PIII: GG and Microst. Evolution

Outline:

Types of grain growth: Stationary vs. Nonstationary

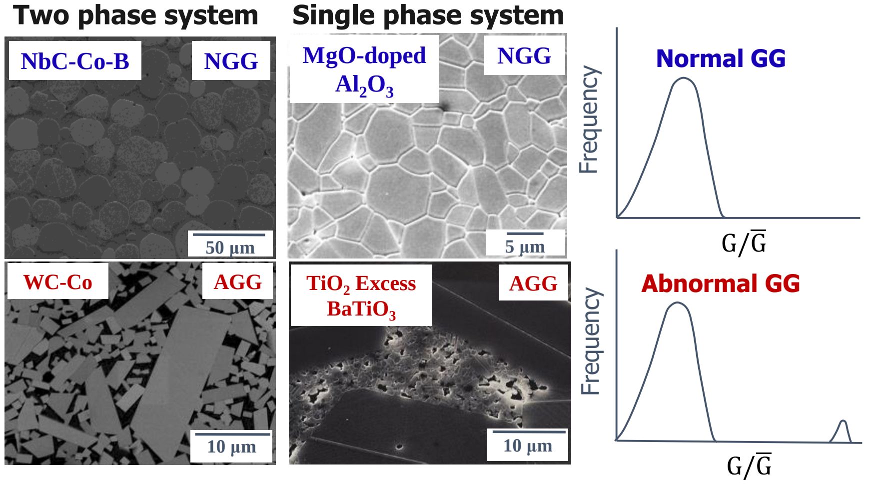
- Liquid phase sintering (LPS)
  - Grain growth in a matrix (Ostwald ripening)
  - Effect of pores on microstructure development
  - Effect of interfacial energy anisotropy
- Solid state sintering (SSS)
  - Grain growth in a pure dense system
  - Effect of 2^{nd} phase particles on grain growth
  - Effect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



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

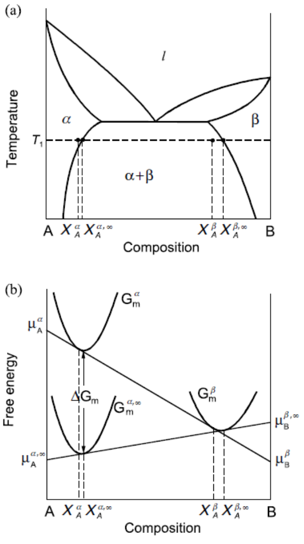
C. W. Park and D. Y. Yoon, *J. Am. Ceram. Soc.*, **83,** 2605 (2000).
D. Y. Yang and S.-J. L. Kang, *Int. J. Refract. H. Mater.*, **27**, 90 (2009)

KAIST, S-J L. Kang

Chap. Liquid Phase Sintering

Qn: Why grain growth takes place during sintering?

Driving Force



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

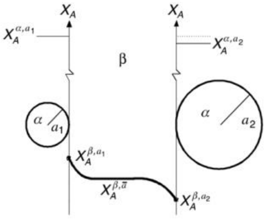


Figure 15.1. (a) Typical phase diagram showing limited solubility of $X_A^{\alpha,\infty}$ and $X_B^{\beta,\infty}$ at temperature T_l and (b) schematic of the molar free energy versus composition at the temperature for α precipitates with a flat interface ($K=0$) and with a finite radius of curvature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

KAIST, S-J L. Kang

Lifshitz-Slyozov-Wagner (LSW) Theory

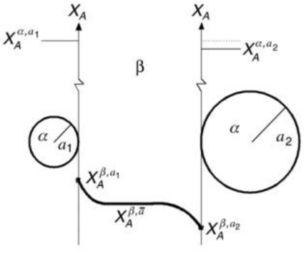
Basic Assumptions: (i) infinitely dispersed system (meaning?)
(ii) constant interface mobility (meaning?)

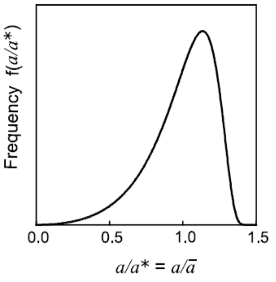
Diffusion-controlled GG (by LSW)

Interaction btw. average-sized grain and an individual grain

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

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





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?)

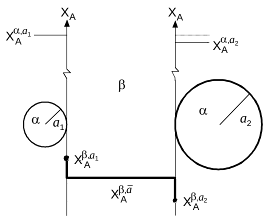
Interface Reaction-controlled GG (by Wagner)

Interaction btw. average-sized grain and an individual grain

$$\frac{da}{dt} = K(C_{\bar{a}} - C_a) = \frac{2K\gamma C_\infty V_m}{RT}\left(\frac{1}{\bar{a}} - \frac{1}{a}\right)$$

$$\bar{a}_t^2 - \bar{a}_o^2 = \frac{64}{81}\frac{K\gamma C_\infty V_m}{RT}t$$

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



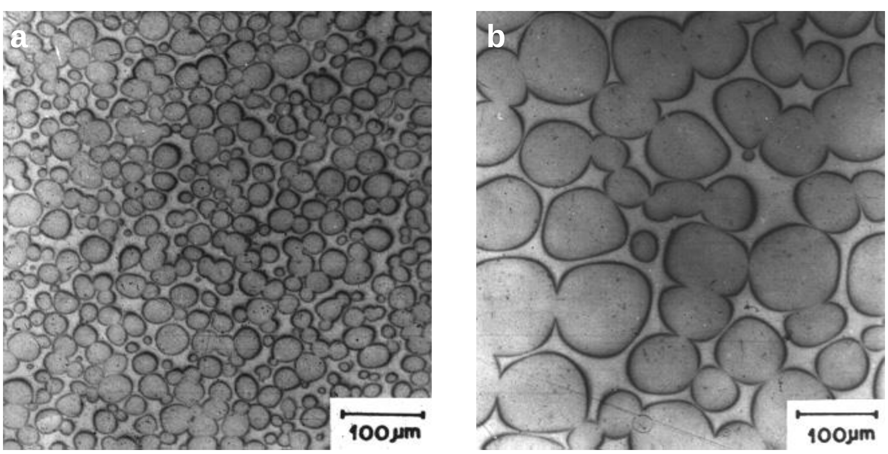
Physically Wrong!

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

KAIST, S-J L. Kang

Normal Grain Growth

Stationary Grain Growth

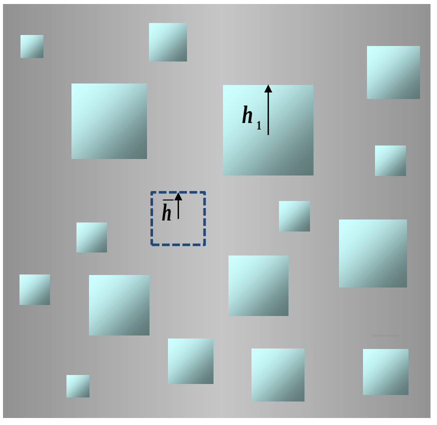


Microstructure of 70W-30Ni alloy annealed at 1540°C for (a) 30 min. and (b) 15 h.

