Grain growth in sintering of clustered powder compacts

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A theoretical model of grain growth in sintering of clustered powder compacts is outlined, showing that the microstructure evolution is stepwise continuous in time and its general trends can be predicted independently of the particular system and process being considered. The dependence of coarsening on densification can be accounted for by introducing a densification-scaled time variable (intrinsic time). The theory is successively applied to systems where particular local mechanisms of matter transport are supposed to operate, respectively in the initial/intermediate and the intermediate/final stage of sintering. The obtained mathematical models are solved numerically to follow the evolution of three regularly packed clusters. The model predictions are in good agreement with experimental data obtained by other researchers. © *2000 Kluwer Academic Publishers*

1. Introduction

Grain growth in porous and non-porous compacts has been largely investigated under many aspects [1, 2]. The traditional approach to a quantitative description of the coarsening phenomenon consists in phenomenological laws accounting for the evolution of the average grain size. Usually this parameter is considered to increase continuously in time according to a law of the type

$$r^n - r_o^n = k(t - t_o) \qquad (1)$$

where r, r_o is the average grain size, respectively at the beginning of the process (i.e. at $t = t_o$, where t_o is an induction time) and at time t, k is a rate parameter, n is an exponent which, depending on various kinetic aspects involved in the process, can assume integer values in the range 1 to 4 [3].

The above law has been adapted to describe grain growth phenomena of several systems with sufficient accuracy. In the sintering of porous compacts of crystalline powders grain growth may accompany densification and the two phenomena are expected to be interrelated [4]. In certain compacts, where the particle size has initially a bimodal or multimodal distribution, coarsening may alter the size distribution, so that, to follow the evolution of microstructure, more information is required than the sole time law for the average grain size [5, 6]. In the case of clustered powder systems quite often the evolution of average grain size does not reflect the evolution of microstructure. In fact, the coarsening

law obeyed by the aggregates may be different from that for a single cluster. Lange [7] has pointed out peculiar phenomena that can be observed when densification and grain growth inside a single cluster is followed. To understand and to model the basic phenomena which may occur in sintering of clustered systems is very important *per se*, but can also contribute to a more complete knowledge of the behaviour of systems which are usually described by phenomenological laws. In fact, size heterogeneities associated with bimodal or multimodal distributions or other phenomena which may occur during sintering (e.g. neck rupture [8] and particle re-arrangement in porous compacts [9], tend *de facto* to cluster the system, and then its average behaviour can be deeply influenced by local evolution in single clusters.

It is known that grain growth, like densification, is the result of different local mechanisms of matter diffusion, depending on the considered material, the stage of sintering and the sintering temperature [10, 11]. Any formulation of a coarsening law which is not merely phenomenological, must therefore take into account one or more of such mechanisms. Nevertheless, it is possible that all of these mechanisms of grain growth have physico-mathematical features in common, which may lead to a similar way of operating. It is the aim of the present paper to show that this is the case. A second aim is to point out which aspects and parameters are expected to depend on the particular system under study and which are in common to all or many different systems.

In the first part of the paper a theory of grain growth for an arbitrary confined system of sintering particles is derived from rather general hypotheses, showing that the evolution of such a system is discontinuous, through a number of time intervals corresponding each to annihilation of an individual particle or a sort of particles. Number of particles, mean and standard deviation of the grain size population are discontinuous functions of time and undergo jumps at the end of each interval. Also, individual particles which have been growing in a step, depending on the number and the type of the connected particles, may begin to become smaller and some of them, eventually, may disappear in a successive step. The dependence of coarsening on densification is accounted for, in that the cross-sectional area through which matter is exchanged between contacting particles is a function of system densification. The complication due to a joint action of the two phenomena can be conveniently removed by introducing a densification-scaled time variable (*intrinsic time*), proper of a given system of which densification curves are known. The theory is successively applied to different grain growth mechanisms, expected to drive matter diffusion both in the initial/intermediate and the intermediate/final stage of densification, so arriving at definite mathematical formulations applicable to special problems. Exemplar solutions of such equations have been obtained numerically for three models of clusters (one bi-dimensional and the others 3-dimensional) where the particles are regularly packed and the size heterogeneity is confined initially to one or two sorts of particles. The study of the numerical results, which are in accord with the general predictions, permits to conclude about the stepwise evolution of relatively small clusters and to calculate approximately the duration of the steps in intrinsic time.

2. Theory

Consider, in general, a network of N particles, all of approximately the same shape, so that the volume and other geometrical quantities of an individual grain can be determined by one parameter (called henceforth equivalent particle *radius*) with shape factors assumed to be the same for the whole system and not significantly changing in the course of the process. Let the network be formed by n_1 particles of radius r_1, n_2 particles of radius r_2, ..., n_i particles of radius r_i, etc. (with $i = 1, 2, \ldots, m$) at a given time, and let each particle of radius r_i be connected by grain boundaries with n_k^i particles of radius r_k ($k = 1, 2, \ldots, m$, with the possibility for some of the coordination numbers n_k^i of being zero). The total volume change for the n_i particles in the unit time will be

$$\frac{dV_i}{dt} = -\sum_k n_k^i \frac{dV_{i \to k}}{dt} \qquad (2)$$

where $dV_{i \to k}/dt$ is the rate of volume (conventionally positive when emitted) which particle (i) exchanges with particle (k). This volume change can be due to several mechanisms of matter transport: surface diffusion, vapour transport, and lattice / grain boundary diffusion [12].

The rate of exchanged volume is related to the flux of atoms moving from particle (i) to particle (k) across an exchange cross-section. Under the hypothesis of independence of the different fluxes each $dV_{i \to k}/dt$ can be calculated as though the two particles were isolated.

