KCerS 2026 Spring
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한국세라믹학회

Grain Growth in Ceramics

Lecturer: **Suk-Joong L. Kang (강석중),**
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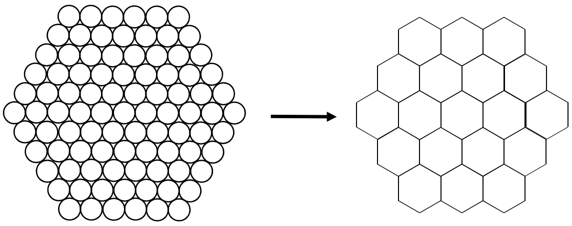
References:

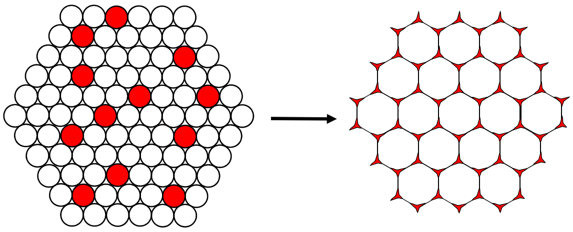
- “Sintering: densification, grain growth and microstructure” Elsevier (2005)
- “Problems and solutions in sintering science and technology” KAIST (2024)
- “Interface structure-dependent grain growth behavior in polycrystals” Chap. 12 in “Microstructural design of advanced engineering materials, pp. 299-322, D. Molodov (ed.) Wiley-VCH (2013)
- Selected papers and book chapters

Densification and Grain Growth

Solid-state sintering (SSS)



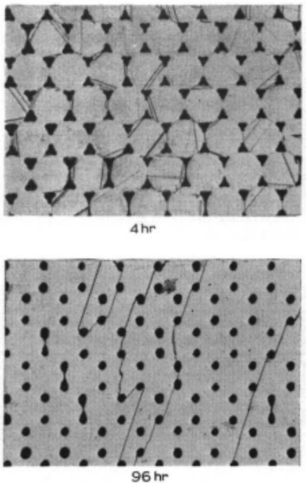
Liquid-phase sintering (LPS)

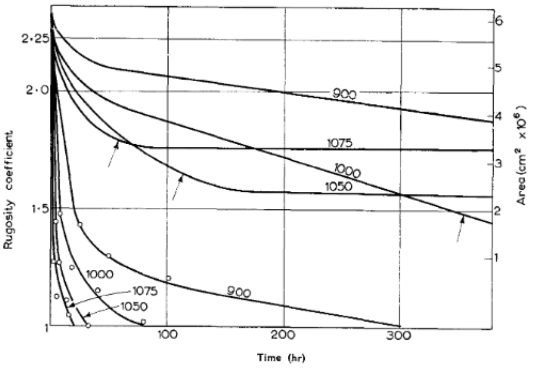


S.-J. L. Kang, “Liquid phase sintering: Fundamentals” in “*Encyclopedia of Materials: Technical Ceramics and Glasses,*” A. Leriche and F. Cambier (eds), Elsevier (2020).

Densification and Grain Growth in SSS

Cu **at 1075 °C**





Void area and rugosity coefficient during isothermal sintering of 0·0128 cm dia. wires. Arrows indicate the approximate time when grain growth occurred.

Suppression of GG, in particular AGG

Alexander and Balluffi, *Acta Metall.*, **5**, 666 (1957).

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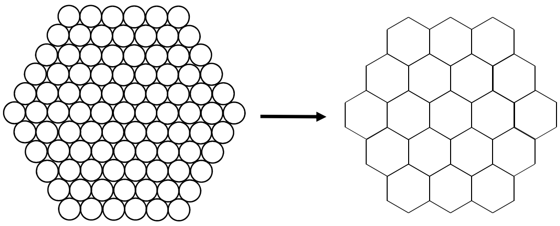
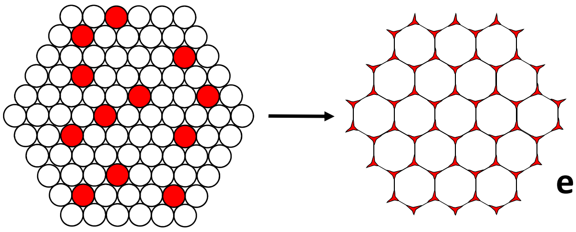
Densification and Grain Growth

Solid-state sintering (SSS)



e.g., Sintering of WC
at 1900–2200 °C

Liquid-phase sintering (LPS)



Role of Liquid:

- Mass flow (densification)
- Path for atom diff. (shape accommodation & grain growth)

e.g., Sintering of WC-Co
at 1350–1450 °C

S.-J. L. Kang, "Liquid phase sintering: Fundamentals" in "*Encyclopedia of Materials: Technical Ceramics and Glasses,*" A. Leriche and F. Cambier (eds), Elsevier (2020).

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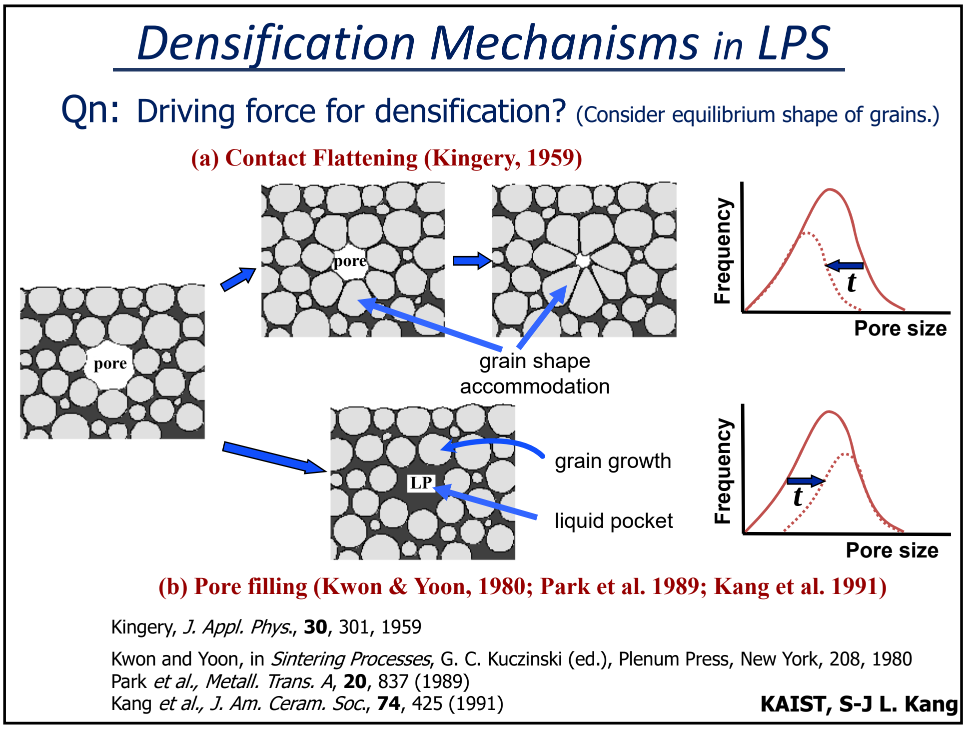

Densification Mechanisms in LPS

Qn: Driving force for densification? (Consider equilibrium shape of grains.)

(a) Contact Flattening (Kingery, 1959)

(b) Pore filling (Kwon & Yoon, 1980; Park et al. 1989; Kang et al. 1991)

Kingery, *J. Appl. Phys.*, **30**, 301, 1959

Kwon and Yoon, in *Sintering Processes*, G. C. Kuczinski (ed.), Plenum Press, New York, 208, 1980
Park *et al., Metall. Trans. A*, **20**, 837 (1989)
Kang *et al., J. Am. Ceram. Soc.*, **74**, 425 (1991)

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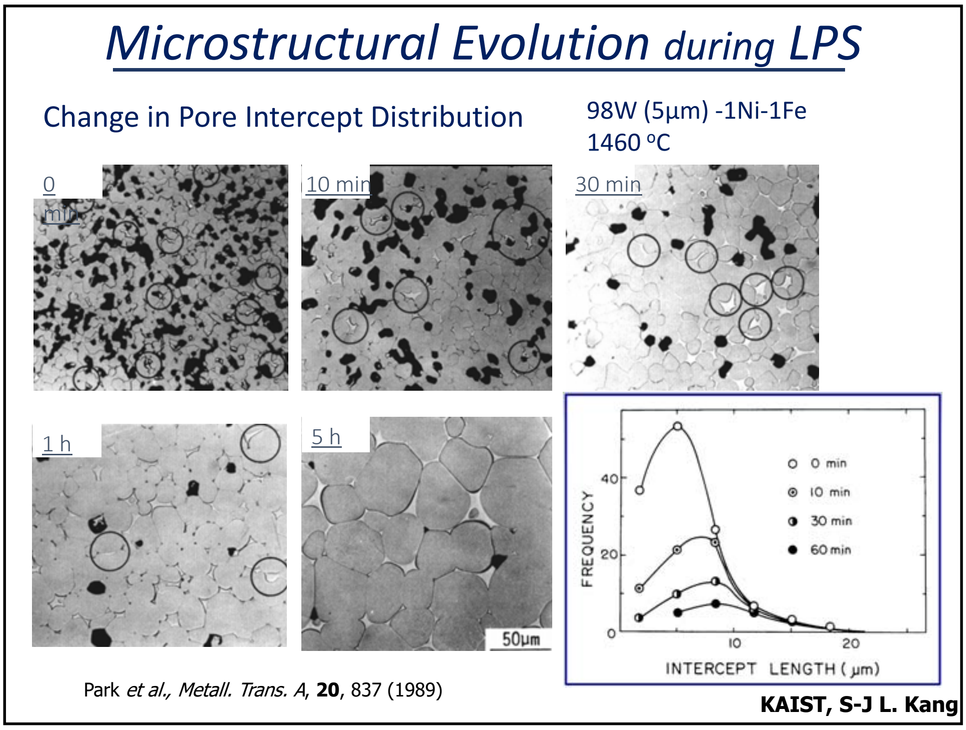

Microstructural Evolution during LPS

Change in Pore Intercept Distribution

98W (5μm) -1Ni-1Fe
1460 °C

Park *et al., Metall. Trans. A*, **20**, 837 (1989)

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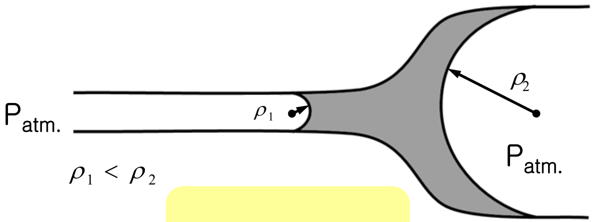
Flow (redistribution) of Liquid

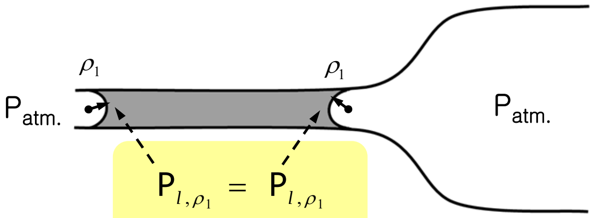
due to uneven capillary pressure



$$P_{l,\rho_1} = P_{atm.} - \frac{2\gamma}{\rho_1}$$

$$P_{l,\rho_2} = P_{atm.} - \frac{2\gamma}{\rho_2}$$

$$P_{l,\rho_1} < P_{l,\rho_2} < P_{atm}$$



$$P_{l,\rho_1} = P_{l,\rho_1}$$

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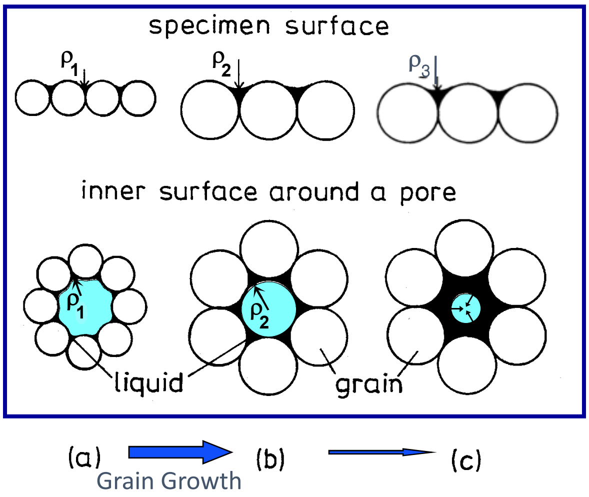
Pore Filling Mechanism of LPS



