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Sintering models and the development of instabilities

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A mathematical model is developed to describe, at least approximately, the densification and reorganization of a random stacking of particles due to internal transport of material. In this model, local stresses due to time varying coordination of particles are allowed which are found to alter the overall sintering behaviour significantly. Further, variations on stacking density and coordination on both a local and a global scale are investigated for their influence on small and large scale particle reorganization during sintering. It is found that these local variations will easily give rise to the development of a porosity of high coordination along with local densification. The overall effect is that this porosity disappears after a large sintering period when grain growth has become already substantial.

Global variations in coordination are seen to be responsible for defect formation. A number of criteria will be derived to estimate under which conditions this formation of defects may be expected. The present model will be discussed with the help of own and a number of examples found in the literature.

1. Introduction

Most of the theories presented until now on the sintering of metal or ceramic particles to a dense structure are based upon the mutual approach of spherical particles of a uniform size, shape and stacking. Further, for the models to describe the densification of a material, a macroscopic extension of the interactions between the individual particles is generally assumed. In this way a statistical mean is found where deviations due to local strain fields and stacking densities are omitted. Generally, the models proposed have proved to be very helpful to relate the observed shrinkage due to sintering to more fundamental processes such as lattice, surface, grain boundary diffusion or a vapourization–condensation mechanism. All the models lead to a particular behaviour of the shrinkage rate in relation to particle size, porosity and grain growth. These models, however, give no indication for the development of defects due to reorganization effects between the particles mutually but, on the other hand, give results for the overall behaviour of a compact which in most cases can be fitted reasonably well to the experimental data. Deviations are normally attributed to internal particle rearrangement effects and creation of a pore system which is slowly removed during progressive sintering. When these deviations occur, however, they have a detrimental influence on the strength of the materials so that suitable criteria have to become available to prevent them. The purpose of this paper is to formulate a simplified statistical model starting from simple and generally accepted and verified expressions for the two sphere approach to describe the densification in a random, but locally fluctuating particle packing where also stresses are allowed.

In a second step, a locally fluctuating particle packing and collective stresses governing the reorganization are allowed. It will be shown that instabilities which are defined as extensive reorganization of the stacking and substantial pore opening can be explained in this way.

Finally, a number of situations will be presented and which can be explained with the help of the suggested model. In this model, it is not intended to give a rigorous treatment of the rearrangement effects, rather the simplest possible and approximate mathematical model will be derived to give at least a qualitative description of and insight into the most important effects to be expected.

2. Overall densification as a global extension of the two-sphere approach

In the present analysis we will start from the approach of Arzt [1] where a random fault free packing is described as a relation between the number of particle contacts and the average distance between the individual particles. This relation is presented by the following expression

$$G(z) = G_0 + C(z - 1) \qquad (1a)$$

where z is the densification parameter, equal to the free particle radius divided by half of the centre-to-centre distance, $G(z)$ is the coordination number, G_0 the coordination number at $z = 1$, and C the slope of the linearized $G(z)$

The differential form is given by

$$\partial_z G(z) = G_0 \delta(z - 1) + C \qquad (1b)$$

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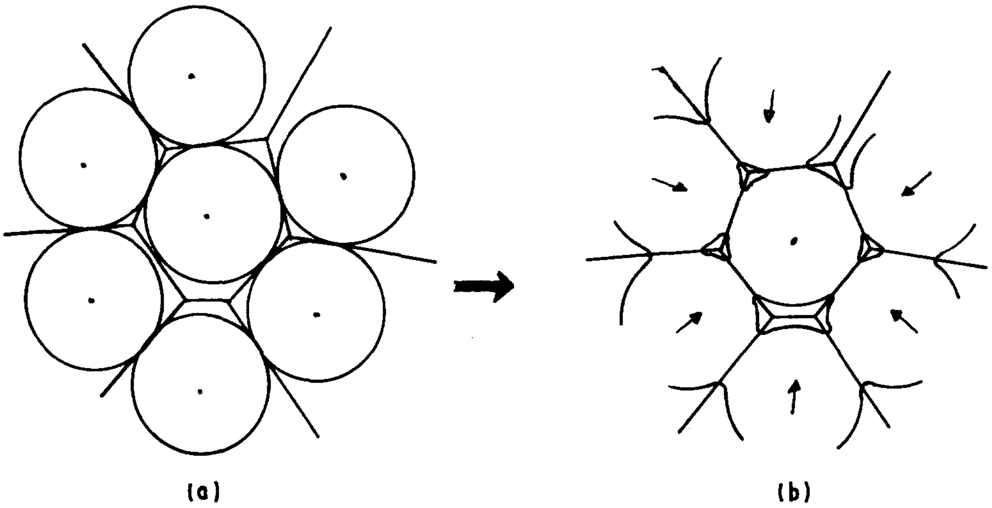

Figure 1 Particle stacking and Voronoj cell (a) before ($z = 1$, $t = 0$) and (b) during densification ($z > 1$, $t > 0$).

where δz is the increase of the densification from the initial value $z = 1$. Further we will use the shorthand notation for derivatives $\partial_x = \partial/\partial x$, $\partial_{xx} = \partial^2/\partial x^2$, $\partial_t = \partial/\partial t$ etc. The expression for $\partial_z G(z)$ by a normal δ-function, which evidently is a simplification, shall be shown to be of particular convenience throughout the development of the model.

Further, each single particle and all material transport is accommodated during the whole densification process in one single cell (Voronoj cell), Fig. 1, such that each cell shrinks along with the particle. During this process, the dimensionless densification parameter, z, increases from its starting value of $z = 1$ by the amount δz.

This approach is different from Artz's analysis [1], where the sintering process is visualized as a gradual growth of the particle while the cell volume and shape are kept constant and which leads to a description of the material transport which is scaled up by a factor of z^3.

Further, there exists a direct connection between the overall density of the material and the densification parameter z. Starting from the density $\rho = \rho_0$ at $z = 1$ we find that in the case of a three dimensional stacking [1]

$$\frac{\rho}{\rho_0} = z^3 \qquad (2)$$

where ρ_0 is the initial density and ρ the actual density.

If the stacking is now allowed to shrink such that no transport of material takes place across a cell wall, the area where two particles are in contact will initially grow rapidly and later more gradually. During this process, new contacts between the particles are created, however, due to a mismatch between the rates of centre-to-centre approach as a consequence of already existing and newly created contact zones, stresses will locally develop and influence the material transport in a cell and therewith the overall behaviour of the compact. If we introduce a parameter τ giving the reciprocal value of the relative distance from the cell face to the particle centre (Fig. 2), we find by geometrical arguments that the total amount of material to be transported away by any mechanism should be

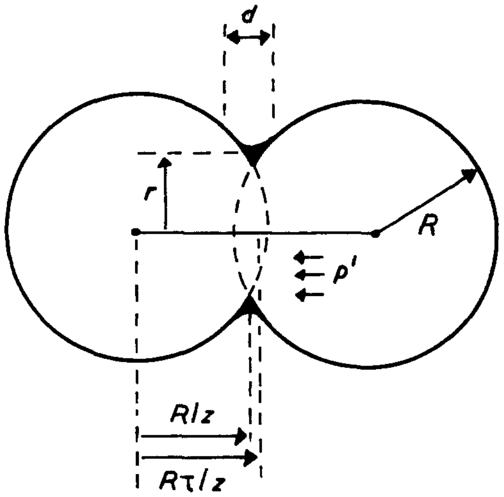

Figure 2 Neck growth and approach of two spherical particles.

$$V(\tau, z, R) = \frac{\pi}{3}\frac{R^3}{z^3}(2z^3 - 3\tau z^2 + \tau^3) \qquad (3)$$

where τ is the local integration parameter, R the free particle radius, and V the volume.

