Effective Diffusion Distance for Aggregated Nanocrytalline Zirconia Ceramic Powders During Sintering

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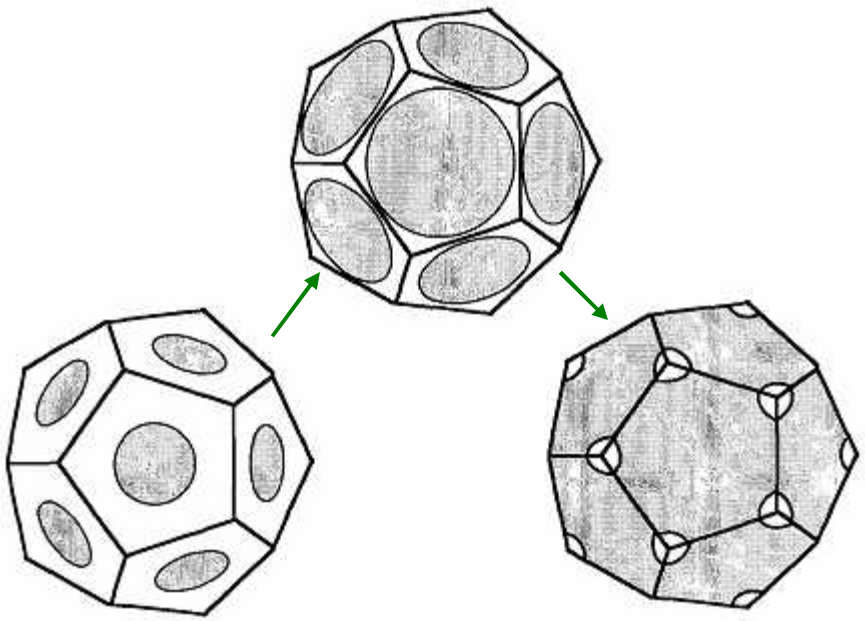
Outline

- Introduction
  - *Traditional Models*
  - *Aggregated Particles*
- Experiments
- Results
- Introduce of a New Effective Diffusion Distance
- Summary

Traditional Models

- Traditional models: a grain and its associated porosity, at each stage of sintering (after DeHoff).



- Relationships between densification rate and grain size.

* $$\frac{\dot{\rho}}{\rho} = \frac{3\gamma\Omega}{kT}\left(\frac{\Gamma_v D_v}{G^3} + \frac{\Gamma_b \delta D_b}{G^4}\right)$$

- Expected relationships for different mechanisms: (From Coble)

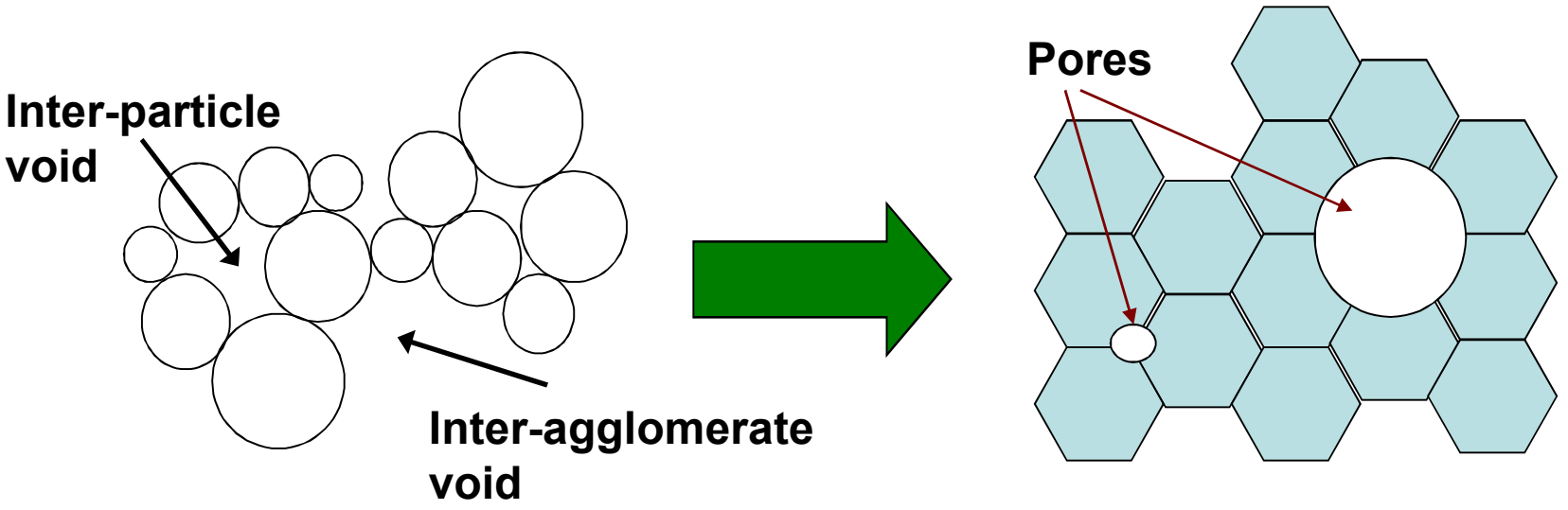
Grain Boundary Diffusion $\Rightarrow \frac{\dot{\rho}}{\rho} \propto \frac{1}{G^4}$

