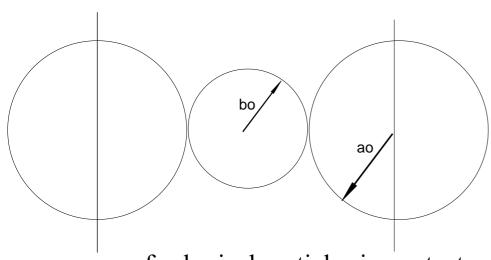
SINTERING OF POWDERS AND DENSE MATERIALS Experimental, Mechanical, Thermal approaches and Modelling

Pr Ange Nzihou, EMAC Pr Roberto Santander, USACH

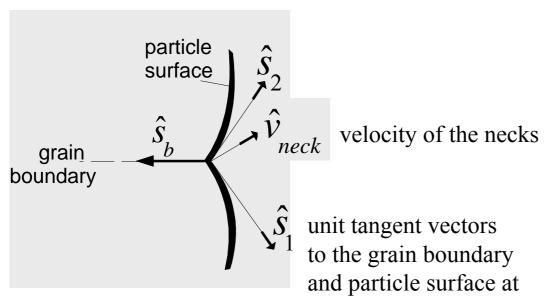
I SINTERING OF POWDERS AND DENSE MATERIALS Experimental, Mechanical, Thermal approaches

Pr Ange Nzihou

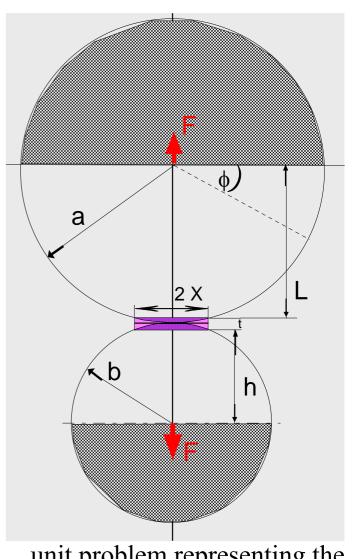
Geometry of the problem



a row of spherical particles in contact

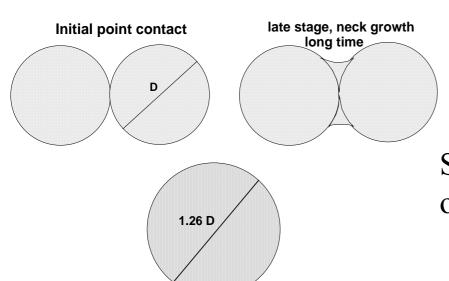


the necks

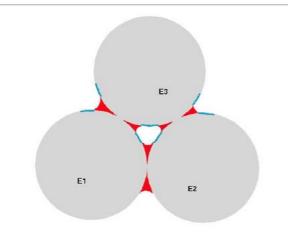


unit problem representing the geometry during neck formation

SINTERING



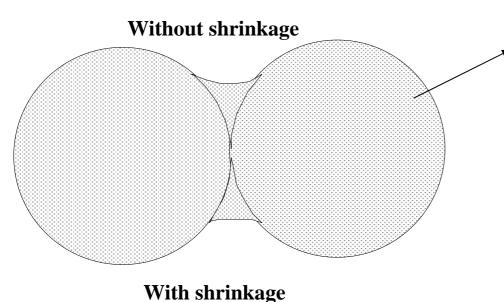
Sintering model with the development of the particle bond during sintering



infinite time

Microstructural scale
In boundary, important atomic
motion

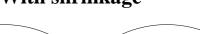
MACROSCOPIC DESCRIPTION

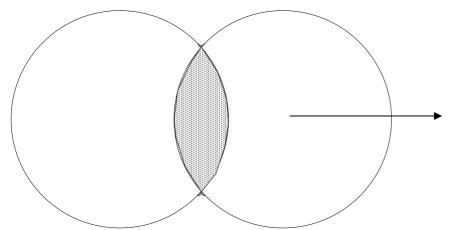


Principal mechanisms

Evaporation –condensation Superficial diffusion

- •Formation of pores
- Mechanical resistance
- •Chemical reactions
- •Dimensional variation contingent on temperature





Principal mechanisms

Volume diffusion flows (viscous and plastic)

PHYSICAL CHEMISTRY ASPECT

DRIVING ENERGIES:

Surface Energy:

•Surface tension

 $\gamma = dW/dS$

Energy linked to the presence of physical defects:

- Proximity of curved surfaces
- •In the crystalline network, there exists a concentration of C de lacuna expressed as flows(thermodynamic statistics):

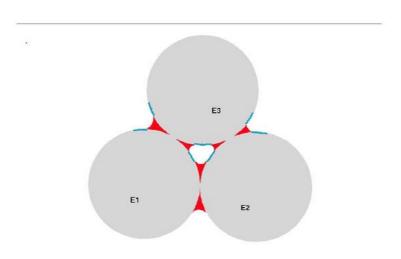
$$C_0 = \frac{n}{N} \approx \exp(E_f/kT)$$

Energy linked to the presence of pressure:

• If the interface is curved, the pressure of the vapor, in equilibrium with the solid, changes depending on the curvature of the surface

