

High Temperature Materials

**By
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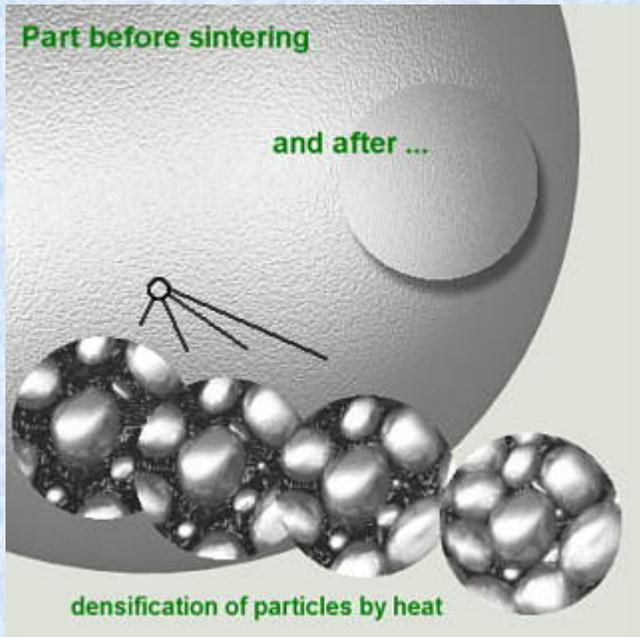
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Sintering and Consolidation of Ceramics

Solid State Sintering

The Phenomenon of Sintering

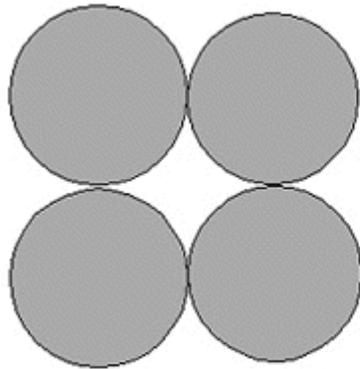


What is Sintering?

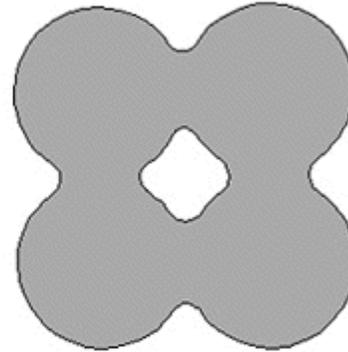
Sintering commonly refers to processes involved in the heat treatment of powder compacts at elevated temperatures, usually at $T > 0.5T_m$ [K], in the temperature range where diffusional mass transport is appreciable.

Successful sintering usually results in a dense polycrystalline solid. However, sintering can proceed only locally (i.e. at contact point of grains), without any appreciable change in the average overall density of a powder compact.

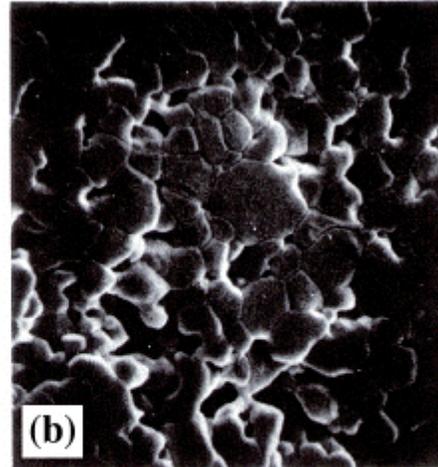
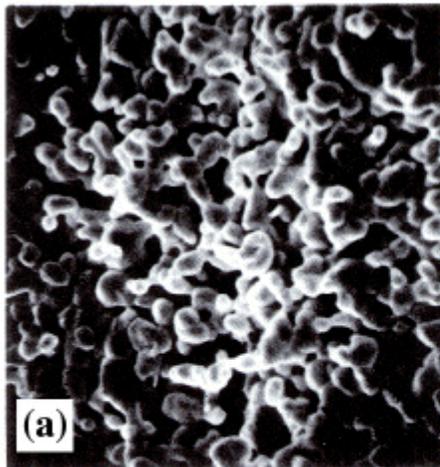
Sintering is thermal treatment of fine-grained material at a temperature below the melting point of the main constituent, for the purpose of increasing its grain size and strength by bonding together the particles. Theories about what happens exactly during sintering have provided the subject matter of innumerable conferences and learned scientific papers. Suffice to say that atomic diffusion takes place and the welded areas formed during compaction grow until eventually may be lost completely. Re-crystallization and grain growth may follow, and the pores tend to become rounded and the total porosity, as a percentage of the whole volume, tends to decrease.



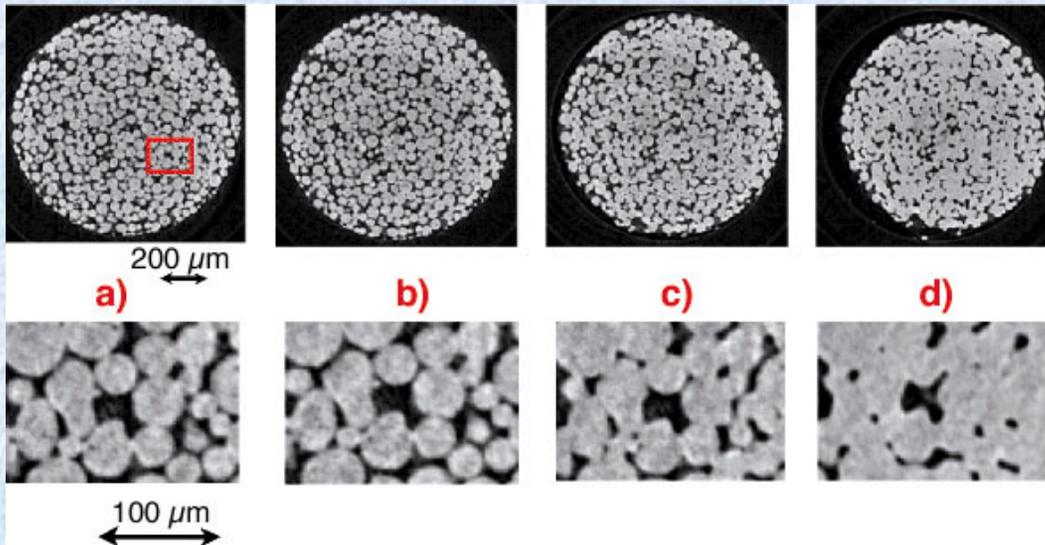
Representation of the initially unsintered powder particles.