Volume Diffusion $\Rightarrow \frac{\dot{\rho}}{\rho} \propto \frac{1}{G^3}$

*:J. D. Hansen, etl, *J. Am. Ceram. Soc.*, **75** 1129-35 (1992).

Aggregated Particles

- The use of flocculated and aggregated particles in 3D printing: non-ideal distribution of pores



- Microstructure is different from the traditional model structure

? $\frac{\dot{\rho}}{\rho} \propto \frac{1}{G^4}$ or $\frac{\dot{\rho}}{\rho} \propto \frac{1}{G^3}$?

Experimental Procedures

ZrO_2-3mol%Y_2O_3 powders (300 nm aggregated particles by 28 nm crystallites)

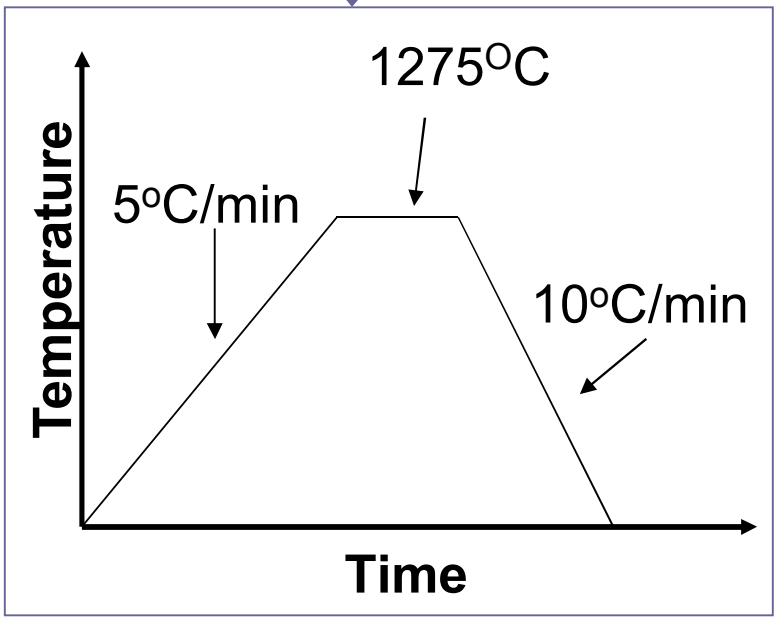
Uniaxial Pressing

(51 MPa)

Green bodies (0.446)

Isothermal Sintering

(6 samples were held for 0.1, 0.5, 1, 5, 10 and 50 hours respectively)



