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SINTERING AND MICROSTRUCTURES
(Lectures I and II)

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AN INTRODUCTION TO SINTERING

This presentation serves as an introduction to the fundamental step of the prodution of nearly all the ceramic materials: "sintering" which means "the bonding of powdered materials by solid-state reactions at temperatures lower than those required for the formation of a liquid phase".

Historical Background

The "ceramic" art dates back to the earliest days of man-kind civilization. Its fabrication processes did always rely on sintering powder compacts based on clays and other minerals. Therefore, from this point of view, through the centuries, sintering has been an extensively applied art. Along with bodies formulations, sintering belonged to the secrets of the ceramic ware producers. It is worth recalling that in Western Europe porcellain ceramic could be reproduced only in the 18th century, by the German alchemist Boettger (1682 -1719) who produced both "porcellain" and "stoneware" according to a procedure which gave birth to the still-leading German ceramic industry.

On the other hand, outside the realm of the "china-ware" production, sintering has been for a very long time a forgotten art. In fact, in the early days, long before metallurgy could reach the high temperatures needed for the "foundry" works, sintering of metal powders was the only viable metallurgy process.

Ancient Egyptian technologists became rapidly aware that iron metal parts could be fabricated by hammering the "iron sponge" obtained by the reduction of fine iron ores. For a long time, the forging a presintered metal used to be the only technique available to produce iron parts and tools. Precious metals, like gold and platinum, which were naturally available as grains and powders, have also been worked through "powder metallurgy operations" before the fusion processes could be at hand. In fact, as soon as furnaces grew in temperature, the powder metallurgy was overshadowed by the foundry techniques.

It is interesting to realize that sintering to produce Platinum compacts by the sintering technique of Wollastone became a viable method in 1803. He used platinum metal powder, obtained by the decomposition of some chemical precursor, to make compacts which where fired and forged. Again this procedure was surpasses about 60 years later by the fusion method devised by Sain-Claire Deville, who could have a relatively easy access to coke gas and oxygen to heat up the fusion crucible.

Powder metallurgy, based on the sintering process, is presently a widely spread technique. Light bulbs Tungsten wires, cemented carbides and near-net shape parts of various alloys are produced with the solid state sintering operation.

Therefore, most of the theory and practice of sintering stems from the powders metallurgy. Only from the late '-40ies some interest rose for the sintering of "non-metals". The drive rose from the refractories industry development and the rising nuclear fuels production. Oxides, caribides and nitrides received more and more attention due to their increasing role in high-technology applications: thermomechanical, electronic and bio-medical.

Sintering or Syntering?

This question has a quite obvious answer. The correct spelling reports "sintering" . But the sound of this word recalls another word "synthesis" which in turn has the general meaning of "the combining of separate materials or abstract entities into a single or unified entity". Philosophy tells us that in the synthesis, both the "thesis" and its apparently opposite "anti-thesis" comply with each other in a mutual agreement.

The prefix "syn-" in ancient Greek means "together" and the verb "tithenai" means to put, to place. Therefore, in the synthesis the parts loose their original identity. But, it is not the case when powdered particles "sinter" to build a "sintered" compact. Their nature, say chemical composition and structure, remains the same as before, only shape and relative dimensions should possibly change. In fact, if the chemical composition or the structure are modified, in this case there is not only a sintering process but a more complex solid state reaction accompanied by sintering phenomena.

If we take what above into account, we are forced to think at different roots of the two words "sin-tering" versus "syn-thesis" because they mean different phenomena.

It is generally reported that "sintering" derives from the german word "sinter", the mineralogy term which pertains to a "siliceous or calcareous matter, deposited by springs or formed around the vent of a geyser". But the word is also considered a derivative of "cinder = ashes" which in old English was written "sinder". Does sintering recall " ashes" because it is a product of the firing of materials? It might be. In fact, firing is an essential step of the sintering process.

However, the mineralogy term "sinter" has the physical meaning of "bonded particles" or "joint particles", it is reasonable that the original Greek prefix "syn-" (together) and verb (tithenai = to place) must have originated the modern term of "sintering" through German.

It is a good thing that the spelling bacame different, at least in English , eventually through the German vocabulary. In fact, sintering should not imply any variation of the chemical composition which is obvious in all the chemical syntheses. If this happens, as it very often does, we are facing phenomena to be named differently as: reaction sintering, vitrification and liquid phase sintering.

Synthesis - sintering opposites.

Opposite to the chemical sysnthesis we have the chemical "analysis" which is meant to take apart the chemical constituents of a substance, either as simpler components or elements. The energy involved in the synthesis - analysis cycle is made up by breaking and forming chemical bonds. It takes energy to break down a chemical compound into its constituents.

On the other hand, an operation opposite to sintering can be found in the "grinding - milling" processes which ultimately build up new "surface" into the material but does not change its physio-chemical nature. Grinding needs a certain amount of energy of which a subtantial part is stored in the new formed surface.

Finally we have these two process operation pairs "synthesis - analysis" and "sintering - grinding". The first implies the variation of the chemical composition which, on the contrary, remains unchanged within the second pair of processes.

Sintering is related to the elimination of a substantial fraction of the solid-gas interface of the starting materials. This is accomplished by thermal treatments, firings. This latter enhances atom mobilities and allows the "sintering driving force" to exhert its action which utimately gives a solid, impervious body with a limited amount of entrapped porosity, eventually near to the theoretical density. The driving force of sintering derives from the surface energy of matter and related phenomena.

General references

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SURFACE ENERGY

We meant that "grinding" can be considered the opposite of "sintering" because in grinding a solid piece is reduced to fine particles, increasing their surface area. Part of the grinding energy remains stored in the particles new surface. Let us recall that in a single phase the "Gibbs freee energy" may vary according to the equation

(1) $dG = VdP - SdT + YdA + udn$,

being Volume, Pressure, S(entropy), Temperature, Area, n (moles number), "Y" surface energy, "u" chemical potential. The variable "Y" is the reversible work needed to create a unit area of surface under condition of constant T, P and amount of matter.

(2) $Y = (dG/dA)$ at const. T,P,n.

A process is "spontaneous" if it is accompanied by a reduction of the system's free energy content, then, any transformation leading to a surface energy reduction will be spontaneous.

The primary driving force for sintering is the reduction of the "free surface energy content" of the system. This is accomplished by reducing the area of surfaces and interfaces within the compact. This can be achieved by a combination of two processes:

a) coarsening - conversion of many small particles into fewer and larger ones;

b) densification - replacement of gas/solid interface with solid/solid interface.

Sintering is evidence of the combined effects of both processes.

Sintering categories

There are three broad categories of consolidation

1) Vitrification - when the composition and processing temperature produce an amount of liquid sufficient to eliminate the gas phase present between the reacting grains. This is the process on which the "clay" ceramics production is based.

2) Liquid phase sintering - as in the previous case a liquid film is formed but not enough to allow the removal of the gas phase; therefore, to reach full density, a change in grain shape and size is necessary.

3) Solid state sintering - densification is achieved only by the change in partcles shape by diffusion through lattice, grain boundaries and, eventually, through the gas phase. change of grain size and shape without any liquid phase contributio

The first two categories could also be considered "react sintering" processes. In order to reach the densification in any these categories, we have at our disposal these five variables:

- 1. Temperature -- 2. Time - 3. Particle size - 4. Compositi (additives). - 5. Pressure.

In this introduction the elementary concepts of solid sta sintering will be presented.

DRIVING FORCE

The driving force for sintering (reduction in excess surface fr energy) is translated into a driving force acting at the atomic lev by means of the curvature differences which necessarily occur different parts of the three dimensional compact. If the surfac curvature were all the same, then no driving force would act on t system after the particles had reached their minimum surface energ This minimum is met by spheres of fluid phases. Not necessarily minimum surface energy corresponds to a spherical surface when th material is a crystalline solid. Facetted bodies are frequent an related with the different surface energies of the crystal lattic planes.

Let us consider two parts of the same solid phase, with fla surfaces, separated by the vapor phase: they are in equilibrium if th transfer of (dn) moles does not change the total free energy content. This happens if the chemical potential (u) is equal in both parts o the solid phase.

This is not true if the surfaces have different curvature radii an the addition of (dn) moles of mass does increase both volume an surface of the part. As in the case of small drops in the presence o a large mass of fluid. In fact, experience has always shown that small particles are unstable in the presence of large ones. Small drops ten to disappear increasing the mass of the larger ones. Matter within the small drops must be at a higher chemical potential.

PRESSURE DIFFERENCE ACROSS A CURVED SURFACE

It has been recognised that it needs a certain amount of work to form and expand the volume of a bubble (for instance within a liquid).

The work of expansion (PdV) is stored in the energy of the inner bubble surface, formed within the liquid (YdA) under reversible equilibrium conditions. Energy must not get dispersed in other parts of the liquid through other mechanism as mass movement or swirl.

$$PdV = YdA \quad (a)$$

The sphere's geometry requires that $dV = 4\pi r^2 dr$ and that $dA = 8\pi r\, dr$.
By substituting dV and dA in (a) we obtain the relation:

$$\Delta P = Y(dA/dV) = Y(2/r)$$

This is the pressure difference across a sphere's surface o radius "r" and surface tention "Y". If the volume is a cylinder, than the relation becomes $P = Y/r$. In general, for a surface with two curvature radii (r and R) the relation becomes

$$\Delta P = Y(1/r + 1/R)$$

This equation dates back to the work of P.S. de Laplace in 1806.

The presence of a pressure difference across a curved surface can be also recognized by the rise of a liquid which wets the surface of a capillary tube. The liquid makes a concave "meniscus": above which there is a lower pressure than above the flat liquid surface. This latter pushes the liquid column up. The case of water in a glass tube.

The reverse is true when the liquid builds a "convex" meniscus across which there is a pressure higher than that above the flat surface. The former pushes down the liquid to a lower level with respect to the flat surface. Case of Hg in a glass tube.

In general it can be seen that, with reference to a "flat" surface,

a) pressure across a concave surface is lower;
b) pressure across a convex surface is higher.