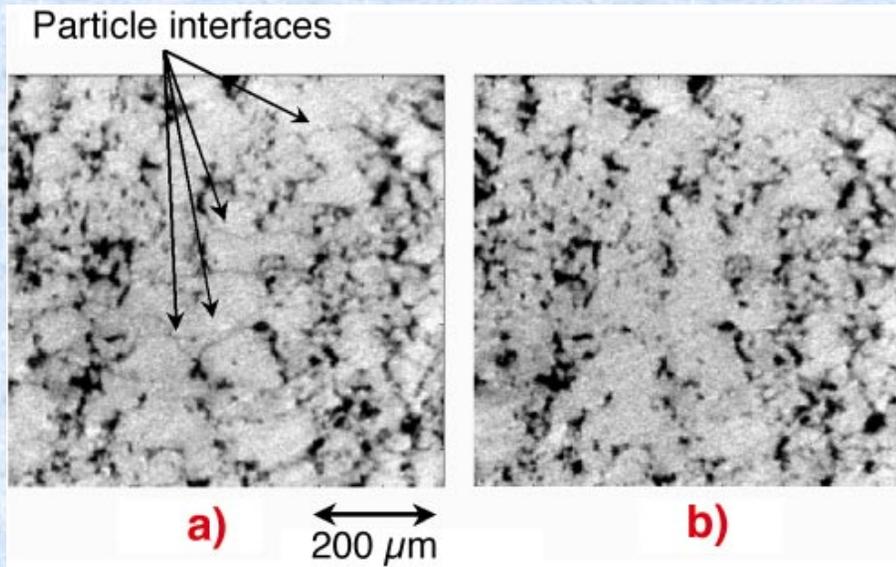
Representation of Sintered Powder Particles



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 Ceramics, 2nd Edition, p.483, Copyright 1976 by John Wiley &

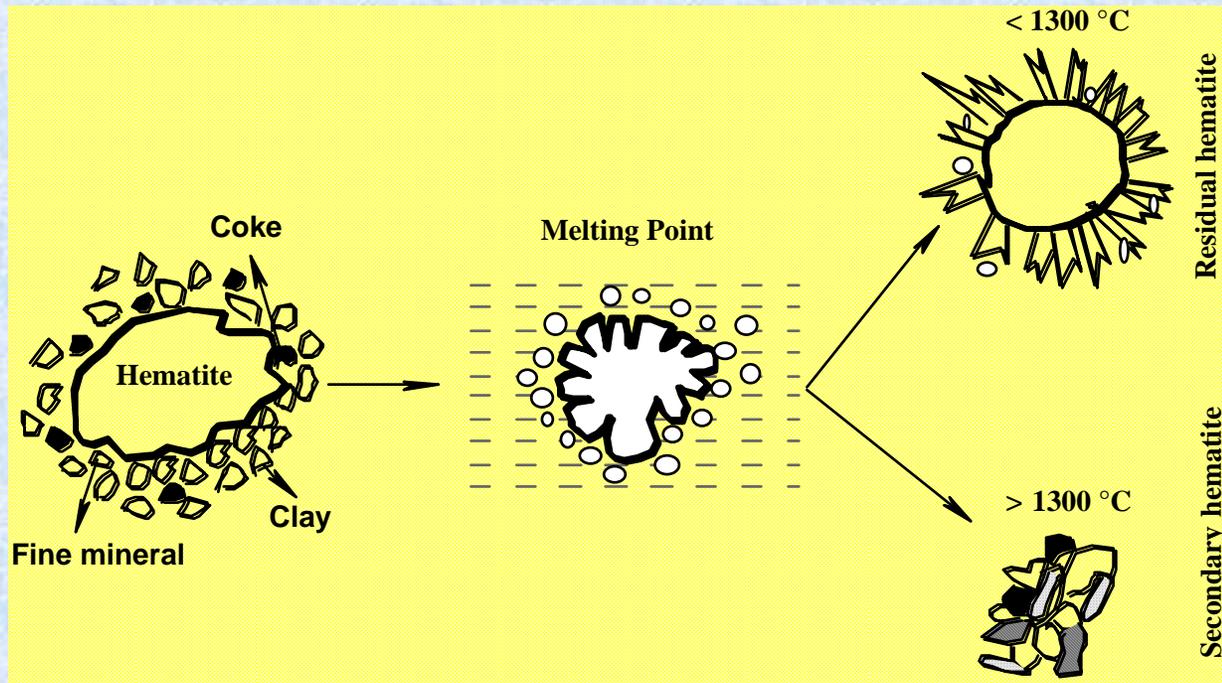


Reconstructions (virtual slices) perpendicular to the cylindrical axis showing Cu particles at different stages of the sintering process: (a) before sintering, (b) after sintering at 1000°C, and (c) after sintering at 1050°C. Identical regions (inside the rectangle of (a)) are shown at a higher magnification below.



Reconstructed slices of a compacted Distalloy sample before (a) and after (b) sintering at 1130°C. The direction of prior compaction is along the vertical direction in the paper plane

Development of sinter texture



N. Menad, H. Tayibi, Fernando Garcia Carcedo and A. Hernández

Minimization methods for emissions generated from sinter strands: a review

J. of clean production, Pages 740-747, 2005

Basic Thermodynamics of Sintering

The driving force for sintering is a decrease in the surface free energy of powdered compacts, by replacing solid-vapor interfaces (of surface energy Γ_{SV}) with solid-solid (Γ_{SS}) interfaces, where $\Gamma_{SS} < \Gamma_{SV}$.

