STRENGTH EVOLUTION IN SINTERING AS A BASIS FOR DENSIFICATION AND DISTORTION CONTROL

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Abstract
Sintering to full density enables powder metallurgy products to compete with castings and forgings. Subsieve powders with high inherent sinterability provide one means to attain densification, but at a substantial cost penalty when compared with readily available coarse compaction grade powders. Unfortunately, for large powders the sintering stress that causes densification is small and often insufficient to overcome the inherent compact strength that resists densification. In such cases, only slow diffusion controlled densification occurs. This study examines sintering densification by comparing the sintering stress and component strength during heating. Rapid densification occurs when the in situ strength is reduced to levels comparable to the sintering stress. Based on this concept, alloys are identified for full density sintering using thermal softening concepts borrowed from casting alloys.

Introduction
Sintering involves heating a packed powder to a temperature where atomic motion leads to growth of weld bonds between contacting particles. With higher temperatures or longer holds at the peak temperature, more cumulative atomic motion occurs, leading to improved interparticle bonding. For small powders, densification usually accompanies particle bonding. However, high temperatures, long times, and small particle sizes are not always economically viable for production sintering operations. Thus, most powder metallurgy sintering is performed under conditions where little densification occurs [1].

An early model for sintering by atomic diffusion was formulated by Kuczynski [2]. A teaching from this and many subsequent models is that long times are required to induce densification of large particles. As an example, 127 μm copper spheres change from 60% to 67% density after 300 h at 1020°C; but 9 μm copper spheres go from 70% to 94% density after 1 h at 900°C [3]. The 14-fold particle size reduction allows for more sintering densification in a shorter time and at a lower temperature [4].

The strong sensitivity to particle size can be explained by the balance between the
sintering stress, as generated by the capillary forces associated with small particles, and the compact strength due to combined parent material strength and neck growth between particles. From a mechanics view, deformation occurs when the applied stress exceeds the material strength. Considering the high temperatures associated with sintering, densification can be treated as a viscous flow process involving the sintering stress and evolving strength. One reason densification does not occur with large particles traces to the compact strength evolution during heating [5, 6]. Engineering materials exhibit increased atomic diffusion and lower strength when heated. For example, pure nickel loses 35% of its room temperature strength by 600°C while the grain boundary diffusion rate increases 10^{13} fold. On the other hand, powder compacts are weak at room temperature and strengthen during heating with growth of the interparticle bond. Surface transport is favored at low temperatures, resulting in bond growth and strengthening without densification. This sinter bond growth in the early portion of a heating cycle adds strength faster than the parent material loses strength due to thermal softening. In this regard, sintering contrasts with conventional metallurgy, since the powder compact strengthens while the parent material is weakening. A surprising result is that sinter strengthening goes on for most of the heating cycle. It is the increasing strength compared with the sintering stress that delays densification to high temperatures. Consequently, if sintering densification is desired, then long times, thermal softening, or high sintering stresses are required. Particle size affects sintering densification because it influences both the sintering stress and strength evolution.

Sintering Rates

Most sintering starts by growing bonds between contacting particles without densification. The sintering rate depends on atomic mobility and the microstructure stress as determined by an inverse function of the particle, grain, or pore size:

\[
\text{sintering rate} = \text{mobility} \cdot \text{stress}
\]  

(1)

Since the 1940's, many investigators have modeled sintering using various concepts for atomic motion [3]. Olevsky [7] contrasted 36 different models, showing that most follow the character established by Mackenzie and Shuttleworth [8] and Coble [9]. Thus, smaller powders, smaller grains, and smaller pores have more interfacial energy and contribute higher stresses, inducing faster sintering for any given temperature. With respect to sintering shrinkage, most of the models can be collected into a generic form as follows:

\[
\frac{1}{L_0} \frac{dL}{dt} = - \frac{A}{\eta} \frac{f(V_s)}{G^n} \Sigma^n
\]  

