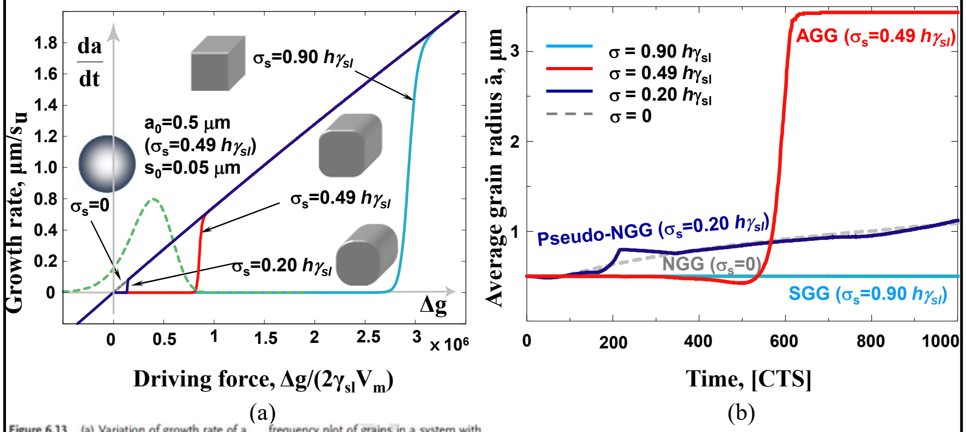
II. Effect of Δg_c (T, Dopant, P_{O_2})



KAIST, S-J L. Kang

Simulation of Grain Growth

Effect of Step Free Energy

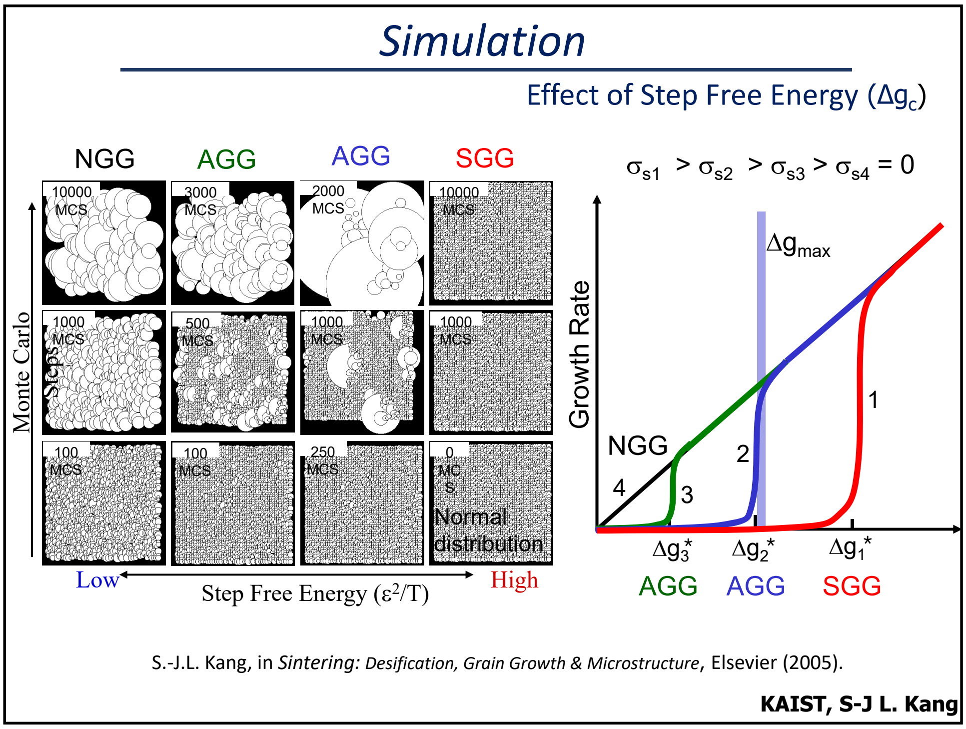


(a) (b)

Figure 6.13 (a) Variation of growth rate of a grain with respect to the driving force normalized to $2\gamma_{sl}V_m$ for various critical driving forces, which are governed by the step free energy σ_s of facets. Schematic equilibrium shapes of a grain for different step free energies are also shown. The dotted curve shows the frequency plot of grains in a system with $\sigma_s = 0.49\,h\gamma_{sl}$, where the average grain radius is 0.5 µm and the standard deviation is 0.05 µm; (b) Variation of the average radius of grains with calculation time steps for systems shown in panel (a). For the calculation, the data used in Ref. [84] were utilized.

S.-J. L. Kang, "Sintering" in Ceramic Science and Technology vol. 3, 143-167, Riedel and I.-W. Chen (eds), Weily-VCH (2012).
S.-J. L. Kang *et al., J. Am. Ceram. Soc.,* **92**, 1464 (2009).
Y.-I. Jung *et al., J. Mater. Res.,* **24**, 2949 (2009).

KAIST, S-J L. Kang

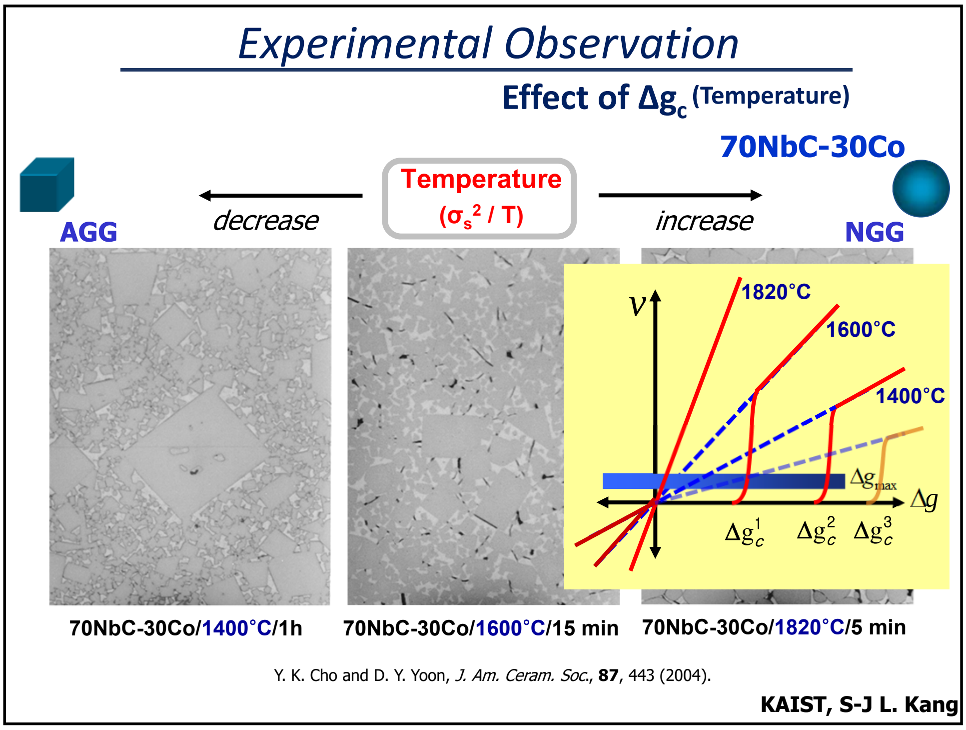


Simulation

Effect of Step Free Energy (Δg_c)

S.-J.L. Kang, in *Sintering: Desification, Grain Growth & Microstructure*, Elsevier (2005).

KAIST, S-J L. Kang



Experimental Observation

Effect of Δg_c (Temperature)

70NbC-30Co

70NbC-30Co/1400°C/1h **70NbC-30Co/1600°C/15 min** **70NbC-30Co/1820°C/5 min**

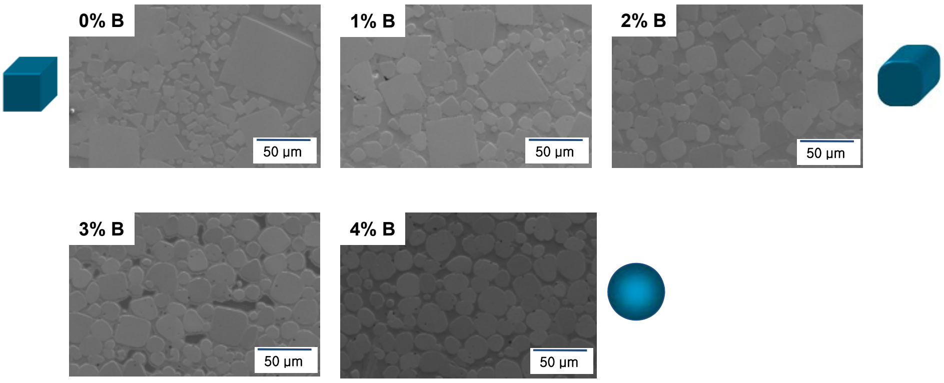
Y. K. Cho and D. Y. Yoon, *J. Am. Ceram. Soc.*, **87**, 443 (2004).

KAIST, S-J L. Kang

Experimental Observation

Effect of Δg_c (Dopant)

NbC-Co-B (at 1450°C for 2 h)



J. H. Lee, M.S. Thesis, (KAIST, 2005)

KAIST, S-J L. Kang

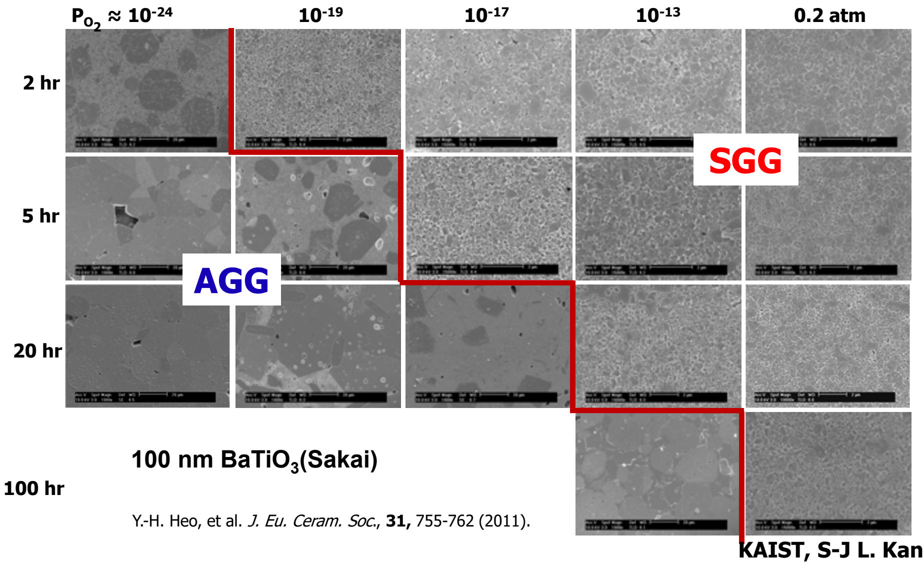
Experimental Observation

Effect of Δg_c (P_{O_2})

Medium σ_s

$BaTiO_3$ -2SiO_2-8TiO_2 (mol%), 1280 °C

Very High σ_s



100 nm $BaTiO_3$(Sakai)

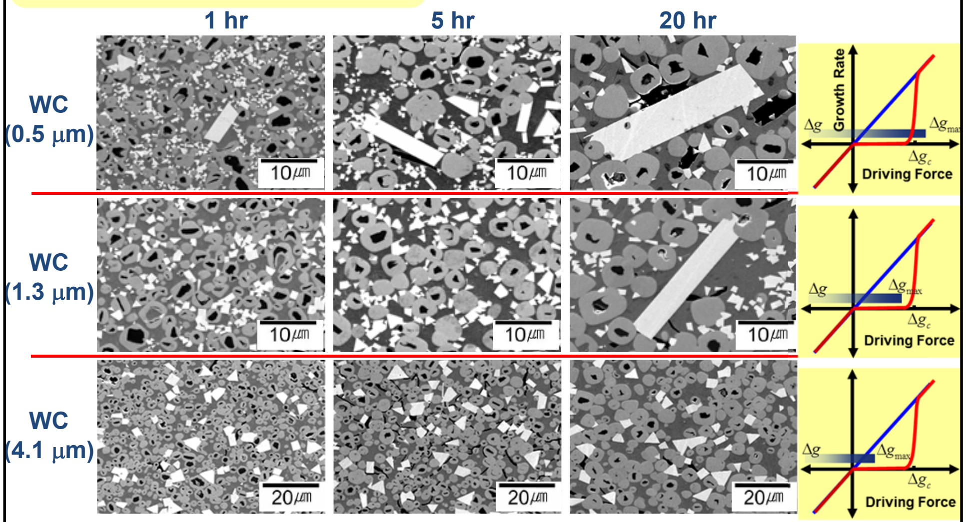
Y.-H. Heo, et al. *J. Eu. Ceram. Soc.*, **31,** 755-762 (2011).

