JOURNAL OF MATERIALS SCIENCE 28 (1993) 2757–2762

Statistical treatment of the sintering defect model and ceramic morphology development

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A model is formulated to account for structural and collective reorganization effects in a random packing of spherical particles which, during sintering, is undergoing global densification as a consequence of reduction of the total free surface energy. This model is found to describe, both qualitatively and quantitatively, the rearrangement of the stacking in such a way that areas with high local coordination tend to contract at a relatively high rate and zones with low coordination densify at a reduced rate or even decrease their density. Statistical effects arising from peculiarities in the particle packing can also be analysed with the help of the mathematical description given. It is found that the rearrangement may also give rise to structural defects and ultimately lead to poor mechanical properties.

1. Introduction

In an earlier publication [1], it was shown that local variations in coordination of individual particles of a stacking, constituting the green structure of a ceramic body, can lead to structural reorganization. This effect will severely influence the structure of the densifying material and ultimately give rise to unwanted defects. However, this model did not give a rigorous statistical treatment of the spectral distribution of the stacking density and the related pore-size distribution. Although it does show that, even in a random and globally homogeneous packing, defect formation will readily occur, it is not easily interpreted in terms of overall changes taking place in the complete structure.

This paper envisages reformulation of the model such that the analysis can be carried some steps further to lead to a number of interesting conclusions on the densification of a structure during the early phase of sintering where reorganization is seen to occur vigorously. First, a general equation describing the effect of local departures from the average particle to particle distance will be derived. This equation will constitute the basis for the description of the spectral development of the local stacking parameter. Secondly, it will be shown that even a close-packed random stacking of monosized spherical particles always exhibits minor deviations from the average stacking density and therefore leads to fluctuations in the final structure.

2. Deviations from the average densification due to variations in the particle coordination

In our earlier paper [1], it was shown that a stacking of spherical particles having local variations in their individual coordination will exert a pressure on its immediate surroundings. This pressure is determined by both the total average densification of the structure and the difference between the local and average coordination. If we assume that somewhere in the stacking of particles there exists a gradient in the local coordination, we must conclude that a force is acting on the particle under consideration into the direction of the area with highest coordination. This force, F, is a direct consequence of a gradient in the free surface energy due to the sintering of the particles and is given by the following expression

$$F = \pi\gamma R^2 \frac{\partial G}{\partial z}\left[1 - \frac{1}{(2z-1)^2}\right]\frac{\partial z}{\partial x} \qquad (1)$$

where G is the coordination, γ the surface tension and R the particle radius. The parameter z expresses the local density of the stacking with $z = z(x, t)$ such that

$$z = (\rho/\rho_0)^{1/3} = R/r \qquad (2)$$

where $2r$ is the centre-to-centre distance of adjacent particles, ρ the local and ρ_0 the starting density of the packing.

Fig. 1 shows schematically two mutually approaching spherical particles along with the different parameters introduced.

Equation 1 deviates slightly from that given before [1], in that the effect due to the increased coordination by densification is neglected. Also the contribution of the neck zone being formed, when two particles decrease their centre-to-centre distance, is taken into account, which has led to the fact that in Equation 1 the factor $2z - 1$ appears instead of z. The force, F, generates a pressure which stimulates densification in zones with a relatively high stacking density and causes dilution at places where the stacking density is lower than average. Fig. 2 depicts our visualization of

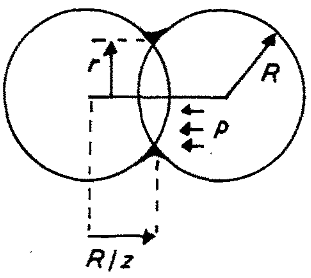

Figure 1 Two spherical particles coalescing due to internal mass transport.