Zirconia Ceramics

Collect density data

Section and Polish

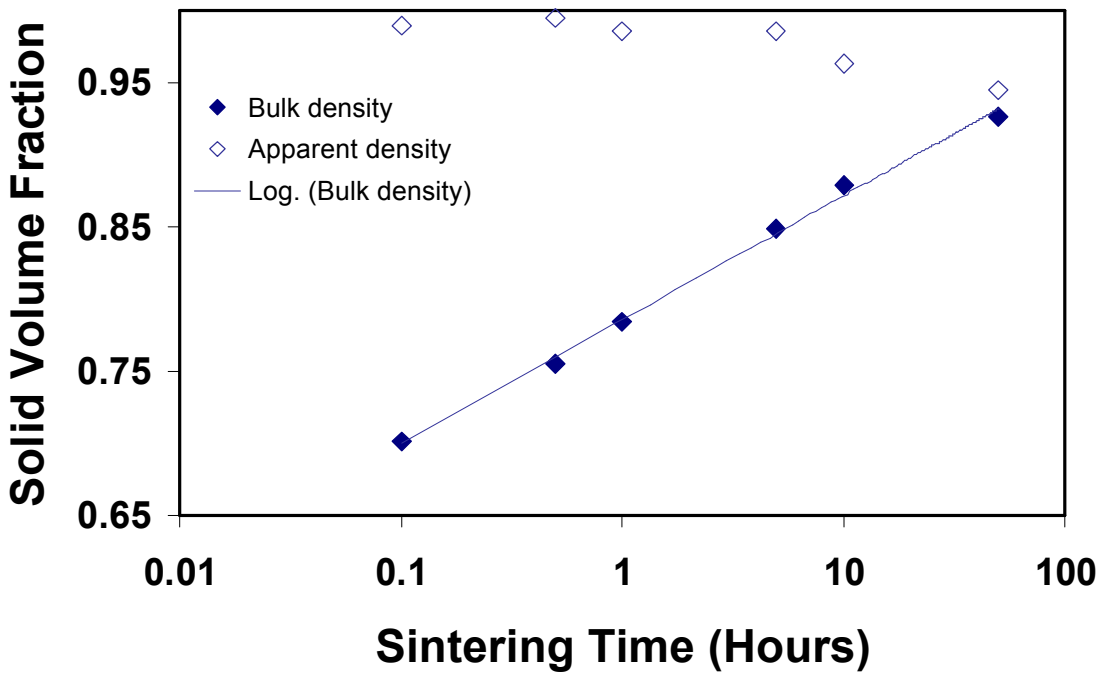
Collect surface features by SEM

Densification Results

- 50% of pore volume removed after 0.1 hr

→ Intermediate stage sintering

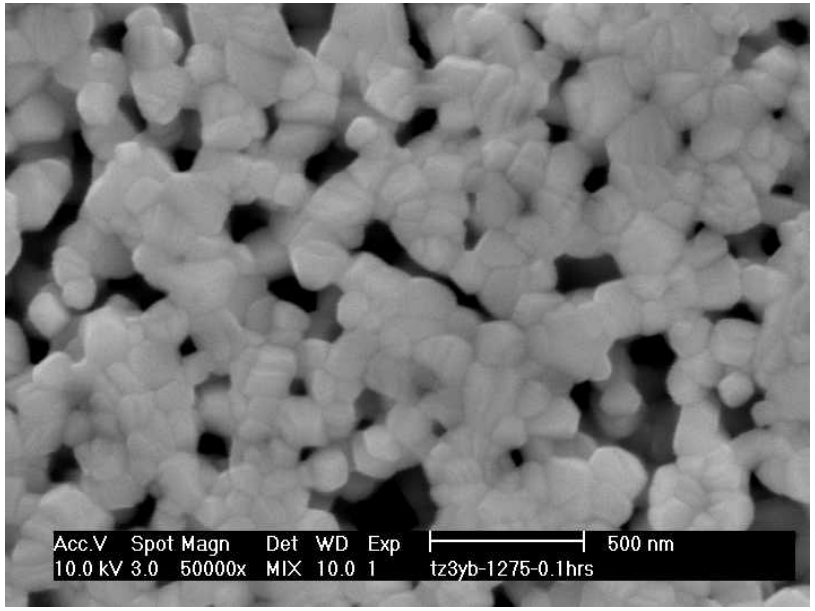
- Pores close when SVF approach about 0.96
- Semi-log dependence of SVF on sintering time