KAIST, S-J L. Kang

Experimental Observation

Effect of Δg_{max} (Initial Particle Size)

70(25TiC-75WC)-30Co, 1450 °C



B.-K. Yoon, B.A. Lee and S.-J.L. Kang, *Acta Mater.*, **53**, 4677 (2005).

KAIST, S-J L. Kang

Experimental Supports for the Principle

Experimental Observations and Interpretations
(Two-Phase Systems)

•Effect of Δg_c (T, Dopant, P_{O_2})

- Sialon, Si_3N_4 (Kang and Han, 1995)
- $SrTiO_3$ (Chung *et al.*, 2002 (Dopant, P_{O_2}))
- NBT-BT (Moon and Kang, 2008)
- $BaTiO_3$ (Chang and Kang, 2009)
- NBT-BT (Moon *et al.*, 2011 (Dopant))
- NbC-Co (Cho and Yoon, 2004 (T))
- NbC-Fe (Oh *et al.*, 2000 (Dopant))
- PMN-PT (Wallace *et al.*, 2002 (Dopant))
- SiC (Jang *et al.*, 1996 (P_{O_2}))
- PMN-PT (Kim *et al.*, 2006, (Dopant, T))
- KNN (Fisher *et al.*, 2009)
- $BaTiO_3$ (Heo *et al.*, 2011 (P_{O_2}))
- Alumina (Park *et al.*, 2002 (Dopant))
- NbC-Co (Lee and Yoon, 2005 (Dopant))
- (Nb,Ti)C-Co (Choi *et al.*, 2002 (Dopant))
- WC-Co (Lee *et al.*, 2003 (Dopant))
- $SrTiO_3$ (Sano *et al.*, 2007) etc.

•Effect of Δg_{max}

- $BaTiO_3$ (Jung *et al.*, 2003)
- WC-Co (Park *et al.*, 1996)
- TiC-WC-Co (Yoon *et al.*, 2005)

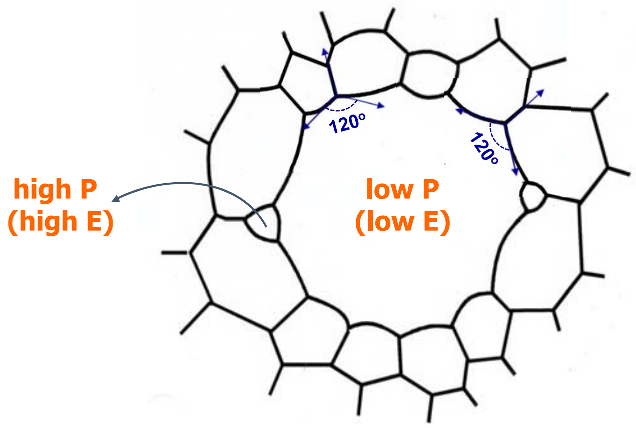
KAIST, S-J L. Kang

Chap. Solid State Sintering

GG: Increase in average grain size

Result of boundary migration

Driving Force



in 2-D

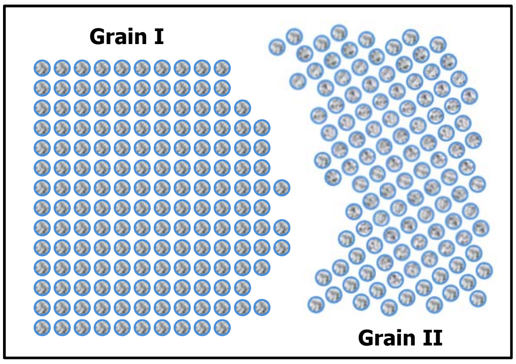
γ = const.

θ = 120°

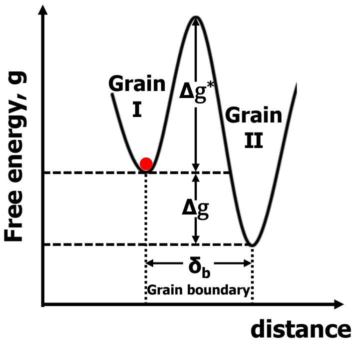
KAIST, S-J L. Kang

Atomic Motion in Boundary Migration

Δ**g (Capillary energy)**$= (2\gamma_b/\mathrm{r})\,V_\mathrm{m}$



Random jump of atoms across the boundary



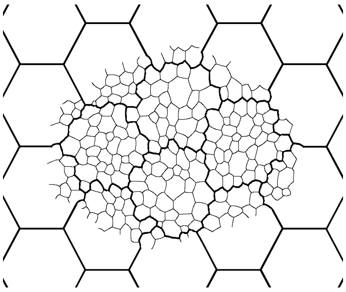
Diffusion Control :

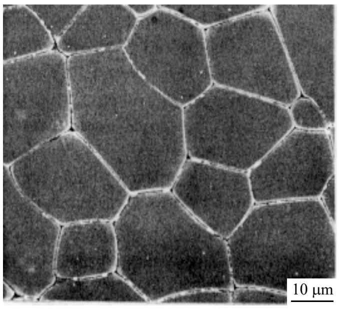
$$M_b = \frac{D_b^{\perp}}{RT} \propto exp\left(-\frac{\Delta g^*}{RT}\right)$$

Kang *et al., J. Ceram. Soc. Jpn.,* 124, 259 (2016).

KAIST, S-J L. Kang

Driving Force for Grain Growth





Etched and polished section of Al_2O_3

Driving Force for the Growth of a Grain

$$\Delta \mathbf{g} = 4\gamma_b \left(\frac{1}{\bar{G}} - \frac{1}{G}\right) \propto \left(\frac{1}{\bar{G}} - \frac{1}{G}\right)$$

The mean field concept is adopted.

KAIST, S-J L. Kang

GG in Pure Materials

The Boundary mobility is assumed to be constant irrespective of the driving force.

$$\textbf{Mobility = const.} \neq f(F_b)$$

The boundary energy is also assumed to be constant, γ_b **= constant**

$$\frac{d\bar{G}}{dt} = \alpha \bar{v}_b = \alpha J \Omega$$

$$= \alpha \frac{D_b^{\perp}}{kT} (\nabla P) \Omega$$

$$= \alpha \frac{D_b^{\perp}}{RT} \frac{2\gamma_b}{\bar{R}_o} \frac{V_m}{\omega}$$

$$\frac{d\bar{G}}{dt} = \frac{D_b^{\perp} 2\gamma_b V_m}{\beta R T \bar{G} \omega}$$

$$\bar{G}_t^2 - \bar{G}_{t_o}^2 = \frac{4 D_b^{\perp} \gamma_b V_m}{\beta R T \omega} t$$

Parabolic law or Square law

For an individual grain,

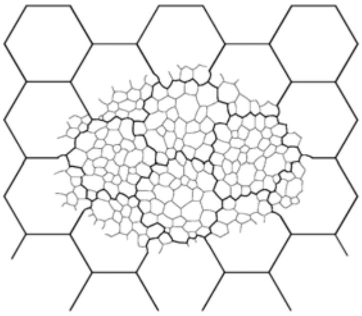
$$\frac{dG}{dt} = M_b [4\boldsymbol{\gamma_b} \left(\frac{1}{\bar{G}} - \frac{1}{G}\right) / \omega] \, V_m$$

Normal Grain growth:

Invariable distribution of relative grain size (stationary GG)

KAIST, S-J L. Kang

Some Considerations on Grain Growth



- Grain growth in terms of topology

From C – E + P = 1,

$$\sum(6-n)P_n + h_o - h_i = 6$$

- von Neumann equation

For a 2-dim. system where *M* is constant,

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \frac{\pi M \gamma_b}{3}(n-6)$$

- Deviation from NG behavior due to

(i) γ, $M_b \neq$ const.

(ii) Presence of 2nd phase particles   Mb = constant

(iii) Solute segregation $\neq$ f(Δg) → AGG(X)

(iv) Non-constant mobility of the boundary

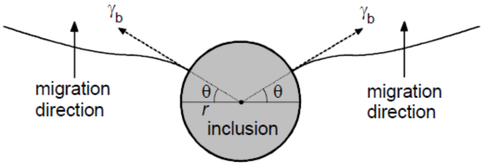
M_b = f(Δg) : This condition is related to the boundary structure

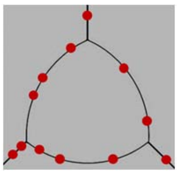
KAIST, S-J L. Kang

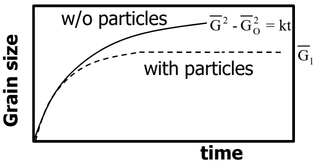
Effect of 2nd Phase Particles

Smith-Zener Effect

Qn: What is the thermodynamic basis of the Smith-Zener effect?







For uniform distribution of second phase particles

$$F_d = \gamma_b \sin\theta \times 2\pi r \cos\theta$$
$$= \pi r \gamma_b \sin 2\theta$$

$$F_d^\sigma = \frac{3 f_v \gamma_b}{2r}$$

$$\frac{\mathrm{d}\overline{G}}{\mathrm{d}t} = \frac{D_b^\perp}{RT}\frac{1}{\omega}\left[2\gamma_b \frac{V_m}{\beta\overline{G}} - \frac{3 f_v \gamma_b V_m}{2r}\right]$$

$$\overline{G}_l = \frac{4r}{3 f_v \beta} \quad \text{or} \quad \overline{R}_l = \frac{2r}{3 f_v \beta}$$

Qn: Ostwald ripening of particles?   In reality, such a high drag?

Addition of BT particles to Ni powder in fabrication of MLCC:
an application example of Zener drag

Smith CS. AIME, **175**, 15 (1949). Manohar PA, et al., *ISIJ Inter.*, **38**, 913 (1998).

KAIST, S-J L. Kang

Effect of solute segregation

Solute/Impurity segregation

Qn: Why solutes segregate at the grain boundary?

