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Characterizing Microstructure Heterogeneity and Its Affect on Sintering and Modeling Sintering

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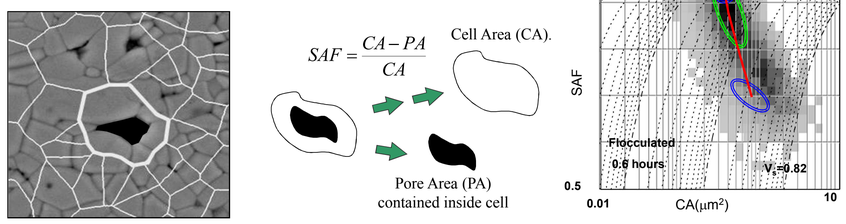
Introduction

Controlled sintering behavior is essential to the reproducible manufacture of high performance, specialty ceramic components, particularly those made from ultra-fine powders. In a homogeneous powder compact, the interdependence between microstructure and densification is defined by the idealized grain-pore geometry assumed in classical models for the sintering. However, sintering behavior can deviate significantly from classical model predictions in real ceramic microstructures that are heterogeneous. To better understand and control sintering in a real, heterogeneous ceramic powder compacts, the interdependence of microstructure and densification in different ceramic powder systems need to be characterized, and compared and contrasted with predictions based on classical and adapted models. Densification is characterized using different constant heating rate dilatometric sintering experiments and the master sintering curve approach. Microstructure is characterized using quantitative image analysis and pore boundary tessellation, with an emphasis on characterizing the meso-scale properties, pore size distribution, pore number, and pore spacing. The advantage of complementing dilatometry techniques with quantitative stereology, pore boundary tessellation and porosimetry to characterize microstructure evolution will allow insight into the implications of microstructure heterogeneity on densification.

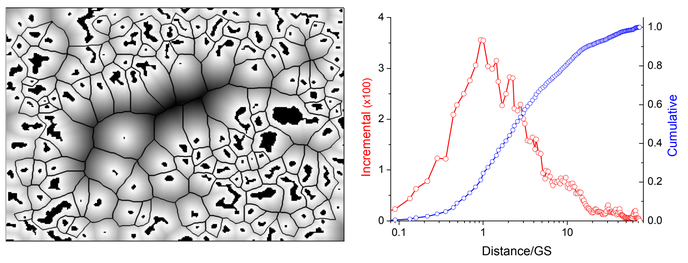
Tessellation**

Tessellation segments the section into cells using the pore areas as the feature of interest.

The Cell Area (CA) and the Pore Area (PA) are calculated and used to determine the Solid Area Fraction (SAF):

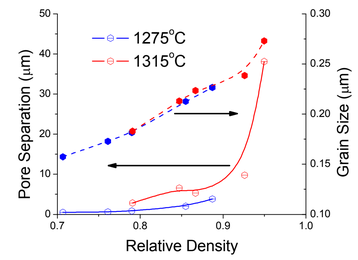


Dilation of tessellated images can be used to determine the effective diffusion lengths

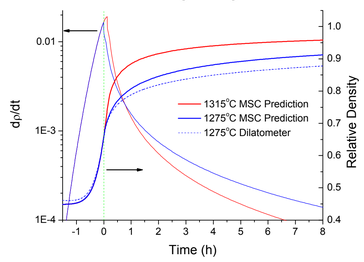


Understanding how the effective diffusion length changes during sintering is a step toward making more quantitative predictions with sintering models

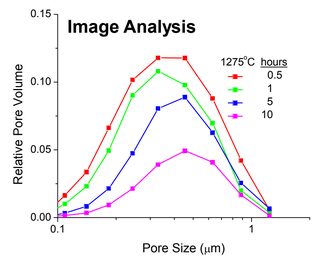
Pore Separation

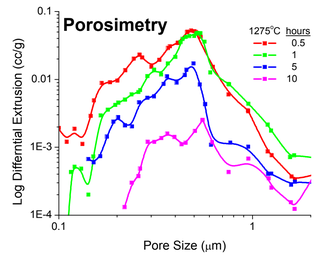


Pore separation increases faster than grain growth



Porosimetry





A simple Hg porosimetry experiment captures the same information as exhaustive image analysis

Typically intrusion results are reported; However, intrusion only reveals the minimum neck diameter not the pore size information