$$\rho = 0.7863 + 0.0389\mathrm{Ln}(t),$$

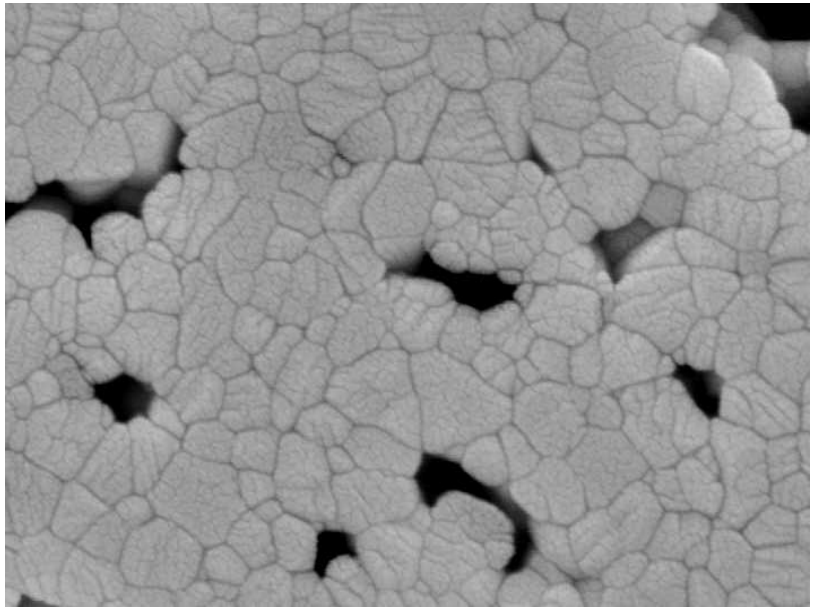
Microstructure

Zirconia-- 0.1 hours



500 nm

Zirconia -- 5 hours



500 nm

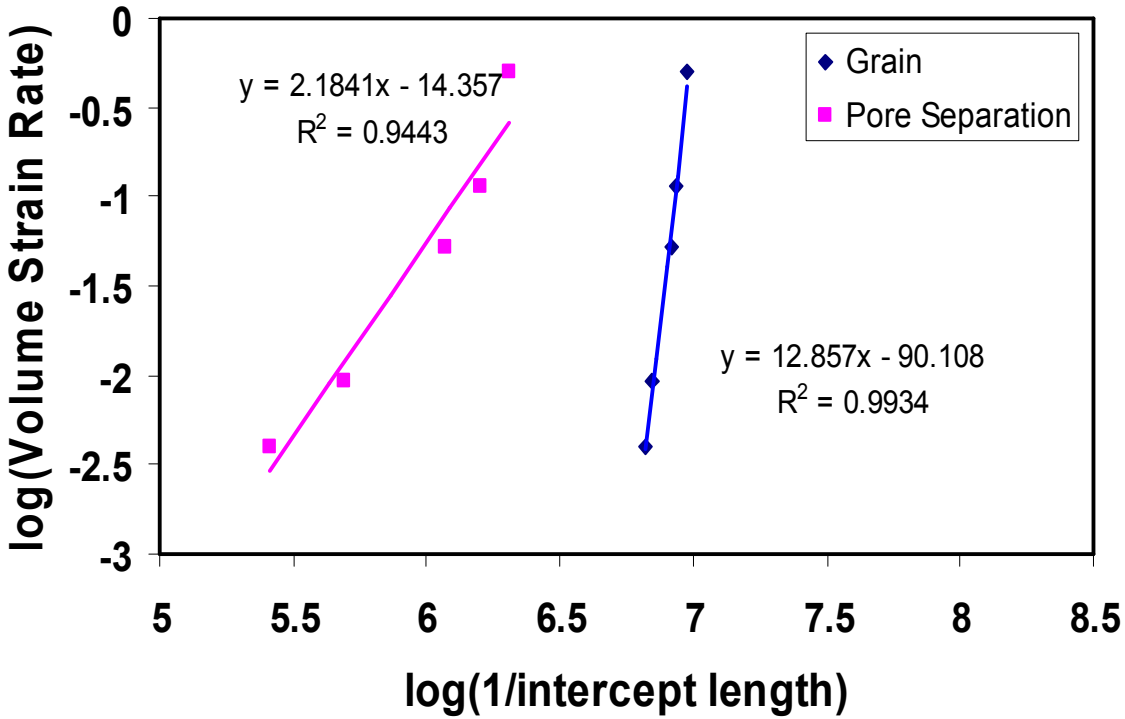
- Non-ideal structure
- Multiple grains between pores
- Pore elimination occurs during sintering

? $\frac{\dot{\rho}}{\rho} \propto \frac{1}{G^4}$ or $\frac{\dot{\rho}}{\rho} \propto \frac{1}{G^3}$?

Results of Intercept Length

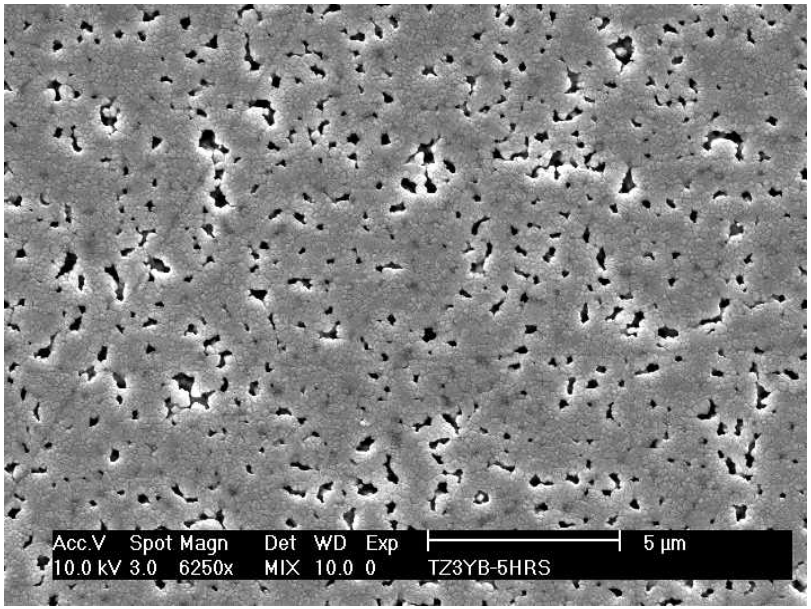
- Grain size exponent is 12.9
- Exponent for pore separation is 2.2
- Inter pore distance can better scale the diffusion length than grain size
- Power law relationship does not fit the data well for pore separation, perhaps due to change in microstructure geometry