The total volume to be transported up to a densification of z is then

$$\begin{aligned}\Delta V &= \int_1^z V(\tau, z, R)\partial_\tau G(\tau)\,d\tau \\ &= \frac{\pi R^3}{3z^3}G_0(z-1)^2(2z+1) \\ &\quad + \frac{C\pi R^3}{12z^3}(z-1)^3(3z+1) \qquad (4)\end{aligned}$$

To find an expression for the densification of the material, we should formally equate this volume to the amount of material which can be transported away from all the contact zones with the cell faces which already exist from the beginning and which are being newly created during the process. At this stage, we should consider the transport phenomena more closely in order to take into account the influence from local stresses due to mismatch in the ratio for centre-to-centre approach of adjacent spheres.

In the present analysis we will start from the approach of Coble [2] and Kingery and Berg [3] and consider both lattice and grain boundary diffusion the dominant mechanisms for material transport. Transport due to lattice diffusion results in removal of material from the contact area of the particles to the neck zone through the interior of the particles. Grain boundary diffusion, on the other hand, differs from lattice diffusion in that transport occurs along the contact zone of neighbouring particles. This area is regarded as a predecessor for the grain boundary between grains in a densified structure.

In Appendix 1, it is shown that the expressions for centre-to-centre approach can be represented in the following way for lattice and grain boundary diffusion, respectively,

$$\left(\frac{\Delta L}{2R}\right)_{\mathrm{l}} = -\left(\frac{4\alpha D_{\mathrm{l}}\Omega\gamma t}{R^3 kT}\right)^{1/2} \tag{5a}$$

$$\left(\frac{\Delta L}{2R}\right)_{\mathrm{b}} = -\left(\frac{6D_{\mathrm{b}}\Omega\gamma\omega t}{R^4 kT}\right)^{1/3} \tag{5b}$$

where $\Delta L/2R$ is the relative change in the centre-to-centre distance of the spheres, α a geometrical parameter close to 2, Ω the atomic volume, γ the surface energy, ω the diffusion zone width, D_{l} and D_{b} the diffusion coefficients for lattice diffusion and boundary diffusion, respectively.

If we impose a densification of $z = 1 + \delta z$ we will have

$$\delta z = -\frac{\Delta L}{2R} \tag{6}$$

This means that, if during the densification process a new contact is created, the approach of the two particles initially occurs very rapidly. On the other hand, each particle is part of a structure that cannot reorganize instantaneously so that tensile stresses in a new contact zone and compressive in the older ones are generated to modify the transport pattern in such a way that the approach rates of the new contacts are diminished and the older ones enhanced. In the case we are not taking into account this effect of local stresses, we will encounter singularities during the integration to find the overall shrinkage.

This problem can be easily circumvented when we modify these expressions by defining a total contact pressure over all contact surfaces bounded by one single cell. Equilibrium requires that the sum of the forces in one cell due to mismatch effects should vanish and leads to an expression for the modified material transport equation. This procedure is given in more detail in Appendix 2.

The total modified transport for both lattice and grain boundary diffusion is summed up and equated to the expression ΔV given in Equation 4, to finally obtain by setting $z = 1 + \delta z$ and linearizing the system (Appendix 2) for lattice diffusion

$$\mathrm{d}_t\delta z = \frac{2D_{\mathrm{l}}\Omega\gamma\alpha}{kTR^3\delta z}\left[1 + \left(\frac{C}{2G_{\mathrm{o}}} + \frac{7}{2}\right)\delta z\right] \tag{7a}$$

and for grain boundary diffusion

$$\mathrm{d}_t\delta z = \frac{2D_{\mathrm{b}}\omega\gamma\Omega}{kTR^4(\delta z)^2}\left[1 + \left(\frac{C}{G_{\mathrm{o}}} + 5\right)\delta z\right] \tag{7b}$$

Obviously the original expression for centre-to-centre approach (Equations 5a and 5b) is found in the limit for $\delta z \to 0$. These equations show that the creation of new contacts between the individual particles may give a substantial contribution to the overall sintering behaviour, especially in the case of grain boundary diffusion which in ceramic systems turns out to be the main contribution to the overall effect. It will be shown later that it is just this effect that gives rise to enhanced defect formation as a consequence of reorganization.

For the further development of the theory, it is helpful to define an apparent compressibility, η, for the particle stacking, therefore we assume an external pressure, acting on a matrix, which we imagine for the moment to be solely responsible for the densification. In the basic equations for matter transfer the action of the external pressure is introduced easily by replacing γ for $\gamma + pR/4$ (Appendix 1), where in the case of a pressure assumed to be responsible for densification only we should take the limit for $\gamma \to 0$. This compressibility is defined in the following way

$$p = \eta\mathrm{d}_t\rho = 3\eta\rho_{\mathrm{o}}z^2\,\mathrm{d}_t z = 3\eta\rho_{\mathrm{o}}z^2\,\mathrm{d}_t\delta z \tag{8}$$

where p is the pressure.

In the present case, where reorganization is not yet assumed and an overall densification occurs, we can find the explicit expressions for $\eta_{\mathrm{l,\,b}}$, where the indices l and b refer to lattice and grain boundary diffusion, respectively.

Introducing the expression $\gamma + pR/4$ for γ into Equation 7a or 7b, substituting the results into Equation 8 and linearizing for δz we finally obtain

$$\eta_{\mathrm{l}} = \frac{2kTR^2\delta z}{3\Omega D_{\mathrm{l}}\alpha\rho_{\mathrm{o}}}\left[1 - \frac{\delta z}{2}\left(\frac{C}{G_{\mathrm{o}}} + 11\right)\right] \tag{9a}$$

for lattice diffusion and

$$\eta_{\mathrm{b}} = \frac{2kTR^3(\delta z)^2}{3\Omega D_{\mathrm{b}}\omega\rho_{\mathrm{o}}}\left[1 - \delta z\left(\frac{C}{G_0} + 7\right)\right] \tag{9b}$$

for grain boundary diffusion.

3. Occurrence of defects as a consequence of internal reorganization in a nearly random packing

It is easily shown by geometrical arguments that the total covered surface area of a particle in one single cell is equal to

$$\Delta O(R, z, G_{\mathrm{o}}, C) = \int_1^z \pi R^2\left(1 - \frac{\tau^2}{z^2}\right)\partial_\tau G(\tau)\,\mathrm{d}\tau$$
$$= G_{\mathrm{o}}\pi R^2\left(1 - \frac{1}{z^2}\right) + C\pi R^2\left(\frac{2}{3}z - 1 + \frac{1}{3z^2}\right) \tag{10}$$

where O is the surface area.