- Solute Segregation at GB
- Many models and theories of GB segregation.
- The simplest one is McLean's model that assumes
  mono-layer segregation of a single adsorbate
  without interference btw solvent and solute atoms
  (no site-to-site interaction, *cf: regular solution model*).

$$\frac{X_B^b}{X_A^b} = \frac{X_B}{X_A}\exp\left(\frac{-\Delta E}{kT}\right)$$

Derived by use of (i) statistical thermodynamics or
(ii) the mass action law

ΔE: free energy of segregation

Qn: What can be the factors that affect solute segregation?

KAIST, S-J L. Kang

Effect of solute segregation

Solute/Impurity drag

Qn: Drag force of the segregated solutes against the boundary migration?

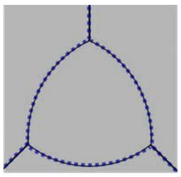
Qn: The difference btw the Smith-Zener drag and the solute drag?

Derivation of the drag force

(i) calculation of C(x) from eq.

$$D\frac{\partial C}{\partial x} + \frac{DC}{kT}\frac{\partial E}{\partial x} + v_b(C - C_\infty) = 0$$

(ii) calculation of the net drag force

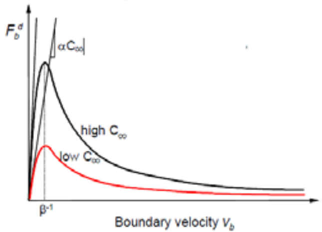


$$F_b^d = -\int_{-\infty}^{\infty} n(x)\frac{\mathrm{d}E}{\mathrm{d}x}\mathrm{d}x$$

$$= -N_v\int_{-\infty}^{\infty} [C(x) - C(\infty)]\frac{\mathrm{d}E}{\mathrm{d}x}\mathrm{d}x$$

An approximated solution: $F_b^d = \dfrac{\alpha C_\infty v_b}{1 + \beta^2 v_b^2}$

α: the drag force per unit concentration of solute and
per unit velocity of moving boundary when $\beta^2 v_b^2 << 1$.
β: the time required for solute atoms to diffuse
one unit distance. (the inverse of the drift velocity)

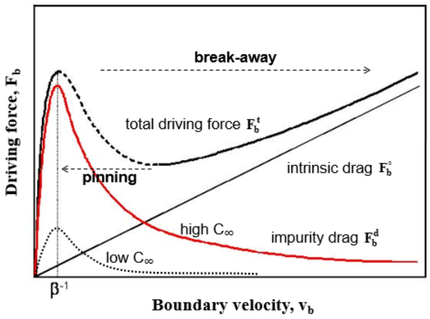


KAIST, S-J L. Kang

Effect of solute segregation

Boundary migration

$$F_b^t = F_b^o + F_b^d = \frac{v_b}{M_b^o} + \frac{\alpha C_\infty v_b}{1+\beta^2 v_b^2} = v_b\left(\frac{1}{M_b^o} + \frac{\alpha C_\infty}{1+\beta^2 v_b^2}\right)$$



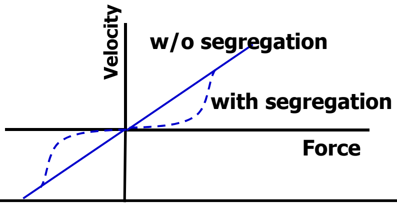
Two extreme cases

$v_b \ll \beta^{-1}$

$$v_b = \frac{F_b^t}{(1/M_b^o) + \alpha C_\infty} \approx \frac{1}{\alpha C_\infty} F_b^t$$

$v_b \gg \beta^{-1}$

$$v_b \approx M_b^o F_b^t$$



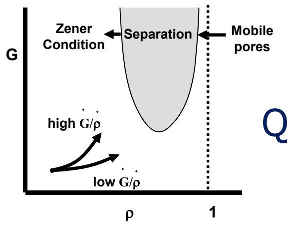
Qn: Boundary mobility in McLean model?

Drag = *f*(segregation, diffusivity)

KAIST, S-J L. Kang

Microstructure Development

in porous materials

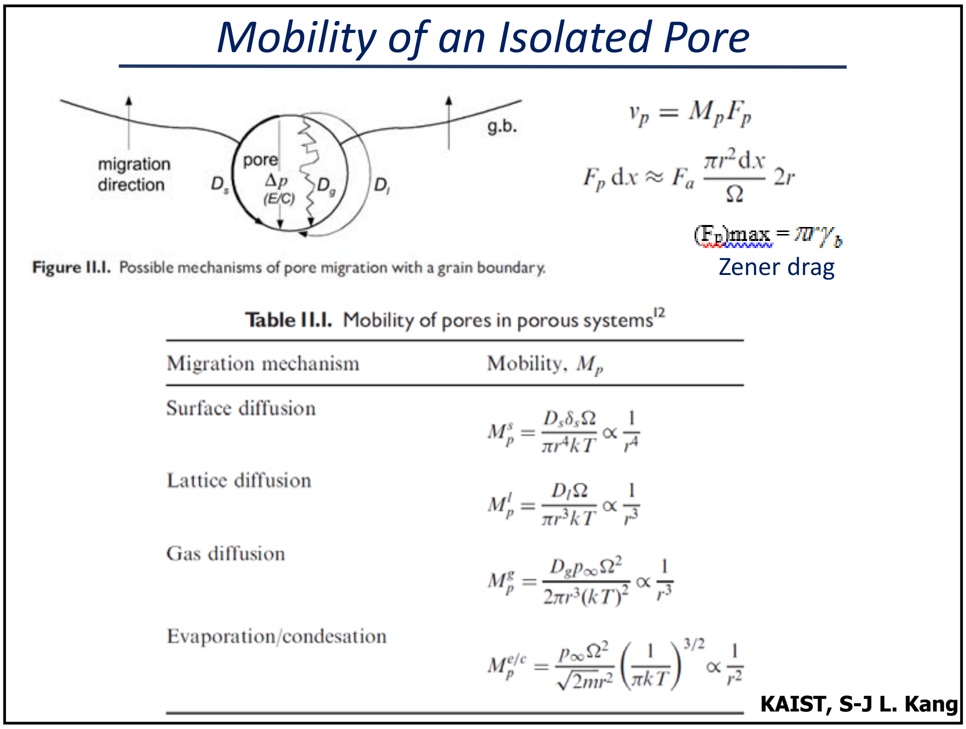


Qn: What are the potential parameters that affect the trajectory of microstructural evolution?

A few points of consideration:

- Densification is governed by driving force (pore size) and densification mechanism.
  Pore size varies with grain size.
- Grain growth is affected by grain size (driving force) and boundary migration mechanism.
  Boundary control vs. Pore control (pore migration mechanisms)
- Location of pores
  4-grain corner, 3-grain edge, 2-grain boundary

KAIST, S-J L. Kang



Mobility of an Isolated Pore

Figure II.I. Possible mechanisms of pore migration with a grain boundary.

$$v_p = M_p F_p$$

$$F_p\,\mathrm{d}x \approx F_a \frac{\pi r^2 \mathrm{d}x}{\Omega} 2r$$

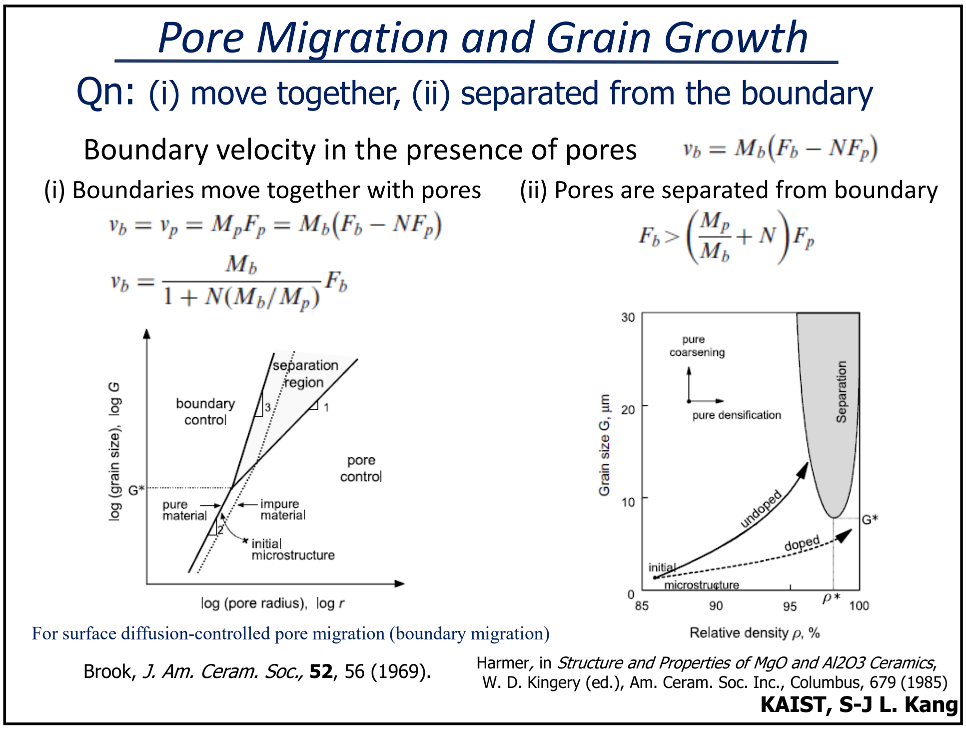
$$(F_p)\mathrm{max} = \pi r \gamma_b$$

Zener drag

Table II.I. Mobility of pores in porous systems[12]

Migration mechanism	Mobility, M_p
Surface diffusion	$M_p^s = \frac{D_s \delta_s \Omega}{\pi r^4 kT} \propto \frac{1}{r^4}$
Lattice diffusion	$M_p^l = \frac{D_l \Omega}{\pi r^3 kT} \propto \frac{1}{r^3}$
Gas diffusion	$M_p^g = \frac{D_g p_\infty \Omega^2}{2\pi r^3 (kT)^2} \propto \frac{1}{r^3}$
Evaporation/condesation	$M_p^{e/c} = \frac{p_\infty \Omega^2}{\sqrt{2m r^2}} \left(\frac{1}{\pi kT}\right)^{3/2} \propto \frac{1}{r^2}$

KAIST, S-J L. Kang



Pore Migration and Grain Growth

Qn: (i) move together, (ii) separated from the boundary

Boundary velocity in the presence of pores $v_b = M_b(F_b - NF_p)$

(i) Boundaries move together with pores

$$v_b = v_p = M_p F_p = M_b(F_b - NF_p)$$

$$v_b = \frac{M_b}{1 + N(M_b/M_p)} F_b$$

(ii) Pores are separated from boundary

$$F_b > \left(\frac{M_p}{M_b} + N\right) F_p$$

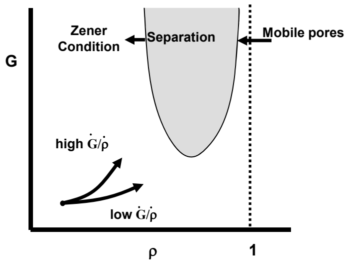
For surface diffusion-controlled pore migration (boundary migration)

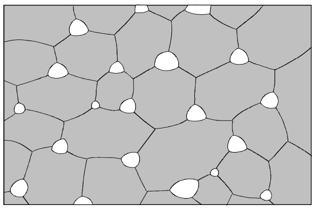
Brook, *J. Am. Ceram. Soc.*, **52**, 56 (1969).

