Strengthening Porous Metal Skeletons by Metal Deposition from a Nanoparticle Dispersion

by

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ABSTRACT

The accuracy of solid freeform fabrication processes such as three-dimensional printing (3DP) and selective laser sintering (SLS) must be improved for them to achieve wide application in direct production of metal parts. This work seeks to reduce sintering and deformation of porous metal skeletons during liquid-metal infiltration by reinforcing the skeletons with metal deposits. This can be accomplished by depositing a metal from a suspension of nanometer-scale iron particles. The nanoparticle deposits from the suspension concentrate in regions of high stress when the solvent is removed by drying. The particles are sintered to create a dense structure that reinforces the porous skeleton—reducing deformation and creep. Generically, this work studies a process for metal deposition from a liquid carrier with unique transport characteristics compared to traditional metal deposition processes such as plating, chemical vapor deposition, evaporation, and sputtering.

This process of depositing metal from nanoparticle suspensions is studied using a commercial product of iron nanoparticles. The processed iron particle suspension contains significant carbon from the organic dispersants used to stabilize the suspension. Gas adsorption, X-ray diffraction, and SEM imaging were used to show that the carbon aids reduction of any iron oxide on heating and strongly influences the densification characteristics.

The iron nanoparticles are applied to porous steel skeletons produced by sintering stainless steel powder. These are then heated to typical steel infiltration temperatures of 1284 °C. The nanoparticle deposits are shown to reduce creep deflections at infiltration temperatures by up to 95% and reduce shrinkage by up to 60%. The best results are obtained by repeating the process of applying the nanoparticles, drying the solvent, and sintering them to 700 °C up to four times. The performance in magnetic materials can also enhanced by applying a magnetic field along the magnetic particles. This magnetic field concentrates the nanoparticle deposits into the contact points between the skeleton particles where they provide optimal benefit.

Thesis Supervisor: Emanuel M. Sachs
Title: Fred Fort Flowers '41 and Daniel Fort Flowers '41 Professor of Mechanical Engineering
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<td>Angle from the axis of symmetry of a particle bond to the surface of the particle measured from the center of the particle.</td>
</tr>
<tr>
<td>$\alpha_{\text{max}}$</td>
<td>The value of $\alpha$ which lies at the interface between the particle and the neck bond</td>
</tr>
<tr>
<td>$\beta$</td>
<td>Neck concentration fraction—the fraction of deposited material deposited in the necks</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Thickness of grain boundary diffusion region</td>
</tr>
<tr>
<td>$\epsilon$</td>
<td>Strain</td>
</tr>
<tr>
<td>$\epsilon_1$, $\epsilon_2$</td>
<td>Strain in bar 1 and bar 2</td>
</tr>
<tr>
<td>$\dot{\epsilon}$</td>
<td>Strain rate</td>
</tr>
<tr>
<td>$\dot{\epsilon}_1$, $\dot{\epsilon}_2$</td>
<td>Strain rate in bar 1 and bar 2</td>
</tr>
<tr>
<td>$\dot{\epsilon}_{\text{bond}}$</td>
<td>Average strain rate in an interparticle bond</td>
</tr>
<tr>
<td>$\dot{\epsilon}_{\text{particle}}$</td>
<td>Average strain rate in a particle</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Surface energy</td>
</tr>
<tr>
<td>$\Delta p$</td>
<td>Pressure difference across an interface due to the surface energy of the interface</td>
</tr>
<tr>
<td>$\rho$</td>
<td>Density</td>
</tr>
<tr>
<td>$\rho_{\text{skeleton}}$</td>
<td>Effective density of a porous metal skeleton</td>
</tr>
<tr>
<td>$\rho_{\text{water}}$</td>
<td>Density of water</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Stress</td>
</tr>
<tr>
<td>$\sigma_{\text{avg}}$</td>
<td>Average stress over an area. Does not compensate for pores on the area</td>
</tr>
</tbody>
</table>
$\sigma_{\text{bond}}$ Average stress across an interparticle bond

$\sigma_{\text{homax}}$ Homogenous stress at the outer surface of the cantilver where it is at its peak. The homogenous stress is the stress calculated if a homogenous material is assumed—no corrections are made for pores

$\sigma_{\text{particle}}$ Average stress across a sectioned particle

$\sigma_{\text{solid}}$ Average stress over the solid material in an area. Stress is compensated for the average porosity

$\Gamma_b$ Grain boundary sintering scaling factor that incorporates kinetic affects related to the microstructure

$\Gamma_v$ Volume sintering scaling factor that incorporates kinetic affects related to the microstructure

$\Omega$ Atomic volume – the average volume associated with a single atom in a crystal lattice

$a$ Lattice parameter, in a cubic lattice it is the length of the side of the cube

$a_s$ Area fraction of interparticle bonds on a cross section

$A'$ Prefactor for a power law creep expression that does not include any microstructural, temperature or process parameters. Should be of order unity

$A$ Prefactor in the power law creep equation that combines many microstructural, material, and process parameters

- Length of the diagonal along face of a cubic unit cell
- Burger's vector in creep and diffusion modeling

$b$ Kinetic coefficient in generalized representation of the sintering rate equation

$B$ Collection of kinetic and stress terms in the creep rate equation that simplifies the expression for the activation energy

$B_l$ Structural dependent factor that relates the ratio of the neck diameter to the particle diameter to the area fraction of bonds on a cross section

$c$ Coordination number—the average number of bonds per particle

$c_n$ Concentration of particles in the binder by volume

$c_v$ Proportionality constant between the strain rate at a particular location and the tip deflection rate

$d$ Grain size
- Particle diameter
- Diffusivity

\( D \)  
Frequency factor in the diffusivity equation

\( D_o \)  
Grain boundary diffusivity

\( D_v \)  
Diffusivity in the grain volume

\( E \)  
Elastic modulus

\( E^* \)  
Effective elastic modulus relating creep rate to stress for diffusional creep (stress exponent of one)

\( f \)  
packing fraction, fraction of the total volume occupied by powder

\( f_{bond} \)  
volume of additional neck material obtained per unit part volume by applying nanobinder

\( f_{closepacked} \)  
Packing fraction of a close-packed structure, approximately equal to 0.74

\( f_{pc} \)  
Packing fraction of a primitive cubic cell

\( g \)  
Acceleration due to gravity

\( G \)  
Shear Modulus

\( h \)  
- (neck volume model) Distance from the plane of symmetry of an idealized cylindrical neck bond to the interface between the idealized bond and the particle.  
- (cantilever stress model) thickness of the cantilever perpendicular to the neutral axis

\( k \)  
Boltzmann’s constant

\( k_p \)  
Parabolic rate constant

\( l \)  
- (neck volume model) Distance from the axis symmetry of an idealized cylindrical neck bond between equal sized spheres and the surface of the bond  
- (cantilever stress model) length of the cantilevered portion of the bar

\( L \)  
Distance between two adjacent particles. \( L \) decreases when there is sintering shrinkage

\( m \)  
Exponent in the generalized sintering rate equation that relates grain size to rate of neck growth. Value depends on the sintering mechanism
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n_s$</td>
<td>Exponent in the generalized sintering rate equation that relates neck growth rate to time. Its value depends on the sintering mechanism.</td>
</tr>
<tr>
<td>$n$</td>
<td>Stress exponent in the creep equation. Strain rate is proportional to stress to the power of $n$.</td>
</tr>
<tr>
<td>$n_a$</td>
<td>The number of times binder is applied.</td>
</tr>
<tr>
<td>$\bar{p}$</td>
<td>Volume fraction of pores in a sample.</td>
</tr>
<tr>
<td>$p$</td>
<td>Pressure.</td>
</tr>
<tr>
<td>$q$</td>
<td>Exponent in a generalized creep equation that relates the dependence of creep rate on the microstructure length scales. Its value varies with the creep mechanism.</td>
</tr>
<tr>
<td>$Q$</td>
<td>Activation energy for creep process.</td>
</tr>
<tr>
<td>$r$</td>
<td>Particle radius.</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant.</td>
</tr>
<tr>
<td>$R_1, R_2$</td>
<td>Principal radii of curvature of a surface.</td>
</tr>
<tr>
<td>$s$</td>
<td>The binder saturation-fraction of pore space filled with binder during an application.</td>
</tr>
<tr>
<td>$t$</td>
<td>Time.</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature.</td>
</tr>
<tr>
<td>$T_m$</td>
<td>Melting temperature.</td>
</tr>
<tr>
<td>$T_o$</td>
<td>Arbitrary reference temperature.</td>
</tr>
<tr>
<td>$v$</td>
<td>Pore volume per unit mass of material.</td>
</tr>
<tr>
<td>$v_b$</td>
<td>Volume of a single neck (interparticle bond) between two particles.</td>
</tr>
<tr>
<td>$v_{binder}$</td>
<td>Volume of binder material added per unit volume of the part.</td>
</tr>
<tr>
<td>$V_{bonds}$</td>
<td>Half of the volume of all the bonds on a particular particle. The other half of the bond volume is attributed to the neighboring particle.</td>
</tr>
</tbody>
</table>
\( V_{\text{particle}} \) The volume of a single particle

\( W_{\text{dry}} \) Weight of a dry porous part

\( W_{\text{submerged}} \) Weight of a submerged porous part

\( W_{\text{wet}} \) Weight of a wet porous part directly after submerging. Excess water is removed from the surface with a paper towel

\( x \) Horizontal position

\( X \) Diameter of the neck bond between two particles

\( \frac{X}{D} \) Ratio of the bond diameter to the particle diameter, a dimensionless measure of bond size

\( y \) Vertical position

\( \Delta y \) Vertical tip deflection of a cantilever bar

\( \dot{\Delta y} \) Rate of vertical tip deflection of a cantilever bar

\( \Delta y_o \) Reference vertical tip deflection rate, value is arbitrary

\( \Delta y_{\text{treated}} \) Vertical tip deflection of a nanobinder treated cantilever bar due to creep at high temperatures

\( \Delta y_{\text{untreated}} \) Vertical tip deflection of an untreated cantilever bar due to creep at high temperatures
1 Introduction

This thesis shows that suspensions of nanometer particles can be added to porous powder metal forms to substantially reduce dimensional changes during high-temperature processing. This chapter reviews the motivation for reducing dimensional changes, alternative methods to improve the dimensional stability, and the rationale for studying this option.

1.1 Motivation

The advent of computer control opened the way to a new class of manufacturing procedures called solid freeform fabrication (SFF). SFF processes can create complex geometry, geometries that would be very difficult or impossible by many other applications and do it without specialized tooling. [1].

While the various SFF processes are each unique, most of them are additive processes in which the parts are built up in layers. As a class, these processes are applicable to all classes of materials, but individual methods are limited as to the materials and/or properties that are achievable.

The quick production time and low cost of variation also make SFF processes potentially attractive in manufacturing of tooling such as injection molds and direct production of low volume parts. In some cases such as ceramic mold production for metal
Introduction

castings, SFF processes have achieved significant market penetration. However, in the direct production of metal components, SFF processes have made limited progress. These applications are still limited by the inability of these processes to simultaneously achieve good production rate, accuracy, and material properties.

Laser-based methods manage to attain two of the three required attributes (accuracy/resolution, material properties, and rate), but never all three. Direct melting as practiced by Optomec and POM Group produces parts with good resolution and material properties but requires long build times. Aeromet uses larger laser sources to increase build time at the cost of resolution.

Powder-based SFF processes like Selective Laser Sintering (SLS) and 3D printing (3DP) build parts more quickly with good resolution. However, the printed parts are porous and must be densified, typically by bronze infiltration. The resulting parts are inferior to wrought materials and designers are reluctant to accept these uncharacterized materials. An SFF process that can produce metal parts of standard accepted alloys with reasonable rate and accuracy can dramatically increase the application of SFF.

Recent developments in post-processing of powdered metal parts have enabled the production of metal parts by two SFF processes, Three-Dimensional Printing (3DP), and Selective Laser Sintering (SLS), with properties comparable to wrought tool steels. This new process, homogenous steel infiltration is discussed in Section 1.1.4. Since good material properties and acceptable rates are now possible in these systems, this work seeks to increase the dimensional accuracy of these processes. These processes are summarized below.

The goal of this work is to increase the final accuracy of the parts by reducing dimensional changes during processing. Thus, parts may combine the improved material properties from steel infiltration and the good rates of 3DP and SLS with reasonable accuracy.
1.1.1 THREE-DIMENSIONAL PRINTING (3DP)

Three-dimensional Printing (3DP) is an SFF process in which geometries are produced by selectively applying a liquid binder to a loose powder as illustrated in Figure 1-1. In 3DP, components are built up layer by layer in an iterative process. First, a layer of powder is spread. Then an ink-jet style printhead is moved across the powder under computer control to selectively bind the powder together where positive geometric features are desired. The part is lowered, and a new layer of powder is spread over the top. The process is then repeated until the entire geometry is complete. [2]

![Figure 1-1](image)

**Figure 1-1 The basic 3DP Process.** A liquid binder is printed into thin powder layers to form geometry. The process is repeated with additional layers until the entire geometry is formed.

Parts can be produced from any powdered material including metal, ceramic, and plastic. The composition can be adjusted locally by adding dopants to the binder. Overhangs are inherently supported by the surrounding powder during printing. However, if loose powder needs to be removed from cavities, holes must be provided for extraction. 3DP applications include ceramic casting molds, carbide cutting inserts, metal injection mold tools, appearance models, gas filters, tissue scaffolds and many more.

Once the part geometry is formed, the part must be post-processed to achieve the final properties desired. The procedures depend on the material system and the final properties desired. The basic process is as follows:
1. **Binder curing** – Some binders require further treatment to develop sufficient strength to be handled. This may range from drying water-soluble polymer binder to sintering colloidal silica binders at 1200°C.

2. **Part removal** – The green part is removed from the powder bed and powder is extracted from the cavities. In the green parts, open pores constitute approximately one third of the part volume.

3. **Binder removal** – In some systems such as metal bound with water-soluble polymers, the binder is extracted via thermal and/or chemical processes.

4. **Densification** – In most cases, the porous printed parts must be densified. This can be accomplished by sintering or by infiltration.

   The specific steps are customized for each material system and can be adjusted to produce a wide variety of final material properties.

   Part resolution may be controlled by the size of the powder particles or the binder droplets. While it is difficult to spread powders below 1-10 μm, sub micron powder may be deposited from a slurry to enable higher resolution geometry [3]. While smaller droplets can be produced from some commercial printheads, typical drop sizes in current 3DP machines are 25-45 μm. The accuracy of as-printed metal parts is typically 1-2 particle diameters (100 μm) [4] although the motion systems or printhead instability may introduce additional errors.

   3DP production rate scales very well. Typically, the printing time dominates the layer formation time. However, this can be reduced by increasing the speed of the motion system and the number of printing nozzles. With online diagnostics, the software can compensate for differences in droplet alignment and flow rate between printheads to maintain high print quality with large numbers of nozzles. One 3DP licensee, ProMetal, produces machines with 128 jets. Multiple parts may also be produced simultaneously in the same bed. However, post-processing may require more time than printing.

### 1.1.2 SELECTIVE LASER SINTERING (SLS)

In selective laser sintering (SLS), parts are built up from layers of powder as in 3DP. However, in this case, a polymer binder is mixed into the powder. The primary powder can be metallic, ceramic, or polymer. To form geometry, a laser scans the surface...
and melts the polymer. The melted polymer then flows between adjacent particles and bonds them together. A new layer is spread and the process repeats until the entire geometry is formed. Typical laser powers for this process are between 25 W and 200 W. The process is illustrated in Figure 1-2. [5]

![Figure 1-2 The basic Selective Laser Sintering (SLS) Process for metal parts. A polymer is mixed into a metal powder. When a laser is scanned over the powder, the polymer melts and bonds neighboring metal particles together. The process is repeated on additional layers until the entire geometry is formed.](image)

After the part has been formed, it can then be removed from the powder bed for post-processing. The post-processing options are very similar to 3DP, sintering or sintering followed by infiltration. In-plane part resolution is controlled by the laser spot size and the powder size. Powder size is limited in turn by the ability to spread the next layer of material. For optimum layer spreading, the layer thickness is at least two times the particle diameter.

Systems with higher laser power may be used to sinter powder together via liquid phase sintering. Powders used for this method generally have a low melting point component to create the liquid-phase at a moderate temperature. The parts do not densify completely and may require additional sintering and/or infiltration. [6]
SLS rate is often limited by heat transfer considerations. Excessive heat could evaporate or decompose the binders while too little heat prevents bonding. In the regions where positive geometry is desired, the entire thickness of the powder layer must be heated into the target temperature range to achieve good bonding within and between layers. After each layer is spread, it may be preheated briefly before scanning. The cost of adding parallel lasers to increase scanning rates would generally be prohibitive. Fortunately, the laser beam can be scanned at high rates due to the modest inertia of the beam scanning mirrors, especially as compared to a 3DP printhead and fluid delivery system.

1.1.3 POST-PROCESSING OPTIONS

Material properties of 3DP and SLS components vary significantly with the material and post-processing methods used. Some parts, including filters, casting molds, and appearance models, can or must be left in a 40-60% porous printed condition. In these cases, they are used in the as-printed state or are sintered for additional strength but with minimal shrinkage. However, most applications require a dense final part. There are two options for densification as summarized in Figure 1-3.

![Figure 1-3 Post processing options for 3DP and SLS parts.](image)

3DP
- Print Binder & Cure

SLS
- Melt polymer w/ Laser

15-20% Shrinkage
Small Parts
Good Properties
Many materials

1.5-4% Shrinkage
Large Parts
Heterogenous Composition
Limited Material Systems

Best Dimensional Stability

Binder is removed and the part is strengthened. Most parts are densified to near full density. This can be done by either sintering or infiltration. Sintering is the usual approach for small parts and infiltration is used for larger parts.
Sintering to full density can be applied to parts printed in small (<20 µm) powder. Sintering to full density requires heating to homologous temperatures ($T/T_m$) where the diffusional processes that produce densification are active. Sintering to full density is generally limited to small parts, as large parts tend to distort from slight variations in the sintering shrinkage. Total linear shrinkage is between 15-20% depending on initial density. Although the dimensional changes are large, this process can be applied to virtually any material composition and produces material properties characteristic of standard alloys.

Infiltration processes offer an alternative with reduced processing shrinkage. However, as the infiltrant must have a melting point below that of the printed skeleton, bronze and other low melting temperature alloys are the typical infiltrants for iron-based skeletons. The typical final part is a heterogeneous mixture of bronze infiltrant and steel powder. The strength and wear properties are reduced relative to steel. Further, designers are uncomfortable with these unusual composite materials.

This work focuses on metal parts that are densified by liquid-metal infiltration. Steel is used as the demonstration material as it is currently the most-used metal material for both of these processes.

1.1.4 HOMOGENOUS STEEL INFILTRATION

Recent work by Lorenz, et al. [7,8] showed how a melting point depressant such as silicon could be used to produce an infiltrate of similar composition to the skeleton. During and after infiltration, the melting point depressant diffusional homogenizes and isothermally solidifies as illustrated in the phase diagram in Figure 1-4. The final product is both dense and compositionally homogenous.
Introduction

Figure 1-4 Transient Liquid Phase Infiltration [9]. A skeleton with composition “A” is infiltrated by a similar alloy but with the addition of a melting point depressant (MPD). After infiltration, the infiltrant solidifies as the melting point depressant homogenizes by diffusion. The final part is completely solid at the infiltration temperature.

Figure 1-5 Homogenous steel infiltration [10]. The process is similar to transient liquid phase infiltration, except that the final composition is in a two-phase field. The persistent liquid phase allows infiltration to continue even if the melting point depressant diffuses very quickly into the skeleton.

When this method was applied to steels using carbon as a melting point depressant, the carbon diffused into the skeleton very quickly, solidifying the infiltrant at the base of the skeleton before it was filled with infiltrant. Kernan et al. [10] modified this method to
permit the use of fast diffusing melting point depressants such as carbon in steel. By choosing a final composition that is in a two phase liquid-solid field at the infiltration temperature, a liquid phase is maintained despite the diffusion of the carbon from the infiltrant into the skeleton as seen in Figure 1-5. The persistent liquid phase fills the pore space and allows infiltration to proceed until the skeleton is completely densified. This process can produce final compositions of standard tool and stainless steels. Samples of D2 tool steel produced by this process achieved impact energy and hardness performance comparable to standard wrought D2 as shown in Figure 1-6. While the steel infiltrated system can reach hardness of 60 Rockwell C, the best bronze infiltrated alloys available from a commercial distributor have a peak hardness of 35 Rockwell C. [11]

![Hardness Measurements: Air Quenched](image)

Un-notched Charpy bar 9 mm x 9 mm

--- Steel Infiltration D2
—— Commercial D2

Figure 1-6 Hardness and impact strength of D2 tool steel produced by homogenous steel infiltration are comparable to commercial D2 material with the same heat treatment [10]. Samples prepared by steel infiltration are comparable to the wrought material in both hardness and impact strength.

1.2 Sources of Dimensional Change

After printing by 3DP or SLS, parts are typically accurate to within a constant offset of approximately 0.10 mm [4]. While this accuracy is inferior to machining processes, it is competitive with casting and, given the reduced time and tooling costs of the methods, is favorable in many applications. Unfortunately, there can be significant
additional dimensional changes during subsequent sintering and infiltration processes that improve the properties of the final part. The major sources of these errors during processing of metal parts by infiltration are discussed below.

1.2.1 SHRINKAGE

During post-processing of 3DP and SLS parts, the polymer binder (if any) decomposes and new bonds between the skeleton particles form by sintering. These bonds form by the net movement of material from convex to concave surfaces. The transport is highest where the change in curvature is highest such as in the contact points between particles. The mechanism and path of transport depends on the material and temperature, but in metals transport is typically by diffusion.

The movement of material from one region of the particles to another can cause a net movement of the particles closer together. At the macro scale, this is observed as shrinkage. In many powder applications, sintering shrinkage is desirable as it increases the strength and density of the part. However, in post-processing 3DP and SLS parts for densification by infiltration, the shrinkage is undesirable as it can reduce the accuracy of the final part.

Typical shrinkage during infiltration of a steel 3DP part with bronze is approximately 1.5% ±(0.25%) [4]. Stucker et al [12] measured similar shrinkages in SLS parts made from the commercial material LaserForm ST-100 and infiltrated with bronze. Another material tested showed less shrinkage, but the shrinkage was sensitive to different parameters.

While enlarging the initial geometry can compensate for the average shrinkage, the variation in shrinkage from part to part represents an error that increases with size. Shrinkage can also vary spatially within a single part due to spatial variations in the initial density or sintering temperature. Spatial variations can cause part warpage. Indeed, Dalgarno and Stewart [13] reported that in a test of SLS parts, large flat, horizontal surfaces experienced the most geometric error.
Since diffusion is an activated process, the rate of transport depends exponentially on temperature and begins to become significant at about one half of the absolute melting point of the material. Diffusion pathways with reduced activation energies like surfaces and grain boundaries dominate at these lower temperatures. As the temperature increases, diffusion through the bulk lattice dominates the process. These bulk processes account for most of the shrinkage during sintering.

Transport by bulk diffusion increases enormously when the infiltration temperature is raised from 1100 °C for bronze infiltration to 1285 °C for steel infiltration. Fortunately, the shrinkage does not increase as much since the driving force for sintering decreases as sintering progresses. However, shrinkage does increase significantly at higher temperatures and smaller powder sizes.

1.2.2 DEFORMATION

Parts may deform at higher temperatures. One possible cause is differential shrinkage. As the total shrinkage is modest, the deformation due to differential shrinkage is generally not severe. Where it is a problem, it may be decreased by reducing the overall shrinkage and reducing variations in temperature and local powder packing density.

The other possible source of deformation is creep. Creep is time-dependent plastic deformation. It can occur by many different processes depending on the material, temperature, and stress level, but general conclusions can be made by expressing the temperature as a fraction of the melting point temperature on an absolute temperature scale and the applied stress as a fraction of the modulus of elasticity.

A general expression for the rate of creep strain ($\dot{\varepsilon}$) as a function of temperature and stress is

\[
\dot{\varepsilon} = A\left(\frac{\sigma}{G}\right)^n \ e^{-Q/RT}
\]
where $Q$, the activation energy, and $n$, the stress exponent, characterize the mechanism of creep strain. $A$ is a prefactor generally dependent on temperature, $\sigma$ is the applied stress, and $G$ is the shear modulus. $R$ is the universal gas constant. $T$ is temperature on an absolute scale.

During infiltration, the stress comes from the self-weight of the part and is most significant at the base of overhangs in the part geometry. The stress in the parts during post-processing is generally low and is independent of temperature. The stress exponent ($n$) at the high homologous temperatures and low stresses characteristic of the infiltration conditions is typically one [14]. The exponential term arises from a dependence on diffusion as a mechanism in the creep process and the activation energy ($Q$) is typically the same as for diffusion.

The temperature increase from 1100°C in bronze infiltration to 1285°C for steel has a substantial impact on the rate of diffusion. Using a lattice diffusion activation energy of 280 kJ for iron [15], the relative rate of diffusion would change by a factor of 18. This leads to a substantial increase in the creep deflections at the higher temperatures. Figure 1-7 graphically illustrates this substantial difference.

**Figure 1-7** Illustration of the increased creep rate at steel infiltration temperatures. Two initially straight bars with unsupported overhangs were heated to 1100°C and 1284°C, representative of bronze and steel infiltration respectively. While no deflection is visible in the 1100°C specimen, the 1284°C specimen has deflected dramatically.
### 1.2.3 TRADE-OFFS BETWEEN SHRINKAGE & DEFORMATION

The creep rate may be decreased by reducing the applied stress. While this can be done by redesigning the part, we do not wish to increase the geometrical constraints on the process. Instead, increasing the size of the bonds between powder particles can reduce the stress. As shown in Figure 1-8, typical particle bond diameter after sintering at 1285°C for one hour is less than 20 μm. If the size of these bonds can be increased, the local stress and thus the creep rate will be reduced.

![Figure 1-8 SEM image showing small bonds in sintered powder.](image)

Figure 1-8 SEM image showing small bonds in sintered powder. SEM image of the fracture surface of a 410 SS part made from 63-90 μm powder and sintered at 1284°C for 1 hour. The bonds are very small relative to the powder size.

Increased sintering strengthens the bonds between powder particles. This can decrease the deformation rate of a part, but unfortunately, it also increases the part shrinkage. On the other hand, shrinkage can be reduced, but the creep deformation would
Introduction

increase. This tradeoff could be optimized to get the best compromise between shrinkage and deformation, but this is not likely to provide a substantial improvement. Moreover, the optimum treatment would vary with powder composition and size.

The goal of this work is to demonstrate an option that reduces shrinkage and creep deformation simultaneously or can at least improve one metric without substantial impact on the other.

1.3 Previous Efforts To Improve Dimensional Stability

Little has been done to address the deformation component of the dimensional stability because it was not a substantial error source before the development of the steel infiltration method and the associated increase in infiltration temperature. However, significant effort has been made previously to reduce the shrinkage and due to the connections between shrinkage and deformation, some of the shrinkage mechanisms are also very relevant to reducing deformation.

1.3.1 ADJUSTING THE FURNACE CYCLE

It is possible to adjust the shrinkage and deformation by changes in the furnace cycle. For example, since both deformation and shrinkage are time-dependent processes, they could be reduced by faster heating and cooling rates that would reduce the overall time at elevated temperatures. Typical ramp rates vary from 1 K/min to 8 K/min. At the slower rates, an infiltration at bronze malting temperatures could require 24 hours allowing even slow deformation processes to become significant. However, these rates are typically limited by the capabilities of the furnace or the rate of heat transfer in the parts. Fast ramp rates can create temperature gradients in the parts that can induce differential shrinkage and warpage. The debinding process must also be executed slowly to allow the gases generated to diffuse out of the part so that the internal gas pressure does not create defects.
1.3.2 PRECOMPENSATION

Initial geometry can be compensated for predictable errors so that the error of the final geometry is reduced. This is standard practice in casting to compensate for solidification and cooling shrinkage and is also widely applied in SFF processes. Unfortunately, this can only compensate for the average value of the dimensional change. While casting shrinkage is a primarily a function of the material and the casting temperature, shrinkage in SFF processes also depends on factors like the initial packing density, heating rate, temperature uniformity, powder composition, powder size, and furnace atmosphere purity. These factors can vary significantly from batch to batch and from location to location. In some cases, significant variations can even occur based on local geometric effects [16]. Spatially varying compensation factors must then be applied, possibly requiring process modeling of each part. This could be a significant burden on low lead-time, high variability processes.

Compensating for creep deformations is even more challenging than shrinkage compensation. Creep deformation is dependent on powder packing fraction, powder size, powder composition, furnace atmosphere, and heating rate like the shrinkage. Additionally, it is sensitive to geometrical errors in the part that can change the stress applied to the part. The average stress in a cantilever bar loaded by self-weight varies linearly with thickness and to the third power with length such that geometrical variation in the SFF process may be amplified during post processing.

Some of these challenges, particularly with respect to shrinkage compensation may be overcome using more detailed models of the parts, the manufacturing process, the errors of particular machines and the furnace temperatures so that the parts may be compensated for local shrinkage variations. Lynn-Chamey and Rosen [17] developed correlations between part accuracy and build parameters. Tong et al. [18] applied error-mapping techniques developed for precision machines such as coordinate measuring machines to map errors in SLA parts across the workspace to permit software compensation for repeatable errors. Seefried has implemented an efficient method for deriving the materials models required for such a process using reaction kinetics [19]. However, these processes
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are limited by the cost, quantity, and accuracy of the input data. Jacobs [20] hypothesized that random shrinkage variation will always exist and that it scales with the average shrinkage value and presented several data sets to support this view. Thus a fundamental improvement in the part accuracy requires a reduction in the original error or at least its variation.