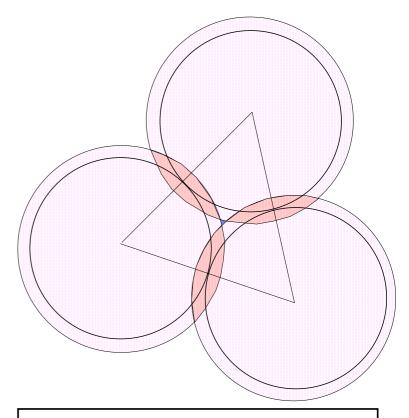
SINTERING MECHANISMS IN SOLID PHASE

1-TANGENT SPHERES



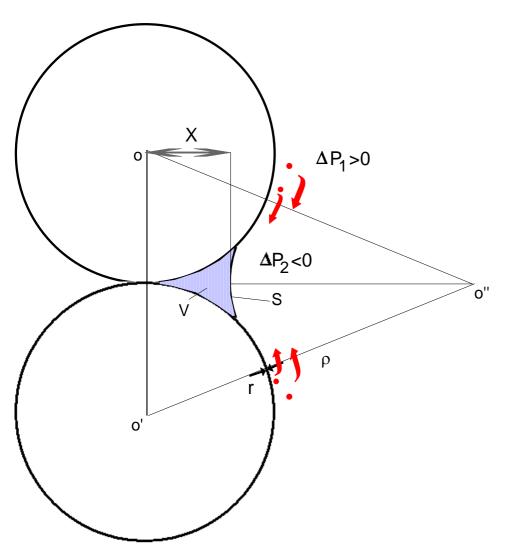
- 1. Evaporation –condensation
- 2. Superficial diffusion
- 3. Volume diffusion

2- SECANT SPHERES



- 1. Viscous flow
- 2. Volume diffusion
- 3. Intergranular diffusion
- 4. Microcreep

1.1-TANGENT SPHERES: Evaporation - condensation

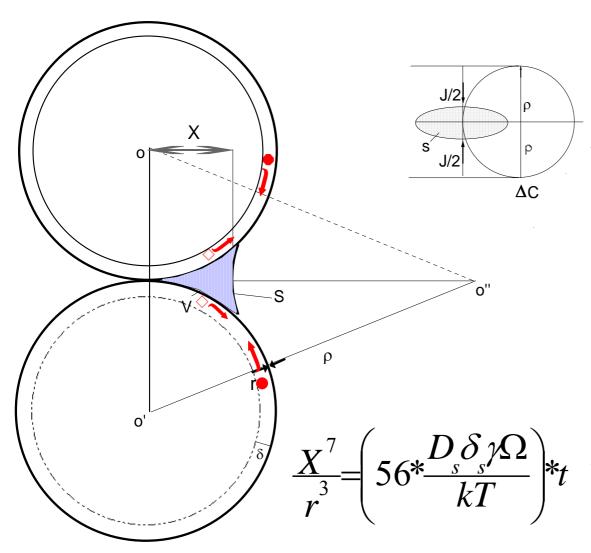


• That a transfer of atoms will be established, by the gaseous phase from the sphere's surface toward the lateral surface of the bridge. $\Delta P_1 > 0$ et $\Delta P_2 < 0$

$$\frac{X}{r} = \left[\frac{3\pi\gamma P_0 \Omega}{dkT} * \left(\frac{M}{2\pi RT} \right)^{1/2} \right] *_t$$

 Ω =volume atomique

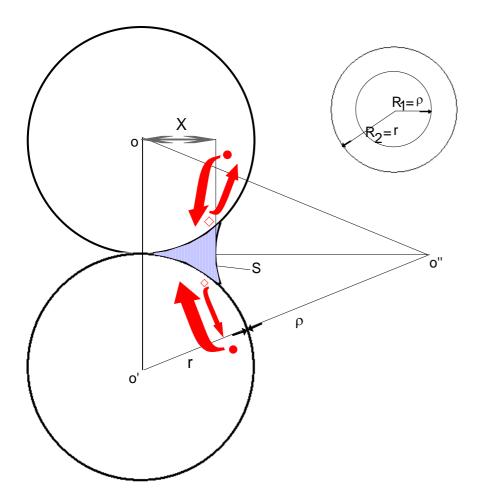
1.2-TANGENT SPHERES: superficial diffusion



- •In proximity to the bridge's surface, there exists and excess of lacunas; however, Nearby the sphere's surface far from the threshold—there exists a defect of lacunas.
- •The extra lacunas will diffuse. If a flux of lacunas is established, there will be an equivalent flux of atoms in the opposite direction which will therefore contribute to build up the bridge.

This exchange of lacunas and atoms will only be restricted to the superficial layer δ_s

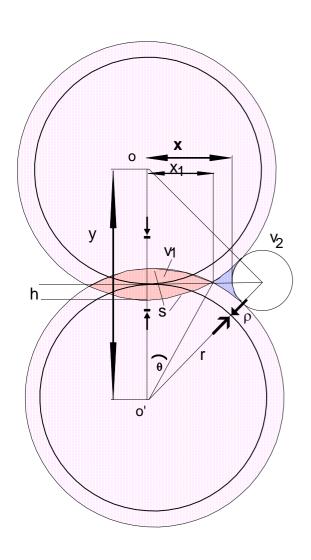
1.3-TANGENT SPHERES: Volume diffusion



- Based on the presence of an excess of lacunas neighboring the bridge's surface, and of a defect of lacunas nearby the sphere surfaces far from the bridge.
- This diffusion of lacunas (and of atoms) is speculated to operate on the volume and no longer on the surface

$$\frac{X^{5}}{r^{2}} = \left(\frac{5\pi}{2} * \frac{D_{\nu} \Omega}{kT}\right) *t$$

