

Model Materials for Liquid Phase Sintering - The Case for Tungsten Heavy Alloys

Randall M. German and Pavan Suri

*Center for Innovative Sintered Products, Pennsylvania State University, University Park, PA 16802, USA
(at the time of this paper, Pavan Suri was Senior Staff Researcher, Production Engineering Research Laboratory,
Matsushita Electric Works, Ltd., Osaka 571-8686, Japan)*

Abstract

An analysis of tungsten heavy alloys is performed with respect to their suitability as model systems for liquid phase sintering, based on the following factors: 1) confirmation of basic phenomenological models such as rearrangement, solution-precipitation, and skeleton formation, 2) development of microstructure-property links such as fracture toughness dependence on contiguity, and 3) constitutive equations for sintering densification and distortion. We conclude the tungsten heavy alloys are an excellent model system based on much prior data and documented microstructure-property links to composition (W-Ni, -Ni-Fe, -Cu, -Cu-Ni, -Cu-Sn, -Ni-Co, -Mo-Ni-Fe), processing data, known thermodynamic and kinetic attributes, and well documented processing behavior. This agrees with the early work by Lenel who described liquid phase sintering of isotropic systems as the "heavy alloy mechanism." Experiments performed with tungsten heavy alloys now challenge long-established concepts in liquid phase sintering leading to novel computer models for densification and distortion.

Introduction

The formation of a liquid phase during sintering increases the sintering rate, as long as the solid is soluble in the liquid. Since humans are impatient, liquid phase sintering is the most common form of sintering - used in products ranging from porcelain to radiation shields [1]. The most important commercial products are based on WC and related carbides sintered in a matrix of cobalt, variously known as cemented carbides or hardmetals. These compositions account for nearly 25% of all commercial sintered products. However, this anisotropic system proves nonideal in modeling. The development of tungsten heavy alloys (W-Ni-Fe or W-Ni-Cu) in the 1930's provided an important theoretical basis for the liquid phase sintering process.

The attributes of liquid phase sintering are well established [1] and the criteria include the following:

- 1) the solid phase must be soluble in the liquid, but with a modest solvation energy (nonreactive)
- 2) the liquid phase should have a low solubility in the solid
- 3) the liquid must wet the solid (which is the usual case based on the first two criteria)
- 4) the liquid must segregate to the solid-solid interfaces (reflected by a decreasing liquidus and solidus).

The segregated liquid provides a capillary force on the solid grains that works to eliminate porosity and reduce interfacial area. Since diffusion rates in liquids are relatively high in comparison with solid-state diffusion,

there is faster bonding and densification as compared to equivalent solid-state sintering. If the solvation energy is high, then the process is better termed reactive sintering, giving very different trajectories to densification and microstructure evolution [2].

In liquid phase sintering, densification is associated with a unipolar solubility; a low liquid solubility in the solid combined with a high solid solubility in the liquid. When surface energies are dominant, liquid phase sintering densification occurs in the classic stages introduced by Lenel [3] and Kingery [4]. Mixed powders are heated to a temperature where liquid forms. During heating there is solid-state sintering, in part driven by the chemical concentration gradient in the microstructure. Solid-state diffusion during heating yields considerable densification prior to formation of the first liquid [5]. Subsequent densification depends on the amount of liquid. Three stages of densification are encountered after the liquid forms - rearrangement, solution-precipitation, and final stage solid skeleton sintering. If there is a high liquid level, then full density can be achieved via rearrangement upon liquid formation. At low liquid contents the solid skeleton inhibits densification, requiring the participation of solution-precipitation events, where mass transport through the liquid controls densification. Residual porosity is eliminated by solid-state sintering of the rigid solid skeleton.

For wetting liquids, the solid-liquid surface energy is lower than the solid-vapor surface energy, resulting in a reduced system energy. During rearrangement the

compact exhibits viscous response to the capillary action. The elimination of porosity increases the compact viscosity. As a consequence the densification rate continuously decreases. Full density is possible by rearrangement if enough liquid is formed. Since monosized spheres pack to 74% density in theory, probably at least 26 vol.% liquid is needed to obtain full density by rearrangement. However, rearrangement is inhibited by particle contacts formed through compaction or solid-state sintering during heating.