Thermodynamically, then, sintering is an irreversible process in which a free energy decrease is brought about by a decrease in surface area.

Basic Thermodynamics of Sintering

At a typical specific surface S of ceramic powders $S = 1-10 \text{ m}^2/\text{g}$ and $\Gamma_{SV} = 1 - 2 \text{ J/m}^2$. The resulting excess of surface energy of $\Gamma_{SV} = 1-20 \text{ J/g}$ is small compared with the heat of chemical reactions ($> 1 \text{ kJ/g}$) but still sufficient to drive the sintering processes. Some mechanisms can lead to a waste of sintering driving force without assisting densification. These are the grain coarsening mechanisms, which are driven by the same force as sintering.

The change of system energy dE due to sintering is therefore composed of the increase due to the creation of new grain boundary areas, $dA_{SS} > 0$, and due to the annihilation of vapor-solid interfaces, $dA_{SV} < 0$. The necessary global thermodynamic condition for the sintering to proceed is

$$dE = \Gamma_{SS} dA_{SS} + \Gamma_{SV} dA_{SV} < 0$$

The sintering process will stop when $dE = 0$

$$\Gamma_{SS} dA_{SS} + \Gamma_{SV} dA_{SV} = 0 \quad \text{or} \quad \Gamma_{SS} / \Gamma_{SV} = - dA_{SV} / dA_{SS}$$

Basic Thermodynamics of Sintering

The sintering progress can be represented by plotting the total free surface area A_{SV} , vs the total surface area of the grain boundaries A_{SS} . At the start of sintering, all surface area equals the free surface area, since no grain boundaries exist yet, $A_{SV} = A_{SV0}$ and $A_{SS} = 0$. As sintering proceeds, A_{SV} decreases and A_{SS} increases, in such a way that a monotonically decreasing curve is obtained with the slope $-dA_{SV}/dA_{SS}$. If, at any point during sintering, the value of the slope reaches Γ_{SS}/Γ_{SV} , the sintering must stop due to the above equilibrium condition. **The principal objective of sintering is the elimination of porosity**, i.e. a minimum A_{SV} , possibly $A_{SV} = 0$ and A_{SS} large, meaning little grain growth. It is thus desirable that the sintering stop condition is reached when the slope dA_{SV}/dA_{SS} close to zero, i.e. $\Gamma_{SS} \ll \Gamma_{SV}$. Through this type of thermodynamic considerations it is suggested that sintering can be encouraged through manipulation of the doping and/or the environment, so the surface energy is maximized.

Classes (Categories) of 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. This is defined as **Solid State Sintering**, with predominant mass transport (i.e. densification mechanism) through solid-state diffusion.

However, 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**.

If the liquid component of the sintering system has low viscosity (e.g. molten cobalt in the “classical” system of WC/Co) the process is defined as **Liquid Sintering**. In this system the predominant densification mechanism is through rearrangement of the solid particles “submerged” in and wetted by the low viscosity liquid, and through dissolution and re-precipitation of the solid.

Why Ceramics have to be sintered?

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 melting-solidification of ceramics.

However, some ceramic refractories, such as Al_2O_3 , $\text{Al}_2\text{O}_3/\text{ZrO}_2$, are manufactured through the melting / casting / solidification process. If made properly, they are superior to the sintered versions, and the processing costs of large, ~ 1 m tall blocks is lower.

•Why do we need Sintering?

The principal goal of sintering is the reduction of compact porosity. Sometimes the initial spaces between compacted grains of ceramics are called “voids”, to differentiate them from the isolated spaces = pores, which occur in the final stages of sintering. The sintering process is usually accompanied by other changes within the material, some desirable and some undesirable. The largest changes occur in

- strength, elastic modulus
- hardness, fracture toughness
- electrical and thermal conductivity
- permeability to gases 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

•Why do we need Sintering?

Sintering is a widely used but very complex phenomenon. The fundamental mechanisms of sintering are still a matter of controversy. Experimental quantification of changes in pore fraction and geometry during sintering can be attempted by several techniques, such as:

- Dilatometry
- Buoyancy
- Gas absorption
- Porosimetry
- Indirect methods (e.g. hardness)
- Quantitative microscopy

The description of the sintering process has been derived from model experiments (e.g. sintering of a few spheres) and by observing powdered compact behavior at elevated temperatures. The following phenomena were observed and modeling was attempted:

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

The development of microstructure and densification during sintering is a direct consequence of mass transport through several possible paths (one of these paths is usually predominant at any given stage of sintering):

- GAS phase (evaporation/condensation)
- LIQUID phase (solution/precipitation)
- SOLID phase (lattice diffusion)
- INTERFACES (surface diffusion, grain boundary diffusion)
- VISCOUS or PLASTIC FLOW, under capillary pressure (internal) or externally applied pressure (pressure-sintering, hot-pressing, hot-isostatic-pressing)

Since certain mechanisms of mass transport can be dominant in some systems, two broad categories of sintering are recognized:

1 Solid-state sintering

where all densification is achieved through changes in particle shape, without particle rearrangement or the presence of liquid

2 Liquid-phase sintering

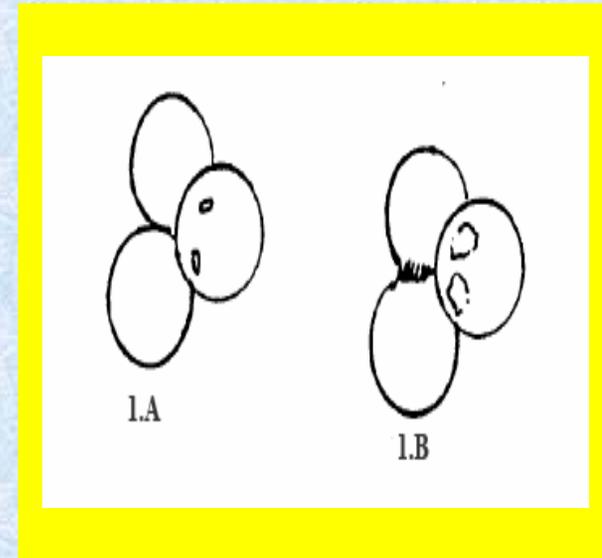
where some liquid that is present at sintering temperatures aids compaction. Grain rearrangement occurs in the initial stage followed by a solution-re-precipitation stage. Usually, the liquid amount is not sufficient to fill the green-state porosity in normal liquid-assisted sintering of ceramics. In many instances, supposedly Solid State Sintering proceeds in the presence of previously undetected (or transient) small amounts of liquid (perhaps introduced as impurities during the powder preparation stage, such as silicates in oxide ceramics Al_2O_3 , ZrO_2).