1.4 3DP Binder Changes

In Three-Dimensional Printing (3DP), the binding material that is applied to the powder can also alter the shrinkage and/or deformation during processing. It may also be possible to make changes to the SLS binders to affect the shrinkage performance, but these are limited by the process requirement that the binder be thermally activated via laser illumination. Some of the previous 3DP efforts to reduce the dimensional changes during processing are reviewed below.

1.4.1 BINDER S

A 3DP licensee, ProMetal, found that parts produced using a polymer fugitive binder developed at MIT, did not have sufficient dimensional stability or processing strength to enable production of high aspect ratio structures. They developed a proprietary binder with improved performance. This binder, called “Binder S”, creates a persistent carbon deposit that appears to strengthen the skeleton through all stages of processing and to dramatically improve the dimensional stability of printed steel parts. Unfortunately, the residual carbon can impact the homogenous steel infiltration system. It is also undesirable in other material systems such as titanium and nickel superalloys where the carbon can be very detrimental to the final properties. [21,22]

1.4.2 METAL SALTS

Many metal salts can be dissolved in a liquid for printing and reduced to pure metal at a low to moderate temperature. The deposited metal could then bind the powder
together with greater strength than the polymer parts. Hopefully, the metals would also reduce the sintering rate by filling the area around the contacts and reducing the total surface energy.

![Image](image.png)

65 μm Molybdenum powder
Copper necks from copper nitrate

30 μm Molybdenum powder
Copper-Silver necks from copper and silver nitrate

Figure 1-9 SEM images of bonds created from copper and silver nitrate printed into molybdenum powder and then reduced to form metal necks [23]. The deposited metal forms continuous bonds between the particles.

Initial success was found printing silver and/or copper nitrate. The solutions produced very effective, strong bonds on heating as illustrated in Figure 1-9. Shrinkage in these parts was very low (0.15 %) and models suggested that it was a function of the compressibility of the powder under the compressive stress on the powder from the surface tension of the liquid metal bonds. However, the melting point of the silver bonds was too low to use this material system for liquid-metal infiltration, and the only dense parts produced were infiltrated with epoxy. [23, 24, 25]

Other material systems were investigated for use in an infiltration system. These included molybdenum, iron, nickel, and copper. Unfortunately, these salts did not form strong bonds between the powder particles as would be required to increase the strength or decrease the shrinkage. The only strong bonds were achieved when the metal was melted such that it could flow to the necks between the particles. [25]
1.4.3 METAL POWDERS

Yoo [24] explored adding fine suspended powders to reduce the sintering shrinkage. Perhaps, such particles could be deposited at particle contacts during drying. The smaller size could reduce the sintering temperature enough that they could form strong bonds while the skeleton particles did not sinter, allowing a printed part to be removed from the powder bed after low-temperature heating.

While suspensions of fine iron particles were created and explored as a binding agent, there were many difficulties. The iron particles settled relatively quickly in the suspension. Further, the difference in sintering temperatures was insufficient to develop good strength unless the powder was oxidized before printing. After lengthy efforts, low shrinkage skeletons were obtained, but the final shrinkage after infiltration was unchanged. Additional efforts using suspensions of fine brazing alloys and sintering activators showed little improvement [26].

1.4.4 SUPPORTED PARTS

Given these many challenges, manufacturers commonly pack parts in a coarse refractory ceramic powder to support them during infiltration. This support can substantially reduce creep deformation. However there are also several difficulties with the process.

While supporting the parts is helpful, it is not an entirely satisfactory solution. It is not easily applied to produce consistent parts at higher volumes and it does nothing to improve the shrinkage. In fact, shrinkage can be a major source of problems since the supporting powder may restrain the shrinkage, causing defects in the part. There are also geometries that are difficult or impossible to support or extract the supporting powder after processing. Supporting powder also reduces the heat transfer to the part, potentially requiring slower heating rates or leading to increased thermal gradients.

There is an additional problem specific to the steel infiltration process. Steel infiltrant cannot touch the skeleton until both the infiltrant and the skeleton are at the
infiltration temperature whereas the bronze infiltrant is typically placed in contact with the part for the entire thermal cycle. It may be more difficult to apply a steel infiltrant to a supported part.

1.5 New Binder System for Increased Dimensional Accuracy

This thesis presents a new method for improving the dimensional accuracy of metal parts densified by infiltration of a porous metal skeleton with metal infiltrant of a similar composition to the skeleton. The primary method for creating these skeletons is by 3DP or SLS, but other processes may also be suitable.

As in previous work, the improvements are achieved through the use of a novel binder. The proposed method deposits metal into the skeleton from a metal colloid to strengthen the bonds, reducing creep deflection at high temperatures and possibly reducing shrinkage. The subsequent chapters summarize this work.

In Chapter 2, the binder system is described and the process by which it can be incorporated into 3DP and SLS production processes are summarized. Necessary conditions for successful implementation are reviewed. Chapter 3 characterizes the iron colloid selected for studying this concept. The densification characteristics of the colloid material in simplified geometries are also studied. Chapter 4 shows how this suspension can be applied to a 3DP or SLS part to dramatically reduce the high temperature creep rates. Shrinkage of specimens with and without iron colloid treatment are compared. The iron colloid is shown to reduce the linear shrinkage compared to untreated specimens. Chapter 5 reports measurements of important deformation parameters and compares the performance against predictions. Chapter 6 summarizes the work and proposes possible future work.
1.6 References


2 Nanobinder Overview

This thesis shows that suspensions of nanometer particles can be added to porous powder metal forms to substantially reduce dimensional changes during high-temperature processing. This chapter reviews the ways in which dimensional stability can be improved, and then proposes a binder-based approach for reducing dimensional changes during liquid-metal infiltration. The proposed binder is a suspension of nanoparticles that strengthens the bonds between the particles for reduced deformations. The requirements of this approach, the process of applying the binder, and the important conditions for successful implementation are then reviewed. Simple models of ideal performance are developed to explain the rationale for this approach. In later chapters, these will be compared against measurements of actual binder performance.

2.1 Concept for Improved Dimensional Stability

As discussed in chapter 1, dimensional changes in powder metal parts occur during the sintering and infiltration process stages. These are classified into two categories: shrinkage and deformation. Shrinkage generally arises during sintering of the skeleton particles. Deformation comes from creep of the particles and the bonds between particles. Several methods for reducing each of these are discussed below. One of these methods, deposition of material into the powder to create/strengthen interparticle bonds, is selected for its potential to decrease errors from both sources.
2.1.1 CREEP REDUCTION

Creep rate is governed by the temperature, material, and applied stress. The temperature and powder material are set by the processing constraints for infiltration and the desired final properties. Thus, the primary method for reducing the creep is through reducing the applied stress. The applied stress is primarily from self-weight of unsupported structures. The applied load is primarily a function of geometry. These loads are modest, so the average stresses induced in the parts are also modest. Consider the bar specimens illustrated in Figure 2-1. The stress at the base of the overhang is given by

\[ \sigma_{avg} = \frac{3 \rho l^2}{h} \]

where \( \rho \) is the average density of the skeleton. If these are made from steel powder \( (\rho = 7.8 \text{ g/cm}^3) \) with a packing fraction of 60%, the peak stress at the base of the cantilever is approximately 29 kPa assuming a homogenous material. The bar thickness \( (h) \) is 5.5 mm and the length \( (l) \) is 33 mm. However, the skeleton is in fact very porous. Since the area fraction of pores in a random section will be the same as the volume fraction of the pores, the average stress can be adjusted for the reduced pore areas by dividing by the relative packing fraction \( (f) \). The average stress over the solid material is then

\[ \sigma_{solid} = \frac{3 \rho l^2}{hf} \]

The revision increases the stress estimate to 58 kPa.
Equation 2-2 would provide an adequate estimate of the stress with geometrically uniform pore structure such as cylindrical pores running lengthwise along the cantilever. It would also be representative of the average value on a random cross section as illustrated in section A of Figure 2-2(A). However the sintered powder produces a very different pore structure. The entire load is carried locally through the collective sinter bonds, which have a small fraction of the particle area. The part could be sectioned as illustrated in section B in Figure 2-2 (A,C) so that it only cuts through the particle bonds. Now, the entire load is supported by a much smaller area, dramatically increasing the stress.

![Figure 2-2](image)

**Figure 2-2** Average stress in a powder bed depends on the way it is sectioned. A) Schematic representation of the powder bed and two possible sections through the powder. Dark regions represent solid material and the light regions pores. B) Illustration of the area fraction of a random cross section through a powder bed. C) Illustration of area fraction of a cross section through the bonds. The cross sectional area is much smaller than the random cross section.

This small bond area can be estimated if some assumptions are made regarding the basic structure. Such a model is developed for the case of primitive cubic packing in 2.3.4. A primitive cubic structure has a relative density of 0.52, similar to the density of a spread powder bed (0.45-0.55).

The size of typical sinter bonds were measured by SEM imaging of broken bonds in samples prepared from 410 SS powder 63-90 μm powder sintered at 1300 C for one hour and then broken. From these measurements, the ratio of average bond to average particle diameter (X/D) is calculated as 0.15. Using Equation 2-26 for the primitive cubic structure, the average bond stress estimate increases to more than 1.0 MPa. This only includes the impact of the area changes at the sinter bonds. Inclusion of stress concentration factors would increase the stress further.
Thus, the stress in the small sinter bonds is increased more than 15 times relative to the average powder stress. As the size of the bonds increases, this stress increase is reduced substantially. This can be accomplished by adding new bond material with a melting point as high or higher than the bulk material. Substantial benefit could be obtained by treating just the highest stress regions such as the outer surface of the base of unsupported overhangs.

2.1.2 SHRINKAGE REDUCTION

Shrinkage occurs by sintering as material is transported from low energy positions on convex surfaces or in the particle bulk to high-energy positions in high curvature, concave regions as illustrated in Figure 2-3. While it is possible to impede shrinkage by altering the surface conditions as by introducing an oxidizing atmosphere or coating the powder with a higher melting point material, this would decrease the sintering rate. The smaller interparticle bonds would likely leave the structure weaker and more susceptible to creep deformation. Likewise, using larger particles would decrease the relative size of the sinter bonds and limit the minimum feature size and layer thickness of the 3D printing process. The infiltration temperature cannot be lowered to reduce shrinkage without switching to a lower melting point infiltrant that produces poorer properties in the final part.

Another alternative would be to create the neck bonds by adding material to the neck from an external source. The bond size could be maintained or even enlarged so that
the skeleton strength and creep rate are not compromised and yet, the part would not shrink as long as the bonds were formed entirely from outside material. This alternative is compatible with reducing the creep rate as discussed above. However, unlike creep, which occurs primarily in small highly stressed regions, the sintering shrinkage is largely uniform throughout the sample. Thus, the material must be deposited uniformly in order to achieve a reduction in shrinkage.

2.2 Proposed Method for Improved Dimensional Stability

Creating bonds between powder particles by adding material rather than by diffusional transfer from other regions of the powder particles has the potential to increase the dimensional stability both by reducing creep deformation and by reducing shrinkage. There are many developed methods for depositing material that might be amenable to strengthening powder skeletons such as those produced by 3DP or SLS. However, there are many requirements for a successful method. These requirements will be reviewed first and then candidate application methods are compared against these requirements. The material deposits necessary to increase the bond sizes in the part can be applied using a liquid binding agent by either of two methods as discussed below.

2.2.1 MATERIAL DEPOSITION REQUIREMENTS

The processing and application requirements impose many constraints on the characteristics of a material and method for reinforcing skeletons for increased dimensional stability. These are reviewed below.

Metallurgically Compatible

Since the final material properties are important, the binder must not have a detrimental affect on the material properties of the finished part. The original polymer binder systems relied on a “fugitive binder” that would decompose during post-processing and leave minimal residue. Although these may leave some carbon residue, carbon is an important constituent in steel alloys. If necessary, the carbon composition of the powder can be reduced to compensate for any carbon added by the binder. However, the carbon
residue is a problem in other material systems such as titanium. This motivated research into silver nitrate binders for 3DP of titanium parts [2].

Low Creep Rate at high Temp

The bonds created from the binder must have a low creep rate at the processing temperature to achieve significant reductions in deformation. This requires that the melting point of the deposited material be above the processing temperatures. Much higher melting points are preferable as the rate of self-diffusion in a material generally scales with the material’s melting point. Increasing the required diffusion distances can also reduce creep. Since diffusion usually involves sources and/or sinks at pores and grain boundaries, fully dense materials with large grains have lower creep rates. Porous structures, particularly open pores, can create very short diffusion distances with large surface area for fast surface diffusion. Creep will be reduced most by dense, large-grained neck structures containing high melting-point materials.

Process Specific Requirements

The deposited material could be used to form the original bonds between the particles or it could be applied after the initial bonds are formed by another process such as 3DP or SLS. In the first case, the binding material can be printed into the part as the basic liquid binder in the 3DP system. It might also be possible to apply the material in a thermally active form that would permit bond formation by SLS. Other methods might also be devised, but they are beyond the scope of this work. The current work will consider direct application only through 3DP.

The requirements of each of these application options are considered below.

Direct Bonding through 3DP

A successful direct bonding binder must meet several requirements. First, it must be printable through an ink-jet style printhead. To meet this requirement, it must have moderate to low viscosity (<10 cP for drop on demand, higher for continuous jet) and be free of large particles or agglomerates that might clog the printhead.
Second, the binder must wet the powder well enough to absorb on contact. If not, the binder drops may coalesce into large drops on the powder surface. Once the binder absorbs into the powder, it should be able to travel through and deposit to a depth at least equal to the layer thickness. Any dissolved or suspended constituents must not deposit exclusively on the top surface.

Third, after printing, it must bond the skeleton sufficiently to allow handling of the part with low risk of damage. This strength must be developed without bonding together unprinted powder surrounding the skeleton so that the part can be removed from the skeleton. This may be expressed as a ratio of printed region cohesive strength to unprinted cohesive strength that exceeds a critical value. The strength of the printed regions can be developed by post-processing in the powder bed, but at too high of temperatures the untreated powder bed will begin to sinter and develop cohesive strength. The exact temperature limit depends strongly on the material and the powder size, but for moderate-sized (>50 μm) steel powder particles 900-1000 C is the approximate upper limit beyond which sintering of untreated powder becomes excessive. [3]

Fourth, the part strength must be maintained through the processing so that the part does not deform excessively at temperature. This is a limitation of the polymer-based binders as they soften and then decompose on heating, leaving the skeleton very weak until it is heated to higher temperatures where metallic interparticle bonds form by sintering.

This application method should allow for uniform distribution of the deposits as would be required for shrinkage reduction. It could also be applied locally in just the high stress regions or in higher concentrations in these regions by local deposition control to maximize the reduction in creep. A conventional polymer binder could be applied on other regions to form the geometry.

Secondary Strengthening

The binder could also be applied to the part after geometry formation by infiltration in place of or in conjunction with direct printing of the binder. The primary requirement for binder application by infiltration is that the active material be dissolved or suspended in a liquid carrier and transported a distance of at least ½ the maximum part thickness. This
requirement may be relaxed if only the outer surface needs to be treated. Although pressure may be applied to aid infiltration of poorly wetting fluids, it is helpful if the fluid wets the porous structure.

The final location of the deposited material in an infiltrated skeleton would be strongly influenced by the drying conditions of the sample as has been shown in studies of supported catalysts [4, 5]. It is possible to achieve either uniform distribution or localized distribution simply by varying the deposition conditions. Higher drying rates favor increased deposition at the surface while at slower rates, the deposits can be distributed uniformly or concentrated to the surface. See Chapter 4 for further discussion.

2.2.2 CANDIDATE METHODS

Traditional metal deposition methods include evaporation, chemical vapor deposition (CVD), plating, and sputtering. Each of these suffers transport limitations that make it difficult or impossible to deposit into the pores of a porous skeleton. As the deposition material is transported into the pores it begins to deposit. As the pores increase in depth, the deposition material is depleted until no further deposition can occur. In CVD and plating processes, the material can be deposited into pores by slowing the deposition process so that the transport processes are not rate limiting. However, this typically requires very slow deposition rates. Yuen deposited titanium nitride coatings on sintered powdered by CVD. He found that the coatings of the powder were only 5% as thick as dense bars coated under the same conditions. [6]

Additionally, these alternative deposition processes could not be applied directly in the 3DP process for direct binding. Only the plating approaches have liquid agents that can be deposited via ink jet printing. However, the concentration of deposit material in the liquid is too dilute to create significant deposits from a single application and the material systems for electroless plating are limited.

From a practical standpoint, many of these processes also require specialized equipment and careful chemical control that may be difficult or costly to implement for these applications.
2.2.3 PROPOSED DEPOSITION METHOD: NANOBINDER

A new binder could strengthen the skeleton with metal added through the printed binder or in a second infiltration step by depositing metal or its oxide in the powder from a colloid. The proposed binder is a colloidal suspension of metal or metal oxide particles that are deposited in the powder interstices when the solvent dries. This binder has been termed a “nanobinder” as it is based on several of the unique properties of nano-sized particles.

In recent years, metal colloids of many common metals have been developed. These include iron, nickel, cobalt, gold, silver, and platinum [8-18]. Particular effort has been focused on gold and silver due to their high stability, low oxidation rate, and ease of manufacture, while iron and cobalt have received attention for their magnetic properties [12,13].

Metal nanoparticles have been produced by many different techniques including evaporation, grinding, thermal spray, and chemical precipitation [14-17]. Of these chemical precipitation is most easily adapted to creating colloids as the nanoparticles are immediately stabilized in a solvent on nucleation. Careful control of the nucleation and growth with possible addition of size selective precipitation techniques allows the production of highly monodisperse colloids [18]. These colloids are stable relative to settling although some metals such as iron may be very susceptible to oxidation. Many nanometal colloids are now available commercially.

Much interest in nanometal colloids arises from the unique thermal properties of the small particles. In 1976, Buffat [19] showed that the melting point of small gold particles decreases substantially with size, inversely proportional to the particle radius as shown in Figure 2-4. At sizes below 10 nm, these effects are very pronounced. Since then, the same relationship has been measured in other materials [20].

These small particles also have drastically reduced sintering temperatures. Nanostructured iron powders with an average grain size of 40 nm produced by levitation melting in liquid nitrogen began sintering at 100 C [21]. By comparison, micron-scaled iron and steel particles do not start sintering until 700-900 C [24]. The sintering temperatures and activation energies of nanoparticles are reduced significantly [23].
Figure 2-4 Relationship between particle size and melting point of gold nanoparticles. The melting point decreases substantially below the melting point of bulk gold at small particle sizes. The effect is particularly significant at particle sizes below 10 nm. [24]

2.2.4 NANOBDINDER PROCESSING

The goal of the nanobinder is to produce a fully dense, compositionally homogenous part with no dimensional change. The particle-level process is illustrated in Figure 2-5. First, the skeleton powder is filled with the nanobinder. This is then dried, depositing the colloidal material into the skeleton, preferably in the neck regions. This deposit is then heated to densify by sintering. At this stage, the part is strengthened. It is then densified by infiltration. If this is done in the proper compositions of skeleton and infiltrant, the final product can homogenize by diffusion to create a spatially uniform composition.

Figure 2-6 compares the implementation of this process to the original “fugitive” polymer binder. In the case of direct binding, the nanobinder is substituted for the polymer binder in the initial printing. The binder curing stage is then changed from drying to a sintering stage of 700-800 C before the part is removed from the powder bed. At this point, the part is ready for infiltration without concern for debinding and the associated defects. If the nanobinder is applied as a secondary binder by infiltration, the part must be debound as in the fugitive binder and then sintered to develop handling strength. The nanobinder is then applied and cured before infiltration. It may be possible to combine the curing and infiltration into a single furnace run. Both nanobinder methods require a minimum of two
furnace runs while the original fugitive binder approach requires one or two runs depending on the details of the process.

In contrast to alternative deposition processes, the nanobinder allows temporal separation of the material transport and deposition processes. The material is printed or infiltrated into the skeleton with little deposition until the suspended particles are either chemically destabilized or the solvent is dried. In theory this process can be used to deposit material into pores and holes of considerable depth although the resulting deposition will not necessarily be uniform.

Figure 2-5 Particle-level schematic of part preparation using the nanobinder. The pores between large (50-100 μm) skeleton powder particles are filled with the nanobinder liquid. The liquid is then dried to deposit the nanoparticles onto the larger skeleton particles. Heating to moderate temperatures densifies the nanoparticles so that they strengthen the bonds between the skeleton particles. The remaining porosity is eliminated by infiltration with metal to achieve a homogenous final part composition with improved dimensional accuracy.
2.2.5 BENEFITS OF PROPOSED BINDER

Due to the reduced sintering temperatures, nanoparticles can form strong structures at very low temperatures by sintering—bonding the larger particles together while untreated powder remains unbonded as required for a 3DP binder. A 10 nm particle is more than two to three orders of magnitude below the average pore size in a 3DP or SLS powder bed allowing it to be transported easily through the required distances.

The skeleton can be strengthened by adding a nanocolloid to the part and drying it so that the deformation rate during metal infiltration is dramatically reduced. Since the bonds are formed from added metal, no shrinkage is required although some shrinkage by normal sintering processes may still occur in parallel with the bond formation resulting in a
net increase in strength without any change in the shrinkage. It may even be possible to reduce the shrinkage if the material is applied to the bonds throughout the part.

Table 2-1 compares the characteristics of various deposition processes against the requirements of a powder reinforcement for increased dimensional stability. The proposed colloid binder is the only one that could operate as a direct binder. It also minimizes the required process equipment as described below and can be applied for deposition in thick part sections.

Table 2-1 Comparison of possible metal deposition processes. Favorable characteristics are bolded.

<table>
<thead>
<tr>
<th></th>
<th>Evaporation</th>
<th>CVD</th>
<th>Sputtering</th>
<th>Electroplating</th>
<th>Electroless Plating</th>
<th>Metal Colloid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposit inside Skeleton</td>
<td>No</td>
<td>Limited</td>
<td>No</td>
<td>Maybe</td>
<td>Maybe</td>
<td>Yes</td>
</tr>
<tr>
<td>Apply During Printing</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Vacuum Required</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Concentrate Material at the neck</td>
<td>No</td>
<td>Limited</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
</tr>
<tr>
<td>Deposition Speed</td>
<td>Slow</td>
<td>Slow</td>
<td>Slow</td>
<td>Fast</td>
<td>Fast</td>
<td>Fast</td>
</tr>
<tr>
<td>Deposit micron thickness</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td>Applicable to many materials</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Additionally, the metal colloid may increase the handling strength of printed parts if it is applied as a primary 3DP binder. The metal bonds created through this process may achieve higher strength than polymer bonds. Such an increase would reduce damage during handling and simplify the manufacture of larger components. However, as polymer binder concentration is much higher than the iron nanobinder, the bond sizes produced by polymer-only binder may be large enough to offset the difference in strength between the bond materials.
2.2.6 CHALLENGES TO SUCCESSFUL IMPLEMENTATION

The primary challenges to successful implementation of the metal colloid binder are concentrating deposits in the necks, densification of the deposits, oxidation of the nanoparticles, and cost of the nanobinder material. While each of these topics is addressed in detail in a later chapter, a brief summary of each issue is provided below.

Concentration of the particles to the necks

The quantity of material additions required to create a neck bond of a given size is highly dependent on the location of the deposits. If the deposits are uniform across the particle surfaces, much more material is required than if it could be deposited exclusively at the contact regions. Section 2.3 shows that the volume of material required to increase the bonds is very small if it is deposited efficiently.

Concentrating the material in the bond locations makes more efficient use of the metal colloid and allows the liquid-metal infiltrant to fill the remainder of the pore space. The quantity of metal that can be deposited in the skeleton per application is limited by the available pore space and the concentration of the metal in the colloid. Inefficient deposition of the nanoparticles would increase the number of applications and/or particle concentration required. A uniform coating could begin to choke the flow of infiltrant and slow the infiltration time.

Fortunately, as the colloid solvent is evaporated, the fluid will minimize its surface area by evaporating from large pores first with the final liquid evaporating from the smallest pores at the contact points. Thus, the liquid has the potential to concentrate the nanoparticles in the contact regions. Additionally, magnetic forces may be applied to magnetic fluids to improve the concentration as discussed in chapter 4.

Densification of the particles

This process requires that the nanoparticles densify by pressureless sintering, typically very difficult to accomplish due to the agglomerates that form in nanopowders [25]. Thus, most nano powders are densified under pressure [26, 27]. However, when deposited from a well-dispersed suspension, the agglomerates can largely be eliminated, making pressureless sintering feasible [28, 29]. Extensive grain growth has been reported...
in the later stages of pressureless sintering, but in the nanobinder application, large grains are desirable for reducing creep rates.

An additional challenge may be caused by shrinkage during densification. Shrinkage of the nanoparticle deposits could be 20% if it densifies from an initial dried density of 50% increasing to 30% shrinkage for a 35% initial density. While monodisperse nanoparticles tend to pack in high density, close-packed arrays [30, 31, 32], they are coated with protective ligands that may create gaps between the particles of 1-3 nm, a very large fraction of the particle diameter (2-12 nm typical). This could reduce the effective density of the metal to less than half the close-packed density. The large sintering shrinkage could lead to fracture of the bonds or delamination from the relatively immobile skeleton particles. Although sintering processes might heal some of these fractures during heating, it is preferable to reduce shrinkage by drying the colloid deposits to a high density.

Oxidation

When iron particles oxidize, their volume doubles. Many other metals have similar expansions during oxidation. This can reduce the initial density of iron in the dried deposits and increase the shrinkage as discussed above. For this reason, it is assumed to be desirable to apply a metal to the part. However, if this is not a limiting factor, a metal oxide may be applied and then reduced by heating in a reducing atmosphere. This would be advantageous as oxide colloids are much more easily stabilized and are widely available for more metals than are metallic colloids.

Preventing oxidation of a metal colloid can be very challenging. While bulk iron oxidizes very slowly at room temperature in dry air, the large surface area of nanometer powders accelerates this process enormously. For example, if oxidation rates between 260-500 C [33] are extrapolated to room temperature, a 10 nm thick film of iron could oxidize in seconds. Fortunately, the protective ligands that cover the particles as well as the solvent reduce the oxidation rate. Chapter 3 reviews some measurements of the oxidation rate of a metallic iron colloid. Chapter 4 compares the performance of metal and metal oxide colloids.
**Nanobinder Overview**

**Binder Cost**

One concern regarding the use of a metal colloid to stabilize powder metal skeletons is the material cost. These materials are typically produced in small batches in well-controlled environments that might not easily scale to large production. Fortunately, progress is being made on producing these colloids in higher volumes at lower cost [34]. A substantial cost reduction might also be achieved if a method is developed to use metal oxide colloids. Additionally, the colloid material requirements are relatively small for these parts (~1 wt% of the skeleton) and can be reduced further by targeted application to specific regions such as those with the highest stress. Some application areas such as jewelry are less sensitive to price. Gold and silver colloids are also easier to make than colloids of transition metals.

**2.3 Process Modeling**

Simple models of the nanobinder process permit upper bound estimates of the potential for material deposition and dimensional stability improvement. Some relationships are developed based on the ideal case and expected deviations from ideal are noted.

**2.3.1 APPROXIMATE NECK VOLUME**

This analysis assumes that the benefits are achieved entirely from the formation of additional material to either create or enlarge the bonds between particles.
Figure 2-7 Comparison of actual bond geometry and simplified geometry. (Left) The actual geometry of bonds between equal-sized spheres is compared to a simplified cylindrical model. Actual neck have curvature as illustrated, but the approximate geometry on the right will be used for the analysis below. The exact case is calculated numerically in the following section for comparison. (Right) The parameters used in modeling the bond volume are illustrated.

The impact of this material on the bond sizes can be estimated by modeling the skeleton particles as monosized spheres. The diameter of the bonds \( (X) \) is normalized by the particle diameter \( (D) \). The bonds between these particles will be modeled as illustrated in Figure 2-7, neglecting the curvature of the bond. With these assumptions, the diameter of the volume of the bond with a given neck diameter \( (X) \) can be calculated by integration. The differential volume illustrated is given by

Equation 2-3

\[
dv = 2\pi hdl
\]

where,

Equation 2-4

\[
l = \frac{D}{2} \sin \alpha
\]

Equation 2-5

\[
dl = \frac{D}{2} \cos \alpha d\alpha
\]

Equation 2-6

\[
h = \frac{D}{2} (1 - \cos \alpha)
\]
Nanobinder Overview

The total volume of a single bond \((v_b)\) is found by integrating

\[
v_b = 2 \int_0^{\alpha_{\text{max}}} 2\pi h dl = 4\pi \frac{\alpha_{\text{max}}^3}{8} \left[ (\sin \alpha \cos \alpha - \sin \alpha \cos^2 \alpha) \right] d\alpha
\]

**Equation 2-7**

\[
v_b = \frac{\pi D^3}{2} \frac{\alpha_{\text{max}}}{\alpha_{\text{max}}^{\alpha_{\text{max}}}} \int_0^{\alpha_{\text{max}}} \left( \sin \alpha \cos \alpha - \sin \alpha \cos^2 \alpha \right) d\alpha
\]

**Equation 2-8**

\[
v_b = \frac{\pi D^3}{2} \left[ -\frac{\cos^2 \alpha}{2} + \frac{\cos^3 \alpha}{3} \right]_0^{\alpha_{\text{max}}}
\]

where \(\alpha_{\text{max}}\) is given by

**Equation 2-9**

\[
\alpha_{\text{max}} = \arcsin \left( \frac{X}{D} \right)
\]

For small values of \(\alpha_{\text{max}}\), the bracketed term approaches zero. Indeed, the small angle approximation gives a value of zero. However, the actual values, while small, are significant. Cosine approximations yield erroneous results, even when including the quadratic terms of the Taylor expansion of the cosine function.

