An Update on the Theory of
Supersolidus Liquid Phase Sintering

Randall M. German
Brush Chair Professor in Materials
Director, Center for Innovative Sintered Products
P/M Lab, 147 Research West
Pennsylvania State University
University Park, PA 16802-6809

Abstract

Prealloyed powders usually melt over a range of temperatures. This feature is useful in performing supersolidus liquid phase sintering, where liquid forms inside the particles when heated just over the solidus temperature. Densification by supersolidus liquid phase sintering is sensitive to time-temperatures. A major difficulty arises when a narrow temperature range exists between densification and distortion. The supersolidus liquid phase sintering process has been analyzed from a theoretical standpoint to improve densification behavior. Accordingly, this study examines the interplay of processing variables to obtain full-density, distortion-free shapes from prealloyed powders.

Introduction

The formation of a liquid during sintering is a common technique to enhance densification. Typically, liquid phase sintering begins by mixing two or more small powders of differing compositions [1]. On heating, one powder melts or reacts to form a liquid between the particles that engulfs the more refractory phase. If the particle size is small, then capillary forces from the wetting liquid enhance densification [2]. The process consists of several overlapping steps involving solid-state diffusion, particle rearrangement, solution-reprecipitation, and solid skeleton densification. After sintering the product is a composite of grains that were solid during sintering interlaced with a solidified liquid. An advantage from the liquid phase comes when the particles are small and the liquid is wetting.

Supersolidus liquid phase sintering (SLPS) uses an alloy powder, which is heated to a temperature between the liquidus and solidus [3]. The liquid forms inside the particles and spreads to form pendular bonds at the particle contacts. The combination of a weakened, semisolid particle and capillary force from a wetting liquid gives rapid viscous flow sintering densification. The process is fast as liquid forms to fragment the particles into isolated grains even when starting with large particles. Thus, SLPS is applicable to atomized powders that are normally too coarse for use in traditional liquid phase sintering. One attractive option is to use powder injection to shape the prealloyed powder while avoiding green density gradients. If the molded shape can be retained

during densification, then SLPS and injection molding provide an important technological base for fabrication of high performance, net-shape components. One target application would be formation of various cutting inserts from tool steels.

Overview of the Model

The current theory of SLPS evolved from observations on particle fragmentation and microstructure evolution during densification. Viscous flow of the semisolid particles in response to capillary forces is the primary densification mechanism; the semisolid particles turn mushy and flow once liquid spreads along the grain boundaries. The viscosity decreases as the liquid volume fraction increases, so more liquid gives faster sintering. However, this lower viscosity leads to distortion. The fast transport rates in liquid also contribute to rapid grain growth. A detriment of grain growth that with isothermal sintering the liquid spreads on the grain boundaries since less liquid is required to coat larger grains; thus, the semisolid system viscosity decreases due to coarsening, even a constant temperature. Temperature controls the solid-liquid ratio, but not the microstructure softness, yet it is the main process control parameter. Densification depends on attaining a critical temperature [4]. Indeed, most SLPS systems exhibit a step function when sintered density is plotted versus sintering temperature. Likewise, distortion follows closely behind densification, so often narrow sintering temperature ranges are required to obtain full density without distortion.

Improved understanding of SLPS is provided by a new model that enables exploration of compositions and sintering cycles better suited to the process. The model is based on earlier calculations and observations on capillarity and viscous flow [3-9] adapted to the morphology associated with SLPS. As an example, for a prealloyed tool steel powder compact, a carbon-rich liquid forms in the particles on heating over the solidus temperature. Observations on quenched particles show the liquid forms along grain boundaries, inside grains, and at pendular bonds between particles. Liquids in the particles make the particles soft and easily deformed by grain sliding while liquid between the particles generates a capillary force that induces densification. The combination of a low strength, capillary force, and grain sliding gives rapid densification.

Tool steels contain many alloying additions, with complicated phase relations. For this model, assumptions are necessary on the liquidus and solidus temperature changes with composition. Observations on tool steels during SLPS captured by Takajo *et al.* [10] show the carbide morphology changes during cooling. Quenched SLPS tool steel gives a microstructure similar to that observed in traditional liquid phase sintering. Key features are associated with the particles, grains, necks, grain boundary liquid, and pores between the particles. Table 1 summarizes the liquid formation and densification events as related to the solid content and fractional coverage of grain boundaries by liquid. The primary focus for SLPS is on the semisolid state, where the structure is viscous, yet has a small yield strength that provides resistance to slumping and distortion.

