SINTERING THEORY

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Sintering of Ceramics

Removal of pores between particles at high temperatures



Scanning electron micrographs of an aluminum oxide powder compact sintered at 1700 C for (a) 2-1/2 min. and (b) 6 min. 5000 X (From W.D. Kingery, H.K. Bown, and D.R. Uhlmann, Introduction to Ceramis, 2nd Edition, p.483, Copyright 1976 by John Wiley &



Sintering/Powder Metallurgy

Not only ceramics but metal and alloy powders were also sintered into useful shapes.





PLZT ceramics made using compaction and sintering. (*Courtesy of Dr. Gene Haertling*.)

Examples of Functional Ceramics

Function	Application	Examples of Ceramics
Electrical	Capacitor dielectrics	BaTiO ₃ , SrTiO ₃ , Ta ₂ O ₅
	Microwave dielectrics	Ba(Mg _{1/3} Ta _{2/3})O ₃ , Ba(Zn _{1/3} Ta _{2/3})O ₃ BaTi₄O ₉ , Ba₂Ti₀O ₂₀ , Zr _v Sn _{1-v} TiO₄, Al₂O ₃
	Conductive oxides	In-doped SnO ₂ (<i>ITO</i>)
	Superconductors	YBa ₂ Cu ₃ O _{7-x} (<i>YBCO</i>)
	Electronic packaging	Al ₂ O ₃
	Insulators	Porcelain
	Solid-oxide fuel cells	ZrO ₂ , LaCrO ₃
	Piezoelectric	$Pb(Zr_x I_{1-x})O_3(PZT), Pb(Mg_{1/3}Nb_{2/3})O_3$
	Electro-optical	PLZT, LINDO ₃
Magnetic	Recording media	γ -Fe ₂ O ₃ , CrO ₂ ("chrome" cassettes)
	Ferronulas, creat caras	Fe3U4 Niekolizine forrite
	Inductors, magnets	Manganese zinc ferrite
Ontical	Fiber optics	
Optical	Glasses	SiQo based
	Lasers	Al_2O_3 , vttrium aluminum garnate (YAG)
	Lighting	Al_2O_3 , glasses.
Automotive	Oxygen sensors, fuel cells	ZrO ₂
	Catalyst support	Cordierite
	Spark plugs	Al ₂ O ₃
	Tires	SiO ₂
1	Windshields/windows	SiO ₂ based glasses



Examples of Functional Ceramics/Con't

Mechanical/Structural	Cutting tools	WC-Co cermets <i>SiAION</i> AI ₂ O ₃
	Composites Abrasives	SiC, Al ₂ O ₃ , silica glass fibers SiC, Al ₂ O ₃ , diamond, BN, ZrSiO ₄
Biomedical	Implants Dentistry Ultrasound imaging	Hydroxyapatite Porcelain, Al ₂ O ₃ <i>PZT</i>
Construction	Buildings	Concrete Glass Sanitaryware
Others	Defense applications Armor materials	PZT, B ₄ C
	Sensors Nuclear	SnO ₂ UO ₂ Glasses for waste disposal
	Metals processing	Alumina and silica-based refractories, oxygen sensors, casting molds, etc.
Chemical	Catalysis Air, liquid filtration Sensors Paints, rubber	Various oxides (Al ₂ O ₃ , ZrO ₂ , ZnO, TiO ₂)
Domestic	Tiles, sanitaryware, Whiteware, kitchenware, Pottery, art, jewelry	Clay, alumina, and silica-based ceramics, glass-ceramics, diamond, ruby, cubic zirconia and other crystals

* Acronyms are indicated in italics.



Thermal Properties of Selected Advanced Ceramics

Material	Melting Point (°C)	Thermal Expansion Coefficient (×10 ⁻⁶ cm/cm)/°C	Knoop Hardness (HK) (100 g)
Al ₂ O ₃	2000	~6.8	2100
BN	2732	0.57ª, —0.46 ^b	5000
SiC	2700	~3.7	2500
Diamond		1.02	7000
Mullite	1810	4.5	_
TiO ₂	1840	8.8	_
Cubic ZrO ₂	2700	10.5	_

^a Perpendicular to pressing direction. ^b Parallel to pressing direction.