The presence of a pressure difference across a curved surface influences the free energy of the matter underneath that surface. An increase in pressure increases the free energy. In fact if we consider constant T, A and n and apply the ideal gas law ($V = RT/P$), from the relation (1) a simple VdP increase can be written as:

$(RT/P)dp$ that is $RT\, d\ln P$;

By integrating between P and P°

$$V\Delta P = RT \ln(P/P^\circ) \quad \text{but } V\Delta P = V\cdot Y(2/r)$$
$$\text{Therefore } \ln(P/P^\circ) = (VY/RT)(2/r)$$

The pressures can be related with the concentration $C(r)$ and $C(\infty)$. Concentrations under the curved (r) and the flat surfaces (∞). The relation, first proposed by W. Thomson Lord Kelvin in 1871, links the surface energy (Y) curvature radius (r) and concentration $C(r)$, $C(\infty)$ under the curved and flat surface respectively. It is important to point out that this relation does not contain any "mass" value and it can be extended also to "vacancy" species. In this more general approach, the Thomson equation can be read as follows:

"any time there is a curved surface, the radius (r) is positive when it is within the dense phase of the species being considered". The dense phase is "vacuum" for the "vacancies" and the "solid" mass for the "atoms". Viceversa, the radius is negative when it is in the dispersed phase. Summarizing

1) from the point of view of atoms:

a) pressure is higher above a convex surface,
b) pressure is lower above a concave surface.

2) from the point of view of "vacancies":

a) they are concentrated above a convex surface which is "concave" when looked at from the point of view of solid matter;
b) they are diluted under a concave surface that is convex from their point of view of the atoms.

Therefore in a powder compact the vacancy concentration will be different at regions of different curvatures resulting in vacancy gradients and, thus, vacancy flow. The rate of mass transport is described by Fick's law of diffusion

$$J = -D\, dc/dx$$

where J is the vacancy flux, D the diffusion coefficient and dc/dx the concentration gradient.

This flow of vacancies is exactly equivalent to the flow of atoms in the opposite direction. It is often helpful in the case of ceramic materials to consider the alternate representation of the driving force for atom movement: namely that a flow of atoms stems from the normal pressure difference which occurs in regions close to the surface different curvatures. This representation leads to a diffusion flow which can be written as follows:

$$J = -(D/RT)dP/dx$$

being dP/dx related to dc/dx throufh the chemica potential (du/dx), via the relation $C\ (\text{mol}/V) = 1/V$ and $(1/V) = (P/RT)$.

The flux J is given as moles/(area x time) whereas the diffusion coefficient D has the dimensions of an area/time.

SINTERING STAGES

The sintering behaviour has been considered to take place in stages.
(I) Initial - first 5 % shrinkage,
(II) intermediate -
(III) final - through the last 10%.

Although there is not a clear cut between the stages and some authors omit the intermediate stage, the complexity of the problem forced the theories to be focussed to the initial and final points only.

(I) Initial stage

The individual particles of the green compact remain identifiable and begin to grow bonding necks at their points of contact. A grain boundary is formed at the junction point. The initial stage is considered exhausted when about 5% of the theoretical shrinkage has been accomplished.

Modelling of the early stage of sintering dates back to the work of Frenkel (1945) and particularly to the work of Kuczynski (1949) who analysed a simple joint sphere-plate. He experimentally measured the rate of growth of the neck between the sphere and the plate. By using either metals or glasses, he gave the kinetics equations for diffusion controlled (metals) and for viscous flow (glasses) mechanism.

After his work, the following generalized expression has been proposed to link x (neck radius), r (particle radius), K (constant containing T,Y,D,P,L,k) and t (time)

$$x^n = r^m K t$$

The (K) constant includes terms as: surface energy, atomic volume, Boltzman constant, absolute temperature and the appropriate coefficient of diffusion D, being this latter defined by the actual trasport path of matter: either through the bulk (lattice), the surface, or the vapor phase, besides the case of viscous flow.

The following cases have been proposed with the appropriate exponents of the kinetics equation (n) and (m):

Transport mechanism	(n)	(m)
1 Viscous flow	2	1
2 Vapour phase	3	1
3 Bulk diffusion	5	2
4 Surface diffusion	7	3.

This approach was concerned only with the mechanism of neck growth and did not considered either densification or grain growth; nevertheless is stimulated further modelling in sintering.

In fact, the two-spheres model for neck growth was proposed by Kingery and Berg with two different alternatives:

a) neck growth without densification,
b) neck growth with densification that is a center to center approach.

Taking different materials to study - viscous flow (glass), evaporation -condensation (NaCl) and bulk diffusion (Cu or Ag) the kinetics equation could be fairly confirmed from evaluation of the relative shrinkage $\Delta L/Lo$ vs time and the observation of the neck growth rate. These experiments indicated several alternate paths for matter transport during the initial stage of sintering, in addition to the first one, based on vacancy movement from the neck to the surface regions with different curvature radii.

The model's picture became more and more complicated as grain boundaries and dislocations became element of the sintering process as route for matter transport. There is a most signigicant difference between these pathways of matter transport

	Source	Path	Densif.	Coars.
1.	Surface	Surface	-	+
2.	Surface	Lattice	-	+
3.	Surface	Vapor	-	+
4.	Grain.bound.	G.Bound.	+	-
5	Grain. "	Lattice	+	-
6.	Bulk (disl.)	Lattice	+	-

Any transport originating from the surface and moving either via surface, vapor or lattice, will not cause any shrinkage but just neck's growth and eventually coarsening.

On the other hand, any material transport originating from the particle's volume, moving through dislocations and grain boundary (even along the surface) into the neck, shall produce shrinkage.

Simultaneous sintering mechanisms could make their detection quite difficult. Efforts met little success and only at the very early stage of sintering, unless the mechanism was unique throughout a large part of the process. It is common procedure to assume that the effect of each mechanism is simply "additive". There are conditions in which one is predominant to be eventually discovered.

II - Intermediate stage

This step is valid up to a 92% density in which the system is considered to consist of a set od uniform grains sharing faces with cylindrical pores running along each three-grain edge and meeting at four-grain corners. The solid is a truncated octaegron, with 14 faces and 36 edges and 24 co ners, named tetrakai-decaedron which fills completely space volume. The pore phase is supposed to run along the edges and to be consequently continuou of the labyrinth type.

Coble derived equations to expresse the change in porosity during the intermediate stage of sintering by considering the diffusion of atoms from the grain boundary to the adjacent pore either directly along the grain boundary (Dgb) or through the lattice (Dl).

The porosity was considered (Pj) as the ratio between pore volume and grain volume at the "j" stage. The equations with A and B representing constants are

for lattice diffusion $Pi-Pj = ((A\ Dl\ Y\ v)/(l^3 kT))\ t$

for grain boundary diff $Pi-Pj = ((BDgb\ Y\ v)/(l^4 kT))\ t$

The lattice diffusion model predicts that the volumetric porosity decrease is linear in time. Because each of these models is really only an order of magnitude calculation, the difference in the specific constant used is almost insignificant. They do indicate, however, that the rate should decrease as sintering proceeds. In fact being "l" the length of the edge of the grain in contact, the grain growth effects the pore shrinkage. In the formulas "l" is the edge length proportional to grain size; "v" is the atomic volume.

However, these equations are applicable only over a density range small enough that no change in grain size occurs. The combination of the Kuczynski rate exponents and the grain size dependencies have been widely used to establish the predominant sintering mechanism at various interval in the sintering process.

If we take into account the time dependence of the grain size and insert it in the above equations, the the following relation is obtained for the porosity

$$P = -(\text{const})\ \ln t$$

Isotermal density vs time data calculated for alumina have substantiated a semi logarithmic dependence over a significant range of density change. Nevertheless, over a certain limit there is a non linear dependence. The evidence is taken to support the assumption that a lattice diffusion mechanism is operating during the intermediate stage of sintering and that grain growth rates significantly affect the obserbed rates of sintering.

III - Final stage

The final stage begins when, as a consequence of densification, the pores have become isolated, mainly at four-grain corners. Some pores may lie on grain boundaries and, depending on grain growth behaviour, some may be left within grains. The pores are usually modelled as spherical, but recently more realistic geometries have been observed specially at grain boundaries.

The final stage is complicated, because the porosity decrease (density increase) is not linear with the logarithm of time. The pores are closed at the four-grains corners. The ambient gas trapped in the pores at closure may inhibit the rate of further shrinkage. Sometimes there is an inversion of the density through a top value after either prolonged firing or, more often, higher temperature treatment.

Reason for failing the full density approach lay in many factores. The porosity is not ideally distributed as it is assumed in the model. The distribution of the pores affects the shrink rate: larger pores shrunk less rapidly and, eventually, if very large they might even have grown larger. Because of these complications quantitative evaluation of the final stage is considered much less precise than in the initial stage.

However, although complicated from the model point of view, the attainment of fully dense allumina bodies indicated that there is no intrinsic limitation to the achievement of complete pore closure.

DENSIFICATION AND TREATMENT OF DATA.

Density versus time graphs have been reported for nearly all the ceramic bodies, from early stage through the intermediate, down to the final stage of sintering. The densification parameter alpha = (d'-d°)/(dt-d°) is given where (dt) is the theoretical density, d° the initial and d' the actual density.

The rate which may be evaluated from alpha versus time graphs, have been used to assess the temperature dependence in order to compare it with any supposed model mechanism.

Agreement with kinetics models would be considered evidence that a given mechanism is operative during sintering. The objection to this practice results from the fact that the models are operative for the initial stage of sintering and they cease to be valid at a limiting value of at most 5%. shrinkage.

Grain growth during the final stage

In most policrystalline materials there is a grain boundary movement so that small grains are eliminated and large grains are increased. Again the driving force is due to the different curvatures radii of the grain faces. Three grains contacts should give a 120 degree contact angle and four grain junction should give the tetrahedral angle of 109.5 degree. At these angles the surface tensions are equally effective on all the boundaries.

Grains having six sides have straight boundaries which form 120 degree with each other. Grains having fewer than six will have concave boundaries if looked at from the grain's center. Grains with more that six sides will have convex boundaries, if looked from inside of the grain.

To decrease their total area, boundaries will move toward the centre of curvature:

a) thus grains with less than six sides will move toward their centre and shrink
b) grains with more than six sides will move their boundaries outside and grow larger.

