

Chapter II

Theoretical Part

Viscous Sintering

Sintering has been the classical domain of conventional and technical ceramic materials, while melting has been the predominant process in glass and metal production. It is true, though, that sintering has been playing a major role in metallurgy for a long time already. Sintering of glasses, by contrast, is a relatively new process. It was developed in connection with special applications, such as vitrification of nuclear wastes, production of filters, biomaterials, pre - forms for optical fibers, etc., The development of viscous sintering was also boosted by the progress in the production of ultrafine powders (by plasma precipitation, or by sol - gel technology). These materials exhibit a "glass - like" behavior. In specific, they often sinter via viscous flow. The intrinsic advantage of viscous sintering lies in the combination of conventional ceramics forming technology, high chemical versatility, and relatively low process temperatures.

The objective of a sinter process is the conversion of a compact of small particles (green body; pre - form) into a monolith by the application of heat. As a common feature of all sinter processes, the decrease and dissipation of surface energy is the primary step. Distinctive features consist in the presence or absence of further driving forces (e.g., by chemical reactions), in the location of the process temperature relative to the liquidus temperature of the system, and predominant transport (i.e. dissipative)

mechanism. The process of liquid phase sintering, solid state sintering, and viscous sintering, are shown in the following list:

Table 2.1 Comparison of Three Types of Sintering

	Liquid phase sintering	Solid state sintering	Viscous sintering
Starting materials	crystalline, many compositions	crystalline, one component	amorphors, one component
Sintering temperature	clearly above T_{liq} of the system	closely below T_{liq} of the system	distinctly below T_{liq} of the system
Additional driving force	chemical reactions	none	none
transport mechanism	liquid phase diffusion	solid state diffusion	viscous bulk flow
sinter aids	act by lowering the eutectic temperature	act by providing high - diffusivity paths in the grain boundaries	temperature, and, in turn, the glass transition temperature, T_g of the system

In a conventional ceramic process, the chemical reaction from kaolinite to metakaolinite and then to mullite predominates.

