Sintered ceramics with controlled microstructures: numerical investigations with the Discrete Element Method

Christophe L Martin, Zilin Yan, David Jauffres, Didier Bouvard and Rajendra K Bordia

Univ. Grenoble Alpes, CNRS, SIMaP, F-38000 Grenoble, France
Department of Materials Science and Engineering, Clemson University,
161 Sirrine Hall, Clemson, SC 29634–0971, United States

The modelling of processes involving powder needs taking into account the particulate nature of the materials involved. The Discrete Element Method (DEM) is well suited for this task. It allows the macroscopic behavior of an assembly of particles to be calculated from the contact forces generated between each particle. Particle rearrangement, a significant signature of powder materials, is explicitly taken into account. We show that DEM has demonstrated use and significant potential for understanding the link between defect formation and initial microstructure. We present diverse examples of application on free and constrained sintering.

Key-words: Sintering, Model, Discrete element model, Defects

1. Introduction

Sintering of powders induces the growing of interparticle necks by solid diffusion mechanisms, the driving force being the reduction of the free surface energy of the system. It usually results in overall shrinkage of the powder compact. The numerical simulation of sintering has been extensively developed in the last years, either at the scale of the whole part with the finite element method (FEM),1 or at the scale of a few particles also with FEM2 or with Monte Carlo type methods.3 In large-scale analysis, the material is considered as a continuum and its behavior is described through constitutive equations, in which parameters are deduced from experimental data or from micro-mechanics-based models. This approach is suitable for simulating the processing of macroscopic components. However, it does not allow important phenomena related with the particulate nature of the material to be investigated. For example, particle rearrangement, local defect formation, percolation effects, and grain coarsening are difficult to understand and simulate. In particular, particle rearrangement may play a significant role when the particle packing is heterogeneous in size or microstructure, or when sintering is constrained. Because these continuum models work at a much larger length scale than the particle, they relate only indirectly to the microstructure.

For more realistic conditions, the Discrete Element Method (DEM) offers an interesting alternative. In DEM, the mechanical equilibrium of each particle is treated by calculating the interactions between contacting particles, hence the rearrangements phenomena that characterize particulate materials are explicitly taken into account. The first attempts to use discrete simulations for sintering were initiated in the 1990’s5,6 using an implicit scheme to compute particle rearrangement. The contact laws that described the interactions between sintering particles considered solely grain boundary and surface diffusion for mass transport. This is actually sufficient for most practical conditions. Later, thanks to a collaboration between late Prof. Shima from Kyoto University and researchers from Univ. Grenoble Alpes, the compaction of powders was modelled taking into account plasticity and explicit dynamic rearrangement of particles.7 Building on this initial DEM code, named dp3D, we developed in 2006 a sintering module that could tackle composites and could model particle coarsening (with a very simplistic approach).8 The sintering module was integrated in the DEM code dp3D, developed at the SIMaP laboratory in Grenoble. Sintering with DEM was developed at about the same time by the Fraunhofer Institute for Mechanics of Materials. Particle rearrangement and crack formation during constrained sintering were investigated.9 The same team tackled the issue of anisotropic shrinkage during sinter forging.9 Constrained sintering, this time considering the effect of a substrate, was also the subject of further attention.10 These studies showed that when the sintered microstructure at the length scale of a several tens of thousands of particles is of interest, the DEM is a powerful simulation tool.

In parallel, it is important to mention the work of Prof. Wakai, who uses a different method which in the future could be advantageously combined with DEM. Based on the FEM Surface Evolver program, the morphological evolution of several grains can be modelled, taking into account surface and grain-boundary diffusion mechanisms and their coupling.5,11 Although the method does not allow for the treatment of a large number of particles as in DEM, it treats their morphological transformations in a much more satisfactory manner. Indeed in DEM, particles are only represented as spheres that are progressively truncated at the contacts with other particles as sintering proceeds, which is a rude significant simplification.