The growth law is related to the rate at which a boundary will move. The movement is due to the excess pressure which, in turn is inversely proportional to the curvature radius. Therefore, the grain boundary migration rate is inversely proportional to the radius of curvature. Small radii require small grain size. Then, in the average the rate at which grains will grow, will be inversely proportional to their diameter.

$dD/dt = K/D$ that is $D'^2 - D^{\circ 2} = Kt$

where D' is the instantaneous diameter, D° the initial value at time zero. Therefore, plotting log G versus log t one expects a straight line with a slope of one-half. This relationshi is commonly observed at least for moderate amounts of grain growth. There are deviation from the 0.5 value and from linearity due to various defects: most important of which is the presence of inclusions which impede boundary movement. In some way, pores can be also considered impurities which pin down the grain boundary movement.

Summary

This introduction to the sintering phenomena could be summarized as follows:

1) The most important sintering mechanism is certainly that based on lattice diffusion with grain boundaries as vacancy sinks. It explains, sometimes in a quantitative manner, the shrinkage of many materials like Al_2O_3, UO_2, BeO, Fe_2O_3, CaF_2, Fe, Cu, Ag and others.

However in particular materials other mechanisms have been demonstrated to be actively present as surface diffusion (ice),) evaporation condensation (NaCl, ZnO (H_2), Fe_2O_3 (HCl) and grain boundary diffusion (Al_2O_3).

The attainment of pore free, full density is in principle possible but is severely hindered by pore and particle size distribution within the green body, prior to sintering.

If we wish to control the sintering process then we must choose the conditions to affect the "rate-controlling" mechanism of the process. This mechanism determines the rate at which everything proceeds and it is the one that we must identify, characterise in terms of how is it affected by the processing variable (t,T,r,P,c).

As a final remark let us remember the densification of alumina which can occur by either lattice diffusion or grain boundary diffusion of atoms from the boundary to the neck. In order to obtain shrinkage, Al_2O_3 must reach the neck from the boundary, both Al and O ions must move.

The overall rate will be determined by the rate at which the solwer of the two ions can move. Furthermore, the important and effective pathway for the slow ion will be the one along which it can move fastest. This leads to the important conclusion that the overall process is controlled by the slow atom moving along its fastest path.

In addition, the actual controlling step will be the slowest step along this latter pathway - it generally assumed that the slowest is the diffusion process itself.

This wide choice for the rate controlling mechanism is one of the features which makes the understanding and control of sintering so complicated.

Some criticism

There are two assumptions in the sintering theories so far presented:

1. that temperature gradients need not to be considered
2. that sintering is driven only by differences in surface curvature in a "continuum".

Experimental observations and other atomistic views have warned us that there might be consequences from the previous approximations which may leed to doubtful deductions. Therefore, sintering under temperature gradients must be taken into considerations . Furthermore, the facetted nature of the crystal surfaces and the discontinuous structure of matte must be considered to influence the microstructural changes that occur during the firing "sintering" of ceramic bodies.

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AN INTRODUCTION TO SINTERING

FONDAMENTAL STEP IN CERAMIC PRODUCTION AND POWDER METALLURGY PROCESSES

> "BONDING OF POWDERED MATTER BY SOLID STATE REACTIONS AT TEMPERATURES LOWER THAN THOSE REQUIRED FOR THE FORMATION OF A LIQUID PHASE"

—●—o—

CERAMIC PROCESS

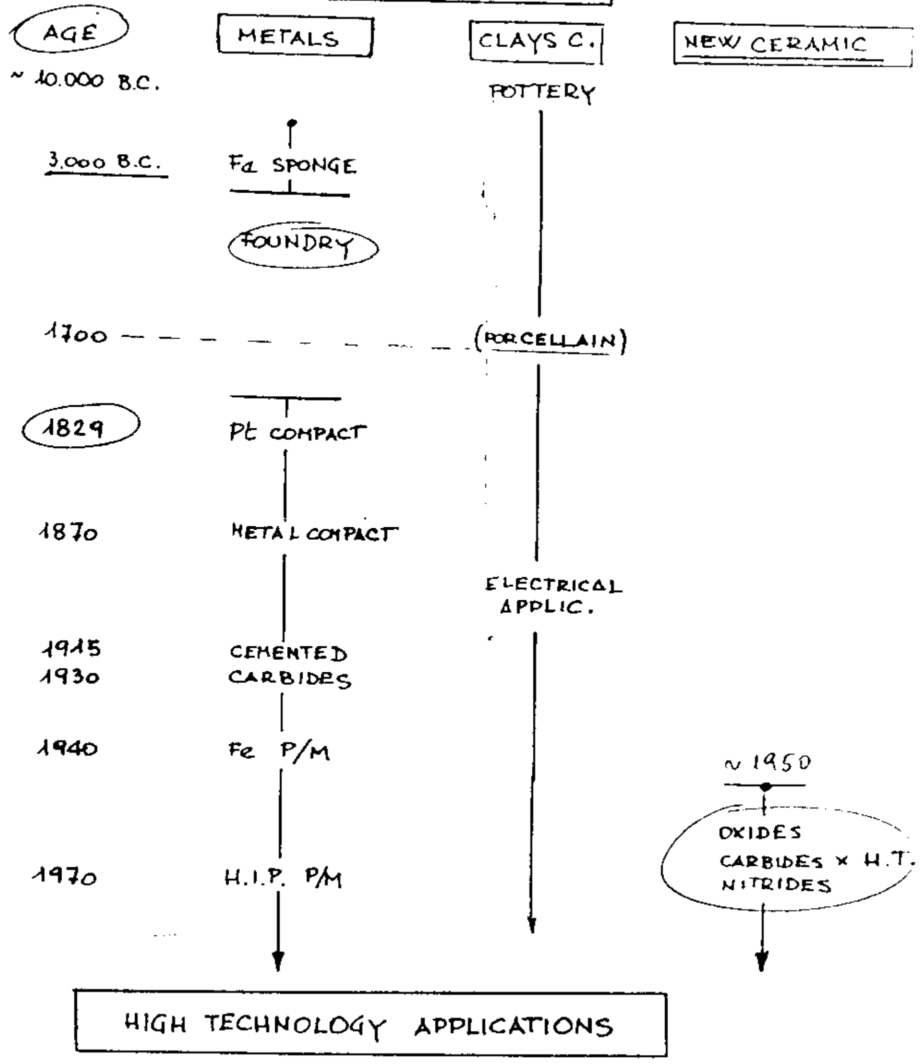
POWDERS → **FORMING** → GREEN BODY COMPACT → **SINTERING** → CERAMIC PRODUCT

SINTERING = EVIDENCE OF VARIOUS PHENOMENA WHICH TAKE PLACE DURING THE **FIRING** PROCESS

—o—

THE SAME IS VALID FOR THE POWDER METALLURGY

HISTORY BACKGROUND



SINTERING or SYNTERING ?

PHILOSOPHY
THESIS + ANTITHESIS
SYN·THESIS

CHEMISTRY
A + B
C

ANCIENT GREEK
SYN - TOGETHER
THITENAY - TO PUT

In Synthesis the parts loose their original identity

This is not the case for sintered particles their chemical and phisical nature is maintained

DIFFERENT SPELLING = DIFFERENT ORIGIN ?

In old English "SINDER-CINDER" means ASHES
Does SINTERING mean to reduce to ashes ? May be
Firing is essential to sintering.

However there is a GERMAN word in Mineralogy
SINTER

"A SEDIMENTARY ROCK" siliceous or calcareous deposits formed at geysers springs of CEMENTED joint particles.

The joint-bonded meaning is present.
But it is a good thing the spelling became different.

SYNTHESIS - SINTERING OPPOSITES

ANALYSIS ⟷ SYNTHESIS

SINTERING ⟷ ?

BONDING ⟷ DEBONDING (GRINDING)

—o—

AS IT TAKES ENERGY TO BREAK DOWN CHEMICAL COMPOUNDS IT TAKES ENERGY TO GRIND MATERIALS

—o—

GRINDING PRODUCES NEW SURFACE AREA

SINTERING ELIMINATES A SUBSTANTIAL FRACTION OF THE SOLID-GAS INTERFACE OF THE POWDERS TO CONVERT IT IN SOLID-SOLID INTERFACE AND REDUCES THE OVERALL SURFACE AREA.

—o—

This is accomplished by FIRING which enhances atomic mobilities and allows the "DRIVING FORCE" to exert its action.

ULTIMATELY A SOLID CLOSE TO ITS THEORETICAL DENSITY CAN BE OBTAINED

—o—

SINTERING SCIENCE AND TECHNOLOGY ARE AIMED TO THE ATTAINMENT OF THIS FULL DENSITY

SURFACE ENERGY

A part of the grinding energy remains stored in the powder as new surface area.

The GIBBS FREE ENERGY of a single phase material varies as:

$$dG = VdP - SdT + \gamma dA + \mu dn$$

γ = surf. energy
μ = chem. pot.
n = n. of moles

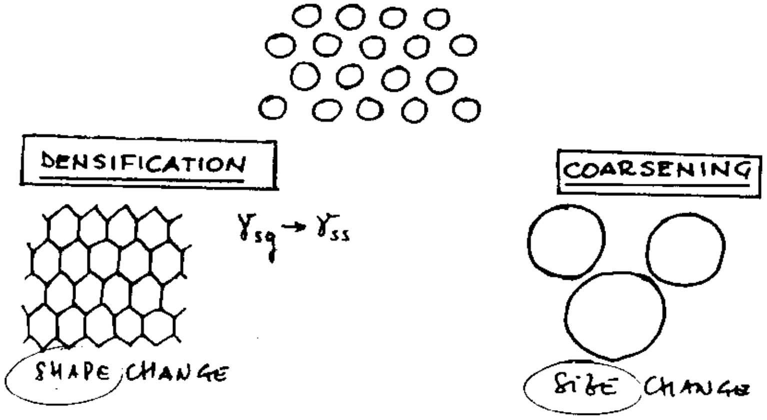
therefore $\gamma = \left(\frac{dG}{dA}\right)_{T,P,n}$

Spontaneous process = decrease of G

Any transformation at (T, P, n const) leading to a surface area reduction is "spontaneous"

DRIVING FORCE FOR SINTERING IS THE REDUCTION OF THE "FREE SURFACE ENERGY CONTENT"

This can be accomplished by two processes



DENSIFICATION

1) VITRIFICATION – mainly silicate systems
T and comp. make a substantial amount of liquid phase which bonds residual particles

2) LIQUID PHASE –
T and comp. make a thin film of liquid which enhances mobility and diffusion to change particle shape and size.