2.1-SECANT SPHERES: Viscous flow



- The formation of a linking zone between spheres carried out by viscous flow of Newtonian-type material
- the displacement of atoms carried out under the influence of a cut which is proportional to the gradient of speeds

$$\sigma = \eta \frac{d\varepsilon}{dt}$$
 $\eta = viscosit\acute{e}$ $\varepsilon = \frac{dl}{l}$

$$\left(\frac{x^{2}}{r}\right)^{1/n} = K\left(\frac{n\gamma}{\eta}\right)^{1/n} *t$$

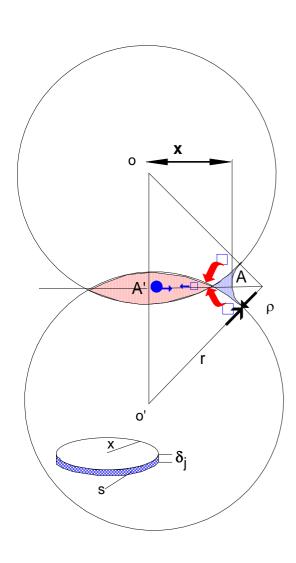
2.2-SECANT SPHERES: Volume diffusion

• Similar to those previously mentioned.

$$\frac{x^{5}}{r^{2}} = \left(20\pi \frac{D_{v} \Omega}{kT}\right) *t$$

• The model considered a variation of the distance between the centers of the spheres

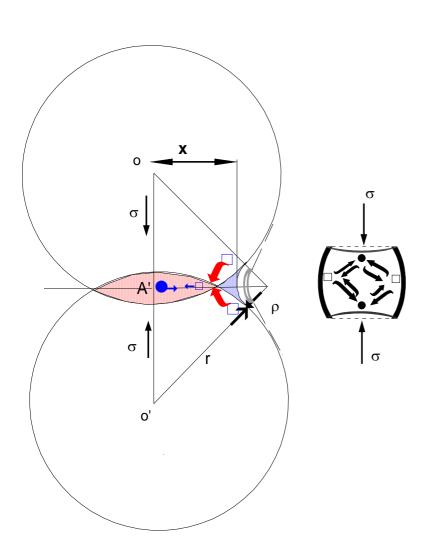
2.3-SECANT SPHERES: Intergranular diffusion



- The experimental observations show that in the majority of cases, it forms a neck within the linked zone, being AA'.
- Les lacunas, finding themselves in excess neighboring the concave surface of the bridge, will be able to diffuse toward this grain joint, instead of spreading to surfaces with a larger radius of curvature meaning the surfaces of the two spheres.

$$\frac{x^{6}}{r^{2}} = \left(96 \frac{D_{j} \delta_{j} \Omega}{kT}\right) *t$$

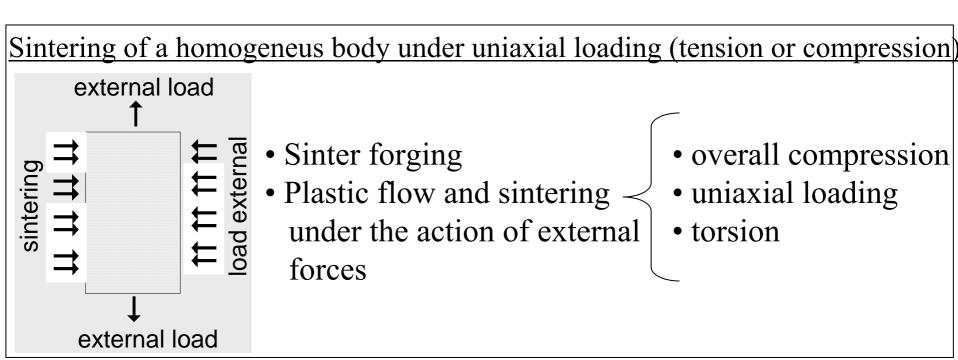
2.4- SECANT SPHERES : Microcreep mechanism

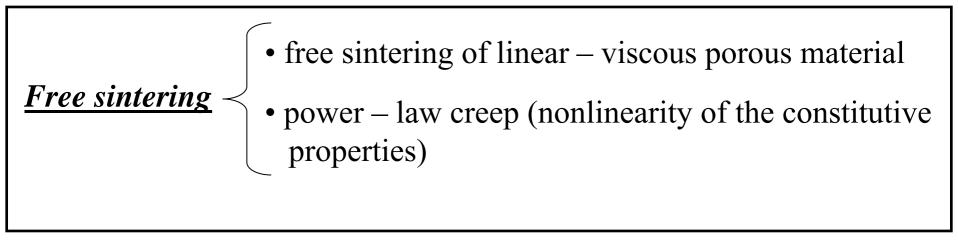


- Creep indicates a flow of material occurring at a given temperature under the influence of a constant.
- Volume subject to the strain of compression σ_1

$$\sigma \cong \gamma \left(\frac{1}{\gamma_1} + \frac{1}{\gamma_2} \right)$$

Cases:

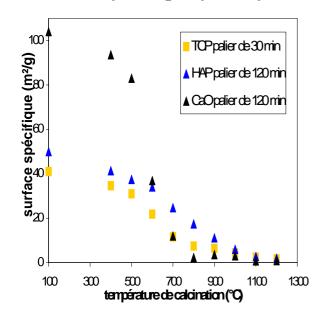




Evolution des solides traités (contenant des polluants)