(2)

where \( L_0 \) is the original length, \( L \) is the instantaneous length, \( A \) is a combination of material and geometric constants, \( t \) is the time, \( \eta \) is the viscosity, \( G \) is the grain size (or other controlling microstructure feature), the grain size exponent \( m \) is typically 3, and the stress exponent \( n \) is often near 1. The density amplification function \( f(V_s) \) relates the actual (local) stress to the bulk (or applied) stress through various functions of the fractional solid \( V_s \) content or fractional solid density. The stress function \( \Sigma \) includes several factors that enhance or retard densification and deformation during sintering, including the capillary stress from the particles, applied stresses
(hot pressing or hot isostatic pressing as examples), gravity, trapped gas, or rigid inclusions. These ideas are similar to creep concepts, to the point where they have been applied to high temperature diffusional creep of sintered materials [10-13].

Sintering shrinkage is traced to dislocation motion and atomic diffusion, leading to the concept of an effective viscosity \( \eta \). Mackenzie and Shuttleworth [8] used this concept to estimate the effective viscosity of copper during sintering at 850°C as ranging from 2\( \cdot \)10\(^8\) and 3\( \cdot \)10\(^{11}\) Pa\( \cdot \)s. Such a high value has been verified by other experiments; for example, Schatt [14] found a value of 2.3\( \cdot \)10\(^9\) Pa\( \cdot \)s for copper sintering at 800°C, Hsueh, et al. [15] suggest a viscosity of 10\(^{13}\) Pa\( \cdot \)s for 65% dense alumina at 1275°C, Cai et al. [16] found 10\(^{11}\) Pa\( \cdot \)s for alumina-yttria at 1000°C, and Lal [17] measured a viscosity of 10\(^9\) Pa\( \cdot \)s for 68% dense bronze sintering at 800°C. Since sintering is usually a multiple mechanism process, links have been proposed between the active diffusion mechanisms and the effective viscosity [12,15].

During sintering, both densification and distortion show evidence of a threshold strength [8,18-20]. Gravity induces microstructure connectivity to give this threshold strength, since there was more distortion in microgravity than in parallel runs performed on Earth [21]. Three-dimensional coordination number measurements confirm that gravity induces a higher coordination number that resists deformation during sintering when compared with microgravity sintering [22,23]. Calculations based on the height to first distortion provide an estimate of the in situ threshold stress [24], giving values from 0.2 to 25 kPa [17,25]. Accordingly, sintering compacts exhibit a threshold stress that must be exceeded to induce densification.

**Sintering Stress**

The sintering rate depends on the sintering stress \( \Sigma \) which consists of several contributions. In the absence of applied pressure, a measure of the stress acting on the microstructure can be derived from the Laplace equation. This local sintering stress \( \sigma_L \), defined as the surface energy times the surface curvature (inverse of the microstructure size), is given as,

\[
\sigma_L = \gamma \frac{1}{g} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)
\]

where \( \gamma \) is the interfacial energy, \( g \) is a geometric constant, and \( R_1 \) and \( R_2 \) are the curvature radii at the surface. For a sphere, the two radii are the same and \( g \) equals 1. Various approximate solutions are available for the sintering geometry based on characteristic curvatures [26-33]. In these, the dominant effect is from the particle size, giving a compressive force distributed over the sintering bond area (stress) that depends on the sintering situation [3]. In late stage sintering, high grain boundary energies and low dihedral angles inhibit densification. Otherwise, the sintering stress is dominated by the scale of the microstructure - small particles generate higher stresses and sinter densify easier than large particles.

Rapid sintering densification can be understood via analysis of the local sintering stress when compared with the temperature dependent in situ component threshold stress \( \sigma_T \), effectively employing a Bingham response model. At low temperatures the threshold strength is high and the compact resists densification. Alternatively, at higher temperatures, thermal softening lowers the threshold strength, allowing densification in response to the sintering stress.

