Gravitational Effects on Distortion in Liquid Phase Sintering

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Abstract

During sintering, powder compacts gain strength through low-temperature interparticle bonding, usually induced by solid-state surface diffusion, followed by further strength contributions from high-temperature densification. In cases where a liquid phase forms, sintering densification is accelerated and shape retention is sustained while the open pores contribute capillary forces that give strength to the compact to resist distortion. Unfortunately, sintering densification requires the compact to become thermally softened to a point where creep strain rates often reach levels near 10^{-2} s^{-1} (1% per second) when the liquid forms. Our measurements show the *in situ* viscosity during rapid sintering densification often falls below 1 GPa-s. Thermal softening of the solid which occurs at high temperatures further substantially reduces the strength. Therefore, the *in situ* strength provides a means to separate compact densification (as required for high performance) from distortion (as required for net-shaping). There are two points of substantial weakness during heating - prior to significant interparticle bonding and during final pore closure. This research examines the interplay that allows densification without distortion. Most surprising is the beneficial role of gravity, where the deviatoric stress acting on the powder structure induces skeletal formation to reduce distortion in contrast to sintering in the absence of gravity.

Introduction

Microgravity liquid phase sintering results have been obtained by the CISP team at Penn State that show surprising results - when sintering in microgravity, components exhibit less densification and more distortion. Microgravity data and observations are supplemented by extensive Earth-based experimentation. Based on the observations, we believe strength and viscosity evolution during sintering are the keys to understanding how components densify during liquid phase sintering. Further, the

contrast and comparison of gravity effects with parallel microgravity experiments provides insight on how powder systems densify. Such insight on the role of gravity suggests routes for minimized distortion.

Basically, during heating a powder compact gains strength through low-temperature interparticle bonding, usually induced by solid-state surface diffusion, followed by further strength contributions from high-temperature sintering densification. In cases where a liquid phase forms, densification is accelerated because of solid transport in the liquid, capillary forces, and liquid lubrication leading to grain sliding along contacts. As long as there are solid bonds or open pores in the sintering body, then there is sufficient rigidity to avoid distortion. However, rapid sintering densification leads to a loss of structural rigidity. Substantial weakness occurs when the pores are closed by rapid densification. This is because the solid skeleton is dissolved by newly formed liquid – a condition that is evident with high liquid contents or when pores rapidly coalesce. When this semisolid system also rapidly densifies, then the capillary forces associated with open pores are also lost, leaving saturated pores and no secondary source of strength. In a sense, liquid phase sintering is analogous to building sand castles at the beach. The extremes exist as -
1) loose, dry sand with no strength and poor ability to hold shape
2) sand with all of the pores saturated with liquid, and although there is more strength there is still no ability to hold shape
3) intermediate (three phase conditions) consisting of solid grains, wetting liquid, and pores, where the liquid pulls the grains into contact and gives the greatest strength.

Most surprising is the gravitational role in suppressing distortion; the deviatoric stress acting on the solid grain structure induces grain-grain contact to reduce distortion at full densification on Earth. In contrast, sintering in microgravity results in significantly more distortion. This is illustrated below (Fig. 1) for 83 wt.% tungsten heavy alloy compacts sintered from identical green compacts in the same furnace for the same time-temperature pathway, but the one on the right was processed in microgravity.

Figure 1. WNiFe compacts.
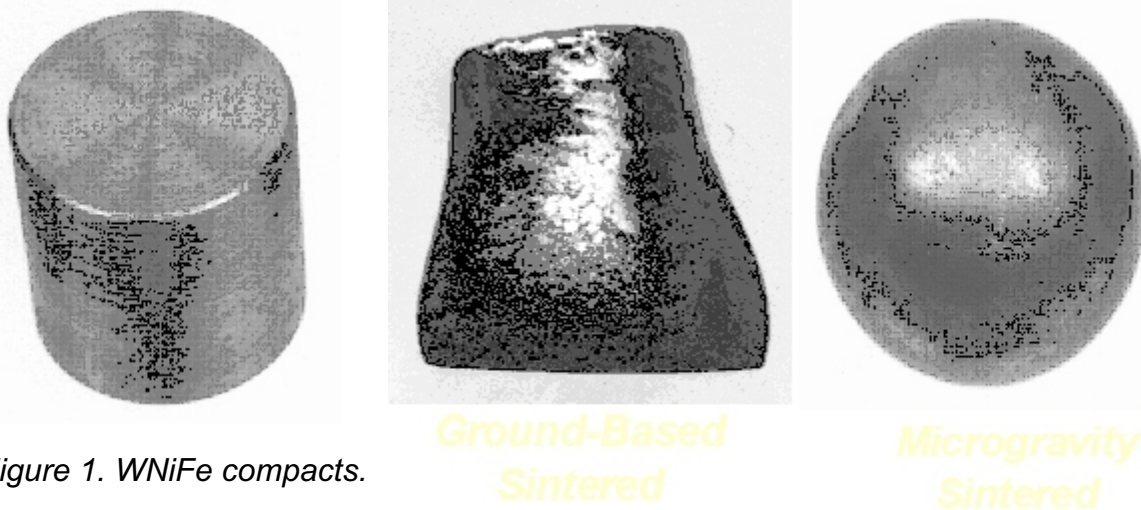
The left-most image shows the presintered W-Ni-Fe compact after outgassing at 1400°C and machining into a right circular cylinder. The center compact followed 1g sintering at 1500°C for 2 h, while the right-most image was processed in µg using the same time, temperature, composition, powder, heating cycle, and furnace.