Typical evolution

Reduction of the specific surface area



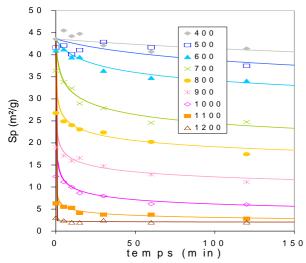
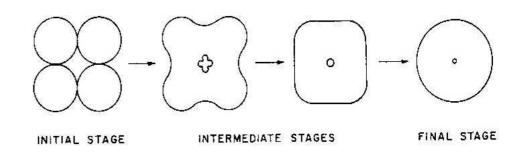
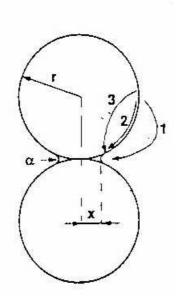


Illustration of the sintering phenomenon:





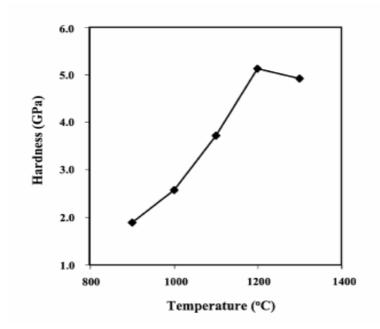
$$j_{i} = -\frac{D_{i}}{RT} \operatorname{grad}\sigma, D_{i} = D_{0i}e^{-E\hat{i}^{T}RT}$$

- Diffusion in gas phase (1)
- Surface diffusion (2)
- Volume diffusion (3)

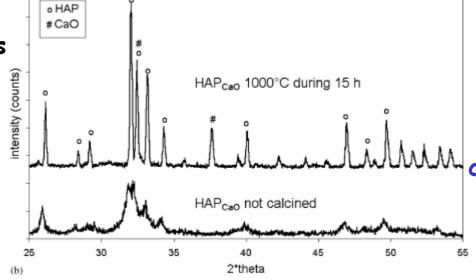
Kinetics:
$$-\frac{dS}{dt} = kS$$

Effect of Calcination on HAp properties

Other physical changes



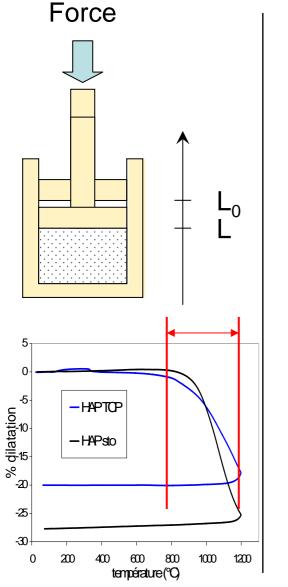




Amorphous to cristalline structure

Calculation of properties during the sintering

Density and porosity calculation from TMA, Thermomechanical Analyzer



Shrinkage

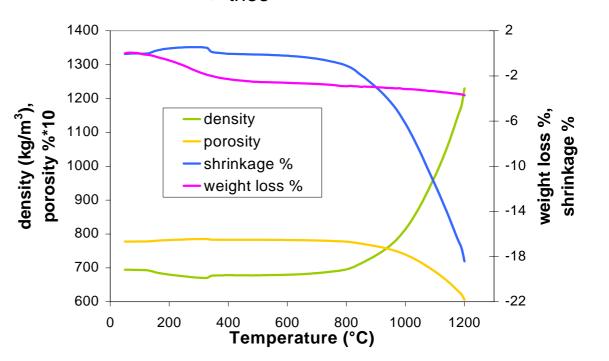
$$\frac{\Delta V}{V_0} = 1 - \left(\frac{L}{L_0}\right)^3$$

Density

$$\rho = \frac{m}{V} = \frac{m_0 - \Delta m}{V_0 - \Delta V}$$

$$\rho = \frac{m_0 (1 - \frac{\% TG}{100})}{\pi R_0^2 h_0 (1 + \frac{\% dilatation}{100})^3}$$

Porosity:
$$\varepsilon = 1 - \frac{\rho}{\rho_{\text{theo}}}$$



Modeling for the description of the sintering process

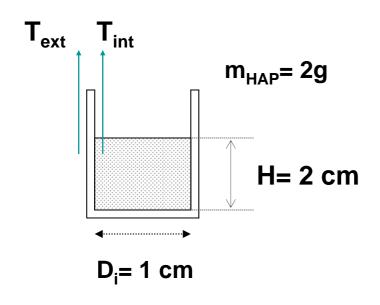
Typical representation of processes involved:

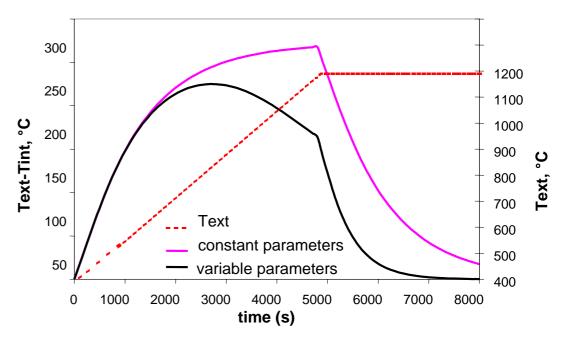
$$(\rho(T,t)c_{p}(T)\frac{\partial T}{\partial t} = \frac{1}{r^{2}}\frac{\partial}{\partial r}\left(\lambda r^{2}\frac{\partial T}{\partial r}\right) + (\nu\Delta H)$$

v: Kinetic of reaction

Continious measurement of the properties:

$$\alpha = \frac{\lambda(T,t)}{\rho(T,t)C_{p}(T,t)}$$







SINTERING OF POWDERS AND DENSE MATERIALS MODELLING

Pr Roberto Santander

Model for Sintering and Coarsening of Rows of Spherical Particles

Literature:

- Parhami F. et al; Mechanics of Materials 31 pp 43-61 (1999)
- Svoboda and Riedel; Acta Mettal. Mater Vol 43 N 1pp 1-10 (1995)
- Olevsky E; Materials Science and Engineering R23 (1998)

Goal:

Model for the formation of interparticle contacts and neck growth between powder particles by grain boundary and surface diffusion.