Integrating the usual flux equation [13] over the exchange area A_{ik}, the rate of volume change can be written in the form

$$\frac{dV_{i \to k}}{dt} = k(T)\Gamma \varphi^-(r_i, r_k, \alpha) A_{ik} \qquad (3)$$

where $k(T)$ is a kinetic factor accounting for diffusivities and other lattice properties, Γ is the local driving force of diffusion, normally with the dimension of a surface energy, and $\varphi^-(r_i, r_k, \alpha)$ is a function of geometry of the particles, including a shape factor α. The product $\Gamma \varphi^-(r_i, r_k, \alpha)$ is proportional to the gradient of chemical potential between the regions where the exchange of matter occurs. For this reason $\varphi^-(r_i, r_k, \alpha) > 0$ whenever $r_i < r_k$, so that, according to Equation 3, at a joint between any two particles the larger particle tends to receive matter from the smaller one.

If the particles are identical $dV_{i \to k}/dt = 0$; in any case $dV_{i \to k}/dt = -dV_{k \to i}/dt$. Thus the geometrical function must obey the following conditions:

(i) $\varphi^-(r_i, r_i, \alpha) = \varphi^-(r_k, r_k, \alpha) = 0$

(ii) $\varphi^-(r_i, r_k, \alpha) = -\varphi^-(r_k, r_i, \alpha)$.

Accordingly $\varphi^-(r_i, r_k, \alpha)$ is an odd function with respect to commutation of the variables r_i, r_k.

The area of the exchange cross-section is not a constant throughout the process, but normally changes with densification of the whole system. Densification can be expressed by linear shrinkage ε_d, which is a function of time and will be regarded as a global variable of the system. Then, in the absence of important sintering inhomogeneities, the exchange area can be expressed in the form of a product

$$A_{ik} = \varphi^+(r_i, r_k, \alpha) g(\varepsilon_d) \qquad (4)$$

where $g(\varepsilon_d)$ is a global process function and $\varphi^+(r_i, r_k, \alpha)$ is a local function depending on the particle geometry. Since A_{ik} is, obviously, independent of the commutation of radii, $\varphi^+(r_i, r_k, \alpha)$ is an even function. Substituting Equation 4 in Equation 3 and successively Equation 3 in Equation 2, while taking into account that $dV_i = -4\pi \alpha r_i^2 dr_i$ a set of m differential equations for the m time functions $r_i(t)$ will be obtained, with the general form

$$\frac{dr_i}{dt} = -\frac{\Gamma}{4\pi r_i^2} k(T) g(\varepsilon_d) \sum_k n_k^i \psi(r_i, r_k, \alpha)$$

$$(i = 1, 2, \ldots, m) \quad (5)$$

where $\psi(r_i, r_k, \alpha) = \alpha^{-1}\varphi^-(r_i, r_k, \alpha)\varphi^+(r_i, r_k, \alpha)$ is a new function with the same parity of $\varphi^-(r_i, r_k, \alpha)$. All functions and parameters in Equation 5 have a definite sign, say positive, except ψ, the sign of which depends

on the permutation of the radii but remains definite for a fixed permutation.

The complexity of the system makes it impossible to predict whether an individual particle will grow or become smaller in the course of the process, because in Equation 5 the summation on the right may include both positive and negative contributions, depending on the actual size of the neighbouring grains and their evolution. It is also possible that a particle, which grows at a given stage of the process, becomes smaller in a successive step.

The total number N of particles during the system evolution is not a constant. In fact the particle which, at a given time instant, is the smallest of all, tends to become smaller and smaller and eventually to disappear, being incorporated in the neighbouring ones. At the instant $t^{(i)}$ when the i-th sort of particles disappears, N will decrease by n_i units. Successively the second smallest particle or sort of particles will disappear, and so on until there is only one sort of equal particles left and the process of coarsening comes to an end. This is an ideal situation, because inhibiting agents intervene in the coarsening of real systems [14]. At any rate, the evolution of the system is characterised by a set of m intervals separated by time instants $t^{(i)}$, through which the number of particles is progressively reduced. The $t^{(i)}$ values form as a bounded set of eigenalues which is proper of a given system. In each of these intervals some predictions can be made concerning the behaviour of the system momenta, which are defined as

$$M_p = N^{-1}\Sigma_i n_i r_i^p \qquad (6)$$

where p is a positive integer. Note that $M_1 = r$ is the mean radius, $4\pi\alpha N M_3/3$ is the total volume of the system (a quantity which is conserved through the whole process), and M_2 is related to the standard deviation Δ by

$$\Delta^2 = N^{-1}\Sigma_i n_i (r_i - r)^2 = M_2 - r^2 \qquad (7)$$

Differentiating Equation 6 with respect to time and introducing Equation 5, one obtains

$$\frac{\mathrm{d}M_p}{\mathrm{d}t} = -\frac{\Gamma}{4\pi} p N^{-1} k(T)$$
$$\times \sum_i \sum_k n_i n_k^i r_i^{p-3} \psi(r_i, r_k, \alpha) \qquad (8)$$

Taking into account the topological identity (valid for all i, k)

$$n_i n_k^i = n_k n_i^k \qquad (9)$$

which is self-evident, it is possible to re-write Equation 8 as follows:

$$\frac{\mathrm{d}M_p}{\mathrm{d}t} = -\frac{\Gamma}{84\pi} p N^{-1} k(T)$$
$$\times \sum_i \sum_k n_i n_k^i (r_i^{p-3} - r_k^{p-3}) \psi(r_i, r_k, \alpha) \qquad (10)$$