For a given alloy and temperature, the model calculates the liquid volume fraction and this liquid is partitioned among the three locations. Liquid at the interparticle necks provides the capillary force for densification, while the liquid on the grain boundaries lubricates grain sliding during densification. As grain growth occurs, the liquid on the grain boundaries spreads to progressively coat more of the structure. As the solid-solid bonds are wetted, the overall system rigidity and viscosity decline. Densification occurs due to the lower viscosity, but distortion occurs due to the lowered rigidity. Liquid that forms inside the grains plays no role in densification. If a high

fraction of internal liquid forms, then densification is delayed to a higher liquid content.

Table 1. System Behavior and Classification

region	state	approximate solid content	typical fractional coverage	behavior
I	Solid	1.00	0.00	small densification, solid-state
II	Rigid	0.95 to 1.00	0.00 to 0.70	slow, diffusional creep
III	Mushy	0.75 to 0.95	0.70 to 0.80	viscous flow, high viscosity
IV	Semisolid	0.60 to 0.90	0.80 to 0.90	rapid densification by viscous flow
V	Fluid-like	<0.60	1.00	shape loss
VI	Liquid	0.00	---	fluid

Temperature is an important control parameter since it dictates both the liquid content and grain growth rate. The solid grain connectivity depends on the fractional coverage of grain boundaries by liquid. With no liquid, densification and grain growth are by slow solid-state processes. A high level of grain boundary coverage by liquid permits grain sliding with concomitant densification. However, with too much liquid no solid bonding occurs, consequently the compact fails to hold shape. Thus, a key role of temperature is in determining the structural connectivity in a balance between viscous flow densification and distortion. A critical condition occurs when about 80 to 90% of the grain boundaries are covered with liquid. At this percolation point the semisolid structure lacks long-range connectivity and densifies by viscous flow. With less liquid coverage of grain boundaries, the solid-liquid system has a high viscosity and good shape retention. As temperature increases and more liquid forms, grains grow and densification accelerate.

A key aspect of the model is the fractional coverage of liquid on grain boundaries, since this controls densification independent of the liquid volume fraction. Wetted grain boundaries allow grain sliding in response to the capillary force. Thus, many different combinations of liquid content and grain size can induce densification. Further, it is the connectivity of the solid grain structure that determines the temperature gap between densification and distortion. Under optimal circumstances the body retains slight strength so that densification takes place without distortion. However, grain growth reduces the grain boundary area, releasing the existing liquid to coat a declining grain boundary area, eventually eliminating all solid connectivity. Distortion occurs as solid connectivity is lost, especially after pore closure.

As long as pores remain, the solid-vapor or liquid-vapor surface energy contributes a compressive capillary stress at the interparticle bonds known as the sintering stress. When softened sufficiently, this stress induces densification of the semisolid particles by viscous flow [11-13]. Liu *et al.* [6,8,9] analyzed the relations between neck size, shrinkage, and capillary force during SLPS. Semisolid systems have *in situ* strengths in the range from 0.01 kPa to 100 MPa, while the sintering stress is near 1 MPa. Thus, when liquid spreads in the microstructure, the compact strength declines and sintering is the same as a glass-ceramic or other viscous, loaded suspension.

Mathematical description of the model is published elsewhere [14]. The intent here is to review the model and illustrate its success in explaining prior observations. Current research is focused on isolation of processing parameters to reduce distortion in the densified products, using austenitic stainless steel as the test material.

Simulation

If you can not model a process, then it is not understood. Thus, computer simulation efforts force us to isolate and decide on what material and process parameters must be understood to model SLPS. Many of the simulation parameters are known from the experimental definition - green density, particle size, composition, heating rate, atmosphere pressure, maximum temperature, hold time, and grain size as examples. Sensitivity analysis shows that only a few parameters significantly influenced the predicted density and microstructure. For example, the temperature for the onset of densification is dominated by the amount of liquid on the grain boundaries. This "fractional coverage" parameter in turn depends on the solid-liquid ratio (temperature), grain size, and partition of liquid in the microstructure (usually about 50% of the liquid occupies grain boundaries).