<u>Mechanical Properties of Selected</u> <u>Advanced Ceramics</u>

Material	Density (g/cm ³)	Tensile Strength (psi)	Flexural Strength (psi)	Compressive Strength (psi)	Young's Modulus (psi)	Fracture Toughness (psi √in.)
Al ₂ O ₃	3.98	30,000	80,000	400,000	56×10^{6}	5,000
SiC (sintered)	3.1	25,000	80,000	560,000	$60 imes 10^6$	4,000
Si ₃ N ₄ (reaction bonded)	2.5	20,000	35,000	150,000	$30 imes 10^6$	3,000
Si ₃ N ₄ (hot pressed)	3.2	80,000	130,000	500,000	$45 imes 10^6$	5,000
Sialon	3.24	60,000	140,000	500,000	$45 imes 10^6$	9,000
ZrO ₂ (partially stabilized)	5.8	65,000	100,000	270,000	$30 imes 10^6$	10,000
ZrO ₂ (transformation toughened)	5.8	50,000	115,000	250,000	$29 imes 10^6$	11,000



Outline

- The need to understand sintering
- Classes (Categories) of Sintering
 - Solid state sintering , liquid phase sintering, viscous flow
- Driving force for sintering
- Solid state sintering
- Material transport
 - Densifying mechanisms
 - Coarsening mechanisms
- Stages of sintering
 - Initial, intermediate, final
- Liquid phase sintering
 - Wetting, dihedral angle, Rayleigh instability
 - Permanent, transient
- Grain and pore growth
 - Normal, abnornal

Intering Kinetics

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Processing of Advanced Ceramics



What is the Purpose of Powder Processing?

- To obtain a dense random packing prior to sintering
- To sinter the ceramic to a high density



Dense random packing: 62-64% of theoretical density



Need to Undestand Sintering

Ceramic processing is based on the sintering of powder compacts rather than melting/solidification/cold working (characteristic for metals), because:

ceramics melt at high temperatures

Solidified microstructures can not be modified through additional plastic deformation and re-crystallization due to brittleness of ceramics.

the resulting coarse grains would act as fracture initiation sites

Low thermal conductivities of ceramics (<30-50 W/mK), in contrast to high thermal conductivity of metals (in the range 50-300 W/mK) cause large temperature gradients, and thus **thermal stress and shock in meltingsolidification of ceramics**

 Therefore we need to understand how a powder compact behaves at elevated temperatures



Need to Undestand Sintering

The sintering process is usually accompanied by changes within the material

- Strength, elastic modulus
- Hardness, fracture toughness
- Electrical and thermal conductivity
- Permeability to gases and and liquids
- Average grain number, size and shape
- Distribution of grain size and shape
- Average pore size and shape
- Distribution of pore size and shape
- Chemical composition and crystal structure



Sintering/Firing/Densification

Sintering: processes in heat treatment of powder compacts at elevated temperatures, T > 0.5T_m[K], appreciable mass transport by diffusion.

• GOAL

- A dense polycrystalline solid (usually)
- To provide strength



Classes (Categories) of Sintering

Solid State Sintering The majority of *non-silicate*ceramics are processed through high-temperature treatment and sintering of powder compacts with little (<2 vol%) or no liquid phases. The predominant mass transport (i.e. densification mechanism) through <u>solid-state diffusion</u>.

Liquid Phase Sintering If the liquid component of the sintering system has low viscosity (e.g. molten cobalt in the "classical"system of WC/Co). The predominant densification mechanism is <u>through rearrangement of the solid</u> <u>particles</u> "submerged" in and wetted by the low viscosity liquid, and through <u>dissolution and re-precipitation</u> of the solid.

Viscous Flow Most silica-containing ceramics, including traditional porcelains as well as advanced silicon nitride, sinter in the presence of viscous glass-type liquids, with predominant mass transport (i.e. densification mechanism) through viscous flow. This is defined as Viscous Sintering.