Methodology:

Model is based on a Thermodynamic Variational Principle arising from the governing equations of mass transport on the free surface and grain boundaries

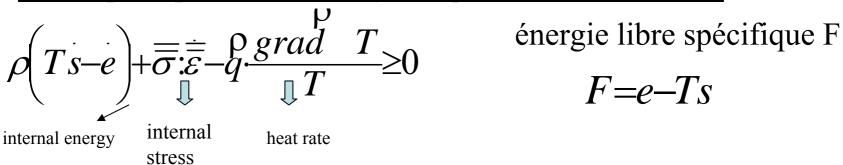


Maximization of the rate of dissipation of Gibbs free energy (for a pair of particles through grain boundary and surface diffusion)

Phenomenological model of sintering based upon the ideas of thermodynamics of irreversible processes

- 1. Porous medium is considered as a two phase material (phase of substance body skleleton and phase voids –pores)
- 2. The skleton is assumed to be made of individual particles having nonlinear viscous incompresible isotropic behavior.
- 3. The voids (pores) are isotropically distributed.
- 4. The overall response is therefore isotropic
- 5. The free energy F per unit mass of porous medium is by hypothesis, a function of the absolute temperature T and of the specific volume v.

Second principle de la thermodynamique des milieux continus



Phenomenological model of sintering based upon the ideas ofthermodynamics of irreversible processes;

Phenomenological model of sintering based upon the ideas of thermodynamics of irreversible processes

Clausius' inequality – Duhem with hypothesis F=F(T,v) and

grad
$$T=0$$

$$\sigma \longrightarrow \text{Cauchy stress tensor}$$

$$\varepsilon \longrightarrow \text{strain rate tensor}$$

$$\varepsilon = \overline{\varepsilon}^{e} + \overline{\varepsilon}^{p}$$

$$\sigma_{ij} = f(\varepsilon_{ij})$$
but not on $T^{\&}$

$$S = \frac{\partial F}{\partial T}$$

$$\sigma_{ij} - P_{L} \delta_{ij}$$

$$\sigma_{ij} = f(\varepsilon_{ij})$$

$$\sigma \longrightarrow \text{Cauchy stress tensor}$$

$$\varepsilon \longrightarrow \text{strain rate tensor}$$

$$\varepsilon = \overline{\varepsilon}^{e} + \overline{\varepsilon}^{p}$$

$$\sigma_{ij} = f(\varepsilon_{ij})$$
but not on $T^{\&}$

$$\sigma_{ij} = f(\varepsilon_{ij})$$

where
$$P_L = \frac{\partial F}{\partial v}$$

where $P_L = \frac{\partial F}{\partial v}_T$ Laplace pressure or sintering stress (result of the collective action of local capillary stresses in a porous material)

Phenomenological model of sintering based upon the ideas of thermodynamics of irreversible processes

The condition (X)



Is satisfied if there exists a dissipative potential D defined as a homogeneous function of order m+1 of the strain rate \mathcal{L}_{ii}

$$\sigma_{ij} - P_L \delta_{ij} = \frac{\partial D}{\partial \mathcal{X}_{ij}}$$

$$\sigma_{ij} - P_L \delta_{ij} = \frac{\partial D}{\partial \mathcal{R}_{ij}}$$
 and $\mathcal{R}_{ij} \frac{\partial D}{\partial \mathcal{R}_{ij}} = (m+1)D \ge 0$

$$D=f(v)$$
 or $D=f(\theta)$

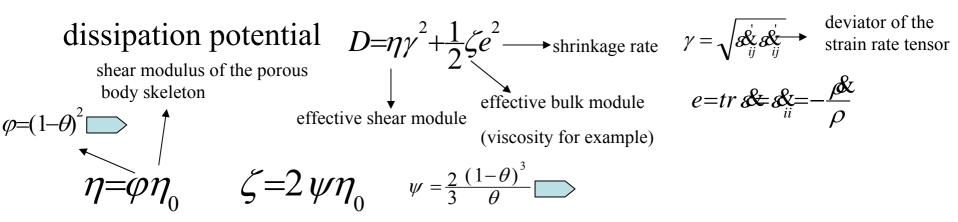
$$D=f(v)$$
 or $D=f(\theta)$ $\theta=\text{porosity}=\frac{V_{pores}}{V_{total}}$

For D, cases three-

- 1. Linear incompressible viscous material with voids
- Incompressible nonlinear viscous material
- 3. Nonlinear viscous porous material

Phenomenological model of sintering based upon the ideas of thermodynamics of irreversible processes

Linear viscous incompressible material with voids



the potential D can be expressed as:
$$D=(1-\theta)\eta_0W^2$$

$$W=\sqrt{\frac{\varphi\gamma^2+\psi e^2}{1-\theta}}$$

The constitutive law is:

$$\sigma_{ij} = 2 \eta_0 (\varphi s_{ij} + \psi e \delta_{ij}) + P_L \delta_{ij}$$

Phenomenological model of sintering based upon the ideas of thermodynamics of irreversible processes