Simulations were conducted using a constant heating rate to a hold temperature, with an isothermal hold at the peak temperature. Density calculations were performed with a forward time step iteration, using a variable step size typically between 1 and 6 s. After each iteration the system parameters were recalculated and rate terms checked to determine the size of the next time step. As liquid forms the system viscosity decreases, requiring smaller computational time steps to avoid mathematical instabilities. Accordingly, during rapid densification, the time step was reduced in proportion to the densification rate and reached 0.01 s. A typical SLPS simulation required about 2000 time steps, or about 1 s execution time on a 1998 vintage personal computer.

Liquidus and solidus temperatures were estimated from differential thermal analysis data. Other material properties were determined from standard handbooks. The grain growth rate constants for both the solid and liquid phases were extracted from grain size data obtained on quenched samples.

Stability tests were conducted to reduce errors from the solution technique. Also tests were conducted for sensitivities to the input parameters, showing the peak temperature was a major factor, followed by time at the peak temperature, heating rate, and grain growth rate constants. The simulations proved insensitive to several of the parameters.

Calculation Results

Early simulation results were applied to various tool steel powders. For example, a tool steel simulation requires definition of the carbon content (dictates the solidus and liquidus temperatures), green density, particle size, initial grain size, grain growth behavior, heating rate, peak temperature, hold time, and process atmosphere pressure. The resulting map showed the density, grain size, and other sintering metrics as functions of the peak temperature and hold time. Higher temperatures (more liquid) required less time for densification. With lower sintering temperatures there is less liquid, so densification is delayed until sufficient grain growth occurs spread the liquid to pass the percolation limit, thereby reducing the system viscosity. Once the fractional coverage on grain boundaries is large enough (via grain growth), continued sintering causes rapid densification, giving full density without distortion.

Table 2 provides a summary comparison of several calculations and experiments. To condense considerable data, this table simply compares the experimental report of temperature and time leading to densification with the predicted values. For each case the model was used to replicate the experimental conditions where possible (heating rate, particle size, grain size, solidus temperature, and so on). The close agreement between predicted and measured conditions provides support for the ideas evoked in this model.

Table 2. Comparison of Experimental and Model Densification Conditions

alloy	ref.	D, :m	actual			model		
			density	T, EC	t, s	density	T, EC	t, s
Ni-Cr-Co	4	30	0.95	1110	900	0.98	1110	900
SKH53	19	12	0.99	1226	3600	0.99	1230	3600
bronze	18	132	0.86	875	600	0.86	875	600
bronze	16	132	0.92	875	3600	0.92	875	3600
Fe-C	17	62	0.92	1420	600	0.95	1420	600
Ni-Si-B	18	69	0.97	1000	900	0.94	1000	900
D7 - 2.29% C	23	40	0.99	1255	3600	0.97	1255	3600
T1 - 0.6%C	15	45	>0.99	1330	3600	>0.99	1370	3600
T1 - 0.8%C	15	45	>0.99	1310	3600	>0.99	1327	3600
T1 - 1.15%C	15	45	>0.99	1250	3600	>0.99	1251	3600
T1 - 1.36%C	15	45	>0.99	1215	3600	>0.99	1208	3600
T1 - 1.63%C	15	45	>0.99	1188	3600	>0.99	1230	3600
316L-B	20	80	0.98	1225	1200	0.99	1230	1200

For example, calculations were performed using tool steel data from Wright *et al.* [15] which included data for the solidus and liquidus temperatures at various carbon levels. That study provided the temperatures for the onset of densification, full densification, and component distortion. Model predictions and experimental determinations were within 16EC of each other. At 0.6% C the prediction was high by 56EC, accounting for most of the difference. Likewise the densification temperatures agreed with an average error of 18EC, again with the greatest disagreement at 0.6%C. Finally, the experimental distortion temperatures were compared with those calculated. The disagreement is largest at 0.6% C, with a difference of 74EC, and an average difference between experiment and prediction of 28EC. For the other four carbon contents, the solid content at the distortion temperature ranges from 52 to 61%, but for 0.6% C there is 83% solid at the reported distortion temperature. The systematic disagreement between model and experiment for the 0.6% C case seems anomalous. Otherwise, the model was in reasonable agreement with experiment.