Besides the sintering stress associated with curved surfaces, other factors affect the
sintering response and should be included in determining the net sintering stress and densification rate, including external applied stress, and retarding effects from inclusions or trapped gases. The effect of applied pressure can overwhelm the inherent sintering stress, residual gas pressure, and inclusion effects. Consequently, many compositions that resist sintering can be densified by the application of an external pressure. The sintering stress represents the local stress at the interparticle bond. On the other hand, a bulk stress calculation would distribute that same force over the entire compact cross-section. The bulk stress associated with sintering depends on the local sintering stress, number of contacts per particle, and effective area over which the stress is distributed. Conversion to a bulk stress is needed for comparison with experimental strength tests. Unless compressed to provide mechanical interlocking, the initial contacts are points and only weak van der Waals or similar forces give strength. Sintering grows bonds between the grains, measured by the contact diameter $X$. These bonds are the origin of strength during sintering. Assume the bonds are randomly oriented with respect to the test axis. Then the bulk sintering stress $\sigma_b$ depends on the solid volumetric fractional density $V_s$, packing coordination $N_C$, neck size to particle size ratio $X/D$, and sintering stress $\Sigma$ as follows:

$$
\sigma_b = \Sigma V_s \frac{N_C}{\pi} \left( \frac{X}{D} \right)^2
$$

The average neck size to particle size ratio $X/D$ is 0.474 to 0.512 if a typical polyhedron grain shape is assumed ($N_C = 14$ or 12) at full density ($V_s = 1$). For comparison, a tetrakaidecahedron is often assumed as a grain shape in sintering. It has an equivalent neck size ratio $X/D$ of 0.56. The upper limit will be assumed as 0.5.

Early sintering is dominated by neck growth via surface diffusion with little shrinkage, while late in sintering there is slower or no neck growth, but an increase in density and coordination number. As sintering progresses, the local sintering stress decreases while the bulk sintering stress remains nearly constant. The calculated sintering stresses are consistently larger than the measured zero creep stresses, suggesting the threshold strength and sintering stress are similar during periods of densification. This implies densification requires a sintering stress relatively close to the strength.

As a new perspective, consider that atomic motion increases with temperature, while the capillary stress reflects the microstructure scale as determined by particle size. As expressed earlier, the sintering rate depends on the product of mobility and stress. Thermal softening is necessary to lower the component threshold strength to a level comparable to the sintering stress. With larger particles and lower sintering stresses, more thermal softening is required for densification. When the temperature dependent strength drops to approach the sintering stress, then shrinkage occurs in inverse proportion to the effective viscosity. Several studies have shown the onset of rapid shrinkage correlates with plastic flow. Hence, the key to understanding sintering densification comes from attention to the relative sintering stress and component strength. The in situ component strength depends on the sinter bond size, density, and parent material thermal softening behavior.

**Sintering Strength**

A component’s in situ strength arises from the sinter bonds formed between contacting
particles. These bonds grow at the initial particle contacts and spread across the particle interfaces. They are the source of strength, as evident by examination of fractured samples after sintering. The strength of the sintered structure depends on the inherent material strength $\sigma_o(T)$ at the test temperature (grain size corrected) and the percent of interface area involved in the bond and stress concentration factor associated with the sharp neck radius.

In sintered porous structures, the initial sintering strength varies with the square of the neck size $X$ to particle size $D$ ratio $(X/D)^2$ and coordination number $N_c$, giving a measured in situ sinter bond strength $\sigma_s$ as

$$\sigma_s = \frac{\sigma_o}{K} V_s \frac{N_c}{\pi} \left( \frac{X}{D} \right)^2$$  \hspace{1cm} (5)

where $K$ is the stress concentration factor that reduces the test strength in proportion to the neck curvature. From stress concentration concepts, it is inversely proportional to the curvature at the base of the neck, which depends on the neck size ratio.

The maximum neck size ratio $X/D$ is near 0.5, but in cases where the dihedral angle $\phi$ is below 60° the final neck size is limited as follows:

$$\frac{X}{D} = \sin \left( \frac{\phi}{2} \right)$$  \hspace{1cm} (6)

In solid-state sintering, the dihedral angle $\phi$ links the solid-solid (grain boundary) energy with the solid-vapor surface energy, while in liquid-phase sintering it links the solid-solid (grain boundary) energy to the solid-liquid surface energy. Thus, if not limited by the dihedral angle, then the peak neck size ratio $(X/D)$ is near 0.5. If the dihedral angle is under 60°, then the peak sintered density and strength are limited by the dihedral constraint. Densification induces new grain contacts leading to further strengthening.