2. Incompressible nonlinear – viscous material

- •incompressible material $\rightarrow \theta=0$ $\Rightarrow \varphi\rightarrow 1$ and $\psi\rightarrow\infty$ •incompressible matric $\rightarrow e\rightarrow 0$ $\Rightarrow \psi e^2\rightarrow 0$ therefore $W\rightarrow\gamma$
- •the dissipative potential of a linear viscous fluid is $D=\eta_0 \gamma^2$
- an extension into nonlinear –viscous behavior is obtained by

material parameter depends on temperature
$$D = \frac{A}{m+1} \gamma^{m+1}$$

• the deviatoric stress is obtained from

$$\sigma'_{ij} = \frac{\partial D}{\partial \mathcal{R}_{ij}} = A \gamma^{m+1} \mathcal{R}_{ij} \qquad (\mathcal{R}_{ij} = \mathcal{R}_{ij})$$

Phenomenological model of sintering based upon the ideas of thermodynamics of irreversible processes;

Nonlinear – viscous porous material

• using a power law dependence, the dissipation of a porous material is

• matrix incompressible, nonlinear-viscous
$$D = \frac{A}{m+1} (1-\theta) W^{m+1}$$
• matrix incompressible, nonlinear-viscous
$$D_{matrix} = \frac{A}{m+1} \gamma^{m+1}$$
• matrix incompressible, nonlinear-viscous
(incompressible nonlinear viscous material)
$$m=1 \quad we \quad have \quad A=2\eta_0$$
(linear viscous porous material)

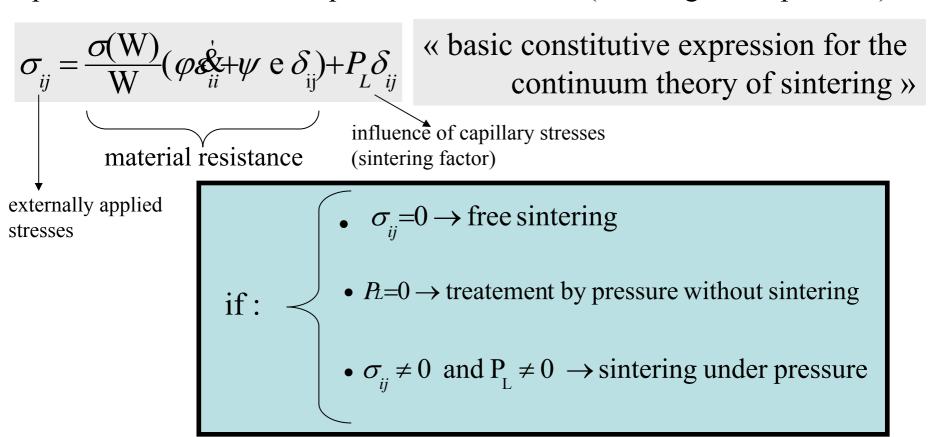
• constitutive law
$$\sigma = AW^{m-1}(\varphi \mathcal{E}_{ii} + \psi e \delta_{ij}) + P_L \delta_{ij}$$
 if
$$\tau = A\varphi W^{m-1} \gamma \qquad p = A\psi W^{m-1} e + P_L$$
 substituting leads to the following relationship between the equivalent stress σ and the equivalent strain rate W

if
$$\tau = A \varphi W^{m-1} \gamma \qquad p = A \psi W^{m-1} e + F$$

$$\sigma = A W^n$$

Phenomenological model of sintering based upon the ideas of thermodynamics of irreversible processes;

- a generalization of the relationship, $\sigma = AW^m$ between equivalent stress and equivalent strain rate $\sigma = \sigma(W)$ arbitrary function of W
- in this general case, the constitutive relationship for a nonlinear —viscous porous material can be represented in the form (sintering under pressure):



Phenomenological model of sintering based upon the ideas of thermodynamics of irreversible processes

we have

$$\tau = \frac{\sigma(W)}{W} \varphi \gamma$$
 and $p = \frac{\sigma(W)}{W} \psi e + P_L$

• an important relationship between the invariants of stress – strain rate state is:

$$(p-P_L) \varphi \gamma = \tau \psi e$$

Model Formulation

• At hight temperature, atoms travel along the free surfaces and the interparticle contacts to reduce the total free energy of surfaces and interfaces of the system.

ENERGY BALANCE BETWEEN SOURCES AND SINKS

$$\prod = G_s : \text{ rate of change of the free energy of system} \\
R_s : \text{ one-half of the rate of energy dissipation}$$

$$\mathcal{C}_{s} = \gamma_{s} A_{s} + \gamma_{b} A_{b} - Fv$$

$$R_{s} = \frac{1}{2} \int_{A_{b}} \frac{1}{D_{b}} \int_{b}^{\rho} \cdot \int_{b}^{\rho} dA_{b} + \frac{1}{2} \int_{A_{s}} \frac{1}{D_{s}} \int_{s}^{\rho} \cdot \int_{s}^{\rho} dA_{s}$$

 $\gamma_s \wedge \gamma_b \rightarrow$ surface and grain boundary energies per unit area

$$D_{s} = \frac{\delta \overset{f}{D}\Omega}{kT} \qquad D_{b} = \frac{\delta \overset{f}{D}\Omega}{kT}$$

 $A_{s} \wedge A_{b} \rightarrow$ surface and grain boundary areas

 $F \rightarrow \text{applied force}$

 $v \rightarrow$ velocity of one end of the row of particles to the other

 $D_{b} \wedge D_{c} \rightarrow \text{diffusion parameters}$

 $\vec{D}_{k} \wedge \vec{D}_{c} \rightarrow \text{grain boundary and surface atom diffusivities}$