$P_1^{surf} = P_1^{pore}$ $P_2^{surf} = P_2^{pore}$ $P_3^{surf} > P_2^{pore}$

$$P_l^{surf} = P_{atm.} - \frac{2\gamma}{\rho_s}$$

$$P_l^{pore} = P_{atm.} - \frac{2\gamma}{\rho_p}$$

- ***Critical Moment :***
  Complete Wetting of Pore Surface

Park *et al., Metall. Trans, A.,* **17A**, 1915 (1986)
Kang *et al., J. Am. Ceram. Soc.*, **72**, 1166 (1989)

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Implications of GG for Densification

Grain Growth in SSS

- Pore coalescence and growth
- Pore entrapment and densification limit
- Suppression of grain growth is beneficial for densification

Grain Growth in LPS

- Grain growth is essential for densification in LPS (pore filling mechanism)
- Densification kinetics is governed mostly by grain growth kinetics

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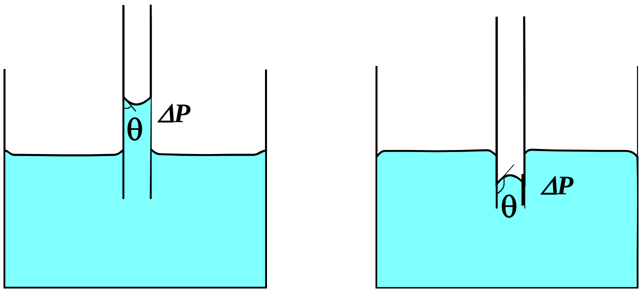
Capillarity

Capillary action of a glass tube



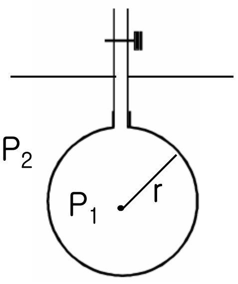
$\theta < 90^o$ $\theta > 90^o$

Young-Laplace Eq.

Qn: Pressure difference btw two adjacent phases with a curved interface

- Blow of a soap bubble
- Inflate a balloon
- Water droplet and Gas bubble

Curved interface



$$PdV = \gamma dA$$

$$P_1 - P_2 = \frac{2\gamma}{r}$$

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Capillarity and Chemical Potential

System with two incompressible phases that are separated by a curved interface

$$d\Omega = 0 = d\Omega^{\alpha} + d\Omega^{\beta} + d\Omega^{\sigma}$$
$$= -P^{\alpha}dV^{\alpha} - P^{\beta}dV^{\beta} + \gamma dA$$

$$P^{\alpha} - P^{\beta} = \gamma\frac{dA}{dV^{\alpha}}$$
$$= \gamma K \qquad K = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$

$$P^{\alpha} - P^{\beta} = \left(\frac{1}{r_1} + \frac{1}{r_2}\right)\gamma$$

Cf: Energy change of compressible fluid due to a curved interface

Deformation energy

$$W = -\int_0^P PdV = -\int_0^P P\left(\frac{\partial V_m}{\partial P}\right)_T dP = V_m\kappa\int_0^P PdP$$
$$= \frac{1}{2}V_m\kappa P^2$$

$$\mu_r^{\alpha} = \mu_{\infty}^{\alpha} + \gamma K V_m^{\alpha}$$ **Gibbs-Thompson Eq.** Only to phase α

$$\mu_r^{\beta} = \mu_{\infty}^{\beta}$$

Freezing point of liq. ↓ Melting point of fine powder ↓

For r <10^{-8}m, the size effect becomes significant (~0.1).

For r > 0.1μm, the size effect is insignificant.

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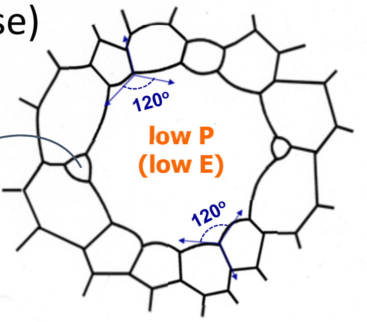
Driving Force for Grain Growth

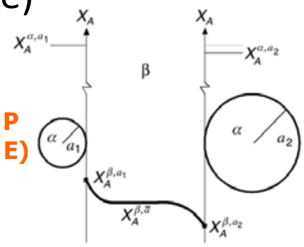
SSS (single phase)



high P
(high E)

low P
(low E)

LPS (two-phase)



high P
(high E)

low P
(low E)

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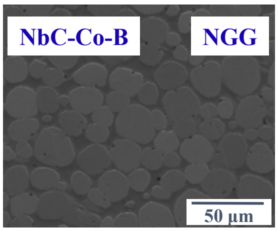
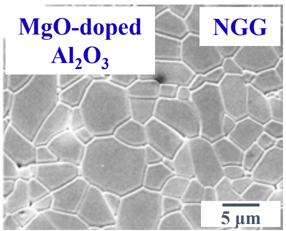
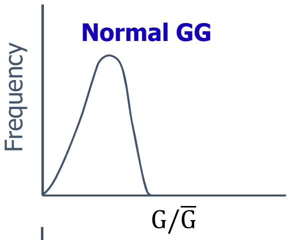
Grain Growth and Microstructure

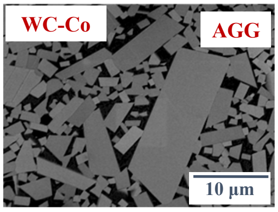
Two Extreme Cases: Normal and Abnormal

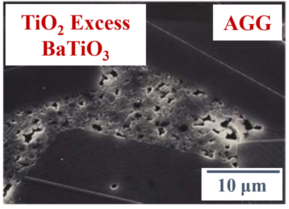
Two phase system **Single phase system**

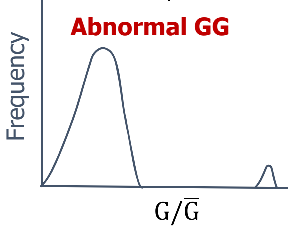












J. H. Lee, M.S. Thesis, (KAIST, 2005).
Yang and Kang, *Int. J. Refract. H. Mater.*, **27,** 90 (2009).

Park and Yoon, *J. Am. Ceram. Soc.*, **83,** 2605 (2000).
Choi and Kang, *Mater. Sci. Forum*, **475-479**, 3891 (2005).

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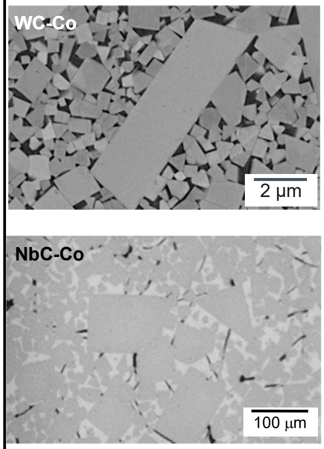
Characteristics of AGG

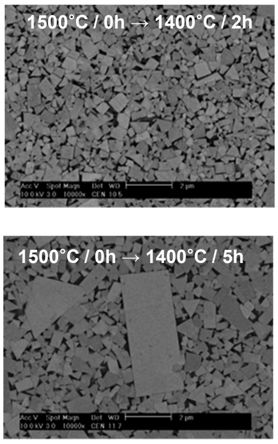
(a) Systems with faceted or partially faceted grains



Cho *et al.*, *J. Am. Ceram. Soc.*, **87**, 443 (2004).
S. M. Kim, M. S. Thesis (2004).

(b) Incubation of AGG

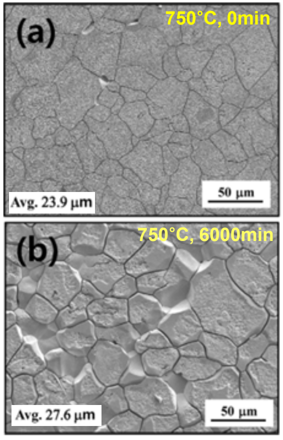
WC-8Co



Yang *et al.*, *J. Am. Ceram. Soc.*, **94**, 1019 (2011).

(c) Stagnant grain growth after impingement of abnormal grains

Pure Ni (180nm)



Jung and Kang, *Acta Mater.*, **69**, 283 (2014).

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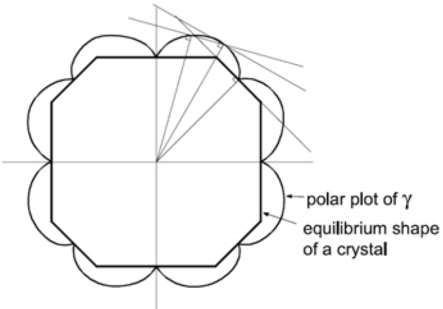
Equilibrium Shape of a Single Crystal

Equilibrium Shape: $\sum(\gamma_i A_i)_{\min}$

Polar plot of surface energy γ (γ-plot)



Wulff construction

(γ of a plane ∝ the distance from the center to the corresponding γ point)

Herring, *Phys. Review,* **82**, 87 (1951)

S.-J. L. Kang, in “*Sintering: Densification, Grain Growth and Microstructure*,” Elsevier, Oxford (2005)

Wulff Theorem

Under equilibrium

$$\mathrm{d}F=\sum_i \gamma_i \mathrm{d}A_i+\left(\frac{\partial F}{\partial n^c}\right)_{T,V}\mathrm{d}n^c+\left(\frac{\partial F}{\partial V^c}\right)_{T,V}\mathrm{d}V^c+\left(\frac{\partial F}{\partial n^s}\right)_{T,V}\mathrm{d}n^s+\left(\frac{\partial F}{\partial V^s}\right)_{T,V}\mathrm{d}V^s=0$$

$$\sum \gamma_i \mathrm{d}A_i+(\mu^c-\mu^s)\mathrm{d}n^c-(P^c-P^s)\mathrm{d}V^c=0$$

$$\sum_i\left[\gamma_i-\frac{h_i}{2}(P^c-P^s)\right]\mathrm{d}A_i+(\mu^c-\mu^s)\mathrm{d}n^c=0$$

$$P^c-P^s=\frac{2\gamma_i}{h_i}\equiv K_w$$

K_w:Wulff constant

$$\mu=\mu^o+\frac{2\gamma_i V_m}{h_i}$$

cf. Gibbs-Thompson eq.

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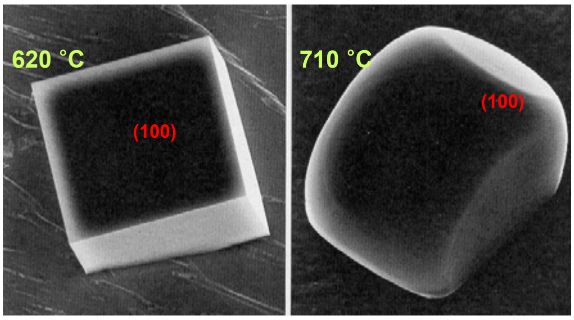
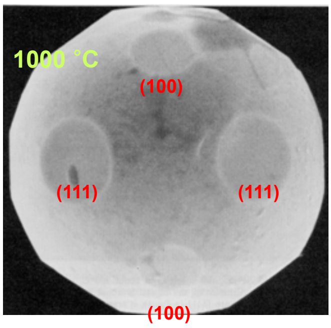
Equilibrium Shape of Single Crystals

Examples

NaCl



Gold



Simple calculation of surface energy using the broken bond model

$$\gamma_\theta = \frac{U_b}{2a}(\cos\theta + \sin\theta) = \frac{U_b}{a\sqrt{2}}\cos(\theta - \frac{\pi}{4})$$

Heyraud and Métois, *J. Crystal Growth*, **84,** 503 (1987).
Heyraud and Métois, *J. Crystal Growth*, **50,** 571 (1980).