Assuming the contribution to the free energy, U, due to the none covered surface area per cell is most important, we find

$$U = \gamma[4\pi R^2 - \Delta O(R, z, G_o, C)]$$

and the force, F, acting on the particle in the cell due to a gradient in the densification parameter z, as well as the value of G_o and C is given by the expression

$$F = -\partial_x U = \gamma\partial_x \Delta O(R, z, G_o, C) \qquad (11)$$

where an explicit and unique dependence of z, G_o and C on x has to be assumed.

This equation formally leads to derivatives of z, G_o and C and is important in determining the nature of an instability. To show that this force leads to instabilities we can write by assuming that G_o and C are constants

$$F = \frac{\gamma\pi R^2}{z^3}\left(2G_o + \frac{2Cz^3}{3} - \frac{2C}{3}\right)\partial_x z$$

for $\partial_x z > 0$ we have $F > 0$ and the force will tend the particles to zones where z is the largest, see also Fig. 3.

At this point, a problem occurs due to the fact that we may have a force acting on a particle, while it should not necessarily lead to actual displacement of the particles themselves. This is most easily seen when we calculate the free energy of a particle in relation to its distance from the neighbours and conclude that a local minimum is found when it finds its centre precisely midway. Also the total free energy of a stacking in a non-densifying field is found to be a minimum when no local departures from homogeneity occur, however, when we have a homogeneously densifying field superposed on a locally varying $\partial_t z$, a situation is obtained where instabilities develop and the total free energy decreases. It is evident, however, that this free energy decrease is much lower than in the case of homogeneous densification. The condition for this to occur is worked out mathematically in Appendix 3 and leads to a formally more precise definition of the free energy to be attributed to the system.

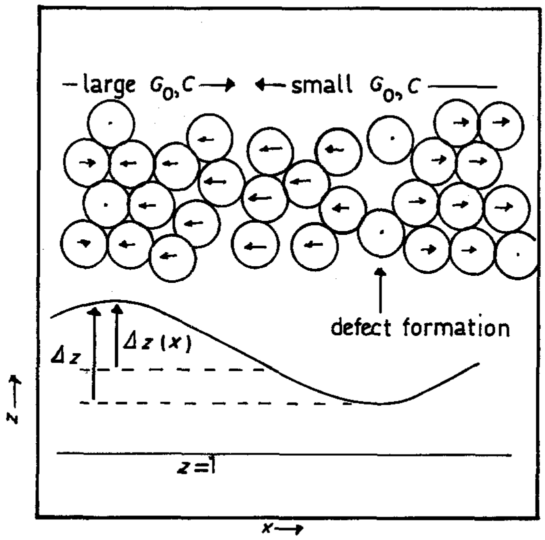

Figure 3 Spatial variation in densification coordination parameters leading to collective reorganization of particles.

To find an expression for the total accumulated force acting on a particle when a reorganization effect occurs in one direction, but which is homogeneous over a broad field perpendicular to this direction, we should integrate Equation 11, where the boundaries are carefully chosen. Two circumstances occur, one for a densifying field and one for a field of reducing z. The situation is further explained in Fig. 3.

Starting from

$$F = \gamma\partial_z \Delta O(z, R, G_o, C)\partial_x z$$

the pressure which causes densification and dilution which for the present case will be assumed to be isotropic, is defined by

$$\frac{1}{2R}\int_{z(\partial_x^- z = 0)}^{z} F\,\mathrm{d}x = \pi R^2 p \qquad (12a)$$

with $z(\partial_x^- z = 0) = z - \frac{1}{2}\Delta z$, where $(\partial_x^- z = 0)$ refers to the minimum value of z. This integral attains its maximum value for $z = z(\partial_x^+ z = 0)$ which is equal to

$$\frac{1}{2R}\int_{z(\partial_x^- z = 0)}^{z(\partial_x^+ z = 0)} F\,\mathrm{d}x = \pi R^2 p \qquad (12b)$$

where $z(\partial_x^+ z = 0)$ refers to the maximum value of z and

$$\begin{aligned} z(\partial_x^+ z = 0) &= z + \tfrac{1}{2}\Delta z \quad G_o(\partial_x^+ z = 0) \\ &= G_o + \tfrac{1}{2}\Delta G_o, \quad G_o(\partial_x^- z = 0) \\ &= G_o - \tfrac{1}{2}\Delta G_o \\ C(\partial_x^+ z = 0) - C(\partial_x^- z = 0) &= \Delta C \end{aligned}$$

The actual local pressure obviously is given as a function of $z(x)$ by Equation 12a, but since we are only interested in the extremum we should integrate up to the maximum of z.

This pressure gives rise to densification which should be highest at the location of maximum coordination and the highest value of z. The densification due to this pressure should be compensated by a decreasing density. This decrease should be highest where the coordination has a minimum, because of the symmetry of the problem as expressed by the boundary conditions of Equation 12b, the fact that the densification is linear in the isotropic pressure, Equation 8 and also because of continuity of the total number of particles involved in the instability, we should conclude that the maximum decrease in z is equal to the maximum increase of z where coordination is highest. For the present problem this means that we can attribute the pressure given by Equation 12b to the diluting zone but with a negative sign.

Substituting Equation 10 into Equation 11 and integrating as prescribed by Equation 12b with the proper boundary conditions and then linearizing, it is found that

$$p = -\frac{\gamma}{R}(G_o\Delta z + \Delta G_o\delta z) \qquad (13)$$

where second-order terms are neglected.

Essential for the assumption that complete reorganization can take place is a.o. the fact that this pressure p, should be isotropic whereas the force responsible for

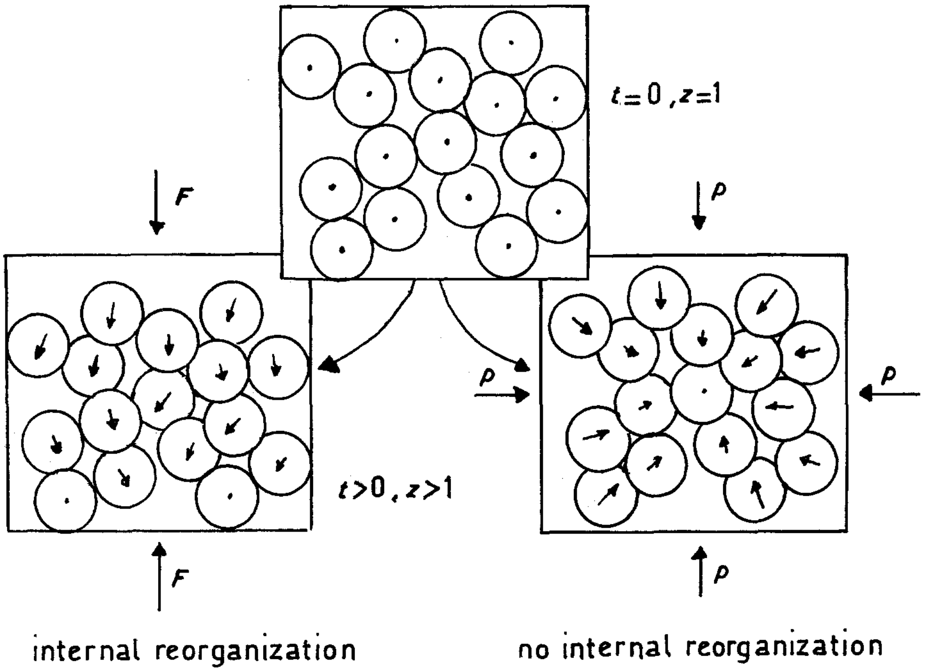

Figure 4 Evolution of the stacking with and without internal reorganization.