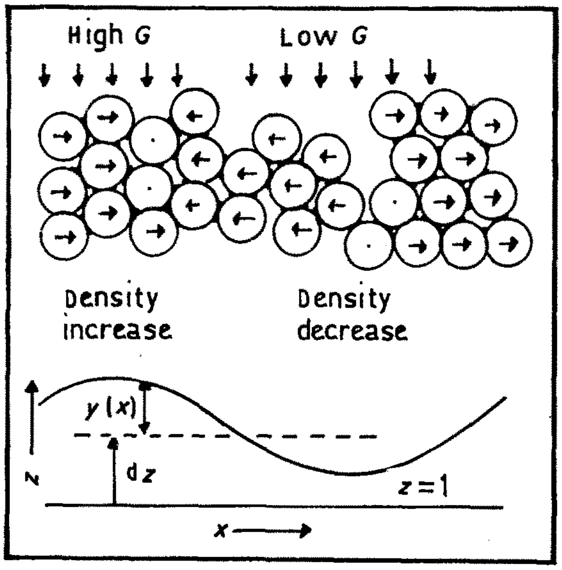

Figure 2 A particle stacking with a gradient in the local coordination, resulting in a variation of the stacking parameter, z.

a stacking and its tendency to rearrange according to the model proposed.

We may define two pressures, p^+ and p^-, by

$$\pi R^2 p^- = \frac{1}{2R}\int_{z\,(\partial_x^+ z = 0)}^{z} F\mathrm{d}x \qquad (3a)$$

and

$$\pi R^2 p^+ = \frac{1}{2R}\int_{z\,(\partial_x^- z = 0)}^{z} F\mathrm{d}x \qquad (3b)$$

which are the pressures in the stacking accumulating by adding up the forces from the location with lowest density, $z(\partial_x^- z = 0)$, to the actual $z(x)$ and by adding from the place with highest density, $z(\partial_x^+ z = 0)$. The prevailing pressure in the system, p, is the sum of $p^+/2$ and $p^-/2$. If we substitute Equation 1 into Equations 3a and b, we obtain for the stacking pressure

$$p = \frac{2\gamma}{R}\bar{G}(z - \bar{z}) + \frac{2\gamma}{R}\delta z(G - \bar{G}) \qquad (4)$$

where average values for the densification $\bar{z} = z(\partial_x^+ z = 0)/2 + z(\partial_x^- z = 0)/2$ and the coordination $\bar{G} = G(\partial_x^+ z = 0)/2 + G(\partial_x^- z = 0)/2$ are introduced to account for the fact that the stacking as a whole will densify at a rate to be superimposed on the local densification or dilution of the structure due to reorganization. Further, δz is the average densification of the structure and may be set equal to $\bar{z} - 1$. Following the analysis used previously [1], we can correlate the pressure, p, with a densification rate $\mathrm{d}z/\mathrm{d}t$ and find

$$\frac{\mathrm{d}z}{\mathrm{d}t} = \frac{2\gamma}{3R\rho_0 z^2\eta}[\bar{G}(z - \bar{z}) + \delta z(G - \bar{G})] \qquad (5)$$

The parameter η in this equation should be considered as an apparent plasticity and is basically determined by the choice of the mechanism of material transport during sintering of the structure [1]. This equation gives a description of a locally varying change of the parameter z as a consequence of variations in the local stacking density and coordination only. As indicated before, the effect of an overall and homogeneous density increase of the structure as a whole, should be included in this expression for $\mathrm{d}z/\mathrm{d}t$. This quantity has been calculated [1], although the explicit form is not of much importance for the present analysis.

If we sum up the total effect of changes in the density due to rearrangement and homogeneous densification, we get

$$\frac{\mathrm{d}(z - \bar{z})}{\mathrm{d}t} = \frac{2\gamma}{3R\rho_0 z^2\eta}[\bar{G}(z - \bar{z}) + \delta z(G - \bar{G})] \qquad (6)$$

which is the general equation describing the variation with time of the departures from the average of the local stacking density depending on the actual local stacking density, the overall densification in the structure, δz, and the variation in the coordination compared with the average.