An important discovery was that grain growth had to be modeled using a combination of solid and liquid processes. Grain growth data from Tandon [16] showed a variable rate of grain growth which could be fit with a partition of mechanisms.

Another test of the model used a nickel-base alloy. The 30 :m powder was heated at 10EC/min to various temperatures between 1080 and 1150EC for 15 min in hydrogen [4]. The experimental densification temperature was 1105EC. The simulation predicted a density of 0.63 for 15 min at 1105EC, but 0.95 for 1110EC, with distortion after 15 min at 1120EC, which is lower than the reported distortion temperature of 1140EC. Simulations with variations in the particle size and initial grain size revealed shifts in the densification temperature of about 2EC. A peak fractional density of 0.98 is predicted with a trapped atmosphere, which matches well with the experimental result. Densification is predicted in less than 15 min. The experimental results show slower densification, with a higher density before the rise and a lower density after densification, reflecting model assumptions of a single grain, particle, and pore size. In reality these are all distributed parameters. Accordingly, actual densification should occur over a range of times in response to the differences in local conditions.

Lund and Bala [17] reported sintered densities near 100% for a Fe-0.9C composition formed from a mixture of two steel powders, one with a 3.8% C level. Using the SLPS model, this powder was predicted to densify at 1420EC in 10 min under vacuum, but to a density of 0.95 when sintered in helium. Experimental densities were 0.94 to 0.97 for vacuum sintering and 0.91 to 0.93 for helium sintering under these same conditions. Experimentally, densification occurred over a broad range of temperatures, a feature not captured in the model. However, the predicted densification temperature proved accurate.

Murley and German [18] studied SLPS using spherical, prealloyed Ni-Si-B powder. Densification occurred experimentally near 990EC while the model predicted densification at 980EC. The simulation predicts distortion by 995EC, which is lower than the observed distortion temperature of 1010EC.

Miura *et al.* [19] conducted SLPS experiments with a 12 :m water atomized alloy powder. Grain growth parameters were adjusted to match the grain sizes of 16 :m after 1 h at 1226EC and 52 :m after 1 h at 1240EC. Because of the small particle size, solid-state sintering produced a density of 0.78 before formation of the first liquid. For 1 h vacuum sintering the predicted temperature for the onset of densification is 1225EC, with full densification by 1230EC, and distortion by 1300EC. The experimental report was full densification at 1226EC, in close agreement with the prediction. No data were provided on distortion.

Tandon [16] reported experiments with 132 :m prealloyed bronze heated at 10EC/min to 875EC in hydrogen. The model predicts a sharper densification event as compared with the experimental result. He also studied SLPS sintering of boron doped stainless steels [20]. Model predicted densification occurs between 1215 and 1230EC, which agrees with reported densification between 1205 and 1230EC. At the point of rapid densification (fractional density of 0.815), the system viscosity is 3 MPa·s, with a pore size of 40 :m, and capillary force of 1.4 MPa, while the strength is about 0.6 MPa.

Slumping and Component Shape Control

A problem with SLPS is the loss of component shape during sintering. An excess softening leads to gravity induced distortion [21]. The model was applied to the sintering of a 1.2% C tool steel powder to determine the combination of processing conditions required for full densification while monitoring the grain boundary coverage by liquid as a predictor of distortion. Above approximately 1255EC the model predicts compact distortion since all grain boundaries would be covered by liquid.

One key finding from the simulation is that a temperature decrease after the onset of rapid densification is a means to control grain boundary coverage by liquid, thereby sustaining solid-solid bonding to resist distortion. Prior work demonstrates use of such a technique to reach full density [22]. By lowering the temperature, densification can be sustained while ensuring shape control.

The model's value was demonstrated using conditions corresponding to a report by Kim *et al.* [23] on a prealloyed D7 tool steel. The experimental report gave a carbon content of 2.29%, starting temperature of 20EC, particle size of 40 :m, initial grain size of 1 :m, liquidus temperature of 1271EC, solidus temperature of 1235EC, solid density of 7.64 g/cm^3, liquid density of 6.0 g/cm^3, heating rate of 5EC/min, and gas pressure in the pores of 0.1 MPa. The compacts were 72% dense after a deoxidation treatment at 1000EC. Because of extensive grain growth during sintering, the results were insensitive to the initial grain size. Final heating was at 5EC/min to hold temperatures between 1190 and 1270EC for times up to 1 h. Although sintering was in vacuum, densification was inhibited by outgassing that resulted in gas filled pores that resulted in surface blisters. Accordingly, the simulations were run with a residual gas pressure of 0.1 MPa. Close agreement between experimental and simulated grain sizes occurred with grain growth rate constants of 1 :m^3/s for solid state and 11 :m^3/s for liquid phase processes. The predicted densities proved very accurate, with a peak density of 97% at 1255EC.

