

4. Firing and sintering

4.0 Introduction

Firing is the high-temperature treatment in ceramic technology, by which the consolidated powder compact (green body) is transformed into a rigid ceramic (dense or porous) and *sintering* is the corresponding process occurring in the material. Note that sintering is sometimes used in the more special meaning of achieving highest density (we prefer the first definition and call the latter state “densely sintered”). It includes (always) strengthening of the microstructure (→ neck growth and / or particle gluing by a glass phase) and (mostly) densification (→ elimination of porosity accompanied by shrinkage) and coarsening of the microstructure (→ grain growth and possibly pore growth). The driving force of sintering is a reduction of Gibbs free energy (chemical potential or free enthalpy) by replacing high-energy free surfaces (solid-vapor) by low-energy grain-boundaries (solid-solid) and finally by minimizing also the grain boundary area (via grain growth). Externally applied pressure can be used to enhance this intrinsic driving force (→ pressure-assisted sintering, including hot isostatic pressing, to eliminate residual porosity without excessive grain growth).

4.1 Solid-state sintering (SSS)

Dihedral angle φ (ranging from 0 to 180 °, but in many sintering models assumed to be equal to 180 °) defined by $\gamma_{ss} = 2\gamma_{sv} \cos \frac{\varphi}{2}$, where γ_{ss} = grain-boundary energy (solid-solid) and γ_{sv} = surface tension (solid-vapor) (→ determines neck and pore shape).

Monitors of sintering: porosity (relative density), shrinkage (approximately related to the neck size / particle size ratio via the Exner-Petzow relation), relative surface area loss (German relation).

Driving forces: vacancy concentration gradient under curved surfaces (Kelvin equation → diffusion mechanisms) and possibly partial pressure difference over curved surfaces (Young-Laplace equation → vapor transport, i.e. evaporation-condensation mechanisms).

Mechanisms:

- *Densifying sintering mechanisms:* surface diffusion, volume diffusion from the surface, evaporation-condensation (mainly in halides),
- *Non-densifying sintering mechanisms:* grain boundary diffusion, volume diffusion from the grain boundary, viscous flow (not SSS, mainly in glasses), plastic flow (mainly in metals),
- *Grain and pore growth via Ostwald ripening* (dissolution of small objects in favor of large objects).

Geometrical models (two-sphere model, random close packed structure of monosized spheres with a packing fraction of 64 %, during sintering coordination numbers increasing from approx. 7 for a rcp structure with 64 % to approx. 14 for a dense structure of space-filling tetrakaidecahedra – Coble model), *scaling laws* (sintering times scaling with grain size ratios

via scaling exponents of 4 for surface and grain boundary diffusion, 3 for volume diffusion, 2 for vapor transport and 1 for viscous or plastic flow – Herring model).

Stages of sintering and analytical models: initial (neck growth), intermediate (densification), final (grain growth); analytical models (→ see Table) and relations by Frenkel (viscous flow, not SSS), Kuczinski, Kingery-Berg, Coble and Zener (→ see Extended Lecture Notes).

4.2 Liquid-phase sintering and vitrification

Dihedral angle φ (usually smaller than in SSS) defined by $\gamma_{ss} = 2\gamma_{sl} \cos \frac{\varphi}{2}$, where γ_{sl} = interfacial energy (solid-liquid) and contact angle (wetting angle) θ defined by $\gamma_{sv} = \gamma_{sl} + \gamma_{lv} \cos \theta$, where γ_{lv} = surface tension (liquid-vapor) (→ wetting and spreading, agglomerate penetration and particle segregation).

Stages of sintering and analytical models: initial (heating, melting, particle rearrangement), intermediate (solution and reprecipitation – contact flattening / grain shape accommodation / Kinergy model, Ostwald ripening and coalescence), final (skeletal sintering and coarsening – reaction-controlled or diffusion-controlled grain growth e.g. according to the square-root-of-time and the cubic-root-of-time law / Lifshitz-Slyozov-Wagner model, respectively).

Typical liquid-phase sintering has a liquid (melt) content of maximally 15 vol.%. When the liquid content is higher, at least 25–30 vol.% (but typically much higher, e.g. 50–80 vol.% in porcelain), the process is commonly called *vitrification*. Vitrification (where the viscous flow mechanism alone is sufficient to bring about complete densification – Frenkel’s model in the initial stage, Scherer’s model in the intermediate stage and the Mackenzie-Shuttleworth model in the final stage) is the common process in firing traditional clay-based ceramics.

4.3 Pressure-assisted sintering

External pressure can be used to enhance the driving force (change in overall surface energy by replacing free surfaces by grain boundaries) for densification without enhancing the driving force for grain growth. *Models of pressure-assisted sintering* (e.g. hot pressing and hot isostatic pressing) are based on *creep equations* (Nabarro-Herring creep by volume diffusion, Coble creep by grain boundary diffusion → see Extended Lecture Notes).

Complex exercise problem: Consider for porous ceramics the results of microscopic image analysis (porosity and pore size), evaluated using the *commercial software Lucia G[®]*, and discuss these results in comparison to those obtained by the Archimedes method (porosity) and via mercury porosimetry (porosity and pore size). *Additional explicit questions:*

- a.) Which size measures are used in microscopic image analysis and how are these 2D size measures related to the true (3D) size measures determined e.g. by tomographic techniques? Discuss the principal difference between the pore size distributions determined from microscopic image analysis and those obtained from mercury porosimetry.
- b.) What are the necessary preconditions (practical and theoretical) to obtain reliable porosity values by microscopic image analysis?
- c.) Is the porosity of a final ceramic related to shrinkage during sintering? If yes, how?
- d.) How do grains grow during sintering? Can pores grow during sintering? If yes, how?