This expression has an obvious interpretation: suppose we have a stacking where some densification has already taken place and there is a group of particles which have lower coordination than the average: $\delta z > 0$ and $G - \bar{G} < 0$, then Equation 6 leads to the result that $\mathrm{d}(z - \bar{z})/\mathrm{d}t < 0$ and consequently that $z - \bar{z} < 0$, which further enhances the decrease of the densification rate. The opposite is true for $G - \bar{G} > 0$. The important conclusion of this should be that in a stacking where normally, for statistical reasons, variations in the coordination should exist, a reorganization will be taking place in such a way that in areas with lower than average stacking densities the densification due to sintering will slow down, whereas it will be accelerated in places with high coordination or local density. Equation 6 will be the most important ingredient to arrive at a suitable description for the statistical development of the reorganization of a sintering random stacking of spherical particles.

3. Statistical treatment of the reorganization effect

To proceed further we introduce the following quantities: $a_1(t) = 2\gamma\bar{G}/(3R\rho_0 z^2\eta)$; $a_2(t) = 2\gamma\delta z/(3R\rho_0 z^2\eta)$; $y = z - \bar{z}$ and $\Delta G = G - \bar{G}$, so that Equation 6 transforms into the much simpler expression

$$\frac{\mathrm{d}y}{\mathrm{d}t} = a_1(t)y + a_2(t)\Delta G \qquad (7)$$

It should be noticed in this context, that the parameters $a_1(t)$ and $a_2(t)$ have an explicit dependence on time because in the model proposed, the quantity η starts from zero at $z = 1$ and follows a specific dependence on time determined by the transport mechanism chosen [1]. Now, a space is defined which represents the number of particles, $\phi(h, \xi)\,d\xi$ lying at a specific moment between ξ and $\xi + d\xi$ where ξ is directly connected to the individual value of the densification given by $z(t)$, and h is a measure of the time during which sintering has taken place. The relation between the number density function, ϕ, and ξ and h is given by the continuity equation

$$\frac{\partial\phi}{\partial h} + \frac{\partial}{\partial\xi}\left(\phi\frac{d\xi}{dh}\right) = 0 \qquad (8)$$

where we will propose a solution for ϕ such that the explicit and implicit dependence of ϕ are separated by $u(h)$ and ξ

$$\phi = u(h)\cdot f[u(h)\cdot\xi] \qquad (9)$$

Further we will assume, for the time being, that the relation between ξ and h may be given by

$$\frac{d\xi}{dh} = \alpha(h)\xi \qquad (10)$$

which will later be shown to be a transformation of Equation 7 to the $\phi(h, \xi)$-space. Now it is most important to find out which form the explicit relation between u and h should have such that Equation 9 is a solution of the continuity equation.

After substitution of Equation 9 into the continuity Equation 8, the following identity is obtained

$$\left[f(u\cdot\xi) + u\cdot\xi\frac{\partial f(u\cdot\xi)}{\partial u\cdot\xi}\right]\left[\frac{du}{dh} + \alpha(h)u\right] = 0 \qquad (11)$$

The trivial solution occurs when the first part vanishes, and represents a spectrum in z or ξ which does not vary in time or h. It is of no use for the present analysis. The second condition is given by the equation

$$\frac{du}{dh} + \alpha(h)u = 0 \qquad (12)$$

The interpretation of the result, obtained so far, is that an assumption on the time behaviour of ξ leads via the form proposed for the solution of ϕ to a specific condition on u, which is most easily solved when α is a constant. In this latter case the solution of Equation 8 will be of the form

$$\phi = \phi_0 e^{-\alpha h}\cdot f(e^{-\alpha h}\cdot\xi) \qquad (13)$$

The problem now is to start from Equation 7 and to transform it into an equation of the type given in Equation 10 such that α is a constant. Further, the functon $\phi(h = 0)$ will have to be adjusted to the starting distribution determined by the initial coordination distribution of the particles in the stacking.