Harmer, in *Structure and Properties of MgO and Al2O3 Ceramics*, W. D. Kingery (ed.), Am. Ceram. Soc. Inc., Columbus, 679 (1985)

KAIST, S-J L. Kang

Densification and Grain Growth: Microstructure Development





Densification rate:

$$\frac{1}{\rho}\frac{d\rho}{dt}=\frac{K_1(1-\rho)^k}{G^m\rho}$$

Grain Growth rate:

$$\frac{1}{G}\frac{dG}{dt}=\frac{K_2}{G^n(1-\rho)^l}$$

- $\frac{\mathrm{d}\rho}{\mathrm{d}G}=\left(\frac{K_1}{K_2}\right)G^{n-m-1}(1-\rho)^{k+l}$

Densification	*m*	*k*
D_l	3	1/3
D_b	4	0

Grain Growth	*n*	*l*
D_s	4	4/3
Gas Diff.	3	1
Evap./Cond.	2	2/3
$D_b^{\perp}$	2	0

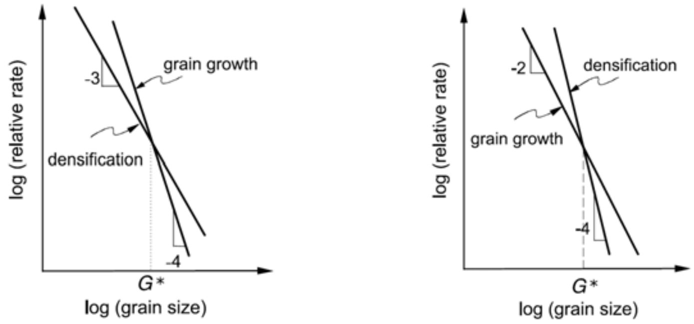
KAIST, S-J L. Kang

Effect of Grain (Particle) Size

Examples

Densification : lattice diffusion
Grain Growth : surface diffusion

Densification : grain boundary diffusion
Grain Growth : evaporation/condensation

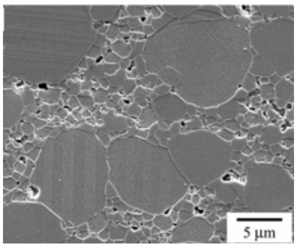


Relative densification and coarsening rates vs. grain size.

KAIST, S-J L. Kang

Abnormal (Exaggerated) **GG**

An extreme type of Grain Growth



0.1 mol% TiO_2-excess $BaTiO_3$ at 1250 °C for 50 h

Bimodal size distribution of grains
- the result of fast growth of a few (some) grains and essentially no growth of matrix grains

Observation of AGG in many different systems
(i) highly pure systems
(ii) highly impure systems
(iii) systems with second phase particles
(iv) systems with a liquid matrix

Phenomenological Description of AGG

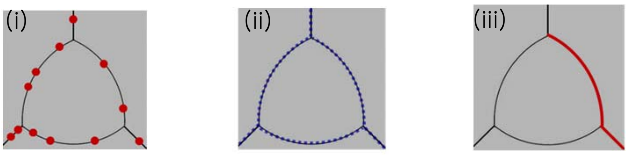
$$\frac{\mathrm{d}G_a}{\mathrm{d}t} = \frac{D_b^{\perp}}{RT}\frac{2\gamma_b}{\beta\overline{G}_m}\frac{V_m}{\omega} \qquad \overline{G}_{a,t} - \overline{G}_{a,t_o} = \frac{2D_b^{\perp}\gamma_b V_m}{\beta RT\overline{G}_m\omega}t$$

Consider the growth of a single crystal into a polycrystal in a single/poly bilayer sample!

KAIST, S-J L. Kang

Suggested Mechanisms of AGG

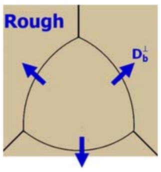
Early Mechanisms



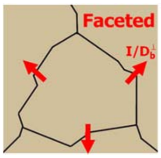
(i) Break-away of grain boundary from second phase particles (since 1950's)
(ii) Break-away of grain boundary from segregated impurities (since 1960's)
(iii) Uneven distribution of a second phase, in particular, a liquid (since 1970's)
"Complexion" hypothesis (since 2000's)
(iv) Anisotropy in boundary mobility and boundary energy (simulation studies)

Recent Mechanism

(v) Change in boundary migration mechanism with respect to the driving force



Kang *et al., J. Am. Ceram. Soc.*, **92**, 1464 (2009).



Kang *et al., J. Am. Ceram. Soc*, **98**, 347 (2015).

KAIST, S-J L. Kang

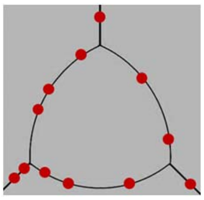
Early Mechanisms of AGG

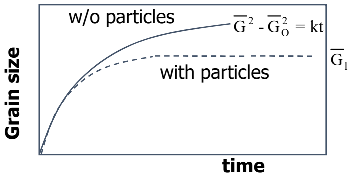
The second phase particle(or pore) drag mechanism

- ***Limit of grain growth*** (Smith-Zener drag)

  Smith CS. AIME 1949;175:15. Manohar PA, Ferry M, Chandra T. ISIJ Inter 1998;38:913.

2^{nd} phase particles





- **Onset of AGG :** particle (pore)/bo

  Brook RJ. J Am Ceram Soc 1969;52:56.
  Rios PR. Acta Mater 1997;45:1785.

  * Uneven distribution of particles or pore
  (local reduction or increase in pinning f

- Valid only for two-phase systems with second phase particles or pores.
- AGG is observed only in some specific systems.
- AGG takes place also in highly porous materials with uniform pore distribution. (eg. $BaTiO_3$)

KAIST, S-J L. Kang

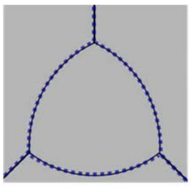
Early Mechanisms of AGG

The solute drag mechanism

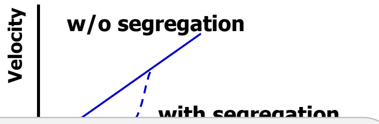
- ***Grain Boundary Migration***

  Cahn JW. Acta Metal 1962;10:789.
  Lűcke K. And Stűwe HP. On the theory of grain boundary modion, in Recovery and Recrystallization of Metal, L. Himmel (ed.) Gordon and Breach, New York, 171-210, 1962

Segregation



Impurity Segregation and Boundary Migration



- AGG is observed only in some specific systems.
- Not possible to explain SGG.
- Not possible to explain the increased tendency of AGG with decreasing particle size.
- Not possible to explain the variation of observed grain growth behavior with respect to the solute concentration in perovskite systems.

- ***Deviation from Normal Beh***

  Abbruzzese G, Buccioni M. Mater Sci Forur
  Kim SG, Park YB. Acta Mater 2008;56:3739.

KAIST, S-J L. Kang

Early Mechanisms of AGG

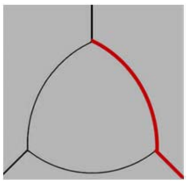
The liquid film enhancement mechanism

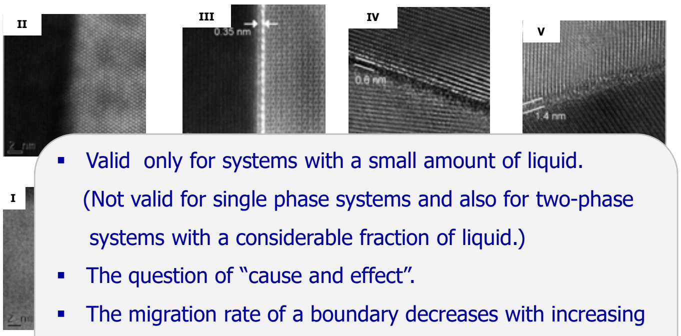
(Highlighted as an introduction of several complexions)

- ***Non-Uniform Distribution of Liquid***

Hennings DFK, Janssen R, Reynen PJL. J Amer Ceram Soc 1987;70:23.
Hibbard GD et al., Scripta Mater 2002;47:83.
Dillon SJ, Tang M, Carter WC, Harmer MP. Acta Mater 2007;55:6208. **(complexion)**

Liquid Phase





- Valid only for systems with a small amount of liquid.
  (Not valid for single phase systems and also for two-phase systems with a considerable fraction of liquid.)
- The question of "cause and effect".
- The migration rate of a boundary decreases with increasing solute segregation and liquid film formation

KAIST, S-J L. Kang

Early Mechanisms of AGG

Effect of anisotropy in γ_b and M_b

$$\nu_b = \mathrm{M}_b \cdot \gamma_b \mathrm{K}$$

Rollett AD et al., Acta Metall., 1989;37:1127
Hwang NM, J. Mater. Sci., 1998;33:5625

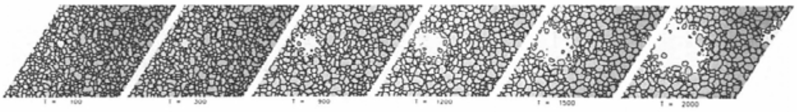
$$\mathrm{M}_b, \gamma_b = \text{const. : NGG}$$

Anderson MP et al., Acta Metall., 1983;32:1127

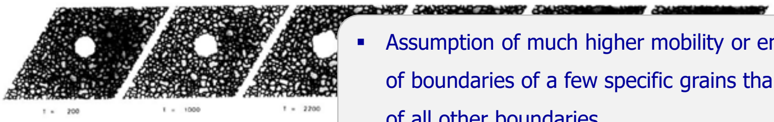
$$\mathrm{M}_b, \gamma_b \neq \text{const. : Formation of AGs}$$

D. K. Lee et al., Scripta Mater., 2008;58:683
Grest GS et al., Acta Metall., 1985;33:509

MC Simulation in a system with GB energy anisotropy (10 times)



MC Simulation in a system with GB mobility anisotropy (7.5 times)

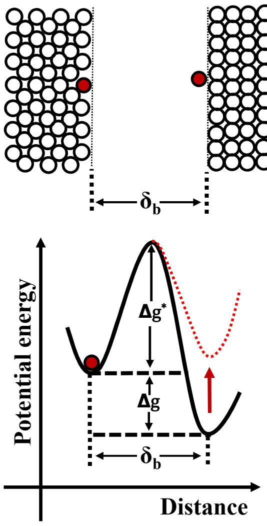


- Assumption of much higher mobility or energy of boundaries of a few specific grains than that of all other boundaries.

KAIST, S-J L. Kang

Common Feature
in the Previous Models and Mechanisms

Diffusion-Controlled Boundary Migration



$$v_b = \frac{D_b{}^{\perp}}{RT}\cdot \nabla g \propto exp\left(-\frac{\Delta g*}{RT}\right)\cdot \Delta g$$

(i) Particle (pore) drag : Reduction of Δg

(ii) Impurity drag : Reduction of Δg

(iii) Liquid Film : Change in Δg^* and δ_b

(iv) Anisotropy of γ_b and M_b :
Change in Δg and Δg^*

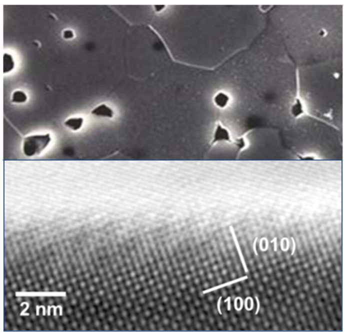
Possibility of Interface Reaction-Controlled Boundary Migration ?

