Integral Work of Sintering Concepts Applied to Liquid Phase Sintering Densification, Distortion, and Microstructure Evolution

Randall M. German, Deborah Blaine, Pavan Suri, Suk-Hwan Chung, and Seong-Jin Park

Center for Innovative Sintered Products, P/M Lab, 147 Research West, Pennsylvania State University, University Park, PA, 16802-6809, USA

Abstract

Experiments involving sintering shrinkage, densification, grain growth, and component distortion during liquid phase sintering have been analyzed using a new predictive tool termed the integral work of sintering. Based on the original master sintering curve concept, this spline-fit, lumped-parameter model has been used to integrate solid and liquid phase sintering. Prior to liquid formation the transport kinetics are slow, so the effective activation energy is high, but on liquid formation densification is rapid and a lower activation energy applies. A combination of these two features into a single integral work of sintering allows accurate prediction of product properties from sintering cycle changes. Alternatively, cycles can be designed to produce desired quality.

Introduction

Materials suited for high temperature applications usually have high melting temperatures, making them difficult to manufacture by conventional methods. Sintering offers an attractive processing route since high-temperature materials can be formed into intricate, fully-dense shapes at substantially reduced temperatures, especially if a liquid is present during the sintering cycle. Liquid phase sintering is inherently a metastable process. The terminal point would be one single grain of solid surrounded by a liquid envelope, and that object would be essentially spherical. Many shapes fabricated by liquid phase sintering are complicated, far from spherical, with small grains and an interspersed liquid network. The elimination of porosity requires sufficient sintering, but avoiding spheroidization, coarsening, and liquid-solid separation requires shorter sintering times. This is a situation where a metastable material proves most valuable – solid grains dispersed in a liquid matrix, but no porosity and minimal loss of geometric complexity. The work of sintering concept provides an important means to ensure sufficient sintering work is applied to a powder compact to achieve densification while avoiding coarsening and distortion.

Integral work of sintering is a means to express complex information in a simplified form. Often sintering relies only on the time at the peak temperature to map property changes. However, considerable sintering occurs during heating to the peak temperature. Hence,
we have used all heating, holds, and cooling cycle components to calculate the total thermal work applied to the sinter body. Atomic motion in sintering is thermally activated. This means that at low temperatures the atoms vibrate $10^{14}$ times per second, but very few of those vibrations lead to a change in position. At the sintering temperature, the atomic vibration frequency is still $10^{13}$ times per second, but the vibration amplitude is much increased. Thus the heating aspect of sintering is to increase atomic motion via diffusion, evaporation-condensation, viscous flow, or plastic flow. For a crystalline material, atomic motion during sintering reaches a rate near six atomic position changes per second. Over time this tremendous rate of motion results in significant microstructure changes, corresponding to major property gains. Detailed sintering calculations require compiled data on the atomic fluxes, geometric progression, and various interactions during sintering. When a liquid forms, the transport rates increase, often leading to 100-fold faster motion. In reality, the problem is too complicated and involves too many material parameters to be solved with any precision.

The alternative is a semi-empirical treatment that lumps all of the details into a simplified plot of property changes versus the integral work of sintering. Originally the concept was introduced for solid state sintering by Su and Johnson [1] and is termed the master sintering curve in that formulation. The integral work of sintering realizes that phase changes, liquid formation events, and other factors require a reformulation of the master sintering curve since the atomic structure changes. The integral work of sintering is a spline-fit combination of a solid and liquid phase regions. It offers a simple model, based on transport events, to link the work of sintering $\Theta$ to some metric of sintering – density, grain size, shrinkage, distortion, or final strength. First formulations treated the fractional density at any time during a sintering. The thermal work needed to obtain any density was estimated and corresponding combinations of heating rate, hold time, and peak temperature were selected to deliver that sintering work without more experimentation.

At the microstructure scale, sintering is very dependent on parameters such as initial density, particle size, grain size, and other parameters including the pore size distribution. Even powder vendors and lot-to-lot variations can change the sintering response of a given material.