### 2.3.2 COMPARISON TO ACTUAL NECK VOLUME

The actual neck geometry is governed by Laplace’s equation

**Equation 2-10**

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

The volume of a particle bond with this shape was calculated numerically for comparison to the approximate geometry considered above. The neck surface was assumed...
to perfectly wet the particles since the particles are made of the same material. Under this condition, the slope of the neck at the interface is tangent to the particle. A surface energy was assumed and then the equilibrium condition was found by iterating on the pressure ($\Delta p$) such that the slope at the bond centerline was zero. Pressure variation through the bond due to gravity and other effects is negligible. The calculated surface is then symmetric about the centerline. The resulting volume was then integrated numerically to calculate $v_b$. Figure 2-8 compares these results to the approximate cylindrical geometry developed above. The approximation underestimates the volume by approximately 6%. This accuracy is more than sufficient for present considerations.

![Figure 2-8](image)

**Figure 2-8** Comparison of bond volume for the exact geometry, bond geometry, and an approximate equation. Exact solution to neck volume as a function of neck size to particle diameter ratio ($X/D$) is very well fit by a fourth order equation. The approximate equation can be used to simplify the analytical relationships.

### 2.3.3 RELATING NECK VOLUME TO DEPOSITION CONDITIONS

Ideally, all of the deposited material would concentrate in the contact regions and would completely densify by sintering. Under these conditions, the quantity of binder material deposited is given by
Nanobinder Overview

Equation 2-11

\[ v_{\text{binder}} = n_a (1 - f) s c_v \]

where

- \( v_{\text{binder}} \) is the volume of binder material added per unit volume of the part
- \( n_a \) is the number of times the binder is applied
- \( f \) is the skeleton packing fraction
- \( s \) is the binder saturation (fraction of pore space filled with binder)
- \( c_v \) is the concentration of particles in the binder by volume.

In reality, all of this added binder material \( (v_b) \) might not be deposited in regions that strengthen the necks to reduce the creep rate and/or shrinkage. A second variable \( (f_{\text{bond}}) \) is then defined as the volume of additional neck material obtained per unit part volume and is expressed as

Equation 2-12

\[ f_{\text{bond}} = \beta(v_{\text{binder}}) = \beta(n_a (1 - f) s c_v) \]

where \( \beta \) is the neck concentration fraction, the fraction of deposited material deposited in the necks.

The volume fraction of bond material \( (f_{\text{bond}}) \) can also be related to the bond volume \( (v_b) \) as follows.

Equation 2-13

\[ \frac{V_{\text{bonds}}}{V_{\text{particle}}} = \frac{v_b}{V_{\text{particle}}} = \frac{2 c_n}{V_{\text{particle}}} \]

where the coordination number \( (c_n) \) is the number of bonds per particle and the bond volume \( (v_b) \) is divided by two because it is shared between two particles. The part volume \( (V_{\text{part}}) \) in turn is related to the total part volume by the packing fraction \( (f) \). These relationships are used to calculate the volume fraction of bond material \( (f_{\text{bond}}) \)

Equation 2-14

\[ f_{\text{bond}} = \frac{V_{\text{bonds}}}{V_{\text{part}}} = \frac{v_b}{V_{\text{particle}}} = \frac{2 c_n}{V_{\text{particle}}} f \]

If the skeleton is composed of monosized spheres, Equation 2-14 simplifies to
Equation 2-15
\[ f_{bond} = \frac{3 \nu c_n f}{\pi D^3 f} \]

Substituting from Equation 2-8 and Equation 2-9, the relationship further simplifies to,

Equation 2-16
\[ f_{bond} = \frac{1}{4} c_n f \left[ -3 \cos^2 \alpha_{\text{max}} + 2 \cos^3 \alpha_{\text{max}} + 1 \right] \]

Equation 2-17
\[ f_{bond} = \frac{1}{4} c_n f \left[ -3 \cos^2 \left( \arcsin \left( \frac{X}{D} \right) \right) + 2 \cos^3 \left( \arcsin \left( \frac{X}{D} \right) \right) + 1 \right] \]

Together, the two expressions for \( f_{bond} \) given by Equation 2-17 and Equation 2-12 relate the material deposition process to the neck size achieved. The process inputs are given in Equation 2-12 and the output is the bond size, typically expressed as \( \frac{X}{D} \).

However, the equations cannot be solved algebraically for bond size as a function of the deposition parameters.

The relationship between \( \frac{v_b}{2V_{\text{particle}}} \) and \( \frac{X}{D} \) is well characterized by the simplified equation

Equation 2-18
\[ \frac{v_b}{2V_{\text{particle}}} = \frac{1}{5} \left( \frac{X}{D} \right)^4 \]

This equation describes the numerical solution of the exact case to within 2% across the range of interest as illustrated in Figure 2-8. The equation can be substituted into Equation 2-14 and solved for \( \frac{X}{D} \) to get

Equation 2-19
\[ \left( \frac{X}{D} \right)^4 = \frac{5 f_{bond}}{c_n f} \]
All the terms in Equation 2-19 are easily measurable except for $c_n$. However, for monosized spheres in the density range of interest, it is typically between 6 and 7.

Substituting for $f_{bond}$ from Equation 2-12 the neck size ratio can be expressed in terms of the application parameters as

Equation 2-20

$$\left( \frac{X}{D} \right)^4 = \frac{5 \beta n_s c_v}{c_n} \left( \frac{1 - f}{f} \right)$$

Equation 2-20 shows that as the neck size ($X$) grows larger, the amount of material that must be added to increase the neck size increases dramatically. The initial application of material may increase the neck size significantly. However, adding additional material will provide much less change in the neck size.

The output of interest to the creep rate is the change in stress due to applying the nanobinder. The relationship between average stress and the neck size will be developed in the next section.

2.3.4 STRESS REDUCTION

The small area of the necks, raises the stress locally high above the average stress. The actual stress increase can be estimated by assuming a structure and a cross-section of that structure. The area fraction of bonds ($a_b$) on the section can be calculated. The average stress in the bonds is related to the average stress across the whole section by the ratio of the areas. An estimate is developed below for a primitive cubic packing structure.

The primitive cubic packing structure, consists of a cube with particles located at each corner of the cube. The length of the sides of the cube is the same as the particle diameter. Each unit cell contains one particle. The coordination number for the particles is 6. The volume fraction of the primitive cubic cell ($f_{sc}$) is then

Equation 2-21

$$f_{sc} = \frac{\frac{1}{6} \pi D^3}{D^3} = \frac{\pi}{6} \approx 0.52$$
This compares favorably with typical 3DP powder bed packing fraction ranges of 0.45-0.60. This structure is easily sectioned along planes perpendicular to the bonds for calculation of the bond area as illustrated in Figure 2-2. The area fraction of bonds is expressed simply as the number of bonds per unit area times the area of each bond. This is expressed as

\[ a_b = \left( \frac{1}{D^2} \right) \times \left( \pi \frac{X^2}{4} \right) = \frac{\pi}{4} \left( \frac{X}{D} \right)^2 \]

The area ratio scales as the square of the neck size ratio \((X/D)\). This would be true for any packing structure. However, the scalar factor is characteristic of the particular structure. So in general, the equation is

\[ a_b = \frac{1}{C} \left( \frac{X}{D} \right)^2 \]

The area fraction of particles in a random section is simply the inverse of the particle packing fraction. The average bond stress \((\sigma_{bond})\) and the average particle stress \((\sigma_{particle})\) are given by

\[ \sigma_{bond} = \frac{\sigma_{avg}}{a_b} \]

\[ \sigma_{particle} = \frac{\sigma_{avg}}{f} \]

where \(\sigma_{avg}\) is the average stress calculated over the entire cross section such as calculated in Equation 2-1 for the case of a cantilever loaded by self-weight. From Equation 2-23-Equation 2-25, the stress amplification in the bonds is

\[ \frac{\sigma_{bond}}{\sigma_{particle}} = \frac{C}{f} \left( \frac{D}{X} \right)^2 \]
Substituting this relationship into the basic power law creep equation, the ratio of average creep strain rates in the bonds to the particles would be given by

\[
\frac{\dot{\varepsilon}_{\text{bond}}}{\dot{\varepsilon}_{\text{particle}}} = \left( \frac{\sigma_{\text{bond}}}{\sigma_{\text{particle}}} \right)^n = \left( \frac{c}{f} \right)^n \left( \frac{D}{X} \right)^{2n}
\]

Equation 2-27

The relative strain rate between the bonds and particles is very sensitive to the stress exponent and the size of the necks. As the size of the neck increases, the difference in strain rates decreases very rapidly, particularly if power-law creep is active \((n>1)\). This effect is illustrated in Figure 2-9 comparing the average strain rates in the particles and bonds for different value of \(n\) and various neck size ratios.

The large difference suggests, that for power law creep, this nanobinder approach should be very effective at reducing the strain rates since even small changes in the neck size ratio can change the strain rates by several orders of magnitude. Further, the strain rates are so much larger in the neck than the particle bulk, that the neck region is very likely to dominate the total strain.

When the stress-strain rate relationship is linear \((n=1)\), the nanobinder process is less likely to have a dramatic impact. In this case, the strain rate ratio varies from approximately 60 at \(X/D\) of 0.1 to less than 10 at \(X/D\) of 0.3. Although the strain rates in the neck bonds will still be much higher than in the particle bulk, the particle volume is much higher than the neck volume. Under these circumstances, the strain in the particle bulk may be a significant fraction of the total strain. The best the nanobinder can achieve is to reduce the strain to that due to the particle average stress alone.
Figure 2-9 Relative strain ratios of neck and particles for different neck size ratios and stress exponents. For power law creep \((n=3)\) the relative strain rates in the bulk and bonds differ by several orders of magnitude for most practical bond sizes. For linear stress strain relationships \((n=1)\), the strain rate differences can still be very significant.

The relative strain rates can be expressed in terms of important process parameters by substituting from Equation 2-19.

\[
\frac{\dot{e}_{\text{bond}}}{\dot{e}_{\text{particle}}} = \left( \frac{\sigma_{\text{bond}}}{\sigma_{\text{particle}}} \right)^n = \left( \frac{c}{f} \right)^n \left( \frac{5f_{\text{bond}}}{c_n^f} \right)^n
\]

If the stress exponent \(n\) is one, the relative strain rates will scale as the square root of the quantity of bond material added. This means, that each additional increase in fluid concentration or additional application cycle is likely to produce less benefit. If the stress exponent is greater than one, the incremental benefit of additional deposits will continue to increase.

The goal of this work is to reduce the total strain of porous metal parts at high temperatures. The total strain is the sum of the strain from the particles and the bond regions. The nanobinder method proposes to reduce the stress and thus the strain in the bonds to achieve an overall reduction. The best this can achieve is to reduce the strain rate to that of the particles under the average stress. As bond size increases and the stresses decrease, the particle strain rates will be increasingly important.
The equations developed suggest the nature of the process scaling. In particular, the contribution of neck strain should decrease with the neck size ratio to the power of $n/2$ as given by Equation 2-27. This hypothesis can be tested by comparing bond sizes measured in the sintered skeletons to the tip deflection. These predictions are tested against experimental data in Chapter 4.

2.3.5 LIMITATIONS OF STRESS ESTIMATES

The preceding analysis has implicitly assumed that the total strain in an area is a weighted average of the strains in the particles and the neck regions where the weights are a combined function of the stress and the volume fraction. The two components of this structure, the particles and the necks, are assumed to be arranged in series so that the load through both is the same. This situation seems reasonable, particularly in a primitive cubic structure. However, the assumption may not be valid in a randomly packed structure.

Further, the properties of the powders are assumed to be the same in tension and compression. In this case, the assumptions are likely to break down at higher strains. In compression, the strength will increase with increasing strain. The deformations in the contact region will increase the contact area between the particles and the local stress will decrease. The compressive stress effectively increases the sintering rate as well. On the other hand, the strength in the tensile region will decrease with increasing strain. The bonds will decrease in diameter under continued strain until they may begin to fracture. Sintering that might otherwise increase the strength of the bonds will be reduced by the tensile stress.

At low packing densities, or with the onset of bond failure that reduces the coordination number of the particles, strain may proceed by rearrangement of the particles rather than deformation. Particle rearrangement could amplify the deformation measured for a given strain rate in the particles and bonds.
2.4 Conclusions

This chapter reviewed possible methods for reducing the dimensional changes of porous metal skeletons at high temperatures and the requirements for successful implementation of these methods. Based on these considerations, a nanobinder is proposed that would deposit metal into the pores to strengthen the skeleton. This reinforcement can reduce the creep rates and possibly the deformation.

The nanobinder consists of a stable suspension of nanoparticles in a liquid solvent. The nanobinder can be applied to a porous metal structure and the solvent extracted by drying to deposit the metal in the structure. The liquid preferentially deposits material in areas of high curvature, which also tend to be the areas of highest stress. Due to their small size, the nanoparticles will sinter at low temperatures so that they can reinforce the skeleton at higher temperatures.

The key to this concept is that the stress at the connections between particles is much higher than in the particles. If the size of the connections can be increased, the stress decreases and thus the strain rate. A simple model was developed that estimates the impact of the bond sizes on the stress in the necks. Relationships between the parameters of nanobinder deposition to the bond size were also developed.
References


3 Densification of monodisperse nanometal particles by sintering

The goal of this work is to create bonds between micron-scale powder particles by depositing metal from dispersions of nanoparticles in a liquid. These bonds should reduce the dimensional and form changes during infiltration of powder-metal skeletons by increasing the skeleton strength without shrinkage. To convert the individual nanoparticles into effective bonds, they must densify to form a solid bond.

This chapter will review the challenges associated with this requirement and previous efforts to understand the drying of nanoparticulate suspensions and the sintering of nanostructured materials. The general properties of the nanoiron product used in this work are then reviewed. Its dried structure is studied by TEM imaging and gas adsorption techniques. The sintering of the particles and the phases are observed by SEM, TEM, XRD, and gas adsorption. These results show that the nanoparticles can be densified by pressureless sintering and that the carbon from the coating ligands and oxygen exposure during process strongly influence the densification and composition of the deposits.

3.1 Nanoparticle Background

Materials with structures on the nanometer scale (<100 nm) have excited substantial interest due to unique properties at small grain sizes. An inverse relationship
between grain size and material strength is well documented for many metals [1-3]. This increasing strength with decreasing particle size has encouraged grain size refinement for improved mechanical strength, leading eventually to the study of nano-sized grains [4,5]. Ultrafine ceramic powders have long been studied for the possibility of reduced processing temperatures and potential increase in ductility [6]. Nano-sized materials are also desired for their reduced processing temperatures, increased reactivity due to high surface area, and novel magnetic, electronic, and optical properties [7-9].

To achieve these small grain sizes, many methods were developed for creating powders with nano-sized grains including vapor phase condensation, solution precipitation, high energy ball milling, and laser ablation [10-16]. Some of these methods such as high-energy milling create micron-scale particles with nano-sized grains while others such as solution precipitation methods create single crystal nano-particles. The size distribution, purity, and agglomeration also depend on the preparation method. Many of the methods most suitable for creating stable nano-dispersions as required for the nanobinder have only been demonstrated at small scales, but significant progress has been made in developing large-scale production abilities [17,18].

3.1.1 BACKGROUND ON CONSOLIDATION OF NANOPARTICLES

For many applications of nano-structured particles, particularly mechanical applications, the particles must be consolidated to form a dense structure. Conventional consolidation processes can be applied to the nanostructured materials, but full densification proves more difficult, particularly if the application requires that the nano-sized grains be maintained through densification. The two primary methods for densifying nanoparticles are melting and sintering.

3.1.1.1 Liquid Phase Densification

Buffat made one of the earliest observations of size-dependent properties [19]. He observed that the melting point of nanometer-sized gold particles was reduced substantially relative to the bulk value. In fact, it is well approximated by a linear inverse relationship as
Densification of monodisperse nanometal particles by sintering illustrated in Chapter 2. Similar reductions have been observed in many other materials [20], and this phenomenon continues to be studied [21-23]. The melting point of the nanoparticles is reduced by their large surface energy.

Many researchers have sought to use the melting point reduction of nanoparticles to densify them by melting. They have typically used dispersions of nanoparticles applied to a substrate to deposit nano-metals at low temperatures for applications such as MEMS devices [24], solar cell metallization [25], and electrical interconnects [26,27,28]. In this previous work, the metal was densified by quick heating to an isothermal hold temperature in an ambient or inert atmosphere. The density of the fired suspension has typically been very low as indicated by electrical conductivities 10-60% of bulk material [25,26, 27]. However, these methods do achieve substantial reductions in processing temperature. Gold lines have been deposited and processed at temperatures as low as 150 C using these methods [26]. It is unclear whether the particles truly melt at these reduced temperatures or simply sinter.

Chung, et al [29,30] used a highly focused laser to dry and cure nanoparticles applied to a glass substrate by ink-jet printing. The resulting structures showed conductivity approaching bulk values suggesting that the material may be approaching full density. When the particles are heated very quickly, the nanoparticles may densify by melting before the surface energy can be reduced by sintering.

3.1.1.2 Nanoparticle Sintering

Sintering rates depend very strongly on the size of the sintering particles. Hansen et al. developed an illustrative model of the shrinkage rate during sintering [31]

\[
\frac{dL}{Ldt} = \frac{\gamma_s \Omega \left( \frac{\delta D_b \Gamma_b}{d^4} + \frac{D_s \Gamma_c}{d^3} \right)}{k T}
\]

where \(D_b\) and \(D_s\) are respectively the grain boundary and surface diffusivity values and \(d\) is the grain size. The first term dominates in early stage shrinkage while the second

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Densification of monodisperse nanometal particles by sintering

dominates in later stages. In both stages, sintering rate increases rapidly with decreasing grain size. Decreasing grain/particle sizes from the micron to nanometer scale should increase sintering rates by a factor $10^9$ to $10^{12}$, sufficient to overcome decreases in diffusivity at lower temperatures. In fact, much of the earliest work in nanoparticles was done in ceramics due to the interest in lowering the required sintering temperatures.

Sintering is an attractive densification method because the basic equipment is simple and it builds on methods and theory that are well developed for micron-scale powders. However, there are important differences between micro- and nano-scale sintering. For example, some experiments show sintering activation energies for nanoparticles similar to diffusion in liquid [36]. A particularly challenging issue in nano-scale particles is the tendency of the nanopowders to agglomerate.

The typical pore size within a powder-agglomerate is a fraction of the particle size while the diameter of pores between agglomerates is several times that of an individual particle. During sintering, the smaller nano-scale pores are quickly eliminated. Densification then continues at a much slower rate proportional to the size of the agglomerate. During this slow stage of the sintering, the grains may grow significantly. The most common densification methods include pressure application before or during sintering to close large interagglomerate pores and increase the densification rate so that a final grain size in the nano-regime is maintained. [32,33,34]

While pressing samples before sintering can help close large pores and increase the initial density for improved sintering, the required pressures are often measured in GPa due to the increased hardness of nanocrystalline materials. Much lower pressures are required during heating when creep processes are significant sources of deformation. The most effective forces are those with high shear components making sinter forging and uniaxial pressing more effective than isostatic pressing. Using applied forces, many researchers have achieved high densities at significantly reduced temperatures. [32,34-39]

Pressure-assisted densification processes can be expensive and difficult to apply to complicated geometries or large components so some effort has been made to develop
pressureless densification methods. Moon [41] achieved some success with liquid phase sintering of W-Cu unpressed parts, but pressureless solid state sintering of agglomerated, unpressed powder was not effective [42]. Wet promising is a promising alternative demonstrated in nano-ceramics that reduces formation of large pores so that the samples may be densified by pressureless sintering.

Wet processing offers an alternative for reducing or even eliminating agglomerates so that pressureless sintering is more effective. Ceramics are commonly processed using colloid and slurry techniques to eliminate pressing operations prior to sintering [34]. Wet processing of metals is not widely practiced due to the difficulty of creating a stable metal dispersion, the relative ease of pressing metal to a high density, and the option of casting complicated geometries. However, at the nanometer scale, chemical synthesis techniques that readily produce unagglomerated metal dispersions are feasible. These dispersions, unlike typical nanopowders, can be made monomodal and monodisperse. Such suspensions are more likely to dry without large pores. Rhodes demonstrated this processing route in nanosized zirconia. [33] Agglomerate free powder, centrifugally cast to 74% density sintered to full density in 1 hour at 1100 C. This is 300 C lower than required for an agglomerated powder of the same crystallite size. Similarly, Markman et al [43] fully densified a colloid of 8 nm cerium oxide powder by centrifugal casting and pressureless sintering at 100 C below the temperature required for cold isostatic pressed samples. This was possible even with some 40 nm agglomerates.

Skorokhod and Ragulya [44,45] have shown that modification of sintering schedules according to the rate-controlled sintering (RCS) theory can substantially improve the densification process of pressed nickel, titanium nitride, and barium titanate. With RCS, densification can be achieved while minimizing grain growth. For example, in the case of nickel nanopowder, a full density, nano-grained sample was achieved at lower temperatures and with a smaller grain size than was possible with traditional constant heating rate sintering schedules.
3.2 Nanoiron Suspension

The nanoparticle suspension used for this work is a commercial product called "Nanolron" produced by NanoMat Inc. Nanolron is a suspension of monodisperse iron nanoparticles with a nominal size of approximately 8 nm. However, particle sizes in particular batches vary in size from 6-10 nm. The particles are supplied in a proprietary solvent with a boiling point of approximately 286°C. The particles can be removed from the original solvent and redispersed in heptane or similar solvent. The maximum concentration of iron in the dispersion is approximately 5 wt% or 0.5 vol%. A NanoMat TEM image of particles dried from their NanoIron dispersion shown in Figure 3-1.

![TEM image of dilute Nanolron suspension dried on a TEM grid. The particles unagglomerated and are very uniform in size. Image courtesy of NanoMat Inc.](image)

3.2.1 NANOBINDER DENSIFICATION

Iron nanomaterials have been studied for their structural and magnetic properties and many methods of synthesizing and processing them have been developed. Particular attention has been given to creating structural components from iron nanopowder via sintering, primarily pressure-assisted sintering. [36-40] After pressing, sintering at temperatures between 700°C and 900°C increased the density to over 90%. Some methods, particularly plasma pressure consolidation [38] more successfully maintained grain sizes
Densification of monodisperse nanometal particles by sintering

below 100 nm. Generally, at high densities, grain growth progresses rapidly and nanograined structures are easily lost.

The proposed nanobinder must be densified after application to the micron-sized powder, presumably by either melting or sintering. Although the melting point of nanoparticles is reduced, it is not likely that the nanobinder could be densified by melting the particles at a reduced temperature for several reasons. First, the experiments that have shown dramatically reduced melting points of nano-particles have been performed on carefully controlled geometries that could not reduce their surface energy by sintering as could happen in the nanobinder [19,20]. Second, if size-effect melting occurred in a packed bed of nanobinder, the liquid state is likely to be transitory, as the surface energy will be reduced very quickly. The nanopowder would likely re-solidify before fully densifying. Third, thick sections of 3DP parts would not be amenable to rapid heating required for melting. In addition, the 8-10 nm particle size of the available nano-iron dispersions would not provide sufficient melting point reduction to melt the particles before the skeleton powder begins to creep or sinter significantly. They might not even melt below the steel infiltration temperature.

Sintering of the nanoparticles is a more promising densification process. Many studies of nanoparticle sintering have been performed and the reduced sintering process temperatures are well documented. For example, Dominguez and Bigot reported measurable sintering as low as 100 C in 40 nm iron particles [36]. The biggest challenge in typical nano-particle sintering is minimizing grain growth to improve the final properties, but this is not a significant issue for the nanobinder. Larger grains will reduce the creep deformation rates. However, the typical nanometal sintering process includes applied pressure before or during sintering to close large pores between agglomerates [36-40] as discussed above.

Pressure assisted sintering of nanoparticle deposits within a micron-scale powder skeleton would be very difficult to achieve. A method would be needed that would apply a pressure to the nanoscale pores in the nanoparticle deposits while applying little or no
Densification of monodisperse nanometal particles by sintering

pressure to the micron scale particles. It might be possible by pressing the part in a fluid with controlled wetting properties. Under pressure a poorly wetting fluid could be forced into the micron-scale pores between skeleton particles but not enter the nanoscale pores that should be eliminated. Thus, a net pressure could be applied to the nanoscale pores. However, this pressure would probably need to be applied while at temperatures of at least 600°C. It would be very difficult to find a suitable fluid and then extract it from the part after processing.

Pressureless sintering is a much more favorable densification route. Pressureless sintering is easily integrated into the existing processing procedures for infiltration of metal parts and could be done in the existing equipment. The nanobinder is an inherently “wet” processing approach with the attendant decreases in agglomeration discussed above. If the nanoparticles are dried without significant agglomeration, the dried deposits will have a narrow pore size distribution suitable for densification by pressureless sintering. While the grains are likely to grow very rapidly during the final stages of densification, the grain growth is desirable for good creep strength. The nanobinder application requires strength at high temperatures where a large grain size would reduce the strain rate.

3.3 Oxidation of Nanoparticles

Many metals, including iron are susceptible to oxidation at room temperature. Nanoparticles, with their large surface area and small sizes, can oxidize very quickly. This may make it difficult to prevent oxidation of a metallic nanobinder during processing. However, it may also be possible to achieve good results using metal oxides that are reduced during later furnace processing.

An important question in handling the nanoiron is its oxidation rate when exposed to air. A slow oxidation rate or a stable oxide passivation layer would simplify handling of the metal colloid.
Measurements have been made of the oxidation kinetics of Iron in air [46]. These have generally used the parabolic model to describe the results. Extrapolation of this data gives estimates of a room temperature parabolic rate constant \((k_p)\) between \(10^{-15}\) to \(10^{-20}\) mg/cm\(^2\) where the rate constant expresses the weight gain due to oxidation per unit area of surface. This can be applied to the case of a 10 nm thick iron layer oxidizing on both sides to estimate the oxidation rate of the iron nanoparticles at room temperature. This predicts an oxidation time between 3 ms and 300 s for the extreme estimates of the rate constant.

This analysis does not include the effects of the surface ligands or the transport of oxygen through the liquid. Both of these could slow the oxidation rate, but it does suggest that the oxidation could be quite rapid.

### 3.3.1 MEASUREMENT METHOD

The saturation magnetization of the sample was chosen to measure the oxidation state of the nanoiron. While oxidation rates are typically measured by weight change, it is difficult to measure the oxidation in the liquid by weight change as there may be some evaporation of the solvent that would offset the weight gain due to oxidation. The saturation magnetization is a property of the material and its crystal structure. It is generally considered independent of particle size, but at the nanometer scale, there are some size dependencies. Surface atoms have a non-equilibrium structure and can react with coatings or the solvent to lower their magnetic response. [47]

The bulk (multi-domain) properties of pure iron and the stable room temperature iron oxides are summarized in Table 3-1. Elemental iron has the highest magnetization. Maghemite \((\gamma\text{-Fe}_2\text{O}_3)\) and magnetite \((\gamma\text{-Fe}_3\text{O}_4)\) are much lower. The magnetization of hematite \((\alpha\text{-Fe}_2\text{O}_3)\) is so much lower that it is generally considered nonmagnetic.
Densification of monodisperse nanometal particles by sintering

Table 3-1 Saturation Magnetization of Iron and its Oxides at Room Temperature

<table>
<thead>
<tr>
<th></th>
<th>Magnetic Order</th>
<th>Saturation Magnetization (emu/g)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Ferromagnetic</td>
<td>218</td>
<td>48</td>
</tr>
<tr>
<td>Hematite (α-Fe₂O₃)</td>
<td>Canted Antiferromagnetic</td>
<td>0.4</td>
<td>49</td>
</tr>
<tr>
<td>Maghemite (γ-Fe₂O₃)</td>
<td>Ferrimagnetic</td>
<td>74</td>
<td>50</td>
</tr>
<tr>
<td>Magnetite (γ-Fe₃O₄)</td>
<td>Ferrimagnetic</td>
<td>84</td>
<td>50</td>
</tr>
</tbody>
</table>

The magnetization at a peak field of 10000 Oe decreased by two orders of magnitude after exposure to air. Such a large decrease is probably a result of oxidation to hematite with some remnants of more magnetic oxides still present. The oxidation rate was measured by placing the liquid nanobinder in an open dish so that it formed a layer of approximately 1-2 mm thickness. At measured times, a small sample cup (volume ~ 70 μl) was filled with suspension and sealed. The weight was recorded, and then the magnetization of the sample at room temperature was measured using a vibratory sample magnetometer at field between ±10000 Oe. Under the applied field, the magnetization of the sample continues to increase until it reaches a limiting value, the saturation magnetization. The saturation magnetization per gram of the samples was then calculated and plotted as a function of air exposure time.

3.3.2 RESULTS

Figure 3-2 summarizes the changes in magnetization with time for two different Nanoiron suspensions. The initial iron concentration and oxidation level of the two suspensions is different, but both are described well by an exponential decay as illustrated in the Figure. The time constants of the processes are similar but vary by 14%.
The magnetization decreases to zero as the metallic iron oxidizes to a nonmagnetic oxide. The process is well-described by an exponential with a time constant of approximately 30 minutes.

Figure 3-2 Magnetization Decay of Nanoiron during air exposure. The magnetization decreases to zero as the metallic iron oxidizes to a nonmagnetic oxide. The process is well-described by an exponential with a time constant of approximately 30 minutes.

The oxidation of the nanoparticles proceeds relatively rapidly with a time constant on the order of 30 minutes. The solutions were almost totally oxidized within two hours of exposure. These oxidation measurements indicate that limited air exposure may be permissible when handling, but the extended air exposure that would be required for printing nanoiron in the 3DP process would result in full oxidation unless the atmosphere were controlled. Drop-on demand printing would be easiest since the binder is not recirculated. In these conditions, only the atmosphere around the powder bed would need to be controlled. Continuous jet printing would be more difficult because the binder is exposed to air in the printhead and may be recycled during operation.

The impact of oxidation state on the processing of the particles must be measured to establish whether the oxygen exposure needs to be controlled. The x-ray diffraction study summarized in Section 3.7.1 below shows that the oxidation state of the iron has a large
impact on the final carbon content of the iron after heating and possibly the speed and temperature at which it densifies. The impact of the nanoiron oxidation state on the nanobinder is considered in the subsequent tests on the structure and evolution of the nanoparticles during drying and sintering. Chapter 4 addresses the impact of particle oxidation on the deformation and shrinkage rates of the material.