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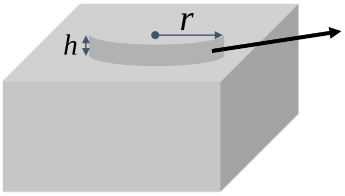
Step Free Energy and Faceting

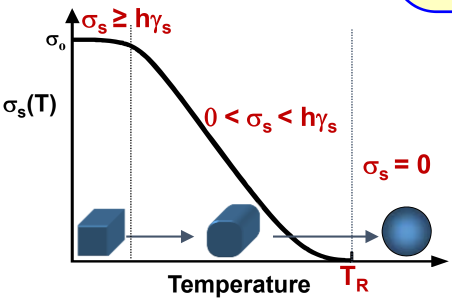


$$\sigma_s(T) = \text{step free energy}$$

$$\Delta g = \pi r^2 h \Delta g_v + 2\pi r \sigma_s$$

$$\Delta g^* = -\frac{\pi\sigma_s^2}{h\Delta g_v}$$: **Critical Driving Force for Nucleation**

σ_s(T) = step free energy



$$\sigma_s(T) = \alpha \exp\left[-A/\sqrt{T_R - T}\right]$$

Infinite order transition

Beijeren, *Phys. Rev. Lett.*, **38**, 993 (1977).
Kosterlitz and Thouless, *J. Phys.*, C6, 1181 (1973).
Leamy and Gilmer, *J. Cryst. Growth*, **24/25**, 499 (1974)

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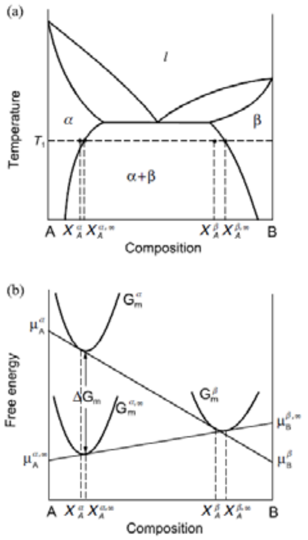
Grain Growth in a Matrix (LPS)

Qn: Why grain growth takes place during sintering?



Driving Force

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

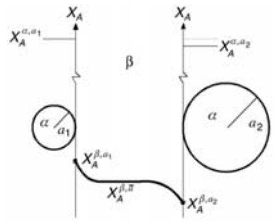


Figure 15.1. (a) Typical phase diagram showing limited solubility of $X_A^{\alpha,\infty}$ and $X_B^{\beta,\infty}$ at temperature T_1 and (b) schematic of the molar free energy versus composition at the temperature for α precipitates with a flat interface ($K = 0$) and with a finite radius of curvature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

S.-J. L. Kang, in "*Sintering: Densification, Grain Growth and Microstructure*," Elsevier, Oxford (2005)

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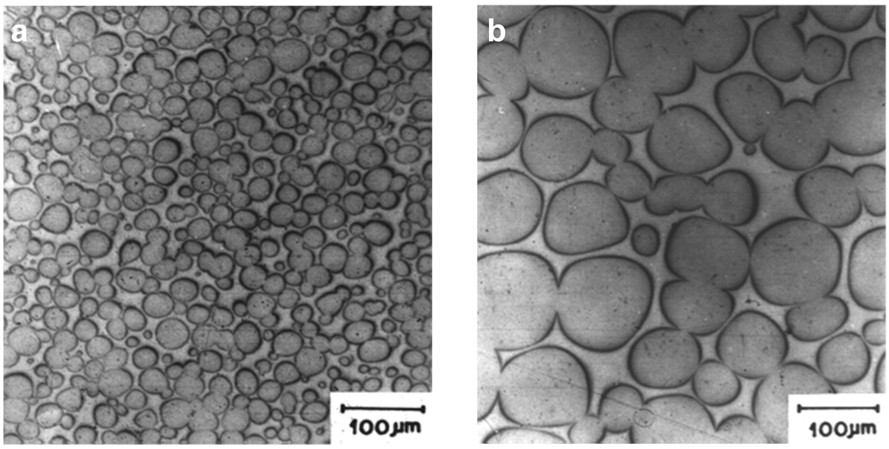
Normal Grain Growth

Stationary Grain Growth



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

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Lifshitz-Slyozov-Wagner (LSW) Theory

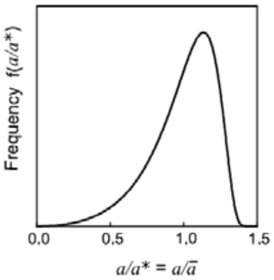
Basic Assumptions: (i) infinitely dispersed system (meaning?)
(ii) constant interface mobility (meaning?)

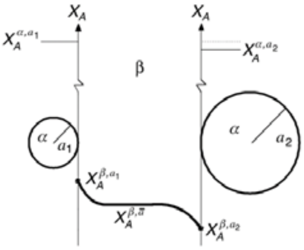
Diffusion-controlled GG (by LSW)

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).

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Lifshitz-Slyozov-Wagner (LSW) Theory

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

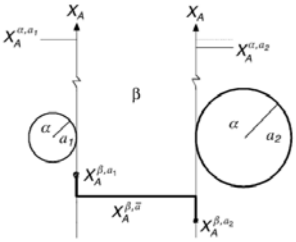
Interface Reaction-controlled GG (by Wagner)

Interaction btw. average-sized grain and an individual grain

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

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

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



Physically Wrong!

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

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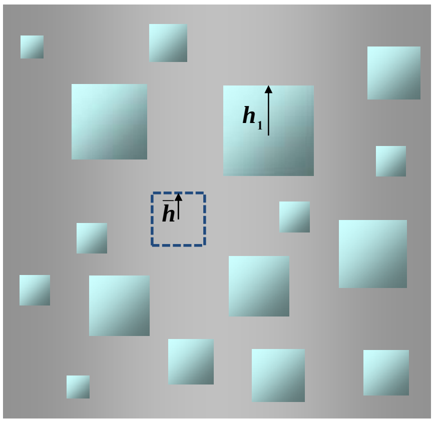
Grain Coarsening in a Matrix

Ostwald ripening: Result of growth/dissolution of individual grains



Interaction of an individual grain with a critical sized grain
(mean field concept)

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

(Difference in Capillary Pressure)

Growth and dissolution of single crystal grains in a liquid matrix

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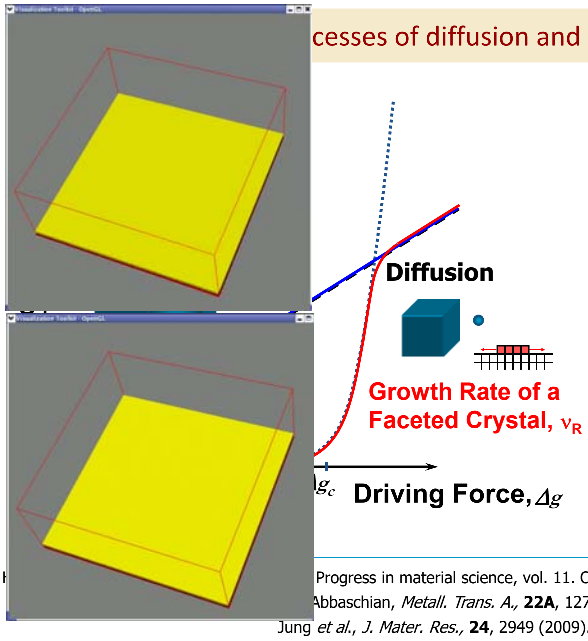
Crystal Growth in a Matrix

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).
Jung *et al.*, *J. Mater. Res.,* **24**, 2949 (2009).

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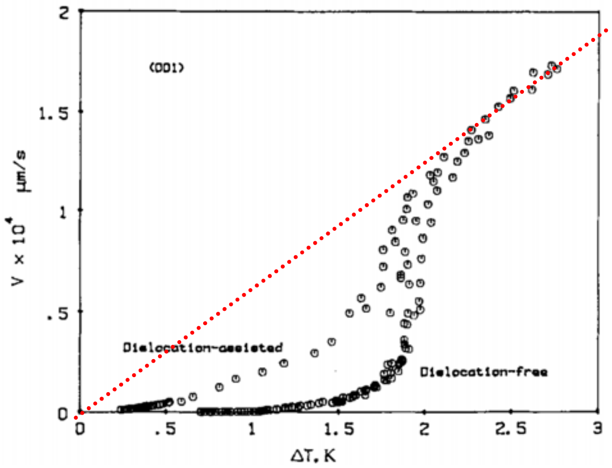
Nonlinear Migration of Faceted Sol./Liq. Interface

Experimental Observation

(001) Ga Single Crystal



Peteves and Abbaschian, *Metall. Trans. A*, **22A**, 1259 (1991).

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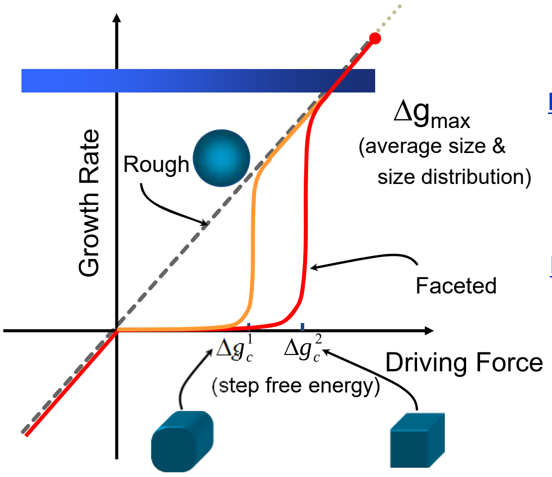
Growth and Shrinkage of Grains in a Liquid Matrix



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

Rounded Grains:

- Linear
- Stationary Grain Growth (LSW theory)

Faceted Grains:

- Non-linear
- Non-stationary Grain Growth

$\Delta g_{\max}\ \ vs.\ \ \Delta g_c$

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

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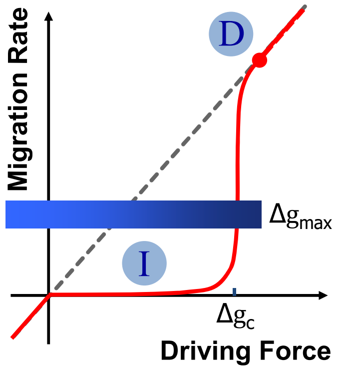
Microstructural Evolution during LPS

Mixed Mechanism Principle of Grain Growth (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**

Jung *et al.*, *J. Mater. Res.*, **24**, 2949 (2009); 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).

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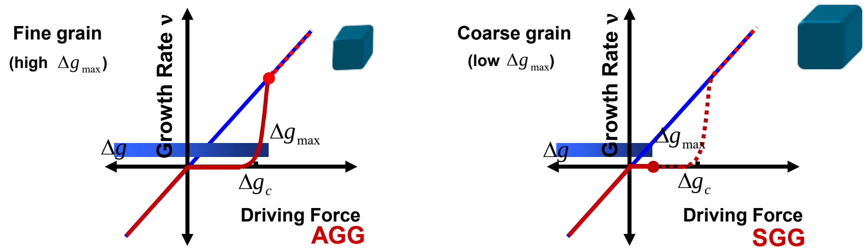
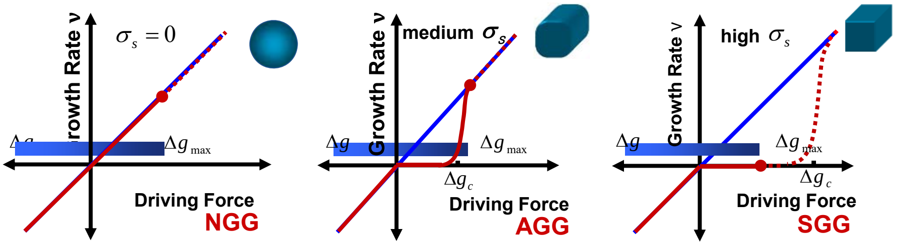
Thought Experiments

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



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



Fisher and Kang, *J. Am. Ceram. Soc.*, **102**, 717 (2019)

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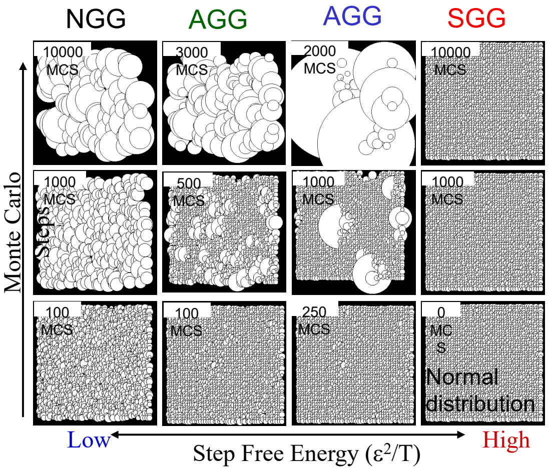
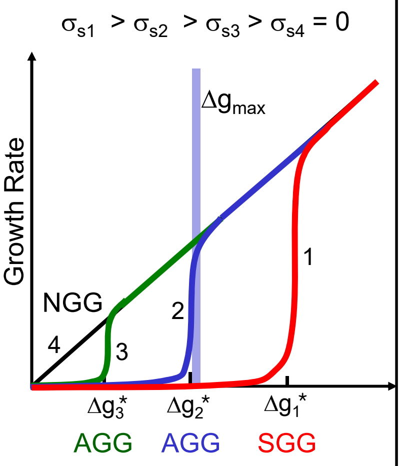
Simulation of Grain Growth