**Integral Work of Sintering Model**

Atomic transport dominates sintering behavior. Early research identified that diffusion plays the primary role in densification [2]. For most materials the transport events follow an Arrhenius activation energy behavior, where the population of active atomic species able to change atomic position scales with the integral of the Boltzmann energy population from the activation energy to infinity. Such calculations are simplified by the integral work of sintering. For example, assume a densification process based on grain boundary diffusion. In this case, the sintering behavior follows [2],

$$\frac{d\rho}{3\rho \ dt} = \frac{\gamma \Omega}{kT} \left[ \frac{\Gamma(\rho)D_o}{(G(\rho))^n} \right] \exp\left( -\frac{Q}{RT} \right)$$

(1)

with $n = 3$ for volume diffusion, and $n = 4$ for grain boundary diffusion. In Equation (1), $\gamma$ is the surface energy, $\Omega$ is the atomic volume, $k$ is Boltzmann’s constant, $\Gamma$ is a collection of material parameters, $D_o$ is the frequency factor for grain boundary diffusion,
is the grain size, \( Q \) is the activation energy for grain boundary diffusion, \( R \) is the universal gas constant, \( t \) is time, and \( T \) is the absolute temperature. Note this densification equation involves material parameters (such as grain boundary activation energy), microstructure parameters (such as grain size), density, and processing parameters (time and temperature). A complex interaction exists between each, especially in an industrial cycle where time and temperature are constantly varying. Thus, solutions to predict final grain size, density, and other relevant parameters are difficult.

An important assumption in classic sintering models is that grain growth can be described entirely as a function of density. This equation is the basis for the master sintering curve [1]. By rearranging Equation (1) so that all the material dependent or constant parameters, except for the activation energy, are grouped together, a density dependent parameter \( \Phi \) is obtained as follows:

\[
\Phi(\rho) = \frac{k}{\gamma \Omega D_0 \beta_0} \int \left( \frac{G(\rho)}{\rho^2} \right) d\rho
\]

The remaining terms are equal to an equivalent parameter \( \Theta \), the work of sintering,

\[
\Theta(t, T) = \int_{t_o}^{t} \frac{1}{T} \exp\left(-\frac{Q}{RT}\right) dt
\]

that depends on time, temperature, and activation energy. While the dominant sintering densification mechanism for most solid-state sintering is grain boundary diffusion. In reality most materials densify through a number of mechanisms, each with a different activation energy and microstructure dependence. Thus, the identification of a single activation energy is only a simplification – leading to what we term an effective activation energy. Thus, even without a melting event, such as encountered in liquid phase sintering, the model is not perfect.

During liquid phase sintering, densification depends on the specifics of the solid-liquid interaction. The dominant event is diffusion of the solid through the liquid between grains. This is similar to grain boundary diffusion, as treated above, except the diffusion path is much faster and the typical activation energy corresponds to either solvation or diffusion of the solid in the liquid. Simply this scales with the melting temperature, so lower melting temperature liquids (if they have solubility for the solid) provide rapid transport rates. For example, the tungsten diffusion along tungsten grain boundaries has an activation energy near 385 kJ/mol, but when liquid nickel is present that activation energy drops to near 240 kJ/mol. Because of this change in effective activation energy on liquid formation, the master sintering curve must be reformulated into two parts, corresponding to the solid state sintering contributions prior to liquid formation and to liquid phase sintering contributions at temperatures where the liquid exists.

Because of such complexities, it is not accurate to use the activation energy for the dominant sintering mechanism in calculating the work of sintering in Equation (3); however, it can be used as a starting point. Usually the activation energy for a particular system is found through curve fitting based on the activation energy that yields the least mean square residual between the model and existing experimental data.
**Construction of the Master Sintering Curve**

Data are collected from designed sintering experiments. It is best to invoke a broad range of heating and hold conditions in a factorial experiment. For example, six experiments might be conducted with fast heating, slow heating, and intermediate heating to both the highest temperature being considered (with the shortest time) and a lower temperature (and longer hold time). Ideally, dilatometry of video imaging is used to provide many points along the heating cycle, versus just six end points. Besides dilatometry, other measures might be video imaging for distortion or bending, thermogravimetric analysis for binder burnout and impurity removal, and thermal conductivity or electrical conductivity or \textit{in situ} elastic modulus measurements for sinter bonding, and finally quenching for quantitative microscopy. From these experiments responses are measured, including the green and sintered densities, shrinkage, mass loss, hardness, grain size, strength, and final dimensional precision or distortion. Consider a model to predict the final sintered density, where the theoretical density $U_{th}$ is taken as the pycnometer density of the system. The fractional density $\rho$ is the ratio of the sintered density $U_s$ at a specific point in the sintering cycle to the theoretical density,

$$\rho = \frac{U_s}{U_{th}}$$

(4)

Once a set of experiments are performed for known heating rates, hold times, and hold temperatures, the fractional density is measured for each system. For a given cycle the integral work of sintering $\Theta$ is calculated from Equation (3) for an assumed activation energy. The relative density is then plotted against the natural logarithm of the work of sintering to form the master sintering curve.