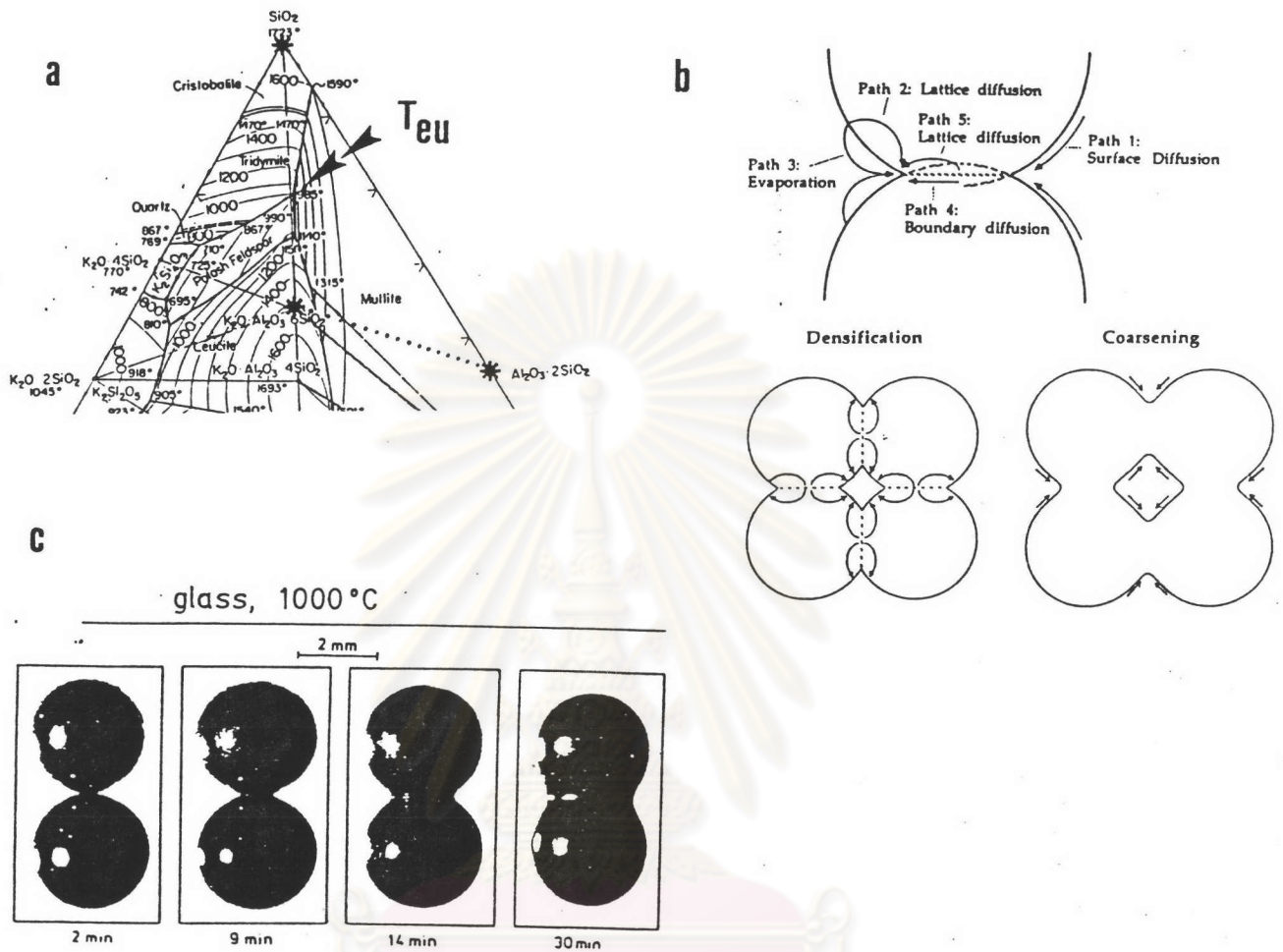


Fig. 2.1 (a) Section of the phase diagram $K_2O - Al_2O_3 - SiO_2$ showing the eutectic which controls liquid phase sintering in conventional ceramic
 (b) Sketch of the key mechanisms in solid state sintering
 (c) Demonstration of the bulk flow in viscous sintering

When taking a closer look to the process of viscous sintering, the nature of the amorphous starting materials must be understood first. Amorphous materials occur as monoliths or as fine particles. As a common feature, they all exhibit a "glass-like behavior". Upon heat treatment, they undergo a gradual softening rather than exhibiting a distinct melting point

(which nonetheless is a well - defined system property even for amorphous materials). To be more specific: They exhibit the typical features of the viscosity - temperature relation known from glasses. These are: a glass transition temperature, T_g , a dilatometric softening point, T_M , a Littleton softening point, T_L indicative of macroscopic form stability, etc. The sketch below illustrates the features:

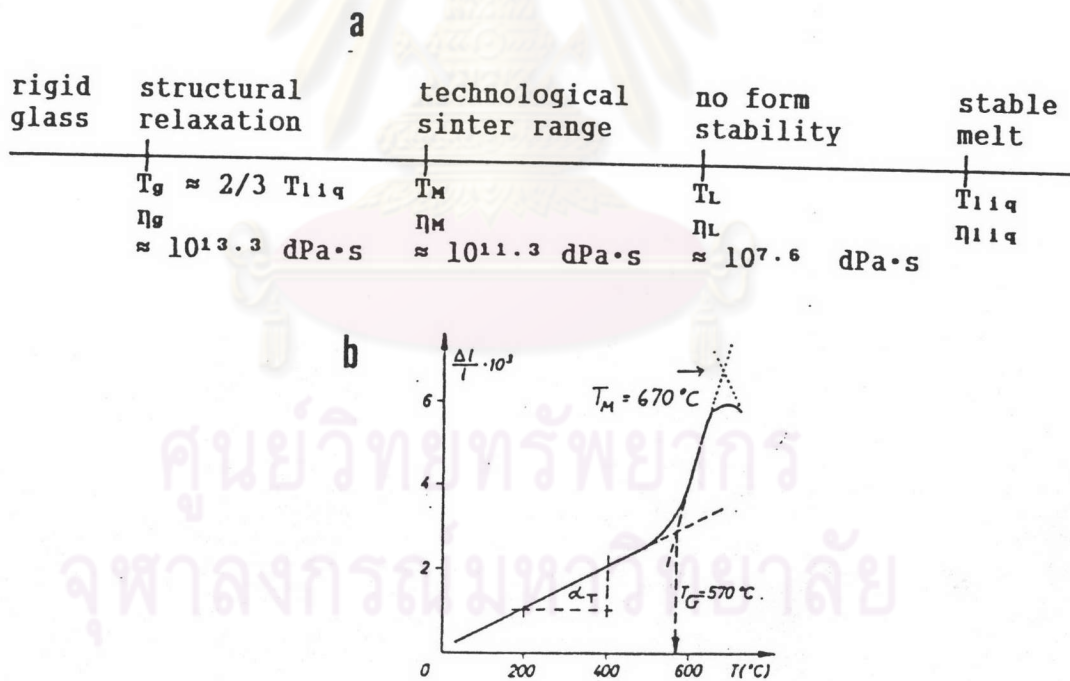


Fig. 2.2 Behavior of a glassy material in terms of the viscosity - temperature relation below T_{liq} ; (a) technological ranges; (b) typical dilatogram.

Studying the behavior of small amorphous particles has shed much light on our understanding of the nature of monolithic glass as well as on the liquid state in general. Both states do not seem to be perfectly homogeneous after all.

The feature which makes a material an amorphous material is the freezing - in of a relaxation mechanism responsible for the establishment of an ordered (crystalline) structure. Macroscopically, frozen - in phases behave like equilibrium phases. They have defined properties such as density, refractive index, heat capacity, etc. Freezing - in can be brought about by

- cooling down a melt
- extracting a solvent
- increasing the size of a molecular array
- precipitation from a fluid phase (plasma, gas, liquid)
- applying a high pressure gradient

fast enough so that no structural relaxation will occur. Indeed, all of the above options correspond to real materials, which are, in the same sequence: technical glasses; glasses derived from a polymeric sol - gel process; technical polymers; hydrogel, pyrogels, alcogel, aerogel precipitates, and other nano - phase materials; meteorite glasses.

The nature of the powders used as starting materials for viscous sintering is to be discussed. Some scientists would feel uneasy to label them as amorphous, because they clearly see traces of crystallinity, e.g., in a high resolution TEM. The fact is faced that on a scale of only a few lattice constants, the terms "crystalline" and "amorphous" merge. Extremely small particles will barely assume the shapes of perfect single crystals with perfect faces; such particles will rather tend to assume rounded boundaries due to the very high surface forces. On the other hand, a small array of

material can barely be arranged in a perfectly disordered way. Chemical forces will impose a distinct near - range order. The common denominator of the otherwise conflicting points of view is the diffuse boundary. It is then a matter of taste rather than of scientific correctness to label these materials as “not perfectly crystallized”, “amorphous”, “nano - crystals”, or “nano - glasses”. And it certainly is a matter of degree rather than of yes/no glassy. There is another class of not - well crystallized materials. In these materials, the disorder consists in a statistical fluctuation of the lattice constants. These materials are “amorphous” in a different sense. They may have quite large grain sizes with sharp boundaries in - between. Although sintering at significantly decreased temperatures, they do not sinter by viscous flow, but by enhanced solid state diffusion.

When powders of the glassy characteristics are sintered to monoliths, then the grain boundaries become invisible, and almost undetectable. It is very suggestive to call the resulting material a glass. In fact, materials derived by viscous sintering and glasses obtained by melting from the same system are virtually indistinguishable. Until today, almost any claim for an experimental proof of the contrary could be dismissed as wrong.