3) SOLID STATE SINTERING –
~~densification~~ is achieved by change of particle shape and size through slow diffusion → lattice, grain boundary and through vapor phase.

1) and 2) may be considered
REACTION SINTERING

SLIDES
1/2/3

SINTERING VARIABLES

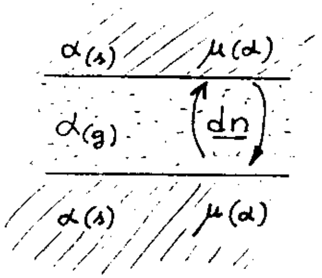
1. TEMPERATURE ↑
2. TIME → TRADITIONAL VARIABLES
3. PARTICLE SIZE ↓ CHEMISTRY ↓↑
4. COMPOSITION (ADDITIVES) ~ Liquid ? phase
5. PRESSURE ↑ HP HIP

— o —

DRIVING FORCE

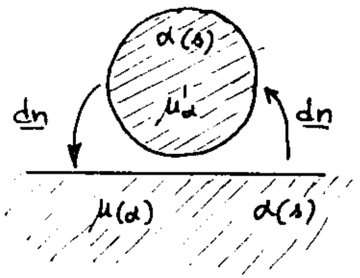
$$dG = -SdT + VdP + \gamma dA + \mu dn$$

SURFACE ENERGY REDUCTION ACTS ON THE ATOMIC LEVEL BECAUSE THERE ARE DIFFERENT SURFACE CURVATURES WITHIN ANY REAL POWDER COMPACT.



Exchange of dn moles does not change "G" if

$$\frac{dA}{dn} = 0$$



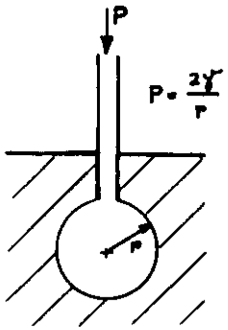
Surface A

Volume V

Exchange of dn moles does change "G" because

$$\frac{dA}{dn} \neq 0 \quad \frac{dV}{dn} \neq 0$$

PRESSURE DIFFERENCE ACROSS A CURVED SURFACE



$$PdV = \gamma dA \qquad P = \gamma \frac{dA}{dV}$$

The reversible expansion work PdV is stored in the surface energy $\gamma \cdot dA$

$dA = 8\pi r\,dr$

$dV = 4\pi r^2 dr$

$$\boxed{P = \gamma \frac{2}{r}}$$ SPHERE

cylinder $P = \frac{\gamma}{r}$; general $P = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$

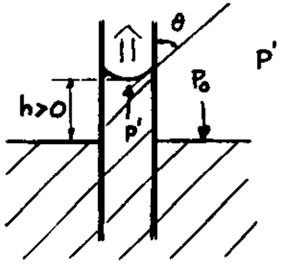
P.S. Laplace 1806

Liquid film (soap) bubble

2 surfaces $P = 2 \times \frac{2\gamma}{r} = \frac{4\gamma}{r}$

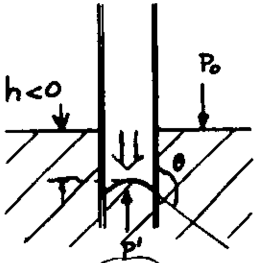
PRESSURE DIFFERENCE CAN BE RECOGNIZED BY CAPILLARY RISE

$$p' = P_0 + \rho g h$$



$p' > P_0$

WETTING



$p' < P_0$

NON WETTING

$$\Delta P = \frac{2\gamma}{r} = \gamma\left(\frac{2\cos\theta}{R}\right) = \rho g h$$

R = capillary

Measure of γ in liquids

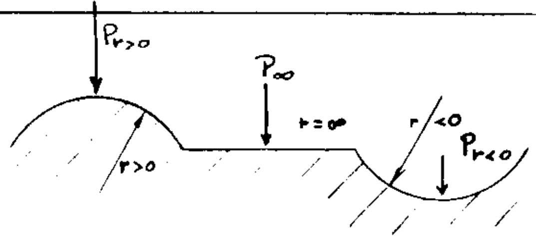
PRESSURE ABOVE CONVEX SURFACE IS HIGHER
" " CONCAVE " " LOWER

$\Delta P = P_r - P_\infty$

$r > 0 \quad P_r > P_\infty$

$r = \infty \quad =$

$r < 0 \quad P_r < P_\infty$



$\boxed{\Delta P = \gamma\left(\frac{2}{r}\right)}$ sphere

If we consider an *expansion*, like the bubble

$$dG = -SdT + VdP + \gamma dA + \mu dn \qquad T, A, n \ \text{const}$$

$$dG = VdP \qquad V = \frac{RT}{P} \qquad dG = RT\frac{dP}{P} = RT\, d\ln P$$

Between P and P° integrating

$$V\Delta P = RT \ln(P/P^\circ) \qquad \text{But} \qquad V\boxed{\Delta P} = V\boxed{\gamma\left(\frac{2}{r}\right)}$$

$$\boxed{\ln(P/P^\circ) = \frac{V\gamma}{RT}\left(\frac{2}{r}\right)}$$

Pressure can be related to *CONCENTRATION* C(r) and C(∞) *under* curved (r) or plane surface (∞)

$$\boxed{P(r) \propto C(r)}$$

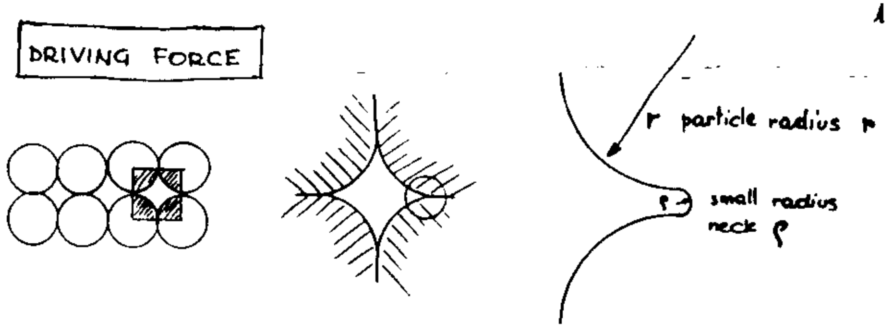
$$\ln\left(C(r)/C_{(\infty)}\right) = \frac{2\gamma V}{rRT} \qquad \boxed{C(r) = C_\infty \exp\left(\frac{2\gamma V}{RTr}\right)}$$

W. THOMPSON 1871

molar quantities
:N atomic $V \to \Omega$; $R \to k$ Boltzman

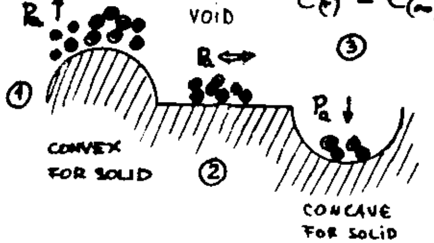
r = CURVATURE RADIUS
$$\begin{cases} r \to \infty & C(r) \to C_{(\infty)} \quad \text{PLANE} \\ r > 0 & C_{(r)} > C_{(\infty)} \quad \text{CONVEX} \\ r < 0 & C(r) < C_{(\infty)} \quad \text{CONCAVE} \end{cases}$$

DRIVING FORCE



FOR ATOMIC SPECIES

$$C_{(r)} = C_{(\infty)} \exp\left(\frac{2\gamma\bar{V}}{rRT}\right)$$

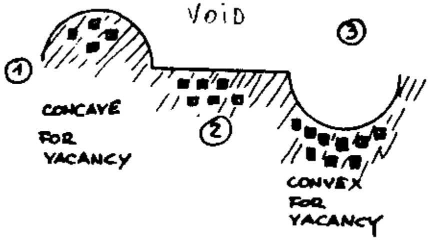


ATOMS

P_a ① (↑) $C_{(r)}$ ↑ $r > 0$

P_a ② ↔ $C_{(\infty)}$ ↔ $r = \infty$

P_a ③ ↓ $C_{(r)}$ ↓ $r < 0$



VACANCIES

P_v ① ↓ $C_{(r)}$ ↓ $r < 0$

P_v ② ↔ $C_{(\infty)}$ ↔ $r = \infty$

P_v ③ ↑ $C_{(r)}$ ↑ $r > 0$

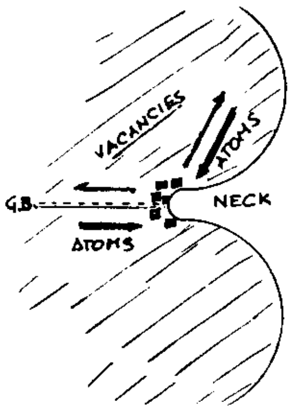
SUMMARY

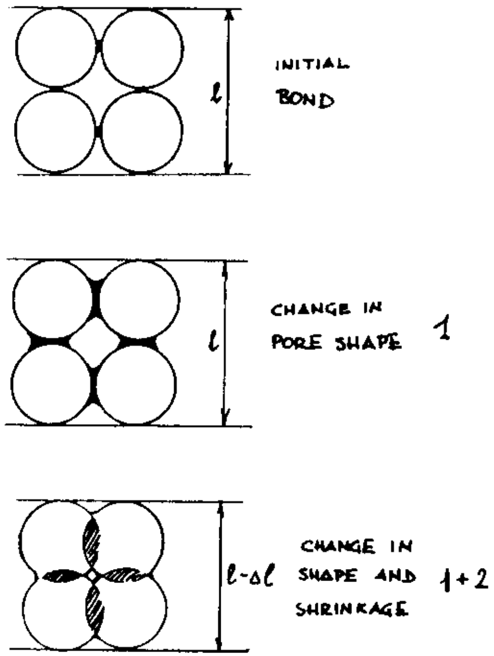
ATOMS - P_a is HIGHER ABOVE CONVEX SURFACE
P_a is LOWER ABOVE CONCAVE SURFACE

VACANCIES - C_v is HIGHER ABOVE THEIR CONVEX SURFACE
C_v is LOWER ABOVE THEIR CONCAVE SURFACE

① The Thompson equation applies to concentration of dilute species and can be applied to VACANCIES in dilute solution in the solid, rather than to atoms themselves.