KAIST, S-J L. Kang 6

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

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

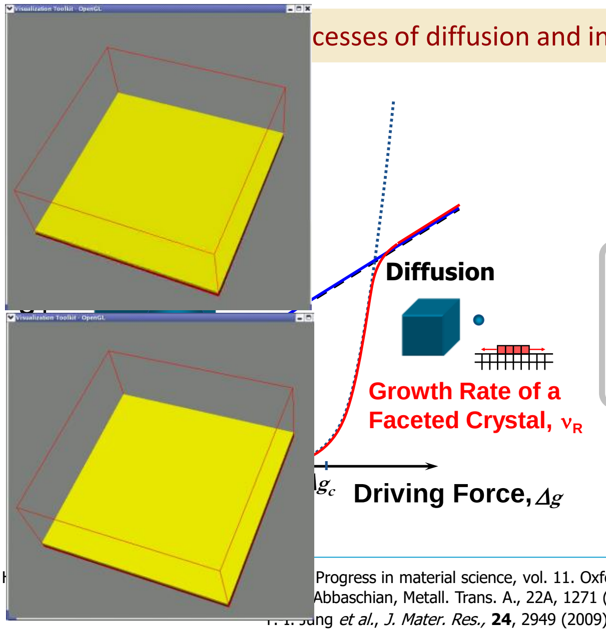
(Difference in Capillary Pressure)

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

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

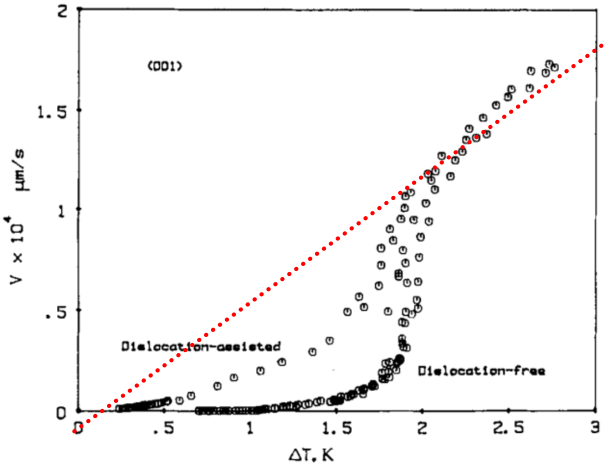
Progress in material science, vol. 11. Oxford, UK: Pergamon Press; 1963. p. 77.
Abbaschian, Metall. Trans. A., 22A, 1271 (1991).
...ung *et al.*, *J. Mater. Res.*, **24**, 2949 (2009).

KAIST, S-J L. Kang

Nonlinear Migration of Faceted Sol./Liq. Interface

Experimental Observation

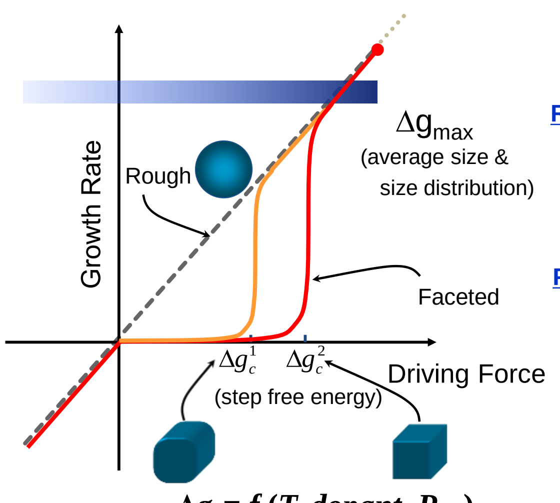
(001) Ga Single Crystal



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

KAIST, S-J L. Kang

Grain Growth and Dissolution in a Liquid Matrix



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

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

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

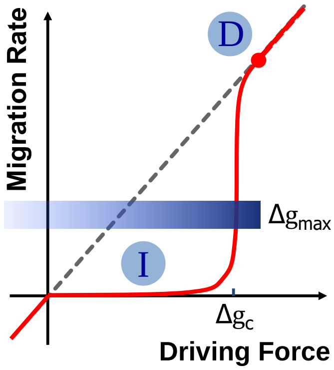
Δg_{max} *vs.* Δg_c

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}

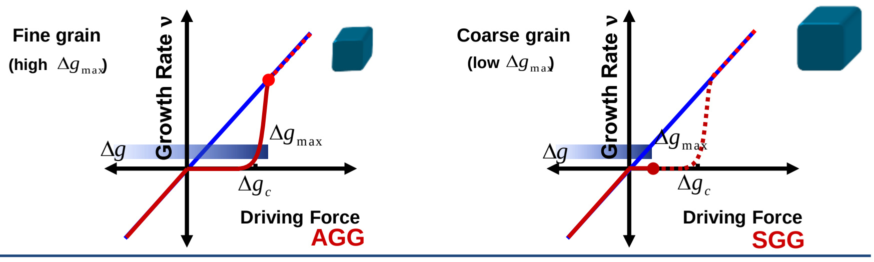
(i) $\Delta g_c = 0$	NGG
(ii) $0 < \Delta g_c << \Delta g_{max}$	PNGG
(iii) $0 < \Delta g_c \leq \Delta g_{max}$	AGG
(iv) $0 < \Delta g_{max} << \Delta g_c$	SGG

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)

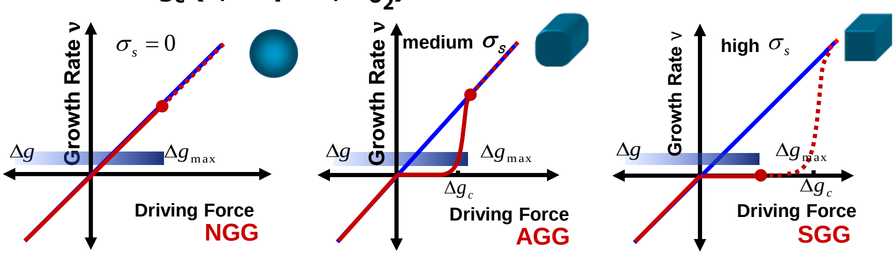
KAIST, S-J L. Kang

Thought Experiments

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



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

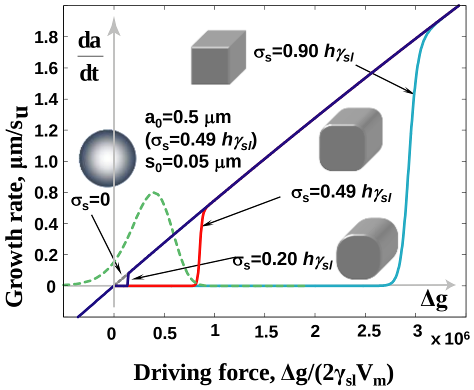


J. G. Fisher and S.-J. L. Kang, *J. Am. Ceram. Soc.*, **102**, 717 (2019)

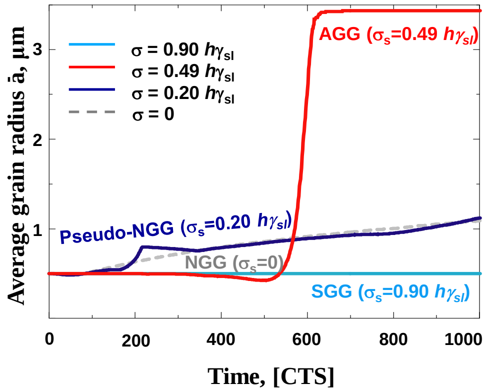
KAIST, S-J L. Kang

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).