The product $(r_i^{p-3} - r_k^{p-3})\psi(r_i, r_k, \alpha)$ (namely, for any r_i, r_k), is positive for $p < 3$, negative for $p > 3$ and

vanishes for $p = 3$. Accordingly, as all other factors in Equation 10 have definite sign, the momenta of order less than 3 decrease in time in the given interval, while the 3rd order momentum is constant, in accord with volume conservation. In particular, the mean radius r is decreasing in time in each time interval where the total number of particles remains constant. The result is rather surprising, since the average particle size of a coarsening system is expected to increase continuously. Nevertheless, r is not a continuous function throughout the process. In fact, at each time eigenvalue, where a number n_i of particles disappears (i.e. one of the r_i decreases continuously to zero), all the momenta defined by Equation 6 undergo a positive jump through a ratio $N/(N-n_i)$. For this reason the average radius will decrease continuously in the intervals between different time eigenvalues, but will increase stepwise at the end of each interval. The final value of r will be, obviously, larger than the initial one, bringing on a reduction of the total surface area, as required by thermodynamics.

As to the standard deviation, which determines the width of the particle size distribution, its behaviour within the intervals cannot be predicted in general, because M_2 and r^2 in Equation 7 are both decreasing functions. Nevertheless if $r_{\max}$ is a value larger than all r_i in a given time interval, as

$$\left| \left(\frac{r_i}{r_{\max}}\right)^{p-3} - \left(\frac{r_k}{r_{\max}}\right)^{p-3} \right|$$
$$> \left| \left(\frac{r_i}{r_{\max}}\right)^{q-3} - \left(\frac{r_k}{r_{\max}}\right)^{q-3} \right|$$

whenever $p < q$, it is possible to establish that $|r_{\max} \mathrm{d}M_2/\mathrm{d}t| < |r_{\max}^2 \mathrm{d}M_1/\mathrm{d}t|$. Correspondingly, the time derivative

$$\frac{\mathrm{d}\Delta^2}{\mathrm{d}t} = \frac{\mathrm{d}M_2}{\mathrm{d}t} - 2r\frac{\mathrm{d}M_1}{\mathrm{d}t} \qquad (11)$$

will be surely positive whenever $r/r_{\max} > 1/2$. In such a case the particle distribution tends to become wider within the considered time interval. The standard deviation will itself undergo a jump at the end of each interval. If Δ' is the value after the jump, we have

$$\frac{\Delta'^2}{\Delta^2} = \frac{N}{N-n_i}\left(M_2 - \frac{N}{N-n_i}r^2\right)\Big/(M_2 - r^2) \qquad (12)$$

Studying the condition under which this ratio is less than unity, one finds that it is absolutely fulfilled provided that the ratio Δ/r is less or equal than unity, or else in the case of $N/(N-n_i) > \Delta/r$. Therefore, it is possible to conclude that the standard deviation may increase continuously within the single interval, but decreases stepwise throughout the whole process, being zero at the final step, when all particles have the same size.

The dependence of the average radius r on the cluster size (i.e. the total number of particles, N) can be established by noting that centered moments of unpair order

are always very small. In particular, from the condition $\Sigma_i n_i (r_i - r)^3 \approx 0$, it is possible to derive the identity

$$Nr^3 \left(\frac{1 + 3\Delta^2}{r^2} \right) \approx \Sigma_i n_i r_i^3 = \text{const} \qquad (13)$$

from where, if $\Delta^2/r^2 \ll 1$, the average radius turns out to be proportional to $N^{-1/3}$.

To solve the set of differential equations (5), the densification law, through which ε_d depends on time, must be known. In the special case of normal growth, as occurring in the final stage of sintering of relatively dense compacts, $g(\varepsilon_d)$ is a constant and the solution is simplified. More in general, suppose that the densification law is given in the form [15]

$$\dot{\varepsilon}_d = k_d(T) \frac{\Sigma}{r^2} f(\varepsilon_d) \qquad (14)$$

where Σ is the driving force for densification, expressed as a sintering stress [16], $k_d(T)$ is a kinetic factor, $f(\varepsilon_d)$ a rate evolution function and r the particle size, which, in the present application can be represented by the average defined above. It is then possible to eliminate the time variable between Equation 5 and Equation 14, obtaining:

$$\frac{dr_i}{d\varepsilon_d} = -\frac{\Gamma}{4\pi\Sigma} \frac{r^2}{r_i^2} \frac{k(T)}{k_d(T)} F(\varepsilon_d)$$
$$\times \sum_k n_k^i \psi(r_i, r_k, \alpha) \ (1 = 1, 2, \ldots, m) \quad (15)$$

where $F(\varepsilon_d) = g(\varepsilon_d)/f(\varepsilon_d)$. Introducing an *intrinsic time x* of the process through the position:

$$dx = F(\varepsilon_d) \, d\varepsilon_d \qquad (16)$$

if the process is isothermal, or if the ratio $k(T)/k_d(T)$ is a constant, the set of equations can be solved *independently of the densification history*, with the intrinsic time as the evolution variable, from:

$$\frac{dr_i}{dx} = -\frac{\Gamma}{4\pi\Sigma} \frac{r^2}{r_i^2} \frac{k(T)}{k_d(T)}$$
$$\times \sum_k n_k^i \psi(r_i, r_k, \alpha) \ (1 = 1, 2, \ldots, m) \quad (17)$$

For some systems where densification and grain growth occur simultaneously, it has been proved [17] that a common thermally activated step exists. In such systems the grain size distribution was shown to be a function of the apparent sample density and not of temperature. This result corresponds to the solution of Equation 17 when $k(T)/k_d(T) = \text{const}$.

