

A discrete nonlinear mass transfer equation with applications in solid-state sintering of ceramic materials

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Abstract. The evolution of grain structures in materials is a complex and multiscale process that determines the material's final properties [1]. Understanding the dynamics of grain growth is a key factor for controlling this process. We propose a phenomenological approach, based on a nonlinear, discrete mass transfer equation for the evolution of an arbitrary initial grain size distribution. Transition rates for mass transfer across grains are assumed to follow the Arrhenius law, but the activation energy depends on the degree of amorphization of each grain. We argue that the magnitude of the activation energy controls the final (sintered) grain size distribution, and we verify this prediction by numerical simulation of mass transfer in a one-dimensional grain aggregate.

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1 Introduction

Ceramic materials have applications in many fields of science and engineering [2]. In particular, the efficient production of dense ceramics with nanosized grains using ultrafine powders is a subject of increased attention. The most common method for achieving densification in ceramics is solid-state sintering, a thermally activated process that involves the diffusion and redistribution of mass by means of various physical processes, leading to a compactified and consolidated final structure. In the case of nanosized powder compacts, a major concern is the considerable grain growth during the densification process. Special consolidation techniques such as hot isostatic pressing, spark plasma and microwave sintering in many cases successfully limit this undesirable phenomenon. The addition of dopants able to limit grain boundary migration is another effective option.

A very effective way to limit grain growth is to promote densification at a lower sintering temperature [3]. Mechanical activation of powders by high-energy ball milling can contribute greatly toward this direction. High-energy mechanical treatment of solids usually leads to the accumulation of excess energy in the structure resulting in plastic deformation and fracturing of crystals [4,5]. The process usually involves initial reduction of grain sizes, followed by plastic deformation of the crystalline structure, whereas excessive milling time may finally lead to grain aggregation [4,6–8]. Grain size reduction leads to an increase of surface energy [9]. Under deformation the lattice structure is transformed, perturbed or completely destroyed. This effect is evidenced by the broadening, decrease of intensity, and finally total disappearance of XRD reflections [5]. This means that the deformation and increase of structural disorder can bring the solid into a nanocrystalline or even completely amorphous state [8,10–12]. Finally, the possible aggregation of grains imposes significant pressure on the grains increasing their contact surface areas [6,7]. This lowers the activation energy for the diffusion processes involved in sintering, thus accelerating the entire process, and reduces the sintering temperatures [9,13].

The alteration of the state of solid materials due to mechanical activation can lead to significant changes in physical and chemical properties. Order-disorder transitions and phase transformations can then take place at much

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lower temperatures. Additionally, nuclei of new phases can often appear at the interfaces possibly followed by subsequent growth of crystallites [6,8,14]. Thus, crystallization from the amorphous state and chemical reactions can be easily accelerated with subsequent treatment, resulting in materials with improved or better-controlled properties [9,14].

Therefore, a central issue for mechanically activated powders is the relations between the properties of the initial powder and the structure of the resulting ceramic material. Improved performance is in many cases achieved by an optimal balance between particle size and mechanical activation effects [15]. Theoretical and computational investigations can help to understand the impact of mechanical activation on the sintering behaviour of nanosized powders, as well as on sintering temperature dependence.

Even though theories of the sintering process has been intensely researched during the last fifty years, there is a lack of quantitative, predictive models for the microstructural evolution during sintering [2]. In the final stage of sintering the densification process is accompanied by grain growth leading to the final pore structure (grain size distribution, geometry and topology of pores). The physical mechanisms responsible for these effects involve various transport processes acting in the bulk and on the surface of grains, at the boundary between grains, as well as the evaporation-condensation mechanism.

Given the complexity of the physical processes and the initial micro-structure, it is not surprising that a variety of mathematical models have been proposed that focus on different stages of the sintering process, based on various simplifying assumptions regarding the number of grains, the geometry and topology of the pore structure, etc. The existing models include continuum diffusion or transport equations [11,12,16] that are solved either analytically (in simplified cases) or numerically, and kinetic Monte Carlo (Potts model) simulation approaches [10]. More specifically in the case of grain growth, computational approaches involve vertex, Monte Carlo Potts, phase field, and cellular automata models [17].