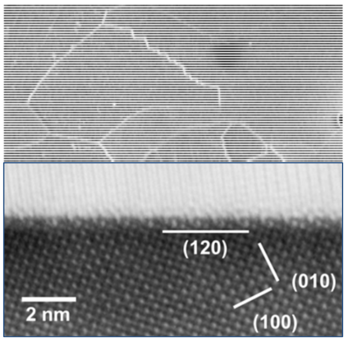
Kang *et al., J. Am. Ceram. Soc.,* **98** 347 (2015).

KAIST, S-J L. Kang

Two Types of Grain Boundaries

Rough (atomically disordered) **Faceted (atomically ordered)**





Ti-excess $BaTiO_3$ **in H_2** **in air**

Variables: *T, dopant, Po_2*

Choi and Kang, *Acta. Mater.* **52**, 2973 (2004).
S.-J. L. Kang, Chap.6, "Sintering" in *Ceramic Science and Technology*
(Ed : R. Riedel and I.-W. Chen) Wiley-VCH, 143-69 (2012).

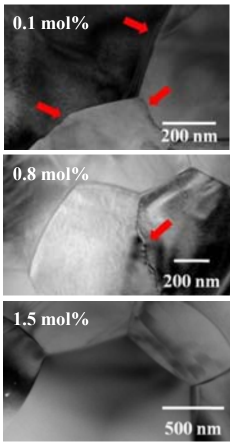
KAIST, S-J L. Kang

Structural Transition of Grain Boundary

- Effect of Dopant -

Change in Δg_c (Dopant)

GB structure in Nb-doped $BaTiO_3$ in air



Low C

High Δg_c
(Faceted GB)

Low Δg_c
(Rough GB)

High C

Degree of faceting with Nb_2O_5 doping

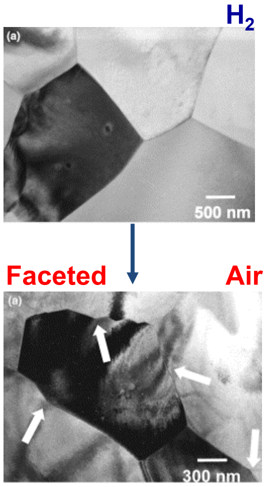
Nd_2O_5 concentration	Fraction of faceted boundaries
0.1 mol%	96 %
0.8 mol%	52 %
1.5 mol%	32 %

An and Kang, *Acta mater.*, **59** 1964 (2011).

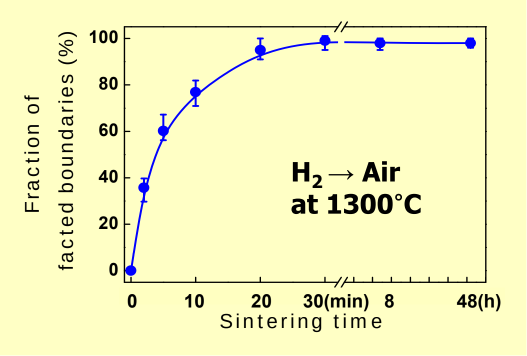
KAIST, S-J L. Kang

Grain Boundary Structural Transition

$BaTiO_3$



Boundary Structural Transition during Sintering

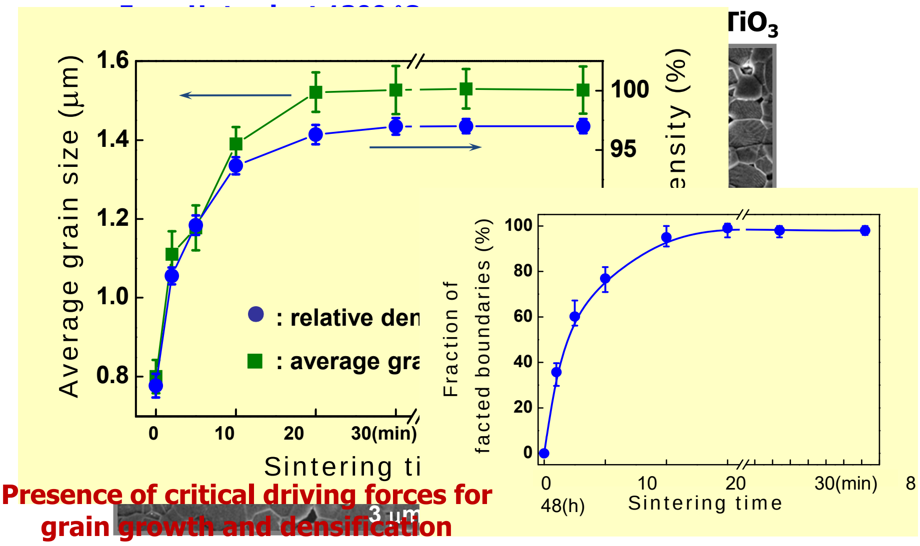


Choi and Kang, *Acta Mater.,* **52**, 2973 (2004).

KAIST, S-J L. Kang

Effect of Boundary Structure on Densification and Grain Growth

TiO$_3$



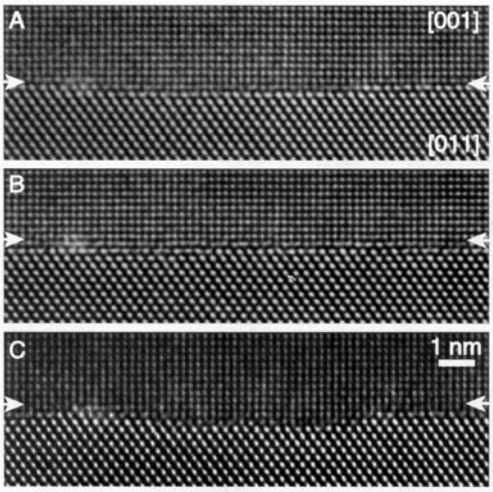
Presence of critical driving forces for grain growth and densification

Choi and Kang, *Acta Mater.* **52**, 2973 (2004).

KAIST, S-J L. Kang

Migration Mechanism of Faceted Boundary

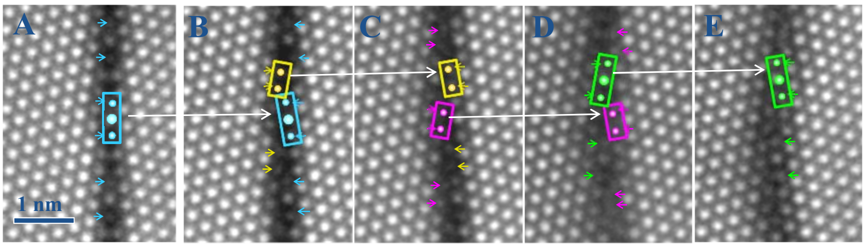
Migration of a Singular GB in Au by the Step Growth Mechanism

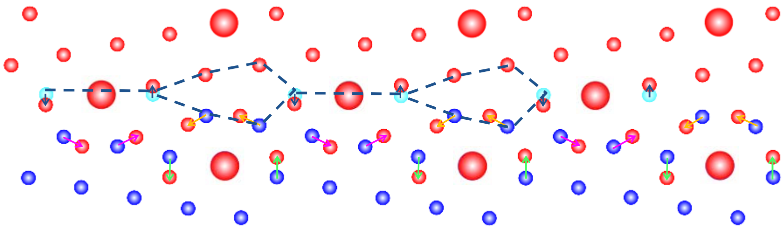


K.L. Merkle and L.J. Thompson, *Mater. Lett.*, **48**, 188 (2001).

KAIST, S-J L. Kang

Migration Mechanism of ∑7 α-Al_2O_3 *Boundary*



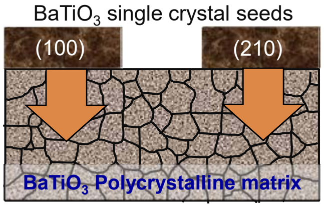


Local Atoms Shuffling: *movement of atoms from ledges to the ledges of the growing crystal*

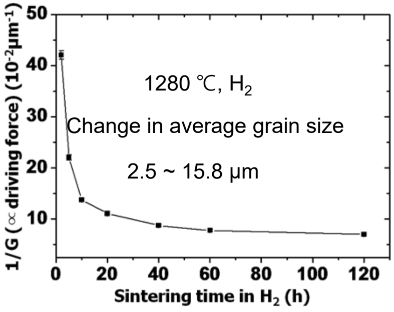
J. Wei, et al., *Nature Materials*, 20, 951, July 2021.

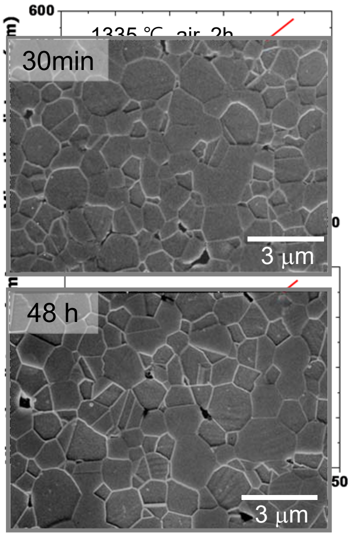
KAIST, S-J L. Kang

Migration Behavior of Faceted Boundary



$$\Delta g \propto \left(\frac{1}{\bar{G}} - \frac{1}{G_{SC}}\right)$$

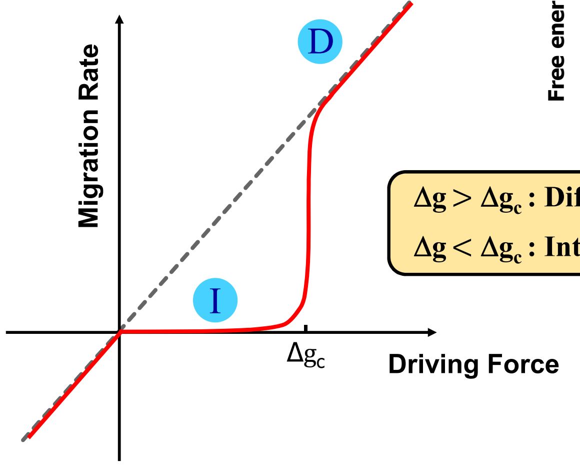


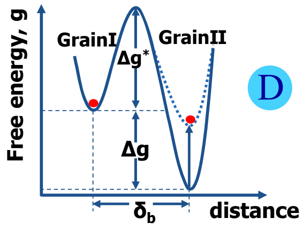


An *et al., Acta Mater.* **60**, 4531 (2012) .

KAIST, S-J L. Kang

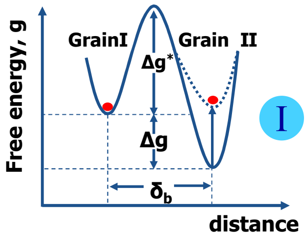
Mixed Control of Boundary Migration





$\Delta g > \Delta g_c$: **Diffusion Control**

$\Delta g < \Delta g_c$: **Interface Reaction Control**



Kang *et al.*, *J. Am. Ceram. Soc.*, **92**, 1464 (2009),
Kang *et al.*, *J. Am. Ceram. Soc.*, **98**, 347 (2015),
Kang *et al.*, *J. Ceram. Soc. Jpn.*, 124, 259 (2016).