Simple model experiments with spheres or rods illustrate sintering phenomena, classified into three stages of sintering, as discussed below.

1. Initial stage of sintering, involving

1A. Local point of contact formation or "fusion", without shrinkage of compact. This is accompanied by smoothing of the free surface of particles.

1B. Neck formation at the contact point, with the resulting concave curvature δn (where $\delta n = 1/r_n$) at the neck, in contrast to the convex curvature on the particle surface of radius r , where $r \gg r_n$. The two radii of the neck curvature, r_n and y , represent an experimental justification for the two-sphere model of sintering.



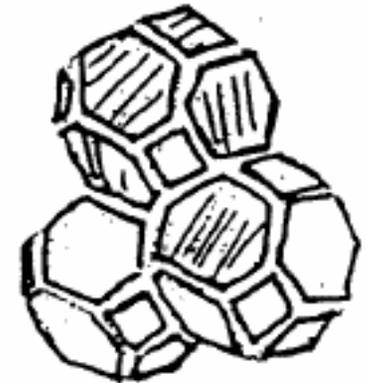
- The processes 1A and 1B result in densification of the sintering component by ~10%. That is, if the relative green density after forming of the particle compact was 60%, the density after initial stage would be about 70% of the theoretical density TD. However, the 10% densification in the initial stage is reached very quickly (seconds or minutes) after exposing powder to high temperature, because of the large surface area and the high driving force for sintering.

2. Intermediate stage of sintering, involving

2A. neck growth,

2B. pores forming arrays of interconnected cylindrical channels,

2C. particle centers approaching one another, with the resulting compact shrinkage.

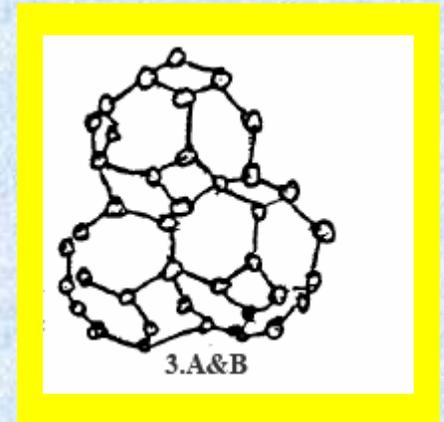


2.A&B&C

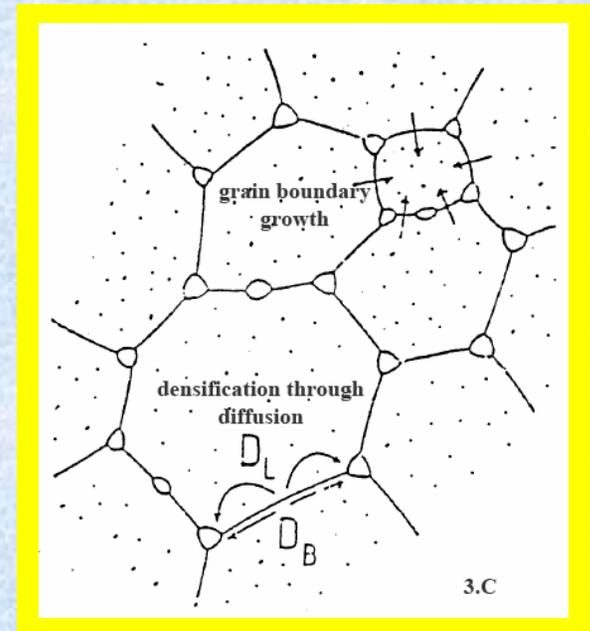
The shrinkage in the intermediate stage can result in additional densification by as much as 25%, or to a total of about 95% of the TD (theoretical density), compare. However, shrinkage does not necessarily have to take place during the intermediate stage of sintering. For example, shrinkage would not occur if matter was transported FROM the particle SURFACE, and proceeded through either gas, solid or along interface as surface diffusion.

3. Final stage of sintering, involving:

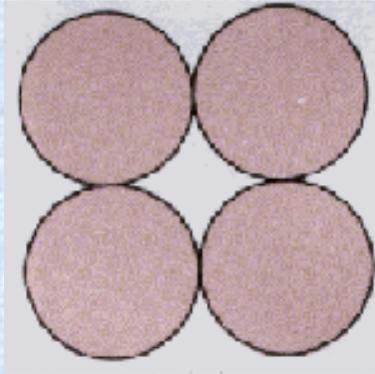
- 3A. Isolation of pores, i.e. relative density exceeding ~93%
- 3B. Elimination of porosity
- 3C. Grain growth



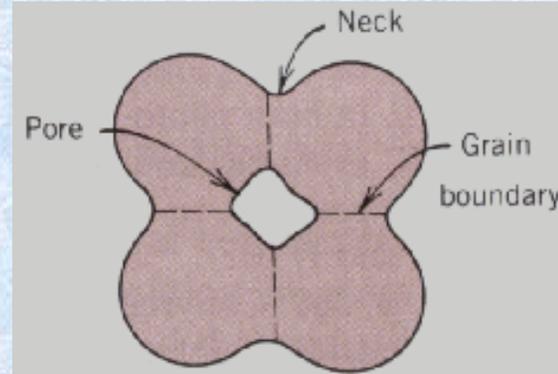
The final sintering stage begins at about 93-95% of theoretical density, when porosity is already isolated. Ideally, at the end of this stage all porosity is eliminated. The complete elimination of porosity in the final stage of sintering can only happen when all pores are connected to fast, short diffusion paths along grain boundaries (or, equivalently, if the grain boundaries remain attached to the pores).