3.4 Drying the Nanobinder

A successful nanobinder that densifies by sintering must dry to a high density with a narrow pore size distribution. Previous work has shown that monodisperse nanoparticles can form suitable structures on drying. This work is reviewed and the structure of the dried nanoiron is analyzed to verify that it is suitable.

3.4.1 NANOCRYSTALLINE SUPERLATTICES (NCS)

When nanoparticle suspensions dry, the particles eventually agglomerate. The nature of the final deposit depends on the stability of the particles during drying, the drying conditions, and the size distribution of the particles. If a repulsive particle-particle force is maintained throughout the drying process, the particles remain separated until the latest stages of drying and eventually form a disordered glassy structure as the surface tension of the solvent compresses the particles. However, if the particles become slightly attractive during drying, the particles may begin to form agglomerates. Under the right conditions, the particles will tend to arrange in a close-packed configuration in two and even three dimensions. The capping ligands of adjacent particles bond them together. Particle-particle separation is less than two ligand lengths indicating that the ligands covering the nanoparticles are interdigitated. This high-level organization is favored by slow changes in stability and high diffusivity of the samples that permit arriving particles to reach low-energy positions in the growing superlattice. Changes in the stability may be achieved by removing solvent through evaporation to increase the particle concentration or by adding small amounts of a poor solvent as by diffusion through a buffer layer.
Densification of monodisperse nanometal particles by sintering

Diffusivity of the particles in their solvent depends on particle size, solvent viscosity, and temperature. These orderly arrays of nanoparticles where nanoparticles are arranged like atoms in a crystal lattice are commonly referred to as nanocrystalline superlattices (NCS).

NCS structures have been formed from particles of many different compositions including semiconductors [59], gold [60-62], silver [63,64], iron [65,66], cobalt [67-69], ceramic [70], and some metal alloys [71,72]. Although Soulantica et al. reported the formation of NCS structures in tin [73] from a polydisperse particle solution, the primary requirement for lattice formation in most systems is a narrow particle size distribution [56]. This can be achieved directly by some synthesis methods while many require secondary size-selective precipitation to narrow the size distribution.

Superlattices are very promising for their potential to produce regular structures based on equilibrium of chemical forces without direct assembly operations. They could be useful in manufacturing photonic crystals [74], data storage structures [75], and sensors [76]. The superlattice structures are formed relatively easily based on the conditions of thermodynamic equilibrium, creating relatively complex structures with minimal external input. Unfortunately, just as in crystal lattices, superlattices have defects. Controlling the defect density is essential to many of the potential applications of superlattice structures.

Superlattice structures provide the essential characteristic for successful pressureless sintering of nanoparticles: a narrow pore size distribution and high packing density. The particles typically arrange in close-packed structures to achieve the highest possible density for monosized particles. Of course, density might be increased further through incorporation of bimodal particle sizes as has been done by Kiely et al. [77], Murray et al. [75]. Additionally, the sintering process may be more accommodating of defects in the NCS structure than data storage or photonic crystal applications. Glassy structures [56] may also provide a sufficiently small pore size distribution to enable good densification, but the initial density will be lower than for a superlattice structure made from the same particles.
3.5 Dried Nanoiron Structure

To verify that the desired high-density, narrow pore size distributions could be achieved in the nanoiron, the dried nanoiron structures were characterized under several different drying conditions. Characterization was performed by transmission electron microscope (TEM) imaging of small samples and gas adsorption pore-size measurement of larger samples. TEM images help to characterize the organizational structure of the nanoparticles. Gas adsorption tests measures the overall structure and can be used to measure how it changes with sintering.

3.5.1 TEM IMAGES

Transmission electron microscope (TEM) samples were prepared by placing small amounts of dispersed nanoparticles on TEM grids with an amorphous carbon support and then removing the solvent by drying. Material was applied by placing the grid upside down on a drop of fluid and then removing it. When applied full strength, the deposits were often thick enough that some areas of the grid were too thick to be electron transparent. Most of the imaged areas were likely multilayered. In order to image individual particles, some solutions were diluted with excess solvent so that individual particles could be obtained. Tests were done with both the heptane and proprietary solvents. Drying was done in a furnace with a controlled atmosphere at temperatures ranging from 120°C to 180°C.

While air exposure was minimized for many of the samples, all samples had at least five to ten minutes of air exposure during transport to the TEM and placement in the microscope. The particles were probably at least partially and possibly fully oxidized at the time of TEM imaging. All TEM imaging was done on a JEOL 2010F with an accelerating voltage of 200 kV.
Densification of monodisperse nanometal particles by sintering

Figure 3-3 shows images of dispersed particles from the heptane and proprietary solvent solutions. The particle sizes measured from the images are very similar as shown in Table 3-2. The standard deviation is approximately ±20% of the average size. A standard deviation of ±5-10% is a typical target for creating superlattice structures [56].

Table 3-2 Particle sizes measured from TEM images of nanoparticles

<table>
<thead>
<tr>
<th>Solution</th>
<th>Avg Particle Size (nm)</th>
<th>Standard Deviation in Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heptane</td>
<td>8.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Proprietary Solvent</td>
<td>8.8</td>
<td>1.3</td>
</tr>
</tbody>
</table>

When drying concentrated solutions on the TEM grids, superlattice structures were observed over most of the sample while there were also areas of more random packing. Samples were dried at temperatures of 120 C, 150 C, and 200 C. Figure 3-4 and Figure 3-5 compare images of samples dried at the two extreme temperatures. The slower drying at 120 C created somewhat larger ordered regions than drying at 200 C, although ordered structures are observed under both conditions. These particles in the ordered regions show up as either bright or dark depending on the imaging conditions. In some cases, as in the 120 C image, both can be observed in the same image. The image of the 200 C sample is somewhat clearer, perhaps due to a thinner deposit. This sample showed two different
packing structures as seen in the close-ups in Figure 3-4(B,C). The particles in the two regions appear to be different sizes, but it is difficult to measure the particle sizes accurately from the image. No images of diluted suspension for viewing individual particles were made of this batch of suspension.

Figure 3-4 TEM images of dried nanoiron deposits after drying at 120°C and heating to 400°C.  
A) Wide area image showing ordered and disordered regions.  
B) Close-up of an area in which dark regions are particles as evidenced by their six-fold symmetry.  
C) Close-up of area in which the bright areas appear to be the particles.

No particles are visible in the disordered regions. This suggests that we may be looking at thick structures where only the orderly packing permits the formation of contrast. When this order breaks down or when it is not oriented with a plane of symmetry along the viewing axis, the structure is no longer visible. The predominant ordered structure is the close-packed plane structure with six-fold symmetry as illustrated in Figure 3-4 and Figure 3-5.
Densification of monodisperse nanometal particles by sintering

Figure 3-5 TEM images of dried nanoiron deposits after drying at 200 C and heating to 400 C. Two different scaled structures are observed as seen in the detail on the right. On top, is a close packed structure, possibly a single layer. Below is a view of another section with larger spacing and at least two layers.

As is typically seen, the particles in these ordered structures appear to have formed close-packed structures with the close-packed planes parallel to the substrate. The close-packed planes are characterized by six-fold symmetry in the particle arrangement. In the FCC lattice, the close-packed planes are the \{111\} planes as illustrated in Figure 3-6 (b). The \{111\} planes form an equilateral triangle in the close-packed plane as illustrated. Figure 3-6(c) is a high magnification image of a lattice-structure produced from the particles imaged in Figure 3-6 (b) with an equilateral triangle illustrated. The diagonal of the face-centered cubic primitive (a) as measured from TEM images of the close-packed structures is 21.9 nm.
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Figure 3-6 Illustrations of close-packed structures. A) Illustration of a face-centered cubic primitive cell with important dimensions labeled. B) Illustration of the close-packed {111} plane in the unit face-centered cubic cell. C) Image of a close-packed plane in the dried nanoiron deposits with an equilateral triangle formed from the {111} diagonal plane of a unit cell illustrated in (B) labeled.

The diagonal length of the unit cell (b) should be twice the diameter of the particles. However, due to the coating ligands, the actual spacing is larger. This reduces the density of the superlattice structure significantly. The volume fraction (f) of the particles in the structure is given by

\[ f = f_{\text{closepacked}} \left( \frac{2d}{b} \right)^3 = \frac{\pi \sqrt{2}}{6} \left( \frac{2d}{b} \right)^3 = 0.74 \left( \frac{2d}{b} \right)^3 \]

Using the measured particles size (Table 3-2) and cube diagonal b (Figure 3-6), the volume fraction of iron in the structure is estimated as 38%. The packing fraction is very sensitive to the particle size measurements. A variation of one standard deviation in the measured particle size (±1.3 nm) would give packing densities as low as 24% and as high as 58%. These changes in packing fraction also have a large impact on the shrinkage required for
densification. This sensitivity also suggests a solution to shrinkage problems. If the particle size can be increased relative to the length of the coating ligands, the density can be increased significantly.

EDS measurements of the iron deposits generally show significant iron, oxygen, copper, and carbon present. The copper is certainly from the TEM grid and much of the carbon signal may be the amorphous carbon support on the grid. However, the oxygen is likely present in the form of iron oxide. Some locations showed traces of silicon. These generally showed anomalously high measurements of oxygen as well. This was attributed to contamination of the sample with Silica from the furnace insulation. Relative concentration of iron and oxygen were compared across many of the samples. While the oxygen content varied significantly, there were approximately equal atomic fractions iron and oxygen in most locations.

3.5.2 GAS ADSORPTION DATA

Surfaces tend to adsorb molecules of gas. The coverage of the surface is a function of the temperature, pressure, adsorbing material, the adsorbent, and the geometry of the sample. For adsorption of nitrogen, the importance of the adsorbing material is minimal. If the temperature is controlled, the relationship between the quantity of adsorbed material and the pressure is primarily a function of the surface area and pore geometry. The quantity of gas adsorbed to a surface as a function of pressure can then be related to the surface area and the pore size distribution of the sample using various models.

The adsorption as a function of relative pressure (absolute pressure/saturation pressure) at a constant temperature is called an adsorption isotherm. Many processes have been developed for measuring an isotherm, but the basic process is similar in all cases. The samples are first degassed in vacuum, possibly with heating to remove adsorbed molecules such as water and carbon dioxide and provide a consistent starting condition for analysis. The pressure is then increased in small increments and the adsorbed quantity measured at each pressure. One common way to do this is to dose the sample with precisely measured
quantities of gas at a controlled temperature. The equilibrium pressure is measured. The adsorbed quantity is calculated from the ideal gas law using the measured total volume.

Gas adsorption isotherms can be related to the pore size distribution by various models. Typically these models assume a simplified pore geometry such as cylindrical or slit (parallel walls) and then calculate the pore filling response as a function or pressure. Density functional theory attempts to account for the continuous variation in gas density in the region near the surface and is generally one of the most accurate models. However, these models are only as accurate as the assumptions that go into them. Samples such as the dried nanobinder do not closely approximate the assumed geometry and so the pore sizes calculated must be considered as approximate measures. The method is most helpful in illustrating the distribution of pore sizes and supporting comparisons between samples.

Gas adsorption techniques were used to provide additional information regarding the pore size distribution to complement the TEM imaging. The pore size distribution was measured using an ASAP 2020 Accelerated Surface Area and Porosimetry Analyzer from MicroMeritics with nitrogen as the adsorptive at a temperature of 77 K. Before measurement, all of the samples were degassed by heating to 200 °C while maintaining a pressure of 5 µm Hg or below for 150 min. After initial measurement of the sample freespace using helium, the samples were degassed again to assure full removal of helium from the micropores present. Pore size distribution was calculated from the adsorption isotherms using the original density functional theory method as implemented in DFTPlus from MicroMeritics. The calculations were performed with the “N2 on Carbon with slit pores using Non-negative regularization and no smoothing” model.

Samples were prepared for analysis by extended drying at a steady temperature followed by a ramp to 400 °C to help remove solvent from the smallest pores. The dried material was removed from the furnace and placed under a nitrogen environment while the deposits were scraped from the drying container and the resulting powder placed in a sample tube for measurement. The fragments of dried material were typically between 100
μm and 5 mm in size. The extra surface area created by breaking the deposits should be small relative to the high surface area of the nanoscale pores.

The samples were dried at 150 °C under a nitrogen atmosphere for 8 days. After the final drying, the samples were ramped from 150 °C to 400 °C over 2 hours and held 1 hour to remove the final deposits. The inert atmosphere was established by evacuating the furnace to 2 Torr and then backfilling with Nitrogen. During drying, the exhaust valve of the furnace remained closed and the tube was pressurized to 5 psi by a connection to a high purity nitrogen source.

3.5.3 RESULTS

The pore size distribution was calculated using density functional theory. Figure 3-7 shows the pore size distribution of the dried nanoparticles as a function of the pore size. While the distribution is bimodal, all the measured pore volume is from pores less than 20 nm. Such pores should densify effectively by pressureless sintering. The spike in pore volume at approximately 1.3 nm could be from the gaps between the particles resulting from the coating ligands. The other discontinuities might be caused by other characteristic pore structures of an orderly packed solid.
3.6 Densification without a Substrate

The simplest case for densification of these nanoparticles is when they are free of constraints from and reactions with a substrate. The unconstrained case will be considered first in this section. The case of sintering and densification on a substrate will be addressed in the following section.

The results of sintering the nanoiron deposits were first examined via TEM imaging. A copper TEM grid with amorphous carbon support was coated with nanoiron as described above and then heated to 700 °C in a forming gas atmosphere. This process minimized particle oxidation until after sintering was completed. After the 700 °C heating, it was imaged. As seen in Figure 3-8, the deposits have formed large, apparently dense nanoparticles 10-30 times the size of the original particles. EDX analysis of the
composition of these particles reveals that they are iron with only trace amounts of oxygen. Many locations showed significant carbon as well. This may be from the amorphous carbon support or because the particles have formed iron carbide. It appears that on heating, the deposits separated into discrete islands that densified completely via sintering.

![TEM Image of Nanoparticles](image)

**Figure 3-8 TEM image of nanoparticles heated to 700 C shows significant sintering creating large particles.** All of the particles observed were formed from 10 nm iron particles deposited on the substrate.

A quantitative view was attained using the gas adsorption technique. This method compiles volume average characteristics of large sample sizes. Loose fragments or powder of dried deposits can be used to approximate the unconstrained sintering case. By repeated gas adsorption analysis after successive processing steps, the evolution of the pore space with heating can be followed.

For these tests, the dried sample from the previous gas adsorption test was returned to the furnace and heated to a higher temperature. The pore size measurement was then re-measured using the same methods as above. This process was repeated at successively higher temperatures to track the evolution of the pores in the dried deposits. Measurements
Densification of monodisperse nanometal particles by sintering

were made after sintering to 600 C, 700 C, and 900 C. All heating was done at 10 C/min with rapid cooling. The peak temperature was held for 10 minutes for each case except 700 C which was held for 20 minutes. Measurements of the sample weight before and after heating showed no significant weight loss during heating, confirming that the samples were unoxidized. Further, the solvent was extracted and the organic ligands decomposed during the initial heating to 400 C and/or degas under vacuum at 300 C.

Figure 3-9 shows the evolution of the pore sizes in the slow-dried sample as measured by gas adsorption. The patterns of the pore size distribution remains remarkably consistent throughout the heating while the total pore volume clearly decreases with some coarsening. The pore volume and surface area of the 900 C sample is too small to produce reliable data, but it continues to support the trend of decreasing total pore volume with some increase in the total pore size.

Figure 3-9 Evolution of pore-size distribution with sintering for slow dried nanoiron. Pore size distribution was measured using gas adsorption. At each successive temperature, the total pore volume decreases with minimal increase in the average pore size.
As discussed in Section 3.7.1 below, x-ray diffraction studies of unoxidized nanooiron showed that most of the material is iron carbide after heating to 700 C. As iron carbide is more refractory than iron, the sintering temperatures should be raised relative to pure iron. If the same material were deposited on an iron substrate, the carbon could diffuse into the substrate so that the deposit would convert from iron carbide to iron. Sintering could then proceed at the faster rate of elemental iron.

Oxidized material might also sinter more rapidly than unoxidized material. On heating, the carbon would react with the oxygen, decarburizing the deposit and allowing faster densification. Evidence of faster sintering in oxidized particles was seen in gas adsorption tests, as well as in layer deposition tests described in Section 3.7.1 below. In the gas adsorption tests, a suspension of nanoiron particles in a heptane solvent was dried at 90 C and then exposed to air to allow oxidation. After drying, the sample was heated to 400 C and then evaluated by gas adsorption. This process was repeated at temperatures of 500 C, 600 C, and 700 C. The pore size evolution is shown in Figure 3-10.

The lower end of the pore distribution is very similar to the slow-dried unoxidized sample. It appears to have substantial order based on the distinct peaks in the pore size distribution. However, there is a second peak in the distribution at 1000 Angstroms. This second peak represents large defects in the dried structure, probably from drying very rapidly at a temperature near the solvent boiling point. Additionally, the temperature is lower than in the previous drying tests so that there is less thermal energy. This lowers the diffusivity of the particles in the suspension and decreases their ability to form close-packed structures. On heating, the large pores increase in size while the small pores disappear. This is a common problem in sintering nanoparticles as discussed above and underscores the importance of controlling the initial sintered structure to achieve densification.
Densification of monodisperse nanometal particles by sintering

The pore distribution was virtually unchanged between 400-500 C and between 600 and 700 C. Additionally, the weight of the sample decreased by 36.8% between these two steps. If the sample were initially $\text{Fe}_2\text{O}_3$, the weight decrease on reduction to metal would be 30%. However, if the oxide were reduced by carbon in the sample to form $\text{CO}_2$, the total weight loss would be 37.1%. This reduction process would explain the weight change and the sudden sintering when heating from 500 C to 600 C.

After heating to 700 C, the gas adsorption data shows significant pores 100 nm and larger—too large to measure with this method. To track further evolution, the sintered deposits were imaged in the SEM after heating through the 700 C cycle. The deposits were reheated to successively higher temperatures to track the evolution of the pores. Figure 3-11 shows representative images of the material after each processing step. The 700 C image confirms the gas adsorption calculation of reduced slow pores with only large pores.
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remaining. Unlike the slow-dried, unoxidized case above, the sample shows limited evidence of densification. The predominate change with heating is pore coarsening.

![SEM images of quick-dried BET samples sintered to progressively higher temperatures.](image)

Figure 3-11 SEM images of quick-dried BET samples sintered to progressively higher temperatures. Pore coarsening is favored over densification.

3.6.1 ESTIMATING DENSITY OF NANO MATERIALS

Density measurement of these nano-structured materials is a significant challenge. The quantity of material and the size of an individual sample are too small for accurate weight measurements as would be required for application of Archimedes method. Many methods are available for measuring porosity from sample cross-sections. However, this method is limited by the ability to prepare representative cross sections without smearing or enlarging nanoscale porosity. If a suitable cross-section could be prepared, SEM imaging
might not have sufficient resolution to detect all the porosity. TEM has sufficient resolution, but it may be difficult to resolve the porosity unless the sample is thin relative to the pore size—a substantial challenge for pores less than 100 nm. Mercury porosimetry requires relatively large sample sizes and could not measure the smallest pore sizes.

A lower bound on the sample porosity can be calculated from the pore volume measured by gas adsorption. Porosity is estimated by assuming the sample composition, in this case iron. Further, all pores are assumed to be open and within the size ranges measurable by the gas adsorption method (1.3 nm to 100 nm). Larger pores can be identified by SEM imaging. The volume fraction of pores (\(\bar{\rho}\)) of the sample is then given by

Equation 3-3

\[
\bar{\rho} = \frac{\nu}{\nu + \frac{1}{\rho}}
\]

where \(\rho\) is the density of the sample material and \(\nu\) is the measured pore volume per gram of material. This estimate is only as good as the assumptions about the composition. If iron composition is assumed, while significant organic coating or residual solvent is in the sample, the volume of the sample is underestimated and the quantity of iron present overestimated. After high temperature processing (600-700 C), the composition assumption should be reasonably accurate since the organic coating should have decomposed, solvents evaporated, and oxides reduced.

Table 3-3 summarizes the porosity estimate from each of the gas adsorption measurements. While this measurement cannot account for closed porosity, experimental and theoretical studies of sintering in micron-scaled powder show that most pores generally remain open until the porosity drops below 15% and they are virtually all closed at a porosity of 5%. The pores close because the cylindrical pores become unstable and pinch off to form isolated spherical pores. [79] Clearly, the 700 C sample is approaching a porosity level where the closed pore volume will increase, but the total porosity calculation is probably still a good estimate. The calculation for 900 C is likely low due to an increase
Densification of monodisperse nanometal particles by sintering

in the volume of closed pores. The measurement accuracy may also have decreased significantly. Due to the decreasing surface area and pore volume with sintering, the sample no longer meets the recommended minimum sample size for good repeatability.

It is difficult to predict exactly how the nanoiron would respond under slower heating cycles characteristic of powder-metal processing. However, it is likely that the slower ramp rates will allow greater densification at a given temperature than was measured in this test.

<table>
<thead>
<tr>
<th>Test Condition</th>
<th>Measured Pore Volume (cm^3/g)</th>
<th>Percent Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>400 C (200 C degas)</td>
<td>0.0859</td>
<td>40.1%</td>
</tr>
<tr>
<td>400 C (300 C degas)</td>
<td>0.0819</td>
<td>39.0%</td>
</tr>
<tr>
<td>600 C</td>
<td>0.0684</td>
<td>34.8%</td>
</tr>
<tr>
<td>700 C</td>
<td>0.0344</td>
<td>21.1%</td>
</tr>
<tr>
<td>900 C</td>
<td>0.0116</td>
<td>8.2%</td>
</tr>
</tbody>
</table>

3.7 Densification on a Substrate

Given the low initial packing density of the nanoparticles, significant shrinkage is necessary to sinter to full density. When sintering loose flakes of dried material, shrinkage proceeds unrestrained. However, when the nanoparticle suspensions are applied to a substrate, new constraints are applied on the densification process. Adhesion forces between the deposited particles and the substrate will resist shrinkage. For densification to proceed, the substrate bonds or the particle-particle bonds will likely fail causing cracks and/or delamination. The situation will be more complicated in the powder where the particles are constrained between two curved substrates. These constraints may impede densification.
Additionally, the deposited material may react with the substrate to encourage or retard sintering. The possible diffusion of carbon from the deposit into the substrate is of particular interest in the iron material system.

3.7.1 PHASE EVOLUTION

Initial study of the densification of nanoparticle layers on planar substrates was done using X-ray diffraction (XRD) of nanoiron applied to substrates. XRD techniques were used to characterize the phases of the material, look for evidence of crystals smaller than 100 nm, and check for existence of single crystal structure. Various x-ray diffraction (XRD) techniques can be used to identify both the crystal structure and orientation of the crystals. There are many XRD techniques, but two were used in this study, powder diffraction and back reflection Laue.

In powder diffraction, a monochromatic beam of x-rays is directed at a collection of randomly oriented crystals in a polycrystalline material. The relative angles between the incident x-ray beam and the detector can be varied to measure the intensity of reflected or transmitted x-rays that meet the Bragg condition at each angle. With a sufficient number of randomly oriented crystals, some will be oriented so that some will meet the Bragg condition for each of the allowed reflection angles. The variation of x-ray intensity with angle will show a series of peaks that are characteristic of the particular crystal structure. If more than one crystal structure is present, the measured response will be the volume-weighted sum of the individual phase responses. Measured peaks can be compared to reference measurements to identify the phases present. Additionally, peaks from small crystals (<100 nm) broaden. The breadth of the peaks can be used to estimate the volume-weighted average crystallite size for crystals below 100 nm. If this technique is applied to a sample with preferential grain orientation, the relative intensities of the different peaks will vary. In the limit, a single crystal will have only one very large peak if it is oriented to perfectly satisfy Bragg’s law or no peaks if it is somewhat misoriented.
Laue X-ray diffraction uses a collimated beam of continuous x-rays directed onto a stationary single crystal specimen. The x-ray beam contains many different wavelengths so that for any crystal spacing, there will be some wavelengths present that meet the Bragg criteria. If the reflected x-rays are recorded on a film, the angles that meet the Bragg condition will show up as bright spots on the film. In other areas, the x-rays will interfere and no signal will be visible. The pattern of dots and its orientation is a function of the crystal orientation. If there are multiple crystals illuminated by the beam, the patterns will overlap. If there are many such crystals, the responses of individual crystals will blend and no pattern will be visible.

XRD was used to better understand the evolution of nanoiron deposited on a substrate. The substrate was a polished single crystal of iron. The single crystals were grown from high purity (99.999% metals basis) iron foils, 2mm thick purchased from Alfa Aesar. Carbon content of the as-purchased samples was measured by combustion infrared detection and determined to be <.005%. The grains in these plates were grown to large sizes by long high temperature annealing cycles at 1300 C and 900 C. The samples were then etched to reveal the grains and cut along grain boundary lines using a low-speed diamond saw to isolate individual crystals. Typical cut grains varied from 5-15 mm on a side. The samples were then mechanically polished on one side using a .05 μm alumina final polish and annealed for several hours at 850 C to remove any small crystallites created during cutting and polishing. After preparation, the crystal orientation was measured using back-reflection Laue and the base diffraction response was measured. The crystals were not oriented with any planes of symmetry so that powder diffraction measurements of the untreated single crystal specimens showed no peaks. Figure 3-12 is a sample powder diffraction measurement of an untreated single crystal specimen. This zero-background substrate permits clear measurements of small quantities of deposited material.

Two nanoiron layers were applied, dried, and sintered on each substrate. After sintering, the layers were examined using the powder diffraction technique with copper Kα radiation. Typical scan speed was 2.5 degrees per minute with the X-ray generator.
Densification of monodisperse nanometal particles by sintering operating at 60 kV and 300 mA. The resulting spectrum was compared to reference data to identify the phase composition. The samples were then returned to the furnace for additional sintering and the process was repeated. All sintering was done with a 10 C/min heating rate and a 10 minutes hold at the sintering temperature. Samples were allowed to cool at 20 C/min except as noted. The same approximate in-plane orientation of the substrate (±5°) was maintained for each powder diffraction analysis.

The nanoiron suspension was applied to the samples in either the oxidized or the unoxidized state. The unoxidized samples were maintained in an inert or reducing atmosphere, nitrogen or argon with 5% hydrogen respectively, during application, drying, and sintering. The oxidized samples were treated with nanoiron from the same batch but were dried in air. Sintering was conducted in a reducing atmosphere of argon with 5% hydrogen. The samples were tested after heating to 700 C, 800 C, 900 C, and 1100 C. Powder diffraction analysis was complemented with back-reflection Laue at several points to verify the status of the single crystal substrate. The deposits were imaged in the SEM after the 900 C and 1100 C heating cycles to examine their morphology.

Figure 3-13 shows the evolution of the XRD pattern of the deposited nanoiron on the single crystal iron substrates. The oxidized solution shows strong iron peaks under all conditions. At the 700 C condition, there are trace amounts of cementite (Fe₃C) present.
However, the unoxidized solution is entirely iron carbide after heating to 700°C. The composition difference between the initially oxidized and the unoxidized samples suggests that the iron oxide is reduced by the carbon from the ligands. The reacted carbon leaves as carbon monoxide or carbon dioxide. This depletes the carbon in the sample such that no measurable iron carbide forms. Conversely, in the unoxidized case, the carbon remains and reacts with the iron to form iron carbide on heating.

No free carbon was detected in either measurement. However, this is likely due to the thin dispersed structure the carbon would form. It started as a 2-3 nm coating on the 10 nm particles. If it were to form a crystalline structure, it would form very broad peaks and if it did not crystallize, there would be no distinct peaks to measure. In either case, it would be difficult to detect small amounts of free carbon. Extra carbon may also have formed other iron carbides with higher carbon concentrations. Some of the peaks for other iron carbides are very close cementite peaks and so it would be difficult to identify trace amounts of these phases.
Densification of monodisperse nanometal particles by sintering

Figure 3-13 XRD data of Nanoiron applied to a single crystal iron substrate. (Top) Oxidized nanoiron solution was dried in air at 150 C to allow it to oxidize. XRD profiles are shown after heating to 700, 800, and 900 C. The sample matches the BCC iron pattern very well in each condition. (Bottom) XRD of solution entirely maintained in inert atmosphere until after the 700 C heating. Initial testing shows very strong iron carbide peaks with only traces of iron. With further heating to 800 and 900 C, the iron carbide peaks disappear and iron peaks grow. The increase in iron peaks results as carbon diffuses into the substrate to convert the iron carbide to iron. The increase in carbon in the substrate also converts some regions to austenite at the sintering temperature. The austenite forms polycrystalline ferrite on cooling that reinforces the iron peaks.
After additional heating to 800 C, the iron carbide peaks disappear. This could be caused by diffusion of the carbon into the substrate or reaction with oxygen in the sintering atmosphere. While both processes likely occur, the increased strength of the iron signals with additional sintering suggests that substantial carbon is diffusing into the iron substrate. During the 800 C sintering, regions with carbon above approximately 0.02% will begin to change phases from ferrite to austenite as evidenced by the phase diagram in Figure 3-14. On cooling, the high carbon region will transform back to ferrite. However, new grains of ferrite may nucleate. The solubility of carbon in iron also decreases significantly so that carbides will be precipitating concurrently. These carbides will slow the growth of the single crystal grain, which might otherwise consume the small grains nucleated near the surface on cooling.

The new grains nucleated on cooling in the high carbon regions will be oriented randomly so that many will reflect the x-ray beams during subsequent diffraction tests—increasing the signal strength. With additional diffusion and heating to higher temperatures, more material will be recrystallized until little or nothing of the original single crystal would remain.
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Figure 3-14 Iron-Carbon phase diagram [80]. Above 740°C, austenite (γ) will begin to form everywhere the carbon concentration is above the solubility limit. This limit is 0.02% at 740°C and decreases with increasing temperature. With such low solubility, small amounts of carbon diffusing into the substrate from the nanoiron layer will cause a phase change.