Further, since there is no buoyancy force on the pore space the compacts distort freely as the pore agglomerate. Also, there is extra liquid since pore filling does not consume excess liquid. Most surprising is the evolution toward hollow spheres, where all of the pores have coalesced into one single central pore and the whole body has spheroidized. The micrograph below shows a microgravity liquid phase sintered compact and the very large pores captured in the process of coalescence. Note the pores are enormous, since the green compact was formed from normal small carbonyl iron, carbonyl nickel, and reduced tungsten, the initial pores were below 1 µm. Now after sintering the pores are up to 200 µm across. This corresponds to a pore coarsening rate 1000 times faster than the grain growth rate. Obviously such behavior is contrary to the earlier suggestions that sintering in space would lead to greater precision. Instead, we now see that microgravity sintering leads to lower performance, an inability to eliminate pores, and more distortion.
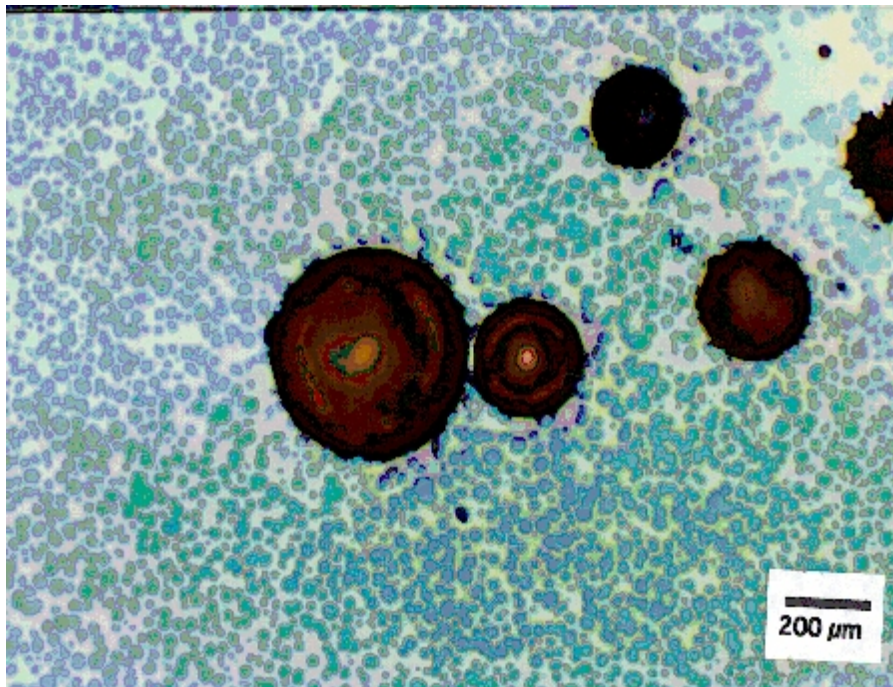

Fig. 2. Coalescence of pores in µg.

Background

Liquid phase sintering is used for net-shape manufacturing [1, 2]. In most systems with a liquid that wets the solid, the liquid enhances densification since it provides a capillary force that pulls the solid grains together, dissolves solid bonds to enable grain rearrangement, and offers a fast mass transport medium [3, 4]. However, liquid phase sintering is generally limited to high solid content compositions due to shape retention

difficulties. In tungsten heavy alloys, the large density difference (over 10 g/cm^3) between solid tungsten grains and the molten matrix (usually an alloy of Ni, Cu, and Fe) induces tungsten grain settling along the gravitational direction, especially for liquid contents over approximately 25 vol.%, resulting in significant distortion [5, 6].