Classes (Categories) of Sintering





Driving Force

Sintering lowers the surface energy by reducing surface area with simultaneous formation of interparticle bonds (neck) by solid state diffusion or alternatively, liquid phase sintering.



Reduction in surface free energy of the consolidated mass of particles

Therefore, usually, particles < 1 µm in size are needed as a starting material

Densification vs. Coarsening

Accomplished by atom diffusion processes that lead to

- <u>Densification</u> of the body (by transport matter from inside the grains into the pores) AND
- <u>Coarsening</u> of the microstructure (by rearrangement of matter between different parts of the pore surfaces *without* actually leading to a decrease in the pore volume). $\Delta(\gamma A) = \Delta \gamma \cdot A + \gamma \cdot \Delta A$

Densification process remove material from the grain boundary region leading to shrinkage

Coarsening processes produce microstructural changes without causing shrinkage



Solid-vapor interfaces (of surface energy γ_{sv}) are replaced by solid-solid (γ_{ss}) interfaces, where $\gamma_{ss} < \gamma_{sv}$.

Rahaman, Ceram. Proc. and Sint. 2nd Ed.

Effect of Temperature on Densification



 The mechanism of mass transfer depends on the material, experimental conditions, and the sintering stage

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TEKNİK ÜNİVERSİTESİ

Umberto Anselmi-Tamburini Basic mechanisms involved in FAST sintering

Densification vs. Coarsening of Hematite Particles

(b)



Hematite sintered at 1000°C in a) air b) an Argon/10%HCl



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TERNİK ÜNİVEDSİTER



Density and shringkage curves for hematite sintered in HCl atmospheres.

HCl in the sintering atmosphere mainly enhanced the grain coarsening mechanisms with only little densification

(Barsoum, 1997)

Solid State Sintering

- Diffusion takes place
 - flow over free surfaces,
 - along grain boundaries,
 - through the crystal lattice,
 - vapor transport,
 - plastic flow,
 - viscous flow,
 - dislocation climb.





Mass Transport During Sintering

Mechanism Number	Transport Path	Source of Matter	Sink of Matter
1	Surface diffusion	Surface	Neck
2	Lattice diffusion	Surface	Neck
3	Vapor transport	Surface	Neck
4	Boundary diffusion	Grain boundary	Neck
5	Lattice diffusion	Grain boundary	Neck
6	Lattice diffusion	Dislocations	Neck

Two factors are important to mass transport in sintering

- stress (or force) → larger with smaller particles and higher surface areas
- mobility → increases with higher temperatures (i.e., diffusion is faster).





Vacancy Flux





Sintering/Stages

- Initial stage; extensive loss of surface area, open pore space.
- Intermediate stage; tubular, rounded pore structure that is open to the compact surface. Gas can permeate through the open pore space.
- Final stage; pores shrink, spheroidize, and no longer connected to the compact surface (closed pores), and difficult to remove. Since open pores are more effective in retarding grain growth, the transition to final-stage sintering gives less grain boundary pinning and usually results in rapid grain growth.

Stage	Process	Surface Area Loss	Densification	Coarsening
Adhesion	Contact for- mation	Minimal un- less com- pacted at high pres- sures	None	None
Initial	Neck growth	Significant, up to 50% loss	Small at first	Minimal
Intermediate	Pore rounding and elongation	Near total loss of open po- rosity	Significant	Increase in grain size and pore size
Final	Pore closure, fi- nal densifi- cation	Negligible fur- ther loss	Slow and rel- atively minimal	Extensive grain and pore growth





Sintering time

Liquid Phase Sintering



liquid phase sintering (98W-1Ni-1Fe(wt%)).