Sintering process

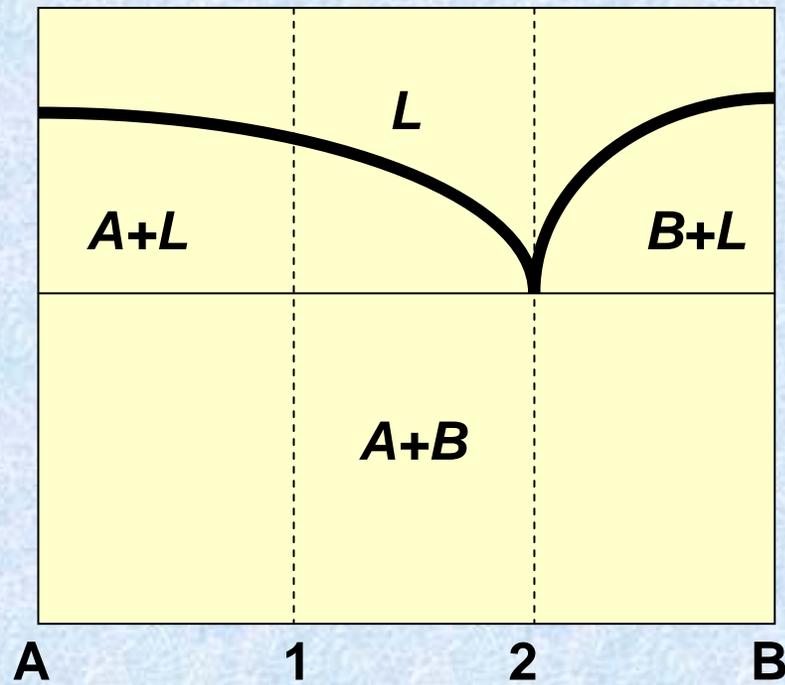
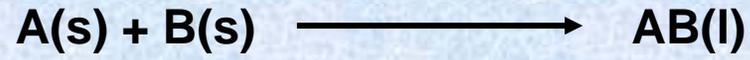


Before sintering



After sintering

Sintering

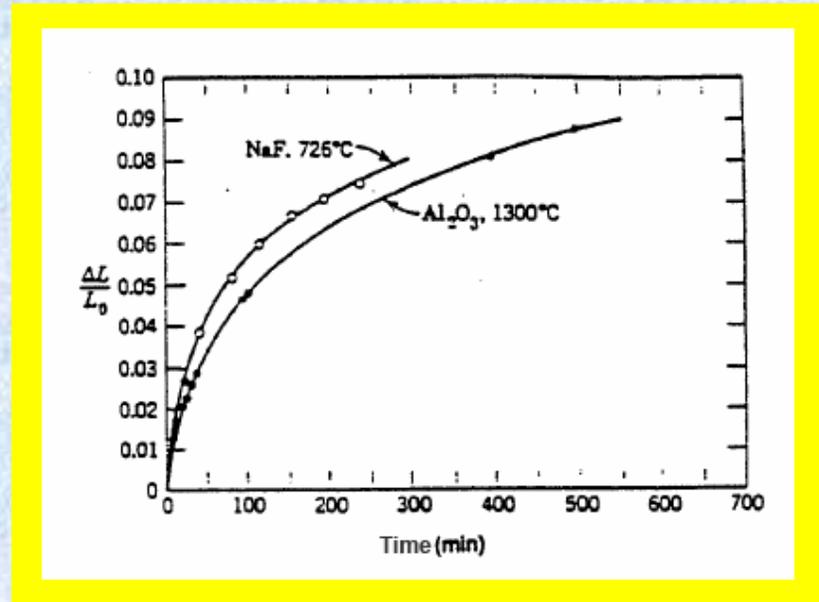


Empirical Modeling of Sintering

A large number of equations describing the variation of porosity P/P_0 (or shrinkage $\Delta L/L_0$) versus time t have been proposed. All of these equations use simplified assumptions of idealized models, or are based purely on empirical observations. These equations usually have forms of:

$$P/P_0 = (a + bt)^c \text{ or } P - P_0 = d \ln(t/t_0)$$

or $(\Delta L/L_0)^n = at$, where:
 $a, b, c, n = \text{constants.}$

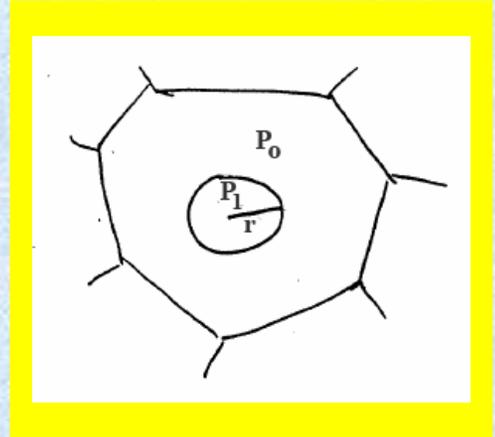


•A remarkable feature of most of these equations is that, using curve-fitting procedures, a nearly perfect fit can be obtained with experimental data on sintering. However, little or no insight into sintering mechanisms is obtained and incorrect conclusions are drawn when physical meanings are attributed to the fitted constants. This is because real systems deviate significantly from idealized models:

- *particles are non-uniformly distributed in space and rearrange during sintering
- *necks grow asymmetrically
- *different sintering stages (neck formation, neck growth, rearrangement, grain growth with or without shrinkage, closed porosity sintering) are controlled by different mechanisms which interact and overlap in a complex way