Percent retained Hg may be useful as a measurement of heterogeneity

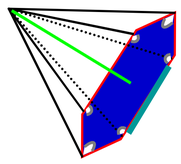
Master Sintering Curve***

Microstructure & Properties: Time-temperature profile:

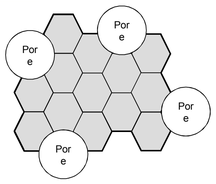
$$\Phi(\rho) \equiv \frac{k}{\gamma_s \Omega D_0} \int_{\rho_0}^{\rho} \frac{G((\rho))^n}{3\rho\Gamma(\rho)} d\rho = \int_0^t \frac{1}{T} e^{-\frac{Q_{app}}{RT}} dt \equiv \theta(t, T(t))$$

$$\Gamma_b = \frac{\alpha C_k C_b}{C_\lambda C_a C_h}$$

α: Chemical potential
C_k: Pore curvature
C_b: Grain boundary diffusion area
C_λ: Diffusion distance
C_a: Cell area
C_h: Cell height

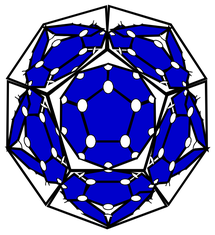


The denominator of Γ changes significantly during sintering

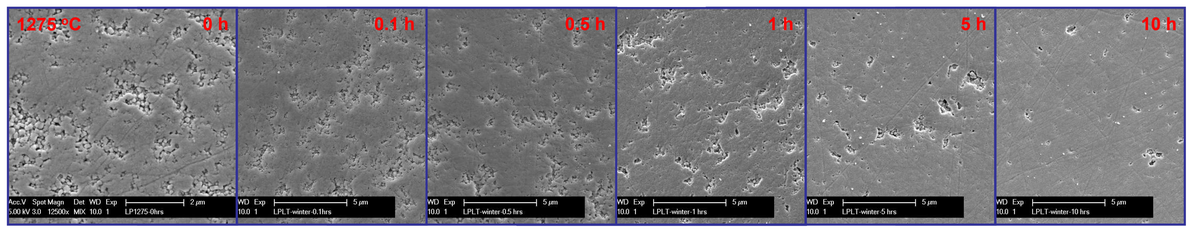


Traditionally, pore spacing is inferred from grain size for analysis convenience

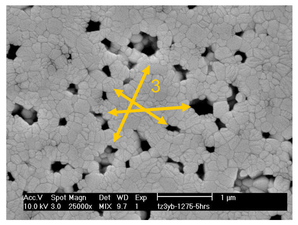
In real systems the pore size and grain size are not correlated, so the pore spacing has to be measured



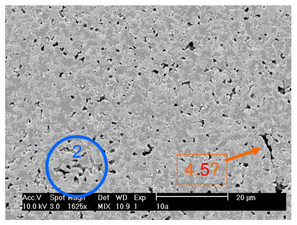
Heterogeneity Evolution



Finer pores are preferentially removed during sintering, leaving more widely spaced larger pores at high density



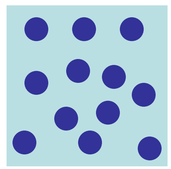
Types of pore couples
1: Classical
2: Pore cluster
3: Inter-agglomerate
4: Inter-granular
5: Stage I induced?



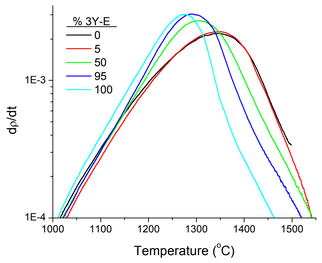
Differential Sintering: Experimental

Material A / Density A
Material B / Density B

$CTE^A < CTE^B$ similarly
$T_s^A < T_s^B$
$\rho^B < \rho^A$
Interface Tensile

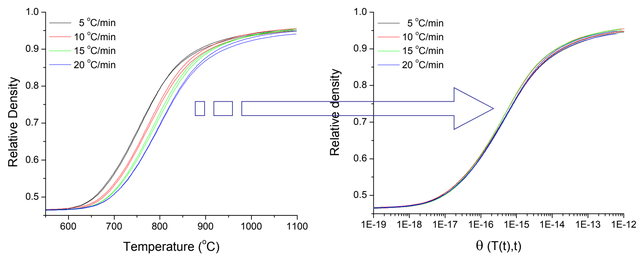


Tensile or compressive stress develops at the interface, Influencing (local) sintering rate and microstructure evolution