② Once the flow equations are known in terms of VACANCIES, the equivalent flow in term of atoms follows.





FLOW OF MATTER

1) COARSENING

2) DENSIFICATION

SINTERING IS THE SUM OF BOTH PHENOMENA

SINTERING STAGES : 3

I	=	INITIAL	FIRST 5% SHRINKAGE
II	=	INTERMEDIATE	in between
III	=	FINAL	ABOVE 90% SHRINKAGE

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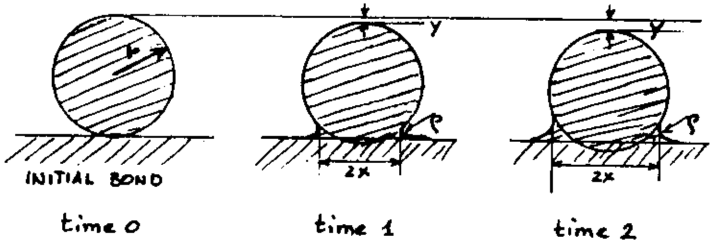
INITIAL FRENKEL (1945) - KUCZYNSKI (1949)

EXPERIMENTS ON JOINT SPHERE - PLATE



SINTERING KINETIC EQUATIONS

$$\boxed{\frac{x^n}{r^m} = kt}$$

found for glass

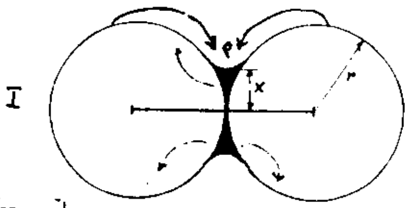
Cu/Ag

transport		n	m
	VISCOUS FLOW	2	1
	EVAPORATION COND.	3	1
	BULK DIFFUSION	5	2
	SURFACE DIFFUSION	7	3

TWO SPHERES MODEL

COARSENING

I



Ia
VAPOR

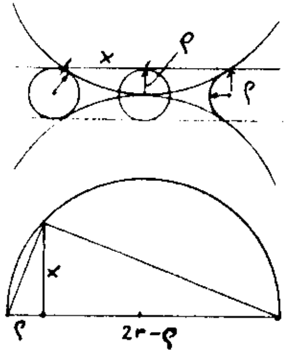
NECK GROWTH

WITHOUT DENSIFICATION

(NO) CENTERS APPROACH

MODEL : VACANCIES MOVE FROM NECK TO SURFACE

Neck radius $\rho = \frac{x^2}{2r}$



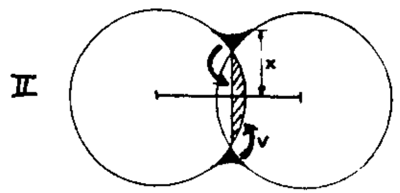
$\rho : x = x : 2r - \cancel{\rho}$ $\quad r >> \rho$

$\boxed{\rho = \frac{x^2}{2r}}$ NECK RADIUS

VIA
- SURFACE DIFFUSION (ATOMS)
- LATTICE DIFFUSION (VACANC.)
- EVAPORATION COND. (ATOMS)

DENSIFICATION + COARSENING

II



NECK GROWTH

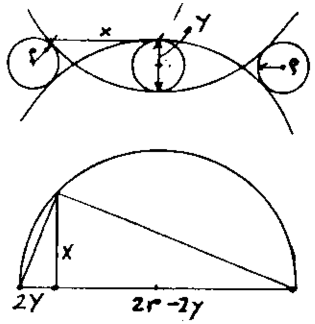
IIa
via G.B.

WITH DENSIFICATION

CENTERS APPROACH (2Y)

MODEL : VACANCIES MOVE FROM NECK TO GRAIN BOUNDARY VIA LATTICE

Neck radius $\rho = \frac{x^2}{4r}$



$2y : x = x : 2r - \cancel{2y}$ $\quad r >> y$

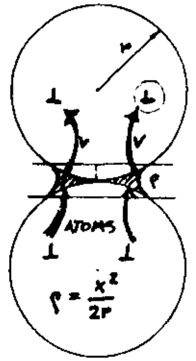
CENTERS $\boxed{y = \frac{x^2}{4r}}$ APPROACH

VIA
- LATTICE DIFFUSION
- G.B. DIFFUSION
- NO : SURFACE / NO VAPOR

TWO SPHERES MODELS

COARSENING

III



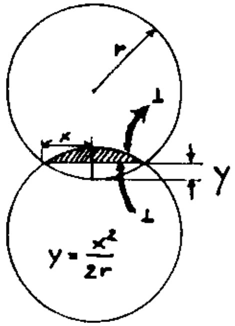
VACANCIES MOVE FROM NECK TO DEFECTS IN THE CRYSTAL (DISLOCATIONS)

ATOMS MOVE THROUGH DISLOCATIONS TO THE NECK

(NO)- CENTERS APPROACH

DENSIFICATION

IV



VACANCIES MOVE FROM THE GRAIN BOUNDARY TO THE LATTICE DEFECTS

ATOMS MOVE THROUGH DISLOCATIONS TO THE GRAIN BOUNDARY ⟷

CENTER'S APPROACH (2Y)

— o —

CASE DENSIFICATION (+ COARSENING) II / IV

$$\boxed{\frac{x}{r} = \left(A\,\frac{\gamma a^3 D}{KTr^3}\right)^{1/5} \cdot t^{1/5}}$$

$$\boxed{\frac{\Delta L}{L} = \left(B\,\frac{\gamma a^3 D}{KTr^3}\right)^{2/5} \cdot t^{2/5}}$$

A : constant   t : time

D : Diffusion coefficient

a^3 : atomic volume

k : Boltzmann

r : particle radius

γ : surface energy

CASE OF COARSENING I / III

FOR EVAPORATION CONDENSATION = NO SHRINKAGE

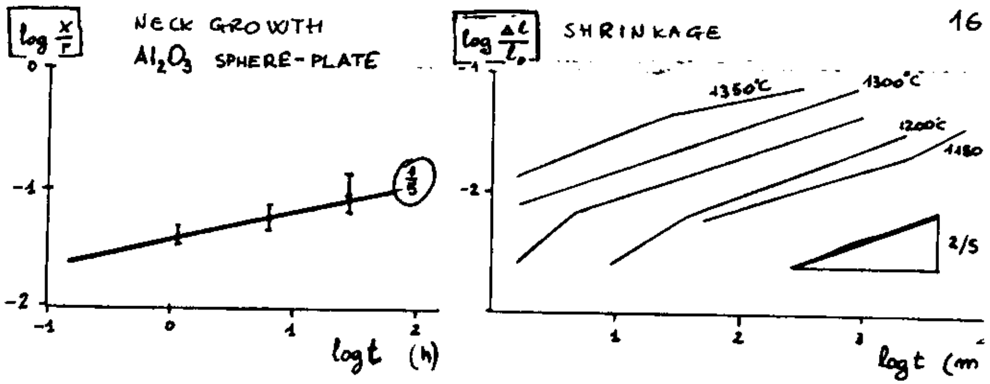
$$\boxed{\frac{x}{r} = \left(A\,\frac{\gamma P a^3}{r^2 k T}\right)^{1/3} \cdot t^{1/3}}$$

FOR SURFACE DIFFUSION = NO SHRINKAGE

$$\boxed{\frac{x}{r} = \left(B\,\frac{\gamma D a^4}{r^4 k T}\right) \cdot t^{1/7}}$$

ALTERNATE PATHS TO NECK (GRAIN BOUNDARY) SINK

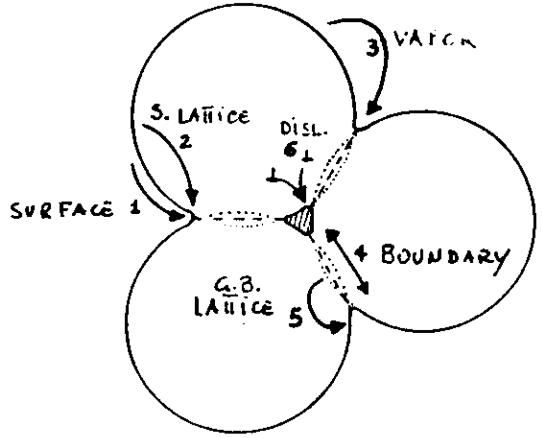
	SOURCE	PATH	DENSIF.	COARS.	CASE
1)	SURFACE	SURFACE	–	⊕	I
2)	"	LATTICE	–	⊕	III
3)	"	VAPOR	–	⊕	I(a)
4)	GRAIN BOUND.	G.B.	⊕	–	II
5)	" "	LATTICE	⊕	–	IIa
6)	BULK	DISLOC.	⊕	–	IV



NECK GROWTH DENSIFICATION

. ALUMINA MICROSPHERES

KINETIC EQUATIONS HAVE BEEN CONFIRMED FOR A LIMITED AMOUNT OF SPHERE / PLATE MODELS



Mechanism Number	Transport Path	Source of Atoms	Sink of Atoms
1	Surface Diffusion	Surface	Neck
2	Lattice "	"	"
3	Vapor Transport	"	"
4	Boundary Diffusion	G.B.	"
5	Lattice "	"	"
6	" "	Dislocations	"

THE ROLE OF PARTICLE SIZE

Besides T and t we can work on "L" particle size
The ΔP acting on CURVED surfaces cause either VISCOUS FLOW (glass) or DIFFUSION (CRYST.)