For this purpose we start with the case of bulk diffusion as the mechanism responsible for the material transport and we need the explicit time dependence of $a_1(t)$ and $a_2(t)$ as given by the equations derived in [1]

$$\frac{dy}{dt} = b_1 y t^{-1/2} + b_2 \qquad (14)$$

If we now put $h = t^{1/2}$ and $\xi = y + [(b_2/b_1)h] + (b_2/2b_1^2)$, we find $d\xi/dh = 2b_1\xi$ with $y = 0$ for $h = 0$, so that it can easily be shown that the correct transformation to solve the continuity equation is found with $\alpha = 2b_1$. Further the fact that $\xi = b_2/2b_1^2$ or $h = 0$ gives a possibility to adjust the distribution to the starting condition, where it may be shown that

$$\frac{b_2}{2b_1^2} = \frac{4\Delta G}{G^2} \qquad (15)$$

In the second case to be considered, grain boundary diffusion, we adopt a similar procedure. In this particular case the basic equation reads

$$\frac{dy}{dt} = c_1 y t^{-2/3} + c_2 t^{-1/3} \qquad (16)$$

and we make the following substitution to transform this equation into the correct type, with $h = t^{1/3}$ and $\xi = y + [(c_2/c_1)h] + (c_2/3c_1^2)$, so that $\alpha = 3c_1$. With the same procedure as before it is found that the starting condition on ξ for $h = 0$ becomes identical to the case of bulk diffusion

$$\frac{c_2}{3c_1^2} = \frac{4\Delta G}{G^2} \qquad (17)$$

If we now start with the distribution function, proposed above, which has been shown to be a solution of the continuity equation when the correct expressions for the quantities ξ and h are introduced, we may take the particular case of $h = t = 0$ and find

$$\phi = \phi_0 f(\xi) \qquad (18)$$

which should necessarily represent the distribution of particles identified by the parameter $b_2/2b_1^2$ or $c_2/3c_1^2$, both being equal to $4\Delta G/G^2$.

We know that a random packing of particles can be characterized by a Gaussian distribution on the basis of their individual coordination [1–4] so that the correct form of the present distribution function $\phi(\xi, h)$ should be

$$\phi(\xi, h) = \frac{e^{-2b_1 h}}{\sigma(2\pi)^{1/2}}\exp\left[\frac{-\xi^2 e^{-4b_1 h}}{2\sigma^2}\right] \qquad (19a)$$

for bulk diffusion as the basic transport mechanism and

$$\phi(\xi, h) = \frac{e^{-3c_1 h}}{\sigma(2\pi)^{1/2}}\exp\left[\frac{-\xi^2 e^{-6c_1 h}}{2\sigma^2}\right] \qquad (19b)$$

for grain-boundary diffusion. The quantity σ gives the scatter of the distribution.

To arrive at the final representation for the distribution as a function of the local densification parameter, y, one more thing still has to be done: we should find a relation between ξ and h for both transport mechanisms under consideration. For this purpose the exact solution for ξ as a function of h is needed, which is given by the transformed equation describing the time dependence of the densification parameter, y, and the explicit connection between ξ and h. The basic equations are

$$\frac{d\xi}{dh} = 2b_1\xi \tag{20a}$$

$$\xi = y + \frac{b_2}{b_1}h + \frac{b_2}{2b_1^2} \tag{20b}$$

for bulk diffusion, and for grain-boundary diffusion

$$\frac{d\xi}{dh} = 3c_1\xi \tag{21a}$$

$$\xi = y + \frac{c_2}{c_1}h + \frac{c_2}{3c_1^2} \tag{21b}$$

From these we may eliminate the factor b_2/b_1 or c_2/c_1, respectively, and develop this result into a Taylor series, followed by substitution into Equations 19a and b. The result is

$$\phi(y, h) = \frac{2e^{-2b_1h}}{(2b_1h)^2\sigma(2\pi)^{1/2}}\exp\left[\frac{-2y^2e^{-4b_1h}}{(2b_1h)^4\sigma^2}\right] \tag{22a}$$

and

$$\phi(y, h) = \frac{2e^{-3c_1h}}{(3c_1h)^2\sigma(2\pi)^{1/2}}\exp\left[\frac{-2y^2e^{-6c_1h}}{(3c_1h)^4\sigma^2}\right] \tag{22b}$$