Transverse rupture strength tests during sintering provide a basis for comparison of the sintering strength with the model. The transverse rupture tests give approximately 1.6 to 2.1 times higher strength when compared to the tensile strength [1]. Alternatively, the stress concentration factor provides an equal, but opposite, compensation when $X/D$ reaches 0.5. As an example of the strength attained during sintering, Lal [17] measured 22 µm loose spherical bronze powder for in situ strength after heating to 75% density at 850°C. Using thermal softening transverse strength data from Shoales and German [6], the calculated bulk in situ strength is 37 MPa while the measured in situ transverse strength is 32 MPa. Similarly, using data from Shoales [5] for compacted 26 µm bronze, gives a predicted strength at 800°C of 46 MPa which compares favorably with a measured value at 48 MPa.

Most metals have surface energies between 1 and 2 J/m², so the direct route to a high sintering stress and rapid densification is via small particles. For example, 10 µm stainless steel powder used in injection molding has a local sintering stress near 6 MPa after 2% shrinkage (corresponding to a bulk stress near 0.7 MPa). As neck growth and densification progress, this stress falls. At 96% density the local and bulk sintering stresses are both about 3.5 MPa. For a larger powder, the sintering stress can be as small as 0.02 MPa. These are not high stresses, so
most large metal powders sinter bond (strengthen) but do not sinter densify. Large powders are sufficiently strong when compared to the sintering stress that they resist densification during sintering. As the particle size increases, the lower sintering stress requires a progressively higher temperature (more thermal softening and more atomic motion) before densification is evident. Thus, small particles sinter densify because of a high inherent sintering stress as compared with the *in situ* strength.

**Atomic Motion**

Besides sintering stress, atomic mobility is a controlling factor in sintering. Sintering will not occur without thermally induced atomic motion, as evident by the lack of sintering in most powders at room temperature. Neck size depends on the cumulative amount of atomic motion over time. Surface transport mechanisms (evaporation-condensation and surface diffusion) move atoms on the pore surfaces, giving particle bonding and compact strengthening, but do not produce densification. Surface diffusion dominates the low temperature sintering of most metals. Bulk transport processes (volume diffusion, grain boundary diffusion, plastic flow, dislocation climb) simultaneously promote neck growth and shrinkage by moving mass from between particles to the interparticle bond. Diffusion processes give slow densification. Plastic flow is active when the microstructure is highly curved, but dislocation generation at the interparticle bonds decays during sintering [14].

Viscous flow densification occurs in metals with liquid phases on the grain boundaries [19]. Sintering additives enhance densification by forming liquid films on the grain boundaries. Schatt [14] shows this leads to an effective viscosity for the system, making it possible to model all forms of sintering with viscous flow concepts using a Bingham model for densification. From an atomistic view, sintering by diffusion processes is slow. On the other hand, for fast sintering of large particles, as desired by industry, rapid densification by viscous or plastic flow is more attractive. A problem is that large particles have low sintering stresses and prove difficult to sinter densify.

An opportunity for sintering densification is apparent when grain boundary wetting liquids form in the microstructure. Mass transport is very rapid in the presence of a liquid phase, often over 100-times faster than in solids. However, formation of a liquid is not sufficient to ensure densification since the solid phase must be soluble in the liquid to generate significant atomic flux [3,10]. It is the combined solubility and atomic mobility that determines the sintering rate. Liquids with no solubility for the solid give no densification benefit beyond that from solid-state sintering of the skeleton. In large particle mixtures, such as Fe-Cu, copper induces interparticle sinter bonding and compact strengthening, but not densification. Consequently, net sintering dimensional change for a 100 µm particle size mixture of Fe-Cu is nearly zero. In this case the low Fe solubility in copper and the high skeletal strength retard densification. If there is no solid solubility in the liquid, then the liquid provides no benefit.