The overall analysis scheme is shown in the attached flow chart. The work of sintering in Equation (3) is calculated for each point by numerical integration using the trapezoidal rule,

$$\Theta \equiv \sum_{i=0}^{n} \frac{I_i + I_{i+1}}{2} (t_{i+1} - t_i)$$

(5)

where $I$ is the integrand of Equation (3) and $n$ is the number of intervals domains. The activation energy changes upon liquid formation, so a spline fit of integral models is required for the events before and after liquid formation.

The relative density plotted against the corresponding work of sintering integral takes the form of a sigmoid curve, given as

$$\rho_s = a + \frac{1 - a}{1 + \exp\left(-\frac{\ln \Theta - b}{c}\right)}$$

(6)

The constants $a$, $b$ and $c$ characterize Equation (6), defining the master sintering curve for the system. Constant $a$ is taken as the initial relative density. Constants $b$ and $c$ are determined using the generalized Newton-Rhapson method by minimizing the error,

$$Err = \left(\sum_{i=1}^{N} \left(\rho_i / \rho - 1\right)^2 / N\right)^{1/2}$$

(7)
where $\rho_i$ refers to the experimentally measured fractional sintered density, and $\rho$ refers to the predicted value using Equation (6).

Normalization is executed by converting all the density data from the sintering experiments to vary between an arbitrary normalized value of 0.5, corresponding to the initial density of the sample, and a normalized value of 1, corresponding to the final density of the sample. This is done through the following normalizing equation:

$$\rho_n = \frac{\rho - 1}{2(1 - \rho_0)} - 1$$  \hspace{1cm} (8)

Normalization of the data causes the individual master sintering curves to collapse onto one curve. Using the normalized master sintering curve, time-temperature-density maps can be constructed independent of initial density.

**Application to Liquid Phase Sintering**

Space limitations in the manuscript do not allow many examples. However, two are shown here to illustrate the general response. They are both for tungsten heavy alloys as part of the Penn State program on Gravitational Effects on Distortion in Sintering targeted at experiments on the International Space Station. For these dilatometry and quenching experiments were combined to monitor the sintering shrinkage and grain size versus integral work of sintering. Alloys inclined to distortion were included in the design of experiments, ranging from 83 wt.% W to 93 wt.% W (balance Ni and Fe in a 7 to 3 weight ratio). Grain size followed an activation energy of 115 kJ/mol as shown in the attached figure. Likewise, distortion, shrinkage, and sintered density were analyzed and the findings from that work will be published in an archival journal by the researchers.

**Conclusions**

Liquid phase sintering involves a complex combination of material, powder, green body, heating cycle, and microstructure parameters. The complexity of the interactions and the experimental effort required to understand the complexity are barriers to making progress. As an alternative, we have found the integral work of sintering concept provides broad, fundamentally sound data on the combinations of heating rate, time, and temperature that allows collapse of experimental behavior into simple plots. Only a single adjustable parameter is required, that being the effective activation energy. This is a lumped
parameter reflecting the cumulative impact of grain growth, pore shrinkage, pore coalescence, neck growth, and general microstructure evolution events. It is linked to the metric under study – density, grain size, distortion, strength, and shrinkage are common parameters examined so far.

\[ G_0 = 3.00 \, \mu m \]
\[ Q = 115 \, kJ/mol \]
\[ k_0 = 1.20 \times 10^{-17} \, m^3/s \text{ for solid state} \]

For 83 %,
\[ k_0 = 2.20 \times 10^{-15} \, m^3/s \]
Error = 3.41 %

For 88 %,
\[ k_0 = 2.40 \times 10^{-15} \, m^3/s \]
Error = 4.18 %

For 93 %,
\[ k_0 = 2.60 \times 10^{-15} \, m^3/s \]

The liquid phase sintering responses of tungsten heavy alloys have been the primary focus for our studies presented here. However, the integral work of sintering has been successfully applied to problems in sintering densification, grain growth, distortion, and shrinkage for molybdenum, zirconia, nickel, stainless steel, and niobium. Further, we have found techniques for including different powders and different vendors, making this a favorable tool for general powder metallurgy process cycle design.

Acknowledgements

Funding was provided by the National Institute for Standards and Technology under the Advanced Technology Program through Polymer Technologies. Additional funding for experiments on liquid phase sintering was provided by the National Aeronautics and Space Administration under the project *Gravitational Effects on Distortion in Sintering*, monitored by Mike Purvey of the Marshall Space Flight Center.

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