2 A nonlinear equation for grain growth

We introduce a model of grain growth applying to the final stage of sintering. The model describes mass transfer between grains in terms of a balance equation. Such a model should account for differences in the initial distribution of grain sizes, which contribute to differential growth of the grains. A stochastic aspect is introduced in the problem, due to the fact that the initial grain configuration is not known. Instead of attempting to model explicitly the various physical mechanisms that contribute to mass transfer, we opt for an effective approach that does not distinguish between the different mechanisms.

The locations of the grain centers are denoted by \mathbf{x} , and those of the nearest neighbors of point \mathbf{x} by \mathbf{x}' . Since the lattice formed by the centres of the grains is irregular, the approach to a continuum limit is not well-defined. Thus, a discrete mass transfer equation is proposed. The

grain masses at time t are denoted by $m(\mathbf{x}, t)$ and $r(\mathbf{x}, t)$ is the grain radius. The grain mass density (assumed constant) is denoted by ρ . The mass and the radius are related via $m(\mathbf{x}, t) = g_n \rho r^n(\mathbf{x}, t)$, where g_n is a geometric factor that depends on the dimension n .

We define by $W(\mathbf{x}' \rightarrow \mathbf{x}, t)$ the transition rate for mass transfer into the grain located at \mathbf{x} from the neighbouring grains at time t . Similarly, $W(\mathbf{x} \rightarrow \mathbf{x}', t)$ represents the transition rate at time t for mass transfer from the grain at \mathbf{x} into the neighbouring grains. The transition rates are assumed to follow the Arrhenius law with an *activation energy* that depends on the degree of amorphization of each grain. The *amorphization degree* represents the fraction of each grain that is in the amorphous state. Grains with higher degree of amorphization are more active, have lower activation energies, and tend to transfer mass more effectively. It is expected that smaller grains (such as those created by mechanical activation) have a higher degree of amorphization. To our knowledge, there are no experimental measurements of activation energies as a function of grain amorphization. Hence, it is necessary to surmise the functional dependence of the transition rates on the grain properties based on intuition and the physical constraints mentioned above. We account for the local dependence of the activation energy by introducing an ‘order factor’ $\phi(\mathbf{x}, t)$, which is inversely proportional to the degree of amorphization of each grain. The $\phi(\mathbf{x}, t)$ should increase with the grain mass, since the fraction of amorphous areas that contribute to activation is reduced in larger grains. The simple linear expression $\phi(\mathbf{x}, t) = \frac{\alpha m(\mathbf{x}, t)}{m_0}$, where m_0 is a reference mass and α a dimensionless constant satisfies this dependence and will be used in this paper.

Based on the above considerations, we propose the following system of equations:

$$\partial_t m(\mathbf{x}, t) = \sum_{\mathbf{x}'} W(\mathbf{x}' \rightarrow \mathbf{x}, t) m(\mathbf{x}', t) - \sum_{\mathbf{x}'} W(\mathbf{x} \rightarrow \mathbf{x}', t) m(\mathbf{x}, t), \quad (1)$$

$$W(\mathbf{x} \rightarrow \mathbf{x}', t) = \lambda \exp \left\{ -\frac{\alpha Q}{RT} \left[\frac{m(\mathbf{x}, t)}{m_0} \right] \right\}. \quad (2)$$

In equation (2), λ is a constant that determines the scale of the transition rates, Q is a constant that sets the scale of the activation energy, and $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ is the gas constant. The local activation energy used in equation (2) is equal to the quantity: $\alpha Q m(\mathbf{x}, t)/m_0$. Hence, the activation energy tends to vanish for small grains ($m \rightarrow 0$), which have a significant volume fraction in the amorphous state. At the same time, the activation energy becomes very large for big grains ($m \rightarrow \infty$), which are predominantly ordered.