S-J. L. Kang; Sintering

Example systems

Sintering processes used for some ceramic systems

Composition	Sintering process	Application
Al ₂ O ₃	Solid-state sintering with MgO additive Liquid-phase sintering with a silicate glass	Sodium vapor arc lamp tubes Furnace tubes; refractories
MgO	Liquid-phase sintering with a silicate glass	Refractories
Si ₃ N ₄	Liquid-phase sintering with oxide additives (e.g. Al ₂ O ₃ and Y ₂ O ₃) under nitrogen gas pressure or under an externally applied pressure	High-temperature structural ceramics
ZnO	Liquid-phase sintering with Bi ₂ O ₃ and other oxide additives	Electrical varistors
BaTiO ₃	Liquid-phase sintering with TiO2-rich liquid	Capacitor dielectrics; thermistors
$Pb(Zr,Ti)O_3 (PZT),$ (Pb,La)(Zr,T)O ₃ (PLZT)	Sintering with a lead-rich liquid phase; hot pressing	Piezoelectric actuators and electro-optic devices
$ZrO_2/(3-10 \text{ mol}\% \text{ Y}_2O_3)$	Solid-state sintering	Electrical conducting oxide for fuel cells
Mn–Zn and Ni–Zn ferrites	Solid-state sintering under a controlled oxygen atmosphere	Soft ferrites for magnetic applications
Porcelain	Vitrification	Electrical insulators; tableware
SiO ₂ gel	Viscous sintering	Optical devices



Surface Tension/ Surface Energy



- Reversible work W_r to increase the surface area by dA
- Surface tension

$$\gamma = \frac{dW_r}{dA}$$

- Energy needed to create surface area dA
- Surface energy

$$\gamma = \left(\frac{\partial G}{\partial A}\right)_{\mathrm{T,P,n_{i}}}$$





Surface Tension/ Surface Energy



Surfaces can be characterized according to their **curvature (radius of curvature)** Extending a surface or changing the radius of curvature of a surface requires work Physical Ceramics Y.M. Chen

Effect of Surface Curvature

The excess surface free energy is due to the different atomic arrangements along the surface relative to the bulk arrangement:



The average bonding of an atom is decrasing from concave over flat to convex surfaces, the partial pressure over the surfaces is increasing in the same order. The surface energy stored in small grains of ceramic materials is the driving force to coalesce (sinter) them together.

Wetting

$$\gamma_{SV} = \gamma_{SV} + \gamma_{LV} \cos \theta$$



Spreading is the process in which the liquid distributes itself to cover the surfaces of the particulate solid. It is expected to be important in the rearrangement stage soon after the formation of the liquid.

Spreading will occur when θ is 0°

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$$\gamma_{LV} + \gamma_{SL} - \gamma_{SV} = 0$$

Dihedral Angle

Liquid

The behavior of the liquid depends on the solid - liquid surface tension.

Equilibrium Dihedral Angle

$$\gamma_{SS} = 2\gamma_{SG(L)}\cos\frac{\phi}{2}$$



In solid-liquid system the liquid will be distributed according to the dihedral angle Brown et al 1007

Rayleigh Instability

At some point the channel becomes unstable and isolated drops form



Intermediate stage of a jet breaking into drops. Radii of curvature in the axial direction are shown.





Isolated pores or liquid phase at grain junctions

http://en.wikipedia.org/wiki/Plateau%E2%80%93Rayleigh_instability#Water_dripping_from_a_faucet.2Ftap_

Liquid Assisted Compaction

Liquid phase promotes the rearrangement of grains. For wetting angles θ < 45° with the liquid distributed along the edges, the grains will be pulled towards the common edge due to the negative curvature of the liquid-solid surface and the associated pressure difference (capillary effect).

Example: ZnO varistors sintered with the addition of Bi_2O_3



Evolution during Liquid Phase

Sintering

Rearrangement

- Liquid melt due to capillary action spreads into the pores and grain rearrangement took place,
- grains rearrange into a more favorable packing arrangement



Solution-precipitation

- Atoms will preferentially go into solution and then precipitate in areas of lower chemical potential where particles are not close or in contact, called contact flattening.
- System is densifies in a way similar to grain boundary diffusion in solid state sintering.
 Ostwald ripening takes place, smaller particles goes into solution preferentially and precipitates on larger particles leading to densification.

S-J. L. Kang; Sintering

Evolution during Liquid Phase

Sintering

Final densification

- Densification of the solid skeletal network
- liquid movement from efficiently packed regions into pores.
- Requirements
- Major phase should be at least slightly soluble in the liquid phase
- "Binder" additive should melt before any major sintering of the solid particulate network occurs, otherwise rearrangement of grains will not occur.