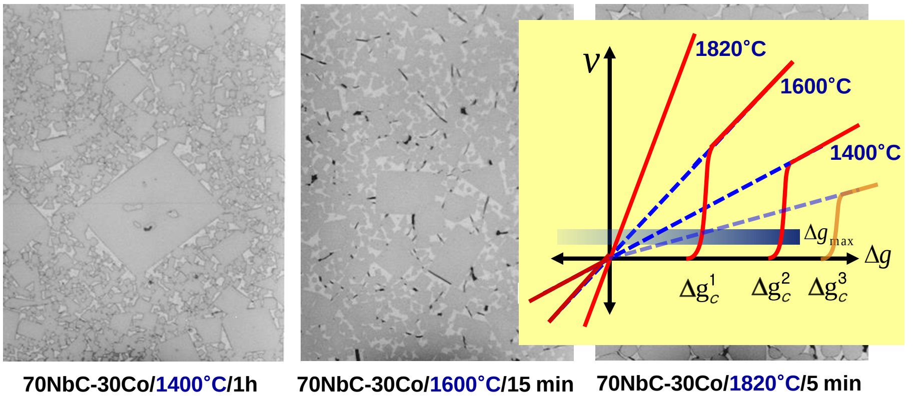
KAIST, S-J L. Kang

Experimental Observation

Effect of Δg_c (Temperature)

70NbC-30Co

AGG ← *decrease* — **Temperature (σ_s^2 / T)** — *increase* → **NGG**



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_{max} (Initial Particle Size)

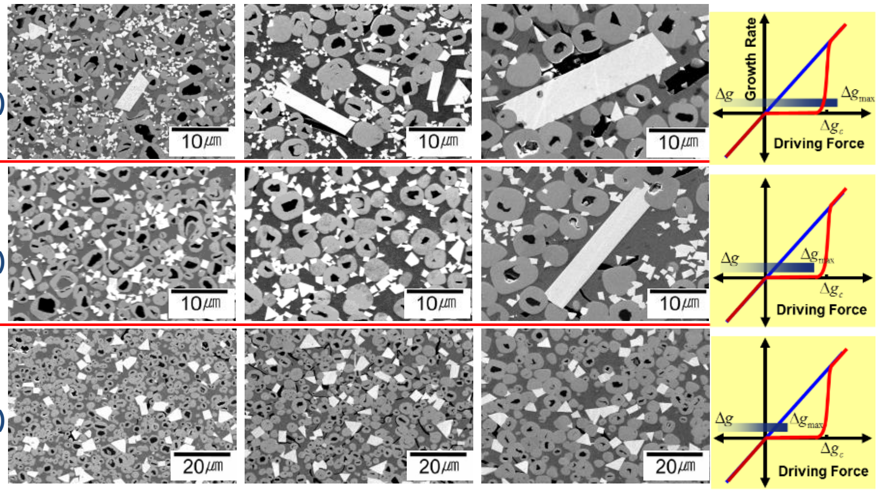
70(25TiC-75WC)-30Co, 1450 °C

1 hr | **5 hr** | **20 hr**

WC (0.5 μm)

WC (1.3 μm)

WC (4.1 μm)



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)

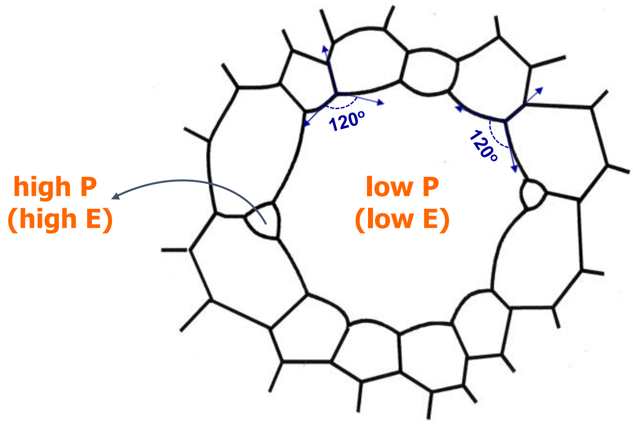
KAIST, S-J L. Kang

Chap. Solid State Sintering

GG: Increase in average grain size

Result of boundary migration

Driving Force



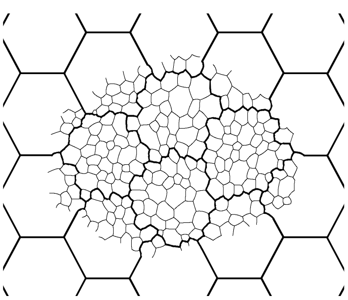
in 2-D

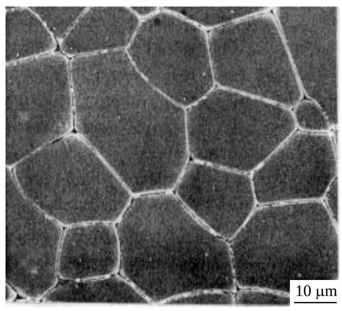
γ = const.

$\theta = 120^o$

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

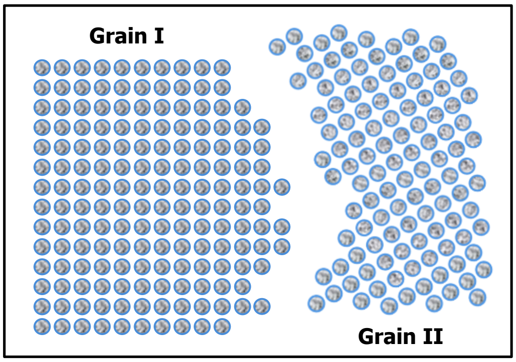
$$\Delta \mathbf{g} = 4\gamma_b \left(\frac{1}{\bar{\bar{G}}} - \frac{1}{G}\right) \propto \left(\frac{1}{\bar{\bar{G}}} - \frac{1}{G}\right)$$

The mean field concept is adopted.