In this context, this article describes recent efforts from the authors to tackle some important aspects of sintering using the DEM code dp3D. In particular, we show how DEM can be used to investigate microstructure evolution at the particle length scale.

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which indent each other by a sintering term, which is always tensile.

\[ T_s = -\eta \pi a_s^2 R_2 \frac{du}{dt} \]  

where \( \eta \) is a dimensionless viscous parameter typically set in between 0 and 0.1. The contact radius \( a_s \), which appears in Eqs. (1) and (3) is a generalization of Coble’s law\(^{(12)}\) for contacts between non-monomodal particles, as proposed by Parhami and McMeeking\(^{(13)}\) and numerically proven by Pan: \(^{(15)}\)

\[ a_s = 2Rh \]  

Coble’s simple equation agrees well with more elaborate solutions that include explicitly surface diffusion.\(^{(16)}\) However, it is clear that it cannot reproduce correctly the growth of a contact that may occur with no increase of the indent value.

Coarsening is not included in the simulations. Also, it should be clear that the numerical model only deals with spherical particles that are indenting each other.

However, the intersected volume between the two particles must be taken care of. In dp3D, this is done through Eq. (4) and by redistributing in the final microstructure the intersected volume around the two particles, \( V_{\text{c}} \), taking care of volume conservation (\( V_{\text{c}} = V_{\text{neck}} \)). The scheme is sketched in Fig. 1(b). The redistribution is carried out on voxelized images that may be used for image analysis and effective properties calculation.\(^{(16)}\) An example of the result of this simplistic volume redistribution scheme is demonstrated in Fig. 2 on a monomodal packing with periodic conditions.

Figure 2 shows the type of microstructure obtained after partial sintering. It indicates an important limitation with DEM. Since DEM only treats pair interaction, it is clear that when contacts impinge on each other the simple Eqs. (1), (2) and (4) cannot apply. Also, the volume redistribution is not exact anymore. Contact impingement may become significant at relative densities as low as 0.85–0.90, and even at lower densities for composite systems.\(^{(17)}\) Here, we will show simulation results in which local density may approach 0.90. The sintering kinetics associated with these simulations is of course questionable but we are confident that the numerical microstructures generated are still realistic. They will thus model two types of materials: porous ceramics for typical applications such as porous electrodes, bone scaffolds and filters, and ceramics before complete densification and for which it is of interest to investigate defect formation.

### 3. Microstructure control using pore formers

A simple manner to control porosity in ceramics is to include pore formers, typically organic powders, which are blended with

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A simple manner to control porosity in ceramics is to include pore formers, typically organic powders, which are blended with
the ceramic powder at the beginning of the forming process. These pore formers are burned out just before sintering, leaving pores in the microstructure after sintering with a controlled size, morphology and distribution. This process can be mimicked in dp3D by removing a prescribed number of particles before sintering. Various pore former/particle size ratios can be tested as shown in Fig. 3.

An alternative and more realistic method consists in mixing the pore formers with the ceramic particles during the compaction process. This method is exemplified in Fig. 4 on a complex microstructure composed of two layers cosintered together. The top layer is made of LSM (La$_{1-x}$Sr$_x$MnO$_3$) and pore formers. The bottom layer is a composite of LSM and YSZ (yttria-stabilized zirconia). The initial green porosity is approximately 0.5 in both layers (once pore formers have been removed). The diffusion coefficients and surface energies have been chosen identical for both LSM and YSZ. The final porosity of the bottom layer is markedly reduced as compared to the top layer due to the fact that YSZ particles are smaller (0.5 μm) than the LSM particles (1μm).

The larger densification of the bottom YSZ–LSM layer is observable from the surface distortion at the interface with the LSM layer that somewhat constrains the bottom layer (free surfaces are otherwise used laterally). It is encouraging to note that the final porosities match correctly the experimental data. This brings some confidence on the appropriateness of our approach. More details concerning quantitative comparison between experimental and numerical microstructures may be found in.