The mass transport from surfaces: evaporation-condensation

The mass transport can proceed through a gas phase, driven by a differential in vapor pressure. Evaporation-condensation takes place because the vapor pressure p_1 on a curved surface of radius r_1 is different from that on a flat surface (p_0 , $r_0 = \infty$) or any other surface at r_2 . This is expressed by the Kelvin equation:



$$\ln (p_1/p_2) = (\Omega \Gamma_{sv} / RT) (1/r_1 + 1/r_2)$$

where Ω = the molar volume of the species. For the simple case of $r_2 = r_0 = \infty$ and $p_2 = p_0$ (that is, for a flat surface), the above equation simplifies to:

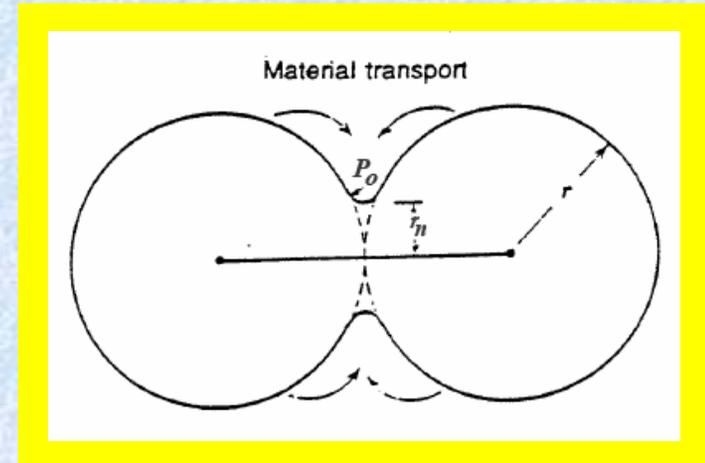
$$\ln (p_1/p_2) \approx (p_1 - p_0)/p_0 = \Delta p/p_0 \quad \text{so} \quad \Delta p/p_0 = (\Omega \Gamma_{sv})/(R T r_1)$$

The mass transport from surfaces: evaporation-condensation

The most important case of evaporation-condensation mass transport is from the surface of convex (spherical) particles ($r > 0$) to the surface of concave necks ($r_n < 0$) where $|r_n| \ll |r|$ at the contact region. No shrinkage occurs in this process and y^3 is a linear function of time:

$$y^3 = \alpha_2 t \text{ and } h/r = \Delta L/L = 0$$

This type of transport dominates at the relatively high vapor pressures of 10^{-4} atmospheres, found for halides (e.g. NaCl at 700°C). The log-log plot of the neck size versus time has a slope close to $1/3$. The evaporation-condensation process is suspected to stop the sinterability of some non-oxide ceramics (such as SiC, B₄C) at very high temperatures $> 2100^\circ\text{C}$



The model for mass transport from surfaces: surface or volume diffusion from surface, D_S

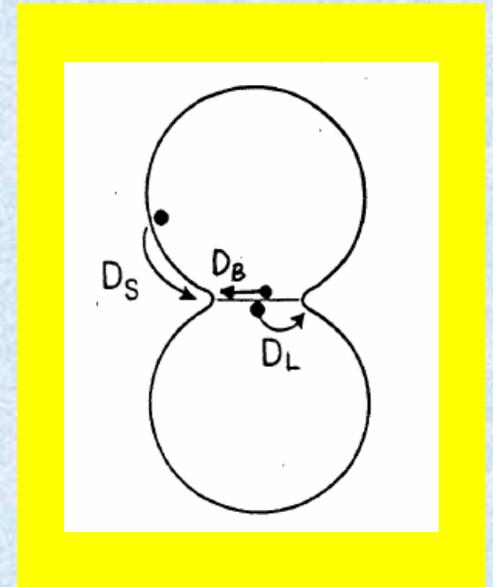
Similar to evaporation-condensation, no shrinkage results from the other two mechanisms of mass transport from particle surfaces to necks through the two possible diffusion paths.

(I) volume diffusion from particle surfaces to necks:

$$y^4 = \alpha_3 t \text{ and } h/r = \Delta L/L = 0$$

(II) surface diffusion, along particle surfaces to necks:

$$y^7 = \alpha_4 t \text{ and } h/r = \Delta L/L = 0$$



The model for mass transport from within the particle volume or from the grain boundary, DL or DB

For mass transfer originating in the particle volume or at the grain boundary, the particle centres approach ($h > 0$) and shrinkage takes place.

(I) for volume diffusion from grain boundary:

$$y^5 = \alpha_5 t \text{ and thus } (h/r)^{2.5} = (\Delta L/L)^{2.5} = \beta_5 t$$

(II) for grain boundary diffusion from grain boundary:

$$y^6 = \alpha_6 t \text{ and thus } (h/r)^3 = (\Delta L/L)^3 = \beta_6 t$$

. Examples of Solid State Sintering

Since ceramics are composed of at least two elements (typically oxygen or nitrogen and metal ions) Both ionic species must diffuse together to maintain the electrical neutrality of the system. Therefore, *it is the diffusion coefficient of the slowest moving ion along its fastest path that controls mass transfer, and therefore densification during solid state sintering.* To enhance sintering, the slowest moving ion must be identified and its diffusion along the fastest path should be "encouraged" through:

Chemical doping,
Atmospheric control
An appropriate time/temperature cycle

Sintering of MgO

MgO sintering proceeds through lattice diffusion. Diffusion of magnesium is faster than oxygen, $D_{Mg} > D_O$. The sintering rate is increased if the diffusivity of oxygen is increased through the creation of additional oxygen vacancies through doping with M₂O (for example Na₂O).

Sintering of Al₂O₃

Another example of solid state sintering is the sintering of Al₂O₃. Initially, it was observed, that small additives of MgO (0.25 wt%) in Al₂O₃ allow the achievement of fine-grained material at full density (which is the ceramist's dream). Additional microstructural observations revealed that MgO eliminates the discontinuous grain growth of Al₂O₃. It was found that grain boundaries do not break away from the pores, which prevents the inclusion of pores trapped inside new large grains, with slow/long diffusion paths for densification. The mechanism by which MgO slows down grain boundary movement in alumina could be as follows

- The majority of MgO doped into Al₂O₃ resides at the grain boundaries, because the dissolution of MgO in Al₂O₃ is small, ~300 ppm. This is due to the relatively large difference in ionic radius: 0.72Å for Mg²⁺ and 0.53Å for Al³⁺
- Any fast migration of the grain boundary would have to incorporate Mg²⁺ ions into the Al₂O₃ lattice, with the resulting increase in internal energy, unless a NEW compound, spinel, forms.