this pressure acts in one direction. We will return to this point later. Further substituting Equation 8 into Equation 13 it is found that

$$d_t z = -\frac{\gamma}{3R\rho_o z^2 \eta}(G_o \Delta z + \Delta G_o \delta z) \qquad (14)$$

which is valid for both lattice and grain boundary diffusion and where η is defined by Equation 9a or Equation 9b.

This equation has the following interpretation. We have an overall and homogeneous densifying field, δz, leading with a local fluctuation in G_o, ΔG_o, to a rate of decrease in z. This decrease in z will further grow and eventually overtake the influence of $\Delta G_o \delta z$ itself. Taking z_o as the amplitude of the instability we should, for this reason, substitute $-2z_o$ for Δz and $d_t z_o$ for $d_t z$

$$d_t z_o = \frac{\gamma}{3R\rho_o z^2 \eta}(2G_o z_o - \Delta G_o \delta z) \qquad (15)$$

At first sight, it may seem curious that a fluctuation in the initial density is not primarily responsible for such instabilities (which, however, are practically coupled to the value of G_o and C). That the onset is not a consequence of a density fluctuation can be seen from Equations 7a or 7b which do not depend on ρ_o. Two sections of the material with different ρ_o's will initially shrink identically. If, for the moment, we take a fixed densification δz and set

$$a_1 = \frac{2\gamma G_o}{3R\rho_o \eta z^2}, \quad a_2 = \frac{\gamma \Delta G_o \delta z}{3R\rho_o \eta z^2} \qquad (16)$$

we find an expression for the time dependence of the departure from stability

$$d_t z_o = -a_2 \exp(a_1 t)$$

This equation gives information on the average value for the centre-to-centre distance of the adjacent particles. It should, however, be remembered that the force due to gradients in z, G_o and C, which acts locally in one direction, gives rise to a rearrangement of the stacking such that we end up with an isotropic pressure which locally changes the density. Now we define a local relative displacement of the particles due to densification and reorganization as $d_t\xi$ (Fig. 4), we should set (Appendix 4)

$$d_t\xi = -\frac{3}{z} d_t z_o \qquad (17)$$

where ξ is the relative position of the centre of the particle. The total change of the centre-to-centre distance due to both homogeneous densification and defect forming now is the sum of $d_t\xi$ given in Equation 17 and the value of $-d_t\delta z$ given by Equation 7a or 7b. This latter is rewritten with the help of Equation 9a or 9b as

$$d_t \delta z = a_3 = \frac{4\gamma}{3R\eta z^2 \rho_o}$$

The total centre-to-centre distance taken in the direction of the displacement leading to the defect is then given by

$$d_t\xi + d_t\left(\frac{\Delta L}{2R}\right) = d_t\xi - d_t\delta z = -\frac{3}{z} d_t z_o - d_t \delta z$$

$$= \frac{3}{z} a_2 \exp(a_1 t) - a_3. \qquad (18)$$

This equation shows that an initial densification occurs which is equal to $a_3 - a_2$: the overall shrinkage reduced by the effect of local fluctuations in the particle coordination. This fluctuation further grows out into a defect in the structure when $d_t\xi - d_t\delta z > 0$. If $d_t\xi - d_t\delta z < 0$ one may expect that an instability will lead to locally enhanced porosity, but ultimately stabilizes when the matrix is sufficiently dense to inhibit reorganization.

It should be stressed that this latter condition underestimates the severeness of instabilities for complete densification. The criterion should therefore be considered as indicative.

The latter requirement for stability is

$$a_3 - \frac{3}{z}a_2\exp(a_1 t) > 0.$$

If this condition is solved by substitution of the parameters: a_3 and a_2 we obtain

$$\exp(a_1 t) < \frac{4z}{3\Delta G_o \delta z} \tag{19}$$

where the right-hand side appears to be independent of the choice for the mechanism for densification. To evaluate the left-hand side, one should take the explicit relation assuming any form of material transport and remembering that t measures the time lapse from the onset of the reorganization. It is of particular interest to find out how much densification we have until a situation is reached where condition 19 is violated. Substituting Equation 5 into Equation 6 we obtain

$$\Delta t = \frac{kTR^3}{4D_l\Omega\gamma\alpha}2\delta z\Delta(\delta z) \tag{20a}$$

for lattice diffusion, and

$$\Delta t = \frac{kTR^4}{6D_b\Omega\gamma\omega}3(\delta z)^2\Delta(\delta z) \tag{20b}$$

for grain boundary diffusion.

Replacing in Equation 19, t for Δt: the growth time of the instability and working out Equation 19 with the help of the definition for a_1 and Equation 9a and 9b, we arrive at

$$\frac{4z}{3} > \Delta G_o \delta z \exp(\tfrac{1}{2}G_o \Delta\delta z) \tag{21}$$

for both lattice and grain boundary diffusion.

During this period further densification takes place which is equal to $\Delta\delta z$. Defects are being formed when $\Delta\delta z$ and δz are such that Condition 21 is violated.

Condition 21 cannot be used, however, to evaluate the situation where a defect is allowed to form right from the beginning of sintering. This is most easily seen from Equation 15 where η can only be taken constant for δz fixed. In fact, during shrinkage, η starts at zero for $\delta z = 0$ such that an instability growing due to the influence of ΔG_o is more severe than Condition 21 suggests.