Although the mass transfer equation (1) looks similar to the master equation used in the analysis of diffusion processes, it differs from the latter in the following: first, the conserved quantity in the master equation is a probability function, while in equation (1) it is the total mass of the grains. Secondly, the classical master equation is

linear in the probability, while equation (1) is nonlinear in the mass due to the variations in grain activity. Finally, in classical diffusion the transitions tend to generate a uniform steady state, while this is not necessarily the case for equation (1), as shown below.

For a time-independent steady state to exist, the time derivative of $m(\mathbf{x}, t)$ must vanish asymptotically. This is accomplished if the ‘detailed balance’ condition is satisfied, i.e.,

$$\lim_{t \rightarrow \infty} \frac{m(\mathbf{x}, t)}{m(\mathbf{x}', t)} = \lim_{t \rightarrow \infty} \frac{W(\mathbf{x}' \rightarrow \mathbf{x}, t)}{W(\mathbf{x} \rightarrow \mathbf{x}', t)} = \lim_{t \rightarrow \infty} \exp \left\{ -\frac{\alpha Q}{RT m_0} [m(\mathbf{x}', t) - m(\mathbf{x}, t)] \right\}. \quad (3)$$

If a steady state exists in which some grains have $m(\mathbf{x}, \infty) = 0$, while for at least one of their neighbours $m(\mathbf{x}', \infty) \neq 0$, the left hand-side of equation (3) tends to zero. Then the right hand-side becomes $\exp \left[-\frac{\alpha Q m(\mathbf{x}', t)}{RT m_0} \right]$. Since $m(\mathbf{x}, t) \propto O(m_0)$, a steady state with vanishing grain masses can exist only if $\alpha Q \gg RT$. This condition is necessary but not sufficient for an asymmetric steady state. Using as an average estimate for the activation energy the value of 500 kJ/mol [13] and a typical sintering temperature (e.g., 1500 °C), $Q/RT \approx 34$, giving an order of magnitude estimate. The value of α determines the variation of the activation energy due to mechanical activation effects. While a large value of Q/RT is necessary for achieving a non-uniform steady state, very large values slow down considerably the sintering process. We expect that $\alpha \leq 1$, to allow for reduction of the activation energy by mechanical activation. At the opposite limit, if $\alpha Q \ll RT$ the ratio of the transition rates in equation (3) will be close to one, and a uniform steady-state is expected. Assuming that $Q/RT \approx 30$ still holds, the limit $\alpha Q \ll RT$ is obtained for $\alpha \ll 1/30$, implying a drastic reduction of the activation energy. It is not known if this condition is realized in physical systems.

3 Dimensional analysis

We use the Length (L) — Mass (M) — Time (T) system of units for dimensional analysis. The governing parameters [18] of the grain mass equation are $m_0, \rho, \lambda, \alpha Q, \mathbf{x}, t$, and RT . To these, one should add the parameters that determine the initial grain size distribution. If this distribution is approximately Gaussian, the parameters include the mean value \bar{r}_0 and standard deviation $\sigma_{r,0}$. Then, the governing parameters and their dimensions are as follows: $[m_0] = M$, $[\lambda] = T^{-1}$, $[\alpha Q] = [RT] = M L^2 T^{-2}$, $[x] = [\bar{r}_0] = [\sigma_{r,0}] = L$, $[t] = T$, $[\rho] = M L^{-3}$. There are three variables with independent dimensions, i.e., $m_0, \alpha Q, \lambda$. According to the Π -theorem of dimensional analysis [18], the equation (1) can be expressed in terms of six dimensionless combinations of the governing parameters, e.g.,

$$\frac{m(\mathbf{x}, t)}{m_0} = \tilde{m} \left(\lambda t, \frac{\mathbf{x}}{\bar{r}_0}; \frac{\alpha Q}{RT}, \frac{\sigma_{r,0}}{\bar{r}_0}, \frac{\alpha Q}{m_0 \bar{r}_0^2 \lambda^2}, \frac{m_0}{\rho \bar{r}_0^3} \right). \quad (4)$$