**Thermal Softening**

An opportunity for sintering densification of large powders in short sintering times comes through analysis of the material strength evolution during sintering. Wrought materials weaken on heating - thermal softening. For example, the strength of copper drops 10% between room temperature and 200°C, nickel strength drops 35% from room temperature and 600°C, and low alloy steel loses 60% of its room temperature strength by 600°C.
**Figure 1.** The yield strength for bulk, annealed 316L versus test temperature. As with most engineering materials, thermal softening occurs with higher temperatures to a point where almost all strength is lost at the solidus temperature.

Fig. 1 plots the strength of 316L stainless steel versus test temperature and shows a curve fit to give zero strength at the melting temperature. From this plot, the extrapolated 1250°C strength for full density material is 25 MPa, which is above the peak sintering stress for 10 μm injection molding grade powders after just 1% shrinkage. Above 1300°C, the strength falls below 10 MPa, allowing 2% shrinkage before the bulk sintering stress equals the strength. By 1330°C the strength is down to 5 MPa and the sintering stress and *in situ* strength are equal at 72% density, and at 1360°C this density is 94%. Consequently, injection molding grade stainless steel powder is predicted to rapidly sinter densify at temperatures near 1360°C, in agreement with practice. In substantiation of this prediction, Fig. 2 plots sintered density for an injection molded 316L stainless steel powder (nominal size of 15 μm) versus peak hold temperature and shows the density for each temperature where the calculated sintering stress equals the *in situ* strength. Densification increases with temperatures over 1300°C, as predicted based on the combination of sintering stress and *in situ* strength.

Hence, the difficulty in sintering large particles to full density comes from the combination of a low sintering stress and high *in situ* strength. A pressed compact starts with a green strength between 2 and 20 MPa. Unlike a bulk material that thermally softens, sinter bonding increases the compact strength during heating. Details of the *in situ* strength evolution and thermal softening during sintering were unknown until recently [5,6]. Fig. 3 plots these results for the *in situ* strength of die pressed 26 μm bronze powder during heating at 10°C/min. Note the green strength is 10 MPa. Initial annealing occurs up to 400°C, lowering the *in situ* strength.
Figure 2. Sintering densification data for an injection molded 316L stainless steel powder heated to various temperatures for 2 h. First significant densification is evident at 1300°C. The solid line shows the calculation results for the conditions where the sintering stress equals the in situ strength.

Figure 3. Strength evolution associated with the sintering of a 26 μm bronze powder, compacted to 86% density, heated at 10°C/min [6]. The green strength was 10 MPa. Three curves show the in situ strength versus test temperature during heating, the room temperature strength after heating to these same temperatures, and the strength during cooling from a peak sintering temperature of 800°C.
strength to 4 MPa. Beyond 400°C the strength climbs rapidly due to sinter bond growth, and peaks at 600°C. Thermal softening dominates the in situ strength over 600°C. This plot also gives the room temperature sintered strength determined on parallel samples cooled from the same peak temperatures. This latter curve is widely reported as part of sintering studies, showing a progressively higher sintered strength with a higher peak temperature. Finally, thermal softening is evident from strength measurements taken during cooling from a peak sintering temperature of 800°C. Substantial strengthening occurs, with a final room temperature strength of almost 700 MPa, although the in situ strength at 800°C was 50 MPa. This 14-fold strength increase on cooling reflects the thermal softening between room temperature and 800°C.

Although the compacts thermally soften at the higher temperatures, the strength remains high up to nearly the solidus temperature. For these same compacts, parallel dilatometer and differential thermal analysis tests show first melt formation at 861°C. Dilatometer measured in situ dimensional change showed no densification up to 600°C, and significant densification over 800°C where the in situ strength approaches the calculated sintering stress.