Successful simulation of these results provides a platform for exploration of alternative sintering cycles with less distortion. For example, component distortion is linked to liquid films on the grain boundaries. In some cases, liquid coverage of the grain boundaries occurs prior to full densification, a predictor of distortion during densification. For the D7 tool steel results mentioned above, this factor controlled distortion, leading to a maximum sintering temperature of 1244EC. Assuming a maximum temperature of 1240EC to avoid distortion leads to a prediction of full density in 3 h. This is a viable time-temperature combination to give densification without crossing into temperatures where shape retention becomes difficult.

Summary

An update on the theory of supersolidus liquid phase sintering of prealloyed powders is presented. The model uses percolation and rheology concepts to create a response that matches well with observations of rapid densification over narrow temperature or time ranges. The model emphasizes the importance of controlling the liquid coverage of grain boundaries to ensure complete densification. Application of the model to several prior experiments gives a demonstration of its value over a range of alloys, including tool steels, steels, cast iron, stainless steels, bronze, and nickel alloys. The model shows control of densification while avoiding distortion is through control of the grain boundary coverage with the liquid phase.

Acknowledgments

References

1. R. M. German, *Sintering Theory and Practice*, Wiley, New York, NY, 1996.

2. K. S. Hwang, R. M. German and F. V. Lenel, "Capillary Forces Between Spheres During Agglomeration and Liquid Phase Sintering," *Metall. Trans.,* 1987, vol. 18A, pp. 11_17.

3. R. M. German, "Supersolidus Liquid Phase Sintering," *Inter. J. Powder Met.,* 1990, vol. 26, pp. 23_34 and pp. 35-43.

4. T. Tandon, Y. Liu and R. M. German, "Application of Supersolidus Liquid Phase Sintering to High Density Processing of Prealloyed Powders," *Advances in Powder Metallurgy and Particulate Materials - 1995,* vol. 2, MPIF, Princeton, NJ, 1995, pp. 5.37-5.49.

5. R. M. German, "A Quantitative Theory for Supersolidus Liquid Phase Sintering," *Powder Met.,* 1991, vol. 34, pp. 101_ 107.

6. Y. Liu, R. Tandon and R. M. German, "Rheological Modeling of Supersolidus Liquid Phase Sintering," *Sci. Sintering,* 1995, vol. 27, no. 2, pp. 71-88.

7. R. Tandon and R. M. German, "Particle Fragmentation During Supersolidus Sintering," *Inter. J. Powder Met.*, 1997, vol. 33, pp. 54-60.

8. Y. Liu, R. Tandon and R. M. German, "Modeling of Supersolidus Liquid Phase Sintering: I. Capillary Force," *Metall. Mater. Trans.,* 1995, vol. 26A, pp. 2415-2422.

9. Y. Liu, R. Tandon and R. M. German, "Modeling of Supersolidus Liquid Phase Sintering: II. Densification," *Metall. Mater. Trans.,* 1995, vol. 26A, pp. 2423-2436.

10. S. Takajo, M. Nitta and M. Kawano, "Behavior of Liquid Phase Sintering of High Speed Steel Powder Compacts," *J. Japan Soc. Powder Powder Met.,* 1986, vol. 36, pp. 398-401.

11. R. Lapasin, V. Sirtori and D. Casati, "Rheological Characterization of Solder Pastes," *J. Elect. Mater.*, 1994, vol. 23, pp. 525-532.

12. A. Jagota, P. R. Dawson and J. T. Jenkins, "An Anisotropic Continuum Model for the Sintering and Compaction of Powder Packings," *Mech. Mater.*, 1988, vol. 7, pp 255-269.

13. J. G. Wang and R. Raj, "Mechanisms of Superplastic Flow in a Fine-Grained Ceramic Containing Some Liquid Phase," *J. Amer. Ceramic Soc.,* 1984, vol. 67, pp. 399-409.