Concurrent with rearrangement are various other events; although, the kinetics of rearrangement are initially so fast these other events are overshadowed. As densification slows, solubility and diffusivity effects dominate. This second stage is termed solution-precipitation. The solubility of a grain in its surrounding liquid varies inversely with its size; small grains have a higher energy and solubility than large ones. The difference in solubilities establishes a concentration gradient in the liquid. Material is transported from the small grains to the large grains by diffusion through the liquid. The net result is a progressive growth of the larger grains at the expense of the smaller grains, giving fewer grains with a larger average size. Solution-precipitation not only contributes to grain coarsening, but also to densification via grain shape accommodation, allowing a customized fitting together of the growing grains to better fill space. The amount of liquid determines the diffusion distance and the necessary degree of grain shape accommodation, as commonly observed in tungsten heavy alloys. After liquid phase sintering, the tungsten grains are several times larger than the original particles and are flattened along neighboring faces to allow a high packing density. Although the solid-liquid interface area is minimized by a spherical shape, grain shape accommodation is favored since it eliminates porosity and the high interface energy associated with pores [6].

The final stage of liquid phase sintering is controlled by slow densification of the solid structure which only becomes evident when the earlier stages reach exhaustion. Microstructural coarsening continues and the residual pores enlarge if they contain trapped gas, giving compact swelling [7]. In general, properties of most liquid phase sintered materials are degraded by prolonged final stage sintering. Hence, short sintering times are preferred in practice. The actual level of densification in each stage depends on the amount of liquid. Accordingly, there are many possible variants to this conceptual framework.

The Case for Tungsten Heavy Alloys

Several factors make the tungsten heavy alloys ideal for liquid phase sintering research. First the powders are commonly available in the small sizes normally used for liquid phase sintering, and many compositions are possible; ranging from W-Ni-Fe with a high solid solubility in the liquid and excellent sintered ductility, to W-Mn-Ni, W-Cu-Ni, and even W-Cu-Sn. Generally, these are lower oxide stability systems that are well

behaved with respect to impurity evaporation during heating, especially if the process atmosphere is reducing or vacuum [8]. Further these compositions can be modified for strength, density, ductility, and other properties through selective additions of Re, Ta, Mo, B, P, and C. This provides several technological advantages such as improved density and strength [9]. Further, from an experimental view, the 1000-fold range in available W powder sizes (from under 50 nm up to 60 μm) helps in experiment design.

Another consideration is that the tungsten heavy alloys are well understood. Approximately 12% of all sintering literature deals with some form of tungsten, and about 1/3 of the tungsten papers specifically deal with heavy alloys. Thus, considerable prior data exists to help in understanding and modeling based on this system.

The system thermodynamics are ideally aligned with the requirements for a liquid phase sintering system [1]. The phase diagrams are known and are not too complicated [10]. This means the solubilities and changes in solubility with temperature for both the solid and liquid are established. The solid is soluble in the liquid. The liquid has negligible solubility in the solid, so once the liquid forms it persists during high temperature holds. Surface energies in the tungsten heavy alloys are close to isotropic [6], giving simplified grain growth with little crystal texture or grain rotation during coarsening.

Densification kinetics of the tungsten heavy alloys are well documented, and clearly follow the classic stages introduced in liquid phase sintering theory [11]. During prolonged sintering, these alloys undergo coarsening, and like densification there is considerable data on the kinetics, role of additives, and factors such as the atmosphere, solid-liquid ratio, temperature, and dopants [12]. Further, these data are supported by extensive thermal analysis data, including dilatometry, and even video imaging during densification [13].

From a practical standpoint, the tungsten heavy alloys offer some challenges. First, they are dense, often over 17 g/cc, so gravitational effects are highly amplified. Thus, friction with the sintering substrate is very evident in a top to bottom size and composition difference. The viscous flow of the solid-liquid system leads to solid settling toward the bottom and creation of an elephant foot shape. The density difference between the solid and liquid is also large, up to 10 g/cc in some alloys. One can argue these differences are problematic, but at the same time they amplify the difficulties encountered in other liquid phase sintering systems.

From a microstructure-property-processing perspective, several significant relations have been isolated for tungsten heavy alloys [14]. The effects include relations between composition, density, microstructure, powder characteristics, impurities, and strength, ductility, fracture toughness, and some thermal properties such as thermal conductivity and thermal expansion coefficient. This progress has helped ensure proper rationalization of the properties and applications.

Modeling

The considerable experimental success with the liquid phase sintering of tungsten heavy alloys is coupled by significant modeling progress. The master sintering curve concept is fully developed for tungsten heavy alloys, providing a simple control strategy for pondering different sintering cycle options [15]. Most recently, the tungsten heavy alloys have been included in three-dimensional simulations of densification and distortion [16,17]. These have progressed to a capability to vary gravity so as to examine computationally the options of sintering on Mars or on the Moon. This is most significant, since experimental validation of the predicted densification-distortion trajectories might still be 40 years in the future. On the other hand, microgravity liquid phase sintering experiments have been conducted with several heavy alloys with consistent findings of pore stability (poor densification due to a lack of pore buoyancy) [18]. No other liquid phase sintering system has been the subject of repeated microgravity and ground-based experiments.