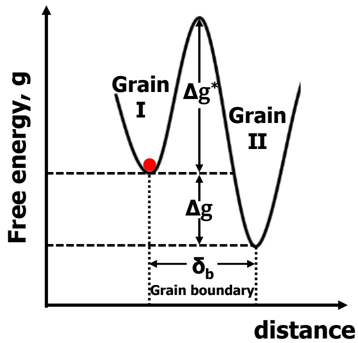
KAIST, S-J L. Kang

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

Classical Law of Normal Grain Growth

Mean Field Concept

$$\frac{dG}{dt} \propto M_b\left(\frac{1}{\bar{G}} - \frac{1}{G}\right)$$

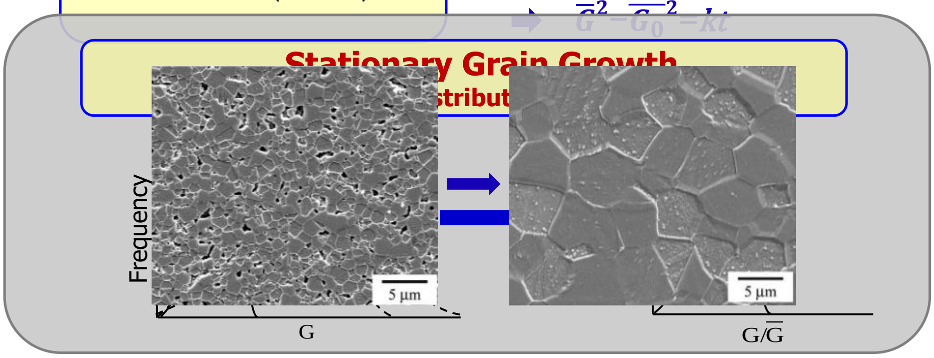
(i) Driving force $\propto \left(\frac{1}{\bar{G}} - \frac{1}{G}\right)$

(ii) Mobility = const. $\neq f(F_b)$

$\Rightarrow \bar{G}^2 - \bar{G_0}^2 = kt$

Stationary Grain Growth

...stribut...

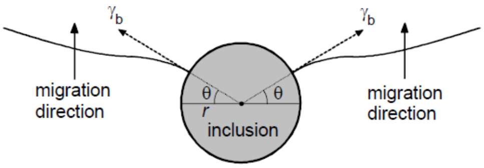


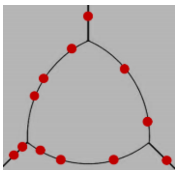
KAIST, S-J L. Kang

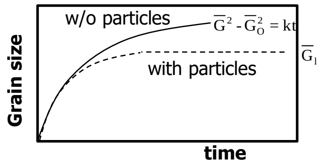
Effect of 2nd Phase Particles

Smith-Zener Effect

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







For uniform distribution of second phase particles

$$F_d = \gamma_b \sin\theta \times 2\pi r \cos\theta$$
$$= \pi r \gamma_b \sin 2\theta$$
$$F_d^{\sigma} = \frac{3 f_v \gamma_b}{2r}$$
$$\frac{d\bar{G}}{dt} = \frac{D_b^{\perp}}{RT}\frac{1}{\omega}\left[2\gamma_b \frac{V_m}{\beta\bar{G}} - \frac{3 f_v \gamma_b V_m}{2r}\right]$$
$$\bar{G}_l = \frac{4r}{3 f_v \beta} \quad \text{or} \quad \bar{R}_l = \frac{2r}{3 f_v \beta}$$

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?

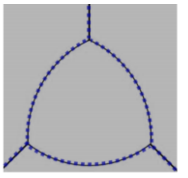
Derivation of the drag force

(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

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

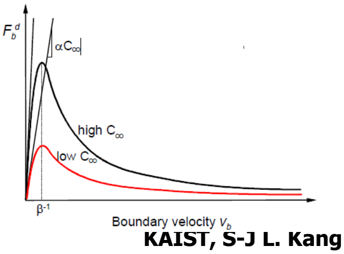
$$= -N_v\int_{-\infty}^{\infty} [C(x)-C(\infty)]\frac{\mathrm{d}E}{\mathrm{d}x}\mathrm{d}x$$



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)

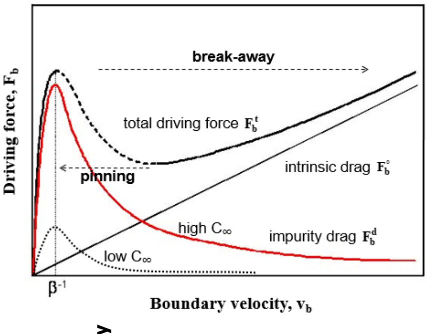


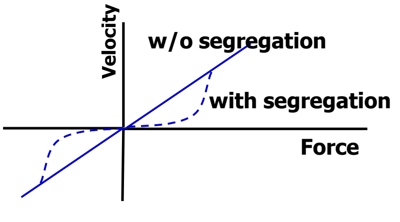
KAIST, S-J L. Kang

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

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

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

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

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

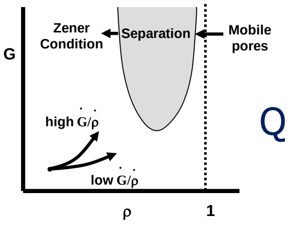
Qn: Boundary mobility in McLean model?

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

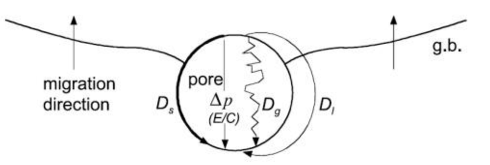


Figure II.I. Possible mechanisms of pore migration with a grain boundary.

$$v_p = M_p F_p$$

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

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

Zener drag

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

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

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 $v_b = M_b(F_b - NF_p)$

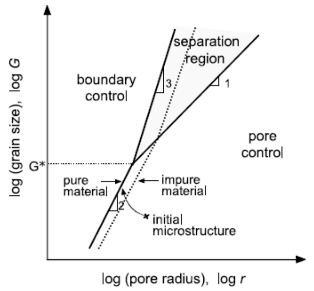
(i) Boundaries move together with pores

$$v_b = v_p = M_pF_p = M_b(F_b - NF_p)$$

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

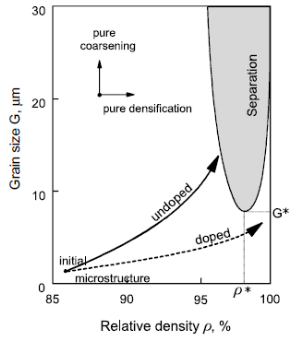
(ii) Pores are separated from boundary

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



For surface diffusion-controlled pore migration (boundary migration)

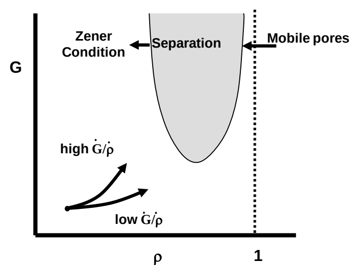
Brook, *J. Am. Ceram. Soc.*, **52**, 56 (1969).