KAIST, S-J L. Kang

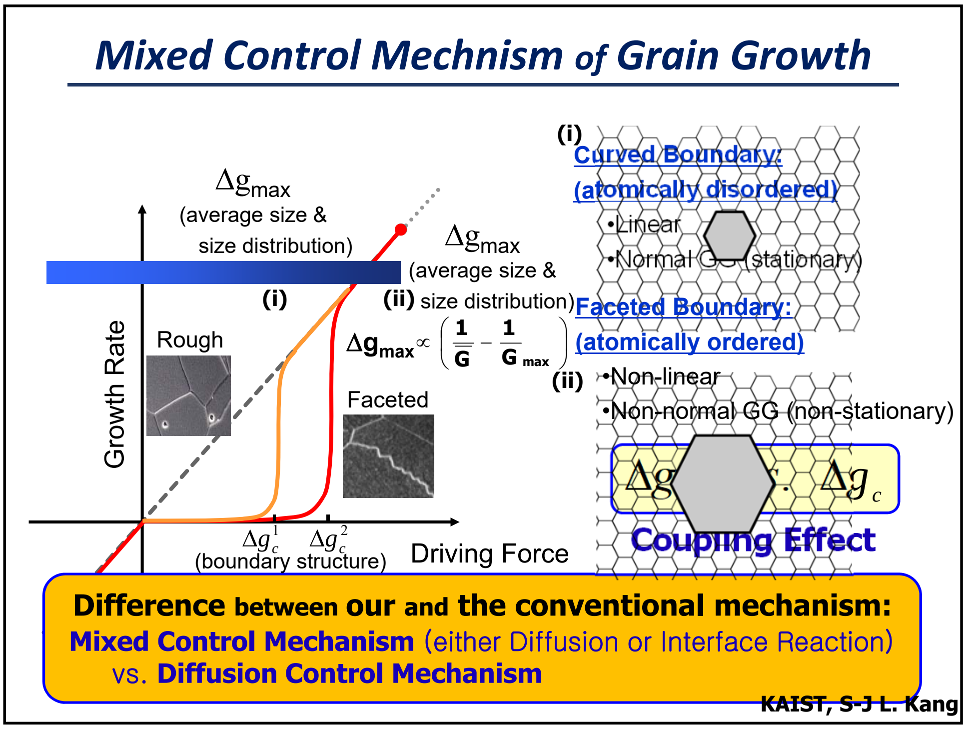
Summary of Recent Findings

- **Migration mechanism of grain boundary**

  is **not** dependent on
  the presence of a liquid (film),
  the presence of solutes, or
  the presence of a 2nd phase (particles)
  at the boundary

  but dependent on
  the morphology (atomic structure) of
  the grain boundary:
  Diffusion control for rough boundary
  Mixed control (diffusion or interface reaction)
  for faceted boundary

KAIST, S-J L. Kang



Mixed Control Mechnism of Grain Growth

(i) **Curved Boundary: (atomically disordered)**

- Linear
- Normal GG (stationary)

Faceted Boundary: (atomically ordered)

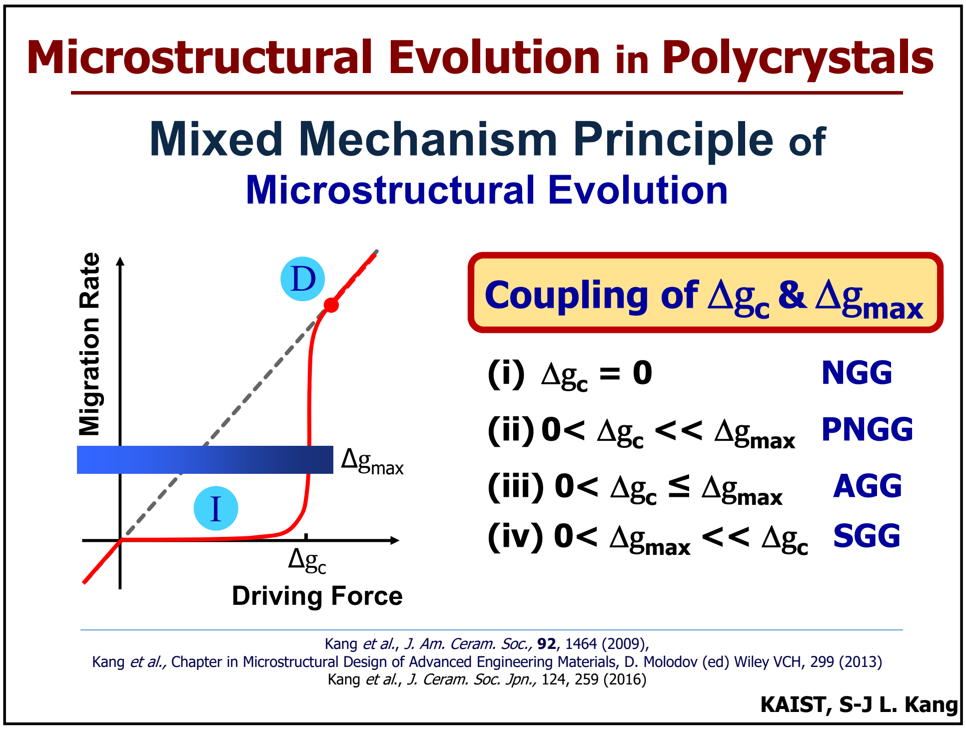
(ii)
- Non-linear
- Non-normal GG (non-stationary)

Δg … s. Δg_c

Coupling Effect

Difference between our and the conventional mechanism:
Mixed Control Mechanism (either Diffusion or Interface Reaction)
vs. **Diffusion Control Mechanism**

KAIST, S-J L. Kang



Microstructural Evolution in Polycrystals

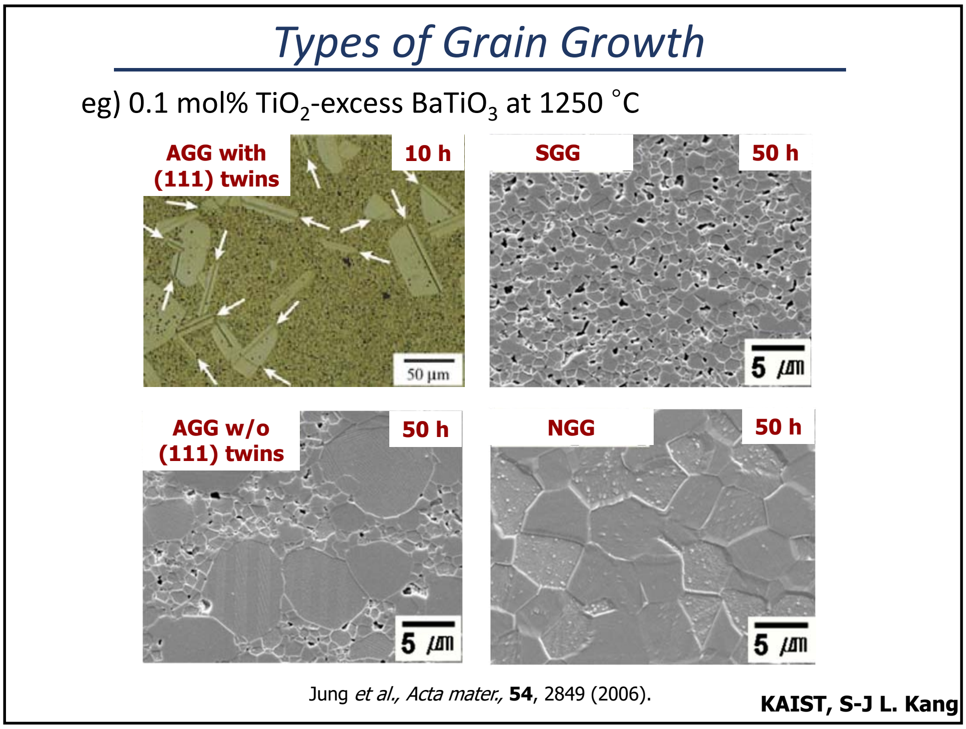
Mixed Mechanism Principle of Microstructural Evolution

Coupling of Δg_c & Δg_{max}

(i) $\Delta g_c = 0$	NGG
(ii) $0 < \Delta g_c << \Delta g_{max}$	PNGG
(iii) $0 < \Delta g_c \leq \Delta g_{max}$	AGG
(iv) $0 < \Delta g_{max} << \Delta g_c$	SGG

Kang *et al., J. Am. Ceram. Soc.,* **92**, 1464 (2009),
Kang *et al.,* Chapter in Microstructural Design of Advanced Engineering Materials, D. Molodov (ed) Wiley VCH, 299 (2013)
Kang *et al.*, *J. Ceram. Soc. Jpn.,* 124, 259 (2016)

KAIST, S-J L. Kang

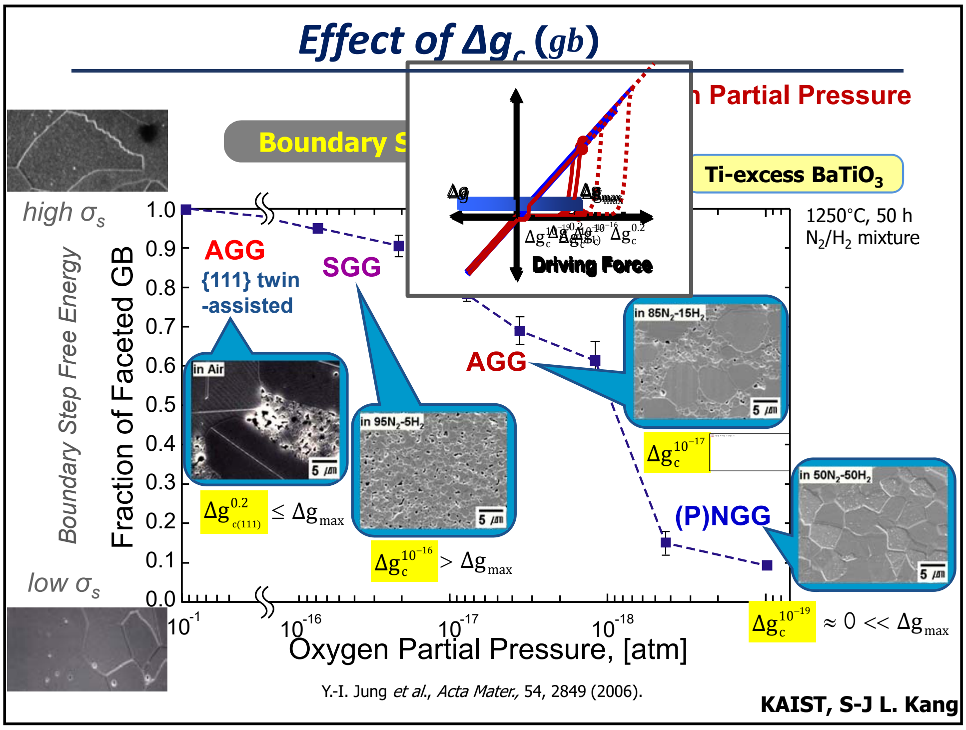


Types of Grain Growth

eg) 0.1 mol% TiO_2-excess $BaTiO_3$ at 1250 °C

Jung *et al., Acta mater.,* **54**, 2849 (2006).