14. R. M. German, "Supersolidus Liquid Phase Sintering of Prealloyed Powders," *Metall. Mater. Trans.*, 1997, vol. 28A, pp. 1553-1567.

15. C. S. Wright, B. Ogel, F. Lemoisson and Y. Bienvenu, "Supersolidus Sintering of High Speed Steels Part 2: Sintering of Tungsten Based Alloys," *Powder Met.*, 1995, vol. 38, pp. 221-229.

16. R. Tandon, "Densification Mechanisms and Microstructural Evolution Leading to High Density Processing of Prealloyed Powders in Supersolidus Liquid Phase Sintering," Ph. D. Thesis, Pennsylvania State University, University Park, PA, December 1995.

17. J. A. Lund and S. R. Bala, "Supersolidus Sintering," *Modern Developments in Powder Metallurgy*, vol. 6, H. H. Hausner and W. E. Smith (eds.), MPIF, Princeton, NJ, 1974, pp. 409-421.

18. P. F. Murley and R. M. German, "Supersolidus Sintering of Coarse Powders and Its Application to Powder Injection Molding," *Advances in Powder Metallurgy,* vol. 3, MPIF, Princeton, NJ, 1989, pp. 103_120.

19. R. Miura, J. Sekiguchi, M. Uchida, Y. Ohwaki and H. Madarame, "Sintering Behavior and

Mechanical Properties of Injection Molded SKH35 High Speed Steel," *J. Japan Soc. Powder Powder Met.*, 1991, vol. 38, pp. 810-813.

20. R. Tandon, Y. Liu and R. M. German, "High Density Processing of Ferrous Alloys via Supersolidus Liquid Phase Sintering," *Advances in Powder Metallurgy and Particulate Materials,* vol. 2, MPIF, Princeton, NJ, 1995, pp. 5.23-5.36.

21. R. M. German, "Manipulation of Strength During Sintering as a Basis for Obtaining Rapid Densification without Distortion," *Materials Trans.*, 2001, vol. 42, pp. 1400-1410.

22. X. Xu and R. M. German, "Evaluation of In Situ Strength Evolution in Sintering of Prealloyed Powders," *Advances in Powder Metallurgy and Particulate Materials - 2000*, Metal Powder Industries Federation, Princeton, NJ, 2000, pp. 5.79-5.88.

23. A. Lal and R. M. German, "The Role of Viscosity in Supersolidus Liquid Phase Sintering," *Advances in Powder Metallurgy and Particulate Materials - 2000*, Metal Powder Industries Federation, Princeton, NJ, 2000, pp. 5.169-5.182.

24. N. Myers, P. Suri, and R. M. German, "High Density P/M Steel," *Advances in Powder Metallurgy and Particulate Materials - 2000*, Metal Powder Industries Federation, Princeton, NJ, 2000, pp. 6.63-6.68.

25. J. Liu, A. Lal, and R. M. German, "Densification and Shape Retention in Supersolidus Liquid Phase Sintering," *Acta Mater.*, 1999, vol. 47, pp. 4615-4626.

26. A. Lal, R. G. Iacocca, and R. M. German, "Densification During the Supersolidus Liquid-Phase Sintering of Nickel-Based Prealloyed Powder Mixtures," *Metall. Mater. Trans.*, 1999, vol. 30A, pp. 2201-2208.

27. N. S. Myers and R. M. German, "Supersolidus Liquid Phase Sintering of Injection Molded M2 Tool Steel," *Inter. J. Powder Met.*, 1999, vol. 35, no. 6, pp. 45-51.

28. R. Raman and R. M. German, "A Mathematical Model for Gravity-Induced Distortion During Liquid Phase Sintering," *Metall. Mater. Trans.,* 1995, vol. 26A, pp. 653-659.

29. I. F. Anderson and A. C. Nyce, "Pressure-Assisted High Temperature Sintering of Metal Alloys and Ceramics," *Indust. Heating*, 1989, vol. 56, February, pp. 22-26.

30. K. T. Kim, H. H. Choi and Y. C. Jeon, "High Temperature Densification of Tool Steel Powder," *Advances in Powder Metallurgy and Particulate Materials - 1996*, MPIF, Princeton, NJ, 1996, pp. 5.9-5.23.