3. Local laws for grain growth mechanisms during densification
3.1. Initial/intermediate densification stage
It is well known that during the initial/intermediate stage of sintering grain boundaries are pinned through
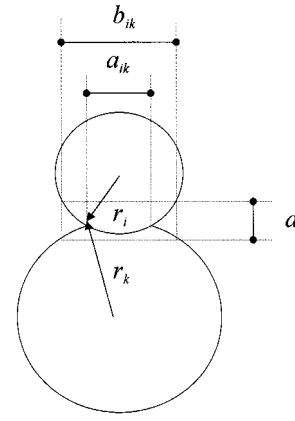

Figure 1 Two-particle model for determination of exchange cross-section in vapour transport.

the pores, so that grain growth can only occur through mechanisms of Ostwald ripening [18] via surface diffusion and/or via vapour transport. The gradient of chemical potential which drives such transport mechanisms is

$$\frac{\delta\mu_{ik}}{d} = \frac{2\Omega\gamma_s}{d}\beta\left(\frac{1}{r_i} - \frac{1}{r_k}\right) \qquad (18)$$

where Ω is the atomic volume of the transported species, γ_s is the surface energy, β is a shape factor relating the local radii of curvature of the surface to the radii of particles, and d is the distance of diffusion. The definition of an exchange cross-section depends on the specific transport mechanism. In the case of vapour transport, matter is exchanged between regions of the free surfaces around the neck, to within a separation distance of the order of d. From a simple geometrical model (Fig. 1) where a_{ik} is the neck cross-sectional radius, and the particle are spheres, one obtains the outer radius of the exchange cross-section from

$$b_{ik}^2 \approx \frac{2dr_i r_k}{(r_i + r_k)} \qquad (19)$$

valid for relatively small d. In the same approximation, the model yields $a_{ik}^2 = 2\varepsilon_d r_i r_k$. Then the exchange area can be expressed as

$$A_{ik} = \pi\left(b_{ik}^2 - a_{ik}^2\right) = 2\pi r_i r_k(\varepsilon_o - \varepsilon_d) \qquad (20)$$

where $\varepsilon_o = d/(r_i + r_k)$ can be regarded approximately as a constant. If the transport mechanism is surface diffusion, A_{ik} could be conveniently defined as the area of the annular cross-section of the neck surface, namely

$$A_{ik} \approx 2\pi a_{ik}d_s = 2\sqrt{2}\pi(r_i r_k)^{1/2}d_s\varepsilon_d^{1/2} \qquad (21)$$

where d_s is the thickness of the surface layer at the neck. Note that both Equation 20 and Equation 21 correspond to the general formulation for A_{ik} given in the foregoing section. It appears from Equation 21 that the exchange cross-section for vapour transport decreases with densification, whereas it is expected to increase if the driving mechanism is surface diffusion. According to the flux equation, the matter flux exchanged by

vapour transport between two particles is given by

$$\frac{dV_{i \to k}}{dt} = \frac{4\pi \gamma_s}{d} k_v(T)(r_k - r_i)(\varepsilon_o - \varepsilon_d) \qquad (22)$$

where $k_v(T)$ is the kinetic factor for vapour diffusion, which is in general different from $k_d(T)$. Correspondingly, in any isothermal run the set of evolution equations turns out to be

$$\frac{dr_i}{dx} = \frac{\gamma_s r^2}{\Sigma d} \frac{k_v(T)}{k_d(T)} \sum_k \frac{n_k^i}{r_i} \left(\frac{r_k}{r_i} - 1 \right) \qquad (23)$$

which is a special case of Equation 17, with $\psi(r_i, r_k) = r_k - r_i$ and where

$$dx = \frac{(\varepsilon_o - \varepsilon_d)}{f(\varepsilon_d)} d\varepsilon_d \qquad (24)$$

defines now the intrinsic time.

3.2. Intermediate/final densification stage

In the intermediate/final densification stage, coarsening is a consequence of boundary migration. The grain boundary, subjected to a given mean pressure p, sets into motion at a velocity [19]

$$v = \lambda p \qquad (25)$$

where v is the mean boundary velocity, p is the mean pressure on the boundary and λ is the mobility, i.d. the velocity under unit pressure, which is proportional to the kinetic factor $k(T)$ and inversally proportional to the diffusion distance d_b. According to Rhines and Graig [20]

$$p = \gamma_b \kappa \qquad (26)$$

where γ_b is the grain boundary surface tension and κ is a conveniently defined mean boundary curvature over a given volume of material. When an isolated pair of polyhedrical grains (i) and (k) of different size are considered, κ is simply the curvature of the grain boundary, with the center in the smaller grain. For a pair of spherical grains of radii r_i, r_k which are in contact through a given dihedral angle, the boundary must be tangent, for equilibrium, to the bisector of the dihedral angle, so its curvature is, approximately, the mean of the surface curvatures $2/r_i$ and $-2/r_k$. In the final stage of densification the dominant grain shape is normally that of a sphere-inscribed polyhedron. In this way the above conclusion applies, as a reasonable approximation, also to polyhedral grains. Accordingly,

$$p \approx \gamma_b \left(\frac{1}{r_i} - \frac{1}{r_k} \right) \qquad (27)$$

In Equation 27 γ_b is a constant depending on the nature of the grain boundary. This argument was discussed in a previous work [16] by two of the present authors.