 $\Omega \rightarrow$ atomic volume

 $k \rightarrow \text{Boltzman's constant}$

 $T \rightarrow$ absolute temperature

 $J_b \wedge J_s \rightarrow$ fluxes of material on the grain boundary and on the free surface

 $\delta_b \wedge \delta_s \rightarrow$ thicknesses within wich diffusion occurs on the grain boundary and surfaces

Model Formulation

Important

- $J \rightarrow$ volume of material passing by diffusion through unit length in unit time
- $c_s^{\&}$ \rightarrow the rate of change of the free energy of the system is the rate of change of the internal energy minus the external work rate. In the system, internal energy is the sum of surface and grain boundary energies
- \prod has a stationary minimum value with respect to compatible variations of J_b , J_s , A_s , A_b and V.

 The Rayleigh Ritz minimization is achieved by setting

$$\delta \prod = \delta \mathcal{C}_{s}^{k} + \delta R_{s} = 0$$

 $\delta\Pi$ must be zero for variations

degrees of freedom of the Variational functional Π

Model Formulation compatibility condition

sum of the principal curvatures of the particle surface

$$A_s = \int_{A_s} v_n dA_s + \sum_{all \ b} \int_{neck} v_{neck} \cdot (\hat{s}_1 + \hat{s}_2) dL$$
motion of the locus of point of connection between the grain boundary and free surface

 $A_b^{\mathcal{K}} = \sum_{all\ b} v_{neck} \cdot \hat{s}_b dL$

$$Fv = \sum_{all \, b} \int_{A_b} \sigma \, dA_b v_b$$

integral of the strees over each grain boundary

rate of motion of the particle surface in the outward normal direction

Equations of conservation

$$J_{s} = -D_{s} \gamma_{s} \nabla_{s} \kappa \quad \text{on } A_{s}$$

$$J_{b} = D_{b} \nabla_{b} \sigma$$
 on A_{b}

Model Formulation

The resulting expressions are coupled linear equations:

$$\begin{bmatrix} \frac{\pi a^2}{xD_s}(2 \times a^2 g_a + L^2 t) & 0 & 0 & 0 & \frac{\pi a L t^2}{4D_s} \\ 0 & \frac{\pi b^2}{xD_s}(2 x b^2 g_b + h^2 t) & 0 & 0 & 0 & \frac{\pi b h t^2}{4D_s} \\ 0 & 0 & \frac{\pi x^4}{8D_b} & \frac{\pi x^4}{8D_b} & \frac{\pi x^4}{8D_b} & \frac{\pi x^4}{8D_b} \\ 0 & 0 & \frac{\pi x^4}{8D_b} & \frac{\pi x^4}{8D_b} & \frac{\pi x^4}{8D_b} & 0 \\ 0 & 0 & \frac{\pi x^4}{8D_b} & \frac{\pi x^4}{8D_b} & \frac{\pi x^4}{8D_b} & 0 \\ \frac{\pi a L t^2}{4D_s} & \frac{\pi b h t^2}{4D_s} & 0 & 0 & 0 & \frac{\pi x t^3}{6D_s} \end{bmatrix} \begin{bmatrix} \mathbf{a} \\ \mathbf{b} \\ \mathbf{c} \\ \mathbf{$$

the set of variables used above are not independent, by imposing volume conservation and geometrical constraints, $L^2 = a^2 - x^2$ and $h^2 = b^2 - x^2$

Model Formulation

$$\begin{bmatrix} a^2 L^2 \left(\frac{t}{x D_s} + \frac{1}{2 D_b}\right) + \frac{2a^4 g_a}{D_s} & \frac{a L b h}{2 D_b} & a L x t \left(\frac{t}{4 x D_s} + \frac{1}{2 D_b}\right) \\ \frac{a L b h}{2 D_b} & b^2 h^2 \left(\frac{t}{x D_s} + \frac{1}{2 D_b}\right) + \frac{2b^4 g_b}{D_s} & b h x t \left(\frac{t}{4 x D_s} + \frac{1}{2 D_b}\right) \\ a L x t \left(\frac{t}{4 x D_s} + \frac{1}{2 D_b}\right) & b h x t \left(\frac{t}{4 x D_s} + \frac{1}{2 D_b}\right) & \frac{t^2 x^2}{2} \left(\frac{t}{3 x D_s} + \frac{1}{D_b}\right) \end{bmatrix} \begin{bmatrix} \mathbf{z} \\ \mathbf{z} \\ \mathbf{z} \end{bmatrix} = \begin{bmatrix} \frac{4 \gamma_s a L}{x} \left(1 - \frac{x}{2a} - \frac{xa}{2L^2} + \frac{x^2}{2L^2}\right) - \frac{2aL}{\pi x^2} F \\ \frac{4 \gamma_s b h}{x} \left(1 - \frac{x}{2b} - \frac{xb}{2h^2} + \frac{x^2}{2h^2}\right) - \frac{2bh}{\pi x^2} F \\ 2 \gamma_s x \left(\frac{a}{L} + \frac{b}{h} - \frac{x}{L} - \frac{x}{h} + \frac{t}{x}\right) - 2\gamma_b x - \frac{2t}{\pi x} F \end{bmatrix}$$

with

$$g_{a} = Ln \left[\frac{a}{x} \left(1 + \sqrt{1 - \left(\frac{x}{a} \right)^{2}} \right) \right] - \frac{L}{a} \qquad t = \frac{1}{x^{2}} \left[\frac{V_{o}}{\pi} - \left(a^{2} L - \frac{1}{3} L^{3} \right) - \left(b^{2} h - \frac{1}{3} h^{3} \right) \right]$$

$$g_{b} = Ln \left[\frac{b}{x} \left(1 + \sqrt{1 - \left(\frac{x}{b} \right)^{2}} \right) \right] - \frac{h}{b}$$