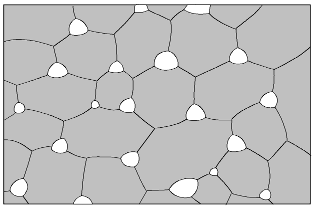


Harmer, in *Structure and Properties of MgO and Al2O3 Ceramics*, W. D. Kingery (ed.), Am. Ceram. Soc. Inc., Columbus, 679 (1985)

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:

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

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

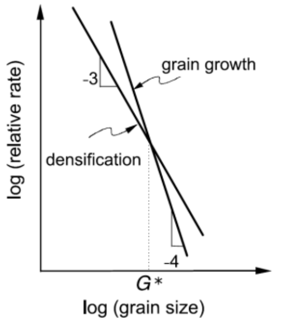
Densification	m	k
D_l	3	1/3
D_b	4	0
Grain Growth	n	l
D_s	4	4/3
Gas Diff.	3	1
Evap./Cond.	2	2/3
$D_b^{\perp}$	2	0

KAIST, S-J L. Kang

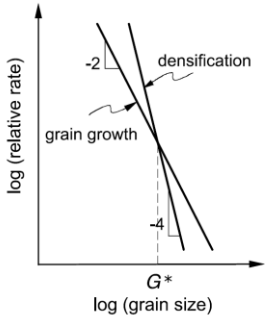
Effect of Grain (Particle) Size

Examples

Densification : lattice diffusion
Grain Growth : surface diffusion



Densification : grain boundary diffusion
Grain Growth : evaporation/condensation

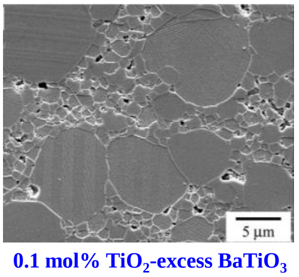


Relative densification and coarsening rates vs. grain size.

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

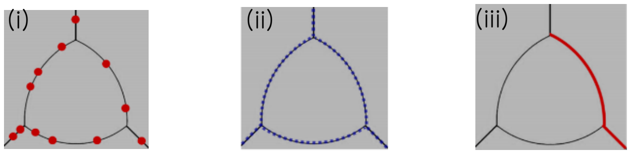
$$\frac{dG_a}{dt} = \frac{D_b^{\perp}}{RT}\frac{2\gamma_b}{\beta\overline{G}_m}\frac{V_m}{\omega} \qquad \overline{G}_{a,t} - \overline{G}_{a,t_o} = \frac{2D_b^{\perp}\gamma_b V_m}{\beta RT\overline{G}_m\omega}t$$

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

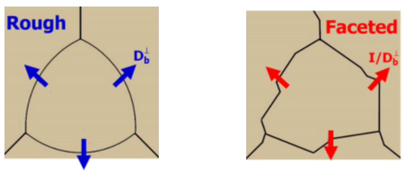
Early Mechanisms



(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

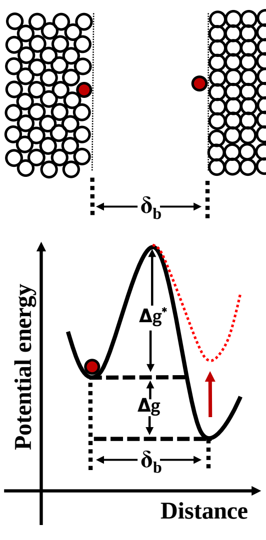


Kang *et al.*, *J. Ceram. Soc. Jpn,* **124**, 259 (2016). Kang *et al.*, *J. Am. Ceram. Soc,* **98**, 347 (2015).

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^*

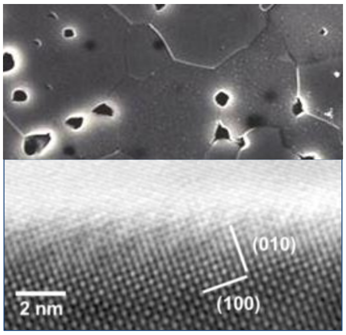
Possibility of Interface Reaction-Controlled Boundary Migration ?

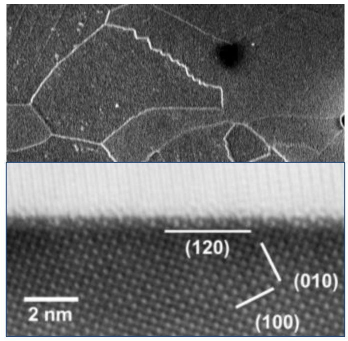
Kang *et al., J. Am. Ceram. Soc.,* **98** 347 (2015).

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**

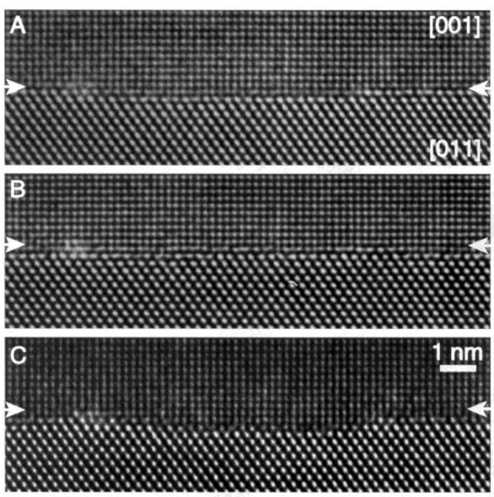
Variables: *T, dopant, Po_2*

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

Migration Mechanism of Faceted Boundary

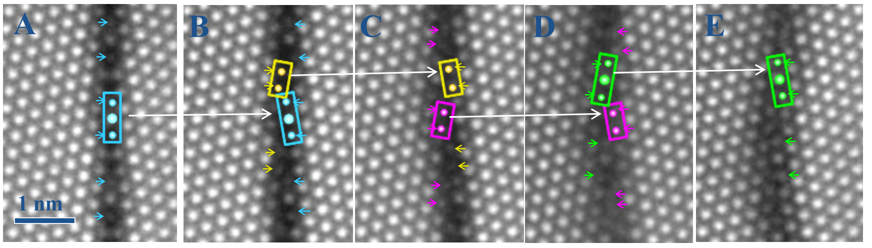
Migration of a Singular GB in Au by the Step Growth Mechanism

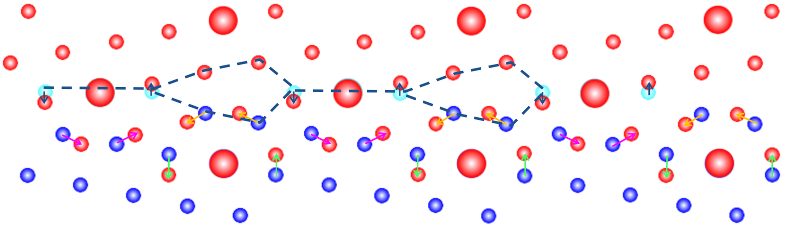


K.L. Merkle and L.J. Thompson, *Mater. Lett.*, **48**, 188 (2001).

KAIST, S-J L. Kang

Migration Mechanism of ∑7 α-Al_2O_3 Boundary



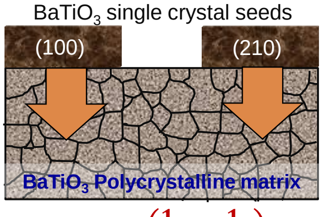


Local Atoms Shuffling: *movement of atoms from ledges to the ledges of the growing crystal*

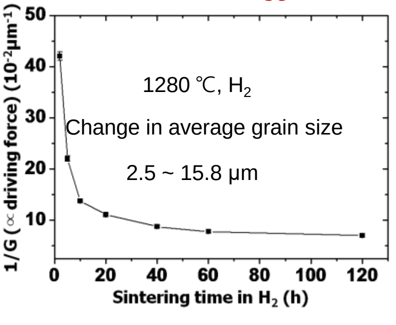
J. Wei, *et al.*, *Nature Materials*, 20, 951, July 2021.