Arguments on the role of MgO in Al₂O₃ sintering continue at the present time

Note that other grain-growth inhibitors can be added to Al₂O₃. For example, submicron ZrO₂ particles (10-20 vol%) residing at the triple points of grain boundaries of alumina effectively inhibit grain growth according to the equation: $r^4 - r_0^4 = a t$, where: r = the average particle size after time t , r_0 = the average initial particle size at $t=0$, and a = constant.

Sintering of SiC

Pressureless sintered SiC requires B and C as additives, which affect the relative diffusion coefficients. Presence of silica impurities in SiC can enhance evaporation-condensation mechanisms through a volatilization reaction



Carbon removes SiO₂ and Si from the surface of SiC according to the carbothermal reduction reaction:



Thus, fewer defects are present at the surface and diffusion along the surface decreases. This slows down the coarsening mechanisms. Simultaneously, boron has been found to selectively segregate toward grain boundary regions, where its role is unclear, i.e. it is suspected that:

Pressure Assisted Sintering

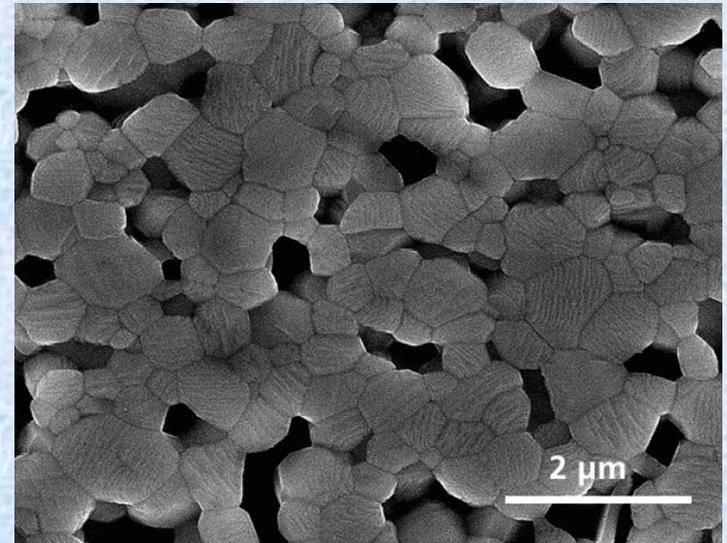
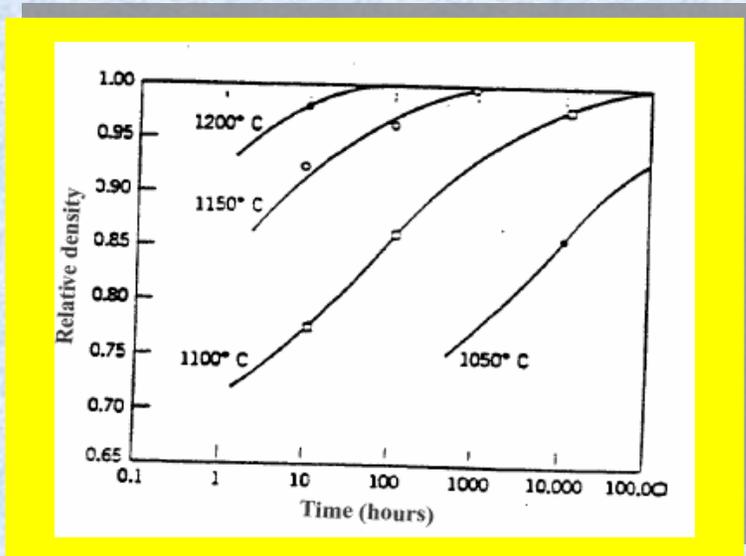
Pressure Assisted Sintering - Technology

Pressure assisted sintering increases the contact pressure of particles and thus the driving force for sintering, compared to pressureless solid state sintering

by ~ one order of magnitude in hot pressing (HP) at 20-40 MPa pressure

by ~ two orders of magnitude in hot isostatic pressing (HIP) at 200 - 300 MPa pressure