At 900°C, any areas with more than .02% carbon will convert entirely to austenite. After heating to these high temperatures, the original single crystal structure should be lost near any surfaces with significant carbon present. Back-reflection Laue tests were performed on the front and backsides of the crystals to check for detectability of the single crystal pattern. Laue patterns were observed on the back of the samples that matched the initial crystal orientation.

Figure 3-15 compares the Laue patterns of the crystals at each stage of the processing. Untreated single crystals show clear patterns characteristic of single crystal specimens. These patterns remain largely unchanged after applying the nanoiron and heating to 700°C. However, the Laue pattern is obscured by a polycrystalline surface layer after heating to 900°C, while the single crystal pattern remains on the backside of the samples. The unoxidized specimen with the highest carbon content has none of the bright spots associated with a single crystal Laue pattern. However, the oxidized sample shows
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some faint spots remaining. This suggests that the polycrystalline layer is thin enough to permit some signal from the single crystal to be observed.

![Image of Laue images from single crystal iron specimens after various processing stages.](image)

Figure 3-15 Back reflection Laue images from single crystal iron specimens after various processing stages. The single crystal pattern can be observed through the initial nanoiron deposit. After heating to 900 C, the single crystal structure remains on the backside of the sample as evidenced by the back Laue images. (Note images have been reversed to maintain a consistent orientation of the pattern.) However, after heating to 900 C the single crystal pattern is obscured on the front side by a polycrystalline surface layer formed on cooling the austenite. Recrystallization is observed where there is significant carbon diffusion. The oxidized solution shows faint traces of the single crystal pattern remain evidencing a thinner polycrystalline layer.

Average crystallite sizes were estimated by analysis of the peak broadening in the XRD patterns for grain sizes below 100 nm. Grains in the oxidized sample were larger than 100 nm after heating to 700 C. However, the average grain size in the unoxidized solution was between 50-100 nm after the same heat treatment. This grain size difference suggests a faster sintering rates for the metallic iron obtained in the oxidized solution than the iron carbide in the unoxidized solution.

This conclusion is supported by SEM images of the deposited layers heated to 900 C. Figure 3-16 shows some images of the samples treated with oxidized solution. The oxidized sample appears to have densified to form metallic deposits. These deposits have delaminated in many locations, but also show areas of attachment. The delaminated regions tend to curve away from the substrate, probably due to differential sintering rates
between the top and bottom of the specimens. There are pores in the regions contacting the substrate while free, delaminated regions appear dense. All the shapes are rounded, evidencing surface evolution via sintering.

The 900 C image of the unoxidized solutions shows some very different features. There appears to be much less detachment from the substrate. However, where the deposited layer has detached, the layers are thicker and more sharply angular than the attached regions. They appear to be made of a higher temperature material that has not evolved via sintering like the regions contacting the substrate. The non-contacting regions are likely iron carbide as measured in the initial test, while the smoother, more sintered, regions that contact the substrate have transformed to iron as the carbon has diffused into the low carbon substrate.

After additional heating to 1100 C, the thick angular structures have disappeared. The morphology of both structures appears similar. The oxidized solution shows evidence of the two deposition layers. In the top layer, the parallel edges of adjacent particles evidence their origin as a continuous layer. The relative size of the fragments and the gaps between them provides some indication of the in-plane shrinkage during sintering. In comparing the two solutions after the 1100 C processing treatment, the deposition fragments are larger and the cracks smaller in the unoxidized case. This suggests a lower shrinkage for this suspension.
Figure 3-16 SEM image of nanoiron deposited on a polished iron substrate for XRD testing. After heating to 900 C, the oxidized solution (top) has densified with significant micron-scale porosity visible. The unoxidized solution (below) shows two distinct regions after the same heat treatment. The lower region contacting the substrate appears to have densified with some micron-scale pores. Delaminated regions have not densified as evidenced by thicker layers and sharper angles. These regions are probably iron carbide while the regions on the substrate have converted to iron and sintered as the carbon diffused into the substrate. After heating to 1100 C, both solutions appear well sintered. The cracks in the unoxidized solution are smaller, suggesting less shrinkage on densification than in the oxidized case. The oxidized nanoiron solution is shown above with the unoxidized solution below.
3.7.2 PORE-SIZE EVOLUTION

The images of the deposited layers show that given identical processing conditions, the regions contacting a substrate densified more rapidly than those that did not. To confirm this trend, the pore size distribution of nanoiron deposited on a substrate was measured and compared to the previous data obtained for deposition without a substrate.

This test required that at least 0.5 g of nanoparticles be deposited on a substrate that could be placed in a sample tube. The bulb at the base of the sample tube can hold approximately 5 cm$^3$. Given these limitations, a lightly sintered powder substrate was used. This substrate has the advantage of also replicating the application conditions discussed in the following chapter. A 410 SS powder sieved to 63-90 μm in size was selected for compatibility with the application tests described in Chapter 4. This material has approximately 0.18% carbon and 12% chromium. The powder was prepared by heating to 900°C for less than 30 minutes followed by rapid cooling (>30 C/min). The sintered bar had just enough strength to be handled.

Nanoiron was applied to the bar until it was saturated and then dried for 14 hours at 150°C. After the drying, it was heated slowly to 400°C and then at 10 C/min to 700°C, held 10 minutes and cooled. After cooling, the process was repeated for a total of four applications. The bar was weighed after each application so that the quantity of deposited material could be estimated. The final gas adsorption sample size was 23.469 g of which approximately 0.614 g was deposited nanoiron. The final bar with the nanoiron deposits was prepared for analysis by breaking it into pieces and grinding it with a mortar and pestle so that the pieces were small enough to place in the sample holder. The final sample was reduced to nearly individual powder grains. All the fractured bonds that resulted from this preparation procedure likely increased the pore volume and surface area. After an initial analysis, the sample was reheated to 900°C for 10 minutes with a 10 C/min ramp rate.

The pore size distribution calculated from these measurements is shown in Figure 3-17. Clearly, the nanoiron applied to the powder has fewer pores than the deposits sintered free of a substrate. The total pore volume is in fact well below the recommended
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measurement limits for the equipment. However, subsequent heating to 900 C does show an additional decrease in the pore volume.

![Diagram of Powder Substrate Effect](image)

**Figure 3-17 Gas adsorption pore size calculations for nanoiron deposited with and without a substrate.** The nanoiron the substrate case was deposited in a 410 SS powder. The material deposited on a powder has significantly less pore volume per unit mass of nanoiron than the material without a substrate showing an increase in the densification of material on a substrate. The pore volume in the substrate case was increased during sample preparation when the bonded powder was broken apart to be poured into the sample tube.

The impact of the 410 SS powder on densification seems smaller than expected from the XRD experiments. This is likely due to the higher carbon content of the 410 SS. The carbon content of the powder of the 410 SS was measured as 0.16%, over the solubility limit (~0.1%) for carbon at 900 C. The carbon content of the iron substrates used for the XRD studies was less than 0.05%. Further, the nanoiron in the powder was approximately 2% of the total sample.
Much of the nanoiron sample was deposited on the outside surface of the bar by the drying process. A sample of the outer edge of the bar was removed for carbon measurement after the sample drying was completed. The carbon content was 0.76%, an increase of 0.6% over the original powder composition. Samples of dried nanoiron contained 9.7% carbon. If the nanoiron were distributed uniformly, this would increase the average carbon composition by 0.2%. The surface of the bar has three times as much carbon as would be expected from uniform distribution. Under these conditions, the substrate powder would be saturated with the carbon and could not act as a carbon sink to increase the densification as was observed in the X-ray diffraction specimens.

Other areas of the sample must have had much lower carbon contents and may have densified very effectively. The gas adsorption measurements represent the combined response of both cases. This explains why the pore volume is smaller than in the case without a substrate but was not dramatically smaller.

3.7.3 MORPHOLOGY EVOLUTION

To better understand the processes that may occur when the suspensions are dried and sintered in the powder, studies were made of the evolution of suspensions dried on a polished flat substrate of 1018 steel. Nanoiron was spin-coated onto the substrate and dried under hot air (>150 °C). The samples then remained in open air for an additional hour before sintering. The nanoparticles should be fully oxidized from this treatment. When sintering from the oxidized state, the initial iron density is at a minimum as the effective density of iron in the sample is reduced by one half during oxidation. Densification shrinkage is maximized, representing, perhaps, the worst case for sintering densification under the constraints imposed by a substrate. Marks were made on the sample to locate particular regions of interest and the sample was then sintered. After sintering, the sample was examined via the SEM. The sample was then sintered to a higher temperature and re-examined. The process was repeated for each sintering temperature. The sample was sintered at 600, 700, 900, and 1100 °C for 10 minutes each with ramp rates of 10 °C/min.
Cracks formed in the applied layer during the initial drying and sintering. While in an application they might be undesirable, they provide observation points for the evolution of the nanoiron coating. Figure 3-18 shows one cracked region and how the structure evolved under subsequent heating cycles.

The first feature of note is the bright thick region along the edges of the cracks. This region is likely thick because it contains much of the material originally deposited in the crack. Without any constraining substrate bonds, this region might have densified completely after heating to 600 C. The interior of the deposited layers appears to have a fine porosity not fully resolved at this magnification. There are also several larger pores that are clearly resolved as at points “a”, “b”, and “c”. After further heating to 700 C, the overall structure is largely unchanged except for some coarsening of some of the holes, probably due to increased sintering in these regions.

After heating to 900 C, the layers are dramatically changed. The structure looks smoother except lines that appear to be grooves or pores along grain boundaries as at points “d” and “e” in Figure 3-18. The deposited material would probably be very dense to form such large grains as pores typically restrain grain growth. There is no evidence of common structure between the substrate and the deposited layer, but this changes with further heating to 1100 C. Now the formerly sharp thick edges along the cracks are rounded and smoothed continuously with the substrate. These changes could be expected from increased sintering at these higher temperatures. Further, the grain boundary grooves are much more prominent as at points “f” and “g” in Figure 3-18 and they are continuous across the substrate and deposited layer. The continuity suggests that there is no longer a grain boundary at the layer-substrate interface. At the high temperatures, substrate grains appear to have grown, consuming the smaller grains in the deposited layer and creating an essentially epitaxial growth. This might be connected with the phase changes between BCC and FCC on heating and cooling to 1100 C forcing recrystallization of both substrate and coating. A similar pattern of structure evolution is seen at other locations as illustrated in Figure 3-19.
Figure 3-18 SEM image of nanoiron deposited on a polished steel substrate and sintered to successively higher temperatures. A) 600 C B) 700 C C) 900 C D) 1100 C

Interestingly, Figure 3-18 shows two distinct grain groove structures. There are sharp grooves as at point “f” and smoother grooves as at point “g”. These may be a result of the recrystallization on cooling through the FCC-BCC phase change in the material. The sharper grooves may represent the cooled grains while the smoother grooves may be remnants of the prior austenite grain structure that has only partially smoothed through surface diffusion. Alternatively, the two grain boundary groove types may result from grain boundaries with different surface energies.
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Figure 3-19 SEM image of nanoiron deposited on a polished steel substrate and sintered to successively higher temperatures. A) 600 C B) 700 C C) 900 C D) 1100 C As the sintering progresses, the pores first coarsen (A, B) and then begin to form distinct grains (C). After further heating, the grain boundaries on the substrate and deposited layer are continuous suggesting that the deposit is epitaxial with the substrate.

These tests suggest that the deposits can densify under the constraints of the substrate. Densification may be aided by recrystallization and the subsequent grain growth. When the nanobinder is deposited on the substrate, it is applied in thin layers. The free surface then provides a ready sink for vacancies as the pores shrink. The large difference in grain sizes between the deposited particles and the substrate favors grain growth of the substrate through the deposited layer.

Although there are cracks and other defects in the deposited layer, these may not inhibit the formation of strong bonds between skeleton powders on application to 3DP skeletons. The bonds are still very thin even when the diameter is increased significantly as by nanobinder deposition. For example, a bond with X/D of 0.25 in a 75 μm powder
would have a maximum thickness of just 2.4 μm. Moreover, just as in the case of the substrate, there is a driving force for densification of this region.

### 3.8 Conclusions

In this chapter, sintering was selected as the ideal method for densifying the nanobinder to form structural bonds in the skeleton powder. However, for this process to succeed, the particles must be dried to a high density with a narrow pore size distribution. These characteristics are possible for monodisperse nanocrystalline dispersions.

TEM imaging of dried nanobinder and gas adsorption measurements of the pore size distribution indicates that the dried samples have a narrow pore size distribution as required for effective densification by sintering. Further TEM and gas adsorption investigation of sintered deposits show that they densify effectively below 1000 C with limited pore coarsening. The total pore volume decreases continuously with increased sintering.

Magnetization measurements show that the oxidation of the nanoiron suspension proceeds rapidly at room temperature. The oxidation rate of the particles was measured in the liquid state by tracking changes in the saturation magnetization of the samples. The oxidation rate was shown to be relatively quick with a time constant of 30 minutes. Dried deposits might oxidize more quickly due to faster oxygen transport in the gas phase.

Sintering of oxidized nanoparticles was studied via x-ray diffraction, SEM observation of deposited layers, and XRD. Nano-sized pores are eliminated at lower temperatures in oxidized than in unoxidized material. Gas adsorption shows that the nano-pores are eliminated below 700 C in oxidized suspensions while some 100-500 nm porosity remains at 900 C in an unoxidized specimen.

X-ray powder diffraction studies show that the iron deposits react with the coating ligands to form iron carbide on heating unless the carbon is removed by reaction with
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atmospheric oxygen or iron oxides. SEM imaging of high carbon (low oxidation) nanoiron deposits show that densification starts in regions attached to the substrate. Delaminated regions appear to densify as the carbon diffused laterally through the layer and then into the substrate.

The effectiveness of oxidized particles in reinforcing steel skeletons will depend on the impact of the carbon deposited into the powder from the nanobinder on the deformation rate. Shrinkage of oxide deposits is also higher than metallic or carbide deposits due to the density differences in the materials. Lower density deposits may decrease the structural strength of the deposits. SEM images of nanoiron deposited on a substrate show wider cracks in the oxidized solutions than the unoxidized solutions. This is likely due to increased shrinkage in the oxidized solutions due to the large volume change when the iron oxides are reduced to metal.
3.9 References

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4 Nanobinder Testing in Porous Metal Skeletons

This work proposes to deposit metal in a porous skeleton to reduce the rate of dimensional changes at high temperatures from creep and shrinkage. The previous chapter examined an iron colloid and its structure during drying and sintering. This chapter examines direct tests of the impact of depositing an iron colloid nanobinder into porous metal skeletons to identify the important parameters in determining the nanobinder performance.

First, the test methods are described and the data is summarized. The effects of important parameters on the creep deformation are then reviewed. The performance is compared against the model developed in Chapter 2 and shown to be inadequate to account for the full benefit achieved. Carbon deposition with the nanobinder is shown to be a significant source of additional benefit. However, nanoiron deposition is shown to be more effective than carbon deposition alone.

4.1 Experimental Methods

When densifying a powder metal skeleton by infiltration, the formed part must first be strengthened. For 3DP and SLS parts, this is often accomplished by removing any polymer binder by thermal treatment and then sintering for additional strength. In a separate furnace cycle, the parts would be reheated for infiltration. Some methods have been developed for debinding, sintering, and infiltration in a single treatment. However,
these methods rely on refractory supporting powders, with the accompanying limitations in geometry and shrinkage discussed in Chapter 2. Stronger parts that are less susceptible to deformation are needed to permit accurate infiltration of complex geometries and to improve the process repeatability of all parts.

During an infiltration cycle, several processes occur concurrently. While the part is heating, the particles sinter and shrink, thereby increasing in strength. The increasing neck bonds formed by sintering will reduce the creep rate by reducing the local stress. However, the sintering rate decreases rapidly with time as the excess surface energy is reduced. The rate of neck growth during the early stages of sintering is approximated by the equation

$$\frac{X}{D} = \left( \frac{Bt}{D^3} \right)^{\frac{1}{n}} = \left( \frac{B}{D^m} \right)^{\frac{1}{n}} t^{\frac{1}{m}}$$

where $B$ is a kinetic coefficient, $D$ is the particle diameter, and $X$ is the neck diameter. This model is based on isothermal vacancy diffusion of equal-sized spheres with mass transport by only one mechanism. While these assumptions are not precise in practice, the model gives insight into how sintering rates scale with time. The exponents, $n_x$ and $m$, are dependent on the sintering mechanism. As time is raised to a power less than one, with typical values of $n_x$ between five for lattice diffusion and seven for surface diffusion, the sintering rate decreases significantly with time.

In contrast, the deflection rate is relatively constant with time as long as the stress remains constant. If parts are sintered for some time before deflection starts, the neck growth rate will be relatively small during deflection making the stress in the particle bonds relatively constant throughout the test. From Equation 4-1 it can be estimated that if the presinter is of the same length as the deflection test, then the additional neck growth during the deflection test would be 10-15% for values of $n_x$ from 5-7. By comparison, the size of interparticle bonds in samples deflected directly after sintering to 1000 C increases at least 3-fold during a deflection test. The 1300 C presintered condition will be referred to as "quasi-static".

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The difference in deflection rate between untreated and treated bars will be minimized under these "quasi-static" conditions. The nanoparticle treated bars will quickly form bonds of significant strength due to the lower sintering temperatures of the nanoparticles. However, after initial densification of the nanoparticles, the rate of continued neck growth decreases significantly. After the initial densification of the nanoparticles, the sintering rate of the untreated parts will be higher than the treated parts because the neck size is smaller in the untreated case. Thus continued sintering strengthens the untreated parts more than the treated parts, decreasing the relative strength difference. However, it is easier to compare the performance of the parts because the bond sizes and relative performance will change more slowly with time.

To permit testing in this quasi steady state regime, a test specimen was designed that allows for full support or for unsupported overhangs depending on the orientation of the specimen. The geometry is illustrated in Figure 4-1 in both the supported and the unsupported positions.

![Figure 4-1 Schematic representation of a deflection test bar in an unsupported position (left) and supported position (right).](image)

4.1.1 PRINTED PART TEST PROCEDURES

The experimental process is outlined in Figure 4-2. It consists of printing the parts, debinding and light sintering, application of the nanoiron, drying the nanoiron, sintering the parts, and then deflecting the parts. Each step is described below. The powder used for these parts is a spherical 410 stainless steel, gas atomized powder sieved to select particles between 63-90 μm in diameter. This powder was selected because it is a standard alloy, readily available which can be infiltrated with steel if desired. [3] The infiltrated alloy has a composition similar to 440C stainless steel but with less chromium.
Figure 4-2  Schematic illustration of the deflection test procedures. Parts are made by 3D printing a polymer binder. The binder is decomposed and the metal skeleton particles sintered together by heating to 1000°C for 30 minutes. Nanobinder is applied by repeated infiltration and drying or by drying from a pool of extra fluid. After drying bars are heated in a supported position for presintering and then in an unsupported position to measure deflection.

The nanobinder selected for this work is the NanoIron product marketed by NanoMat Inc studied in Chapter 3. It consists of unagglomerated, monodisperse iron particles in an organic carrier. The carrier used in these solutions is proprietary to NanoMat but has a boiling point of approximately 286°C. The concentration of the iron in the solutions was approximately 0.5 vol%.

4.1.1.1 Printing Parts
The geometry was formed by three-dimensional printing (3DP) with an acrysol binder. Acrysol is a colloid of polymer particles. This binder was selected because it
leaves a minimal residue after debinding. The dried polymer was heated in a reducing atmosphere (5% Hydrogen, 95% Argon) at 5 C/min. Thermal gravimetric analysis (TGA) of the dried binder was used to measure the weight loss as a function of time and temperature under typical 3DP debinding conditions. The results are shown in Figure 4-3. The residue was approximately 2.5 wt% of the dried residue material. If 10 vol% of a 3D printed part is polymer, the residue will be less than 0.05 wt% of the skeleton weight. Even though this residue is small, it is mostly carbon and can have a small but measurable impact on the properties of the sintered part.

![Figure 4-3](image)

**Figure 4-3** Thermal gravimetric measurements of the decomposition of dried acrysol in a forming gas atmosphere. Final residue is approximately 2.5% of the dried weight. This residue is mostly carbon and can have a measureable impact on the properties of the powder.

4.1.1.2 Debind and Sinter

After printing, the parts were dried and removed from the bed. They were debound by heating in a reducing atmosphere to 600 C for 30 min at a ramp of 5 C/min. The parts were then heated to 1000 C for 30 minutes to sinter for additional strength and cooled at 10 C/min. Throughout this cycle, the bars were oriented in a supported position on an alumina plate.
4.1.1.3 Nanobinder Application

The nanobinder was applied with one of two methods. In the first method, the parts were infiltrated with the nanoiron until saturated. This was usually done in an inert atmosphere and then the parts were quickly transferred to the tube furnace. After sealing the furnace, the atmosphere was purged by pulling down a vacuum and backfilling with forming gas. The bars were then heated to dry at temperatures between 120 C and 300 C. The drying rate was adjusted by controlling the flow of gas through the tube and the temperature. To attain higher concentrations of iron, the samples were heated through the nanobinder sintering step and then the nanobinder application process was repeated until the desired deposition level was achieved.

This method was used to achieve drying rates classified as “quick” or “moderate”. For a “quick” drying rate, the parts are heated to 150 C for 20 minutes and then heated to 300 C in 20 minutes. The “moderate” drying rate maintains the 20-minute hold at 150 C and then heats to 300 C over a period of 200 minutes. Forming gas flow rates for “quick” and “moderate” drying rates were maintained between 1-2 scfh. “Slow” drying rates were attained using the method below with a minimal gas flow and a 24-hour hold at 150 C before heating slowly to 300 C.

In the second method, the bars were placed in a pool of binder inside of an open jar as illustrated in Figure 4-2. The parts were heated in the furnace as described above for the “slow” drying rate. Due to the large surface area of the part, most of the drying occurred at the part surface. As solvent dried from the surface of the part, it was replenished from the remaining pool until most of the original binder pool infiltrated into the part and dried. This allowed deposition of larger amounts of binder in a single application. Gas flow was minimal with the exhaust valve closed and the tube pressurized with inert gas to 1-5 psi positive pressure.

4.1.1.4 Nanobinder Sintering

Nanobinder drying was concluded by heating the parts up to 400 C to aid evaporation of the solvent in the small pores. The nanoparticulate deposits were subsequently heated in a tube furnace under a forming gas atmosphere to 700 C for 10 minutes with a ramp rate of 10 C/min to consolidate the deposits. After this heating, the
structure consolidated sufficiently that the risk of oxidation on exposure to air was reduced. This heating was done with the parts in a supported position as illustrated in Figure 4-2.

4.1.1.5 Sintering
The bars were then sintered in a supported position at 1300 C or 1100 C for 1 hour. The sintering was performed in a ceramic tube furnace with heating rates of 8 C/min below 1100 C and 5 C/min above 1100 C. The sintering atmosphere was forming gas (Argon with 5% hydrogen).

4.1.1.6 Deflection
Finally the bars were heated in the unsupported position through a simulated infiltration cycle. This cycle requires heating to the infiltration temperature of 1284 C at 8 C/min below 1200 C and 5 C/min above. The samples were held at the infiltration temperature (1284 C) for 18 minutes. For these tests, the parts were not infiltrated to avoid irregularities of the infiltration process such as the extra force of the surface tension of the liquid metal. As the infiltrant partially solidifies at the infiltration temperature, infiltration should rapidly strengthen the part and decrease the deflection rate.

4.1.1.7 Test Data
The shape of each bar after the deflection was measured by scanning the bar using a flat bed scanner at 600 dpi. The top surface of the bars was used as a reference edge to measure the vertical deflection at the tip as illustrated in Figure 4-4. The vertical tip deflection was the primary metric from each test, but the entire shape of some of the bars was also measured from the scanned images. Additionally, calipers were used to measure the dimensions of the parts before and after treatment to quantify the shrinkage. The weight was also recorded so that the amount of iron actually deposited in the parts could be measured.

Tests show that deflections for identical samples show good repeatability within a run but significant variation between runs. This variation may be due to differences in atmosphere purity from inconsistent furnace sealing or deposits in the furnace tube from previous runs. To reduce the effect of variations between runs, untreated control specimens were heated through the same treatment cycles as the treated bars to provide a standard of
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comparison. The tip deflection of the treated bars is normalized by the tip deflection of the control bar from the same furnace cycle to calculate a deflection ratio. Lower values of the deflection ratio correspond to greater improvement from the nanobinder treatment. An example of a deflection pair is shown in Figure 4-4.

\[ \text{Deflection Ratio} = \frac{\Delta y_{\text{treated}}}{\Delta y_{\text{untreated}}} \]

Figure 4-4 Scanned images of deflected bars illustrating deflection measurements.

4.1.2 CAST PART TEST PROCEDURES

The initial tests with the iron nanobinder were conducted using specimens produced by 3DP. The dimensions of these specimens varied significantly, with a standard deviation of about 1% of the average value. The weight was even more variable with a standard deviation of 2.3% of the average value. Additionally, large quantities of extra powder are required during printing for filling the space around the printed regions while the residues of the 3DP binder may also affect the properties of the printed parts. Therefore, it was desirable to create specimens using a different method.

A two-piece mold was machined from a plate of machinable alumina. The mold is illustrated in Figure 4-5. The two-piece construction and draft angles on the ends permit removal of samples with little to no shrinkage while maintaining a rectangular cross-section in the deflecting beam. It is assembled using two alumina bolts with single-use washers cut from an alumina fiber blanket. Parts are produced by assembling the mold and then filling it with steel powder. The mold is tapped lightly to pack the powder uniformly and the excess is then removed from the top using a razor blade. Outside dimensions are controlled very accurately by the mold. All parts were produced in the same mold. The density of the parts is a function of how much tapping is done. For maximum consistency in part density, the mold is weighed before and after filling to verify that the weight and thus the density are within the targeted range.
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Figure 4-5 Molded test specimens. (Left) A dimensioned drawing of the parts produced from the alumina mold. (Right) An exploded view of the alumina mold for creating porous skeletons with high dimensional consistency shown with an example part.

The part preparation largely followed the pattern established for the printed parts. After filling the mold, the parts were then sintered with a ramp rate of 5 C/min to 600 C with a 30-minute hold at 600 C. The samples were then heated at 8 C/min to 1000 C, held for 30 minutes and cooled at 8 C/min. The hold at 600 C was included to provide compatibility with polymer binder treatments where they were used for comparison. The sintering atmosphere was argon with 5% hydrogen. An identifying number was scratched onto each bar after sintering and its weight recorded. Specimens were stored in a dry atmosphere until used for deflection testing.

Drops of the nanoiron were applied to the skeleton until saturated. This was done in a nitrogen environment to reduce oxidation. The samples were then removed and placed in a tube furnace for drying. The furnace was evacuated until the nanoiron began to flow out of the skeleton and then backfilled with argon 5% hydrogen gas. An inert environment was maintained throughout drying either by flowing a reducing gas or purging the system and then pressurizing to 5 psi.
The typical drying conditions for these tests replicated the moderate drying conditions of the printed bar tests with a 120 minute hold at 150°C. After the hold, they were cooled to room temperature and removed from the furnace rather than heating to 400°C as in the previous tests. This change was made to provide compatibility with the magnets used to create a magnetic field during some of the tests. During drying, the cantilever bars were supported by their ends so that drying could occur more easily from both the top and bottom surfaces of the cantilever. The printed parts were typically laid on a flat substrate during nanoiron drying.
The samples were then heated to 700°C in 70 minutes, held 10 minutes and cooled back to room temperature at 10°C/min. The purpose of this heating was to densify the nanoiron deposits. The nanoiron application process was then repeated if additional material deposition was desired.

Many specimens were again heated to 1300°C and held one hour before deflection testing to reduce the sintering during testing. This presinter step was done after any nanobinder was applied to the part. The operations were conducted in a large tube furnace with ramp rates of 8°C/min below 1200°C and 5°C/min above 1200°C. The atmosphere was argon with 5% hydrogen.

In practical application, it is not desirable and often not possible to sinter a part with support before infiltrating. This requires an extra processing step that costs both time and money while increasing the part shrinkage. Many geometries may not be as convenient to support during infiltration as were the test bars. In order to test the nanoiron performance under more realistic conditions, some bars were deflected directly after densifying the nanoiron to 700°C.

The parts were deflected with in situ measurement as described in Chapter 5 to gather additional data on the deformation process. To facilitate these other measurements, the heating cycle was adjusted. The parts were quickly heated to 750°C and then heated at 2°C/min to 1284°C. They were held at 1284°C for 60 minutes and then cooled to 600°C in 60 minutes. Since only one sample could be tested at a time, it was not possible to provide a control sample for every test sample. However, several control samples were tested for comparison.

4.1.2.1 Magnetic Field Drying

SEM imaging of the skeletons after nanoiron deposition showed that the nanoiron was not effectively concentrated in the neck regions and that more material was depositing on the surfaces than in the interior. To improve the concentration of the nanoparticles in the contact regions, a magnetic field can be applied across the specimen. Gradients in the magnetic field form in the contact regions between the skeleton particles. The field
gradients concentrate the magnetic nanoiron fluid into the contact regions as the solvent evaporates. This concept was developed by Jan Wilkes.

This method was implemented by placing Samarium-Cobalt permanent magnets at the ends of the bar to create a field along the length of the bar as illustrated in Figure 4-7. Nanoiron was applied to the center of the skeleton until the fluid began accumulating on the magnets. Images of broken bonds after heating to 700°C confirm that applying a magnet field significantly increases the bond sizes relative to samples dried without a magnet. Section 4.4 discusses the impact of the magnet field on the nanobinder performance.