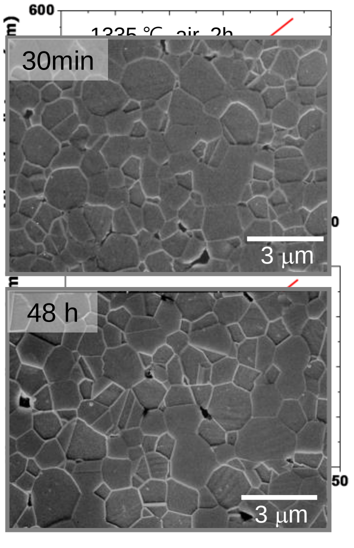
KAIST, S-J L. Kang

Migration Behavior of Faceted Boundary



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

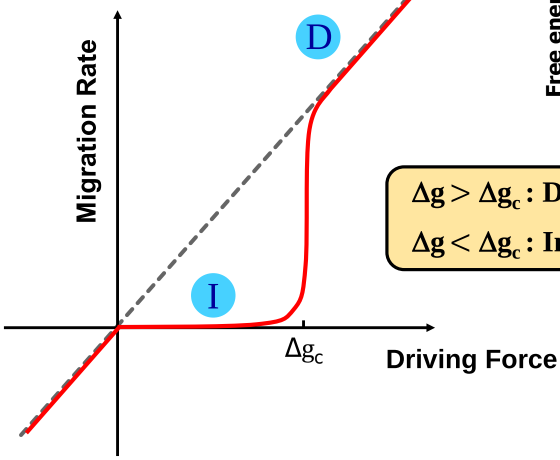


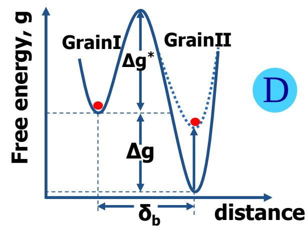


An *et al., Acta Mater.* **60**, 4531 (2012) .

KAIST, S-J L. Kang

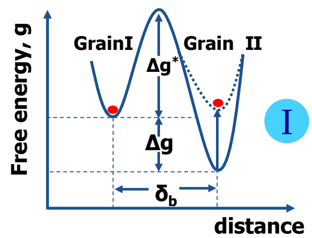
Mixed Control of Boundary Migration





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

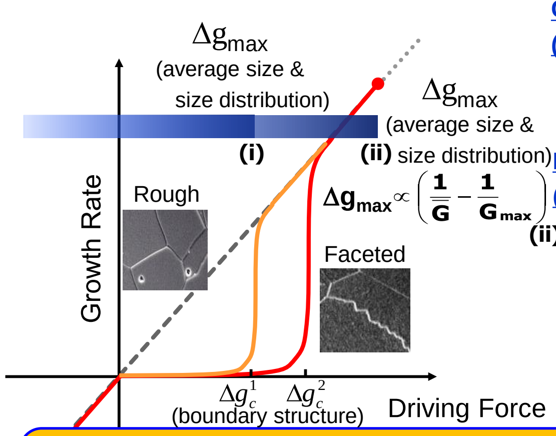
  is **not** dependent on
  the presence of a liquid (film),
  the presence of solutes, or
  the presence of a 2nd phase (particles)
  at the boundary

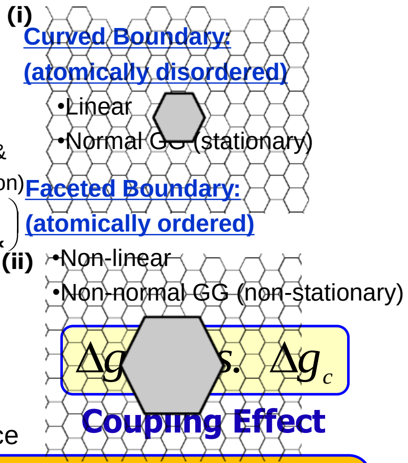
  but dependent on
  the morphology (atomic structure) of
  the grain boundary:

  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



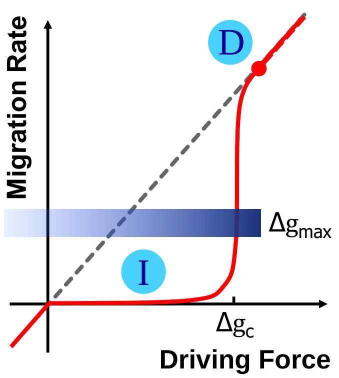


Difference between our and the conventional mechanism:
Mixed Control Mechanism (either Diffusion or Interface Reaction) vs. **Diffusion Control Mechanism**

KAIST, S-J L. Kang

Microstructural Evolution in Polycrystals

Mixed Mechanism Principle of Microstructural Evolution



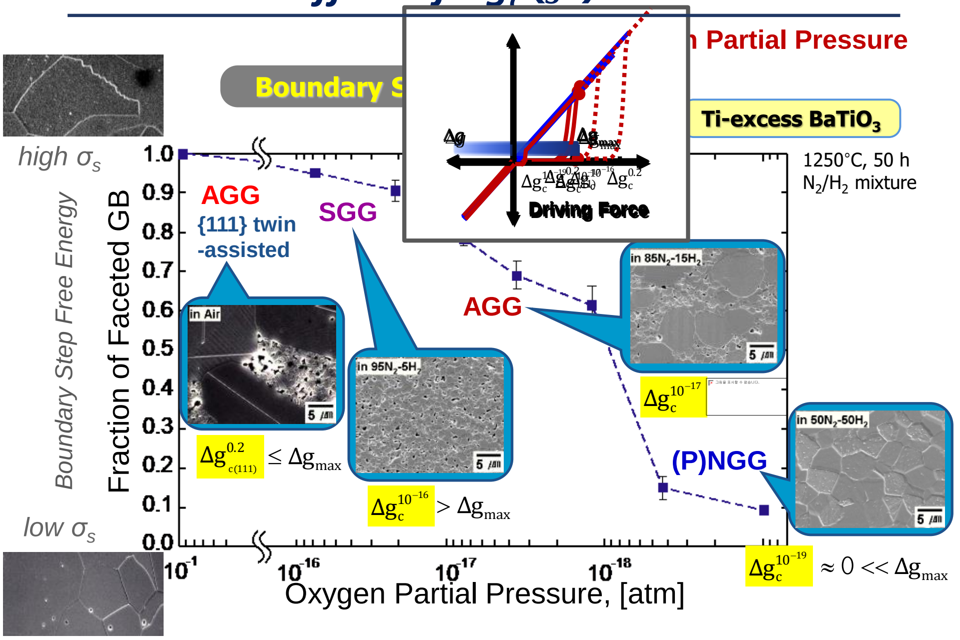
Coupling of Δg_c & Δg_{max}

(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

Effect of Δg$_c$ (gb)