**Mechanical View of Sintering Densification**

A new view of sintering densification comes from consideration of the strength evolution and sintering stress. The focus shifts from concern over atomic motion to consideration of the mechanical response of the compact. Accordingly, densification critically depends on the sintering stress exceeding the threshold strength. The conceptual base for this mechanical view is captured in Fig. 4 via schematic tensile curves over a range of temperatures. The tensile curve consists of elastic and plastic regions, the former being recoverable and not contributing to densification. As temperature increases, the strength and elastic modulus fall and the ductility usually increases, but falls at high temperatures. Densification by plastic flow is expected when thermal softening lowers the flow stress to a level comparable to the sintering stress. When this occurs there must be significant atomic mobility. The larger the sintering stress (smaller the particle size), the lower the temperature for the onset of densification during heating. At high temperatures, slow solid-state densification occurs by diffusional creep, while strengthening from bond growth can occur without densification. Ignoring creep gives a simple notion for full density sintering in short times based on the in situ stress state. For larger particle sizes with low sintering stresses, sintering densification is hindered by the inherent compact strength. If the compact is thermally softened to a level approaching the sintering stress, then it densifies. Unfortunately, because of the low sintering stress, more thermal softening is required for large particles that otherwise resist densification. Supporting this concept is recognition that most sintering occurs during heating to the sintering temperature. Accordingly, isothermal holds are very short in industrial sintering. Indeed, many dilatometer traces show more shrinkage during heating that once isothermal conditions are attained, in line with a dominant role from thermal softening as compared with diffusion controlled densification.

The pathway shown for bronze, where strength increases before densification, has been verified for several materials. For example, mixed 125 μm water atomized iron and copper powders with graphite (2 wt.% Cu and 0.8% C), compacted to 7.37 g/cm³ has a green strength of 12.1 MPa. After heating at 10°C/min the in situ transverse rupture strength increases to 56 MPa at 1100°C, and on cooling to room temperature is over 1000 MPa. The predicted strength at 1100°C is near 44 MPa, while the calculated sintering stress is 3.5 MPa. Since the strength is more than 10-fold higher than the stress, the compact resists sintering densification and only
Figure 4. A schematic of the mechanical view of sintering, showing elastic-plastic tensile stress-strain curves for various temperatures. At higher temperatures there is a lower strength and eventually thermal softening brings the strength to a level comparable to the sintering stress, giving densification.

Figure 5. Distortion versus shrinkage for 22 µm bronze powder during heating at 5°C/min. The component distortion is labeled as "distortion," in situ video imaging of a cantilever section "deflection", and time dependent creep "rate" versus the sintering shrinkage for initially loose (5.2 g/cm³) powder [17]. The results illustrate densification occurs prior to distortion.
slow creep densification occurs in sintering (less than 0.1% shrinkage). Computer simulation suggests a final density of 7.5 g/cm³ (0.6% shrinkage) is possible after 120 h at 1120°C. Alternatively, very high temperatures would give sufficient thermal softening for rapid densification. Thus, a fundamental problem in sintering large powders to full density in short sintering times is the in situ strength. As particle size increases, the sintering stress decreases, yet surface transport controlled sinter bonding increases the strength at the sintering temperature. In short, the resistance to rapid densification results from the strength of the sintering material far exceeding the sintering stress.

A Means for Densification of Large Powders

Many target large particle size powder metallurgy alloys are too strong for sintering densification in conventional cycles. The low sintering stress is inadequate to induce densification. An option is to weaken the sinter bonds formed during heating is via liquid phases. Low strengths are associated with liquid films on grain boundaries, a fact recognized in liquid metal embrittlement, semisolid forming, hot tearing, grain boundary melting, spray deposition, and supersolidus sintering. In castings, when liquid forms on the grain boundaries the tensile strengths often falls below 1 MPa. There is almost no measurable strength when most of the grain boundaries are wetted. The liquid quantity for significant strength loss depends on the alloy composition and dihedral angle; for example Cu alloys containing Bi are sensitive to liquid formation because the dihedral angle is 0°. In high dihedral angle materials, sintering distortion is resisted down to 20 vol.% solid, similar to the point of first observable strength in casting alloys. Both cases represent similar percolation limits.

Casting alloys have been examined for strength versus temperature in the solid-liquid temperature range. The data suggest liquid formation on grain boundaries is a means to tailor strength to match the sintering stress for densification. Tensile tests on iron and aluminum alloys near the solidus temperature give strengths well below 1 MPa when a grain boundary liquid forms. Dahle and Arnberg [27] measured strengths in the 0.001 MPa range with 80 vol.% liquid for various aluminum alloys. As expected, the strength is zero near the percolation limit at 20 vol.% solid, but increases rapidly with solid fraction. Extrapolation to 15 vol.% liquid suggests a strength near 2 MPa. For comparison, a 20 μm powder gives an initial sintering stress in the 2 to 3 MPa range. Thus, sintering densification would be possible when sintering at a temperature that gives near 15 vol.% liquid. Alloys exhibit strength loss and ductility loss near the solidus temperature. Liquid formation on the grain boundaries weakens the structure and provides a means to overcome a high strength during sintering, independent of the particle size.