They pointed out that, in a two-particle system, an excess of vacancies in the grain boundary regions or at free surfaces, due to the elastic compliance of the system, generates a real tensile membrane stress σ_b in the boundary, which must be considered instead of γ_b. This membrane stress is not a constant, but depends on the geometry of the system. For a two-particle model σ_b is evaluated in the Appendix as a function of the particle radii and the sintering stress (Equation A.4). In such a case, replacing γ_b with σ_b in Equation 27, the boundary velocity turns out to be

$$v = \frac{k(T)}{d_b} \frac{\Sigma}{2} \left(\frac{1}{r_i^2} - \frac{1}{r_k^2} \right) r_i r_k (1 - \varepsilon_d) \qquad (28)$$

Calculating the rate of exchanged volume $dV_{i \to k}/dt$ as the product of v through the boundary area $\pi a_{ik}^2 = 2\pi \varepsilon_d r_i r_k$, the volume exchanged by a pair of particles turns out to be

$$\frac{dV_{i \to k}}{dt} = \frac{\pi k(T)\Sigma}{d_b} \left(r_k^2 - r_i^2 \right) \varepsilon_d (1 - \varepsilon_d) \qquad (29)$$

where Σ can be regarded as the driving force for grain growth, which, in this case, would be the same as for densification. Equation 29, introduced in Equation 2, yields the set of evolution equations

$$\frac{dr_i}{dt} = -\frac{k(T)\Sigma}{4d_b} \varepsilon_d (1 - \varepsilon_d) \sum_k n_k^i \left(\frac{r_k^2}{r_i^2} - 1 \right) \qquad (30)$$

being again a special case of Equation 5 with $\psi(r_i, r_k) = r_k^2 - r_i^2$ and $g(\varepsilon_d) = \varepsilon_d(1 - \varepsilon_d)$. Eliminating the time variable through Equation 9 and defining the intrinsic time x by Equation 15, Equation 30 becomes:

$$\frac{dr_i}{dx} = -\frac{r^2}{4d_b} \frac{k(T)}{k_d(T)} \sum_k n_k^i \left(\frac{r_k^2}{r_i^2} - 1 \right) \qquad (31)$$

Comparison of Equation 31 with Equation 23 shows that the substitution of the concept of surface tension with that of membrane stress produces a different dependence on the radii. In fact, the use of Equation 27 would lead to a set of differential equations where $\psi(r_i, r_k)$ is the same as in Equation 23. It has been observed that, for some systems, grain growth and densification have the same activation energy [17]. In such a case Equation 31 can be furtherly simplified by assuming $k(T) = k_d(T)$.

4. Geometrical models for numerical solution

Fig. 2 illustrates three geometrical cluster models (a, b, c) considered for numerical solutions. The particles are numbered according to the size they are expected to assume in the course of the process: particles with the same number will remain equal in size on account of symmetry.

Model (a) is a two-dimensional arrangement of 19 closed-packed spheres, initially of equal radius r_o, except the central sphere which is smaller (with radius
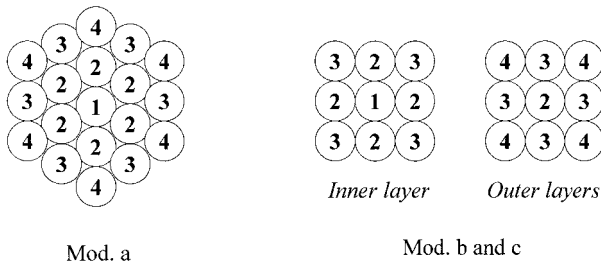
Mod. a

Inner layer   Outer layers

Mod. b and c

Figure 2 Models for numerical simulation: model a (2-d): $N = 19$; $r_{1o} = 0.9 r_o$; $r_{2o} = r_{3o} = r_{4o} = r_o$ model b (3-d): $N = 27$; $r_{1o} = 0.9$ r_o; $r_{2o} = r_{3o} = r_{4o} = r_o$; model c (3-d): $N = 27$; $r_{1o} = 0.8 r_o$; $r_{2o} = 0.9 r_o$; $r_{3o} = r_{4o} = r_o$.

$r_{1o} = 0.9 r_o$). At the beginning of the process matter will flow from particle (1) to the nearest neighbours (2) which, in turn, begin to receive atoms also from sort (3), and so on. Consequently, the initial heterogeneity spreads instantly to the whole cluster population. The symmetry of the system conserves the sorting throughout the process.

Models (b) and (c) represent a 3-d cubic packing of 27 spheres, respectively with two and with three sorts of initial radii, precisely $r_{1o} = 0.9 r_o$ in case (b) and $r_{1o} = 0.8 r_o$, $r_{2o} = 0.9 r_o$ in case (c). The evolution of the system proceeds as in the foregoing instance.

For each of the three models numerical solutions of both Equation 23 (initial/intermediate stage of sintering) and Equation 31 (intermediate/final densification setage) were obtained using the Runge-Kutta method, under the following positions:

i. The mean radius r has been assumed, in a first approximation, constantly equal to r_o;

ii. the ratio r_o/d_b has been given the value of 100 in all cases;

iii. Equation 31 were solved in the special case of $k(T) = k_d(T)$.

The constant in Equation 23 is difficult to evaluate without reference to a particular material. A conventional value of 10 has been therefore adopted. The way the solution is influenced by the value of the constant will emerge in the discussion.