Densification and distortion are the concerns of this research [5, 6, 7]. Unfortunately, in prior work there has been little systematic investigation of distortion. This becomes evident in trying to explain the causes of significant distortion when sintering in microgravity (µg). Seventy-seven powder compacts have been processed in µg conditions, giving the following general results:

■ 1g compacts always densify prior to distorting as demonstrated in by the data shown below (Fig. 3) for a W-Ni-Cu compact

■ gravity induces grain settling, with top-bottom grain size, solid volume fraction, and contiguity gradients

■ grain settling does not occur in microgravity, rather surface to core gradients arise

■ pore elimination (densification) is difficult in microgravity

■ pore coarsening and coalescence produce large pores in microgravity

■ green body homogeneity is a dominant factor with respect to distortion on Earth

■ grain settling induces structural rigidity that limits the extent of distortion on Earth; without grain settling microgravity sintering results in more distortion.

The bottom line is that microgravity samples are more porous and more distorted when compared to Earth-based sintering. Table 1 summarizes the differences between 1g and µg.

Table 1. Comparison of gravity and microgravity sintering macroscopic behavior.

attribute	1g	µg
densification	yes	no
distortion	some	considerable
porosity	little	considerable
pore size	small	large
buoyancy	yes	no
contiguity	high	low

Our research has also determined microstructural links to distortion [5, 8]. For example, Table 2 compares the microstructural features of a W-Ni-Fe composition subjected to

liquid phase sintering for 2 h at 1500 C, with one sample in µg and the other in 1g.

Table 2. Comparison of microscopic attributes of a 78 wt.% W heavy alloy (Ni:Fe=7:3) sintered at 1480°C for 2 h in 1g and µg conditions.

feature	1g	µg
grain size, µm	30.3	26.1
solid fraction	0.74	0.62
solid contiguity	0.22	0.18
neck size, µm	10.5	9.3

Significant knowledge gains have come from the microgravity research, changing how Earth-based liquid phase sintering is performed, resulting in higher precision sintered products. Thus, even with very limited access to microgravity, our findings have resulted in new processing strategies and new industrial practices for higher precision industrial components. Many of the important findings have been published, and a fundamental contribution has been made in terms of a new strength evolution model for sintering [9]. One of the most important findings from the combined 1g and µg studies is that the rules isolated by mankind over many years of Earth-based processing do not carry over into the microgravity environment.
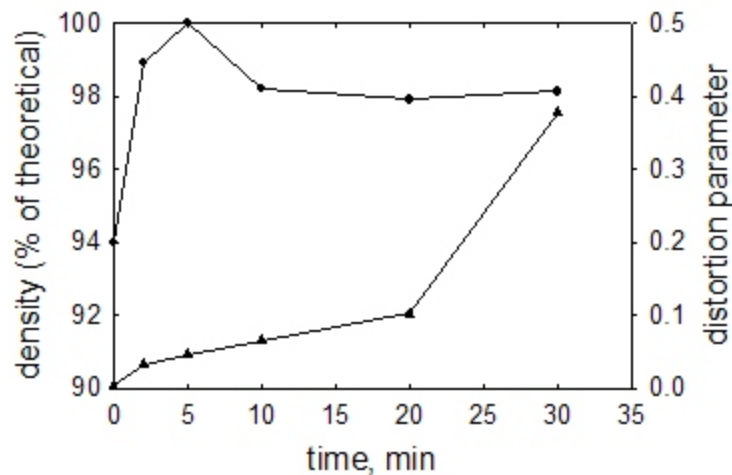

Fig. 3. Distortion parameter and density for liquid phase sintered 80W-16Ni-4Cu with 67% initial porosity and 87 mm pores after sintering at 1480°C using a heating rate of 10°C/min. The samples were water quenched after different hold times.

Discussion

So why do liquid phase sintering systems distort after densification? The key is in the microstructure and the low strength the microstructure passes through when the liquid

forms. Up to pore closure, a combination of solid skeleton and capillarity compression from open pores provide sufficient rigidity to prevent distortion. When sintered on Earth, gravity keeps the grains in contact and this contributes a small yield strength to the compact (estimated at 0.3 kPa in some cases). Thus, Earth-based processing passes through low strength conditions with a small, finite yield strength up to pore closure. If there is an excess of liquid, then densification is rapid, pores close early, and strength depends only on the degree of solid-solid bonding. Inherently sintering densification and distortion depend on many of the same parameters. Full density is possible in the rearrangement stage of liquid phase sintering with a high liquid content [1], but with concomitant distortion. With a low liquid content the solid skeleton forms to resist densification, and this solid skeleton helps retain compact shape. Thus, simple comparative experiments show low solid content samples achieved full density and distort, while high solid content samples densified slowly but did not distort.