Summary

In summary the selection of tungsten heavy alloys as a model system for liquid phase sintering experiments is supported by extensive data. The favorable attributes include considerable history in the study of processing, properties, composition, and microstructure. A wide flexibility in compositions, and nearly ideal behavior when compared to the model liquid phase sintering concepts. The unique situation with the tungsten heavy alloys has resulted in several microgravity experiments, making them the most explored of all powder system in extraterrestrial sintering. Finally, the favorable understanding has resulted in implementation of three-dimensional models for densification and distortion that proves effective for both microgravity and earth, with predictions for intermediate gravity (Mars and Moon) cases that must wait for future space experiments to attain verification.

Acknowledgements

Research on Gravitational Effects on Distortion in Sintering at Penn State is supported by the National Aeronautics and Space Administration. Mike Purvey and Witold Palosz of the Marshall Space Flight Center provide management and technical oversight.

References

- [1] German, R. M., *Sintering Theory and Practice*, John Wiley and Sons, New York, 1996.
- [2] Savitskii, A. P., *Liquid Phase Sintering of the Systems with Interacting Components*, Tomsk, Russia, 1997.
- [3] Lenel, F. V., Sintering in the Presence of a Liquid Phase, *Trans. AIME*, 1948, vol. 175, pp. 878-896.
- [4] Kingery, W. D., Densification During Sintering in the Presence of a Liquid Phase 1. Theory, *J. Appl. Phys.*, 1959, vol. 30, pp. 301-306.
- [5] Farooq, S., Bose, A., German R. M., Theory of Liquid Phase Sintering: Model Experiments on W-Ni-Fe Heavy Alloy System, *Prog. Powder Met.*, 1987, vol. 43, pp. 65-77.
- [6] Kipphut, C. M., Bose, A., Farooq, S., German R. M., Gravity and Configurational Energy Induced Microstructural Changes in Liquid Phase Sintering, *Metall. Trans.*, 1988, vol. 19A, pp. 1905-1913.
- [7] German, R. M., Churn, K. S., Sintering Atmosphere Effects on the Ductility of W-Ni-Fe Heavy Metals, *Metall. Trans.*, 1984, vol. 15A, pp. 747-754.
- [8] Bose, A., Rabin, B. H., German, R. M., Liquid Phase Sintering of Tungsten Heavy Alloys in Vacuum, *Prog. Powder Met.*, 1986, vol. 42, pp. 557-567.
- [9] Bose, A., German, R. M., Microstructural Refinement of W-Ni-Fe Heavy Alloys by Alloying Additions, *Metall. Trans.*, 1988, vol. 19A, pp. 3100-3103.
- [10] Fernandez Guillermet, A., Ostlund, L., Experimental and Theoretical Study of the Phase Equilibria in the Fe-Ni-W System, *Metall. Trans.*, 1986, vol. 17A, pp. 1809-1823.
- [11] German, R. M., Farooq, S., Kipphut C. M., Kinetics of Liquid Phase Sintering, *Mater. Sci. Eng.*, 1988, vol. A105, pp. 215-224.
- [12] German, R. M., Olevsky, E. A., Modeling Grain Growth Dependence on the Liquid Content in Liquid-Phase Sintered Materials, *Metall. Mater. Trans.*, 1998, vol. 29A, pp. 3057-3067.
- [13] Wu, Y., German, R. M., Marx, B., Bollina, R., Bell, M., Characteristics of Densification and Distortion of Ni-Cu Liquid Phase Sintered Tungsten Heavy Alloy, *Mater. Sci. Eng.*, 2003, vol. A344, pp. 158-167.
- [14] Rabin, B. H., Bose, A., German, R. M., Characteristics of Liquid Phase Sintered Tungsten Heavy Alloys, *Inter. J. Powder Met.*, 1989, vol. 25, pp. 21-27.
- [15] Park, S. J., Chung, S. H., Blaine, D., Suri, P., German, R. M., Master Sintering Curve Construction Software and Its Applications, *Advances in Powder Metallurgy and Particulate Materials - 2004*, Part 1, Metal Powder Industries Federation, Princeton, NJ, 2004, pp. 13-24.
- [16] Binet, C., Lencoski, K. L., Heaney, D. F., German, R. M., Modeling of Distortion and Densification During Liquid Phase Sintering, *Metall. Mater. Trans.*, 2004, vol. 35A, pp. 3833-3841.
- [17] Ganesan, R., Griffio, A., German, R. M., Finite Element Modeling of Distortion during Liquid Phase Sintering, *Metall. Mater. Trans.*, 1998, vol. 29A, pp. 659-664.
- [18] Lu, P., German, R. M., Iacocca, R. G., Presintering Effects on Ground-Based and Microgravity Liquid Phase Sintering, *Metall. Mater. Trans.*, 2001, vol. 32A, pp. 2097-2107.