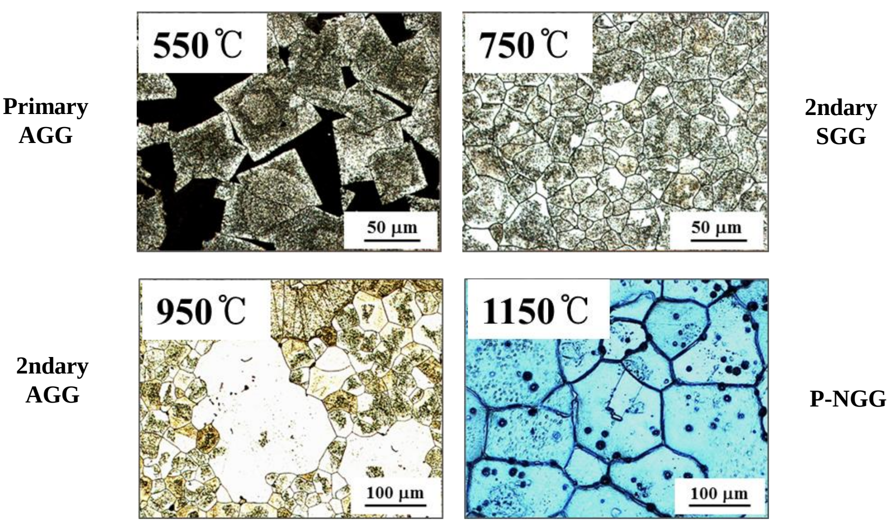
Y.-I. Jung *et al.*, *Acta Mater.,* 54, 2849 (2006).

KAIST, S-J L. Kang

Microstructural Observation during SSS

Effect of Temperature

UFG Ni sintered for 1 h at various temperatures



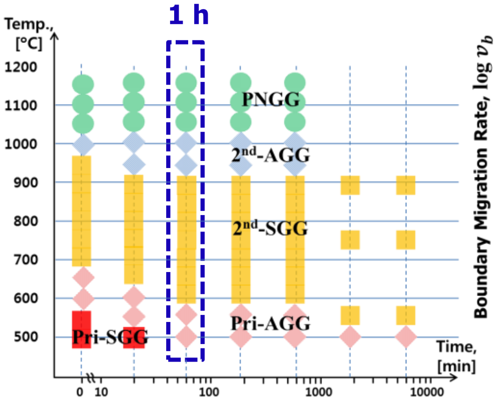
S. H. Jung et al., *Acta Mater.,* **69,** 283 (2014)

KAIST, S-J L. Kang

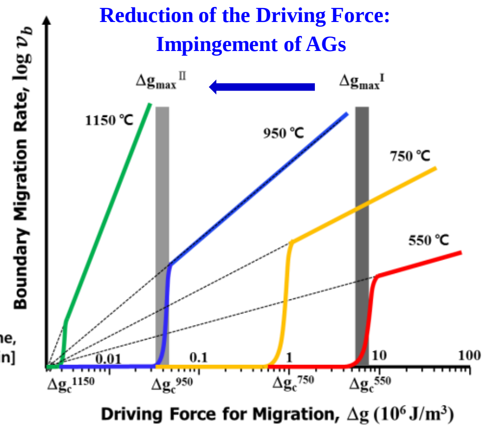
Microstructural Observation during SSS

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)

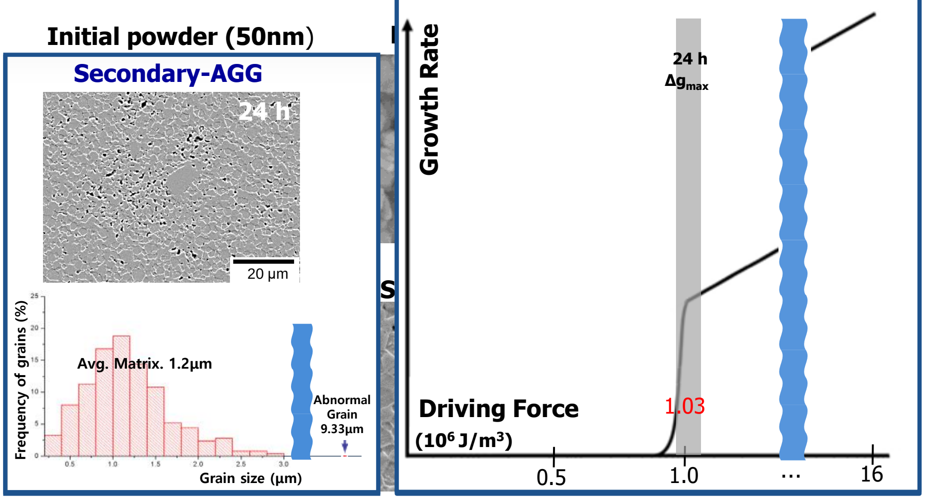
KAIST, S-J L. Kang

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)



S.-J. L. Kang et al., *Ceram. Inter.,* **50**, 37441 (2024)

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)

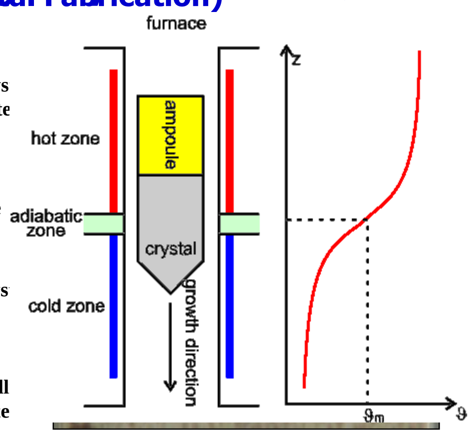
KAIST, S-J L. Kang

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

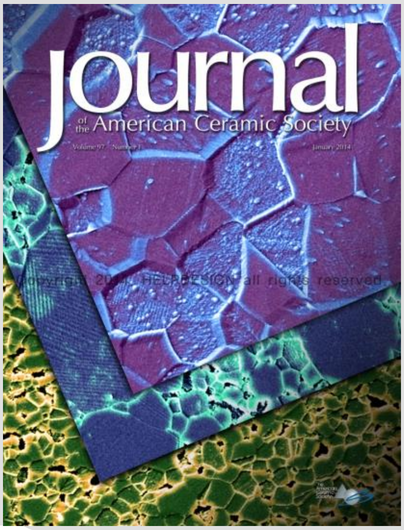


Bridgman Method

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

KAIST, S-J L. Kang

Application Example of the Principle



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

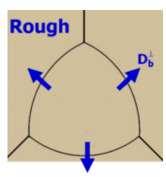
KAIST, S-J L. Kang

Concluding Remarks

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

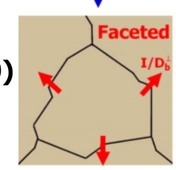
- ***Rough Boundary:***

Linear behavior of boundary migration (Δg_c=0)
Stationary GG: **NGG**



- ***Faceted Boundary:***

Nonlinear behavior of boundary migration ($\Delta g_c \neq 0$)
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)

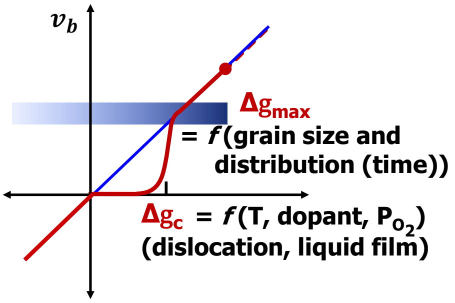
KAIST, S-J L. Kang

Concluding Remarks

Interpretation and Prediction of Microstructural Evolution (GG Behavior)

The Mixed Mechanism Principle of Microstructural Evolution

Coupling of Δg_c & Δg_{max}



- **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. Ceram. Soc. Jpn*, **124**, 259 (2016).