This distribution has a very interesting interpretation. First, we see that it is normalized to unity, which is a consequence of the fact that we have already started with a normalized distribution for the factor $b_2/2b_1^2$ or $c_2/3c_1^2$ which were related to the local coordination of the particles in the stacking. Second, we notice that when h approaches 0, which is the very beginning of the densification of the structure, the distribution becomes infinite at $y = 0$ and vanishes for $y \neq 0$, but it remains normalized to unity. What we are actually saying is that the distribution is of the shape of a Dirac δ-function in the limit of $h = 0$. The physical interpretation obviously is that right at the beginning of sintering, all particles have the same densification. Consequently, the local and individual value of z is equal to the average value $\bar{z}$ which is equal to one. The distribution should show that all the particles have the same y being equal to zero. As the sintering proceeds, particles with different coordination will show different development of y as a function of time or h, in such a way that particles with a coordination higher than average shift to higher values of y and those with lower coordination than average will see their y reducing. The overall effect will be that the distribution is very rapidly broadening.

We can carry the present analysis one step further by calculating a more tractable expression for parameters b_1h and c_1h on the basis of the results given previously [1]: $2b_1h = \frac{1}{2}G\delta z$ and $3c_1h = \frac{1}{2}G\delta z$. Inserting this into the distribution ϕ (y, h) we obtain a surprisingly simple result which relates the distribution to more easily accessible parameters for both cases of bulk and grain-boundary diffusion

$$\phi(y, \delta z) = \frac{8e^{-1/2G\delta z}}{G^2\delta z^2\sigma(2\pi)^{1/2}}\exp\left[\frac{-32y^2e^{-G\delta z}}{\sigma^2G^4\delta z^4}\right] \tag{23}$$

One more thing still has to be done in this respect: to define the quantity σ more explicitly. In two subsequent papers, Belik [3, 4] gives an analysis of the relationship between the coordination number and the packing density in a random stacking and derives a number of distributions of contacts among equal sized spheres at various average coordinations. Cumberland and Crawford [2] give experimental evidence on the particle packing of a model system of gunshot and finds an average coordination which resembles the value of $G = 7.3$ in Belik's analysis, a number which is also adopted by Arzt [5]. From this result it may be concluded that ΔG at a height of $1/e^{1/2}$ amounts to $G/3$, so that, for the present analysis, we can set σ equal to $4/(3G)$. If we further abandon the coordinate y and put $z - \bar{z}$ instead, we will obtain the final result

$$\phi(z, \delta z) = \frac{6e^{-1/2G\delta z}}{G\delta z^2(2\pi)^{1/2}}\exp\left[\frac{-18(z-\bar{z})^2e^{-G\delta z}}{G^2\delta z^4}\right] \tag{24}$$

This result can even be simplified further by normalizing the distribution to its peak value at $z = \bar{z}$

$$\frac{\phi(z, \delta z)}{\phi(\bar{z}, \delta z)} = \exp\left[\frac{-18(z-\bar{z})^2e^{-G\delta z}}{G^2\delta z^4}\right] \tag{25}$$

4. Discussion

In the preceeding section the spectral developmet of the particle stacking was derived on the basis of a specific time dependence of the parameter z which is a measure of the centre-to-centre distance of adjacent particles. This spectral development is found to be expressed as a simple equation, especially when it is normalized to the peak value of the distribution at $z = \bar{z}$. It is also seen that in both cases considered, bulk and grain-boundary diffusion, the same result emerges, which makes the interpretation of the model independent of the choice of any of these as the dominant diffusion mechanism. In fact, because the structure is characterized by a densification parameter, z, and the actual coordination, G, it is easy, knowing the stacking density distribution, to characterize a number of structural changes occurring during sintering.