Liquid improves the mass transport rates, densification, and coarsening.

Exerts capillary pull on the particles equivalent to a large external pressure.



S-J. L. Kang; Sintering

Persistent Liquid Phase Sintering

- Liquid phase exist throughout the high-temperature portion of the sintering cycle.
 - Example: cemented carbides or hardmetals, a sintering mechanism involving the generation of a permanent liquid phase is applied. This type of liquid phase sintering involves the use of an additive to the powder, which will melt before the matrix phase and which will often create a so-called binder phase.

- The process has three stages:
 - Rearrangement
 - Solution-precipitation
 - Final densification



http://www.ipmd.net/Introduction_to_powder_metallurgy/Sintering#sthash.5JEyaWgJ.dpuf

Transient Liquid Phase Sintering

 <u>Transient liquid phase sintering</u> liquid disappears during the sintering cycle, either due to dissolution into the solid (solid solution) or formation of a new phase





http://www.ipmd.net/Introduction_to_powder_metallurgy/Sintering#sthash.5JEyaWgJ.dpuf

Equilibrium Shape of Grains





Wulff's construction to calculate the minimizing surface for a fixed volume

Thermodynamics - Interaction Studies - Solids, Liquids and Gases, edited by Juan Carlos Moreno-Pirajan

(a) SEM image of rutile TiO_2 particles.

The Centre National de la Recherche Scientifique. (b) Theoretical equilibrium crystal shape (ECS) for rutile TiO_2 .

(1994) by the American Physical Society (URL:http://link.aps.org/abstract/PRB/v49/e16721)



Tetracaidecahedron



The polycrystalline structure is of paramount importance to materials science and engineering. It is an example of a space-filling irregular network structure



http://www.susqu.edu/brakke/kelvin/kelvin.html

Pore Stability

Pores can grow or shrink. The two parameters affecting pore growth is the number of surrounding grains and the dihedral angle.



(Small) pores with few neighboring grains have concave surfaces and tend to shrink, whereas

(Large) pores with many neighboring grains have convex surfaces and tend to grow

The surface curvature of the grains around an isolated pore is affected by their number and the dihedral angle.

Pores are important and unwanted elements of a ceramic microstructure. The final pore space in an sintered ceramic is mainly a function of the pore volume in the green body.

Pore Evolution During Sintering



Coordination for pore stability as a function of pore coordination number and dihedral angle. For the dihedral angle 120°, pores surrounded by more than 12 grains will grow. S-J. L. Kang; Sintering

Pore Entrapment

Pores can also be entrapped. Entrapping happens when grain growth is too fast. Slowing down grain boundary mobility will prevent entrapping.

> Doping Secondary phases.....





Density as a function of grain growth for alumina. Adding MgO slowed grain growth and displace the region where pore entrapping (=separation) occurs.

Grain Growth

Two types of grain growth can be distinguished





Normal Grain Growth

- obeying Ostwald's ripening law
- uniform grain size distribution





Grain Growth



- Abnormal Grain Growth, Exaggerated or Discontinuous Grain Growth,
 - we observe few LARGE grains
 - bimodal grain size distribution





Sintering Kinetics

$$\frac{\Delta L}{L} = \frac{const}{kT} \frac{t^n}{r^m}$$

r: particle radius m: 1-1.5 t time (n: 1/3 -2/5) L: length of the sintered body

It is obvious from the above equation that ceramics with small grain size will shrink e.g. densify much faster than coarse green bodies.



Shrinkage and Densification



• A frequent measure of sintering is the linear dimensional change, designated as a shrinkage $\Delta L/L_o$ or density.

Erdem Akça, Ph.D.

Grain Growth

$$G^n - G_0^n = k_0 \exp(-Q/RT)t$$

k= constant T= time Q= activation energy G= grain size G₀= initial grain size n= power exponent When n is 2 It is called the parabolic law for grain growth

Generally describes the growth of grains in pure metals and ceramics

In practice normal growth is not common.

The power exponent in practice ranges from 2 to 4 for ceramics and some metals

The value for n=3 was widely reported. **Cubic Growth Law** Impurities and solute drag greatly effect the grain growth behavior.