Effect of Step Free Energy (Δg_c)





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

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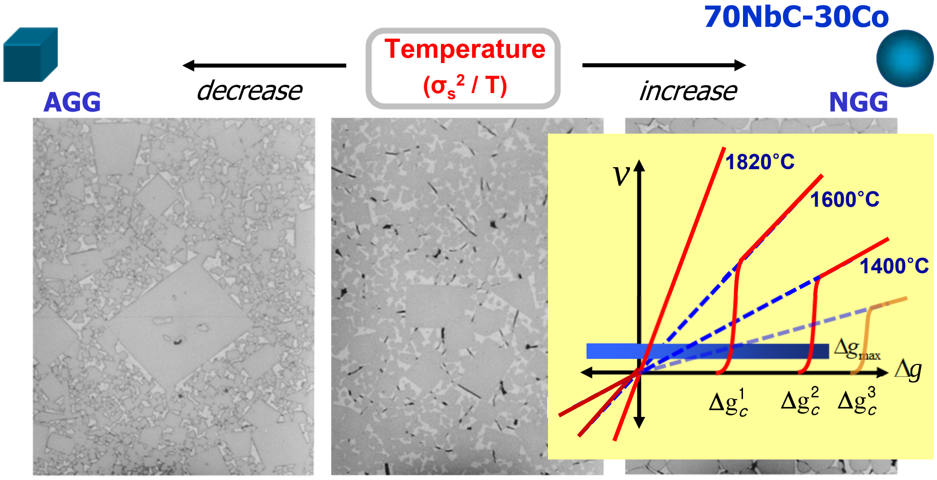
Microstructural Evolution during LPS

Effect of Δg_c (Temperature)

70NbC-30Co



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

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

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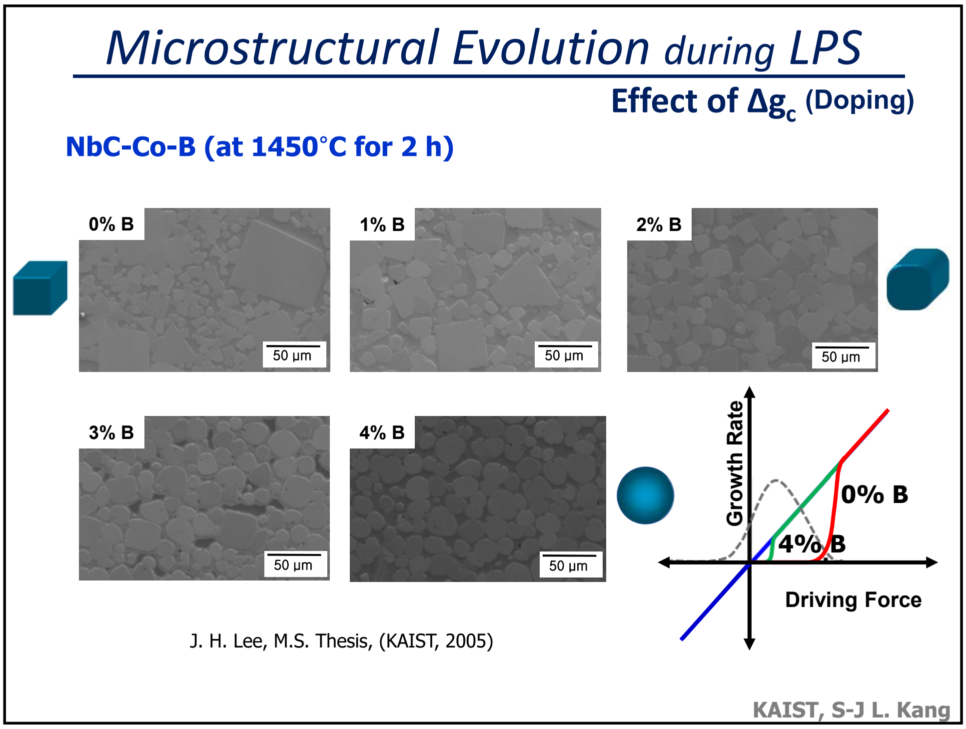

Microstructural Evolution *during* LPS

Effect of Δg_c (Doping)

NbC-Co-B (at 1450°C for 2 h)

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

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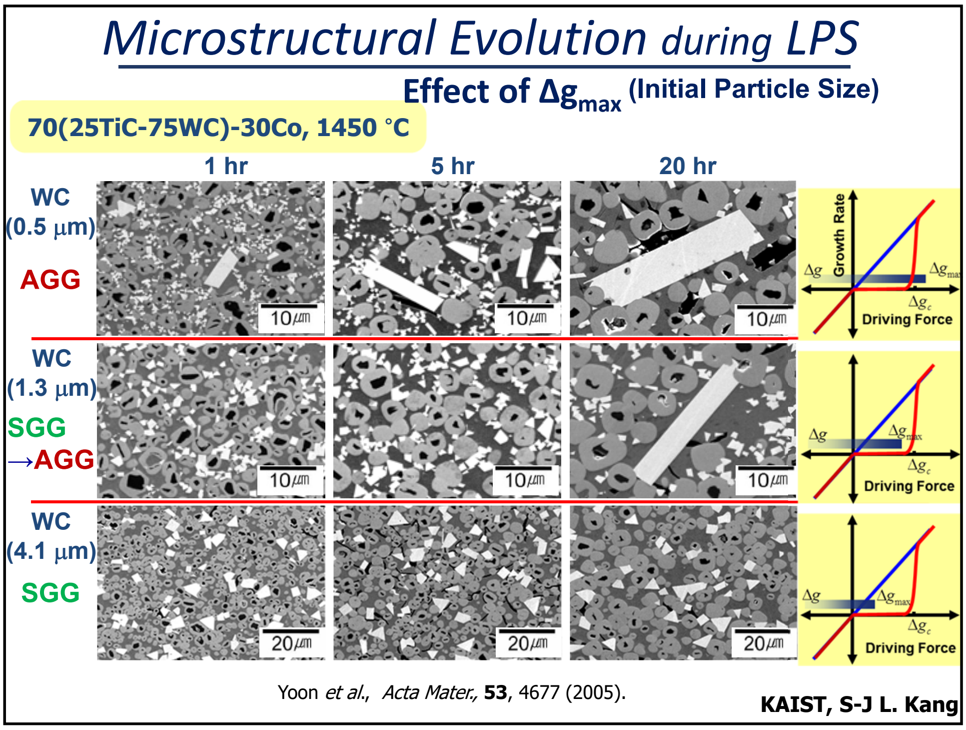

Microstructural Evolution *during* LPS

Effect of Δg_{max} (Initial Particle Size)

70(25TiC-75WC)-30Co, 1450 °C

Yoon *et al.*, *Acta Mater.*, **53**, 4677 (2005).

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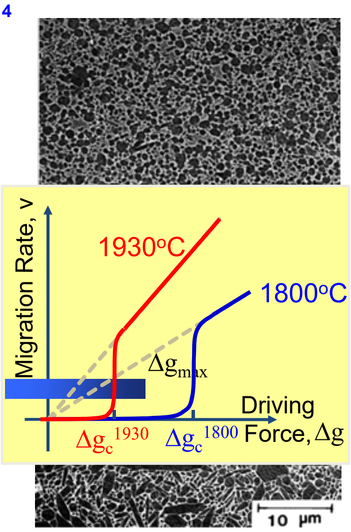
Microstructural Evolution during LPS

Effect of Temperature

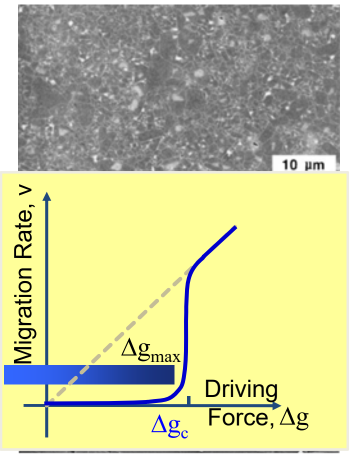
Si_3N_4



Sintered at 1930℃ for 1h in N_2

Effect of Sintering Time

SiC



hot-pressed at 2000℃ for 8 h in Ar

Si_3N_4: Mitomo *et al., J. Ceram. Soc. Jpn.*, **114**, 867 (2006).
SiC: Kim *et al., J. Eur. Ceram. Soc.*, **22**, 1031 (2002).

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))
- 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))
- 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}))
- NbC-Co (Yang *et al.,* 2012 (Dislocation))
- NbC-Co (Cho and Yoon, 2004 (T))
- NbC-Fe (Oh *et al.,* 2000 (Dopant))
- PMN-PT (Wallace *et al.,* 2002 (Dopant))
- $SrTiO_3$ (Sano *et al.,* 2007) etc.

•Effect of Δg_{max}

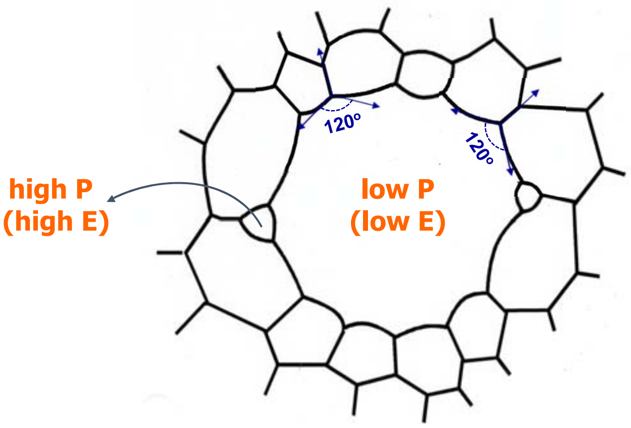
- $BaTiO_3$ (Jung *et al.,* 2003)
- WC-Co (Yang *et al.,* 2011)
- TiC-WC-Co (Yoon *et al.,* 2005)
- WC-Co (Park *et al.,* 1996)

Grain Growth in Solid-state (SSS)

GG: Increase in average grain size

Result of boundary migration

Driving Force



in 2-D

γ = const.

θ = 120°

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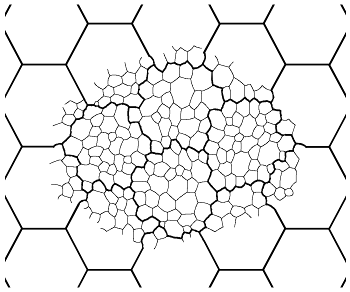
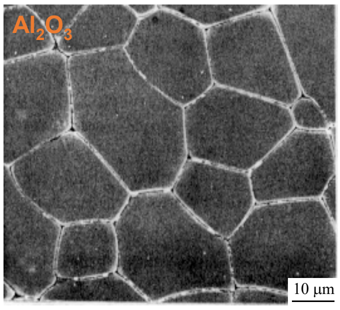
Driving Force for Grain Growth

SSS





Driving Force for the Growth of an individual Grain

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

Interaction of an individual grain with its surrounding grains (an average-sized grain) – mean field concept

atom transport across the boundary

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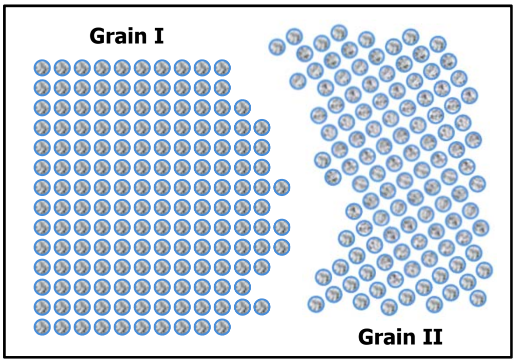
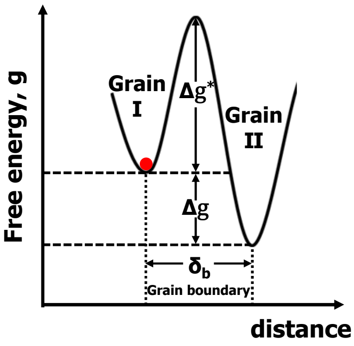
Atomic Motion in Boundary Migration

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



Random jump of atoms across the boundary



Diffusion Control :

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

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

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Classical Law of Normal Grain Growth

Mean Field Concept

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

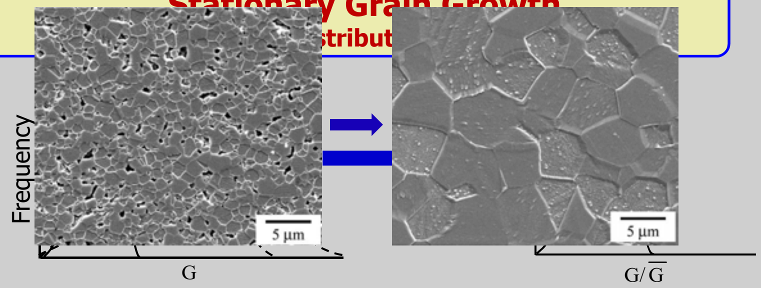
(i) Driving force $\propto \left(\frac{1}{\bar{G}} - \frac{1}{G}\right)$

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

➡ $\overline{G}^2 - \overline{G_0}^2 = kt$

Stationary Grain Growth

stribut



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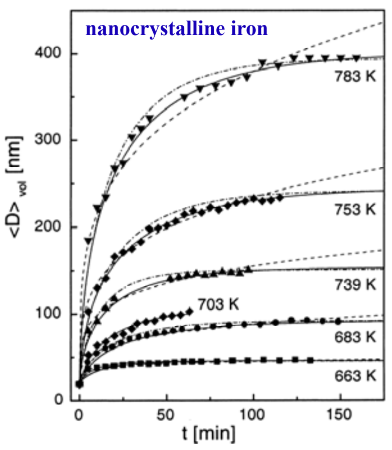
Deviation from Normal GG Behavior

Classical Understanding

NGG: Parabolic Law: G^2-G_o^2 = kt



- **Stationary grain growth**
  relative grain size distribution
  with respect to annealing time
- **Deviation from the ideal law**
  →Nonstationary grain growth
- **Suggested causes: solute, liquid film, 2nd phase particles** (pores)

Natter *et al.*, *J. Phys. Chem. B,* **104**, 2467 (2000).