Example of Viscous Sintering: Porcelains



Sintered nano barium titanate

NETZSCH Dilatometer 402 C

Equipment



Materials

Powdered metal and composite materials

Measurement

Thermal expansion and sintering behaviour

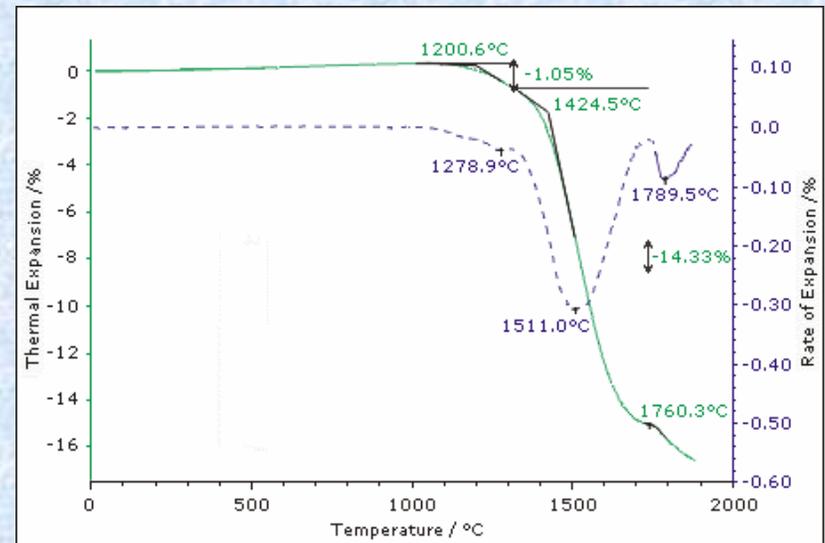
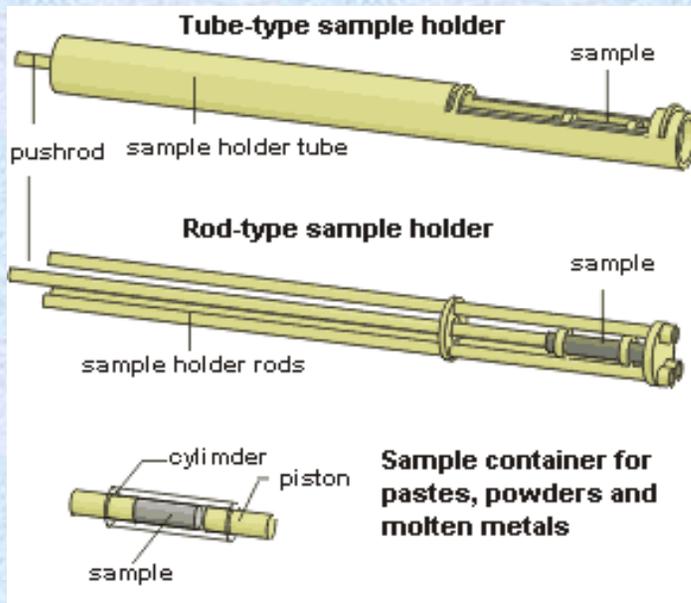
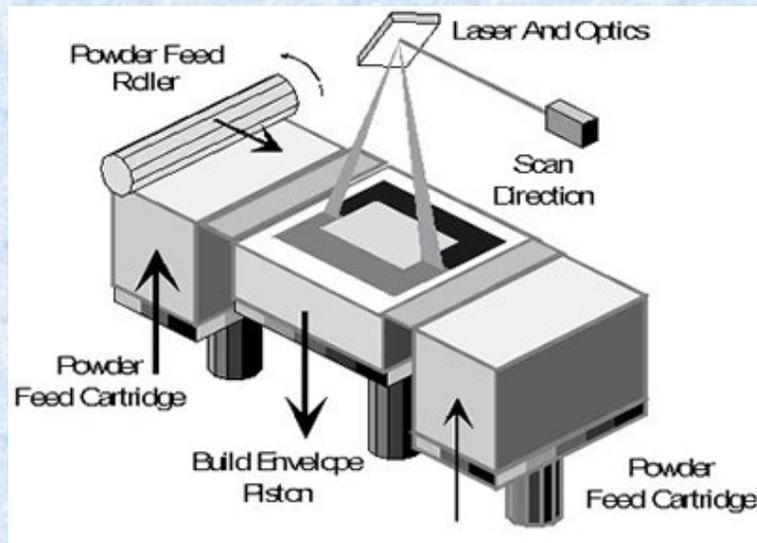


figure shows the thermal expansion and rate of expansion of a silicon nitride green body. The sintering step starting at **1201°C** is due to the influence of the sintering additives. The main shrinkage step occurred at **1424°C** (extrapolated onset). The effect above **1760°C** is most probably due to evaporation of additives

The Laser Sintering Process



Certain proportion of the laser energy is transformed into heat, this depends upon the powder material and its characteristics. Laser output can be minimised through maintaining the powder at a temperature just below its melting point

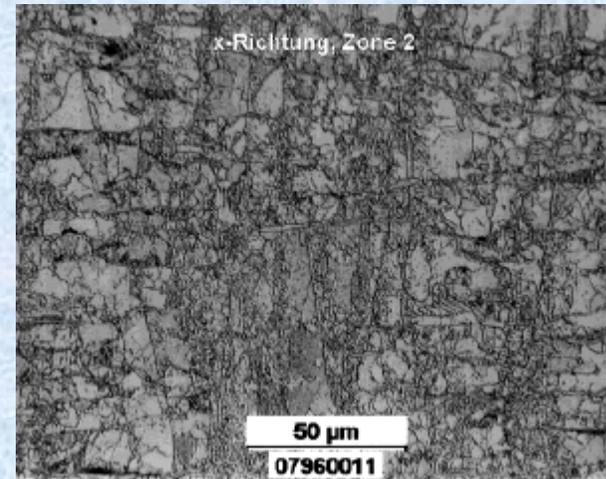


Selective Laser Sintering (SLS)

This process is a well known procedure for rapid tooling/prototyping. Its principle is the following: A powder made from synthetic materials, coated metal powder or mixture of metal powders is deposited in a thin layer. In a next step a Laser beam heats and melts the powder either partially or fully. Repeated application of this procedure creates rapidly full scale objects in one manufacturing step



Surface treated by with SLS



This Figure shows a cut through a sintered aluminium-bronze part. The part has a dense structure with fine grains. Therefore, manufacturing metal forging tools by selective Laser-Sintering seems to be a valuable alternative to conventional manufacturing procedures

Sintering Practice Exercises

1. Name 5 different changes that can occur during heating of a ceramic material.
2. What are the 3 principal sintering processes?
3. What does liquid sintering mean?
4. What does viscous sintering (vitrification) mean?
5. What are the main driving forces during sintering?
6. What are the main driving forces during actual “solid state” sintering?
7. Which transport mechanisms occur during solid state sintering?
8. What is the effect of increased temperature on solid state sintering?
9. Name at least 4 parameters that are crucial during solid state sintering?
10. Describe the different stages of solid state sintering.
11. What requirements must be fulfilled in order to attain total pore elimination during solid state sintering?
12. Why is sintering easier in the presence of a liquid phase?
13. Describe the reaction mechanisms during liquid sintering.
14. How does vitrification differ from “normal” liquid sintering?
15. During the study of a solid sintering process at constant temperature it was discovered that the neck radius, y , is proportional to $t^{0.2}$.
What is the dominating transport mechanism in this sintering process?