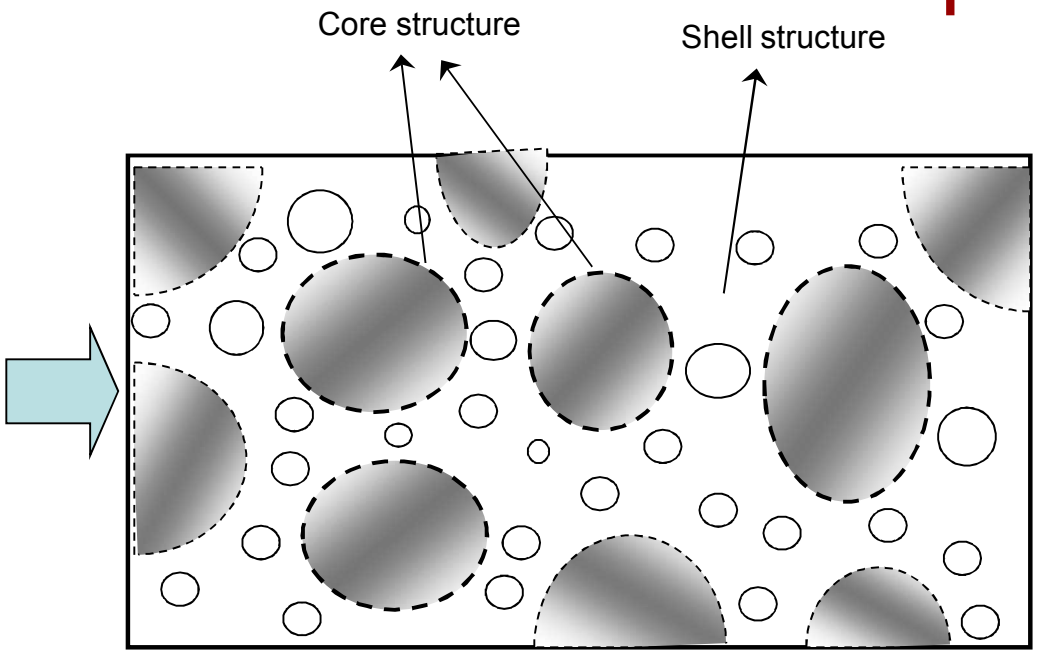
Plot of log volume strain rate against log inverse intercept length