KAIST, S-J L. Kang



Effect of Δg_c (*gb*)

n Partial Pressure

Boundary S

Ti-excess $BaTiO_3$

1250°C, 50 h
N_2/H_2 mixture

$\Delta g_{c(111)}^{0.2} \leq \Delta g_{max}$

$\Delta g_c^{10^{-16}} > \Delta g_{max}$

$\Delta g_c^{10^{-17}}$

$\Delta g_c^{10^{-19}} \approx 0 << \Delta g_{max}$

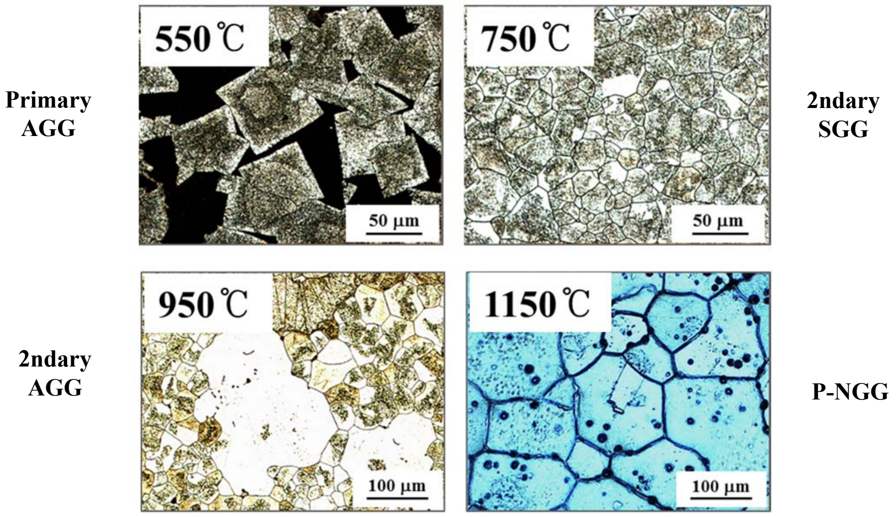
Y.-I. Jung *et al., Acta Mater.,* 54, 2849 (2006).

KAIST, S-J L. Kang

Microstructural Observation during SSS

Effect of Temperature

UFG Ni sintered for 1 h at various temperatures



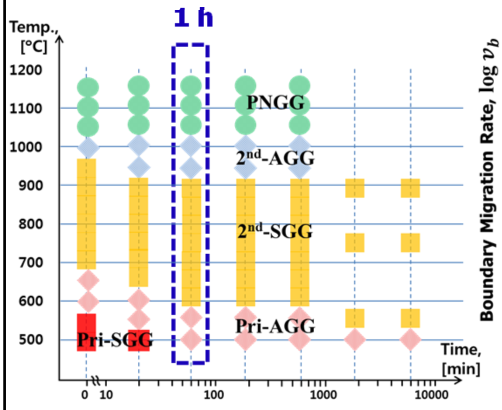
S. H. Jung et al., *Acta Mater.*, **69,** 283 (2014)

KAIST, S-J L. Kang

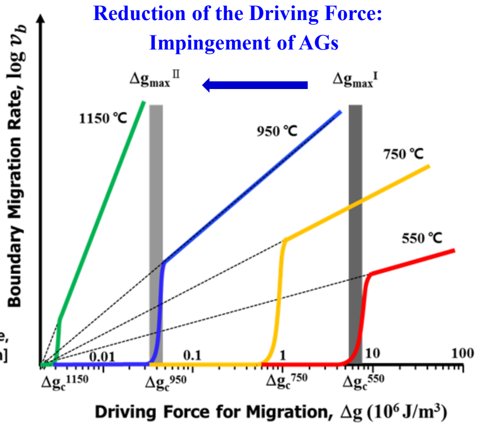
Microstructural Observation during SSS

Effect of Temperature

Grain Growth Behavior in UFG Ni with T



Sintered for 1 h at each temperature



S. H. Jung et al., *Acta Mater.*, **69,** 283 (2014)

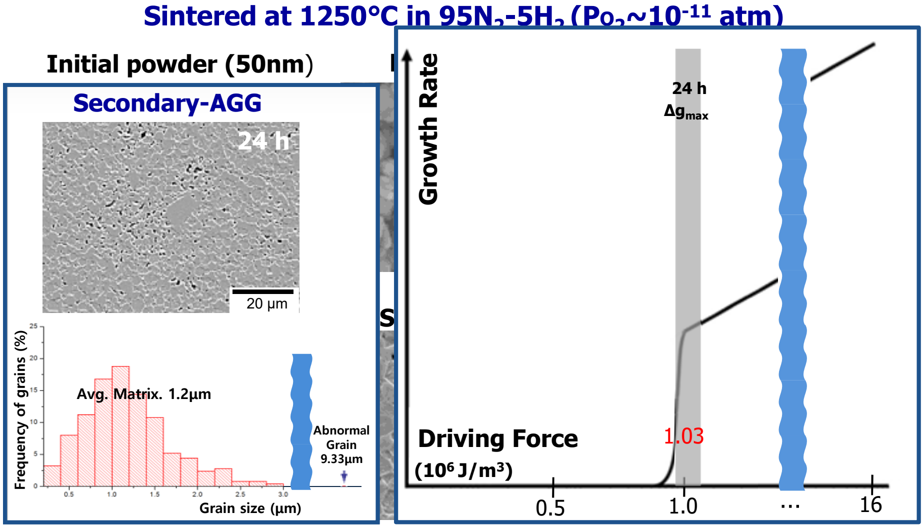
KAIST, S-J L. Kang

Microstructural Observation during SSS

Effect of Sintering Time

Grain Growth Behavior in $BaTiO_3$ (50nm)

Sintered at 1250°C in $95N_2$-$5H_2$ (P_{O_2}~10^{-11} atm)



KAIST, S-J L. Kang

Experimental Supports for the Principle

Experimental Observations and Interpretations
(Single Phase Systems)

- **Effect of Δg_c (T, Dopant, P_{O_2})**
  - $BaTiO_3$ (Lee *et al.,* 2000(P_{O_2}); Jung *et al.,* 2006 (P_{O_2}); Chang and Kang, 2009 (T), An and Kang, 2011 (Dopant, P_{O_2}); Moon, 2018 (t, P_{O_2}))
  - $SrTiO_3$ (Chung *et al.,* 2002 (Dopant, P_{O_2}))
  - Nickel (**Jung *et al.,* 2013, 2014 (T, P_{O_2})**)
  - $Na_{1/2}Ba_{1/2}TiO_3$-$BaTiO_3$-$K_{1/2}Na_{1/2}NbO_3$ (Park *et al.,* 2016 (Dopant))
  - $Na_{1/2}Ba_{1/2}TiO_3$-$BaTiO_3$ (Ko *et al.,* 2016 (T))
  - Nickel (Lee *et al.,* 2000 (T))
  - Cu (Koo and Yoon, 2001)
  - 316L stainless steel (Lee *et al.,* 2001)
  - Alumina (Park *et al.,* 2003, 2004 (Dopant))

- **Effect of Δg_{max}**
  - **$BaTiO_3$ (Jung *et al.,* 2003**; Yang *et al.,* 2006)

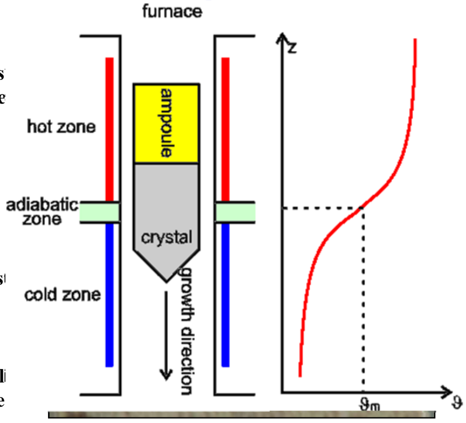
KAIST, S-J L. Kang

Application Example of the Principle

Solid-state Conversion of single crystals (A Noble Method of Single Crystal Fabrication)

Conventional Methods of Single Crystal Fabrication

Czockralski Method

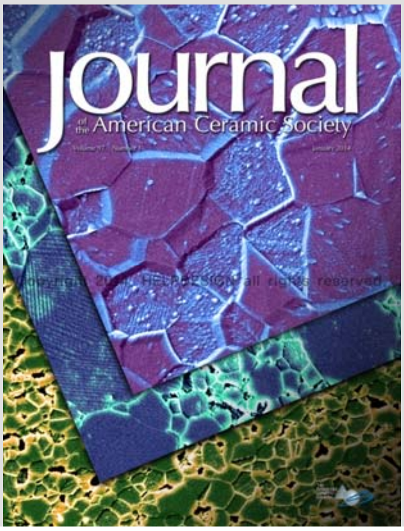


Bridgman Method

Kang *et al., J. Am. Ceram. Soc.,* **98** 347 (2015). (*Feature article*)

KAIST, S-J L. Kang

Application Example of the Principle



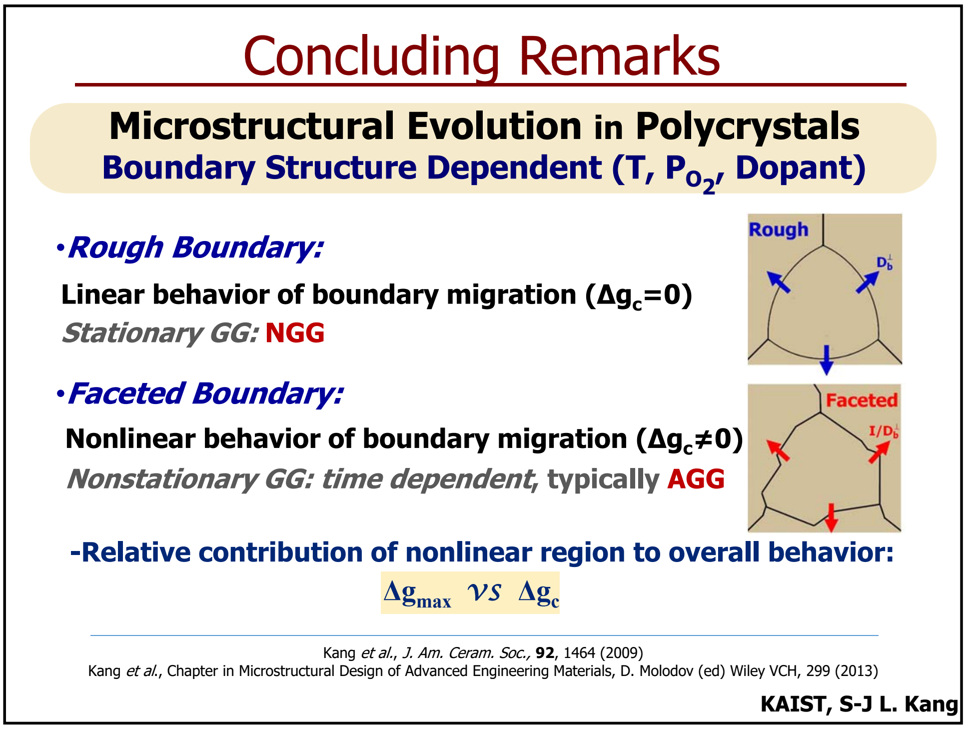
journal

Solid-State Conversion of Single Crystals: The Principle and the State-of-the-Art

Feature

Kang *et al., J. Am. Ceram. Soc.,* **98** 347 (2015).