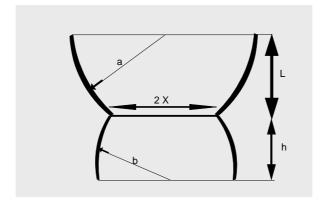
Numerical Procedures

• initial conditions $\longrightarrow a = a_o$ $b = b_o$ and x = 0

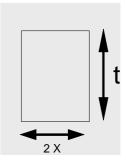
Case 1: very small value of x, instability numerical asymptotic approach

Case 2: elimination of the circular disc

• Runge Kutta



Case 3:elimination of the spherical surfaces



Case 1: very small values for the magnitude of x

• in the limit where x /a , x /b and t /x are much smalle than 1 and higher order terms in [k] $\{\mathcal{S}\}=\{f\}$ are neglected

$$\mathcal{X} = \frac{\left[4 D_{b} g_{a} g_{b} + D_{s} (g_{a} + g_{b})\right] (2\gamma_{s} - \gamma_{b})}{g_{a} g_{b} x t^{2}} - \frac{4D_{b} F}{\pi x^{3} t} \quad \bigoplus$$

$$\mathcal{E} = -\frac{D_s(2 \, \gamma_s - \gamma_b)}{g_a \, \text{t} \, \text{a}^2} + \frac{\text{t} \, D_b \, F}{6 \, \pi \, \text{x}^3 \, \text{a}^2 \, g_a}$$

$$\mathcal{E} = -\frac{D_s(2 \, \gamma_s - \gamma_b)}{g_b \, \text{t} \, \text{b}^2} + \frac{\text{t} \, D_b \, F}{6 \, \pi \, \text{x}^3 \, \text{b}^2 \, g_b}$$

$$t = \frac{1}{x^2} \left[\frac{V_o}{\pi} - \frac{2}{3} \left(a^3 + b^3 \right) + \frac{x^4}{4} \left(\frac{1}{a} + \frac{1}{b} \right) \right]$$

Of \bigoplus with $1/g_a$ and $1/g_b$ negligible is obtained:

generalization of Coble's

$$x^{6} = 96 D_{b} \left[\frac{4(2\gamma_{s} - \gamma_{b})}{\left(\frac{1}{a_{o}} + \frac{1}{b_{o}}\right)^{2}} - \frac{F}{\pi \left(\frac{1}{a_{o}} + \frac{1}{b_{o}}\right)} \right] Te$$

 $Te \rightarrow time \text{ elapsed}$

are used until:

$$\frac{x}{a} = 0.01$$

Results

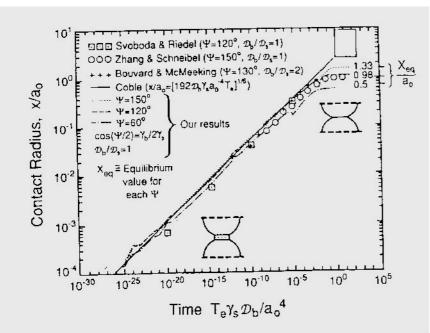
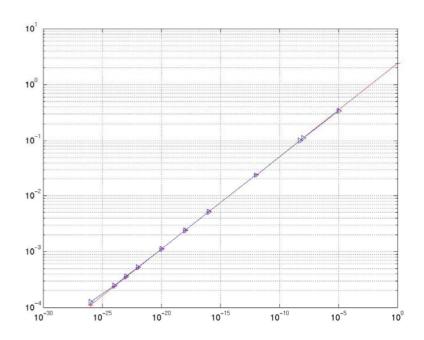


Fig. 3. Contact radius vs. time for the free sintering of a row of identical particles for various dihedral angles.



numerical matlab

paper

Results

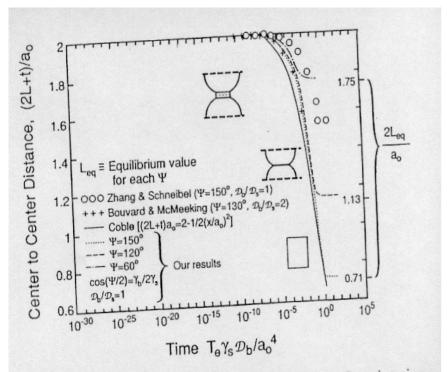


Fig. 4. Center-to-center distance vs. time for the free sintering of a row of particles for various dihedral angles.

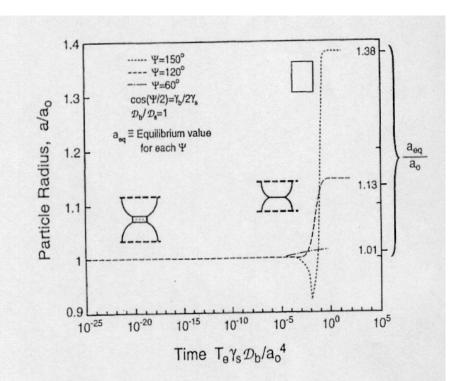


Fig. 5. Particle radius vs. time for the free sintering of a row of identical particles for various dihedral angles.