4. Retarding effect of inclusions

Sintered components can gain some tunable functionalities or superior mechanical properties by the controlled addition of a second phase (inclusions, platelets or whiskers). In the case of a metallic matrix with ceramic inclusions, this comes at the price of a reduction in the densification rates. The versatility of DEM allows for the simulation of the densification of such composites with the possibility to investigate both volume fraction and relative size effects. Another interesting effect is dispersion of inclusions. Figure 5 shows for example that for the same volume percentage of inclusions, dispersion can be tuned quite differently in the initial green compact.

Inclusion/inclusion interactions are governed by Hertzian laws. Metallic/metallic interactions are given by Eqs. (1)–(3), while metallic/inclusion interaction is adapted from Eq. (1), simply by removing the sintering term and keeping only the viscous part. Material parameters in Eqs. (1) and (2) were taken from Nickel for the matrix particles.

Figure 6(a) shows that, as expected, as volume fraction of inclusions increases, the densification rate decreases drastically for a given relative density. For example, the matrix sinters approximately ten times faster than the 20 vol.% composite. Also, we have observed that monomodal composites with 30 vol.% inclusions do not sinter, in accordance with percolation models.

More interestingly, Fig. 6(b) demonstrates that the matrix/inclusion to size ratio $\mu$ also has a significant effect. As inclusions become smaller with respect to the matrix particles, a larger number of inclusions are able to decorate the matrix particles. Thus a larger number of sintering contacts (matrix-matrix) are

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**Fig. 3.** Partially sintered numerical microstructure obtained by removing clusters of particles that mimic pore formers. Relative density is 0.70. a) No pore former; 20% volume of pore formers with pore former to particle size ratio: b) 1, c) 7.

**Fig. 4.** Evolution of the porosity along the height of a bilayered composite electrode before sintering (blue curve) and after sintering (black curve). The corresponding final microstructures are shown on the right hand side. Arrows indicate the experimentally measured average porosity for each layer.

**Fig. 5.** Two composites with 10% vol. of inclusions. a) Well dispersed. b) Agglomerated. Size ratio matrix/inclusion, $\rho$, is 3.
replaced by non-sintering ones (matrix-inclusion) leading to higher retardation of densification.

Although not as pronounced as the relative size effect, the dispersion of inclusions also plays a role [see Fig. 6(b)]. The two curves related to the 20 vol.% composite (linked by the pink arrow) indicate that well dispersed inclusions are more effective than agglomerated ones to retard sintering. In that case, the agglomerate was approximately composed of 15 inclusions, leading to agglomerates with nearly the same size as the matrix particles.

The size effect of inclusion was observed experimentally by Ueyama et al.:23) it was found that adding 30 nm BaTiO3 particles suppressed sintering of a Ni electrode film. The addition of 50 nm particles was much less effective in retarding sintering. Sugimura and Hirao,24) also demonstrated the retarding effect of BaTiO3 (30–100 nm) on the sintering of Ni powder (200 nm), but found that agglomerated inclusions had a smaller retarding effect than well-dispersed larger inclusions. These results are in qualitative agreement with the present simulations.

5. Effect of the green packing

The effect of the initial green microstructure can also be investigated with DEM. We compare the densification of two different microstructures that have been compacted uniaxially up to 0.58 relative density: a homogeneous microstructure and a microstructure made of aggregates that were not allowed to break during compaction. The aggregates are approximately spherical and 2 μm in size and their internal relative density is 0.70. This type of aggregates mimic calcined aggregates for example. Particles are 200 nm in size (with ± 5% dispersion) for both microstructures. The material parameters were taken as representative of fine Al2O3 particles.25) Conditions are periodic in all three directions.

Fig. 6. Densification rate versus density for composites. a) Effect of volume fraction. b) Effect of matrix/inclusion size ratio, ρ. The pink arrow indicates the curve when inclusions are agglomerated [Fig. 5(b)] instead of well dispersed [Fig. 5(a)].