Figure 4-7 Drying nanoiron in a magnetic field concentrates deposits into the contact areas between particles. (Top) Illustration of the method used for applying the magnetic field. Permanent magnets were placed at the ends of the bar. (Lower left) Illustration of magnetic field lines in the skeleton. Gradients in the magnetic field form at the particle contacts. (Lower Right) Nanoiron in the bars concentrates in the areas with gradients in the magnetic field.

4.2 Data Summary

The deflection data from the printed parts is summarized in Table 4-1 with information regarding the sintering conditions and the weight of the nanoiron added to the specimens. Table 4-2 reports similar data for the cast specimens.
Table 4-1 Summary of data from deflection tests.

<table>
<thead>
<tr>
<th>Bar #</th>
<th>Sintering Temp</th>
<th>Specimen Type</th>
<th>Drying Method</th>
<th>Tip Deflection (mm)</th>
<th>Weight Change (%)</th>
<th>Relevant Control Bar</th>
<th>Deflection Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>1300</td>
<td>Test</td>
<td>Quick</td>
<td>0.54</td>
<td>1.09%</td>
<td>V</td>
<td>0.18</td>
</tr>
<tr>
<td>III</td>
<td>1300</td>
<td>Test</td>
<td>Moderate</td>
<td>1.55</td>
<td>0.57%</td>
<td>V</td>
<td>0.52</td>
</tr>
<tr>
<td>V</td>
<td>1300</td>
<td>Control</td>
<td>Moderate</td>
<td>2.99</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vi</td>
<td>1100</td>
<td>Test</td>
<td>Moderate</td>
<td>2.51</td>
<td></td>
<td>VIII</td>
<td>0.43</td>
</tr>
<tr>
<td>Viili</td>
<td>1100</td>
<td>Control</td>
<td>Moderate</td>
<td>5.85</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-I</td>
<td>1100</td>
<td>Test</td>
<td>Slow</td>
<td>6.48</td>
<td>-0.30%</td>
<td>2-II</td>
<td>0.82</td>
</tr>
<tr>
<td>2-II</td>
<td>1100</td>
<td>Control</td>
<td>Slow</td>
<td>7.92</td>
<td>-0.08%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-VII</td>
<td>1100</td>
<td>Control</td>
<td>Slow</td>
<td>7.11</td>
<td>-0.16%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-VIII</td>
<td>1100</td>
<td>Test</td>
<td>Slow</td>
<td>6.19</td>
<td>0.45%</td>
<td>2-VII</td>
<td>0.87</td>
</tr>
<tr>
<td>3-IX</td>
<td>1100</td>
<td>Test</td>
<td>Slow</td>
<td>5.74</td>
<td>0.62%</td>
<td>2-VII</td>
<td>0.81</td>
</tr>
<tr>
<td>3-II</td>
<td>1100</td>
<td>Control</td>
<td>Slow</td>
<td>6.73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-III</td>
<td>1100</td>
<td>Test</td>
<td>Slow</td>
<td>5.88</td>
<td>0.55%</td>
<td>3-II</td>
<td>0.87</td>
</tr>
<tr>
<td>3-VII</td>
<td>1100</td>
<td>Test</td>
<td>Slow</td>
<td>5.87</td>
<td>1.04%</td>
<td>3-II</td>
<td>0.87</td>
</tr>
<tr>
<td>5-ii</td>
<td>1300</td>
<td>Control</td>
<td>Moderate</td>
<td>3.68</td>
<td>-0.10%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6-vii</td>
<td>1300</td>
<td>Test</td>
<td>Moderate</td>
<td>1.73</td>
<td>0.67%</td>
<td>5-II</td>
<td>0.47</td>
</tr>
<tr>
<td>6-ix</td>
<td>1300</td>
<td>Control</td>
<td>Moderate</td>
<td>3.96</td>
<td>-0.08%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specimen</td>
<td>Description</td>
<td>Material</td>
<td>Initial Weight (g)</td>
<td>Weight loss %</td>
<td>Deflection Ratio</td>
<td>Max. defl.</td>
<td>Shrinkage</td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td>----------</td>
<td>-------------------</td>
<td>---------------</td>
<td>-----------------</td>
<td>------------</td>
<td>-----------</td>
</tr>
<tr>
<td>C-2</td>
<td>Control</td>
<td>410 SS</td>
<td>18.704</td>
<td>0.00%</td>
<td>yes</td>
<td>2 K/min</td>
<td>N/A</td>
</tr>
<tr>
<td>C-3</td>
<td>Treated with Acrysol</td>
<td>410 SS</td>
<td>18.685</td>
<td>0.60%</td>
<td>yes</td>
<td>4 K/min</td>
<td>5.26</td>
</tr>
<tr>
<td>C-4</td>
<td>Treated with Binder S</td>
<td>410 SS</td>
<td>18.773</td>
<td>1.2%</td>
<td>yes</td>
<td>8 C/min to 5 C/min</td>
<td>6.914</td>
</tr>
<tr>
<td>C-5</td>
<td>Control</td>
<td>410 Ss</td>
<td>18.604</td>
<td>0.00%</td>
<td>yes</td>
<td>1 K/min</td>
<td>19.464</td>
</tr>
<tr>
<td>C-6</td>
<td>Control</td>
<td>410 Ss</td>
<td>18.571</td>
<td>0.00%</td>
<td>yes</td>
<td>1 K/min</td>
<td>0</td>
</tr>
<tr>
<td>C-7</td>
<td>Control</td>
<td>410 Ss</td>
<td>18.571</td>
<td>0.00%</td>
<td>yes</td>
<td>1 K/min</td>
<td>19.464</td>
</tr>
<tr>
<td>C-8</td>
<td>Control</td>
<td>410 Ss</td>
<td>18.571</td>
<td>0.00%</td>
<td>yes</td>
<td>1 K/min</td>
<td>19.464</td>
</tr>
<tr>
<td>C-9</td>
<td>Control</td>
<td>410 Ss</td>
<td>18.618</td>
<td>0.00%</td>
<td>yes</td>
<td>2 K/min</td>
<td>1.007</td>
</tr>
<tr>
<td>C-10</td>
<td>Control</td>
<td>410 Ss</td>
<td>18.825</td>
<td>0.67%</td>
<td>yes</td>
<td>2 K/min</td>
<td>0.388</td>
</tr>
<tr>
<td>C-11</td>
<td>Control</td>
<td>410 Ss</td>
<td>18.825</td>
<td>0.67%</td>
<td>yes</td>
<td>2 K/min</td>
<td>0.388</td>
</tr>
<tr>
<td>C-12</td>
<td>Control</td>
<td>410 Ss</td>
<td>18.825</td>
<td>0.67%</td>
<td>yes</td>
<td>2 K/min</td>
<td>0.388</td>
</tr>
<tr>
<td>C-13</td>
<td>Quick dry</td>
<td>410 Ss</td>
<td>18.801</td>
<td>0.00%</td>
<td>yes</td>
<td>2 K/min</td>
<td>0.548</td>
</tr>
<tr>
<td>C-14</td>
<td>2 hrs @ 150 C, supported at ends</td>
<td>410 SS</td>
<td>19.319</td>
<td>0.70%</td>
<td>yes</td>
<td>2K/min</td>
<td>3.766</td>
</tr>
<tr>
<td>C-15</td>
<td>2 hrs @ 150 C, supported at ends</td>
<td>410 SS</td>
<td>19.303</td>
<td>0.80%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-16</td>
<td>Ferrofluids, shr @ 100 C drying</td>
<td>410 SS</td>
<td>19.303</td>
<td>0.80%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-17</td>
<td>oxidized nanotom of recent batch</td>
<td>410 SS</td>
<td>18.827</td>
<td>0.30%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-18</td>
<td>oxidized nanotom of recent batch</td>
<td>410 SS</td>
<td>18.827</td>
<td>0.30%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-19</td>
<td>oxidized nanotom of recent batch</td>
<td>410 SS</td>
<td>18.827</td>
<td>0.30%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-20</td>
<td>oxidized nanotom of recent batch</td>
<td>410 SS</td>
<td>18.827</td>
<td>0.30%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-21</td>
<td>oxidized nanotom of recent batch</td>
<td>410 SS</td>
<td>18.827</td>
<td>0.30%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-22</td>
<td>oxidized nanotom of recent batch</td>
<td>410 SS</td>
<td>18.827</td>
<td>0.30%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-23</td>
<td>oxidized nanotom of recent batch</td>
<td>410 SS</td>
<td>18.827</td>
<td>0.30%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-24</td>
<td>oxidized nanotom of recent batch</td>
<td>410 SS</td>
<td>18.827</td>
<td>0.30%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-25</td>
<td>oxidized nanotom of recent batch</td>
<td>410 SS</td>
<td>18.827</td>
<td>0.30%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-26</td>
<td>oxidized nanotom of recent batch</td>
<td>410 SS</td>
<td>18.827</td>
<td>0.30%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>231</td>
</tr>
<tr>
<td>C-27</td>
<td>Acrsol-treated D2</td>
<td>410 SS</td>
<td>18.938</td>
<td>0.00%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>0.362</td>
</tr>
<tr>
<td>C-28</td>
<td>Acrsol-treated D2</td>
<td>410 SS</td>
<td>18.938</td>
<td>0.00%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>0.362</td>
</tr>
<tr>
<td>C-29</td>
<td>Acrsol-treated D2</td>
<td>410 SS</td>
<td>18.938</td>
<td>0.00%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>0.362</td>
</tr>
<tr>
<td>C-30</td>
<td>Acrsol-treated D2</td>
<td>410 SS</td>
<td>18.938</td>
<td>0.00%</td>
<td>yes</td>
<td>new 2K/min</td>
<td>0.362</td>
</tr>
<tr>
<td>C-31</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.263</td>
<td>1.41%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.136</td>
</tr>
<tr>
<td>C-32</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-33</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-34</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-35</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-36</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-37</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-38</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-39</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-40</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-41</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-42</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
<tr>
<td>C-43</td>
<td>2 hr at 150 C drying</td>
<td>410 SS</td>
<td>19.195</td>
<td>2.70%</td>
<td>no</td>
<td>new 2K/min</td>
<td>0.154</td>
</tr>
</tbody>
</table>
The best results were obtained by drying the material under a magnetic field with four binder applications. The particular batch of nanoiron had a particularly high concentration of iron particles and the total deposit was 2.7% of the untreated bar weight. This bar, deflected without presintering, deflected only 1.5 mm compared to 29.5 mm for a bar that was not treated with nanoiron. These test bars are compared in Figure 4-8.

![Treated Bar](image1)

![Untreated Bar](image2)

Figure 4-8 Photo comparing the deflection of 410 stainless steel bars with and without nanoiron treatment. The treated bar received four applications and was dried under a magnetic field. Both bars were deflected without prior sintering except the 1000 C sintering required to create the initial geometry.

4.3 Drying Conditions

Of particular interest to this process is the relationship between the nanobinder benefit and the drying conditions. These relationships were studied in tests with the printed parts. Figure 4-9 summarizes the measured deflection ratios as a function of the drying conditions and the weight of material added to the parts. Interestingly, the deflection ratio appears to be more strongly related to the drying conditions than the quantity of material added.
In the initial tests with printed bars, slow drying was studied most extensively. Slow drying favors the formation of dense deposits that can sinter to a high density as observed in the previous chapter. It was believed that slow drying would also favor deposition of the iron at the particle contacts where they could enlarge the bonds between particles. However, Figure 4-9 shows that this method provided the least benefit.

The slow dried bars reduced deflection approximately 15% when the nanoiron was applied in a single application, independent of the quantity of material added. This limited benefit could be evidence of poor concentration of the fluid to the contact points between the particles. When the nanoiron was applied in multiple applications, the level of benefit improved significantly, but it was still less than other samples with comparable nanoiron depositions that were dried more quickly.

It is clear that the drying rate strongly influences the binder performance. Faster drying substantially reduces deflection with a 50-60% reduction for moderately dried samples and 80% reduction for the quick dried sample. Two factors contribute to the large
differences associated with drying conditions: bond repair during multiple applications and concentration of nanoiron at the surface at high drying rates. The results of additional tests confirming the importance of these factors are summarized in the following sections.

Slower drying may also have allowed increased oxidation of the nanoparticles. The effect of oxidation on the nanobinder performance is addressed in section 4.4 below.

4.3.1 MULTIPLE APPLICATIONS

The quicker dried samples used multiple applications of nanoiron to achieve the final deposits while most of the slow-dried samples were dried from a large pool. After drying and heating to 700 C for 10 minutes, cracks form in the deposits due to sintering shrinkage. These cracks are observed when treated parts are imaged in SEM as in Figure 4-10. When cracks form during the first applications, they can be filled at least partially by subsequent applications as illustrated schematically in Figure 4-10. This effect was observed when comparing bonds in samples with different numbers of nanoiron applications as illustrated in Figure 4-10. In these and other tests with multiple applications, the parts were heated to 700 C and held 10 minutes between applications of nanobinder to permit sintering and densification of the particles.
Nanobinder Testing in Porous Metal Skeletons

When the nanoparticles begin to sinter, they shrink. The shrinkage is accommodated by cracking and/or delamination of the deposited bond material. If the sample is heated for deflection at this point, the bonds can provide little direct strengthening. However, if the nanobinder is applied another time, new deposits form in the cracks of the previous deposit and enlarge the bond diameter. While these deposits will also shrink, the final flaws will be smaller. The smaller the flaws the more quickly they can be closed by sintering.

The significance of this effect is clearly seen by comparing the deflection of the slow dried samples in which the nanobinder was applied in a single application to those with multiple applications in Figure 4-9. Applying at least two applications of nanoiron to the parts substantially decreased deflection. However, deflection was still not as low as in the more quickly dried samples. An additional factor must be important.

Figure 4-10 Applying the nanobinder multiple times both enlarges the bonds and heals cracks formed by sintering shrinkage. (Top) Schematic illustration of bond repair by multiple applications of nanobinder. (Bottom) Images comparing bonds sintered to 700°C in samples with 1, 2, and 4 applications and dried under a magnetic field. The size of the cracks in the bonds shrinks with additional applications.
The shrinkage required for densification is a strong function of the initial packing density. For the nanoparticles, the packing density is in turn related to the relative thickness of the ligand coatings and the particle diameter. If the relative thickness of this coating can be reduced, the metal density of the deposit will increase significantly so that shrinkage will be reduced.

4.3.2 DRYING RATE

The drying rate can affect nanobinder performance by changing the location of the deposits through the part thickness. During drying, the solvent evaporates primarily from the surface of the part. The solvent evaporation begins a series of opposing transportation processes illustrated in Figure 4-11. The balance of these transport processes determines whether the material is deposited uniformly or is concentrated in either the center or the outer surface. [4, 5]
Nanobinder Testing in Porous Metal Skeletons

Figure 4-11 Illustration of the process of drying the nanobinder from a pore. (Top) A pore is shown partially filled with nanobinder. On drying, gradients in particle concentration may develop as illustrated by color gradients in the field. If drying is quick enough, most of the particles will be concentrated on the outside of the pore as illustrated. (Bottom) Transport processes occurring during drying of the nanobinder. The relative magnitude of the transport processes determines how the particles are distributed after drying is complete. They can be uniformly distributed or concentrated on the outside or inside.

As the surface is depleted of liquid, material begins to flow from the interior of the part. The outward flow of liquid will carry suspended nanoparticles outward. However, the continued surface evaporation increases the surface concentration of particles creating a concentration gradient that favors diffusion of the particles back to the part center. The relative magnitude of the two particle transport mechanisms determines the distribution. If
the convective flow of particles to the outside dominates over the diffusive flux, the particles will be concentrated on the outside surface.

The concentration of the nanoparticles may also play an important role. If the initial concentration of the particles is near the maximum stable concentration, the particles will begin to agglomerate or precipitate with very small increases in concentration. This would limit the gradient in particle concentration that could be sustained before the nanoparticles would deposit on the outer surface.

The convective flux is determined by the drying rate while the diffusive flux depends on the coefficient of diffusion in the liquid. For a given particle size and liquid, the diffusivity will be determined primarily by the temperature. The drying rate is also a function of the temperature as well as the gas flow conditions around the part. Higher temperatures increase the diffusivity and the evaporation rate.

If the particles were concentrated on the outside of the part, this would increase the deflection reduction achieved by a given quantity of the nanobinder. Bending loads applied by gravity loading cause the cantilever deflection. Under bending, the stresses are highest on the top and bottom surfaces of the parts. If the deposits are concentrated in these regions, we would expect to achieve greater shrinkage reduction than if they were distributed uniformly through the part.

A test was devised to determine whether the higher drying rates were concentrating the material deposits at the outer surface of the parts. Cylindrical specimens were produced from spherical 63-90 μm copper powder by sintering at 700 C for 30 minutes in an alumina mold. Nanoiron was applied to these parts and then dried with either the slow, moderate, or quick drying conditions. After drying, the deposits were sintered to 700 C for 10 minutes to densify them. The part was sectioned for observation by cutting with a hacksaw. Sectioning tears apart the bonds between particles exposing the broken bonds and the outer surfaces of the particles for examination. The deposition pattern was observed optically from the color contrast between the black nanoiron deposits and the red copper and chemically by using Energy Dispersive Spectroscopy (EDS) in the SEM to measure the iron concentration as a function of distance from the top surface.
Figure 4-12 shows an optical photograph comparing both treated specimens to an untreated specimen. The treated specimens show a dark region around the exterior of the part where the nanoiron is concentrated. The dark region of the quicker dried specimen is somewhat darker and narrower than for the moderate drying conditions. The slow-dried sample is similar in appearance to the quick dried sample.

The EDS measurements were made on a Hitachi S-530 with a 20 KV accelerating voltage. The iron concentration was measured by sampling the entire field of view at a magnification of 500X to average out the local spatial non-uniformity of the deposits. The calculated iron concentration is not an absolute value, but rather a relative measure since EDS probes primarily the near surface region. Measurements were made, starting near the top surface and moving toward the bottom surface along the centerline of the original cylinder. Figure 4-13 summarizes the measured concentration distribution. The data gives a clear indication that faster drying causes more material to deposit near to the surface.
Dried Nanolron distribution

![Graph showing the distribution of iron deposits in copper plugs for various drying conditions.](image)

Figure 4-13 Distribution of iron deposits in copper plugs for various drying conditions. Concentration measurements made using EDS across the whole field of view at a magnification of 500X down the centerline of a cylinder of sintered copper powder. The faster drying rates concentrate more material in a thinner region on the outside of the sample. Since the bending stresses are highest on the outside, this the effectiveness of the nanobinder increases.

SEM micrographs were made of the cross-section of the treated specimens at each point where the iron concentration was measured. All images were made at a magnification of 500X. Figure 4-14 compares images of the three treated samples taken at similar distances from the top surfaces. The iron deposits are seen as circles of deposits where there were contacts between adjacent particles. They also have formed lines between adjacent circles. Under all drying concentrations, more iron is deposited at the surface than in the interior. In the quicker dried samples, the deposits seem to be thicker and larger than in the slow-dried sample. The slow-dried sample still has some evidence of the chains of deposited material observable 2.5 mm from the surface while the quicker dried samples do not. These images provide qualitative confirmation of the EDS measurements.
Figure 4-14 Images of Copper specimens after nanoiron deposition under various drying conditions. Nanoiron deposits on the spherical copper powder are seen as circles where particles contacted. The deposits also form lines of deposited material connecting these contacting locations. Other large fragments may be from the iron deposits as well. Nanoiron deposits decrease with increasing distance from the top surface under all drying conditions, but decrease is somewhat less rapid for the slow dried sample. Scale bar represents 100 μm.

4.4 Magnetic Field

The nanoiron can act as a magnetic “ferrofluid”. The particles are stable enough in the fluid that they do not precipitate or agglomerate under an applied magnetic field, but rather move the fluid to the areas of largest field. If a magnetic field is applied to a powder
skeleton, the field is strongest at the contact points between the particles. If nanoiron is applied to the bar, the magnetic field will create a strong driving force for locating the fluid at the contacts between the particles. The magnetic field can also reduce the transport of the nanoparticles to the exterior of the part during drying so that the deposition pattern is more spatially uniform. The increased neck size should improve the nanobinder performance. Spatial uniformity may also help in reducing shrinkage and distortion. This concept was developed and implemented by Jan Wilkes.

![SEM images showing the effect of drying under a magnetic field.](image)

**Figure 4-15** SEM images showing the effect of drying under a magnetic field. (Top) Bond size in the center of samples dried without a magnetic field (left) are much smaller than those dried with a magnetic field (right). (Bottom) The nanoiron deposits on the outer surface of parts dried without a magnet field (left) are much larger than those dried with a magnetic field (right). Images taken after sintering to 700 C.

This concept was implemented in the bars by placing samarium cobalt permanent magnets at the ends of the bar as illustrated in Figure 4-7. Nanoiron was then applied to the center of the bar as before and continued until the fluid began to collect on the magnet.
Nanobinder Testing in Porous Metal Skeletons

The particles were dried at 150°C and then the magnets were removed before heating to 700°C. In some cases, this process was repeated to achieve higher levels of deposition.

Samples of the base of several parts were partially cut off and then fractured after heating the deposits to 700°C. The fracture surface was examined to view the bonds created and compare them to similar specimens dried without a magnet field. The increase in bond size from the magnets can be seen from Figure 4-15. Figure 4-16 also clearly shows that the bonds whose axis is approximately parallel to the magnetic field are larger than those perpendicular to the magnetic field.

Figure 4-16 SEM images comparing bonds aligned with magnetic field to those perpendicular to the magnetic field. (Top) Illustration of the field orientation. (Bottom) Bond sizes with their axis parallel to the magnetic field are larger than those with an axis perpendicular to the magnetic field.
Figure 4-17 Deflection ratios for nanoiron specimens dried with and without a magnetic field. Samples dried under a magnetic field have lower deflections than comparable samples dried without a magnetic field. Data includes samples that were presintered at 1300°C and samples deflected directly after processing the nanoiron.

These samples were then heated and deflected using the 2 K/min deflection cycle. The total deflection of the bars with and without magnets is compared in Figure 4-17. Drying under a magnetic field improved the performance (reduced the deflection ratio) of the samples by nearly 50%. As seen in Figure 4-15, the bonds formed under the magnetic field are clearly larger. If it weren’t for the redistribution of deposits to the exterior of the part, the performance difference between the two cases might be much larger.

4.5 Other Factors Affecting Deflection

4.5.1 OXIDATION STATE OF THE SOLUTION

The nanoiron suspension oxidizes readily in air converting the iron nanoparticles into iron oxide particles as documented in Chapter 3. Comparisons of oxidized and unoxidized material showed that the oxidized material tended to densify at lower temperatures but with higher shrinkage. While lower temperature densification is desirable, the high shrinkage is likely to reduce the structural integrity of the nanoiron.
material. When the dried bonds are heated, the bonds will break due to volume change during reduction of iron oxide to iron. This will leave a highly porous deposit that will require large shrinkage to densify, if it densifies at all. This suggests that the oxidized material would be less suitable for reducing the creep in the porous metal than the unoxidized solutions. However, oxidized particles can be handled more easily and are cheaper to produce. The effect of oxidation was specifically tested to quantify the relative difference.

This effect was tested by dividing a quantity of nanoiron from the same batch into two samples. One sample of nanoiron was left in open air for several days to permit full oxidation while the other was maintained in an inert environment. Afterwards, each solution was used to treat one bar. Nanoiron was applied to each bar twice and dried using a moderate drying cycle. They were sintered to 1300°C for one hour and deflected with a constant heating rate of 2 K/min. Figure 4-18 shows the two bars after deflection and compares them to an undeflected bar. The bar treated with unoxidized suspension performed better than the oxidized specimen with tip deflections of 5.0 and 7.2 mm respectively. For reference, an untreated bar deflected 13.5 mm.

![Deflection comparison of parts treated with oxidized and unoxidized nanoiron](image)

**Figure 4-18** Deflection comparison of parts treated with oxidized and unoxidized nanoiron. The bar treated with oxidized nanoiron deflected more than the bar treated with unoxidized nanoiron. Total amount applied was similar in both cases. The bars are pictured upside down so that high temperature deflection moved the tips upward.
This test confirms that oxidation negatively affects the nanobinder performance with 40% higher deflection than unoxidized. However, the sample still shows significant improvement when the nanoparticles are fully oxidized. The oxidized nanoiron solutions have the advantage of depositing less carbon into the substrate in conditions where carbon is undesirable. Thus, while the oxidation may decrease performance, it may prove favorable in application due to its lower cost and ease of handling. These suspensions may also be stable at higher concentrations so that more material can be deposited in a single application.

4.5.2 SAMPLE DENSITY

The density of the samples has a very large impact on the deflection rates of the parts. In cast parts, the part volume is very tightly controlled. The weight is an accurate indication of the part density. Samples with lower density deflected much more than a sample with identical preparation but higher weight. The density difference need not be large for a significant change in the total deflection.

This effect is seen in comparing untreated bars C-10 and C-25. C-25 weighs 4% more than C-10. The greater density of C-25 reduced the deflection from 18.6 to 13.5 mm. While increasing density increases the loads on the cantilever, it also increases the average number of contacts between the particles. The latter effect dominates to create a net decrease in deflection with increasing density in these uniform cross section bars.

Thus it is seen that increasing the density can effectively decrease creep deformations of the parts. Every effort should be made to maximize the initial density of powder metal parts before infiltration to achieve maximum stability. This also shows the importance of controlling the density when comparing deflections between samples. The sample weights of the cast bars used for comparing deflections varied by approximately ±0.25%.
4.5.3 PRESINTER IMPACT

Sintering before deflection reduces deflection tremendously. In the tests with printed specimens, samples were presintered to either 1300°C or 1100°C for one hour. The higher sintering temperature reduced the deflection of the control specimen by approximately 50% from 6-8 mm to 3-4 mm. One of the cast specimens was deflected directly after sintering in the mold at 1000°C for 30 minutes. The tip deflection of this sample was 29 mm compared to 13.5 mm for samples of the same geometry and weight presintered to 1300°C before deflection.

4.6 Deflection Reduction Mechanisms

It is clear that the nanobinder treatment can be very effective in reducing the creep deformation of porous metal skeletons. However, the mechanism is uncertain. Possible mechanisms include the reduction in stress due to increased bond sizes, chemical effects from adding additional carbon, or structural effects from increasing the number of bonds between particles. The tests conducted to date are not sufficient to fully quantify the relative importance of each of these effects. However, several tests do provide indications as to the significance of carbon deposition. Bond size measurements provide some indication of the effect of the nanobinder on strengthening the bonds. Each of these is considered below.

4.6.1 BOND SIZE MEASUREMENTS

In chapter 2, a model of the nanobinder performance was developed from the assumption that the creep strain was dominated by strain in the bonds where the stress is much higher than in the particle bulk. Under the simplest scenario, the creep deformation would be related directly to the stress in the bonds and the creep would decrease as the area fraction of bonds increased. If the structural characteristics of the skeleton such as packing fraction remain constant, Equation 2-27 in Chapter 2 can be simplified to
The stress exponent \((n)\) is assumed to be one based on the measurements reported in Chapter 5.

This relationship can be tested for deflected bars by fracturing the part after deflection and comparing the measured bond sizes to the difference in the total tip deflection or the tip deflection rate. These results can also be scaled by the number of bonds per unit area to compensate for differences between parts. If the neck strain rates control the total strain, then the differences in tip deflection or deflection rate should be nearly proportional to the difference in neck strain rates. In most cases though, the actual strain rate was not measured, just the total deflection which is proportional to total strain. If the structure experiences little change during deflection, the total strain may be used as an indicator of strain rate. The bars that were presintered at 1300 C before deflection best meet this condition. Under these assumptions the ratio of strain rate and strain are both expressed as

\[
\frac{\dot{\varepsilon}_1}{\dot{\varepsilon}_2} = \frac{\varepsilon_1}{\varepsilon_2} = \frac{\sum \left( \frac{X}{D} \right)^2}{\sum \left( \frac{X}{D} \right)}
\]

where the summation is across all of the bonds in the measurement area. For the narrow particle size used in the powders, the powder diameter will be considered constant and this reduces to

\[
\frac{\dot{\varepsilon}_1}{\dot{\varepsilon}_2} = \frac{\varepsilon_1}{\varepsilon_2} = \frac{\sum X_2^2}{\sum X_1^2}
\]

This relationship was tested by examination of two sample pairs. The samples were prepared by making a cut in the bars so that a piece could be broken off the structure. The fractures pass through just the bonds of the particles so that many bonds are visible for
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measurement. The number of bonds was counted in a representative area and their diameter was measured.

The first pair of specimens was bars C-18 and C-25. C-18 was dried under a magnetic field with two applications of nanoiron. C-25 was an untreated bar. Both were presintered at 1300 C before deflection. The second pair was C-29 and C-32. These were not presintered. C-29 has no nanoiron treatment while C-32 received four applications with a magnetic field applied during drying. Specimens with magnetic field drying were selected as they provide more uniform nanobinder distribution. The results of the bond size measurements are summarized in Table 4-3.

<table>
<thead>
<tr>
<th>Bar</th>
<th>Average Neck Size</th>
<th>Number of Bonds</th>
<th>Predicted Deflection Ratio</th>
<th>Actual Deflection Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-25</td>
<td>23.8</td>
<td>23</td>
<td>0.78</td>
<td>0.18</td>
</tr>
<tr>
<td>C-18</td>
<td>25.8</td>
<td>26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-29</td>
<td>23.5</td>
<td>65</td>
<td>0.40</td>
<td>0.05</td>
</tr>
<tr>
<td>C-32</td>
<td>28.4</td>
<td>99</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The 1300 C presintered pair (C-18 and C-25) shows very little difference in bond size and area in the measured sample, but they differed in total deflection by a factor of 0.18. The second pair did show a significant difference in bond size and number. However, Equation 4-4 predicts that the ratio for treated to untreated tip deflections would be 0.4. Actual deflection difference was one-eighth this amount. However, the bond sizes in this sample would have changed significantly with time during the sample so that the final deflection may not be a good indication of the deflection rate related to the measured neck size difference. This does not explain the even larger difference between measured and predicted results in the presintered specimen pair.