To demonstrate the effects of constrained sintering, a corollary heterogeneous structure was produced by mixing granules of different zirconia powders (3YB and 3YB-E) that have different sintering behavior

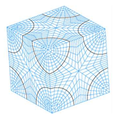
Even though the MSC is based on an ideal (homogeneous) structure, it also predicts densification in real (heterogeneous) structures reasonably well at low and intermediate densities



Microstructure and property details are generally not employed in the construction of the MSC

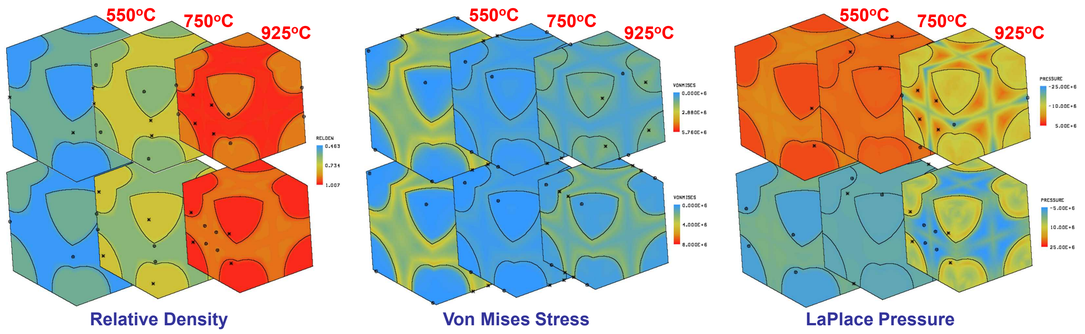
$$\rho = \rho_o + \frac{\rho_f - \rho_o}{\left[1 + \exp\left(-\frac{\log(\theta) - \log(\theta_o)}{a}\right)\right]^b}$$

Differential Sintering: FE Modeling



The SOVS model* has been incorporated into Sandia's SEACAS FE code to modeling sintering

Numerical modeling can be used to calculate parameters that are difficult to determine experimentally.



Summary

Microstructural heterogeneities introduced during processing affect densification and microstructure evolution during sintering, and need to be characterized and modeled to more accurately predict final stage sintering in real systems

Impact

Through science-based understanding and predictive modeling, the cost and time to develop integrated ceramic packages such as LTCCs and SOFCs will be reduced, while increasing reliability.

The stresses developed in multi-component ceramic structures can result in reduced performance or failure. A combination of experiment and numerical modeling can sufficiently define the critical parameters for successful part production.

Future work

Develop a large consistent set of experimental data to develop representative models for heterogeneous sintering.

Evaluate the effect of particle size, consolidation technique and density differences on heterogeneous microstructure evolution.

Fully characterize heterogeneous microstructure evolution with the complementary techniques of LVDT and video based dilatometry, porosimetry and tessellation using the Master Sintering curve as a guide.

Automate image processing to increase tessellation throughput.

Integrate grain growth, anisotropy and heterogeneous microstructure evolution into Sandia's FE code.

Determine the magnitude of forces and microstructural variation that lead to sintering induced heterogeneous microstructure evolution.

Determine if designed microstructural heterogeneities, such as, localized dopants, particle size variations or secondary phases, can be used to minimize or eliminate heterogeneities, or conversely create heterogeneities to achieve a given property.

*M. W. Reiterer J. G. Arguello and K. G. Ewsuk, "An Arrhenius-Type Viscosity Function to Model Sintering Using the Skorohod–Olevsky Viscous Sintering Model Within a Finite-Element Code." J. Am. Ceram. Soc., 89 [6] 1930–1935 (2006).
** R.J. McAfee and I. Nettleship, "A Mesoscale Description of Microstructure Evolution for Sintering Ceramics." Acta Mater. **53** 4305 (2005).
*** H. Su and D.L. Johnson, "Master Sintering Curve: A Practical Approach to Sintering." J. Am. Ceram. Soc. **79** [12] 3211 (1996).

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lookheed Martin company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000