The flux (flow) is the amount that crosses unit Area in unit time. The flux J is linked to the applied force, F, chemical potential gradient $-d\mu/dx$

Diffusion law $\boxed{J = -D\frac{dc}{dx}}$ c = concentration

We shall link J with the PRESSURE difference $\boxed{\frac{dP(r)}{dx}}$ at different curvature surfaces (r).
$C(r) \propto P(r)$ and by applying the law for diluted species $P(r) = C(r)RT$ then we obtain the same "J"
$\frac{1}{RT}\cdot\frac{dP}{dx} = \frac{dc}{dx}$

$\boxed{J = -\frac{D}{RT}\frac{dP}{dx}}$ by mole; or $\boxed{J = \frac{-D}{kT}\frac{dP}{dx}}$ by atom

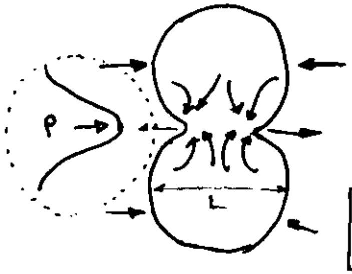
Thus relation can be obtained using concepts as: B (mobility) = velocity under unit force
F (force) = gradient of chemical potential
c (concent.) .- $J = c \times$ velocity

$$J = cBF = -cB\frac{d\mu}{dx} = -cBRT\frac{d\ln c}{dx} = -BRT\frac{dc}{dx}$$

then $-D = BRT$ or $-D = BkT$

VISCOUS FLOW

How does "L" effect sintering via viscous flow of the whole mass?



There is a $\boxed{\text{STRESS "}\Delta P\text{"}}$ across surfaces: push on convex
pull over concave

$\boxed{\Delta P = \frac{\gamma}{\rho}}$

If we consider the neck (ρ) rim of radius ρ.-
The $\boxed{\text{"STRAIN RATE"}}$ ($\dot{\varepsilon}$) in a viscous body is proportional to the applied $\boxed{\text{STRESS}}$ (ΔP) factor (η) $\boxed{\text{VISOSITY}}$

$\boxed{\dot{\varepsilon} \propto \frac{1}{\eta}\cdot\frac{\gamma}{\rho}}$

By applyin the SCALING LAW "$\rho \propto L$"
"Large particles build large necks"

then $\dot{\varepsilon} \propto \frac{\gamma}{\eta L}$, being the "time" invers. prop. to $\dot{\varepsilon}$ (rate)
we obtain the relation for the "sintering time"

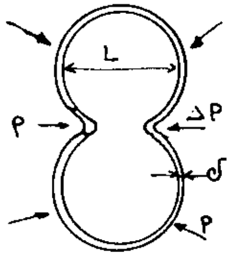
$$\boxed{t_{visc} = (K)\,\frac{L\eta}{\gamma}}$$

In case of viscous flow SINTERING (time) is directly proportional to size "L"

Small particles with low viscosity and high surface tension need a short time to sinter!

LIQUID PHASE SINTERING | How does "L" work ?

Liquid allows atoms to dissolve at high P points to diffuse (D_ℓ) to low P locations and reprecipitate out!



Flux $J \propto -\frac{D_\ell}{kT}\frac{\Delta P}{\Delta x}$ $\Delta x \propto L$
moving distance ∝ L

is proportional to the $\Delta P = \frac{\gamma}{\rho} \propto \frac{\gamma}{L}$
using SCALING LAW approach

then $\boxed{J} \propto -\frac{D_\ell}{kT}\frac{\gamma}{L}\cdot\frac{1}{\Delta x} = \boxed{-\frac{D_\ell}{kT}\cdot\frac{\gamma}{L^2}}$

The $\boxed{\text{AREA}}$ through which atoms move is $\boxed{A \propto L\cdot\delta}$ proportional to film thickness δ × length which is linked to "L" size of particle.

The $\boxed{\text{VOLUME}}$ of matter to be moved scales with "L" size.

$$\boxed{V \propto L^3}$$

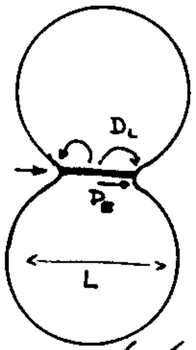
the $\boxed{\text{TIME}}$ required to sinter to a required stage

$$\Delta t = \frac{\text{Volume to be moved}}{\text{Rate of flow} \times \text{atomic vol.}} \propto \boxed{\frac{V}{J\cdot A\cdot\Omega}}$$

$$\Delta t_{liq} \propto \frac{L^3}{-\frac{D_\ell}{kT}\frac{\gamma}{L^2}\cdot L\,\delta\,.\,\Omega} = \boxed{\frac{L^4\,kT}{-D_\ell\,\gamma\,\delta\,\Omega}}$$

Time gets shorter with "small" L", large D_ℓ, γ; δ and Ω.
at const. T.

SOLID STATE SINTERING | How does "L" operate on it?



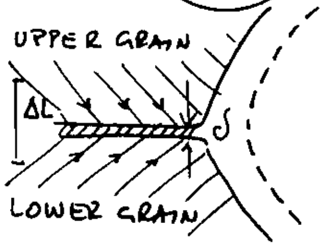
Atoms at necks experience pressure difference. Owing to the presence of a GRAIN BOUNDARY atoms can move to their SINK via LATTICE (D_L) or the same G.B (D_{GB}).

The volume to be moved is $\boxed{V \propto L^3}$

The Area of transit is $\boxed{A_{GB} \propto L\cdot\delta}$

where δ is the G.B thickness ∥ G.B.
A is the G.B area

The Time needed to move V is given by the relation with flux(J)·A_{GB}·Ω



$$t_{\substack{SS\\GB}} = \frac{V}{J\cdot A_{GB}\cdot\Omega} = \frac{L^3}{-\frac{D_{GB}}{kT}\frac{\gamma}{L^2}\cdot L\,\delta\,.\,\Omega}$$

Being $\boxed{J = -\frac{D}{kT}\cdot\frac{\Delta P}{\Delta x}}$

and, as before $\frac{\Delta P}{\Delta x} = \frac{\gamma}{\rho}\cdot\frac{1}{\Delta x}$

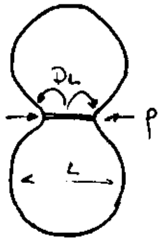
By SCALING LAW $\frac{\Delta P}{\Delta x} \propto \frac{\gamma}{L^2}$

$$\boxed{t_{\substack{SS\\GB}} = \frac{L^4\,kT}{-D_{GB}\cdot\gamma\cdot\delta\cdot\Omega}}$$

This relation recalls the "liquid phase" where D_{GB}/D_ℓ must be exchanged.

Again "t" gets shorter for "L" small; large D, γ, δ and atomic volume.

SOLID STATE VIA LATTICE DIFFUSION



Atoms may diffuse from the BOUNDARY to the NECK by way of the LATTICE "D_L"
The volume to be moved $V \propto L^3$ must cross an Area $\propto$ to L^2 the particle size
$V \propto L^3 \quad A \propto L^2$

$$\text{time} = \frac{V}{J \cdot A \cdot \Omega} = \frac{L^3}{J\, L^2\, \Omega}$$ and if we recall $J = -\frac{D_L}{kT}\frac{\Delta P}{\Delta x}$

and again by SCALING LAW equate $\Delta x \propto L$ and $\Delta P = \frac{\gamma}{\rho} \propto \frac{\gamma}{L}$, then $\frac{\Delta P}{\Delta x} \propto \frac{\gamma}{L^2}$

$$\boxed{\text{time}_{\substack{SS\\ \text{Lattice}}} = \frac{L^3}{\frac{D_L \gamma}{kT L^2} \cdot L^2 \cdot \Omega} = \frac{L^3 kT}{D_L \cdot \gamma \cdot \Omega}}$$

the time dependence through LATTICE scales with L^3!

There are major difficulties!
What path shall atom prefer to move to the neck?
There are several alternative paths and different mechanisms!

All have their own Diffusion coefficient
D_L ; D_{GB} ; D_e ; D_{Vap} ; D_{surf}
However all these can almost always be represented within the precision of the experiment as

$$\boxed{D = D_0 \exp\left(\frac{-Q}{RT}\right)}$$ being all "ACTIVATED" processes.

In fact!

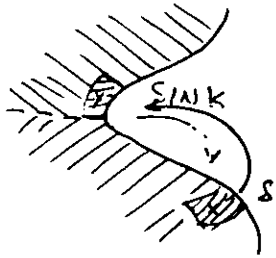
COMPLICATIONS DUE TO SURFACE AND/OR VAPOR PHASE TRANSPORT

These mechanisms allow shape change but do not densify - They consume ΔG, driving force, reduce surface area but give no SINTERING.

1) SURFACE
As in liquid phase we consider a SURFACE thickness then the same equation applies

$$\Delta t_s = \frac{L^4 kT}{D_s \delta_s \gamma \Omega}$$

2) VAPOR PHASE - EVAPORATION ⟷ CONDENSATION
The condensation rate at the NECK is given by the net number of atoms landing on it



$$\boxed{\Delta t_{e/c} = \frac{L^2 (kT)^{3/2}}{\Omega^2 \rho_V}}$$ ρ_V = gas density

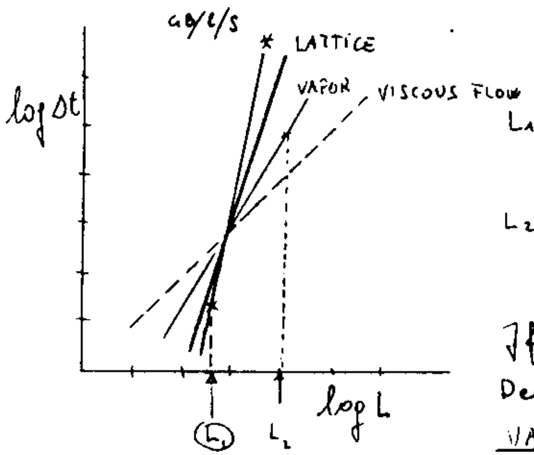
The rate of evaporation at a point is $\propto$ prop. to the difference between actual P and Pequilibrium over surf.
Δ Rate $\propto (\text{Kond})\left(\frac{\gamma}{r_x} - \frac{\gamma}{r_y}\right)$. Time depends on "$L^2$"
Time to sinter via e/c gets shorter if Ω is ↑ and vapor density is high!

SUMMARY OF PARTICLE SIZE INFLUENCE

Considering all processes possible it is evident that "SMALL PARTICLES" SINTER FASTER AND BETTER ?

Time to sinter	Mechanism	Size effect
Δt	VISCOUS FLOW	∝ L
"	VAPOUR PHASE	∝ L^2
"	LATTICE DIFF	∝ L^3
"	* GRAIN BOUND. LIQUID PHASE SURFACE DIFF.	∝ L^4

The diffusion coefficients will make the difference



Which mechanism is most likely for small/large "L"?