Part of the deviations from the model could be a result of non-uniformity in the nanoiron deposits through the thickness. Variation in the bond sizes through the thickness of the bar was observed in specimen C-32. To compensate the measurements were made from an image near the outer edge of the bar near the cantilever base where stresses are
highest. Sample C-18 was not checked for bond size variation through the part thickness. The location chosen for the bond size measurements was probably from near the center of the part. This might explain part of the discrepancy in this case.

However, the very large deviation from the model predictions suggests that there are other important differences. The next section shows that the carbon can have a significant impact, but that the iron is significant as well. Chapter 5 also examines ways in which the deformation mechanisms deviate from the assumptions made in this model.

4.6.2 CARBON DEPOSITION

Carbon is a powerful alloying element in steels. The deposition of carbon with the nanobinder can have a significant impact on the deformations of the part. The carbon content of several samples was measured by combustion infrared detection. In this method, the sample is heated in an oxidizing environment. The carbon reacts with the oxygen. The quantity of carbon is measured by infrared measurements of the exhaust gas. The results for samples of treated and untreated 410 SS as well as nanoiron samples are summarized in Table 4-4. As this is a destructive test, the samples for the tests were typically taken from the thick ends of the bars so that the deflected areas were not damaged.
Up to 10% of the nanoiron deposit may be carbon. This carbon may not be distributed uniformly through the skeleton but concentrated near the surface as illustrated by the iron distribution measurements in Section 4.3.2. The carbon gradients will be reduced by diffusion at high temperatures, but the low solubility of carbon in the iron limits the transport rate.

The carbon could reduce the deflection by reducing the diffusion throughout the skeletons or by creating iron or chromium carbides in the bond areas where the stresses are likely to be the highest. However, the phase diagram of 410 SS (Figure 4-19) indicates that over most of the temperature range where creep is significant, the carbides are not stable. Any reduction in creep rates from the carbides would decrease with time as the carbides dissolved.
However, the carbon may shift the phase composition to reduce or eliminate ferrite at the infiltration temperatures. The test bar with the maximum increase in the carbon content would be the one with 2.7% unoxidized nanoiron, dried under a magnet. If this were dried uniformly, the carbon concentration would increase up to 0.27% for a total of 0.43%. Any composition above 0.25% carbon will remain in the austenitic phase up to the infiltration temperature. This can be accomplished by adding just 0.9 wt% nanoiron could increase the carbon content into the austenitic phase.

Additionally, the carbon may affect the sintering rates of the particles. Sintering proceeds through the same diffusional mechanisms as creep. Generally, factors that affect the creep rate will also affect the sintering rate similarly. Thus, materials with lower creep rates will have lower sintering rates as well. While the lower intrinsic creep rate would tend to lower the deformation, the interparticle bonds will be smaller due to the corresponding decrease in sintering rate. These smaller bonds would be more highly stressed. The net effect may be to increase the deformation rate in a material with a lower intrinsic creep rate.

4.6.2.1 Carbon Additions to Reduce Deformations

To test the importance of the carbon content alone, two skeletons were prepared from 420 stainless steel powder 63-90 μm in diameter using the alumina mold method. 420 SS has the same composition as 410 except with increased carbon and chromium content. The chromium content increases from 11.5-13 % in the 410 to 12-14% in 420. The increased chromium content is necessary to maintain corrosion resistance with the increased carbon in the alloy. The carbon content in the particular powder batch was measured by combustion infrared detection at 0.435%. One of the 420 SS skeletons was presintered at 1300 C. They were both deflected using the typical 2 C/min heating cycle.
Figure 4-19 Pseudobinary phase diagram for 410 SS. The basic 410 composition with 0.16% carbon is single phase austenite (γ) between approximately 950°C and 1200°C. If the carbon is increased to 0.25%, only the austenite phase is stable between 1060°C and the infiltration temperature. Diffusional creep may be lower in the single phase region.

The 420 bar that was presintered to 1300°C deflected only 0.63 mm at the tip—much less than the 13.5 mm measured in a comparable bar produced from 410 SS. This result confirms that the carbon can play a significant role in reducing the creep deflection of the parts, probably due to a decrease of the diffusivity. If similar results can be achieved with smaller changes in carbon content, carbon deposition might be a very useful approach for reducing the deflection of porous skeletons.

This deflection of the untreated 420 SS bar is also less than the best case result achieved by application of the nanobinder to a cast part presintered at 1300°C. The smallest deflection of a presintered nanobinder treated bar is 2.5 mm. However, that was accomplished with a nanoiron deposit of just 0.80% so that the maximum carbon increase
would be less than 0.1%. It is unclear how much of the difference between the 420 SS bar and the 410 bar treated with nanoiron is related to the lower carbon content in the latter. This question is addressed in the following section.

A very different result was observed in the case of the second skeleton deflected without presintering at 1300 C. This 420 SS skeleton deflected 28.4 mm compared to 29.3 mm for a comparable 410 SS bar. By comparison, bars treated with the nanobinder deflected as little as 1.5 mm. This result confirms that there is a substantial benefit from the nanobinder beyond simple carbon addition. It may be that the carbon is concentrated at the neck region, but it is more likely to be related to the quick sintering rate of the nanoparticle deposits.

![Graph showing deflection rate versus temperature](image)

**Figure 4-20** Tip deflection rate versus temperature for a nanoiron treated bar. 410 SS bar treated with nanoiron and deflected with a presintering cycle shows a decreasing deflection rate with increasing temperature. This is likely due to strengthening of the particle bonds due to sintering of the nanoiron. Nanoiron deposition was 1.4 wt% of the total skeleton weight.

This is seen in the plot of deflection rate versus temperature for sample C-31 shown in **Figure 4-20**. This bar received two nanoiron applications and was dried under a magnetic field. The deflection rate was calculated by numerical differentiation of the measured tip deflection versus time and temperature. If applied load and structure are constant, creep rates should increase exponentially with temperature. However, this bar shows a peak and then a decrease in creep rate with temperature. This could be caused by sintering of the nanoparticles during heating. As the nanoparticles sinter, they would reinforce the structure and reduce the local stresses.
If the carbon reduces the rate of creep in the parts by lowering the diffusivity of iron in the matrix, the sintering rate would be reduced similarly. The untreated 420 SS bar would have very small bonds if it were not presintered at high temperature before deflection. On heating, the bonds would begin to grow but they would be under significant stress. On the side of the bar loaded in tension, the sintering process would be slowed and maybe even halted by the applied load. These neck bonds would begin to strain and may start to fail. At this point, the remaining bonds would be more highly loaded and might begin to fail in succession so that the total strain would be amplified. If the carbon did decrease the diffusion rates in the alloy, the sintering would proceed more slowly than in the lower carbon 410 SS. The initial bond sizes in the 420 SS samples would be smaller than for the 410 SS specimens.

The case of bars deflected without prior sintering is of greatest interest in application. In general, the presintering step is not feasible without a supporting powder with its attendant problems. It is also not always desirable to add the extra carbon due to its impact on the final material properties. Increasing the carbon content of the powder can impact the steel infiltration process. As the carbon content of the skeleton increases, the feasible final compositions for steel infiltration change. [10]

Other material systems such as titanium and nickel cannot tolerate carbon deposition as well. Carbon increases the hardness and creep strength of titanium, but also embrittles titanium. When added as an alloying element, carbon is still maintained to 0.06 wt%. [21] While nickel does not form carbides, deposited carbon can form carbides with other alloying elements. Some carbides are more desirable than others, but like titanium, most nickel alloys that contain carbon do so only in small fractions. [22] Thus, carbon deposition in these alloys would need to be eliminated or carefully controlled.

4.6.2.2 Comparing Creep Impact of Carbon Deposition to Nanobinder Application

There are many ways by which carbon might be applied to the nanobinder skeletons to reduce the creep rates. Carbon can be added to the base powder as above. It can be added by coating the powder with polymer, mixing polymer into the base powder, or printing polymer–loaded binders. Many of these processes could be much less
expensive than employing the proposed nanobinder approach. Therefore it is important to determine whether there is a significant performance advantage obtained by using the nanobinder over simply adding carbon to the skeleton.

For this comparison, another specimen with increased carbon was prepared using a 3DP binder developed by Extrude Hone. This binder, Binder S, was deposited into cast bars by infiltration, dried in air to 180°C and then heated in a reducing atmosphere to 600°C for debinding. It was subsequently sintered at 1300°C and deflected. The carbon content of the Binder S treated bar and some of the nanoiron treated bars was measured to quantify the change in carbon content and compare it to the deflection ratio. The measurements are summarized in Table 4-4 above.

The carbon content is increased by nanoiron treatment, but the increase is relatively small for most of the specimens. The increase is actually similar to treatment with the traditional 3DP binder, Acrysol. The proprietary binder used by a 3DP licensee, Binder S, has much higher carbon deposition with an increase of 0.15% over the untreated powder.

Deflection tests were conducted with all of these specimens. While all of the bars deflected less than the untreated bars (deflection ratio < 1), the parts treated with nanobinder consistently showed less deflection (lower deflection ratios) than the carbon treated bars for a given increase in carbon content.

This is graphically illustrated in Figure 4-21 in which the deflection ratio of the various samples is plotted against the increase in carbon content relative to the untreated 410 SS powder. Interestingly, the carbon treated specimens (Binder S, 420 SS) that were presintered to 1300°C fall along a single line while the nanobinder treated parts with the same heat treatment ("Nanobinder Treated") have much better performance for the same increase in carbon content.
Figure 4-21 Deflection ratios for treated and untreated bars plotted against the change in carbon composition of the specimen relative to the basic 410 SS composition. Samples include 420 SS material, polymer binder in 410 SS, and nanoiron treatment of 410 SS powder. The carbon treated parts show significant creep reductions, but smaller than the nanoiron treated parts. Additionally, the nanoiron parts follow similar trends with and without a presinter at 1300 C while the 420 SS bars with carbon added have very high deflection ratios (low benefit of carbon) unless it is presintered at 1300 C.

Specimen C-12 labeled “Nanobinder Surface Carbon” in Figure 4-21 does fall very close to the line for carbon only treatment. The high carbon content in this sample is a product of differences both in the nanobinder application method and the location from which the sample for carbon composition measurement was extracted. The deposits in this sample were concentrated on just the bottom surface by drying with the top and sides partially covered so that most of the evaporation occurred at one surface. The heavy surface deposits are seen in Figure 4-22. While the carbon measurements for all other samples averaged the carbon content through the part thickness, the region used for this measurement was a 1 mm thick slice from surface where the nanobinder deposits were concentrated. This sample represents the extreme in surface concentration achieved during these tests.
Figure 4-22 Large surface concentration of deposits in sample C-12. SEM image of large surface deposits of nanoiron obtained by drying at a quick rate with the sides, tip, and bottom partially covered to reduce evaporation in these regions. Carbon measurements from the surface of a similarly prepared sample were anomalously high.

This sample has low performance (high deflection ratio) both relative to the carbon content measured (Figure 4-21) and the amount of nanoiron deposited (Figure 4-23). For example, specimen C-17 was dried without a magnetic field but with a 25% lower deflection ratio than C-12 with 20% less nanoiron added. This suggests that the deposition method used in sample C-12 was inferior to other methods including magnet drying and drying without a magnetic field but with free drying from multiple surfaces. Yet, even in these low performance conditions, the nanobinder treated sample still performed somewhat better than the carbon only specimens as evidenced by its position below the trend line through the carbon specimens.

The carbon content of magnet-dried specimens should be very uniform through the thickness due to the increased deposition uniformity of these samples. The deflection ratio of the magnet-dried samples that received at least two applications of nanoiron was compared to the other results by estimating the carbon content of these specimens. The carbon content was estimated by assuming a uniform distribution and that 10% of the weight increase from nanobinder application was due to carbon deposits. In the one case
where there was a measurement of the carbon value, this method proved to overestimate the carbon deposition. These data points are shown in Figure 4-21 as the dataset “nanobinder-magnet dry”. This dataset is well below the carbon only line suggesting that the nanobinder does improve performance significantly.

![Graph showing comparison of deflection performance of surface-loaded bar (C-12) to other specimens. The magnet-dried dataset appears insensitive to the presinter condition of the specimens. Specimens with and without a presinter fall along the same line in the figure. In contrast, the 420 SS bars performed dramatically different with and without presinter and cannot be represented by a single trend line. This result confirms that the nanobinder performs an important role in forming the initial structures when the parts are not presintered.](image)

The magnet-dry dataset appears insensitive to the presinter condition of the specimens. Specimens with and without a presinter fall along the same line in the figure. In contrast, the 420 SS bars performed dramatically different with and without presinter and cannot be represented by a single trend line. This result confirms that the nanobinder performs an important role in forming the initial structures when the parts are not presintered.

Taken together, these results show that while it may be possible to reduce the creep deformations by applying carbon to the parts, the nanoiron can achieve improved performance even when presintered at 1300 C. However, the nanoiron is especially valuable in specimens that are not presintered to 1300 C.
4.7 Shrinkage Measurements

The dimensions of the sample bars were measured with calipers after each treatment step. However, these measurements were not sufficiently accurate to detect differences in shrinkage between treated and untreated specimens. More accurate measurements of the cast parts were obtained using an optical comparator. The cast models provided sharp smooth edges for repeatable measurements. All the samples were assumed to start with the same initial length as measured from representative samples after removal from the mold. All the samples that had not been cut for examination were measured on an optical comparator after the deflection cycle. The average shrinkage of untreated bars was 2.6% and of the treated bars 1.3%, a 50% reduction.

Additionally, there was a slight trend for further decreases in shrinkage with increased nanoiron applications as illustrated in Figure 4-24. The data points are insufficient to draw firm conclusions regarding the nature of the relationship.

Shrinkage reduction might be related to the carbon deposited with the nanoiron. However, a sample treated with oxidized nanoiron showed similar improvements as the unoxidized sample. Carbon content of oxidized and unoxidized nanoiron samples heated to 700 C in Argon-Hydrogen atmosphere was measured by combustion infrared detection. The carbon in the oxidized samples was less than 1% compared to 9.7% for the unoxidized case. Carbon deposition from oxidized samples would be negligible. Thus, most of the shrinkage benefit must be from the iron deposition.
Figure 4-24 Variation in shrinkage reduction with quantity of nanoiron added. Total shrinkage reduction is approximately 50% with some increase in shrinkage reduction with increasing nanoiron quantity of deposits. There is not sufficient data to draw conclusions regarding the nature of the relationship. The oxidized nanoparticles are almost as effective at reducing the shrinkage as the unoxidized nanoparticles. Also, the application of a magnetic field during drying does not appear to change the drying shrinkage significantly.

If the carbon deposition is not reducing the shrinkage, then the iron deposition is reducing the shrinkage directly. In untreated skeletons, material is transferred from the particle to form the bonds. This transfer leads to shrinkage. The deposited iron forms bonds between the particles from added material so that the shrinkage mechanisms are reduced.

Surprisingly, the application of a magnetic field does not appear to have a significant effect on the shrinkage. Drying under a magnetic field increases the uniformity of the deposits through the part thickness and concentrates the deposits in the particle contacts. This should be helpful in reducing the shrinkage by the mechanism described. In the samples dried without a magnetic field, a significant portion of the material is deposited on the part surface. It is possible that these deposits reduce the shrinkage rate of the surface piece. The surface would then resist the higher shrinkage rate of the interior and an overall reduction in shrinkage could be measured. Further study is required to fully understand this relationship.
4.8 Conclusions

In this chapter, the nanobinder concept has been tested in cantilever bars of porous metal skeletons produced from 410 SS powder. These parts are similar to parts produced by 3DP or SLS in their structure and density. Nanoiron was applied to these bars under various conditions and then they were heated up to infiltration temperatures. The tip deflection of the bars was measured as an indication of the creep rate. The dimensions of the bars were also measured to compare shrinkage rates of treated and untreated parts.

These tests show that nanobinder can significantly reduce the deflection rate of the porous metal skeletons. The greatest benefit is achieved either by drying quickly to concentrate the material on the outer surface where the stresses are highest or by drying in a magnetic field. The magnetic field concentrates the deposits in the contact regions between the particles. Oxidation of the nanoparticles reduces their strengthening benefit, but they do still provide significant strengthening. Given the lower cost and ease of handling iron oxide particles, it may be desirable to investigate these further.

The nanoiron was also found to reduce the shrinkage of the skeletons by 40-60%. The shrinkage reduction is dependent on the quantity of the nanoiron material added to the part. Shrinkage is not strongly affected by the oxidation state of the particles or by the application of a magnetic field during drying.

A model of the nanobinder performance based on reducing stress in the bonds through increasing their size is not sufficient to explain the reduced creep deflection of nanobinder treated parts. The difference appears to be related by the addition of carbon to the part with the nanobinder. However, the addition of carbon alone is shown to be insufficient. The carbon and iron must be deposited together for best results.
4.9 References


5 Creep of Porous Parts

In the previous chapter, the nanobinder was shown to significantly reduce the deflection of porous metal skeletons when heated to infiltration temperatures. In this chapter, the deflection processes are measured to gain additional insight into the process characteristics and parameters. The basic creep mechanism is identified and the key parameters are compared for treated and untreated specimens. These tests show that the basic creep mechanism (diffusional creep) is unchanged by the application of the nanobinder but that the values of the activation energy are affected. The test methods used are sensitive to changes with time such as sintering that lower the measured activation energies. The differences between the activation energy measured for bars with and without nanoiron treatment is attributed to the carbon composition changes and residual porosity.

5.1 Background

Materials can deform by many mechanisms. The particular mechanisms of deformation provide different macroscopic characteristics such as dependence on time, temperature, size, and stress. These mechanisms vary from the familiar time independent, elastic deformation typical of low stresses at room temperature to time and rate-dependent strain rates that may be observed at high temperatures or at high strain rates.

While there are general trends among similar materials such as metals, the particular areas in which each of these mechanisms is most significant can vary widely.
Ashby developed the concept of a deformation mechanism map (DMM) to graphically display the interdependencies between applied stress and temperature and the mechanisms and/or rate of deformation. Typically the deformation mechanisms are shown as a function of temperature and stress level. The temperature is expressed as the ratio of the current temperature to the melting temperature of the material in an absolute temperature scale. This is termed a homologous temperature. The stress is often shown as a ratio of applied normal or shear stress to the elastic or shear modulus. In general, these maps can vary with grain size, material processing history, and composition. However, most share many common characteristics and similar boundaries. [181]

![Deformation mechanism map for pure iron](figure-5-1.png)

**Figure 5-1** Deformation mechanism map for pure iron. [2] Diffusional processes dominate at lower stresses. At higher stresses, dislocation motion is significant.

**Figure 5-1** shows the DMM of pure iron. At the highest stresses, deformation proceeds by dislocation motion that is independent of temperature. At high temperatures, other deformation processes create slow but significant strains even at relatively low stresses. These time-dependent deformation processes are collectively called “creep”.

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An illustration of the three characteristic creep stages observed during constant load creep testing. Creep tests generally focus on the steady state “secondary creep” stage.

Creep is sometimes divided into three stages called primary, secondary, and tertiary creep illustrated in Figure 5-2. Primary creep is characterized by a high initial strain rate that decreases after a relatively small strain. Secondary creep begins as the initial high strain rate slows down to a long constant rate period. Secondary creep is the longest period in most applications. In the tertiary creep stage, strain rate increases again under a constant load as failure processes begin. Most creep modeling addresses the secondary stage and focuses on predicting the amount of creep expected with time. Design applications may be limited either by the allowable deformation or time to failure. [3]

5.1.1 POWER LAW CREEP MODELS

Creep is characterized by continued deformation at a constant stress rate, but there are many different processes by which the deformation can progress. They all share a dependence on diffusion processes. As diffusion is an activated process with a strong temperature dependence, creep also has a strong temperature dependence. Creep and diffusion generally become significant at a temperature higher than half the material’s melting point in absolute temperature, but it may be much lower for nanostructured materials as has been measured directly [4] and inferred from the decrease in sintering temperature in nanostructured materials [5-39].
Creep of Porous Parts

Although there are many different mechanisms by which creep may occur, they can be well represented by the Dorn equation [10,11],

\[ \dot{\varepsilon} = A' \frac{D G b}{k T} \left( \frac{b}{d} \right)^n \left( \frac{\sigma}{G} \right)^n \]

where \( q, n \) depend on the mechanism of the creep. The Diffusivity, \( D \), is given by

\[ D = D_0 e^{-\frac{Q}{k T}} \]

For general considerations, the exponential term may be removed from the diffusivity and the remaining constants be combined this may be simplified to

\[ \dot{\varepsilon} = A \left( \frac{\sigma}{G} \right)^n e^{-\frac{Q}{k T}} \]

The remaining factors from Equation 5-1 were combined into the single prefactor “A.”

The stress exponent “\( n \)” and the activation energy “\( Q \)” are the critical parameters that help to characterize the active creep process. The activation energy comes from the diffusional processes that are important to the creep mechanism and is generally the same as the activation energy for the active diffusion process. The prefactor “\( A' \)” is a constant that is experimentally determined. While this model has been justified by various derivations, it is essentially an empirical model with values that are determined experimentally for each combination of material, processing, temperature, and stress. Some creep models may include dependencies on the grain size \( (d) \), Burgers vector, temperature, and/or shear modulus in “\( A' \”).

5.1.2 CREEP MECHANISMS

At high temperatures and relatively low stresses, deformation is based on direct diffusional transport. The applied stress fields create a gradient in chemical potential that favors diffusion from surfaces and grain boundaries parallel to the applied stress to those normal to the applied stress. The different diffusional creep processes are characterized by
the diffusion paths that are active. Coble creep is dominated by grain boundary diffusion while Nabarro-Herring creep is dominated by diffusion through the bulk lattice. They can be differentiated by the difference in activation energies between the two processes. They also differ in their dependence on grain size. Coble creep rates are proportional to $d^3$ while Nabarro-Herring creep rates are proportional to $d^2$. Diffusional creep processes are characterized by a stress exponent equal to one and creep rates that depend on grain size.

At higher stresses, dislocation motion may become active, and the stress exponent increases to values greater than one. Typical values of “$n$” for these processes are three to eight or even larger. In these conditions, small stress changes can cause very large changes in strain rate.

During dislocation creep, there are two distinct processes of dislocation motion that operate in series. These are dislocation glide and dislocation climb. The resistance to dislocation glide is very sensitive to solutes in the lattice. Solutes create irregularities in the crystal lattice that increase the difficulty of dislocation motion. Obstacles such as second-phase particles and grain boundaries can also impede dislocation motion. Higher stresses are required to continue dislocation motion past these obstacles. At room temperature, no additional strain is possible until the stress is increased further. If the stress is constant, strain stops. However, at elevated temperatures dislocations may climb past obstacles via diffusion and then continue movement via glide, introducing a thermally activated step to the strain process.

The stress exponent “$n$” for these processes is determined by which part of the dislocation motion limits the strain rate. If the lattice resistance to dislocation motion is increased as by solute atoms or dispersed particles, the dislocation glide process is rate limiting. Under these conditions, “$n$” has a typical value of 3 while “$n$” is typically 4-5 when dislocation glide is rate limiting. Alloys with significant dispersion strengthening experience a threshold stress with “$n$” values that can exceed eight. \[10\] Alternative models have been proposed as by Evangelista and Spigarelli [12] that better explain behavior in this threshold creep regime, but the power-law creep is adequate for this work.
5.1.3 PRIMARY CREEP

During creep tests, secondary creep accounts for the majority of the test time under most conditions. However, the strain contribution of primary creep may be very significant. Primary creep is generally characterized by a change in strain rate with time under constant load and temperature conditions. As the creep processes reach a steady state, secondary creep begins. Primary creep has not been studied or modeled as extensively as secondary creep.

In dislocation creep, primary creep may be characterized by relatively free glide of dislocations that begins to slow as obstacles are encountered and dislocation tangles emerge. Some alloys show little primary creep especially in diffusional creep. When it is observed, it may arise from excess vacancy concentrations created by grain boundary area decreases as the grain boundaries grow simultaneously with creep deformation. Estrin, et al suggested that this process might be particularly important in the case of nanostructured materials with high grain boundary areas [13].

Primary creep may contribute significantly to the deformation of powder metal parts during sintering and infiltration since the overall strain may be relatively low, particularly in the naniron treated parts. This possibility is discussed further in Section 5.4.5.1 below.

5.1.4 CREEP PARAMETERS

Creep mechanisms can be identified by measuring the stress exponent \(n\) and the activation energy \(Q\). Additionally, the grain size dependence can be measured to further distinguish between Nabarro-Herring and Coble creep. Table 5-1 summarizes the expected values of these parameters for each of the major creep processes.
Table 5-1 Summary of Primary Creep Mechanisms

<table>
<thead>
<tr>
<th>Creep Mechanisms</th>
<th>Stress Exponent ((n))</th>
<th>Activation Energy ((E))</th>
<th>Dependence on Grain Size ((d))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nabarro-Herring</td>
<td>1</td>
<td>Lattice Diffusion</td>
<td>(d^2)</td>
</tr>
<tr>
<td>Coble</td>
<td>1</td>
<td>Grain Boundary Diffusion</td>
<td>(d^3)</td>
</tr>
<tr>
<td>Dislocation Glide</td>
<td>3</td>
<td>Lattice Diffusion</td>
<td>None</td>
</tr>
<tr>
<td>Dislocation Climb</td>
<td>5-8</td>
<td>Lattice Diffusion</td>
<td>None</td>
</tr>
</tbody>
</table>

The additional creep parameter not considered in this analysis is the prefactor “\(A\)”. While this value is important for predicting absolute values of the creep rate, it is not necessary to understand how it will scale with modified parameters. The activation energy \(Q\) determines how the process scales with temperature and the stress exponent determines the scaling with stress. These values can be measured by measuring deformation changes with stress and temperature. The prefactor value for the material is difficult to measure using the powder skeletons since the stress and strain levels are non-uniform across the powder particles. A value of “\(A\)” measured from a powder skeleton would depend on the local stress states which is a function of particle size, packing density, and sintering state. Conversely, a detailed knowledge of the local stress state would be required to apply a bulk value of the prefactor to the powder skeletons.

5.1.5 POROUS SKELETONS ON THE DMM

The average stress of the deflection specimens was estimated in Chapter 2 as approximately 58 kPa. For the assumption of simple cubic packing, the average bond stress ranges between 400 kPa and 4 MPa for neck size to particle diameter ratios ranging from 0.1 to 0.3. A deformation mechanism map is not available for the 410 SS used in these tests. However, the data for iron provides some indication of where the test conditions might fall. When the estimated bond stress is plotted on the deformation mechanism map for pure iron (Figure 5-3), it is clear that the skeletons are near the boundary between dislocation and diffusion creep. In fact, the actual stresses in a particular bond may land on both sides of the boundary such that there may be contributions from multiple mechanisms.
Creep of Porous Parts

Figure 5-3 Plot of estimated infiltration conditions on the deformation mechanism map of iron. [2] Under infiltration conditions, the samples are in a diffusional creep regime where the stress exponent should be one. However, the conditions are close to the power law regime. The actual alloys tested could be in a different regime.

5.2 Creep Parameter Measurements

Creep parameters are usually measured using small homogenous samples with constant, uniform stress and temperature. Since stress and temperature are uniform, the strain rate can be calculated directly. Series of samples are tested at different combinations of temperatures and stresses to determine the activation energy and stress exponent for a particular creep mechanism. This process can be repeated for each deformation mechanism to characterize each creep mode. This method requires many samples for each deformation mechanism.

To understand the performance of the nanobinder, the creep characteristics of the powder compacts must be characterized. The sensitivity of the nanobinder performance to temperature and stress will depend on the stress exponent and the activation energy.
Unlike typical creep specimens, the stresses vary throughout the bars due to the porous geometry of the parts making it impractical to determine strain rate as a function of the absolute stress. However, the quantity of interest is not the property of the actual material, but of the porous compact as a whole. In effect, the porous material will have some effective creep parameters that can be determined from the overall response of the material to applied loads. In general these parameters will depend not only on the material, but also on the structure of the powder compact. This structure is a function of the manufacturing method, density, powder size, powder size distribution, and degree of sintering. It would be very useful to develop a method of relating intrinsic material creep properties to the creep of these structures so that predictions of creep performance could be made from a knowledge of the intrinsic material properties. This is beyond the scope of this work. This work compares parts treated by nanobinder to those that are untreated by measuring the effective stress exponent and creep activation energy of each bar type.

These effective creep parameters and mechanisms may not represent the deformation processes at the local levels. Therefore, there may not be complete correlation between values and effective mechanisms measured for the powder and those determined for bulk material at similar temperatures and average stress levels.

5.2.1 CREEP DEFORMATION OF CANTILEVER BEAMS

For beams with small deflections, the strain varies linearly through the thickness of the beam. This constraint arises from basic geometric requirements and is not changed by the deformation mechanism. However, the stress field associated with this strain is determined by the constitutive equations of the material. Linear elasticity gives the familiar linear variation while creep may give nonlinear relationships. Also, creep constitutive equations relate the stress and strain rate rather than the strain.

In the simplest case of diffusional creep where the stress exponent equals one, the results of linear elastic beam calculations can be used to analyze creep of beams by adding a time derivative to the displacement terms. Thus, the linear elastic equation for vertical displacement is the formula for vertical displacement rate when applied to creep processes. This equation must be integrated across time to calculate the displacement magnitude.
Creep of Porous Parts

Additionally, the materials constant of linear elasticity must be replaced with an appropriate materials term for creep deformation. For the case of a cantilever bar, with a uniformly distributed weight, the tip deflection for linear elastic deformation would be

\[ \Delta y = \frac{3 \rho ghl^4}{2h^2 E} \]

This could be modified for deflection via diffusional creep as

\[ \Delta y = \frac{3 \rho ghl^4}{2h^2 E^*} \]

where by analogy to linear elasticity a material constant for diffusional creep would be

\[ \dot{\varepsilon} = \frac{\sigma}{E^*} \]

\[ E^* = \frac{G}{A} \exp\left(\frac{Q}{RT}\right) \]

For values with a stress exponent larger than one, the relationships between deflection rate and applied stresses must be derived. This can be accomplished by assuming a linear strain variation through the height of the beam based on strain compatibility requirements. The moment is found by applying the constitutive equation to the known strain relationship and integrating through the beam cross-section. This derivation was done for the self-loaded cantilever by Pettavin [14], but the linear relationship will suffice here.