In Appendix 5 approximate solutions for Equation 15 are derived in the case that the instability is allowed to grow from the beginning of sintering. The solutions, again, show a surprising similarity for both cases of lattice and grain boundary diffusion. Starting from these solutions and working out the stability requirement as before, the following condition is obtained for both lattice and grain boundary diffusion

$$\frac{4z}{3} > \Delta G_o \delta z \exp(\tfrac{1}{2}G_o \delta z)\left(1 + \frac{G_o \delta z}{4}\right) \tag{22}$$

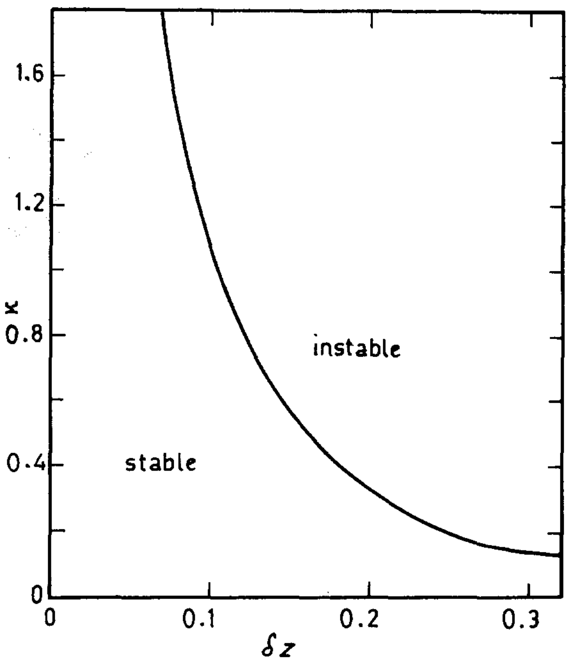

Figure 5 The value for κ as a function of the densification parameter defining a stable and instable regime for growth of defects. $G_o = 7.3$.

which looks very similar to Equation 21. Taking Equation 22, setting $G_o = 7.3$ [1] and $\Delta G_o = \kappa G_o$, the condition can be graphically displayed as in Fig. 5 showing the instable and stable zones.

Values of $\kappa = \frac{1}{2}$ occur quite often [5] in a particle stacking which should lead to a defect formation already at a densification of 16%. It should further be stressed that the present analysis made has so far implicitly assumed that the stacking of particles, although it is rearranged, retains its integrity up to the condition expressed in Equation 22.

If the reduction in coordination is found to occur over an extensive area, or has some local symmetry, we should expect that the instable field experiences no constraint at all resulting in the growth of a large defect (see also Fig. 6).

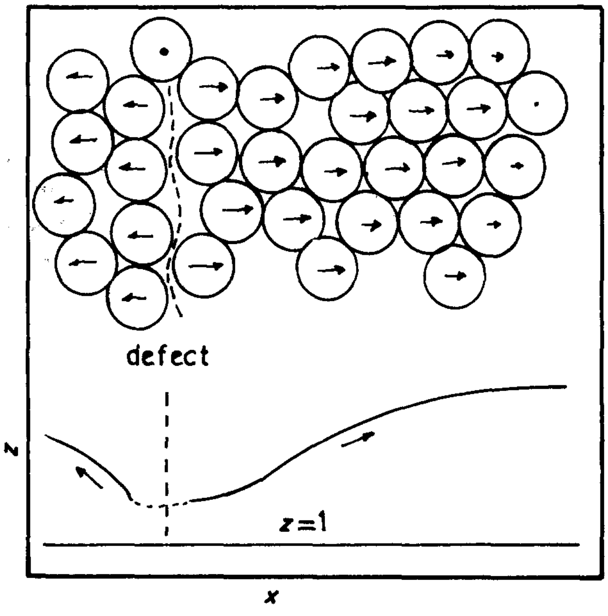

Figure 6 Growth of a large defect under the influence of a variation in particle coordination.

This defect growth rate is calculated in Appendix 5 and reads

$$\mathrm{d}_t\varepsilon - \mathrm{d}_t\delta z = \frac{\gamma}{R\rho\eta}\left[\frac{\lambda}{2Rz^3}\overline{\Delta G}_{\mathrm{o}}\delta z \exp(\tfrac{1}{2}G_{\mathrm{o}}\delta z) \times \left(1 + \frac{G_{\mathrm{o}}\delta z}{4}\right) - \frac{4}{3z^2}\right] \qquad (23)$$

where $\overline{\Delta G}_{\mathrm{o}}$ is the average value of ΔG_{o} over the total length of the instable field, λ, and $\mathrm{d}_t\varepsilon$ is the receding rate of particles on opposite sides of the defect. A stability requirement based upon this condition is far more restrictive than in the former cases since the length is directly compared to the particle size such that $\lambda/2R \gg 1$.

4. The condition on the local homogeneity of the structure

For the model developed until now, it was implicitly assumed that the structure undergoes a homogeneous shrinkage, while collective deviations from the average packing density lead to an extensive defect formation.

Looking, however, on a limited scale, like a small number of individual particles, quite extensive fluctuations in the G_{o} and C value may be found. These deviations may also lead to very local reorganizations and give rise to pore formation on a much finer scale than considered in the former case. The question now arising is the following: if we define an optimum structure as homogeneous and random, on what scale anywhere in the structure should we expect to find representative values to characterize the global stacking, with no chance for defect formation?

The easiest way to arrive at a suitable criterion, taking into account local fluctuations, is to consider a single particle which experiences a force due to a local fluctuation in the densification parameter z but which is constrained in its movement by its immediate surroundings.

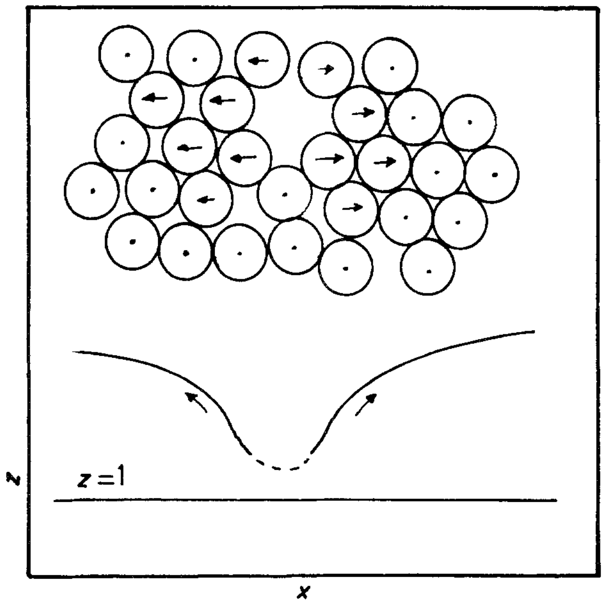

Figure 7 Variation of local density leading to local reorganization and growth of small defects.

The net displacement force again is given by Equation 11, but to find the contact pressure between this particle and its neighbour we should take into account the local constraint from the immediate horizontal neighbours (see Fig. 7).

It is easily shown that the net contact force, ΔF, is given by

$$\Delta F = \tfrac{1}{2}[F(x) - F(x + 2R)] = -R\partial_x F \qquad (24)$$

and the contact pressure p

$$p = -\frac{1}{\pi R}\partial_x F \qquad (25)$$

This pressure is responsible for local densification fluctuations, where it again has to be assumed that complete reorganization occurs leading to an isotropic pressure. Inserting Equations 10, 11 and 24 into Equation 25, making use of the definition of η and linearizing the result, we find after a very lengthy but straightforward calculation

$$\mathrm{d}_t\xi - \mathrm{d}_t\delta z = \frac{2\gamma R}{\rho_{\mathrm{o}}\eta z^6}\Big[G_{\mathrm{o}}\partial_{xx}z - (3G_{\mathrm{o}} - C)(\partial_x z)^2 + 2\partial_x z\partial_x G_{\mathrm{o}} - \frac{2}{3R^2} + \delta z\Big(C\partial_{xx}z + (3G_{\mathrm{o}} - C)(\partial_x z)^2 + 2\partial_x C\partial_x z + \partial_{xx}G_{\mathrm{o}} - \frac{8}{3R^2}\Big)\Big] \qquad (26)$$

for both cases of lattice and grain boundary diffusion.