The low strength transient that allows distortion is traced to the dihedral angle. In low dihedral angles, the reduction in solid-liquid surface energy on first melt formation leads to liquid penetration of grain boundaries [10]. Consequently, densification by rearrangement takes place rapidly, but solid-solid bonds do not form before pore closure. Thus, the disappearing capillary force removes the only source of component strength. Distortion is the consequence of strength loss. Most interesting, samples sintered to full density still distort on reheating to the liquid phase sintering temperature. This demonstrates that newly formed liquid does attack grain boundaries. On the other hand, high liquid content alloys with a high dihedral angle retain shape up to full density.

It is the liquid penetration of grain boundaries that causes compact strength loss. A high solid solubility in the liquid correlates with a low dihedral angle that is a precursor to liquid penetration of grain boundaries. The fractional atomic solid solubility in the liquid can be approximately linked to the dihedral angle by the following empirical expression [10]:

$$k_A = 0.11 - 0.14 \frac{\phi}{2} \tan\left(\frac{\phi}{2}\right) \qquad (1)$$

where k_A is the fractional atomic solid solubility in the liquid, and ϕ is the dihedral angle in radians. High solid solubility in the liquid k_A indicts a low dihedral angle according to Eq. 1. The atomic solid solubility in liquid can also be linked to the dihedral angle by the following empirical equation:

$$\phi = 75 - 638 \, \Delta k_A \qquad (2)$$

where Δk_A is the fractional atomic solid solubility change in newly formed liquid as compared with the solid solubility in the additive, and ϕ is the dihedral angle in radians. Eq. 2 indicts that if the atomic solid solubility in liquid is much larger than the atomic solid solubility in the additive, then the systems have low dihedral angles. In turn, low dihedral angles imply easier liquid penetration of the grain boundaries and often distortion.

Solid volume fraction and dihedral angle are the dominant factors controlling densification and distortion. Table 3 summarizes the interrelation between dihedral angle and solid volume fraction with respect to distortion.

Table 3. Interrelation between solid volume fraction and dihedral angle with respect to distortion during liquid phase sintering.

	low dihedral angle	**high dihedral angle**
low solid fraction	rapid densification large distortion	slow densification little distortion
high solid fraction	intermediate densification intermediate distortion	slow densification no distortion

This table simply shows a high solid volume fraction and high dihedral angle results in slow densification without distortion. On the other hand, low solid volume fraction and low dihedral angle result in rapid densification with shape distortion. The experimental map shown below (Fig. 4) illustrates these interrelations. It consists of five zones densification and distortion zones.

Zone I, densification is via solid-state sintering due to the extremely high solid volume fraction and high dihedral angle with no distortion.

Zone II, a high solid volume fraction and high dihedral angle give slow liquid phase sintering, also without distortion.

Zone III, faster densification results in some distortion.

Zone IV, low solid volume fraction and low dihedral angle result in fast densification, compact strength loss, and consequently large distortion.

Zone V, solid volume fraction is below the percolation limit (0.185 vol.% solid) for compact rigidity and no composition can be sintered without distortion.