Using the notation $\tilde{t} = \lambda t$, $\tilde{\mathbf{x}} = \frac{\mathbf{x}}{\bar{r}_0}$, $u = \frac{\alpha Q}{RT}$, $\mu_{r,0} = \frac{\sigma_{r,0}}{\bar{r}_0}$, $\tilde{m}_0 = \frac{m_0}{\rho \bar{r}_0^3}$, $z = \frac{\alpha Q}{m_0 \bar{r}_0^2 \lambda^2}$ for the dimensionless variable combinations, the mass-transfer equation is expressed as follows:

$$\partial_{\tilde{t}} \tilde{m}(\tilde{\mathbf{x}}, \tilde{t}) = \sum_{\tilde{\mathbf{x}}'} e^{-u \tilde{m}(\tilde{\mathbf{x}}', \tilde{t})} \tilde{m}(\tilde{\mathbf{x}}', \tilde{t}) - \sum_{\tilde{\mathbf{x}}'} e^{-u \tilde{m}(\tilde{\mathbf{x}}, \tilde{t})} \tilde{m}(\tilde{\mathbf{x}}, \tilde{t}). \quad (5)$$

Note that the dependence on the scaled variables $\mu_{r,0}$, \tilde{m}_0 and z is not explicit in equation (5), since these variables involve the initial conditions.

4 Simulations results and discussion

Equation (5) can be solved numerically using a forward finite-difference discretization of the time derivative. This leads to the following updating scheme:

$$\tilde{m}(\tilde{\mathbf{x}}, \tilde{t}_{k+1}) = \tilde{m}(\tilde{\mathbf{x}}, \tilde{t}_k) + \delta t_k \sum_{\tilde{\mathbf{x}}'} \left[\tilde{W}(\tilde{\mathbf{x}}' \rightarrow \tilde{\mathbf{x}}, \tilde{t}_k) \tilde{m}(\tilde{\mathbf{x}}', \tilde{t}_k) - \tilde{W}(\tilde{\mathbf{x}} \rightarrow \tilde{\mathbf{x}}', \tilde{t}_k) \tilde{m}(\tilde{\mathbf{x}}, \tilde{t}_k) \right], \quad (6)$$

where the transition rate $\tilde{W}(\tilde{\mathbf{x}}' \rightarrow \tilde{\mathbf{x}}, \tilde{t}_k)$ is given by $\tilde{W}(\tilde{\mathbf{x}}' \rightarrow \tilde{\mathbf{x}}, \tilde{t}_k) = \exp[-u \tilde{m}(\tilde{\mathbf{x}}', \tilde{t}_k)]$. If $W_{\max,k} = \max_{\tilde{\mathbf{x}}, \tilde{\mathbf{x}}'} \{\tilde{W}(\tilde{\mathbf{x}} \rightarrow \tilde{\mathbf{x}}', \tilde{t}_k), \tilde{W}(\tilde{\mathbf{x}}' \rightarrow \tilde{\mathbf{x}}, \tilde{t}_k)\}$ is the maximum transition rate at time t_k , the time increment δt_k should satisfy the condition $\delta t_k W_{\max,k} \ll 1$. A very small time step would slow down the evolution. Since the transition rates change dynamically during the process, the time step is adaptively updated.

We solve equation (6) for a 1d closed chain (ring) of $N = 1000$ grains. The initial grain distribution is assumed to be Gaussian with $\bar{r}_0 = 10$ in arbitrary units and coefficient of variation $\mu_{r,0} = 0.2$. The reference mass m_0 is taken equal to the mean of the initial mass distribution. First, we consider the case of low activation energy using a dimensionless activation parameter $u = 0.1$. The initial grain size distribution and the evolved distribution after 100 000 steps are shown in Figure 1. In the evolved state the radius of all the grains is approximately equal to the initial mean radius. In this case, the low activation energy leads to a diffusive behaviour that asymptotically drives the system toward a uniform steady state.