L₁: Small particles favour G.B. or Surface mechanism.

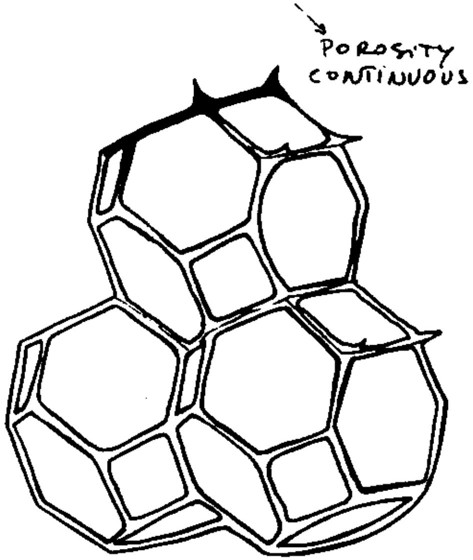
L₂: Larger particles favor the VAPOUR phase

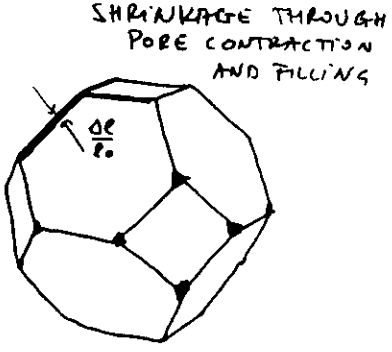
If we wish to achieve $\Delta\ell/\ell_0$ Densification we do not want VAPOR mechanism.

Use particles small and operate in order reduce SURFACE diffusion and increase GB and Lattice diffusion!

INTERMEDIATE STAGE

AFTER SOME GRAIN GROWTH HAS OCCURRED POROSITY BECOMES A CONTINUOS LABYRINTH





IN THE LATEST STAGE PORES REMAIN AT CORNERS - CLOSED.

Porosity is considered as the ratio between PORE VOLUME and GRAIN VOLUME at any "J" stage

$$\boxed{P_i - P_j = \frac{A\, D_\ell\, \gamma v}{\ell^3\, K\, T} \cdot t}$$

LATTICE DIFFUSION

ℓ = GRAIN SIZE

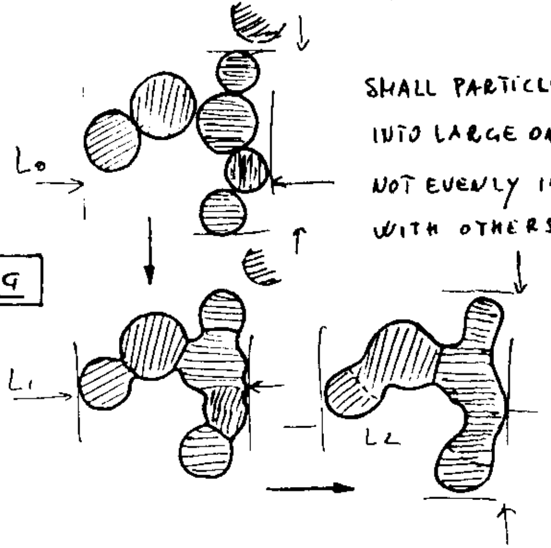
$$= \frac{B\, D_{gb}\, \gamma v}{\ell^4\, K\, T} \cdot t$$

G.B. DIFFUSION

INTERMEDIATE STAGE OF SINTERING

DEFECTS

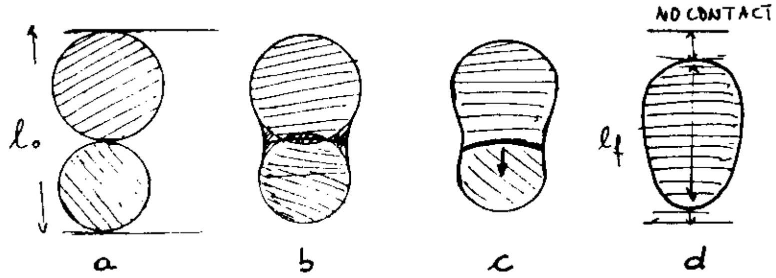
GRAIN GROWTH OF CLUSTER OF PARTICLES WITH DIFFERENT SIZE



SMALL PARTICLES SHRINK INTO LARGE ONES IF NOT EVENLY IN CONTACT WITH OTHERS

COARSENING

$L_2 < L_1 < L_0$



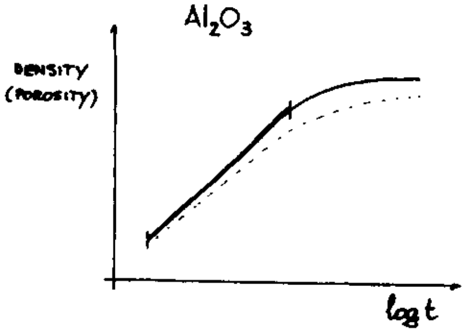
QUALITATIVE GRAIN GROWTH : PARTICLES WITH DIFFERENT DIAMETER

a = CONTACT

b = NECK + G.B. FORMATION

c = G.B. MIGRATION DUE TO CURVATURE

d = FINAL COARSENING



$$\boxed{P = -k \ln t}$$

$k = f(\text{grain size})$

SLIDE 8

ISOTHERMAL DENSITY VS TIME INDICATE LINEAR RELATION HOWEVER DEVIATION OCCUR BECAUSE OF CHANGE IN THE "GRAINS SIZE" → GRAIN GROWTH

FINAL STAGE

1) PORES BECOME ISOLATED AT FOUR GRAIN CORNER
2) PORES LIE ON GRAIN BOUNDARIES
3) SOMETIMES THERE IS A DENSITY DECREASE DUE TO THE ENTRAPPED GASES AND OR PORE COARSENING EXPECIALLY AT HIGH TEMPERATURE

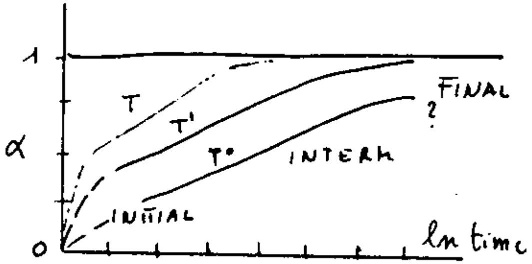
CLASSICAL CERAMICS = BLOATING (REDOX PHENOMENA)

DENSIFICATION AND TREATMENT OF DATA

DENSITY VS TIME

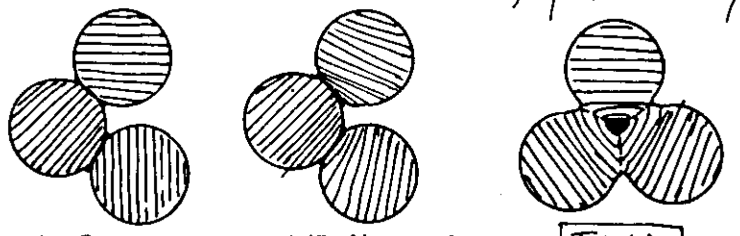
$$\boxed{\frac{d'-d_o}{d_{th}-d_o}=\alpha}$$

d' istantantaneous } meas.
d_o initial (green) }
d_{th} theoretical calc.
XRD

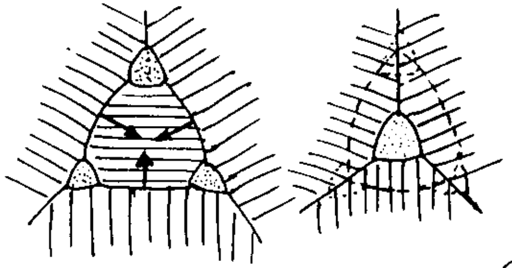


$$d_{th} = \frac{z \cdot M_w}{N V_c}$$

d' = measured
a) afta firing at K(T)
b) by DILATOMETRY



INITIAL INTERMEDIATE FINAL

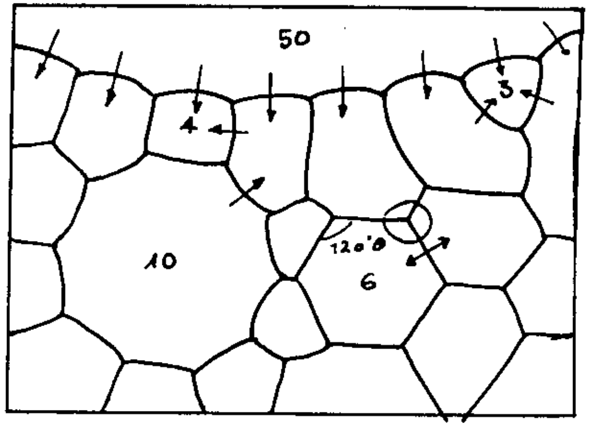


AS THE SMALL GRAIN SHRINKS (SURF. CURV.) THE PORES ARE DRAWN TOGETHER TO FORM A LARGE PORE

DENSITY IS UNCHANGED

SLIDE 7

GRAINS GROWTH



The 50-sided grain has the most strongly curved boundaries and the strongest tendency to grow larger
Driving force is due to diffrent curvature radii.

Surface tensions are in equilibrium at 120° θ for 3 grains contact or 109° in space for 4 grain contact

Grains with n < 6 will SHRINK
" " n > 6 " GROW n = 6 EQUILIB.

The Growth low is $\boxed{\frac{dD}{dt} = \frac{K}{D}}$

1) Boundary move as a funtion of $\Delta P \propto 1/r \propto 1/D$ particle
2) Grain growth rate in a polycryst. is inv $\propto$ to $\bar{D}$ grain.
then $\boxed{D^2 - D_o^2 = k t}$

SLIDE 11

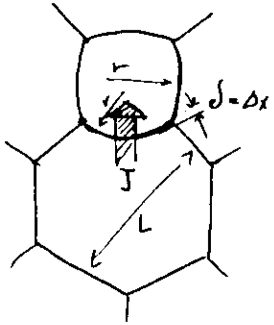
RATE of GRAIN GROWTH

It can be estimated by the flux across the G.B.