A number of very interesting conclusions can be derived from this equation.

(a) Starting with $\partial_x z = 0$ we see that instabilities can only occur when $\partial_{xxx}G_{\mathrm{o}} \neq 0$ and $\delta z \neq 0$. As in Section 2, again, it follows that we should necessarily have some densification to onset an instability.

(b) Once an instability has started, the first terms without δz will rapidly grow. Taking $\mathrm{d}_t\xi = (-3/z)\mathrm{d}_t z$ we see that Equation 26 is of the shape of a time reversed diffusion equation. A fluctuation, once established, will grow into an instability quite easily.

Although the equation has a very complicated structure, unlike in the former case, we do not need to solve it explicitly to find a suitable stability criterion, since it contains more detailed information on the growth of the fluctuation itself. We assume that only non-catastrophic defects occur when $\mathrm{d}_t\xi - \mathrm{d}_t\delta z < 0$ and further that local variations in z, G_{o} and C are expected of the form

$$z = \Delta z \sin\frac{x}{\lambda}, \quad G_{\mathrm{o}} = \Delta G_{\mathrm{o}} \sin\frac{x}{\lambda} \text{ and } C = \Delta C \sin\frac{x}{\lambda}$$

Inserting these expressions into Equation 26, it is readily shown that the worst case occurs for $\sin x/\lambda = 0$ which leads to the criterion

$$\Delta G_{\mathrm{o}}\Delta z < \frac{1}{3}\frac{\lambda^2}{R^2} \qquad (27)$$

It should be stressed again that this surprisingly simple criterion is completely independent of the choice of any of the transport mechanisms considered so far. Further, it is seen in Equation 27 that the distance over which the fluctuation in z and G_0 varies is compared with the radius of the individual particles. A further consequence of the requirement for stability is that nowhere in the structure a z value should be found less than one, which imposes a limit on Δz being equal to δz. We then arrive at

$$\Delta G_0 \delta z < \frac{1}{3}\frac{\lambda^2}{R^2} \qquad (27a)$$

Taking a local variation of ΔG_0 equal to $\frac{1}{2}G_0$, which means that the primary coordination may be locally equal to half the average and $\delta z = 0.16$, as in Section 3, the densification necessary for achieving a structure where local instabilities are not developing, we find that $\lambda > 1.8\,R$, which is about the size of a single particle. Defining now homogeneous randomness, we should state that the value of G_0 and C should fluctuate over more than one cell in order to inhibit formation of defects on the scale of the particles. In other words, a structural unit containing more than eight particles should have an average G_0 which is equal to the global average of the stacking.

5. Discussion

A model is presented to give the following.

(a) An analytical expression for the overall shrinkage of a random stacking of particles assuming two different kinds of local transport mechanisms: lattice diffusion and grain boundary diffusion (Equations 9a and 9b).

(b) A mathematical treatment of a collective reorganization process of a particle stacking where local variations in the coordination (or density) are assumed, leading to a description of the evolution of a defect in a further homogeneously densifying structure.

(c) A determination of the condition for local randomness defined by the average coordination of a local, but as small as possible, number of particles which is representative for the global, although collectively varying coordination.

This model so far, has one limitation which merely defines the maximum value up to which it may be expected to present a description of the reality. The material to be transported away from the contact area is deposited in the neck zone or at the clear faces of the particles themselves. This process gives initially a slightly higher rate of change of the free surface energy with variations in the densification parameter, than calculated in the present case, but later on reduces this effect. For this reason, local destabilizing pressures are higher than assumed here at the beginning, but vanish when approaching full densification. It is estimated that when using a value of $\delta z < 15\%$, the model should give a suitable description of the reality.

Good examples that visualize the collective reorganization during sintering are found in the literature [4–6]. In the case of Petzow's and Exners [5] experiment, it is clearly visible that the collective rearrangement of the particle stacking starts right at the beginning and develops into large structural defects. From the presented microstructure in this latter result it may be found that zones occur where a value of $\Delta G_0 > \frac{1}{2}G_0$ and severe crack formation due to sintering takes place.

The microstructures in the results of Liniger and Raj [4] show a number of possibilities. First, a homogeneous random structure (M5) exhibits rapid and defect free sintering. A second structure (M3, 4) with spatially moderate, but significant, variations in ΔG_0 shows, as expected from Section 3, an initial decrease of the width of the defect, but later on a substantial increase of the defect size. Well organized packings give extremely high local values of $\partial_{xx} G_0$ with rather weak global variations (M1). In this particular case, the local model, presented in Section 4, tells us that we may expect a fine grained high density defect structure and a very low sintering rate as a result. Further, Equation 23 applies to the cases of M3, 4 as well, predicting extensive crack opening during the process.

A similar structure may be seen in the Figs 8 and 9 where, although a normal green structure looks globally homogeneous, high local variations in coordination are present. These local variations have extensions of up to some times the particle size and lead therefore to local and collective particle rearrangement with a pore structure of high coordination as shown in Fig. 9. Prolonged sintering will not give a

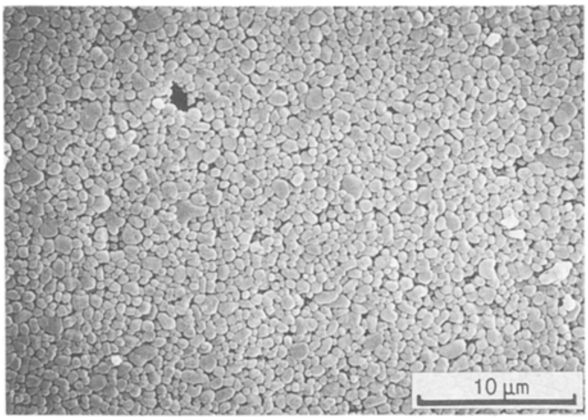

Figure 8 Loose stacking of α-Al_2O_3 particles before firing.

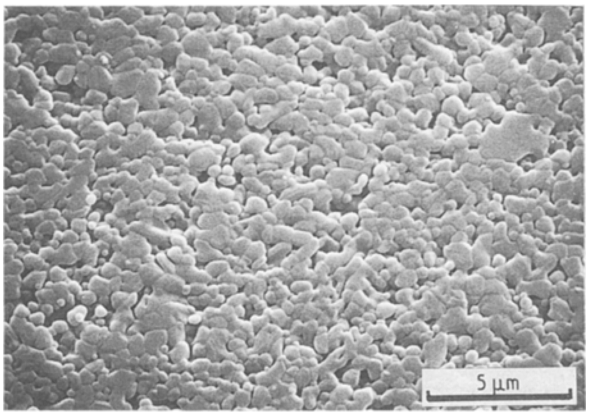

Figure 9 Reorganization and sintering of the stacking shown in Fig. 8 after 0.5 h at 1300 °C.