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

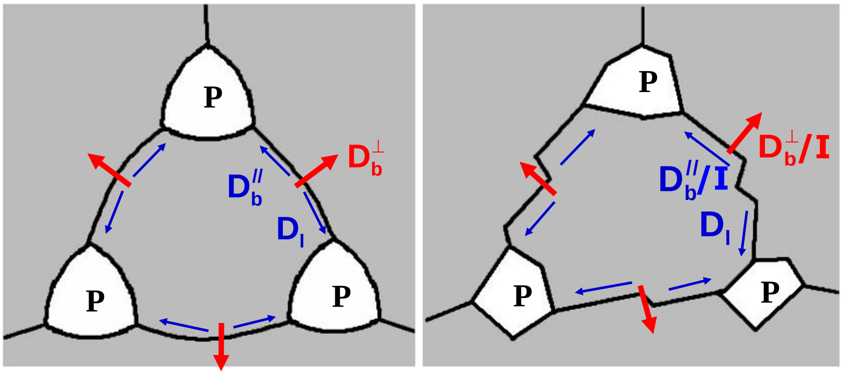
Solid State Sintering

- 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
Diffusion Control

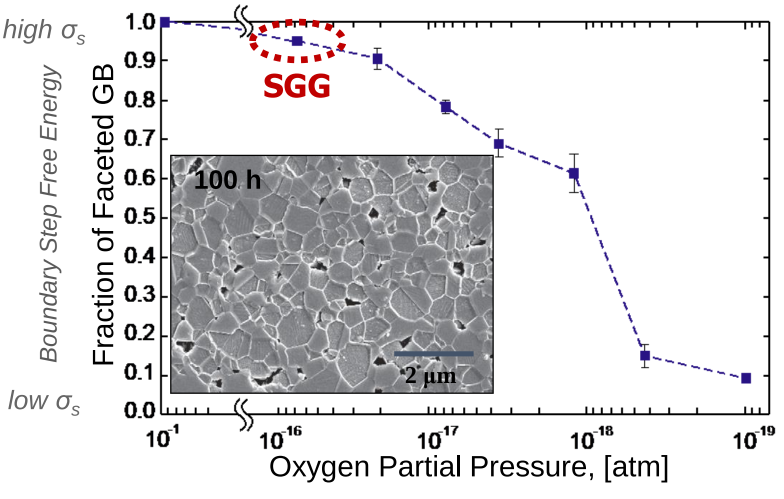
Rate(Δg) : Non-linear
Mixed Control
(Diffusion and Interface Reaction)

KAIST, S-J L. Kang

Fraction of Faceted Grain Boundary

Boundary Structural Change

Ti-excess $BaTiO_3$



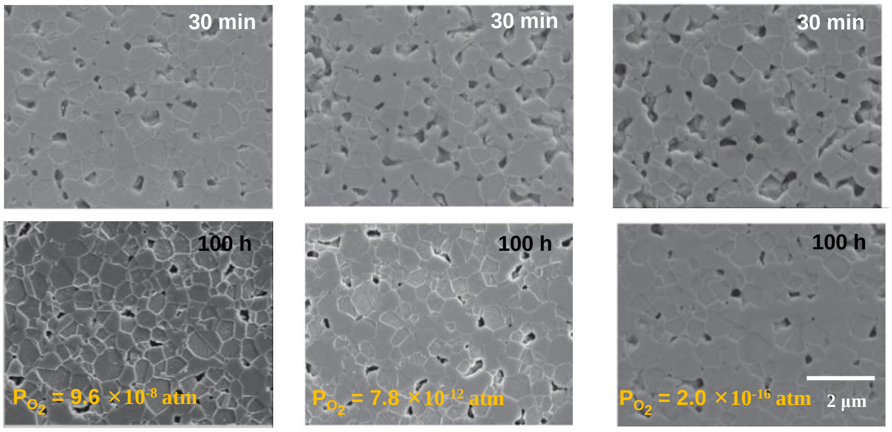
Y.-I. Jung *et al.*, *Acta Mater.*, 54, 2849 (2006).

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

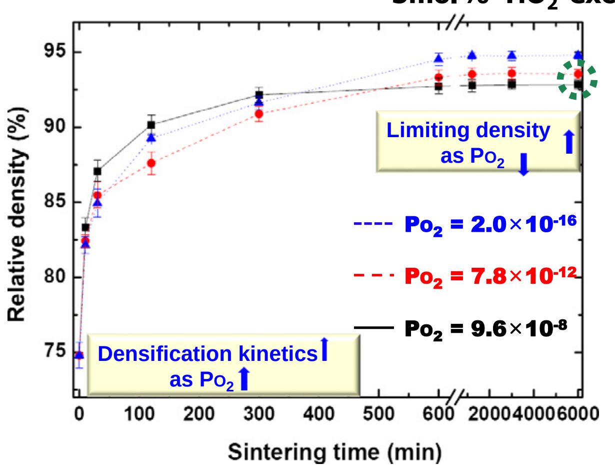


M.-G. Lee et al., *Acta Mater.*, **59**, 692 (2011).

KAIST, S-J L. Kang

Effect of Boundary Structure on Densification

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



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

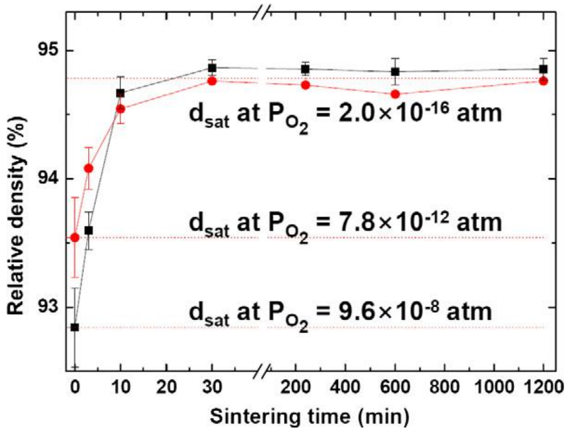
Presintering in H_2
Sintering at P_{O_2} = $10^{-7} – 10^{-16}$

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