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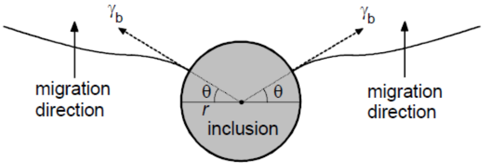
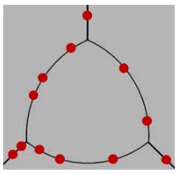
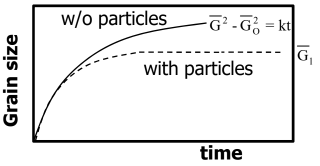
Effect of 2nd Phase Particles

Smith-Zener Effect

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







For uniform distribution of
second phase particles

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

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

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

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

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 *et al.*, *ISIJ Inter.*, **38**, 913 (1998).

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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?

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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?

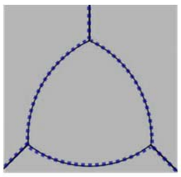
Derivation of the drag force

(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

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

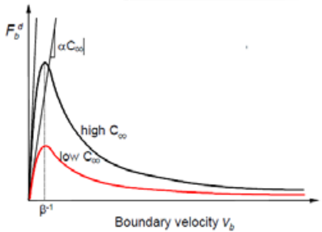
$$= -N_v\int_{-\infty}^{\infty} [C(x) - C(\infty)]\frac{\mathrm{d}E}{\mathrm{d}x}\mathrm{d}x$$



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

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)



Cahn, *Acta Metall.,* **10**, 789 (1962)

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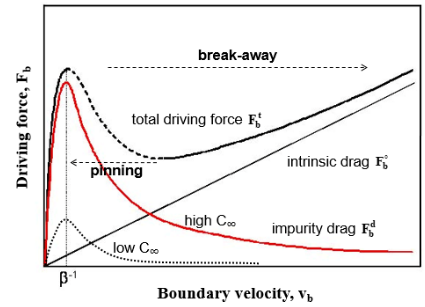
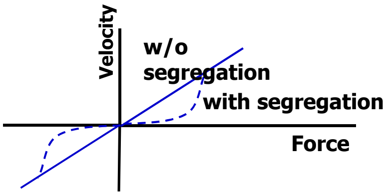
Effect of solute segregation

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)

Cahn, *Acta Metall.*, **10**, 789 (1962)

Luecke and Stuewe, in *Recovery and Recrystallization of Metals,* Himmel L. (ed) Gordon and Breach, N.Y., pp171-210 (1963)

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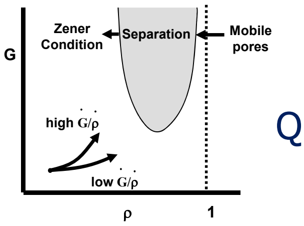
Effect of pores

Microstructure development in porous materials

under the assumption of
diffusion control of atom transport



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

A few points of consideration:

- Densification is governed by the driving force (pore size) and densification mechanism.
  Pore size varies with grain size.
- Grain growth is affected by the 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

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Mobility of an Isolated Pore

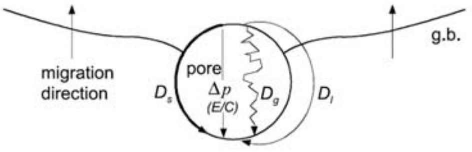

Figure II.I. Possible mechanisms of pore migration with a grain boundary.

$$v_p = M_p F_p$$

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

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

Zener drag

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

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

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Pore Migration and Grain Growth

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

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

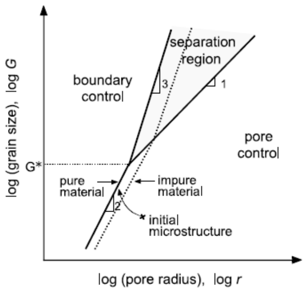
(i) Boundaries move together with pores

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

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

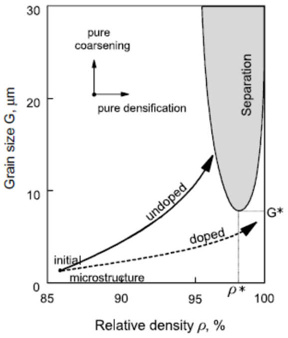
(ii) Pores are separated from boundary

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



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)

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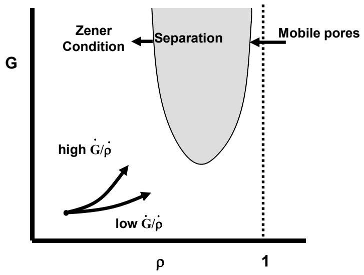
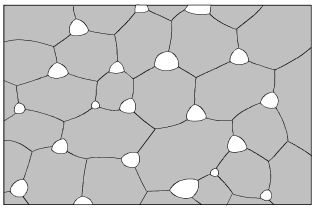
Densification and Grain Growth:

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

S.-J. L. Kang, in "*Sintering: Densification, Grain Growth and Microstructure*," Elsevier, Oxford (2005)

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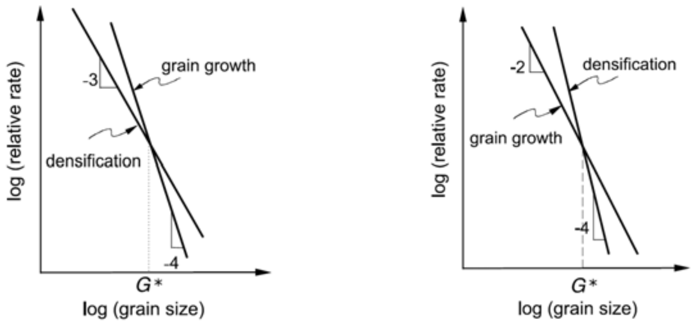
Effect of Grain (Particle) Size

Examples

Densification : lattice diffusion
Grain Growth : surface diffusion

Densification : grain boundary diffusion
Grain Growth : evaporation/condensation



Relative densification and coarsening rates vs. grain size.

S.-J. L. Kang, in "*Sintering: Densification, Grain Growth and Microstructure*, Elsevier," Oxford (2005)

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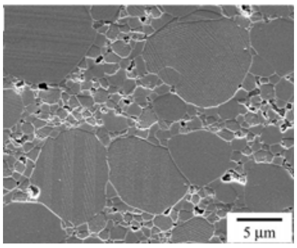
Abnormal (Exaggerated) **GG**

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) 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!

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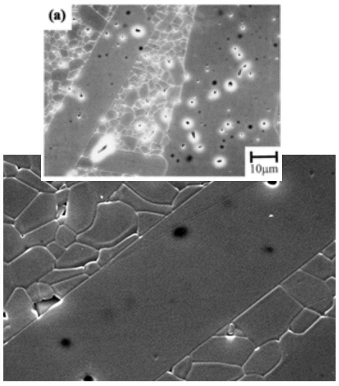
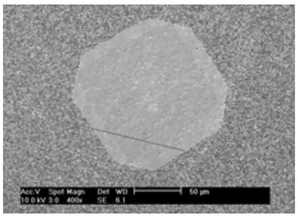
Abnormal grains and faceted boundaries

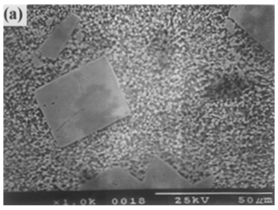
Al2O3



$BaTiO_3$



Ni



Why is the faceted shape of abnormal grains maintained during their growth?

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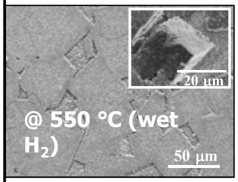
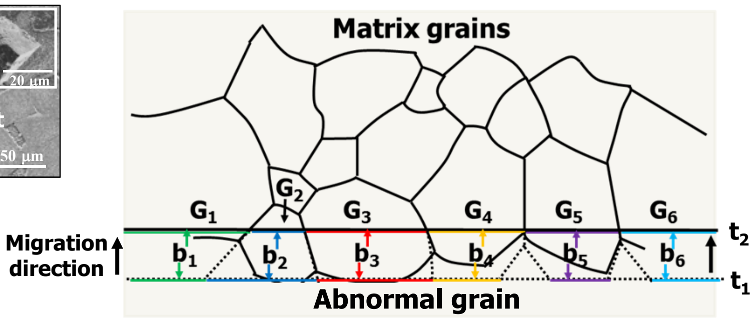
Flat Boundary Migration of Abnormal Grain





$$v_b \propto M_b \cdot \gamma_b \mathrm{K}$$

$$v_{b_1} = v_{b_2} = v_{b_3} = \cdots = v_{b_n}$$

$$M_{b_1} \neq M_{b_2} \neq M_{b_3} \neq \cdots \neq M_{b_n}$$

$$\gamma_{b_1} \neq \gamma_{b_2} \neq \gamma_{b_3} \neq \cdots \neq \gamma_{b_n}$$

v_b : boundary velocity
M_b : boundary mobility
γ_b : boundary energy
K : mean curvature

The maintenance of facet planes of AG during its growth cannot be explained by the classical boundary migration theory.

The facet plane is singular with a very deep energy cusp!

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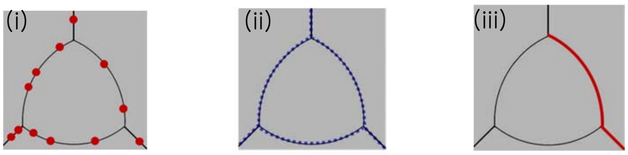
Suggested Mechanisms of AGG

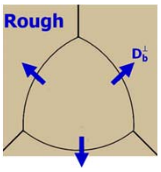
Early Mechanisms

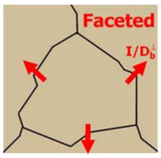


(i) Break-away of grain boundary from second phase particles (since 1950's)
(ii) Break-away of grain boundary from segregated impurities (since 1960's)
(iii) Uneven distribution of a second phase, in particular, a liquid (since 1970's)
"Complexion" hypothesis (since 2000's)
(iv) Anisotropy in boundary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

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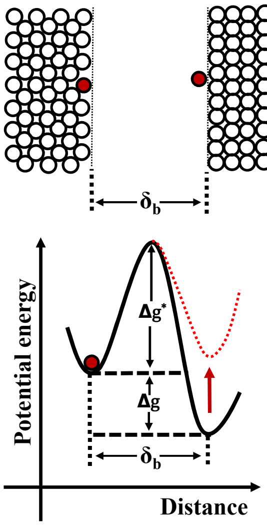
Common Feature in the Previous Models and Mechanisms

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).