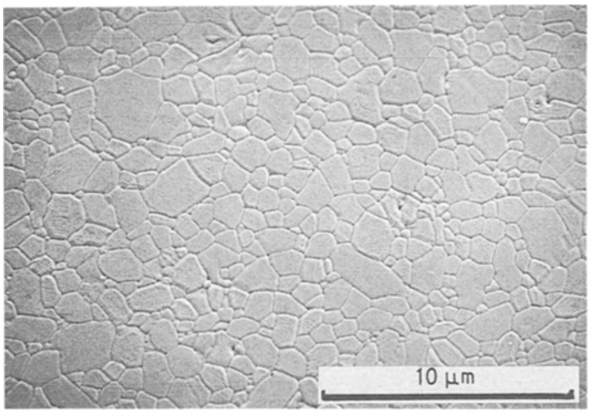

Figure 10 The same material shown in Fig. 8 and after 2 h at 1500 °C.

further reorganization but is mainly necessary to reduce the pore structure which is created by the reorganization effect. It may further be speculated that the grain structure finally obtained when sintering is completed, is not much different from the reorganized structure, where zones with enhanced density form the individual grains as shown in Fig. 10.

This idea might cast some new light upon the structural changes occurring during sintering. Grain growth is preceded by locally enhanced densification due to fluctuations in coordination. This grain growth goes hand-in-hand with pore growth also due to this reorganization. The conclusion should be then that grain growth occurs already in an early stage of sintering, but overall shrinkage is reduced due to formation of a new system of porosity.

As a concluding remark it should be emphasized that also the influence of an externally applied pressure p_{ex} is easily introduced into the criteria. We can simply set $\gamma(p_{ex}) = \gamma(p_{ex} = 0) + p_{ex}R/4$ in the parameter a_3 in Section 3 giving for Equation 21a

$$\frac{4 + pR/\gamma}{3} > \Delta G_o \delta z \exp(\tfrac{1}{2} G_0 \delta z)\left(1 + \frac{G_o \delta z}{4}\right)$$

and similarly in Section 4 for Equation 26a:

$$\Delta G_o \delta z < \frac{1}{3} \frac{\lambda^2}{R^2}\left(1 + \frac{pR}{4\gamma}\right)$$

It can be concluded from this, in accordance with the above given arguments, that an externally applied pressure will suppress defect formation due to both global and local reorganization and increases the sintering rate substantially.

Appendix 1. The transport equations

Consider the situation as shown in Fig. 2 where two spherical particles have a common neck zone and are jointly developing a grain boundary. Vacancies are formed directly under the outer surface of the neck zone area and absorbed at the boundary. This sink should be homogeneous. Standard theory tells us that the total volume displaced per unit of time over the complete circumferential area of neck given by $J\Omega$, is expressed as follows

$$J\Omega = 4\pi D_v \Delta C_v \mathrm{d}\Omega \qquad \text{(A1)}$$

where ΔC_v is the difference in vacancy concentration between the source and sink for the vacancies, d the width of the diffusion field and D_v the vacancy diffusion coefficient. If we have a neck zone with a curvature, σ, and a pressure p' acting on the grain boundary we find for ΔC_v

$$\Delta C_v = \frac{C_o \gamma \Omega}{kT\sigma} + \frac{C_o p' \Omega}{kT} \qquad \text{(A2)}$$

where C_o is the equilibrium vacancy concentration under a flat, pressureless surface. By geometrical arguments it is further easily shown that (Figs 2 and 4)

$$\sigma = \frac{r^2}{4R} \quad \text{and} \quad p' = p\frac{R}{4\sigma}$$

where p is the external pressure acting on the complete stacking of the particles. If we take $C_o \sim C_v$ and Onsager's relation: $D = \Omega C_v D_v$ which couples matter transport to the diffusion of vacancies, it is found that

$$\frac{J\Omega}{d} = \frac{4\pi D\Omega}{kT\sigma}\left(\gamma + \frac{pR}{4}\right) \qquad \text{(A3)}$$

For the case of lattice diffusion, we should take $D = D_l$ and $d = 2\alpha\sigma$ where α should be close to 2 and for grain boundary diffusion we set $D = D_b$ and $d = \omega$, an effective width of the diffusion zone where the actual transport takes place.

Further geometrical arguments tell us that

$$\frac{r^2}{2R^2} \sim -\frac{\Delta L}{2R} = \frac{z-1}{z} \sim \delta z \quad \text{and}$$

$$J\Omega = \frac{2\pi r^3}{R}\mathrm{d}_t r$$

leading to

$$\delta z = \left(\frac{4\alpha D_l \Omega \gamma t}{R^3 kT}\right)^{1/2} \qquad \text{(A4a)}$$

and

$$\delta z = \left(\frac{6 D_b \omega \gamma \Omega t}{R^4 kT}\right)^{1/3} \qquad \text{(A4b)}$$

for lattice and grain boundary diffusion respectively. Equations A4a and A4b are derived differently in Section 2.

Appendix 2. Local stress redistribution

We may write Equation A2 in the following way

$$\Delta C_v = \frac{C_o \Omega}{kT}(p_i + p_i')$$

where p_i is seen as the pressure in the *i*th grain boundary in one cell due to the curvature in *i*th the outer neck zone and p_i' is the pressure due to the force acting externally because of mismatch effects.

The total contact force F working over the cell is equal to

$$F = \sum_i \frac{\gamma}{\sigma_i}\pi r_i^2 + \sum_i p_i' \cdot \pi r_i^2$$

$$= \sum_i 4\pi\gamma R + \sum_i p_i' \cdot \pi r_i^2 = 4\pi R\gamma G(z)$$

where use is made of the result of the geometrical arguments and the requirement that the stress redistribution at equilibrium should lead to

$$\sum_i p_i' \pi r_i^2 = 0$$

The average contact pressure then is equal to

$$\bar{p}(z) = \frac{4\pi R \gamma G(z)}{O(z)}$$

$$= \frac{4\gamma z^2}{R} \frac{G_o + C(z-1)}{G_o(z^2-1) + C(\frac{2}{3}z^3 - z^2 + \frac{1}{3})} \quad \text{(A5)}$$

Adopting now this value for the average contact pressure for a cell where we take in (A3): $\gamma = \gamma_i = \bar{p}\sigma_i = \bar{p}r_i^2/4R$ with $p = 0$ for each individual contact area, we can take the two contributions for both lattice and grain boundary diffusion together and find for the volume transported per particle over the ith contact zone

$$\frac{\mathrm{d}V_i}{\mathrm{d}t} = \frac{\pi \bar{p} \Omega}{kT}\left[\alpha D_1 R\left(1 - \frac{\tau_i^2}{z^2}\right) + 2D_b\omega\right] \quad \text{(A6)}$$

Since we want to know the statistical mean for the densification we should integrate over all contact zones for $1 < \tau < z$, thus

$$\mathrm{d}_t \Delta V = \frac{\pi \bar{p} \Omega}{kT} \int_1^z \left[\alpha D_1 R\left(1 - \frac{\tau^2}{z^2}\right) + 2D_b\omega\right] \partial_\tau G(\tau)\,\mathrm{d}\tau \quad \text{(A7)}$$

If we introduce Equation 4 into (A7) and attribute the various contributions to $\mathrm{d}_t z$ to lattice and grain boundary diffusion we find

$$\mathrm{d}_t z = \frac{4D_1 \Omega \alpha \gamma [G_o + C(z-1)] z^4}{kTR^3 [G_o + \frac{1}{4}c(z^2-1)](z^2-1)}, \quad \text{(A8a)}$$

for lattice diffusion and

$$\mathrm{d}_t z = \frac{8D_b \omega \Omega \gamma [G_o + C(z-1)]^2 z^6}{kTR^4 [G_o + \frac{1}{4}C(z^2-1)](z^2-1)[G_o(z^2-1) + C(\frac{2}{3}z^3 - z^2 + \frac{1}{3})]} \quad \text{(A8b)}$$

for grain boundary diffusion.