5. Results and discussion
Coarsening, as predicted by the general theory, is a stepwise phenomenon, each step being terminated whenever a sort of particles is incorporated in a neighbouring larger sort. The following step is then calculated, eliminating the incorporated particles from the cluster and assuming as new starting radii of the remaining sorts the values obtained at the end of the foregoing step. The whole process is terminated, in ideal conditions, when a sole sort of particles is left. The values of intrinsic time corresponding to the end of these steps form a kind of eigenvalue spectrum, which is proper of a given system. In Table I the data of numerical calculations are summarised for all examined models. In Fig. 3, where the radii of the particles are plotted vs. intrinsic time x, the evolution of models (a) and (b), simulating the behaviour of systems in the initial/intermediate stage of sintering due to vapour transport, can be followed. In
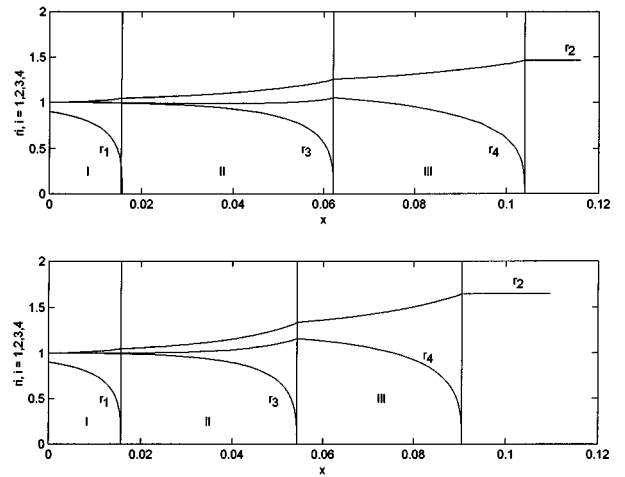

Figure 3 Evolution of particle radii from numerical simulation (initial/intermediate stage of sintering): above model a; beneath model b.
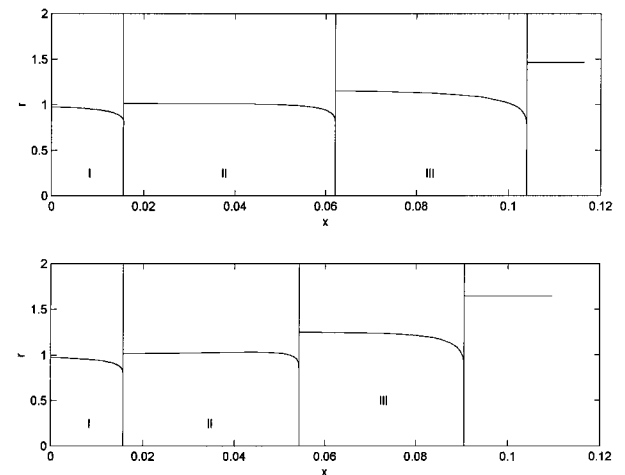

Figure 4 Evolution of mean particle radius from numerical simulation (initial/intermediate stage of sintering): above model a; beneath model b.

Fig. 4 the corresponding behaviour of the mean radius r is shown for both models. The evolution of the radii is quite similar in the 2-d and the 3-d cluster, the latter being only a bit faster (see values of x in Table I). This is an indication that, at least in small regular clusters, the type and dimensionality of particle packing is not expected to have critical influence on the coarsening history. The mean radius decreases slightly within a single step, but at the end of each step undergoes a positive jump through a ratio $N_i/(N_i - n_i)$ (being N_i the total number of particles in the cluster before annihilation of the i-th sort), just as predicted by the theory.

The influence of the diffusion mechanism can be observed comparing the plots of Figs 3b, 4b with those of Fig. 5, simulating the evolution of model (b) in the intermediate/final stage of sintering. The values assumed by the radii at the end of each step are nearly the same in both cases. This would imply: more steps, more coarsening. As the x variable is related to the densification of the system, systems which undergo the same densification would coarsen more when the step duration is shorter, while, for the same step duration, systems which densify the more may exhibit the more of coarsening. The reason for this behaviour is volume