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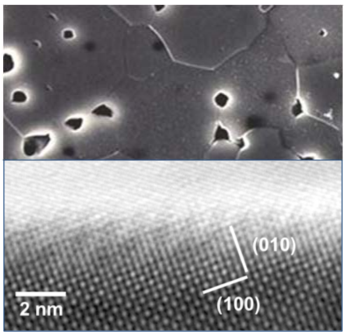
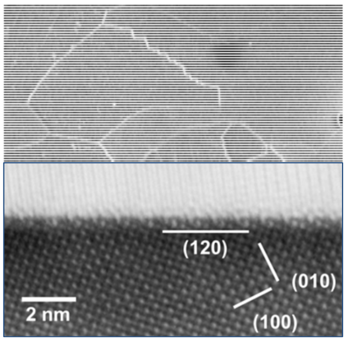
Two Types of Grain Boundaries

Rough (atomically disordered)



Ti-excess BaTiO$_3$ in H$_2$

Faceted (atomically ordered)



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).

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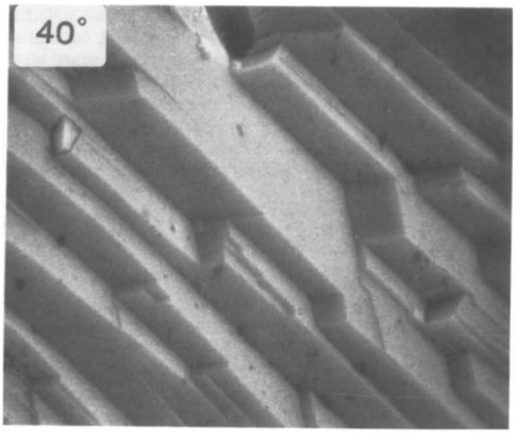
Faceted Grain Boundary in Cu-0.03Bi



Themelis *et al.*, Materials Charaterization, **24**, 27 (1990)

Faceted grain boundaries have been observed since 1950's.

eg) G. Henry, J. Plateau, X. Wache, M. Gerber, I. Behar, and C. Crussard,
Memoires Scientifiques Rev. Metallurg., **56**, 417 (1959). (Ni grain boundary)

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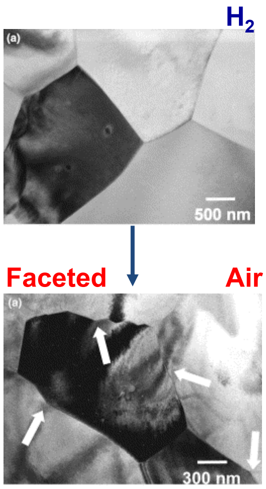
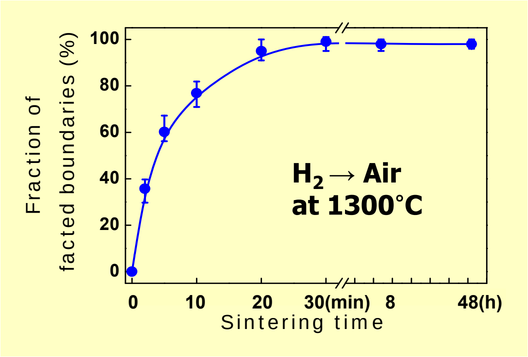
Grain Boundary Structural Transition

$BaTiO_3$



Boundary Structural Transition during Sintering



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

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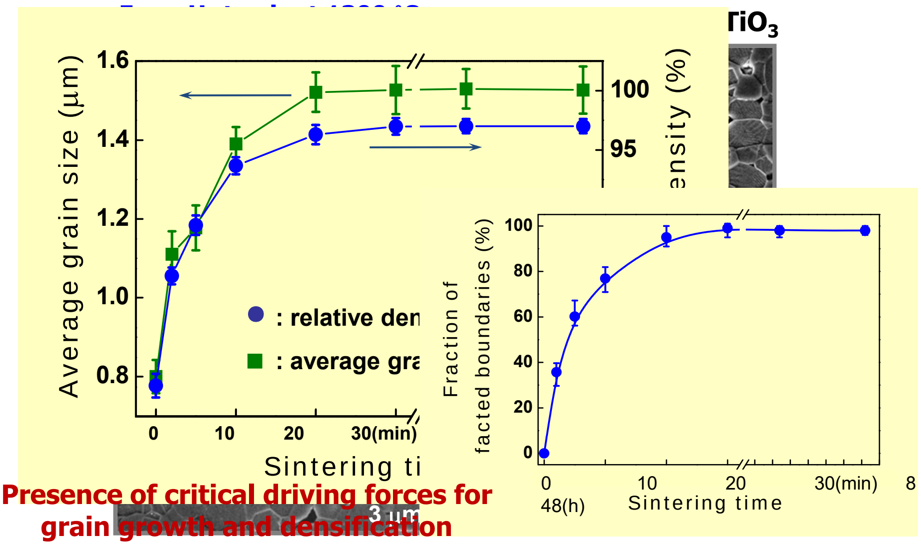
Effect of Boundary Structure on Densification and Grain Growth



Presence of critical driving forces for grain growth and densification

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

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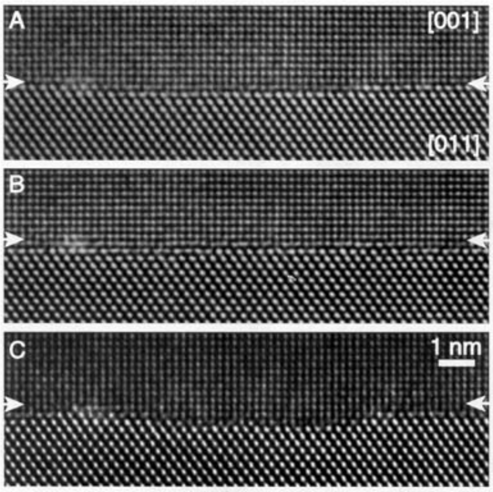
Migration Mechanism of Faceted Boundary

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



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

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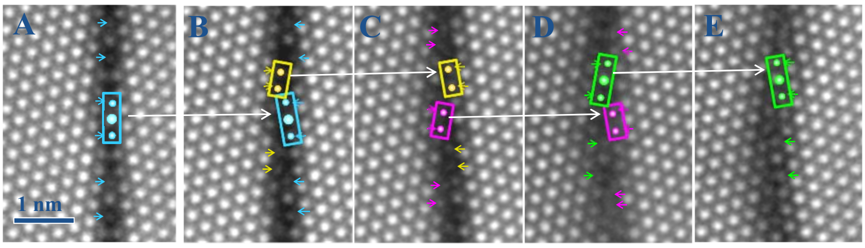
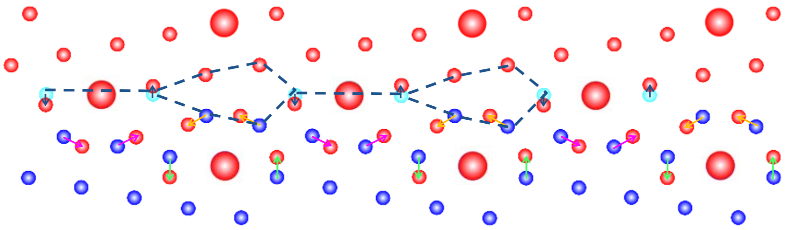
Migration Mechanism of ∑7 α-Al_2O_3 Boundary





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

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

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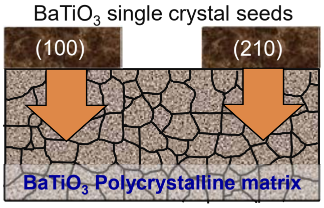
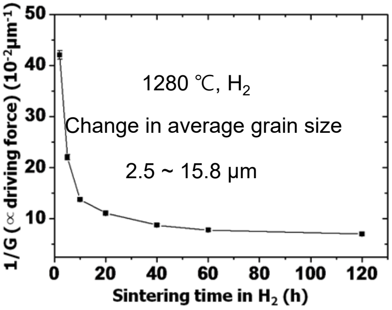
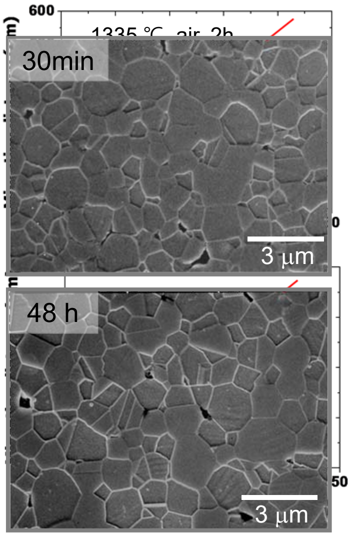
Migration Behavior of Faceted Boundary



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





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

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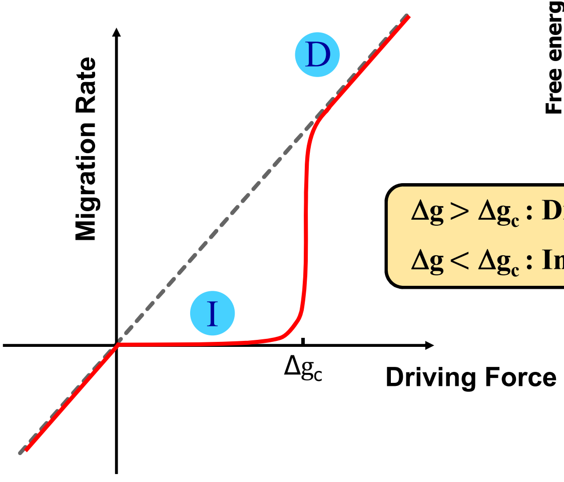
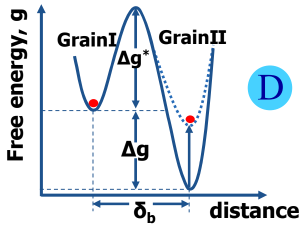
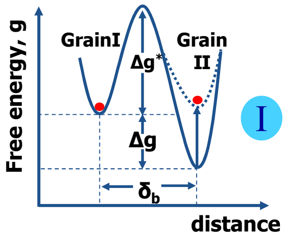
Mixed Control of Boundary Migration





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

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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

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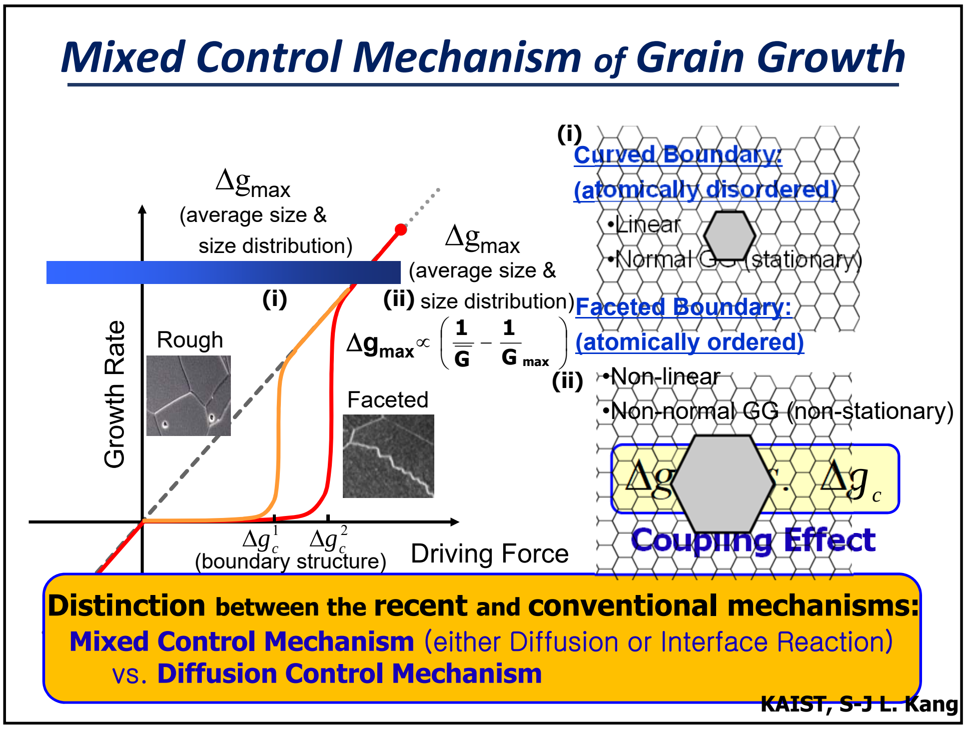

Mixed Control Mechanism of Grain Growth

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

- Linear
- Normal GG (stationary)

Faceted Boundary: (atomically ordered)

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

Δg_{max} vs. Δg_c

Coupling Effect

Distinction between the recent and conventional mechanisms:
Mixed Control Mechanism (either Diffusion or Interface Reaction)
vs. **Diffusion Control Mechanism**