Upon linearization we find the expressions given in Section 2, Equations 7a and 7b.

Appendix 3. Free energy consideration

In the present analysis we start from Equation 10 and write for the free energy density

$$U(r) = U_o + \frac{1}{z^2(r)}(C_1 - \tfrac{1}{3}C_2) - \tfrac{2}{3}C_2 z(r) \quad \text{(A9)}$$

with $C_1 = \gamma\pi R^2 G_o$, $C_2 = \gamma \pi R^2 C$ and U_o is a constant.

To know the complete energy balance, the analysis will have to be taken over three spatial dimensions expressed by $r = (x, y, z)$ and we define a global densifying field δz with a spatial variation $\varepsilon(r)$ by $z(r) = 1 + \delta z + \varepsilon(r)$.

The auxiliary condition will be that

$$\int_V \varepsilon(r)\,\mathrm{d}r = 0 \quad \text{(A10)}$$

The total free energy change due to densification and instabilities will be

$$\Delta U = \int_{\Delta U}\int_V \mathrm{d}\Delta U(r)\,\mathrm{d}r = -2C_1 \delta z V + (C_1 - \tfrac{1}{3}C_2)(1 - 4\delta z)\int_V \varepsilon^2(r)\,\mathrm{d}r \quad \text{(A11)}$$

where Condition A10 has been applied.

Taking Artz's values $G_o = 7.3$ and $C = 15.5$ we see that all coefficients can be taken positive so that for $\delta z = 0$ the occurrence of reorganization is energetically unfavourable. The energy necessary for rearrangement, however, will have to be delivered by the densifying field. This has been implicitly assumed in the models developed in Sections 3 and 4. On the basis of this consideration, it should be emphasized that a single particle during rearrangement will tend to stay midway between its neighbours: each particle stays in its own potential well. The free energy given in Equation A9 should, therefore, be attributed to the potential well as an entity (identified by the cell itself). An instability, as assumed by the function $\varepsilon(r)$, therefore is the collective rearrangement of the cell structure rather than the particles.

Appendix 4. Reorganization

Reorganization for the present model means that particles move collectively under an external force acting in one direction. The stacking is continuously changing in such a way that besides shear forces, also an isotropical pressure is generated which causes local isotropical densification. Under such circumstances the vectorial sum of the displacements of the particles is in the direction of the applied force.

If O is the surface area perpendicular to the force applied, Δl is some arbitrary distance in the direction of the force and N is the number of particles in the volume $\Delta V = O\Delta l$, we find that the relative change of the average centre-to-centre distance of the particles measured in the direction of the applied force becomes

$$\mathrm{d}_t \xi = \frac{1}{\Delta l}\mathrm{d}_t \Delta l$$

With the requirement of reorganization leading to isotropic pressure we then have

$$\begin{aligned} O\mathrm{d}_t \Delta l &= \Delta V \mathrm{d}_t \xi = \mathrm{d}_t \Delta V = \mathrm{d}_t N/\rho \\ &= -(N/\rho^2)\mathrm{d}_t \rho = -(\Delta V/\rho)\mathrm{d}_t \rho \\ &= -3\Delta V z^2(\rho_o/\rho)\mathrm{d}_t z = -(3\Delta V/z)\mathrm{d}_t z \end{aligned}$$

so that

$$\mathrm{d}_t \xi = -\frac{3}{z}\mathrm{d}_t z \quad \text{(A12)}$$

It should be stressed that also an additional increase in density (or coordination) may occur as an explicit consequence of the reorganization itself. This effect, however, depends strongly on the original particle density G_o and the ability of particles to slide across each other. At a high initial density (G_o more than half of the theoretical value for a fully dense structure), this contribution will not be very high.

At lower densities it should be considered that Equation A12 is approximate and underestimates the actual effect.

Appendix 5. Solutions for the $z_o(t)$ behaviour

Starting from Equation 15

$$d_t z_o = \frac{\gamma}{3Rz^2\rho_o\eta}(2G_o z_o - \Delta G_o \delta z)$$

we get by using Equations (7a) and (9a) or Equations (7b) and (9b) for small values of δz

$$d_t z_o = b_1 z_o / t^{1/2} - b_2 \qquad \text{(A13a)}$$

for lattice diffusion and for grain boundary diffusion

$$d_t z_o = c_1 z_o / t^{2/3} - c_2 / t^{1/3} \qquad \text{(A13b)}$$

Approximate solutions are found by standard procedures and read

$$z_o = -b_2 t \exp(2b_1 t^{1/2}) \qquad \text{(A14a)}$$

and

$$z_o = -\tfrac{3}{2}c_2 t^{2/3} \exp(3c_1 t^{1/3}) \qquad \text{(A14b)}$$

for lattice and grain boundary diffusion respectively.

Elementary manipulations then give

$$2b_1 t^{1/2} = 3c_1 t^{1/3} = \tfrac{1}{2}G_o \delta z$$

and

$$b_2 t = \frac{\gamma t \delta z}{3R\rho_o\eta}\Delta G_0 \quad \tfrac{3}{2}c_2 t^{2/3} = \frac{\gamma t \delta z}{2R\rho_0\eta}\Delta G_o$$

Applying the requirement for stability that $-\frac{3}{2}d_t z_o - d_t \delta z < 0$ we obtain by differentiating Equations A14a and A14b using also the expression for $d_t \delta z$ given in Section 3

$$\frac{4z}{3} > \Delta G_o \delta z \exp(\tfrac{1}{2}G_o \delta z)\left(1 + \frac{G_o \delta z}{4}\right) \qquad \text{(A15)}$$

where again it appears that the criteria are the same for both lattice and grain boundary diffusion.

A full loss of constraint at the location where $d_t z$ has its minimum means that the centre-to-centre distance of the particles at the opposite edges of the defect is the sum of the relative movements of all the particles from the defect.

The receding rate is given by

$$d_t \varepsilon = -\frac{1}{2R}\int_{z(\partial_z^- z = 0)}^{z(\partial_x^+ z = 0)} \frac{3}{z} d_t z_o \, dx \qquad \text{(A16)}$$

where x runs along a line of length λ from the defect to the location where the relative movement is equal to zero.

The relative defect growth rate then is calculated by use of Equations (A16), (A13a) and (-b), the expression for $d_t \delta z$ in Section 3 and the fact that the problem is symmetric in z. The result is given in Equation 23.

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