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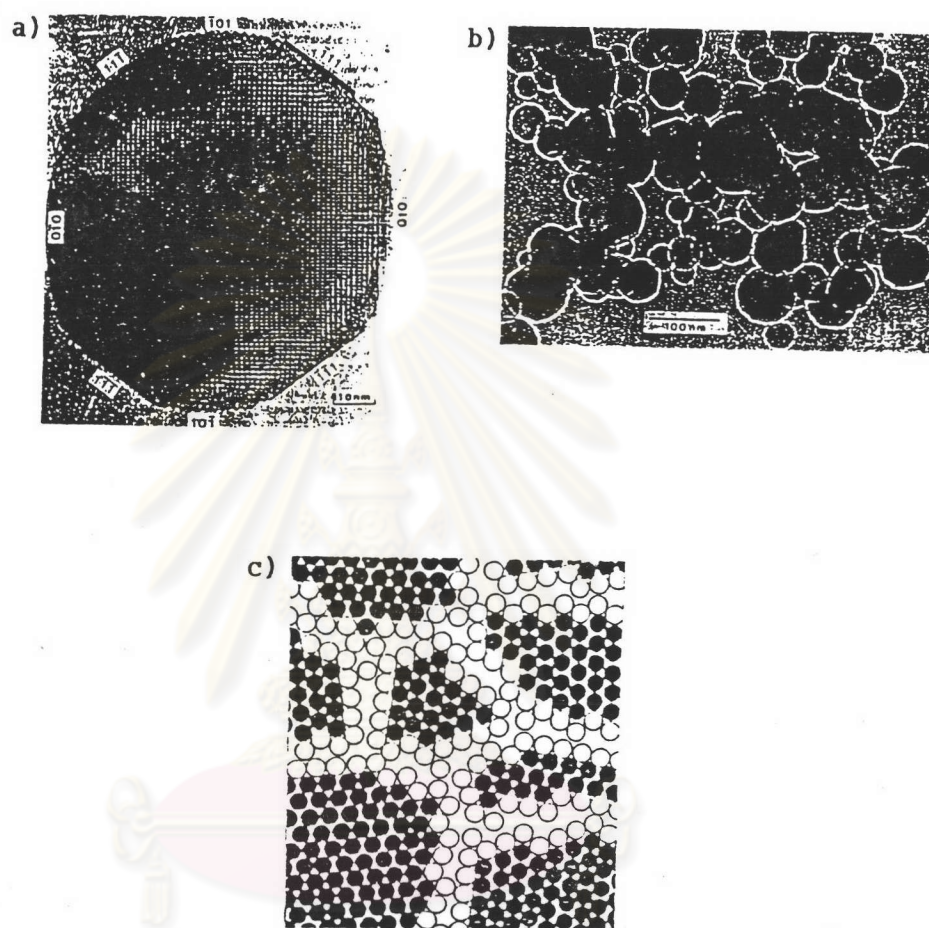


Fig. 2.3 Schematic for sintering Al_2O_3

- (a) Ultrafine Al_2O_3 particle showing both the features of a crystal and the rounded boundary; image width ≈ 90
- (b) Array of ultrafine Al_2O_3 particles; image width ≈ 600 nm
- (c) Sketch of a sintered nano-material with diffuse grain boundaries



Densification Kinetics

Modeling the densification kinetics in viscous sintering is not simple, but at least easier than for solid state or liquid phase sintering. A model based on an array of monosized spheres suggests that the densification rate linearly depends on the so - called capillary velocity σ/η (i.e., the quotient of surface tension and viscosity), and is inversely proportional to the size of particles. Thus the main parameters are temperature and particle size. The time demand for complete densification is approximated by

$$\tau_{\text{sinter}} \approx 1.6 d \eta(T)/\sigma \quad 2.1$$

The model is reported to be quite insensitive towards particle geometry. With uniaxially compacted broken particles (crushed glass), however, an expressed unisotropic densification behavior is observed. In addition to the densification rate, a flow (or "creep") rate occurs. Such problems have to be controlled in the fabrication of the green body already. Thus, as far as fabrication is concerned, much of the know - how from solid state sintering can be used for viscous sintering, too.