The only point is to notice that, as far as the statistical aspect is concerned, a Gaussian distribution in the primary coordination was taken as the starting point. The consequence of this is that a specific packing structure is described, belonging to a globally homogeneous structure. Any other distribution function could have been taken as the starting distribution for Equation 13, because this is only a general solution of the continuity equation.

Fig. 3 shows a schematic drawing of the spectral development together with the relevant features to be dealt with in this discussion.

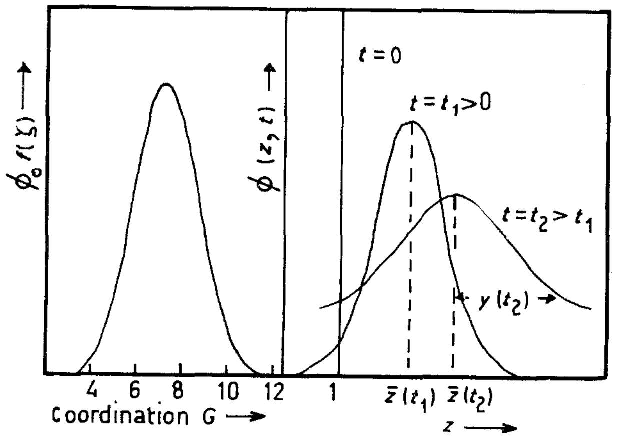

Figure 3 The initial coordination of a random stacking of particles and the spectral development of the rearrangement effect.

If we limit, for the moment, the discussion to globally homogeneous structures which do have reorganization, we should determine the particular values of z in relation to $\bar{z}$ and δz to quantify the frequency of significant structural peculiarities during and due to reorganization. In this respect, two visualizations are possible. One is that in both cases of densification and dilution of the structure, the positions of the adjacent particles relative to one another remain the same. This assumption is believed to apply to dense and/or rigid stackings, where the freedom for any sort of relative movement is highly restricted.

Such a situation will lead to non-densifying situations in areas where $\delta z < \bar{z} - z$. If we substitute this condition into Equation 25 with $G = 7.3$ and $\delta z = 0.1$, it is readily concluded that defects may be expected only in a very limited number of cases.

The second possibility is that the particles will not necessarily maintain their relative positions as can be expected in relatively loose packings. In such a case, certain assumptions will have to be made concerning additional reorganization effects. Because in the present analysis the total densification is assumed to be the sum of the homogeneous effect and the reorganization effect, we should also consider the contribution of any other redistribution separately.

If it is assumed, further, that the distance over which redistribution forces in the structure are piling up is greater than the particle dimensions, we may calculate the projection of the centre-to-centre distance of adjacent particles into the direction of the stacking density gradient, while keeping the lateral projections unaltered. This has been worked out previously [1] and the result reads that local dilutions occur if $(\delta z/3) < \bar{z} - z$. Inserting this into Equation 25, again with $G = 7.3$ and $\delta z = 0.1$, it is concluded that a relatively large number of particles will be connected to places where voids in the structural development occur. In such instances, a drastic reduction of local coordination may additionally induce growth of structural defects.

A second reorganization effect involving sliding of particles and resulting into higher densities can also be assumed, in which case the factor 1/3 will be substantially lower and, consequently, an even greater number of particles will be connected to rapidly growing voids in the structure. A number of typical features, often seen in densifying structures, is explained by the present model. An example of it is shown in Fig. 4, but numerous papers published in the open literature show basically the same tendency [6–9]. It may be tentatively concluded that the redistribution effect of the particles as described above is, in fact, even more serious than the analysis shows. In this respect it may be questioned whether a bimodal powder compact as starting material will inhibit this latter restacking effect. On the one hand, a large difference in particle size in a compact with the correct morphology can greatly oppose restacking but, on the other hand, homogeneous mixtures are very hard to obtain. Bimodality on the basis of particle sizes different by a factor of 2–4 is often seen to give homogeneous morphology and may suppress extensive restacking.