Microstructure Analyses

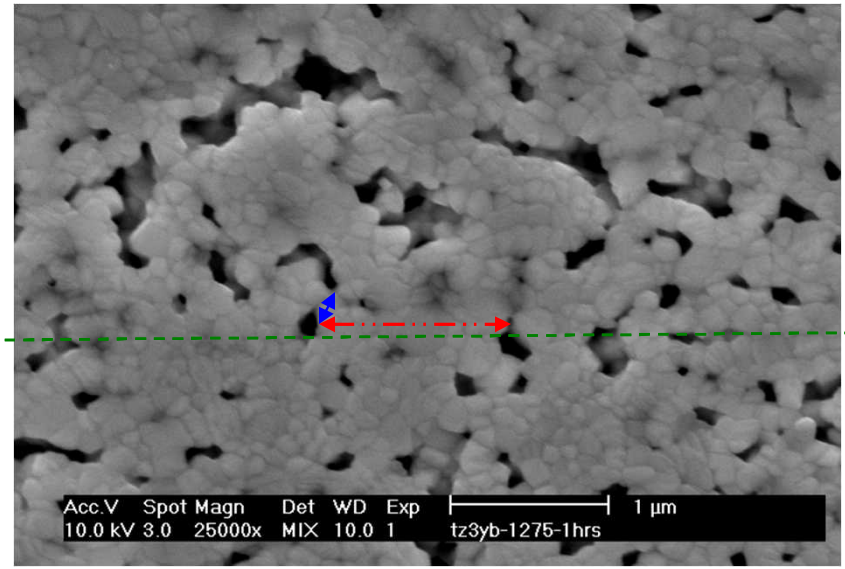
Zirconia– 5 hours

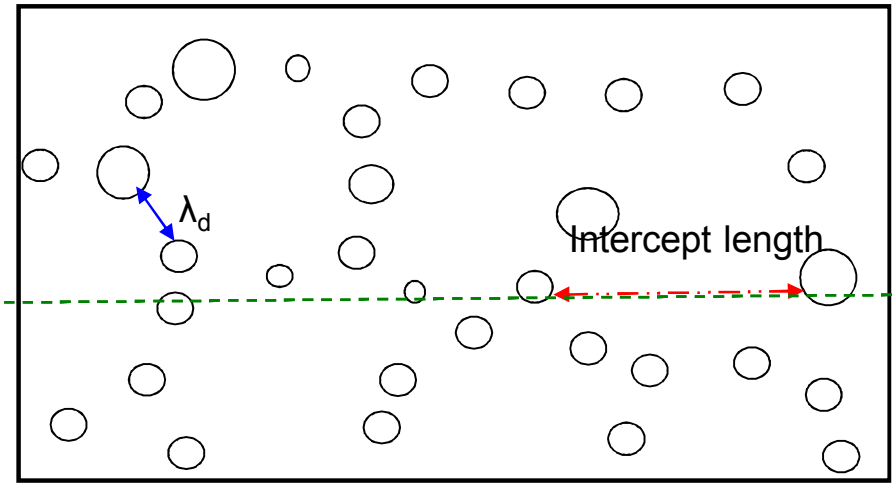




- The pores in this material showed a non-random arrangement. Pores appear to reside more at the boundaries of dense regions containing many grains
- “Core” and “shell” structures

Diffusion Shortcuts





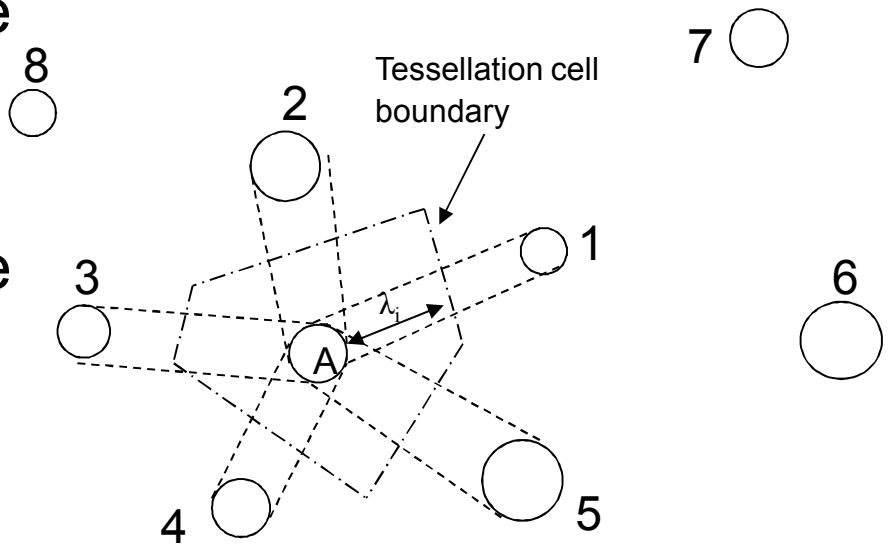
: Intercept length :Diffusion shortcuts

- The flux equation: $J=k(\Delta c)/\lambda$. Longer distance, less mass transferred in limited time
- The intercept length overestimated the diffusion distance in aggregated structure
- Comparison of pore separation and diffusion shortcut

Effective Diffusion Distance

- Flux from the area between pore A and pore 1:

$$J_1 = kc / \lambda_1$$



- Flux from the area between pore A and pore 2:

$$J_2 = kc / \lambda_2$$

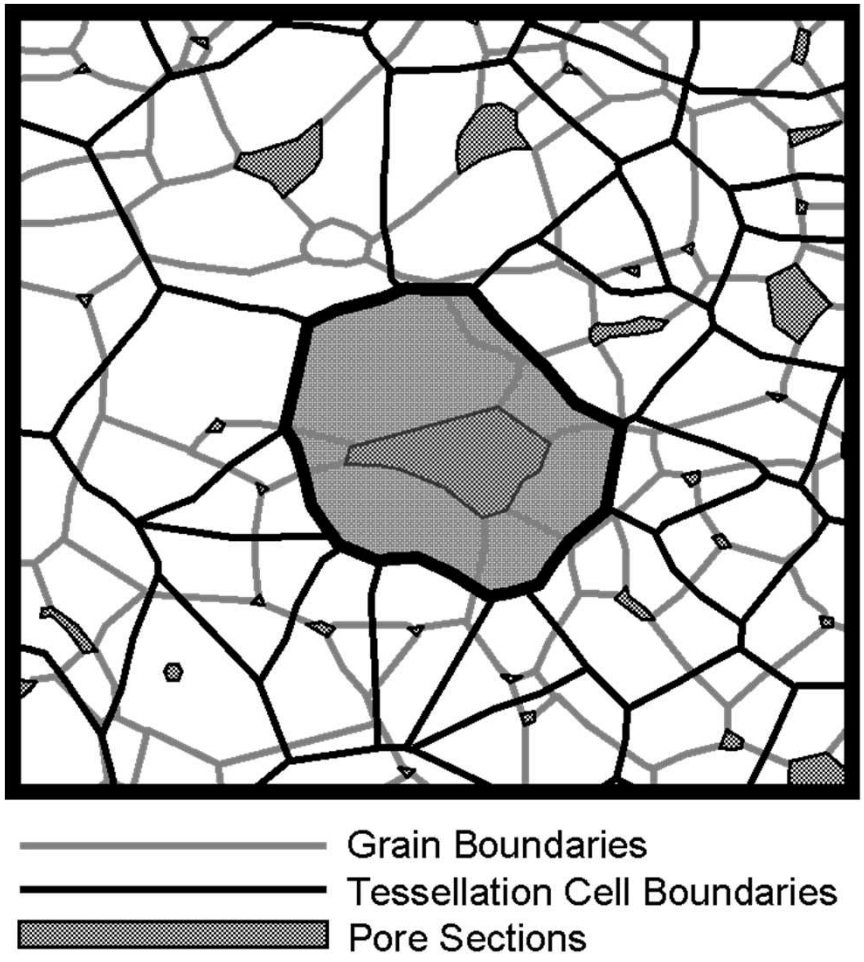
- Flux from areas between pore A and all nearest neighboring pores:

$$J = J_1 + J_2 + \ldots = kc(1/\lambda_1 + 1/\lambda_2 + \ldots) = kc/\lambda_d$$

$$\lambda_d = n/(\sum_i \frac{1}{\lambda_i})$$

- Only the pores in tessellation cells share a boundary with the centering pore A are considered here

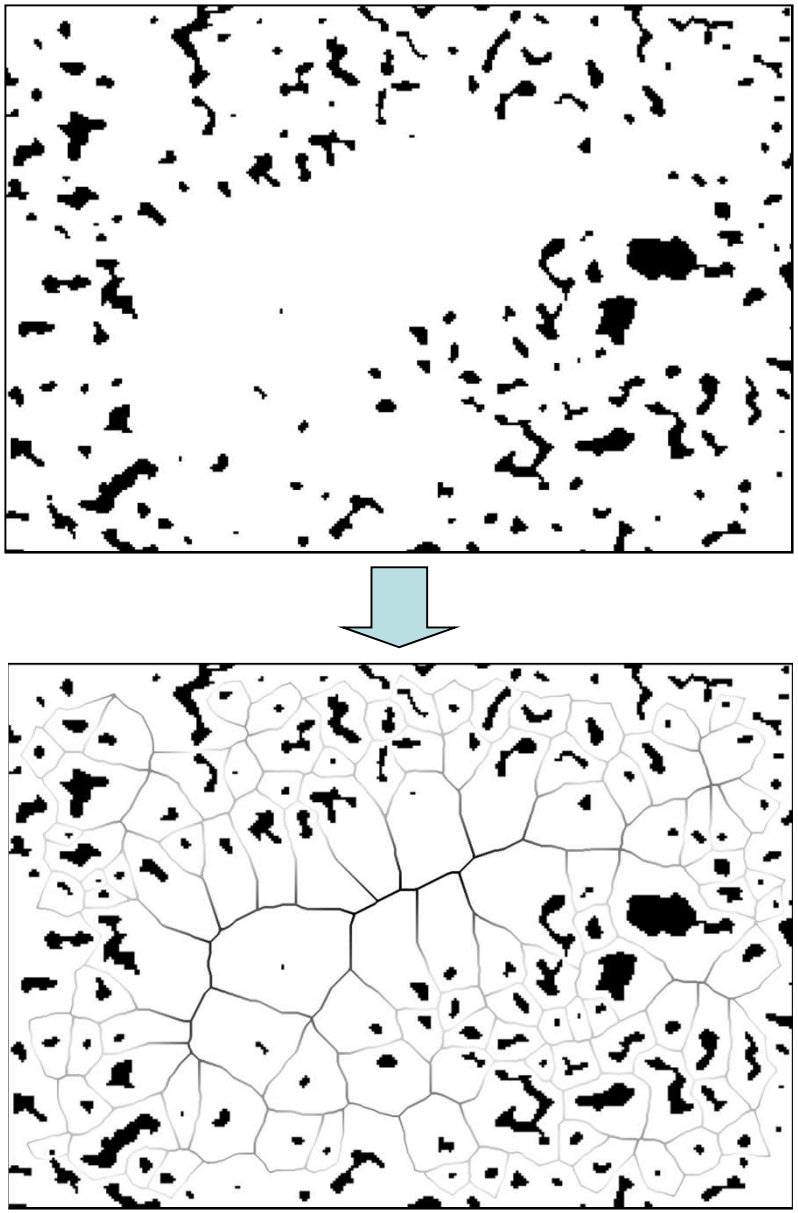
Tessellation



- Similar to construction of a Voronoi polyhedron outside of pore boundaries in two dimensions.
- A tessellation cell contain a pore and fractions of the surrounding grains.
- Tessellation always gives a unique segmentation of the microstructure.
- Sensitive to local arrangements of grains around the pore.