Next, we consider the case of high activation energy. The grain size distribution for $u = 15$ is shown in Figure 2. Here, the larger grains grow at the expense of the smaller ones. The grain radius distribution develops a bimodal structure that includes a fraction of very small grains. The evolution of the grain radius coefficient of variation $\mu_r(t)$, skewness coefficient, $s_r(t)$ and the maximum radius, $r_{max}(t)$ versus time are shown in Figure 3. The time is calculated based on $t_k = \sum_{i=0}^{k-1} \delta t_i$. The coefficient of variation $\mu_r(t)$ increases in magnitude with time as a result of the evolving gap of the distribution. The skewness coefficient $s_r(t)$ also develops a non-zero value as the distribution evolves away from the Gaussian. The $r_{max}(t)$

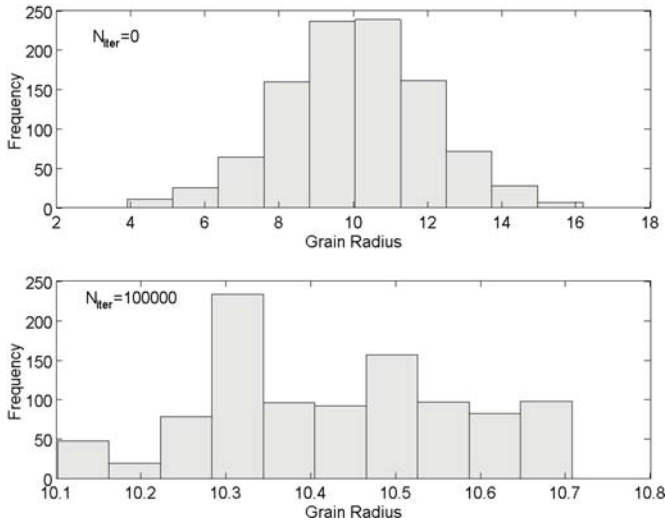


Fig. 1. Grain size distribution at $t = 0$ (top) and $t = 100\,000$ (bottom) for $u = 0.1$ and $\mu_{r,0} = 0.2$.

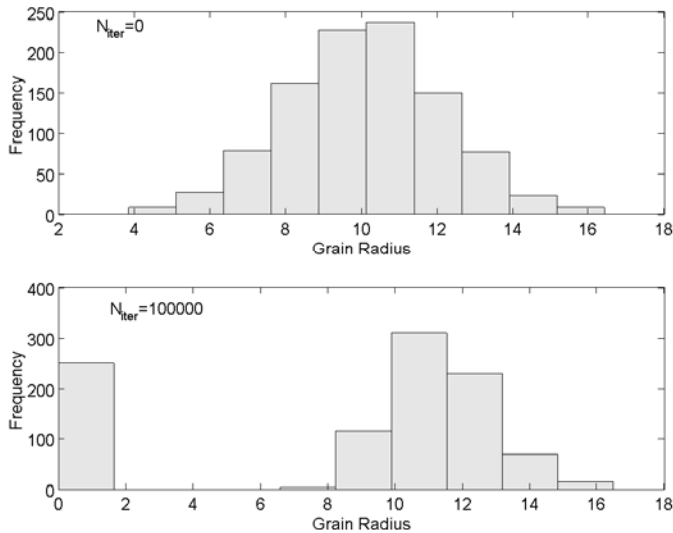


Fig. 2. Grain size distribution for $u = 15$ and $\mu_{r,0} = 0.2$: initial (top) and after 100 000 steps (bottom).

also increases albeit slowly. The plots shown in Figure 3 seem to indicate a smooth approach to a time-independent steady state as the time increases. Also note that if the evolution of the moments were plotted versus the number of steps (instead of the time t_k , the plots would exhibit discontinuities due to the fact that certain steps correspond to significantly larger time increments than others. The spatial configuration of the grains is illustrated in Figure 4 by plotting the initial and final (after 100 000 steps) radius of the first 30 grains: The smaller grains tend to shrink, while the larger grains grow at a considerably slower rate. The asymmetry is due to mass conservation, i.e., the fact that an increase of the grain radius by δr increases the mass by an amount that exceeds the respective reduction