TABLE I Data of numerical simulation

|		Model a (initial/intermediate stage)				
Step number		Initial particle size (relative to r_o)			Mean radius	Intrinsic time
	$r1$	$r2$	$r3$	$r4$	r	x
I	0.9	1.0	1.0	1.0	0.975	0.0157
II	0	1.046	0.994	0.998	1.013	0.0621
III		1.252	0	1.050	1.157	0.104
IV		1.461		0	1.461	
		Model a (intermediate/final stage)				
Step number		Initial particle size (relative to r_o)			Mean radius	Intrinsic time
	$r1$	$r2$	$r3$	$r4$	r	x
I	0.9	1.0	1.0	1.0	0.97	0.0036
II	0	1.048	0.993	0.997	1.01	0.0128
III		1.264	0	1.033	1.148	0.0197
IV		1.461		0	1.461	
		Model b (initial/intermediate stage)				
Step number		Initial particle size (relative to r_o)			Mean radius	Intrinsic time
	$r1$	$r2$	$r3$	$r4$	r	x
I	0.9	1.0	1.0	1.0	0.975	0.0157
II	0	1.049	0.993	1.001	1.014	0.0543
III		1.334	0	1.160	1.247	0.905
IV		1.645		0	1.645	
		Model b (intermediate/final stage)				
Step number		Initial particle size (relative to r_o)			Mean radius	Intrinsic time
	$r1$	$r2$	$r3$	$r4$	r	x
I	0.9	1.0	1.0	1.0	0.97	0.0036
II	0	1.053	0.991	1.001	1.015	0.0111
III		1.342	0	1.152	1.247	0.0167
IV		1.645		0	1.645	
		Model c (initial/intermediate stage)				
Step number		Initial particle size (relative to r_o)			Mean radius	Intrinsic time
	$r1$	$r2$	$r3$	$r4$	r	x
I	0.8	1.0	0.9	0.9	0.9	0.0076
II	0	1.067	0.870	0.904	0.947	0.0250
III		1.280	0	1.021	1.150	0.0470
IV		1.520		0	1.520	
		Model c (intermediate/final stage)				
Step number		Initial particle size (relative to r_o)			Mean radius	Intrinsic time
	$r1$	$r2$	$r3$	$r4$	r	x
I	0.8	1.0	0.9	0.9	0.9	0.00180
II	0	1.074	0.864	0.905	0.948	0.00545
III		1.289	0	1.009	1.149	0.00917
IV		1.520		0	1.520	
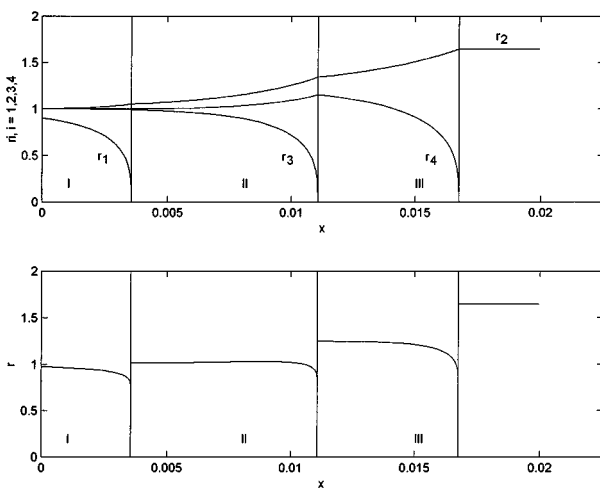
Figure 5 Evolution of particle radii (above) and of mean radius (beneath) from numerical simulation (intermediate/final stage of sintering): model b.

conservation. In fact, on account of Equation 13, the grade of coarsening of a cluster of given composition and size, expressed as the ratio of the average radius r at a given step of the process to the initial average radius r_o, is approximately given by

$$\frac{r}{r_o} \approx \left(\frac{N}{N_i}\right)^{1/3} \tag{32}$$

where N_i is the actual number of particles. The grade of coarsening is, therefore, independent of the mechanism of grain growth, but is determined exclusively by the initial cluster microstructure.

On the opposite, it is the duration of the single step that is influenced by the process, as indicated by the plots. As the constants in the differential equations are in some way arbitrary, it is important to investigate this dependence analytically. In all examined models, within the single step, where coarsening is continuous, one of the particle radii decays dramatically to zero, while the increase of the remaining radii is rather slow (Figs 3 and 5). Then the eigenvalue x_i, corresponding to the instant when the particles of the i-th sort disappear, can be calculated, as a first approximation by integrating Equation 17 in the hypothesis that, during the considered step, the only changing radius is r_i, while the other radii remain constant and equal to the mean

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radius r. Such an integration yields, in general

$$x_i = x_{i-1} + \frac{4\pi r \Sigma}{\Gamma \sum_k n_k^i} \frac{k_d(T)}{k(T)} \int_o^{\theta_i} \frac{\theta^2 \, d\theta}{\psi(\theta)} \qquad (33)$$

where $\theta = r_i/r$ and $\theta_i = r_i^{(i-1)}/r$ being $r_i^{(i-1)}$ the value of r_i at the beginning of the step (or at the end of the foregoing step). The summation $v_i = \Sigma_k n_k^i$ is simply the number of contacts of each particle of the i-th sort. In the simulation of grain growth in the initial/intermediate stage of sintering ($\psi(\theta) = 1 - \theta$), the result is:

$$x_i = x_{i-1} + \frac{\Sigma d}{\gamma_s v_i} \frac{k_d(T)}{k_v(T)} \left[\ln\left(\frac{1}{1-\theta_i}\right) - \theta_i - \frac{\theta_i^2}{2} \right] \qquad (34)$$

while, in the simulation for the intermediate/final stage, where $\psi(\theta) = 1 - \theta^2$, one obtains

$$x_i = x_{i-1} + \frac{4d_b}{r v_i} \left[\frac{1}{2} \ln\left(\frac{1+\theta_i}{1-\theta_i}\right) - \theta_i \right] \qquad (35)$$

Applying Equation 35 to model (b) and assuming for simplicity $\theta_i \approx r_{1o}/r_o = 0.9$ for all steps, the values $x_1 = 0.0038$, $x_2 = 0.0095$, $x_3 = 0.0181$ are calculated, which represent a reasonable approximation to the exact solution (Table I). Application to model (c) with $\theta_1 = 0.8$ for the first step and $\theta_i = 0.9$ for the successive steps, would yield $x_1 = 0.0020$, $x_2 = 0.0077$, $x_3 = 0.0153$, in excess with respect to the numerical solution (Table I); assuming $\theta_i = 0.8$ for all steps a better estimation is obtained ($x_1 = 0.0020$, $x_2 = 0.0050$, $x_3 = 0.0090$), an indication that in a multi-particle system the ratio of smallest to largest radius tends to drive the evolution independently of size of the other particles. Analogous conclusions apply also to the Ostwald ripening simulation.

Following these results and according to Equations 34 and 35, three parameters are expected to influence the duration of the coarsening steps:

i. the mean particle size of the cluster; in particular, a fine-grained compact will undergo slower coarsening than a coarser aggregate, while densification is faster: this is true also of Ostwald ripening, because Σ is normally inversely proportional to r [15, 16];

ii. the coordination number; a porous compact, with low coordination numbers, will coarsen more slowly than a dense compact;

iii. the ratio of smallest to largest radius, which plays in this way the role of an order parameter of the system; compacts with wide particle size distributions or with bimodal distributions may coarsen more rapidly than homogeneous systems.