Previous observations [5, 6, 10] are superimposed on the map using W-Ni-Cu, W-Ni-Fe, W-Ni, W-Cu, Mo-Cu, Mo-Ni, and Fe-Cu. These results agree with the map and suggest it is broadly representative of liquid phase sintering systems with spherical solid grains. For systems with prismatic grains we need more experiments to confirm these.
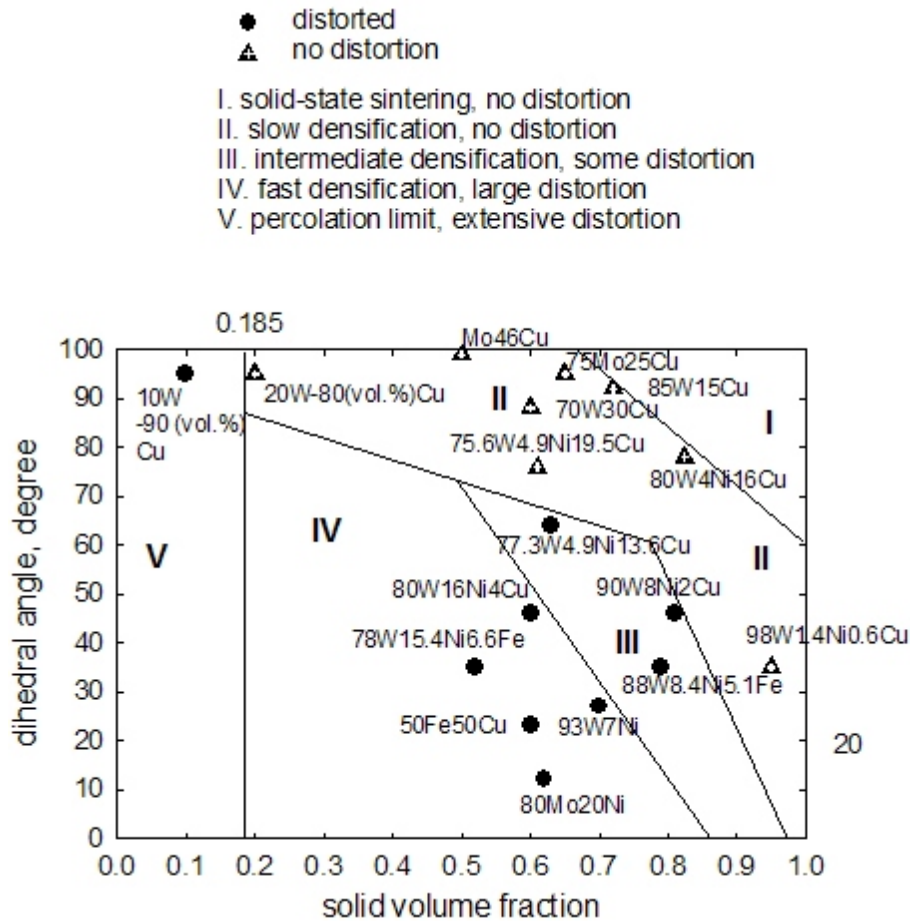
Fig. 4. Densification and distortion map for tungsten heavy alloys during liquid phase sintering.

Strategies For Distortion Control In Liquid Phase Sintering

Various strategies emerge to improve distortion control in liquid phase sintering. Since the compact strength evolution determines densification and distortion onset, the design of compositions for densification without distortion requires manipulation of the microstructure and its evolution to sustain enough compact strength to avoid distortion. As compact strength has contributions from both sinter bonds and capillary forces, in principle, processing strategies that preserve sinter bonds or capillary forces will resist distortion. Liquid phase sintering systems that densify slowly resist distortion; also they do not show a propensity for secondary rearrangement. Most practical systems that resist distortion inherently have high solid volume fractions and high dihedral angles. So one option for distortion control is to use high solid volume fraction and high dihedral angle systems. Systems with low solid solubility in the liquid phase inherently have a high dihedral angle and resist distortion. Compositions with presaturated liquid forming

agents (for example, prealloy matrix) will inhibit dissolution of sinter bonds into newly formed liquid and resist distortion. A slow heating rate at the point of liquid formation also allows solid bonds to reform before capillary forces are lost with pore closure, thereby resisting distortion. On Earth, densification and distortion are sequential events; the first focus is on densification which occurs prior to distortion. Only when open pores are eliminated and no solid skeleton has formed with gross distortion be observed. If a solid skeleton has formed prior to pore closure the compact will resist distortion. One of the surprising observations in microgravity is the migration of pores to the compact center with a sealed, dense outer compact shell. The absence of gravity induced solid grain contacts reduces the skeletal strength and the compact forms a thick shell of dense material.

Conclusions

Solid volume fraction and dihedral angle are dominant factors with respect to densification and distortion during liquid phase sintering. Distortion decreases with increasing solid volume fraction and increasing dihedral angle. Green pores affect distortion during rapid heating, especially when nearly full density is achieved or capillary forces are lost (latter happens in microgravity sintering without densification as pores cluster away from the surface). On Earth, distortion is inhibited until pores close and the compact is nearly fully densified. Hence, distortion follows densification on Earth. Microgravity results in a lower strength compact since there is no grain compression to form a solid skeleton. As pores cluster and coalesce, they become closed but not eliminated. As a consequence, microgravity compacts are weaker with more distortion and less densification. From this insight, new processing strategies emerge to improve distortion control in liquid phase sintering.

Acknowledgments

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