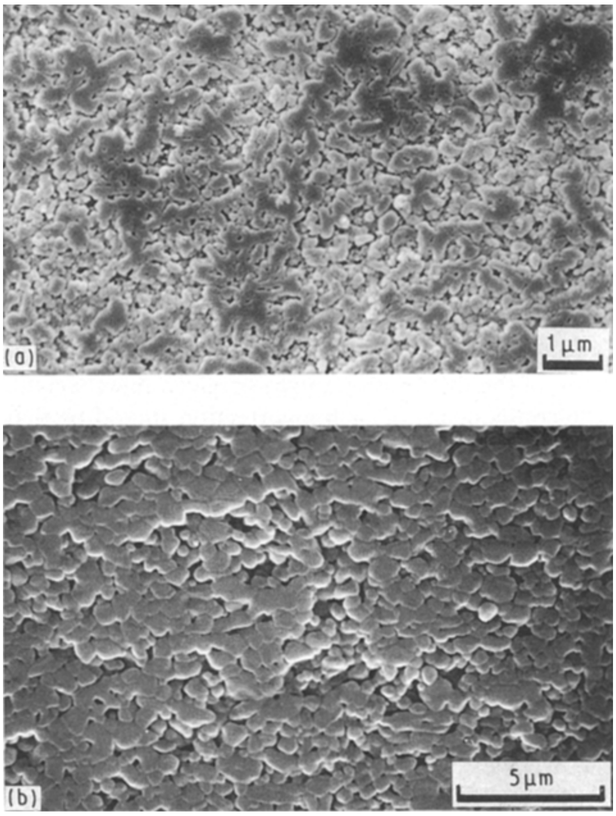

Figure 4 Microstructures of Al_2O_3 (a) at moderate densification and (b) after about 1 h at 1500 °C.

In spite of this conclusion, a shortcoming of the present analysis should be mentioned. It is assumed that Equation 6 remains valid also for areas where, due to reorganization, an enhanced densification is taking place. This should not necessarily be the case, which may be most easily understood by considering the case that the density is approaching its final value, when only structural changes occur but no real development of the particle stacking is allowed. We can easily determine the consequence of the above-mentioned assumption when we calculate the average density of the structure starting from the definition of z in terms of stacking density and integrate over the stacking density function given in Equation 23. It is found in this case that, in first-order approximation, the density is given by $\rho = \rho_0(\bar{z})^3$, which shows that reorganization in the present description does not necessarily lead to deviations in the density change rate from the expected behaviour in the case of a homogeneous packing.

However, it should be assumed that the increase in the parameter z will slow down when more than a few per cent of density increase is achieved, whereas a decrease in areas with lower local stacking density is most likely to accelerate. For this reason integration over the complete z-spectrum should be restricted to z-values lower than a certain maximum, while the left flank of the distribution might be given more weight. The consequence of such a correction should be that due to the reorganizaton the density increase of the structure will significantly lag behind the increase expected for a homogeneous structure. It would be easy to assume an upper limit for the integration, mentioned, and to propose a weighting function, but doing so would introduce some arbitrariness in the result and does not lead to more specific insight into the matter. What is important, however, is that reorganization is leading to a reduced overall densification compared to the case where no statistical variation in the particle coordination is assumed.

At various places in the open literature this point has been raised, but was left unexplained [6–10].

The next point to consider is the case where no globally homogeneous packing exists. This occurs when the processing of a green structure is such that large agglomerates and voids remain. In this respect, an agglomerate should be seen as an area with high coordination and density, whereas a void is an area of reduced coordination. The consequence is that, for the present model, the starting distribution, Equation 13 at $h = 0$ will have an extended tail at both the high and low coordination. It might be represented as the sum of two Gaussian distributions with different values of σ, one to describe the normal globally homogeneous packing and one to describe departures from homogeneity. Integration to find the overall density should, for the above mentioned reasons, be restricted to a maximum for z. The result shows that reorganizaton is responsible for a pronounced reduction in the densifcation rate during sintering.

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Received 2 January
and accepted 2 September 1992