MULTI-SCALE MODELING OF LIQUID PHASE SINTERING AFFECTED BY GRAVITY: PRELIMINARY ANALYSIS

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Abstract

A multi-scale simulation concept taking into account impact of gravity on liquid phase sintering is described. The gravity influence can be included at both the micro- and macro-scales. At the micro-scale, the diffusion mass-transport is directionally modified in the framework of kinetic Monte-Carlo simulations to include the impact of gravity. The micro-scale simulations can provide the values of the constitutive parameters for macroscopic sintering simulations. At the macro-scale, we are attempting to embed a continuum model of sintering into a finite-element framework that includes the gravity forces and substrate friction. If successful, the finite elements analysis will enable predictions relevant to space-based processing, including size and shape and property predictions. Model experiments are underway to support the models via extraction of viscosity moduli versus composition, particle size, heating rate, temperature and time.

Introduction

One of the most important findings from the earlier conducted combined ground-based and microgravity studies [1,2] is that the rules isolated by mankind over many years of Earth-based processing do not carry over into the microgravity environment. New pathways are needed to obtain densification and satisfactory mechanical properties while minimizing distortion and attaining the desired dimensional precision for operating components. In this connection, the understanding of the link between the events occurring at the level of microstructure and the macroscopic behavior of powder specimens during liquid phase sintering (shape distortion, porosity spatial distribution) is of vital importance. This understanding can be gained through the development of a multi-scale model framework taking into account microscopic phenomena and macroscopic shape evolution.

Modeling of micro-scale evolution

At the microscale, simulations should be constructed to show how individual grains bond during sintering by the combined motion of thousands of atoms. Three types of simulations can be applied to this problem in liquid phase sintering:

- *atomistic level* (molecular dynamics) - applied to the study of sintering based on a large ensemble of individual vibrating atoms, providing a means to study time dependent particle coalescence, neck growth and bonding between grains, dihedral angle stabilization, and the roles of factors such as dopants or temperature on sintering [3];
- *viscous models* (surface energy minimization) - wherein an initial configuration is input with prescribed volume fractions, surface energy, and other boundary conditions and allowed to

morph as a viscous solid through a sequence of small steps to a lowest energy configuration, providing a means to identify terminal configurations in multiple grain and multiple phase systems [4];

- *hybrid model* (fine grained Monte Carlo) - relies on computational cells larger than atoms but still involves discrete jumps based on energy minimization rules and appropriate boundary conditions; provides time dependence to the microstructure transformation, enables extraction of important constitutive parameters relating to grain size, grain growth, grain agglomeration, neck growth, and liquid or pore distribution and sizes [5].

The atomistic level simulations provide a means to study the particle coalescence and redistribution of phases, including how additives change particle-particle sintering [3]. Unfortunately, to be relevant these simulations require accurate atomic interaction potentials to compute the total energy of the system. First-principles calculations can provide the most reliable interatomic potentials. An alternative is to use empirical interaction potentials such as the embedded atom method. However, a simulation of sintering requires a very large number of atoms and considerable computational time, making these methods rather slow.

To address these challenges, a hybrid solution to the micro-scale aspects can be employed. The discrete atom level calculation can be replaced by a coarser grid to expedite the simulation, but the time based discrete simulations should enable identification of morphology versus time needed for the mesoscale and component scale models.

Modeling of meso-scale evolution

Kinetic Monte-Carlo (KMC) models have been used extensively to simulate problems of microstructure evolution in multiple grain and multiple phase materials. The first KMC models were used to simulate normal grain growth in single-phase materials [6,7]. It has been shown [8] that very good representation of grain structure, topology and kinetic data could be obtained from KMC simulations. Since then, KMC models have been used to study many other types of microstructure evolution including abnormal grain growth, recrystallization [9], phase transformations, Ostwald ripening [10], pore migration [11] and final-stage sintering [12]. The earliest attempt to simulate sintering using KMC models was limited to final stage sintering and implemented densification by expanding the area of the simulation as densification proceeded. The criterion for densification was to reduce porosity in proportion to the mean distance between pores in the simulation.

While KMC models are fundamentally stochastic, the results of the studies cited above are very stable and have been found to always converge to the same topological and kinetic solutions [13].