Distortion and Dimensional Control

One difficulty with attaining a low in situ strength for sintering densification is concomitant distortion. A compact that becomes too weak will densify, but not retain shape. The threshold stress for densification is low, and progressively falls as temperature increases. This is especially true if liquid aggressively penetrates the grain boundaries during sintering. During this weakening transient, several forces such as gravity act to distort the compact. From video imaging and other tests, distortion seems to occur when the strength falls too much during sintering. For example, distortion in tungsten W-Ni-Fe heavy alloys occurs at 60 vol.% solid where the in situ strength is 0.6 MPa.

To investigate the strength window between densification and distortion, experiments
were conducted with loose powder where the initial strength was as low as possible. To form test compacts, loose 22 μm bronze powder was heated at 10°C/min to 400°C in a crucible to provide handling strength. This presintered structure was removed from its crucible and subsequently tested for sintering shrinkage using dilatometry. Distortion after sintering was quantified using the difference in point-to-point (anisotropic) final dimensions. The 22 μm bronze powder resisted distortion up to 900°C once sinter bonding created in situ strength. This is evident in Fig. 5 which shows densification occurs before significant distortion. Deflection and its rate were measured in situ via video imaging while the distortion was measured after sintering. All three measures show shape preservation to near full density.

It is characteristic of approximately ten sintering systems investigated to date that densification occurs before distortion (beyond distortion from nonuniform heating or green density gradients). Only when the in situ strength is below 1 MPa is distortion detected. Strengths as low as 2 kPa have been measured at the onset of distortion.

To densify large particles in short sintering times, it is important to soften the particles while not lowering the strength to a point where gravity causes distortion. This requires both composition and temperature control. Dimensional control is improved by keeping the component squat. Fig. 6 shows the results of 14 different sintering experiments, where various compositions were examined for distortion as a function of the microstructure [25]. Here the distortion after sintering is plotted versus a material independent strength function ($V_S N_C \sin^2(\phi/2)$). Distortion is clearly linked to a low microstructure strength during sintering.

![Figure 6](image)

**Figure 6.** Sintering distortion as a function of the strength function calculated from experiments with 14 different compositions processed by liquid phase sintering, data from ref. [25].
Liquid Formation Role

In identification of candidate systems for sintering densification, the key is to lower the *in situ* strength to levels comparable to the sintering stress, while not lowering the threshold strength or contiguity to a point where distortion occurs. Liquid phases are a means to weaken a compact to enhance the sintering densification of large powders. In many cases, newly formed liquid penetrates interparticle bonds and disintegrates the solid particles into grains smaller than the original particles by secondary rearrangement.

When an additive particle melts near a solid skeletal sinter bond, there is a possible penetration of the grain boundary in the sinter bond between particles. At equilibrium, the dihedral angle $\phi$ describes the grain boundary groove balance of surface tensions between solid and liquid phases. Differentiation allows analysis for the dihedral angle sensitivity to changes in solid-liquid surface energy,

$$\frac{d\gamma_{SL}}{\gamma_{SL}} = \frac{d\phi}{\phi} \frac{\phi}{2} \tan\left(\frac{\phi}{2}\right)$$

(7)

The momentary decrease in solid-liquid surface energy traces to the reduction in free energy during solid dissolution across the interface into newly formed (unsaturated) liquid. Substantial drops in the solid-liquid surface energy are possible. The concern is with the relative change needed to disintegrate grain boundaries and weaken the solid skeleton. This corresponds to a reduction in dihedral angle $\phi$ to zero, or $d\phi = -\phi$. Accordingly, $d\phi/\phi = -1$, giving a relation for the relative solid-liquid surface energy decrease needed for grain boundary penetration,

$$-\frac{d\gamma_{SL}}{\gamma_{SL}} = \frac{\phi}{2} \tan\left(\frac{\phi}{2}\right)$$