The aggregated and homogenous compacts present noticeably different packing characteristics. The green aggregated compact exhibits a heterogeneous microstructure with dense aggregates and pores in between. Also, while all the contacts between particles in the homogeneous compact are small in size, they are much more spread when considering the aggregated compact. This is because, as indicated in Fig. 7, most of these contacts are large (intra-aggregate contacts), while a few small ones are contacts between aggregates (inter-aggregates).

Figure 7 shows the evolution with densification of the contact size distribution together with their microstructure for the two packings. The large initial contacts inside the aggregates (intra-aggregate contacts) constrain particle rearrangements. Conversely, the numerous small contacts of the homogeneous packing yield significant driving force for densification. Inspection of Eq. (1) reveals that the viscous term, which opposes the approach of the two particles, is proportional to $\alpha_s^4$. Thus, in our model, small contacts between particles are beneficial for densification kinetics.

These remarks explain that the sintering kinetics is affected by heterogeneities, as shown by Fig. 8. This figure indicates that densification time to reach 0.90 density is approximately 50% more for the aggregated microstructure. Finally, we have observed that the initial large pores (one of them is outlined in grey in Fig. 7) that characterize the aggregated green micro-
6. Defect growth during sintering

The fully discontinuous framework in DEM enables the local topological modifications that come with crack formation (branching, bifurcation, healing and new surfaces) to be treated in a natural manner. We take advantage of this feature to investigate the effect of constrained sintering on the growth of defects.

We show here the evolution of a crack that may have been generated during green forming (e.g. ejection after compaction or during drying processes). Figure 9 shows the evolution of an idealized microstructure with an initial crack, which is constrained in the z direction by two planes. Conditions are periodic in the x and y directions. The viscous parameter η is set to 0.1 for the tangential interactions between particles and 0.0 for those between the particles and the two planes [Eq. (3)]. The initial packing density is 0.50 and although the sample shrinks in the x and y directions, it is clear that the constraint in the z direction has deleterious effects on the microstructure. This is because there is a driving force [the sintering term in Eq. (1)] for particles to densify in all three directions. Since the constraint does not allow for densification in the z direction and it is not possible for particles to easily rearrange to compensate for the constraint, local tensile stresses arise.

Thus, the weaker initial crack zone grows in the z direction. But Fig. 9 indicates that cracks that are oriented normal to the constraint also appear in zones that are devoid of noticeable defects. We have actually observed that these cracks nucleate where small heterogeneities are present (typically a smaller number of contacts or a smaller local density).25,26

Other geometries have been tested29 (edge initial crack, no initial crack). They all point to the same conclusion: constraints and lack of particle rearrangement are the necessary conditions for defects to grow. Indeed, Henrich et al.30 have shown that when particle rearrangement is fully active [η = 0 for all particles in Eq. (3)], initial cracks do not degenerate into larger ones.

7. Concluding remarks

We have investigated sintering conditions for which the control of the microstructure (porous ceramics, bilayer, composites) and a better understanding of defect formation (heterogeneities, cracks) can benefit from DEM simulations. The particulate nature of the material to process is taken explicitly taken into account in these simulations. This enables the construction of microstructures that are closer to the real ones (with the restriction that primary particles are spherical). For example, particle size distribution, composites and aggregated or agglomerated packings can be tackled.

The model that characterizes the contact interactions is too simplistic to capture some important features of sintering: coarsening and contact impingement in particular. These are phenomena occurring mostly at the end of sintering. Clearly, DEM simulation is not the best tool for the last stage of sintering. Finite element2,11,13 or kinetic Monte Carlo3 techniques are better equipped for this task. Still, DEM simulations offer a powerful tool for the early and intermediate stages of sintering where most of the defects may initiate. In this context, combined approaches linking phase-field and discrete-element methods as proposed by Shigawara may offer a comprehensive option.27

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