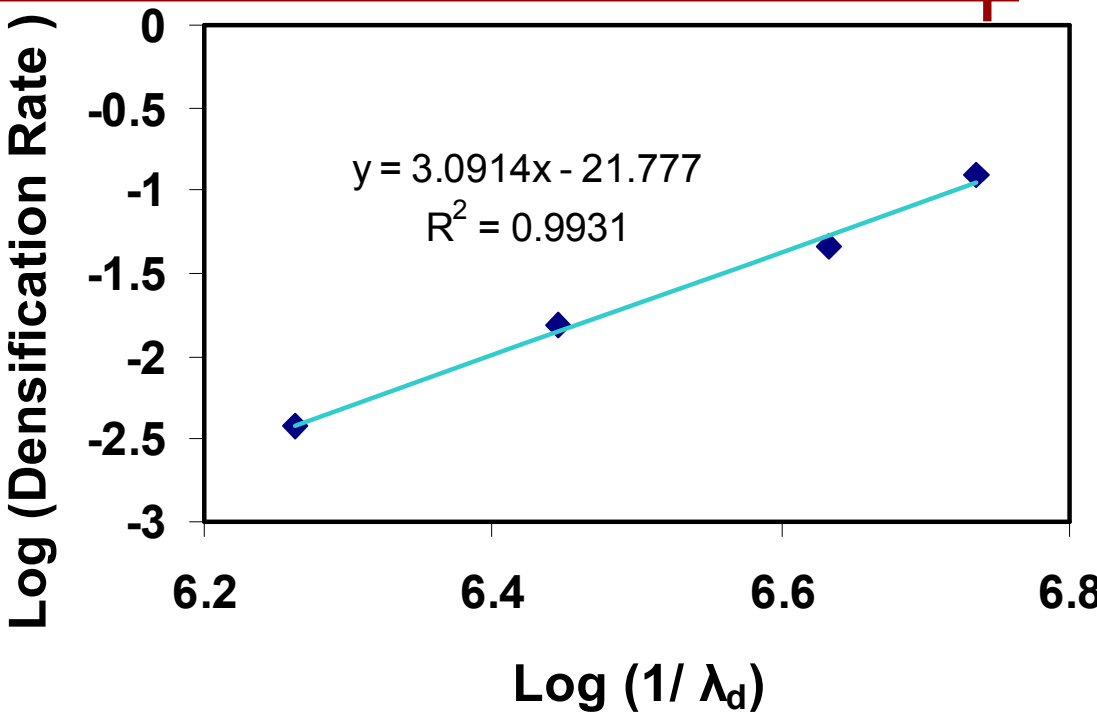
Diffusion Distance Map

- Process SEM images into binary pore images.
- Distance map with the tessellation cell boundaries obtained from pore images.
- The tessellation cell boundaries fall at the maximum distance from all pores.
- The grey scale of cell boundaries represent the distance between the pores. The dark, the further.



Diffusion Distance Fit

- A λ_{di} is calculated for each tessellation cell, then the average value of λd is calculated for all cells in the all images of one single sample
- The exponent value is 3.



- Previous study * show this zirconia ceramic is densify by grain boundary diffusion
- Many possible diffusion path across multiple grains between two pores, the exponent may not present diffusion mechanism

*: J. Kanters, etl, *Advanced Engineering Materials*, **3** 158-162 (2001)

Summary

- Sintering of aggregated nanocrystallines ceramic powders results in non-ideal microstructure
- For these ceramics with multiple grains between pores, inter-pore distance can scale the diffusion distance better than grain size
- The average inter-pore intercept length based on the stereologhical definition of pore separation would be an overestimation for diffusion distance in aggregated structures
- A good fitting relationship between densification rate and the new parameter λ_d is found, suggests λ_d may allow simple one dimensional flux model to be used to analyze ceramics structure which is sensitive to the arrangement of pores


Thankyou!

Grain Scale Measurements

- A few stereological parameters are available to test the geometry of sintering models.

$$S_v^{ss} = 2P_L^{ss} \qquad S_v^{sv} = 2P_L^{sv}$$

$$\lambda_g = 4V_v^s / (2S_v^{ss} + S_v^{sv}) \qquad \lambda_p = 4(1 - V_v^s) / S_v^{sv}$$

$$\Psi = S_v^{ss} / S_v^{sv} \qquad S^{ss} = S_v^{ss} / S_v^{ss} + S_v^{sv}$$