(8)

Larger decreases in solid-liquid surface energy are required to penetrate high dihedral angle grain boundaries. If the dihedral angle is 30° (0.524 radian), then a 7% decrease in the relative solid-liquid surface energy leads to liquid penetration of the grain boundaries. Alternatively, for a 60° (1.048 radian) dihedral angle, the required surface energy reduction is close to 30%. The typical surface energy is less than 100 kJ/mol, so a 7% decrease amounts to 7 kJ/mol energy decrease associated with solvation, which is reasonable for many systems. Wetting systems with low dihedral angles (those with a high solid solubility in the liquid), offer the largest opportunity for grain boundary penetration upon first melt formation. These same characteristics are associated with activated sintering.

Applications

Thermal softening is a natural consequence of atomic motion, which is the same underlying cause of sintering densification. Consequently, temperature is important to sintering densification. Powder compacts densify when they are thermally softened. When the particle size is large, the sintering stress is low and very high temperatures are required to induce sufficient thermal softening and viscous flow densification. Microstructure weakening occurs when liquid phases attack the interparticle bonds formed during heating. Dissolution of sinter
bonds depends on the dihedral angle. For example, the maximum solubility of W in solid Ni is 14.7 at.%. Upon melt formation at 1495°C the solubility of W in liquid Ni increases to 20 at.%. With extrapolations from the thermochemical data, this corresponds to a free energy change of 10 kJ/mol. Such a free energy change will lead to a zero dihedral angle for the newly formed liquid, since the solid-liquid surface energy is momentarily reduced to near zero by solid dissolution into the liquid. The consequence is liquid penetration of the interparticle grain boundary at the sinter bonds, eliminating the strength that would otherwise resist densification.

A high solid solubility in the liquid correlates with a low dihedral angle and easy melt penetration of grain boundaries. A significant link is observed between the dihedral angle \( \phi \) in degrees and the change in atomic solubility on melt formation. Effectively, systems that exhibit an increase in atomic solubility of the solid phase into newly formed liquid have low dihedral angles. In turn, low dihedral angles imply easier melt penetration of the interparticle bonds. Application of this concept leads to a search for sintering systems with low dihedral angles and large solid solubility changes on melt formation.

Because of the loss of structural rigidity, distortion would be expected. However, if pores are not saturated with liquid, then capillary forces from the wetting liquid provide sufficient strength to resist distortion, especially in smaller compacts. As chemical equilibrium is attained, liquid retracts from the grain boundaries and solid-solid bonds reform. For common liquid phase sintering systems, such as W-Ni-Fe and Fe-Cu, liquid pools remain on grain boundaries. Contiguity measurements in W-Ni show solid bonds that existed at 1000°C disintegrate on melt formation. The contiguity passes through a minimum after 3 min and recovers over the next 20 min at temperature. Rapid sintering shrinkage occurs while the microstructure is soft.

Conclusions

Basic stress-strength mechanical ideas are applied to sintering. Unlike bulk materials that thermally soften with heating, the pathway for powder compacts is more complicated. A combination of sinter bonding and thermal softening determines the resistance to densification for both large and small powders. Small powders have higher sintering stresses and prove easier to densify in short times when the \textit{in situ} strength and viscosity fall at high temperatures. On the other hand, large powders have lower sintering stresses such that the \textit{in situ} strength resists densification during sintering. Slow diffusional creep processes give some densification, but not in time frames compatible with industrial powder metallurgy practice.

Liquid phases provide a means to lower \textit{in situ} strength during sintering. A low dihedral angle is preferred, but if the dihedral angle approaches zero and pores are saturated with liquid then all strength is lost and the component distorts. Since liquid wetting and the solid:liquid ratio depend on temperature, good temperature control is required in these processes. With large powders the sintering stress is low, so only a low \textit{in situ} strength will allow densification. A large change in solid solubility on melt formation is a predictor of sintering densification. From these principles, several alloys have been designed for full density processing and thermal cycles defined for improved dimensional control.

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