KAIST, S-J L. Kang



Concluding Remarks

Microstructural Evolution in Polycrystals
Boundary Structure Dependent (T, P_{O_2}, Dopant)

- ***Rough Boundary:***

Linear behavior of boundary migration ($\Delta g_c=0$)
Stationary GG: **NGG**

- ***Faceted Boundary:***

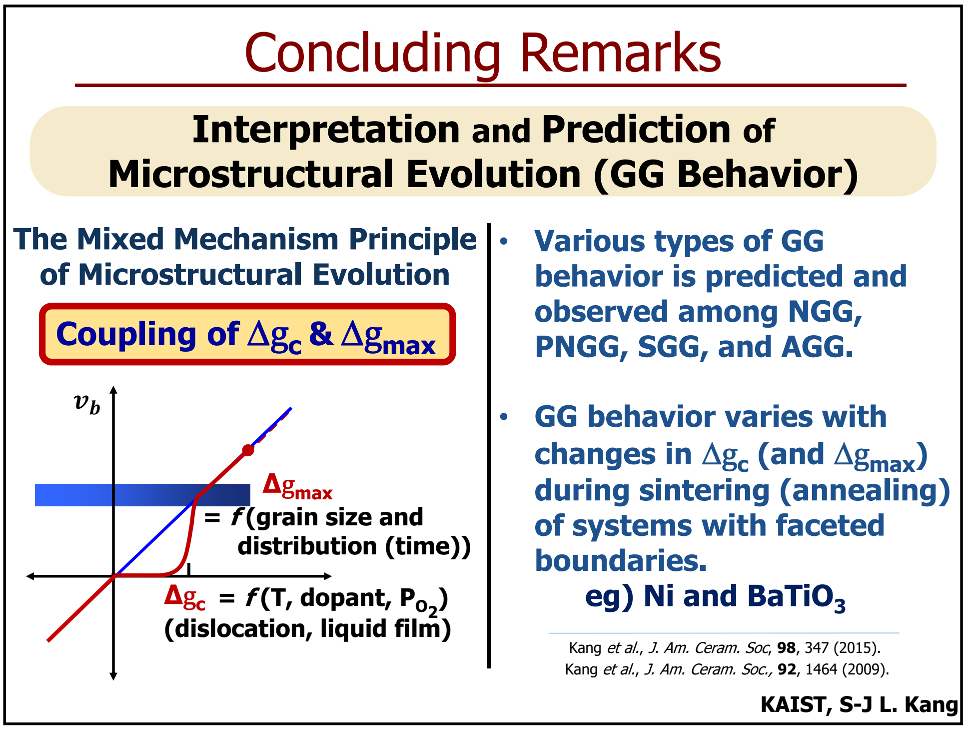
Nonlinear behavior of boundary migration ($\Delta g_c\neq0$)
Nonstationary GG: time dependent, **typically AGG**

-Relative contribution of nonlinear region to overall behavior:

Δg_{max} *vs* Δg_c

Kang *et al.*, *J. Am. Ceram. Soc.,* **92**, 1464 (2009)
Kang *et al.*, Chapter in Microstructural Design of Advanced Engineering Materials, D. Molodov (ed) Wiley VCH, 299 (2013)

KAIST, S-J L. Kang



Concluding Remarks

Interpretation and Prediction of
Microstructural Evolution (GG Behavior)

The Mixed Mechanism Principle of Microstructural Evolution

Coupling of Δg_c & Δg_{max}

Δg_{max} = *f*(grain size and distribution (time))

Δg_c = *f*(T, dopant, P_{O_2})
(dislocation, liquid film)

- **Various types of GG behavior is predicted and observed among NGG, PNGG, SGG, and AGG.**
- **GG behavior varies with changes in Δg_c (and Δg_{max}) during sintering (annealing) of systems with faceted boundaries.**

eg) Ni and $BaTiO_3$

Kang *et al.*, *J. Am. Ceram. Soc*, **98**, 347 (2015).
Kang *et al.*, *J. Am. Ceram. Soc.*, **92**, 1464 (2009).

KAIST, S-J L. Kang

Summary of GG Studies

Liquid Phase Sintering (Ostwald ripening)

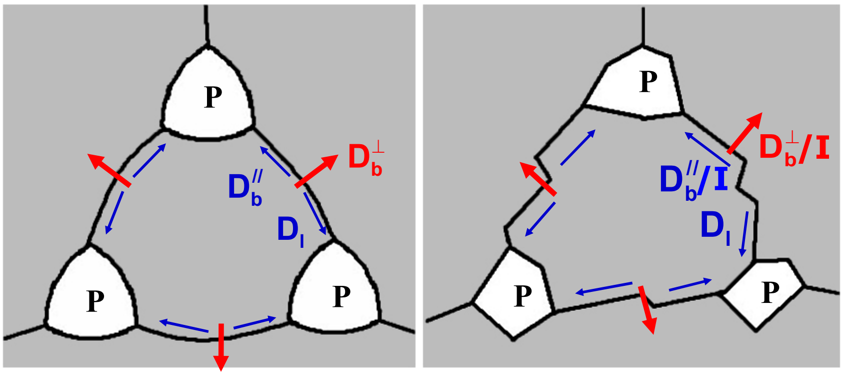
- LSW and modified LSW theories from the 60's to 90's for normal grain growth
- Essentially no fundamental studies on AGG until late 90's
- Development of the Mixed Mechanism Theory of grain growth and Mixed Mechanism Principle of microstructural evolution between late 90's and 2000's

Solid State Sintering

- Theoretical/experimental and simulation studies on GG for pure and impure systems as well as systems with 2nd phase particles and liquid films from the 50's to 2000's
- The early mechanisms fail to explain AGG observed in many different systems.
- The Mixed Control Mechanism of boundary migration and the Mixed Mechanism Principle of microstructural evolution

KAIST, S-J L. Kang

Effect of Interface Structure on Densification



Rough(atomically disordered) **Faceted**(atomically ordered)

Variables : T, dopant, atmosphere(P_{O_2})

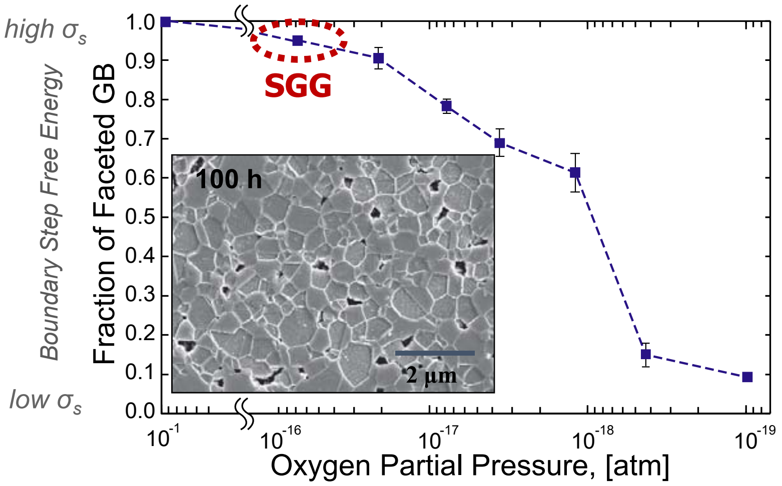
Rate(Δg) : Linear	Rate(Δg) : Non-linear
Diffusion Control	**Mixed Control** (Diffusion and Interface Reaction)

KAIST, S-J L. Kang

Fraction of Faceted Grain Boundary

Boundary Structural Change

Ti-excess $BaTiO_3$



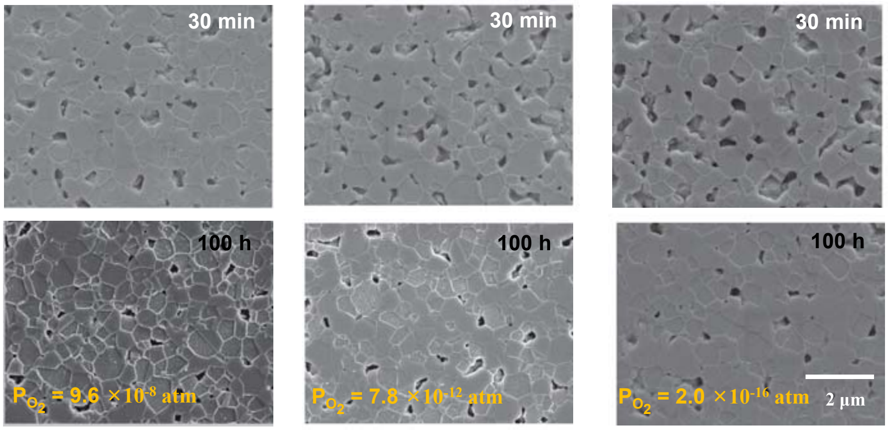
Y.-I. Jung *et al.*, *Acta Mater.*, 54, 2849 (2006).

KAIST, S-J L. Kang

Effect of Boundary Structure on Densification

5 mol% TiO_2-excess $BaTiO_3$

1250°C in H_2 for 30 min
↓
1290°C

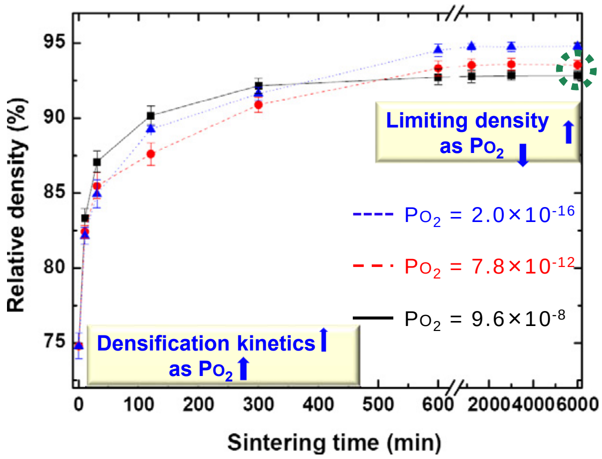


M.-G. Lee et al., *Acta Mater.*, **59**, 692 (2011).

KAIST, S-J L. Kang

Effect of Boundary Structure on Densification

5mol%-TiO_2-excess $BaTiO_3$ at 1290°C



Limiting density ↑ as Po_2 ↓

Densification kinetics ↑ as Po_2 ↑

(94.7 ± 0.2 %)
(93.5 ± 0.4 %)
(92.7 ± 0.4 %)

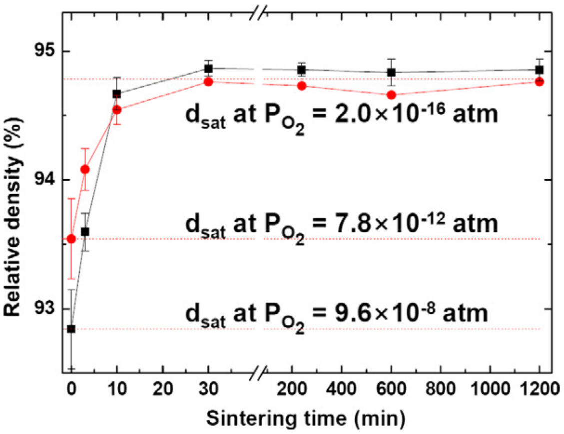
Presintering in H_2
Sintering at P_{O_2} = 10^{-7} – 10^{-16}

No grain growth during sintering

M.-G. Lee et al., *Acta Mater.*, **59**, 692 (2011).

KAIST, S-J L. Kang

Faceting-dependent Limit of Densification



Critical driving force for densification
= f (Degree of faceting)

M.-G. Lee et al., *Acta Mater.*, **59**, 692 (2011).

KAIST, S-J L. Kang

Exercises:

- Dissolution and growth shape of faceted grains
- System NbC-Co:
  - Grain shape at low temperature
  - Growth mechanism of faceted grains
  - Effect of f_l on grain growth behavior
- v_b vs. T for a polycrystal with high solute segregation
- AGG
  - Effects of particle size and temperature

KAIST, S-J L. Kang