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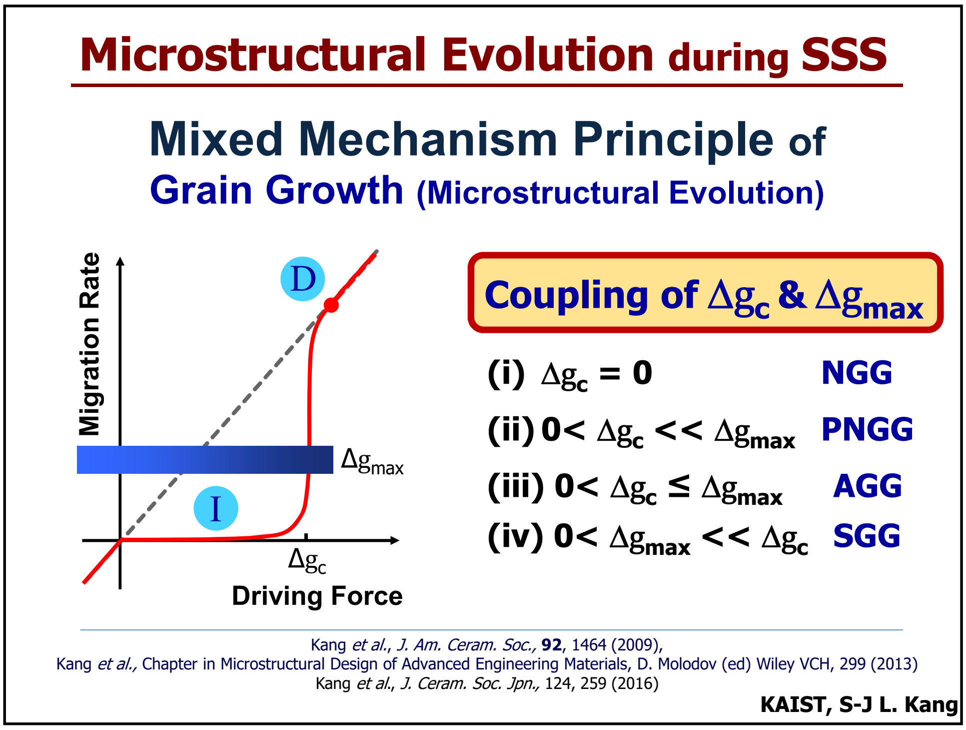

Microstructural Evolution during SSS

Mixed Mechanism Principle of Grain Growth (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)

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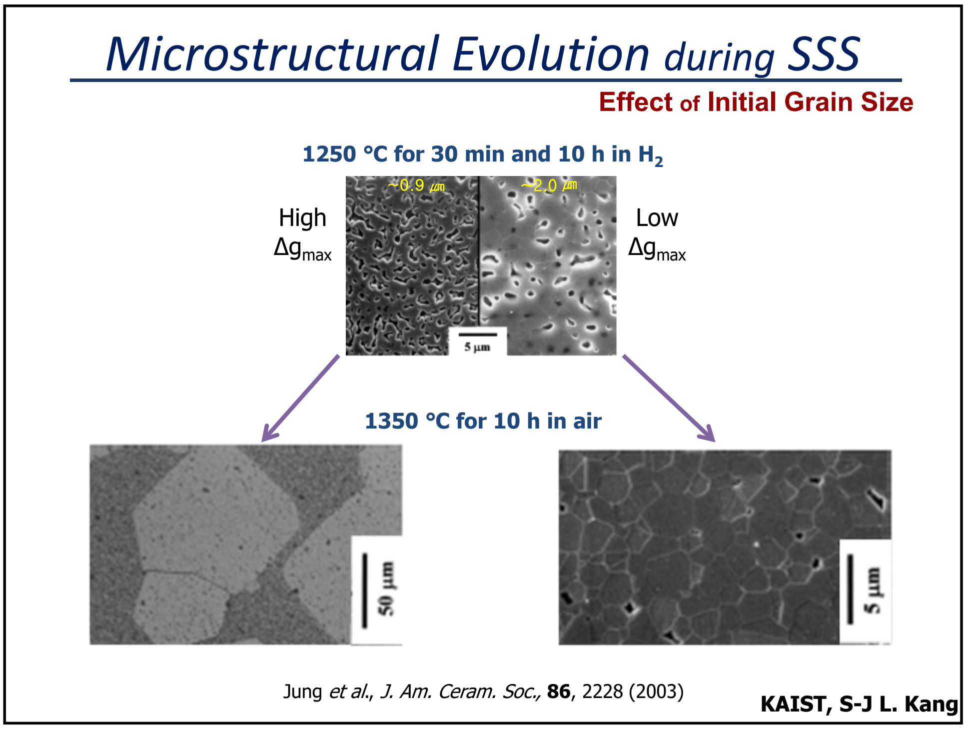

Microstructural Evolution during SSS

Effect of Initial Grain Size

1250 °C for 30 min and 10 h in H_2

1350 °C for 10 h in air

Jung *et al*., *J. Am. Ceram. Soc.*, **86**, 2228 (2003)

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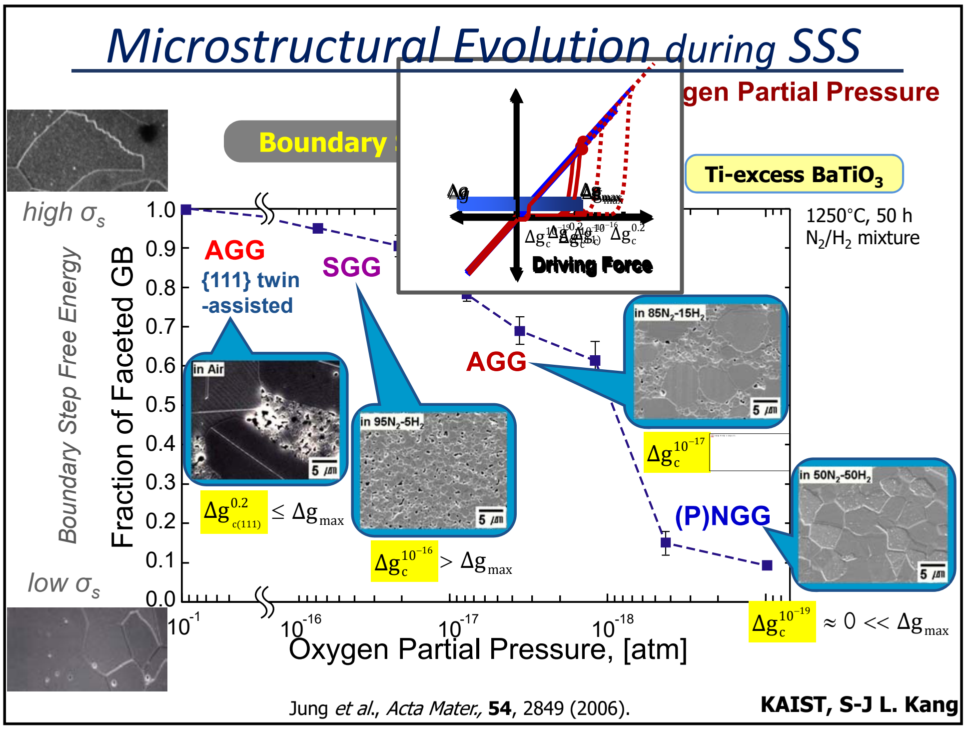

Microstructural Evolution during SSS

gen Partial Pressure

Boundary

Ti-excess $BaTiO_3$

1250°C, 50 h
N_2/H_2 mixture

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

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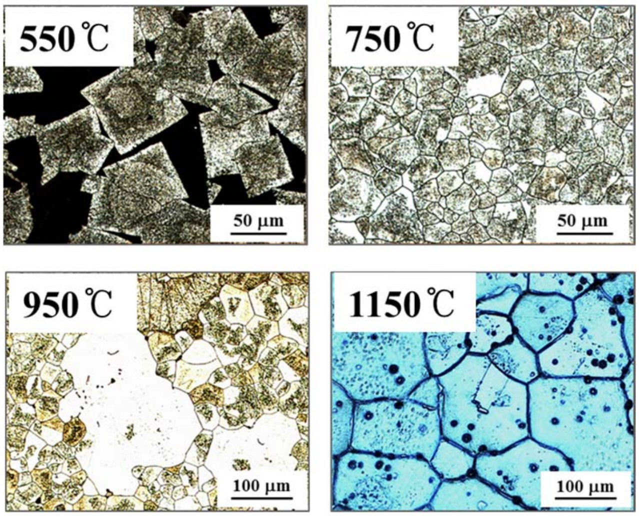
Microstructural Evolution during SSS

Effect of Temperature

UFG Ni sintered for 1 h at various temperatures



Primary AGG

2ndary SGG

2ndary AGG

P-NGG

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

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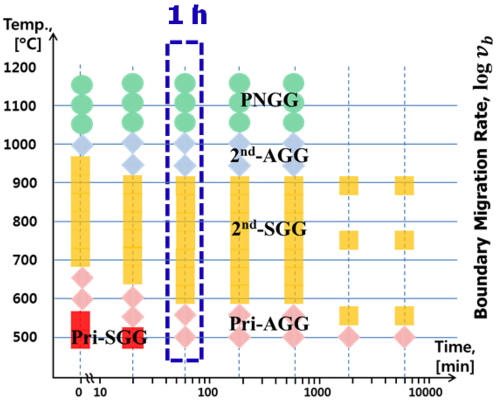
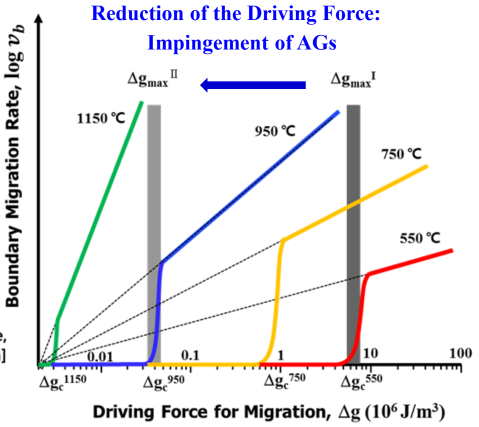
Microstructural Evolution during SSS

Effect of Temperature

Grain Growth Behavior in UFG Ni with T



Sintered for 1 h at each temperature



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

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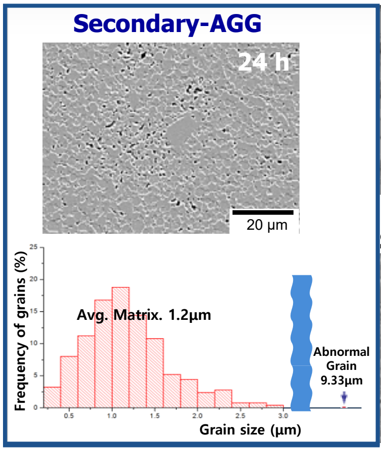
Microstructural Evolution during SSS

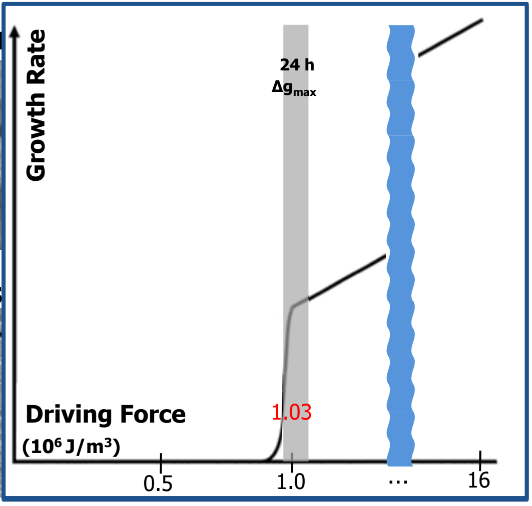
Effect of Sintering Time

Grain Growth Behavior in $BaTiO_3$ (50nm)

Sintered at 1250°C in $95N_2$-$5H_2$ (Po_2~10^{-11} atm)

Initial powder (50nm)





Kang *et al., Ceram. Int.,* **50**, 37441 (2024)

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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}); Lee *et al.,* 2013 (Dislocation); Kang *et al.,* 2024 (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 and Kang, 2016 (T); Jeon *et al.,* 2020 (Dopant))
  - 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 and Δg_{max}**
  - $BaTiO_3$ (Jung *et al.,* 2003; Yang *et al.,* 2006; An *et al.,* 2012)
  - $Na_{1/2}Ba_{1/2}TiO_3$-$BaTiO_3$ (Ko and Kang, 2016)

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Application Example of the Principle