Starting from the late 1940's, many researchers, including Kuczynski [14], Kingery [15], Exner [16] Johnson [17], Coble [18], Ashby [19] and others [20,21,22], have studied microstructure evolution during sintering. These studies initially considered sintering of idealized powder compacts consisting of 2 or 3 spherical particles of equal size, subjected to sintering by various diffusion mechanisms. The main accomplishment of these early models was an understanding of the driving forces, transport mechanisms and densification processes for sintering of crystalline materials. Next, sintering models consisting of repeating unit cells of the same geometry were proposed by DeHoff [23], Bouvard and McMeeking [24], Riedel and co-workers [25,26,27], Slaughter and Nettleship [28], and others [29,30,31]. In these models, researchers extended the two and three particle systems to idealized repeating unit cell models where each cell consists of a grain and the porosity around it. Molecular dynamics simulations used to study the sintering of nano-particles [32,33] showed that additional mechanisms such as particle rotation is active, as previously observed in tungsten heavy alloy LPS.

Continuum mechanics modeling of sintering of two [34], three [35] and a row [36] of particles have given very accurate particle shapes evolution. The application of continuum thermodynamic principles by the finite difference method to simulate the sintering of two particles [37], a row and close-packed particle [24], and unit cells of different packing [29] have given accurate data on the shrinkage kinetics during sintering. A cellular model [38] was used to study sintering by surface diffusion in a multiple particle system and an MC model [12] was used to simulate final-stage sintering of multiple grains. Some of these idealized geometric simulations [24] have been used to obtain the sintering stress, or capillary stress, necessary for modeling sintering at the continuum level.

When including a link to the deterministic micro-scale stress analysis, Monte Carlo model can be used to obtain more general and accurate thermodynamic (sintering stress, bulk and shear moduli) and kinetic data (densification rate, *etc*.) for liquid-phase sintering taking into consideration the gravity influence.

Modeling of macro-scale shape distortion during sintering

Sintering kinetics of real porous bodies is determined by temperature, the properties of the powder particles, and the nature of property interactions during microstructure evolution. Among some of the important aspects are kinematic constraints (*e.g*., adhesion of porous component's end face and its support surface, which depends on gravity and the component mass), externally applied forces and, also, inhomogeneity of properties in the volume under investigation (for example, inhomogeneity of the initial density distribution in the green body).

The complex problems can be solved in terms of a macro-scale description if the local events at the micro-scale are known from a parallel set of local simulations. An approach capable of solving these problems is the continuum theory of sintering [39].

The main constitutive relationship of the continuum theory of sintering is represented below:

$$\sigma_{ij} = \frac{\sigma(W)}{W}\left[\varphi\dot{\varepsilon}_{ij} + \left(\psi - \frac{1}{3}\varphi\right)\dot{e}\delta_{ij}\right] + P_L\delta_{ij} \qquad (1)$$

where φ and ψ are the normalized shear and bulk viscosity moduli, which depend on porosity θ and other structure parameters such as grain size, relative interparticle neck radius, *etc*.; δ_{ij} is a Kronecker symbol; $\dot{e}$ is the first invariant of the strain rate tensor. The effective equivalent strain rate W is connected with temperature, the current porosity, and with the invariants of the strain rate tensor. The effective equivalent stress $\sigma(W)$ determines the constitutive behavior of a porous material. P_L is an effective Laplace stress (sintering stress), which depends on the local sintering stress P_{Lo}, porosity and various pore structure parameters such as relative interparticle neck radius. The porosity θ is the ratio of the pore volume to the volume of a porous body.

The formulation (1) is used for the description of a wide range of powder processing techniques. Parameter σ_{ij} corresponds to the macroscopic stress applied to a representative volume element. The first term of the right-hand part characterizes the porous material's flow resistance, and the second term corresponds to the influence of capillary (sintering) stresses. In the case where the macroscopic stress σ_{ij} is equal to zero, Eq. (1) describes free sintering. In the case when the effective sintering stress P_L is equal to zero, Eq. (1) describes treatment by pressure without sintering. In general, Eq. (1) describes sintering under pressure.