Glassy Phases Versus Crystalline Phases

A glassy phase is in a frozen - in state which is close to, yet distinctly different from the underlying equilibrium. This can be expressed by the Gibbs free energy difference of devitrification, G_{dev} . It is tempting to estimate G_{dev} by an interfacial term, G^x . For structural entities of radius, r , G^x takes the value $3\sigma V^m/r$.

where σ = surface tension

V^m = molar volume (molar mass divided by density).

For r , the critical radius r_0 from nucleation theory is employed, and its value at the glass transition temperature, $T_g \approx (2/3) T_{liq}$ is adopted.

$$G = x_k G_k + G^{mix} + G^x \quad 2.2$$

$$r = r_0(T_g) = \frac{2 \sigma V^m}{H^m (1 - T_g/T_{liq})} \approx 6 \sigma V^m / H^m \quad 2.3$$

where H^m = heat of melting:

T_{liq} = liquidus temperature

Actually, r_0 is smaller at T_g than at any $T > T_g$. Thus prior to being frozen - in, the entities remain subcritical and transient species, but no real phases. They may be called latent compounds. An evaluation of G_{dev} by equation. (3) yields $G_{dev} \approx H^m/2$. The enthalpy difference of devitrification, H_{dev} is derived by the relation $H_{dev} = G_{dev} + T S_0$, where S_0 is the zero point entropy of the glass; according to $S_0 = H^m / (3T_{liq})$. Thus, at $T = 298$ K, H_{dev} assumes values between $0.55 H^m$ and $0.65 H^m$ depending on the value of T_{liq} . In table 2.2, available experimental data for H_{dev} , G_{dev} , H^m , T_g , and T_{liq} are compiled. These data suggest $H_{dev} = (0.60 \pm 0.06) H^m$ and $G_{dev} = (0.53 \pm 0.05) H^m$, which is in good agreement with the above concept.

Table 2.2 Enthalpy and Gibbs free energy differences of devitrification, and heats of melting, in kJ/mol; liquidus and glass transition temperature in K

compound	H _{dev}	G _{dev}	H ^m	T _{liq}	T _g	compound	H _{dev}	G _{dev}	H ^m	T _{liq}	T _g
B ₂ O ₃	18.2	11.3	24.1	723	530	N·C ₃ ·S ₆	77.3	71.1	-	1603	-
C·A·S ₂	71.7	60.2	166.9	1826	1113	N·C ₂ ·S ₃	57.7	53.8	-	1562	838
K·A·S ₄	67.8	61.6	108.8	1693	-	N ₂ ·C·S ₃	87.0	80.3	-	1483	743
K·A·S ₆	89.6	72.5	123.0	1473	926	N ₂ ·S	29.3	24.4	57.7	1393	-
K·S	8.2	-	50.2	1249	-	N·S	37.7	34.7	52.3	1361	684
K·S ₂	12.6	-	35.2	1318	790	N·S ₂	29.3	25.4	35.6	1147	724
L·S	-	-	28.0	1474	700	C·S	-	-	82.8	1817	1065
L·S ₂	54.4	49.7	61.1	1306	735	P ₄ ·S	22.2	18.3	-	1013	-
N·A·S ₆	103.8	92.8	118.6	1391	1018	P ₂ ·S	15.1	12.8	53.6	1018	-
N·A·S ₄	73.7	67.0	-	1523	1130	P·S	8.1	6.7	34.5	1037	695
N·A·S ₂	47.2	44.2	-	1835	1033	SiO ₂	9.5	8.0	9.6	1996	1495

In this thesis work, $T(n,n)$ in °C is used instead of $10^{n,n}$ dPas because a temperature relates to a viscosity level, so in the report, the value of n,n is used. From the equation 2.1, the importance of viscosity is that the sintering time can be calculated.

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