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

Conventional Methods of Single Crystal Fabrication

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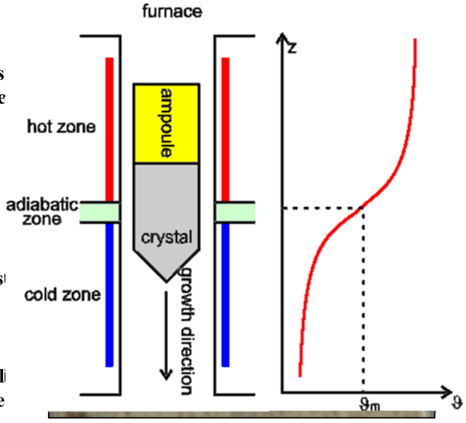
Matrix (Sinte

Czockralski Method



Bridgman Method

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

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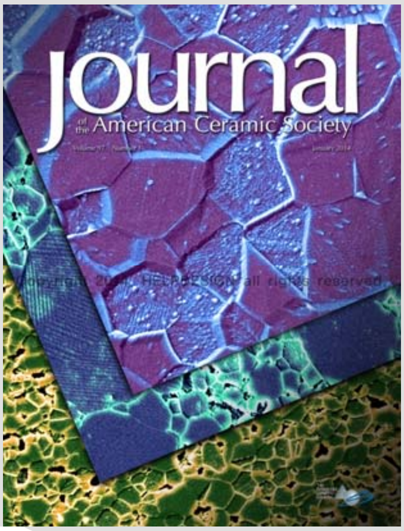
Application Example of the Principle



journal

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

Suk-Joong L. Kang, Ji-Hoon Park, Seok-Young Ko and Ho-Yong Lee

Feature

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

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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

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Exercises:

- Growth of a rectangular cuboid-shaped single crystal of which the equilibrium shape is a cube.
- 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
- AGG
  - Effects of particle size and temperature
- Bi-layer sample of single crystal/polycrystal
  - Driving force for single crystal growth as a function of grain size
  - Migration distance of the single crystal as a function of grain size for a fixed annealing time

S.-J. L. Kang, "Problems and solutions in sintering science and technology", KAIST (2024)

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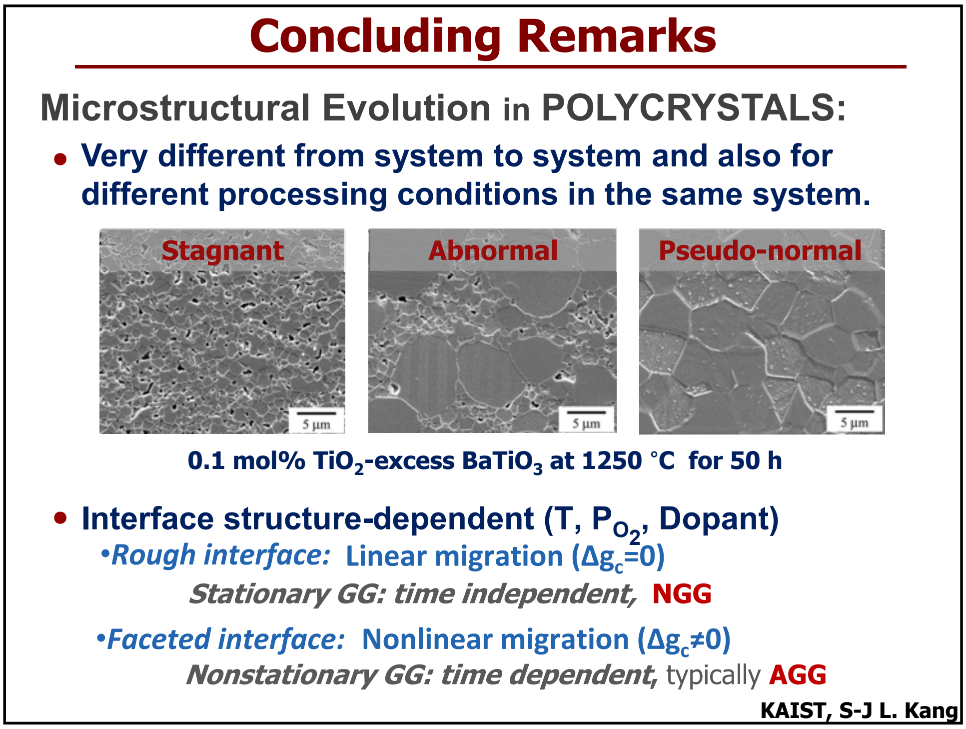

Concluding Remarks

Microstructural Evolution in POLYCRYSTALS:

- Very different from system to system and also for different processing conditions in the same system.

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

- Interface structure-dependent (T, P_{O_2}, Dopant)
  - *Rough interface:* Linear migration ($\Delta g_c=0$)
    - ***Stationary GG: time independent,*** **NGG**
  - *Faceted interface:* Nonlinear migration ($\Delta g_c \neq 0$)
    - ***Nonstationary GG: time dependent,*** typically **AGG**

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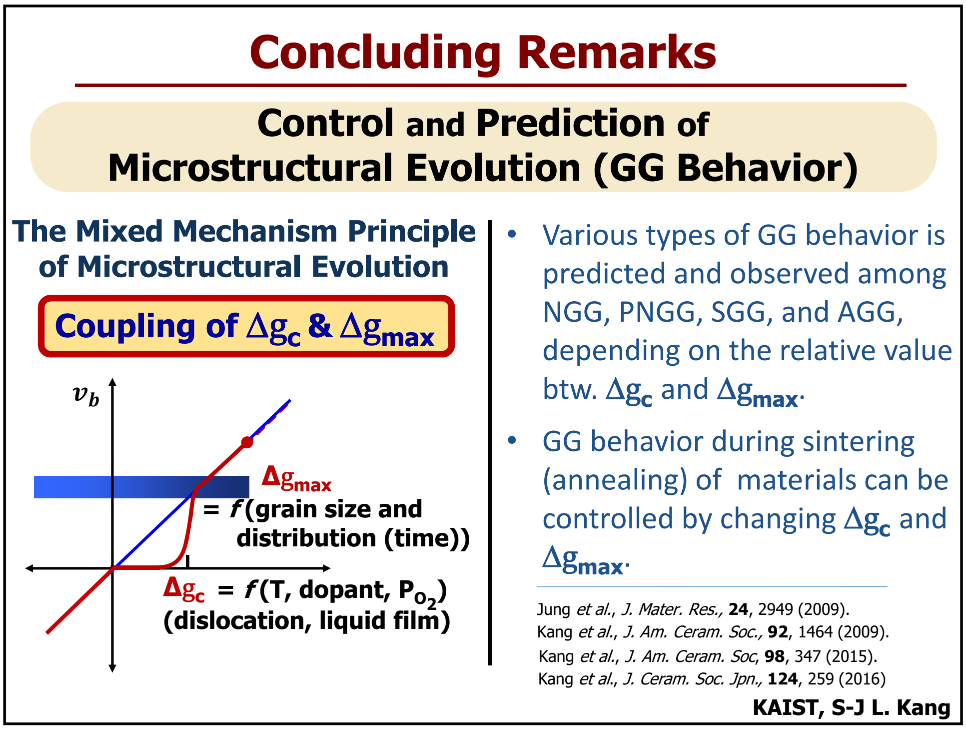

Concluding Remarks

Control 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, depending on the relative value btw. Δg_c and Δg_{max}.
- GG behavior during sintering (annealing) of materials can be controlled by changing Δg_c and Δg_{max}.

Jung *et al.*, *J. Mater. Res.*, **24**, 2949 (2009).
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)

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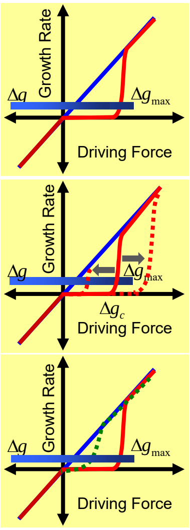
Strategies for Suppressing AGG

- **Reduction of sintering time:** use of incubated AGG behavior
  Yang and Kang, *Inter. J. Refract. Met. Hard Mater.*, **27**, 90 (2009).
  Kang *et al.*, *Ceram. Int.*, **50**, 37441 (2024).
- **Reduction of $\Delta g_{\max}$ for a fixed Δg_c**
  - Use of coarse powder
    Jung *et al.*, *J. Am. Ceram. Soc.*, **86**, 2228 (2003)
    Yoon *et al.*, *Acta Mater.*, **53**, 4677 (2005).
  - Two-step sintering (High + Low)
    Yang et al., *J. Am. Ceram. Soc.*, **94**, 1019 (2011).
    Ko and Kang, *J. Eu. Ceram. Soc.*, **36**, 1159 (2016).
- **Change in Δg_c for a fixed $\Delta g_{\max}$**
  - Doping effect
    Chung *et al.*, *Acta mater.*, **50**, 3361 (2002).
    An and Kang, *Acta mater.*, **59** 1964 (2011).
  - Temperature effect
    Cho and Yoon, *J. Am. Ceram. Soc.*, **87**, 443 (2004).
    Jung *et al.*, *Acta Mater.*, **69**, 283 (2014)
  - Atmosphere (P_{O_2}) effect
    Jung *et al.*, *Acta Mater.*, **54**, 2849 (2006).
    Heo *et al.*, *J. Eu. Ceram. Soc.*, **31**, 755 (2011).
- **Change in growth mechanism**
  (from 2DNG to defect-assisted growth)
  Yang *et al.*, *J. Ceram. Soc. Japan* **120**, 467 (2012).

VC in WC-Co
B in NbC-Co



Fisher and Kang, *J. Am. Ceram. Soc.*, **102**, 717 (2019).

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Potential Research Subjects in Sintering S&T

• Effect of boundary structure on boundary kinetics and sintering

- **Observation and Model/Theory of atomistic motion along and across the boundary in faceted systems**
  eg) Wei J, et al., Nat Mater. 20, 951 (2021).
- **Densification (experimental observation and theory development) with respect to the boundary structure**
  eg) Lee MG, et al., Acta Mater., 59, 692 (2011).
  Dillon SJ, et al., Acta Mater., 242, 118448 (2023).
- **Calculation/simulation of grain growth (microstructural evolution) in faceted systems**
  eg) Jung YI, et al., J. Mater. Res., 24, 2249 (2009).
  Chen K, et al., Acta Mater., 167, 241 (2019)
  Hu J, et al., J. Materiomics, 7, 1007 (2021).
  Kang SJL and Fisher JG, Open Ceramics, 16, 100484 (2023)
- **Further experimental and theoretical studies on the effects of other parameters, such as second phase particles and defects, in faceted systems**
  eg) Lee MG, et al., J. Asian Ceram. Soc., 1, 95 (2013)

Potential Research Subjects in Sintering S&T

- **Development of (new) sintering and other processing techniques**
  - Two-step sintering
  - Spark plasma sintering (Electric field-assisted sintering)
  - Solid-state conversion of single crystals

    Application of these techniques in commercial production
- **Effect of boundary structure on materials properties and processing**
  - Diffusion and Related Phenomena
    - Grain boundary diffusion
    - Sintering (densification)
    - Creep eg) Dillon SJ, et al., Acta Mater., 246, 118718 (2023).
  - Physical properties of materials with microstructural evolution

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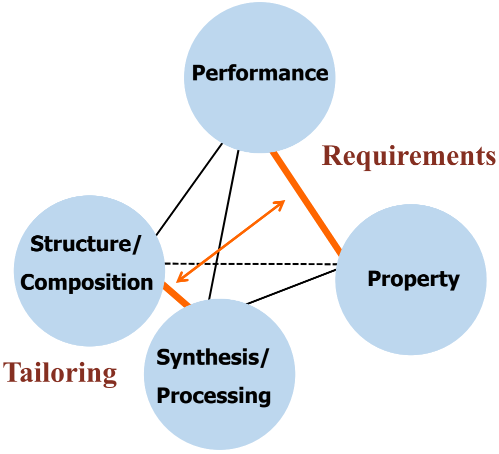
Bordia, Kang, and Olevsky, *J. Am. Ceram. Soc.*, **100**, 2314-2352 (2017).
Kang and Fisher, Open Ceramics, 16, 100484 (2023)

Final Remarks

Four Basic Elements of MSE



Materials Design and Tailoring

Microstructure Tailoring:
Control of
Grain Growth

The Principle of Microstructural Evolution

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Final Remarks

In only one sentence, what statement would contain the most information of our scientific knowledge?

"All things are made of Atoms."

- Richard Feynman -

In two sentences? The second one would be:

"The arrangement of Atoms governs the properties of All things."

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