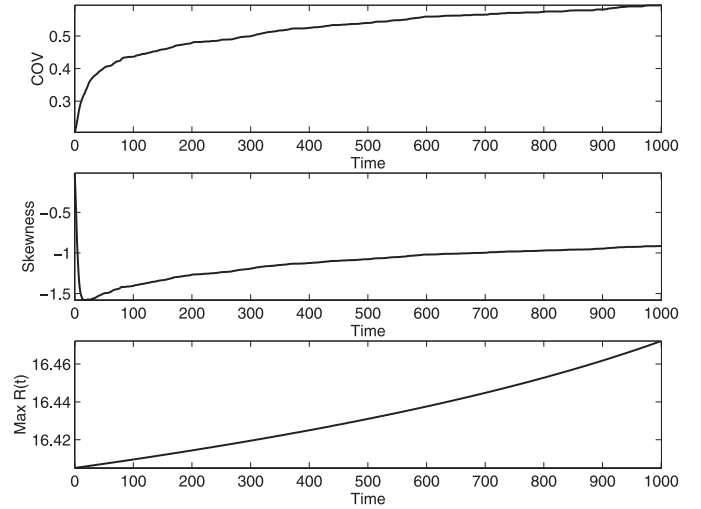


Fig. 3. Coefficient of variation (top), skewness coefficient (middle), and maximum radius (bottom) of the grain size distribution versus simulation time for $u = 15$ and $\mu_{r,0} = 0.2$.

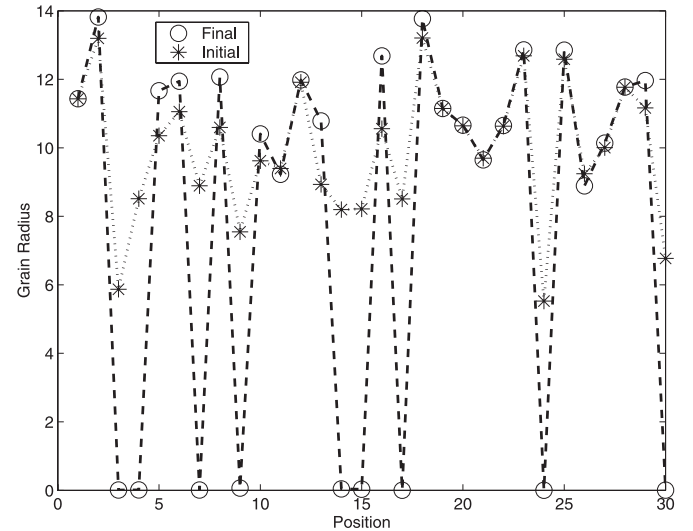


Fig. 4. Initial (*) and final (o) grain sizes for the first 30 sites; $u = 15$ and $\mu_{r,0} = 0.2$.

in mass due to a decrease δr of the radius. A number of grains, the initial size of which is close to the mean radius, do not change appreciably their size.

We note that the model presented here does not include grain coalescence. This can be addressed by solving equation (6) iteratively, with the first iteration ending when the radius of one (or more) of the smaller grains drops below a certain threshold; at this point the smaller grains would coalesce with the largest nearest neighbours. The number of grains would thus be reduced, and the resulting radius distribution would be used as an initial condition for the next iteration of equation (6). This mechanism leads to a coarse-graining of the grain radius distribution. The renormalization group approach may

be a suitable framework for investigating the asymptotic grain size distribution under this coarse-graining procedure.

5 Conclusions

We presented a discrete, nonlinear equation for grain growth in sintered grain aggregates, using transition rates that depend on the degree of amorphization of each grain. The model was solved numerically for a closed chain (ring) of grains. The activation energy was shown to be a crucial factor for the asymptotic grain size distribution, since it leads to a transition from a bimodal steady state (growth regime) to a uniform one (diffusion regime). Various aspects of the model require further study, including the existence of a well-defined threshold between the two regimes, the impact of governing parameters on the grain size evolution, the roles of the initial grain size distribution and the initial grain configuration. Finally, grain coalescence needs to be incorporated in the model (in the spirit discussed in the previous section) in order to observe realistic grain growth.

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