It should be noted that existing model concepts and numerical codes, in particular those based upon the continuum theory of sintering, depend on the accurate determination of the constitutive parameters such as the bulk and shear moduli (ψ and φ) and the sintering stress P_L. This determination, relying on realistic pore-grain structures, can be provided by the microscale simulations (see above). A new synergistic combination of the macroscopic continuum model,

meso-scale Monte Carlo model, and microscale hybrid model simulations should enable a coupled description of liquid phase sintering at different scale levels with effective integration of gravity as an adjustable parameter.

The gravity influence

Studies on microstructural and configuration changes in liquid phase sintering have provided insight into the sintering and composition factors that influence distortion [40-48]. Most of the research in this area analyzed microstructure gradients as influenced by gravity. The influence of gravity-induced grain settling was examined by Kohara and Tatsuzawa [40], Niemi and Courtney [41], and German *et al*. [42-49]. The last group also studied gravity effects on the grain structure under liquid-phase sintering, with emphasis on grain packing [46] and grain coarsening [48]. Experimental evidence of gravity-induced shape distortions is given in several studies [43,47]. A geometry described as an "elephant foot" shape was frequently observed for distorted W-Ni-Fe powder compacts.

A publication by Raman and German [46] provided a first mathematical model for gravity-induced shape distortion during liquid-phase sintering. In this study, the evolution of the shape of a "top hat" (cylinder with flange) was modeled and experimentally observed. However, one of the model assumptions is constant density during the distortion process. This is based upon the hypothesis that bulk densification occurs during heating and is essentially complete prior to liquid formation [49]. In light of this idea, shape change is calculated for an incompressible viscous material in a gravity field [46]. Although qualitative successful for liquid phase sintered tungsten heavy alloys with excessive liquid quantities, such an assumption substantially restricts the model basis and excludes shrinkage and its interplay with gravity forces. The first study which included the analysis of a coupled impact of sintering stresses and gravity has been conducted by Olevsky and German [50,51]. This work, however, was a purely macro-scale analysis, focused on specimen shape distortions without taking into account the evolution of the micro- and meso-structure.

For a full-scale analysis, the gravity influence should be taken into account at both micro- and macro-scales. At the micro-scale, the respective bond energies are to be directionally modified to include the impact of gravity on the site exchanges. The buoyancy and grain settling has to be taken into account by introducing an additional Hamiltonian-based term in the bond energy expressions. In addition, the Potts model should be linked to the finite-element code calculating stresses and strains at the micro-scale in order to determine the gravity stress-effected state of the microstructure and to obtain the final form of the sintering body. The next step in the implementation of these ideas is the utilization of finite-element calculations allowing visco-plastic stress-strain analyses.

At the macro-scale, the continuum model of sintering can be embedded in the following finite-element framework:

$$\left[\int_{\vartheta}[B]^{T}[D][B]\,d\vartheta\right]\{V_n\} = -\int_{\vartheta}[B]^{T}P_L\{1\}\,d\vartheta + \int_{\vartheta} g\,\rho_T\,(1-\theta)[N]\{n_g\}\,d\vartheta \qquad (2)$$

where [B] is the matrix correlating the strain rates with the nodal velocities V_n; [D] is the matrix correlating the stresses with the strain rates ("matrix of viscosities"); ϑ is a macroscopic porous volume under investigation; g is the gravity acceleration; ρ_T is the theoretical density of a fully-dense material; N is the matrix of the finite element shape functions; {1} designates the unit column-vector; and $\{n_g\}$ is a unit vector oriented in the direction of the gravity forces' action.

The development of the respective computer codes based on the described multi-scale modeling concepts is a part of the on-going research. Model experiments are underway to support the models via extraction of viscosity moduli versus composition, particle size, heating rate, temperature and time.

Conclusions

A multi-scale modeling framework for simulation of liquid phase sintering at micro-, meso-, and macro-scale structure levels is described. Both micro- and meso-scale modeling levels can rely on Monte-Carlo simulations, while macro-scale modeling is based on the finite-element approach. The development of the respective computer codes based on the described multi-scale modeling concepts is a part of the on-going research. Model experiments are underway to support the models via extraction of viscosity moduli versus composition, particle size, heating rate, temperature and time.

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