Cartoon Picture of Grain Growth





Whether a grain grows or shrinks is determined by its curvature





In order to lower the material's free energy, large grains grow at the expense of small grains



W.D.Kingery, H.K.Bowen, D.R.Uhlmann, Introduction to ceramics, Wiley

Grain Boundary Pinning

Impurities or dopants are often concentrated at interfaces. When a grain boundary moves, e.g. during grain growth, the solutes concentrated at the interface have to be carried along, thus slowing down the grain boundary mobility called solute drag.

Pores and second phase inclusions have the same effect. The retaining force is a function of the inclusion radius *r* and is given by





Increase of interface area while passing an inclusion

Driving force of a grain boundary

$$F = \frac{\alpha \gamma_b}{G}$$

 α is geometric factor, 2 for spherical grains

Zener Relationship

$$G_L = \frac{2\alpha r}{3f}$$

G_L= limiting grain size r =particle radius f =fraction of second phase

Doping and Grain Boundary Pinning



 Grain size and density evolution of an alumina ceramic with and without MgO doping.

(Barsoum, 1997)

The Role of Mg in Alumina



4. Comparison of microstructures of porous, sintered alumina, sintered without MgO addition (Ett Buckles, (MRS Bucklet IN/JUNE 1996) h a MgO addition prevented discontinuous grain growth (right). Original magnification is 250X. (Press release photo.)

The Role of MgO in Alumina



Figure 3. Translucency comparison of pore-free and normal porous alumina (press-release photo).



Figure 1. The Lucalox high-pressure sodium-vapor lamp. A discharge lamp with a cylindrical envelope of translucent Lucalox ceramic that resists high-temperature sodium vapor. The lamp proper is enclosed in an evacuated glass envelope for protection and to prevent oxidation of the metal end cap of the ceramic tube. The lamp is now available in a wide range of sizes. (1962 press release photo.)



J.E. Burke, (MRS BULLETIN/JUNE 1996)

Sintering of Ceramics

Removal of pores between particles at high temperatures



Scanning electron micrographs of an aluminum oxide powder compact sintered at 1700 C for (a) 2-1/2 min. and (b) 6 min. 5000 X (From W.D. Kingery, H.K. Bown, Uhlmann, Introduction to Ceramis, 2nd .483, Copyright 1976 by John Wiley &

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- increase of interparticle contact area with time
- rounding-off of sharp angles and points of contact
- in most cases, the approach of particle centres and overall densification
- decrease in volume of interconnected pores
- continuing isolation of pores
- grain growth and decrease in volume of isolated pores

Final Remaks



Powder Characteristics

TABLE 2.1 Desirable Powder Characteristics for Advanced Ceramics

Powder characteristic	Desired property		
Particle size	Fine ($< \sim 1 \mu m$)		
Particle size distribution	Narrow or monodisperse		
Particle shape	Spherical or equiaxial		
State of agglomeration	No agglomeration or soft agglomerates		
Chemical composition	High purity		
Phase composition	Single phase		



Densification vs. Coarsening



Only densification followed by grain growth will give good final densities.



(Barsoum, 1997)

Powder Defects/Agglomerates

- Agglomerates are classified into two types:
 - Soft agglomerates in which the particles are held together by weak van der Waals forces and
 - Hard agglomerates in which the particles are chemically bonded together by strong bridges (Neck formation).
- The ideal situation is the avoidance of agglomeration
- At least prefer to have *soft agglomerates* rather than *hard agglomerates*
- Soft agglomerates are easy to handle
- Hard agglomerates are difficult to handle



Powder Defects/Agglomerates

- Lead to heterogeneous packing in the green body
- Differential sintering during the firing stage.
- Serious problems such as the development of large pores and cracklike voids in the fired body
- Agglomerates usually have higher density than green body

Granulation

•The process of collecting particles together by creating bonds between them <u>intentionally</u>



Cracklike void produced by a ZrO_2 agglomerate shrinking away from the surrounding Al_2O_3/ZrO_2 matrix during firing



Reactive Sintering



Reaction energy may be used as driving force for sintering



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