The behaviour of an aggregate of clusters is, obviously, more complicate than that of a single cluster. In the ideal situation of an aggregate of identical clusters, coarsening would occur inside the single cluster, but would stop at the cluster boundaries, because the particles in contact there, being always of the same size, cannot exchange matter. The final result would be, correspondingly, an aggregate of moderately larger grains, all of one size. On the opposite, cluster heterogeneity (as resulting, e.g., from inadequate powder mixing) tends to spread coarsening from a cluster to another, leading to an increased heterogeneity of the sintered compact, as well as to a larger mean particle size. A promising method to reduce the negative effects of coarsening in a large aggregate, is employing agglomerate powders. The available technology (spray drying, etc.) permits to obtain agglomerates with very narrow size distributions. The presence of small size grains inside a single aggregate enhances densification, while clustering reduces coarsening for the reasons said above. Such conclusions are confirmed in a study by Lange [7], who followed the microstructure evolution of a pair of ZrO_2 single crystals and of two polycrystalline ZrO_2-$3Y_2O_3$ particles of approximately the same size, at a temperature of 1400°C for 12 hours. The behaviour of the two samples is quite different. The single-crystal particles undergo relatively small center approach and growth. In the polycrystalline pair densification of the micrograins leads to a nearly complete center approach between the two particles after 12 h, while coarsening remains confined to within the clusters. Moreover, if the evolution of the interior grains is followed, some grains are found to disappear, while others grow in the iniital stage (from 0.3 h to 4 h) and become smaller in the final stage, as it is the case e.g. for particle 3 in all the models (see Table I and Figs 3 and 5). Also, the ratio of final to initial radii of grains undergoing coarsening (about 1.5–2) can be compared with the predictions of the present model, as applied to relatively small clusters.

Concerning the validity of semi-empirical laws as Equation 1, it is clear from the plots of the average radii (Fig. 4) that such laws are not adequate to describe the behaviour of small clusters. In larger systems, however, where the number of steps may be very high and all steps have in the mean the same duration, it is reasonable to suppose that the number of particles surviving a given step is inversally proportional to the elapsed intrinsic time (plus an initial constant x_o related to the initial particle number). Then, from Equation 32, the average radius would be proportional to $(x + x_o)^{1/3}$, independently of the mechanism of grain growth. In such a case the features of the process will determine the true dependence of r on real time through the correspondence of Equation 16.

6. Conclusions

In coarsening of particle clusters, there are:

i. aspects which depend only on the microstructure of the system (i.e. particle shape, size composition, topological parameters, etc.);

ii. apects which are influenced by the local mechanisms of diffusion which drive grain growth and densification.

The aspects which depend only on the microstructure are:

i.1. the process has a stepwise evolution, determined by the disappearing of the particles which are at each

step the smallest, the number of steps being fixed by the initial microstructure;

i.2. the average particle radius decreases continuously through any step where the total number of particles is conserved and undergoes a positive jump at the end of each step;

i.3. the standard deviation of the size population may increase continuously within a single step, but decreases at the end of each step;

i.4. the average particle radius is (approximately) inversely proportional to the cubic root of the total number of particles present in the cluster.

The duration of the steps depends on both microstructural parameters (average particle radius, coordination number of smallest particles, and an order parameter defined as the ratio of the largest to the smallest grain) and on the diffusion mechanisms whereby densification and grain growth are produced, namely

ii.1. on the ratio between the driving forces of, respectively, the densification and the grain growth mechanism;

ii.2. on the ratio between the kinetic factors of the two diffusion mechanisms

iii.3. on the ratio between the kinetic functions of densification and grain growth, which scales the intrinsic time.

Appendix

For a model of two spherical particles of radii r_i, r_k connected by a circular grain boundary of radius a_{ik}, the boundary membrane stress σ_b was shown to be related to the the mean compressive stress Σ acting on the boundary (assumed as the *sintering stress*) [16] by

$$\sigma_b = \Sigma a_{ik} \frac{\sin(\beta_i + \beta_k)}{2 \sin \beta_i \sin \beta_k} \qquad (A.1)$$

where β_i, β_k are the two parts into which the dihedral angle at the neck is divided by the contact plane, so that $a_{ik} = r_i \sin \beta_i = r_k \sin \beta_k$.

The linear shrinkage associated with densification is (in absolute value)

$$\varepsilon_d = \frac{\{r_i(1 - \cos\beta_i) + r_k(1 - \cos\beta_k)\}}{(r_i + r_k)} \qquad (A.2)$$

and, for relatively small ε_d, can be approximated by $\varepsilon_d \approx 0.5 a_{ik}^2 / r_i r_k$. To the same order of approximation,

$$\sin(\beta_i + \beta_k) \approx \left(\frac{a_{ik}}{r_i} + \frac{a_{ik}}{r_k}\right)\left(\frac{1 - 0.5 a_{ik}^2}{r_i r_k}\right) \quad (A.3)$$

Substituting Equation A.2 and A.3 in Equation A.1, one obtains

$$\sigma_b \approx \frac{\Sigma}{2}\left(\frac{1}{r_i} + \frac{1}{r_k}\right) r_i r_k (1 - \varepsilon_d) \qquad (A.4)$$

which shows how the grain boundary membrane stress depends on the geometry of the contacting particles. The dependence of σ_b on the degree of densification is practically negligible, as normally ε_d is much lower than unity.

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