δ = G.B. thickness

$$J = -\frac{D_B}{kT}\frac{\Delta P}{\underset{\to\delta}{\Delta x}} \quad \text{but} \quad \Delta P = \frac{\bar{\alpha}\gamma}{r}$$

$\bar{\alpha}$ = shape factor
r = curv. radius



We assume that the RATE of GROWTH is $\propto$ to BOUNDARY VELOCITY

$$\frac{dL}{dt} \propto V_b = J \times \text{atomic volume } \Omega$$

$$= cm^{-2} \times sec^{-1} \times cm^3 = (cm\ sec^{-1})$$

$$J = -\frac{D_B}{kT}\cdot\frac{\bar{\alpha}\gamma}{r}\frac{1}{\delta} \quad (r \propto L \text{ grain size})$$

$r \to L$

The relative velocity

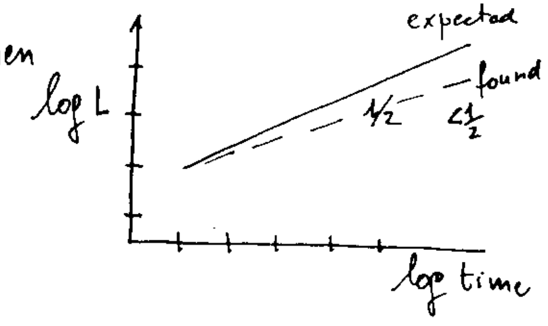
$$\frac{1}{L}\frac{dL}{dt} = \frac{1}{L}J\Omega = \frac{1}{L}\cdot\frac{-D_B V\bar{\alpha}\gamma}{kT}\frac{1}{\delta}\frac{1}{L} = \left(\frac{1}{L}\right)^2\cdot\frac{D_B V\bar{\alpha}\gamma}{kT\delta}$$

$$\left(\frac{1}{L}\right)\left(\frac{1}{L}\right)^{-2} dL = \quad L\,dL = (\text{const})\,dt \qquad \boxed{L^2 - L_0^2 = (k)\Delta t}$$

$$\boxed{\Delta t_{gg} \propto \frac{L^2 kT\delta}{D_B\gamma V\bar{\alpha}}} \quad (a)$$

Time required for a certain grain growth increases with ① L average size, G.B. thickness, whereas it decreases by increa. D_B, surface energy and atomic volume.

Then

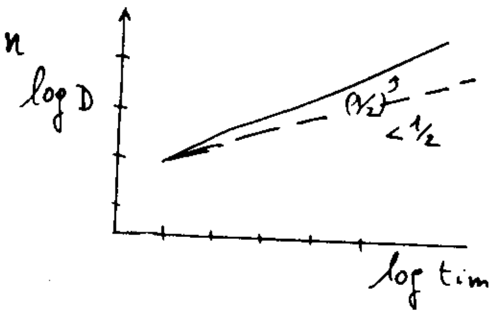


Experimental slopes are lower than 1/2 due to G.B. PINNING
VELOCITY is LOWERED if terms in (a) are changed by PORES + INCLUSIONS

Vide 12

GRAIN GROWTH

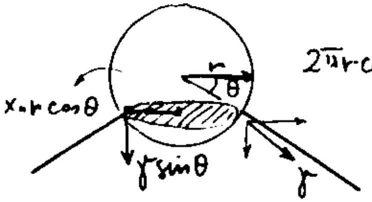
Then



Experimental slopes are ≠ 1/2 due to GB PINNING BY PORES OR IMPURITIES

PORES AND INCLUSIONS PIN G.B. AND SLOW DOWN G.G.

If we think of the boundary energy as surface tension then the force exerted on a pore by the G.B. is given by the action of "$\gamma \sin\theta$" on the $2\pi r\cos\theta$ rim



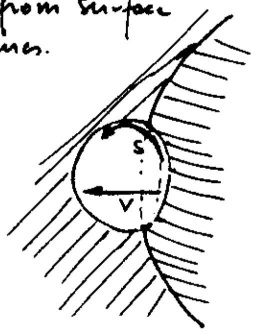
$$2\pi r\cos\theta \times \gamma\sin\theta = 2\pi r\gamma\frac{\sin 2\theta}{2} = \text{Force}$$

$$F = \pi r\gamma \sin 2\theta$$

$$\boxed{F_{max} = \pi r\gamma} \qquad \theta = 45°$$

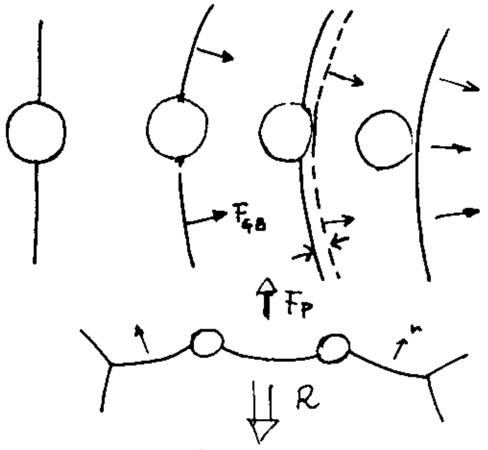
In order to MOVE, PORE must win this FORCE

Driving force to move atoms via SURFACE OR VAPOR comes from surface curvature.



Its ability to move depends on its size (large pores have large F to win); and the "γ" of the G.B.
During the intermediate stage PORES control the rate of G. growth.

GRAIN GROWTH WITH PORES



$F_{GB} = \frac{\gamma\alpha}{R}$

PORES and G.B have different MOBILITIES

PORE WILL REMAIN ISOLATED IF $V_P \neq V_{GB}$

$\vec{V} = \vec{F} \times \text{Mobility}$

$$\boxed{F_P H_P < F_{GB} H_{GB}}$$

BRAKING FORCE F_P

$\Delta F = F_{GB} - N F_P$

$F_P = N(\pi r \gamma)$ max.

N = number of pores or inclusions
r = radius of pore
γ = surface energy GB

GB. AND Pore BECOME SEPARATED IF

$$V_P = F_P H_P < V_{GB} = F_{GB} H_{GB} - N F_P H_{GB}$$

divide by H_{GB} and extract F_{GB}

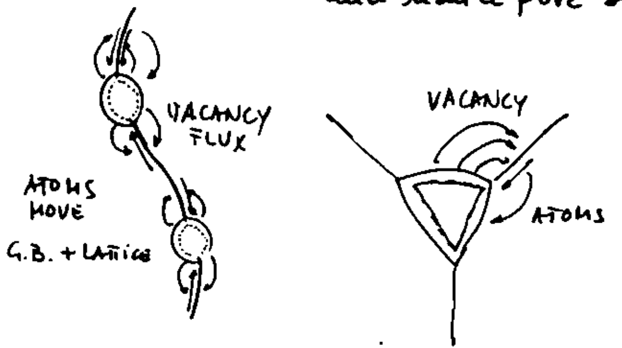
if this $$\boxed{F_{GB} > N F_P + \frac{F_P H_P}{H_{GB}}}$$ PORE AND G.B SEPARATION OCCURS.

GRAIN BOUND. PULLS PORE WITH A FORCE $F = \pi r \gamma \sin 2\theta$ BUT Mobility of PORE MAY BE NOT ENOUGH TO KEEP ON WITH G.B. DIFFUSION MECHANISMS = SURFACE DIFF. OR/AND VAPOR PHASE.

CONCLUSIONS

IN FINAL STAGE THERE ARE TWO PROCESSES:

DENSIFICATION atoms move from the G.B. to the PORES and reduce pore size.



PORE SIZE IS REDUCED BY ATOMS FILLING THE INNER SURFACE OF PORE = TOTAL SURFACE REDUCTION : $\bar{G} \downarrow$

GRAIN SIZE INCREASES

COARSENING the pores are pulled together, merge and increase pore size : Total surface is reduced

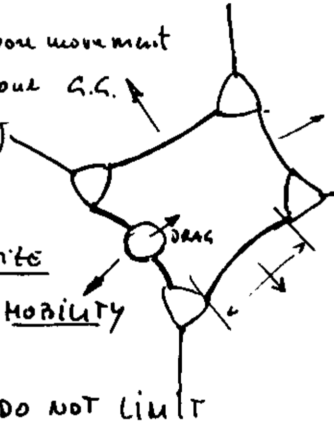
HOWEVER IT IS NEEDED TO INCREASE FIRST AND SUPPRESS THE SECOND

The ease of pore movement acts to favour G.G. (Grain Growth)

Densification REDUCES PORE SIZE

SMALL PORE'S MOBILITY IS LARGER

SMALL PORES DO NOT LIMIT GRAIN GROWTH = COARSENING!



Diffusion distance for densification (l) is increased by Grain Growth which therefore acts to slow densification process.

> SHOULD WE KEEP PORES LARGE TO AVOID GRAIN GROWTH?

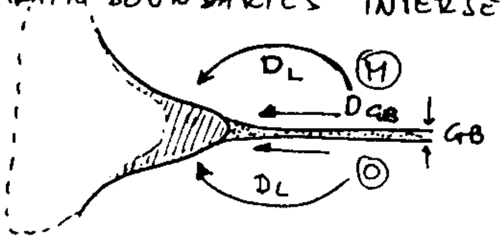
SLIDES!!

[illegible] !!

THE GOAL IS DIFFICULT! THE PATTERN IS CLEAR

AVOID COARSENING INCREASE DENSIFICATION BY PORE PINNING AND REMOVAL OF PORES.

PORES ARE FILLED EFFECTIVELY BY ATOMS FROM GRAIN BOUNDARIES INTERSECTING THEM



WE MUST AFFECT THE RATE CONTROLLING MECHANISM DIFFUSION OF EITHER M and/or O

If atomic species are more than one Al_2O_3, ZrO_2, ... the overall process is controlled by the slow species moving along its FASTEST path.

THEREFORE MAKE FASTER THE PATH OF SLOW MOVING SPECIES G.B./LATTICE

HINTS INTRODUCE ADDITIVES WHICH MAKE GRAIN BOUNDARIES A VIABLE ROUTE FOR ALL THE ATOMS INVOLVED → DENSIFICATION

HENCE, CHANGE EXPERIMENTAL CONDITIONS AND TRY TO ASSESS THEIR EFFECT!

GOOD LUCK!