The total strain rate at a location is found by integrating the strain rate across time,

\[ \varepsilon(x, y) = \int \dot{\varepsilon} \, dt = \int_0^t \left(\frac{\sigma}{G}\right)^n \exp\left(\frac{-Q}{RT}\right) \, dt \]
For the case of self-loaded specimens heated in a uniform temperature field, the stress is independent of time while the deflections remain small and the temperature is independent of location. Under these conditions, the equation can be separated to get

\[
\varepsilon(x, y) = A \left( \frac{\sigma(x, y)}{G} \right)^n \int_0^t \exp \left( -\frac{Q}{RT(t)} \right) dt
\]

The term inside the integral contains all the information about the heat cycle of a specimen. The heat cycle effectively becomes a scalar multiplier on the strain magnitude. The strain distribution is only a function of the stress distribution and the stress exponent.

The independence of the stress field and temperature history will be exploited to extract information about the effective stress exponent of a porous metal cantilever bar both by comparing final deformations of multiple bars with different stress levels and by measuring the final shape of deflected bars. Activation energy can be calculated in turn by measuring the deformation rate at varying temperatures but a constant stress.

### 5.3 Stress Exponent

#### 5.3.1 MEASURING STRESS EXPONENT BY VARYING SAMPLE GEOMETRY

The stress exponent determines the way in which strain rate varies with stress. The stress exponent is usually determined by directly measuring changes in strain rate with stress. However, this requires methods for applying variable stresses in situ. Alternatively, the stress exponent can be determined from the final strain shape of a test piece with a spatially varying stress field. Due to the relatively low strength of a porous metal skeleton, the gravity loading of an unsupported structure such as a cantilever bar applies sufficient stress to cause measurable strains. As the stress varies along the length of the bar, the stress exponent can be determined from the deformed shape.

When such a cantilever bar is heated in a furnace, the stress is constant with time while the temperature is spatially uniform. At high levels of deformation, the assumption of a constant stress field will no longer hold, but the deflections in the ensuing calculations
are small enough to be modeled adequately using small deflection approximations. As discussed above, this reduces the temperature profile effects to a scalar multiple on the final deflection so that the total deflection of different specimens heated through the same cycle may be compared.

This method was implemented by creating a series of cantilever bars with differing lengths to vary stresses between bars and comparing the total deflection of the bars when heated through the deflection cycle. Two sets of bars were created with a different thickness. The 5 mm thick bars were deflected at 1270°C for 10 minutes while the 4 mm thick bars were deflected at 1250°C for 10 minutes. Both sets used a ramp rate of 6°C/min below 1200°C and 3°C/min above.

![Figure 5-4 Specimens for stress exponent testing. The raw sintered bar (left) is produced by sintering powder in an alumina mold. It is milled to produce the deflection specimen (right). The stress during deflection is adjusted by varying the length and/or thickness. Constant thickness specimens are preferred to eliminate errors from surface damage during machining.](image)

The porous metal bars were prepared as for the deflection test specimens from special low carbon D2 tool steel powder 63-90 μm in diameter. The powder was cast in an alumina form and sintered to 1200°C for 30 minutes. These sintered bars were milled to create cantilevers of geometry illustrated in Figure 5-4. The stress in the bars was varied by adjusting the length of the cantilever. Alternatively, stress could be varied by adjusting bar thickness with a constant cantilever length, but the machining process may leave a damaged layer of reduced strength. Maintaining a constant bar thickness assures that the damaged layer remains a constant fraction of the total thickness so that a constant cross-section stiffness is maintained.
The density was measured by applying Archimedes’ principle with a correction for the weight of the water absorbed into the pores. The weight of the samples was measured dry, submerged in water, and wet after immersion. The density of the part is then given by

\[
\rho_{\text{skeleton}} = \frac{W_{\text{dry}}}{(W_{\text{wet}} - W_{\text{submerged}}) \rho_{\text{water}}}
\]

The dimensions of the samples were measured as well to verify their accuracy. The average bar density was 5.0 g/cm³, approximately 64% relative density. Table 5-2 summarizes measurements of the dimensions, estimated stress, and measured deflection of each test bar. The stress at the base of the cantilevers was estimated assuming a uniform distributed load from the bar self-weight with a homogenous material. This means that the stress is averaged across the pores and necks. The homogenous peak stress is given by

\[
\sigma_{h,\text{max}} = \frac{3 \rho g l^2}{h}
\]

where \(\rho\) is the skeleton density, \(L\) and \(h\) are the length and thickness of the bar respectively. The deflection of a cantilever beam with a linear stress-strain rate relationship under these loading conditions is given by Equation 5-4. Substituting from Equation 5-11 and solving for the peak stress,

\[
\sigma_{h,\text{max}} = \frac{2 E^* (\Delta y) h}{l^2}
\]

For the creep deformations, the modulus of elasticity is replaced by an effective modulus \((E^*)\) that is a function of the temperature-time history as well as the creep parameters of the homogenous material.
The deformation mechanism map predicts that diffusion creep is the dominant creep mechanism. To verify the expected linear relationship between stress and strain rate, the stress is graphed against the geometric parameters from Equation 5-12. Figure 5-5 shows the deflected bars and the normalized tip deflection as a function of the average stress at the base of the cantilever. The data is very well represented by a stress exponent of one as indicated by the correlation with the linear fit, confirming that diffusional creep is the relevant deformation mechanism. This does not exclude the possibility of other processes being active where local stresses may be much higher than the average stress, but the overall behavior is captured by a linear relationship between stress and strain rate.
5.3.2 MEASURING STRESS EXPONENT FROM CANTILEVER SHAPE

To minimize the required number of samples, another method was developed for comparing treated and untreated bars that takes advantage of the loading characteristics of cantilever bars. In cantilever bars, the applied moment changes continuously along the length of the cantilever. Thus, the local stress and strain rate change continuously as well. The deflected shape of the bar is then a function of the stress profile and the stress exponent. As long as the stress profile is known, the stress exponent can be determined. This approach requires only one deflection specimen to determine the stress exponent rather than a series of measurements as is required when using uniform stress specimens. Moreover, this same specimen can be used to measure the creep activation energy as described below.
Creep of Porous Parts

The bar shape is normalized to facilitate shape comparisons. The horizontal distance from the base of the cantilever is normalized by the cantilever length. The vertical deflection at each point is normalized by the tip deflection. As long as the deflections are small enough that deviations from linear deflection behavior are minimal, the normalized deflected shape is independent of the deflection magnitude. The cast and printed deflection samples do not meet the requirement of zero slope at the fixed end to be accurately modeled as a cantilever, so the shape of a deflected bar was determined using finite element analysis.

![Figure 5-6 Two-dimensional Ansys model used for predicting the deflected shape of the cantilever bars for different values of the stress exponent. The geometry was meshed using 8 noded 2-D elements.](image)

A two-dimensional model was built in Ansys and analyzed using a creep material model. The bars were modeled in 2D using static analysis with strain rate effects and meshed with 8 node elements as illustrated in Figure 5-6. The modeling conditions are summarized in Table 5-3.

### Table 5-3 Summary of Ansys Modeling Conditions

<table>
<thead>
<tr>
<th>Type of analysis</th>
<th>Structural 2D</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Static analysis with strain rate effect</td>
</tr>
<tr>
<td>Element type</td>
<td>2D, 8-Node structural solid</td>
</tr>
<tr>
<td>Number of nodes</td>
<td>4658</td>
</tr>
<tr>
<td>Material models</td>
<td>Linear isotropic and implicit creep</td>
</tr>
<tr>
<td></td>
<td>Norton creep law: $\dot{\epsilon}_\sigma = C_1 \cdot \sigma^{C_2} \cdot e^{C_3/T}$</td>
</tr>
<tr>
<td>E-modulus</td>
<td>2e11 N/m²</td>
</tr>
<tr>
<td>Poisson ratio</td>
<td>0.32</td>
</tr>
<tr>
<td>Density</td>
<td>4642 kg/m³</td>
</tr>
</tbody>
</table>
The normalized deflection shape was extracted from the finite element results using several different values of the stress exponent in the material model. Figure 5-7 shows the calculated deformed shape and distribution of strain for stress exponents of one and three.

![Deflected Shape with Contours of Von Mises Strain](image)

**Figure 5-7** Ansys modeling of deflected shapes. Comparison of Ansys predictions for deflected shape and Von Mises Strain distribution with a stress exponent of 3 (top) and a stress exponent of 1 (bottom). Higher stress exponents have more localized strain.

The deflected shape of specimens from the deflection tests described in Chapter 4 were measured to compare with the numerical predictions. These specimens were prepared from 410 stainless steel powder of 63-90 μm diameter cast in a mold as described in Chapter 4 for maximum dimensional consistency. They were then presintered to 1300 C for one hour.

The shape of deflected bars was measured by scanning the deflected shapes on a flat-bed scanner and then measuring the scanned images. The non-dimensionalized results
Creep of Porous Parts

are shown in Figure 5-8 for both treated and untreated specimens. The figure shows that the nanobinder treatment did not change the deflected shape of the bars. Both deflected shapes closely match the finite element predictions for a stress exponent of one. These results confirm that the stress exponent is unchanged by the nanobinder treatment and that the deformation creep progresses by diffusion creep under both conditions.

![Deflected Shape of Cantilever Bar](image1)

Figure 5-8 Stress exponent measurement from the deflected shape of the cantilever bars. (Top) Comparison of measured shape of deflected 410 SS bars with and without treatment with nanoiron. No change in shape detected. (Bottom) Comparison of measured shapes to ANSYS predictions for different stress exponents. Good fit is obtained with a stress exponent of one confirming that diffusional creep is the dominate deformation mechanism.

5.3.3 CREEP MECHANISM BASED ON STRESS EXPONENT

The stress exponent measurements confirm that the dominant creep mechanism is diffusional creep as suggested by the iron deformation mechanism map. Diffusional creep
is the only mechanism that creates a linear relationship between stress and strain-rate as measured from all samples regardless of method.

Since grain boundaries serve as both sources and sinks of vacancies in diffusion creep, diffusional distance is related to the grain size. Creep rates in diffusional creep are sensitive to the grain size. In the case of powdered compacts, the upper limit on grain size is the particle size. Therefore, one might expect the creep rate to decrease with increased particle sizes. This effect should be offset somewhat by the reduced sintering of larger particles that would lower the relative bond size.

5.3.4 **EFFECT OF STRESS VARIATION THROUGH TEST SPECIMEN**

The cantilever bar specimens used for measuring the test specimens have wide variation in stress levels. The average stress varies along the bar length and through the bar thickness. The local stresses can be much larger than the average stress and vary between the particles and bonds and between locations in the bonds. Given this large variation, multiple mechanisms may be active simultaneously. Under these conditions, the materials would act as a composite of different materials of varying strengths. The slowest deforming material type would likely dominate the total deformation.

The stress exponent measurements show that diffusion creep is the dominant deformation process in both treated and untreated specimens. As this mechanism is characteristic of the lowest stress levels, the bar could be uniformly deforming by diffusional creep. If some local areas, such as high stress regions of a bond at the base of the overhang were deflecting by a different mechanism, the stress might be sufficient for dislocation creep processes to be active. If this were the case, the affected regions would appear "softer" than lower stressed regions, effectively reducing the stiffness of the structure. In this situation, the deflection shape would remain very similar to a bar with creep only by diffusion. However, the machined test bars would show some non-linearity under these circumstances. To test this possibility, the 4 mm thick bars included a test specimen with a peak homogenous stress 50% above that of the cantilever test specimens. The dataset is still well described by a linear fit. If there are any mixed deflection modes, they only affect a small region.
5.4 Activation Energy

5.4.1 RELATIONSHIP BETWEEN TIP DEFLECTION RATE AND STRAIN RATE

Activation energy is calculated from the change in deformation rate with temperature. Substituting the temperature dependence of diffusivity (Equation 5-2) into Equation 5-1, the creep equation is

\[ \dot{e} = A \frac{D_0 G b}{kT} \left( \frac{b}{d} \right)^p \left( \frac{\sigma}{G} \right)^n \exp \left( \frac{-Q}{RT} \right) \]

Equation 5-13

The activation energy originates from the diffusivity term. It is usually calculated using a series of creep tests at the same stress, each at a different temperature. Strain rate is calculated for each test and the activation energy calculated from the rate data. For this work, the tip deflection rate of a single bar was measured across a range of temperatures to calculate the activation energy from a single specimen. The tip deflection rate is proportional to the strain rate as long as the temperature is uniform and the stress state does not change. The tip deflection rate is then

\[ \Delta \dot{y}_{\text{tip}} = C \dot{e} = A' \frac{CD_0 G b}{kT} \left( \frac{b}{d} \right)^p \left( \frac{\sigma}{G} \right)^n \exp \left( \frac{-Q}{RT} \right) \]

Equation 5-14

"C" is the proportionality constant between the strain rate at a particular location and the tip deflection rate.

Collecting the non-temperature dependent terms and dividing through by reference deflection rate (\( \Delta \dot{y}_o \)) and temperature (\( T_o \)) to nondimensionalize each term, the equation simplifies to

\[ \frac{\Delta \dot{y}}{\Delta \dot{y}_o} = A' \frac{CD_0 G b}{\Delta \dot{y}_o kT_o} \left( \frac{b}{d} \right)^p \left( \frac{\sigma}{G} \right)^n \left( \frac{T_o}{T} \right) \exp \left( \frac{-Q}{RT} \right) = B_1 \left( \frac{T_o}{T} \right) \exp \left( \frac{-Q}{RT} \right) \]

Equation 5-15
Equation 5-16

\[ \ln \left( \frac{\Delta y}{\Delta y_o} \right) - \ln \left( \frac{T_o}{T} \right) = \ln(B) - \frac{Q}{RT} \]

If the terms on the left are plotted against 1/RT, the activation energy is the slope of the best-fit line.

5.4.2 EXPERIMENTAL METHOD

This method was implemented using the cast cantilever bar geometries discussed in Chapter 4. The tip deflection was measured in situ during heating in a tube furnace to calculate the deflection rate and determine the activation energy for the deflection bars. The experimental setup is illustrated in Figure 5-9. Tip deflection is measured optically using a digital camera triggered to take images at constant intervals, typically 100 s. Viewing access is provided by a hole in the furnace sufficient to see the tip of the deflection bar. The pixel resolution of the images is approximately 15 μm with a field of view of approximately 8 mm horizontally by 12 mm vertically. A fiber optic illuminator positioned behind the bar provided lighting. Image quality was maintained at high temperatures where thermal emission in the visible and infrared spectrum is significant by incorporating a neutral density filter with optical density of 2.0 together with heat absorbing glass to reduce infrared transmission. A frame was provided that held the furnace tube perpendicular to the camera. Figure 5-10 shows a representative image taken of a deflecting bar during a test.
Figure 5-9 Schematic of in situ deflection measurement system. (Top) Perspective view of basic quartz tube furnace illustrating the hole through the furnace for observing the tip position. (Bottom Left) Cross sectional view of the furnace illustrating the image acquisition and specimen position. (Bottom Right) Close up of the specimen and reference bar in the furnace.

The test specimens used in these tests were the same cantilever bars sintered in the alumina mold and discussed in Chapter 4. Many of the specimens were used for both stress exponent and activation energy calculations by measuring both the shape and activation energy. Specimens were all produced from 63-90 μm powder, primarily of 410 stainless steel.
The specimen is mounted in an alumina block during the furnace cycle as pictured in Figure 5-11. This block maintains the specimen parallel to the axis of the furnace tube. The specimen position is maintained by a compressed piece of alumina fiber blanket that acts as a spring to bias it against the stop. To subtract errors due to differences in thermal expansion between the specimen and the camera, an alumina reference rod is mounted to the specimen support near the base of the specimen. The stability of the alumina reference rod was verified by measuring its deflection during two hours at 1300 C. No deflection was detected. The difference in thermal expansion between the specimen and the reference rod may introduce some relative motion along the tube axis (horizontal), but only the vertical motions are measured.
Figure 5-11 Furnace used for deflection testing. View of the inside of the furnace with the top removed. The alumina specimen holder holds the sample in the center of the quartz tube.

Figure 5-12 The temperature profile used for measuring the creep rates of the cantilever bars.

A deflection test was executed using a programmed temperature profile as illustrated in Figure 5-12. Ramp rates of 2 C/min were used for the majority of the tests, although rates of 1 C/min and 4 C/min were also used. For each test image, the vertical distance between the top corner of the deflection specimen and the tip of the reference bar was analyzed using the image tracking features in MiDAS2.0 event capture and analysis software produced by Excitex. The temperature corresponding to each image was calculated from the known heat cycle. Deflection rates were calculated numerically from
the measured tip positions. These deflection rates are then fit to Equation 5-16 using a least squares fit, where the slope gives the activation energy. A representative data sets is graphed in Figure 5-13.

![Figure 5-13 Summary of creep rate data illustrating the calculation of the activation energy.](image)

5.4.3 MEASURED ACTIVATION ENERGIES

Since only one specimen is required to measure the activation energy, many different conditions were considered. Some bars were sintered in a supported position at 1300 C before executing the deflection test, while others were used after the initial 1000 C sinter. Some specimens were also infiltrated with polymer-based binding agents for comparison. The calculated activation energies for nanoiron treated and untreated bars are summarized in Table 5-4.
Table 5-4 Summary of activation energies calculated for deflecting bars

<table>
<thead>
<tr>
<th>1300 °C Presintered</th>
<th>1000 °C Presintered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treated Bars kJ/mol</td>
<td>Untreated Bars kJ/mol</td>
</tr>
<tr>
<td>262</td>
<td>313</td>
</tr>
<tr>
<td>269</td>
<td>285</td>
</tr>
<tr>
<td>231</td>
<td>380</td>
</tr>
<tr>
<td>241</td>
<td>345</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>251</td>
<td>336</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>33</td>
</tr>
</tbody>
</table>

5.4.4 IMPACT OF ALLOY COMPOSITION ON ACTIVATION ENERGY OF DIFFUSION

Generally, the activation energy for creep is the same as the activation energy for the controlling diffusion process. Thus, activation energies for diffusion can provide useful information on the characteristics of a creep process. Diffusional activation energies can vary significantly with composition.

In 410 SS, the primary constituents are chromium (~12%) and carbon (~0.15%). Table 5-5 summarizes the variation of activation energy, and frequency factor ($D_o$) for self-diffusion of iron in alloys of chromium and carbon. Values of diffusivity are also calculated for several reference temperatures. Carbon lowers the activation energy while chromium raises the activation energy. However, above 1373 K (1100 °C) the variation in self-diffusivity with carbon content is not very large because significant variations in the activation energy are offset by decreases in the frequency factor ($D_o$). This means that it might be easier to measure a change in the activation energy with composition than a change in the creep rate with composition and that lower activation energies may not necessarily indicate significant changes in diffusion rates.
Table 5-5 Self diffusivity of Iron in alloys with Chromium and Carbon [15]

<table>
<thead>
<tr>
<th></th>
<th>Diffusivity</th>
<th>Diffusivity</th>
<th>Diffusivity</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>1173 K cm²/s</td>
<td>1373 K cm²/s</td>
<td>1573 K cm²/s</td>
</tr>
<tr>
<td></td>
<td>cm³²/s</td>
<td>cm³²/s</td>
<td>cm³²/s</td>
</tr>
<tr>
<td>Q/J mol</td>
<td>Do cm²/s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Variation with Chromium</td>
<td>1.5E-13</td>
<td>1.0E-11</td>
<td>2.5E-10</td>
</tr>
<tr>
<td>Fe</td>
<td>284699</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Fe + 4% Cr</td>
<td>314006</td>
<td>2.1E-13</td>
<td>2.3E-11</td>
</tr>
<tr>
<td>Fe + 8% Cr</td>
<td>376808</td>
<td>1.0E-14</td>
<td>2.8E-12</td>
</tr>
<tr>
<td>Carbon (wt%)</td>
<td>Variation with Carbon</td>
<td>1.2E-11</td>
<td>2.4E-10</td>
</tr>
<tr>
<td>0.10%</td>
<td>275295</td>
<td>0.343778</td>
<td></td>
</tr>
<tr>
<td>0.15%</td>
<td>268537</td>
<td>0.202153</td>
<td></td>
</tr>
<tr>
<td>0.20%</td>
<td>261804</td>
<td>0.119102</td>
<td></td>
</tr>
<tr>
<td>0.30%</td>
<td>248409</td>
<td>0.041581</td>
<td></td>
</tr>
<tr>
<td>0.40%</td>
<td>235111</td>
<td>0.014627</td>
<td></td>
</tr>
<tr>
<td>0.50%</td>
<td>221909</td>
<td>0.005184</td>
<td></td>
</tr>
</tbody>
</table>

The diffusion of chromium and carbon may also be important to the nanobinder performance. The nanobinder will create composition gradients around the particle with low chromium, carbon rich areas in the particle contact regions. On heating, carbon will diffuse into the particles. The chromium gradient will be balanced by iron diffusion into the particle and chromium diffusion into the neck. The diffusivity of these elements will effect both the creep rate and the time required to homogenize the structure via diffusion.

Table 5-6 Diffusivity of Chromium and Carbon in Iron Alloys [15]

<table>
<thead>
<tr>
<th></th>
<th>Diffusivity</th>
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<th>Diffusivity</th>
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<tbody>
<tr>
<td></td>
<td>1173 K cm²/s</td>
<td>1373 K cm²/s</td>
<td>1573 K cm²/s</td>
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<tr>
<td></td>
<td>cm³²/s</td>
<td>cm³²/s</td>
<td>cm³²/s</td>
</tr>
<tr>
<td>Q/J mol</td>
<td>Do cm²/s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusivity of Chromium in Fe Matrix (Austenite)</td>
<td>1.9E-13</td>
<td>1.2E-11</td>
<td>2.5E-10</td>
</tr>
<tr>
<td>Chromium</td>
<td>406114.8</td>
<td>1.80E+04</td>
<td>1.5E-14</td>
</tr>
<tr>
<td>Diffusivity of Carbon in Fe Matrix (Austenite)</td>
<td>1.5E-08</td>
<td>9.0E-07</td>
<td>4.8E-06</td>
</tr>
<tr>
<td>Fe Matrix</td>
<td>150723</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>Fe + 1% Cr</td>
<td>135232</td>
<td>0.0055</td>
<td></td>
</tr>
<tr>
<td>Fe + 2.5% Cr+0.2%C</td>
<td>154910</td>
<td>0.09</td>
<td>1.1E-08</td>
</tr>
<tr>
<td>Fe + 7% Cr+0.2%C</td>
<td>162865</td>
<td>0.12</td>
<td></td>
</tr>
</tbody>
</table>

5.4.5 UNTREATED BARS

The average activation energy of the untreated bars is 336 kJ. This is above the reported values of pure iron (285 kJ/mol) [15,16], but less than would be expected from an alloy of 12% chromium (>380 kJ). Both of these values are much higher than the
activation energy of grain boundary creep (40 kJ/mol) [15] so it is unlikely that grain boundary creep plays a significant role. This suggests that the dominant creep mechanism is Nabarro-Herring or simply Nabarro creep.

The deviation from the expected activation energy values could have several causes. Alloy composition is known to have a strong effect on measured activation energies, but the trends in the available activation energy data do not suggest that this is a significant source of the differences. Other factors such as primary creep, sintering, and diffusion may not change the activation energy, but they may affect the measured value of the activation energy. This measurement method assumes that the change in deflection rate with time is solely a function of the temperature change. Any other factors that change the strain rate with time introduce errors into the activation energy measurements.

The untreated samples were no longer in the field of view of the camera during the 1284 hold. However, the deflection was small enough in many of the treated bars to measure the deflection rate during the isothermal hold. In most of these tests, the deflection rate decreased measurably with time. This suggests that there are kinetic effects that reduce the measured activation energy. Two possible effects are summarized below.

5.4.5.1 Primary Creep
Primary creep is characterized by a decreasing creep rate with time. This could cause a decrease in the measured activation energy in a cantilever bar test. However, this effect should be transitory. As strain accumulates, steady state secondary creep should begin and the slope of the 1/RT plot increase at higher temperatures. None of the data showed such an increase in the slope. However, many of the specimens do show decreasing creep rates during an isothermal hold at 1284 C. However, the tip deflection at this condition is typically large. It is unlikely that the primary creep stage persists at this point. The decreasing rate is more likely caused by continued sintering.

5.4.5.2 Sintering
During sintering, the strength of the porous skeleton increases with time. The increasing strength with time would partially offset increases in deflection rate with temperature. In the cantilever bar method or by measuring the creep activation energy, this
would be observed as a decrease in the measured activation energy relative to the actual value of the activation energy.

However, sintering rates decrease with time. If a bar is initially sintered before deflection starts, the rate of additional sintering during deflection will be significantly reduced. The error in the activation energy measurement will also be reduced accordingly. This is seen in comparing the results in Table 5-6 for untreated bars sintered at 1300 C for one hour before deflection to the specimen sintered to 1000 C for 30 minutes before deflection. The measured activation energy with the 1300 C presinter is 60% larger than in the 1000 C presinter case. Bars treated with nanoiron also show substantial reduction in the activation energy when they are not sintered at 1300 C before deflection. It is probable that sintering continues during the deflection and contributes to a reduction in the measured activation energy. In treated specimens, the nanoparticle deposits may also be sintering.

5.4.6 NANOBINDER TREATED PARTS

The measured activation energy in the nanobinder treated bars is reduced even more than the untreated bars. The average activation energy measured was 251 kJ/mol. They certainly have some reduction due to the same factors as observed in the untreated parts. Primary creep and sintering could still reduce the measured activation energy. However, they are not a likely source of the additional reduction in measured activation energy as the primary creep should be similar to the untreated specimens and the sintering was reduced by the nanobinder treatments as evidenced by the measured shrinkage reduction.

The additional reduction in activation energy may be caused by composition differences or residual porosity in the bonds.

5.4.6.1 Composition Differences

While the untreated bars are compositionally homogenous, the treated bars initially have a distinctly different composition at the particle necks where the nanoiron deposits accumulate. During sintering and deflection testing, the concentration gradients in the structures may be reduced. The composition induced in the structure could affect the
activation energy of the creep process directly since the activation energy varies with composition. Also, the change in composition profile with time by diffusion could introduce additional errors into the activation energy measurements.

The deposited necks should be rich in iron but will also contain significant carbon and little chromium. However, the diffusivity of both carbon and chromium is sufficient to eliminate large composition gradients during presintering at 1300 C for 60 minutes. At 1300 C, the diffusivity of chromium in iron is approximately $5.9 \times 10^{-10} \text{ cm}^2/\text{s}$, and the self-diffusivity of iron is $2.6 \times 10^{-10} \text{ cm}^2/\text{s}$. Given these diffusivities, the characteristic diffusion distance ($\sqrt{4Dt}$) for a one-hour sinter at 1300 C is of the order of the particle radius. Carbon diffusivity is several orders of magnitude faster. After presintering at 1300 C, the remaining composition gradients are likely to be small. However, local composition differences may be significant in the further reduction in measured activation energy in the bars that were not presintered to 1300 C before deflection.

Even after the particle scale composition variation is reduced, the average composition may be affected. The deposited iron dilutes the chromium, decreasing its average concentration slightly, but probably not enough to change the final diffusion characteristics. However, there are also significant carbon deposits with the nanoiron. The carbon composition of nanoiron dried without a metal substrate and heated to 700 C was measured by combustion infrared detection. In the unoxidized case, almost 10% of the deposit is carbon. If the skeleton weight is increased by 1% from the added nanoiron, the average carbon composition of the part will increase by nearly 0.1%. Carbon measurements in several treated bars (Chapter 4) showed less than 0.02% increase in the average carbon composition. Similar carbon increases in austenitic iron reduced the activation energy for iron self-diffusion by approximately 3 kJ/mol (Table 5-5).

The decrease in activation energy could be somewhat higher if the carbon were distributed preferentially to the outer surface of the skeleton. The composition of the outer edge of one specimen was measured as 0.33 %, a substantial increase from the 0.16% composition of the untreated powder. This might reduce the activation energy by 25-30
kJ/mol. These changes are significant, but they do not account for the full 80 kJ/mol difference in measured activation energies between the treated and untreated bars.

A 410 SS bar was treated with a commercial ferrofluid consisting of approximately 10 nm iron particles. During heating and deflection, the oxygen from the particles decarburized the base powder. After sintering and deflecting the specimen, the carbon composition of this specimen was measured as 0.01%. Still, the measured activation energy was 173 kJ/mol. This is much lower than the volume diffusion activation energy for any of the relevant elements or their alloys. Another mechanism must contribute to the low activation energy.

5.4.6.2 Phase Change

The carbon added from the binder could change the activation energy if the added carbon caused a phase change in the steel at the creep temperatures. Consider the pseudo-binary phase diagram for 410 SS steel with respect to carbon composition shown in Figure 5-14. The base powder composition would cross the boundary between austenite (FCC) and mixed austenite/delta phases at approximately 1200 °C. Further heating to infiltration temperatures could convert up to half of the material to delta iron (BCC). Carbon additions from the nanobinder might be sufficient to prevent this phase change entirely and would certainly increase the fraction of gamma iron present. However, measurements of iron self-diffusion in pure iron show that the activation energies of gamma iron (285-311 kJ/mol) are somewhat higher than alpha/delta iron (240-280 kJ/mol), opposite the measured trend [17]. Although a change in diffusivity caused by a phase change might decrease the creep, it does not explain the differences in measured activation energies.
5.4.6.3 Residual Porosity in Nanobinder Deposits

The difference in activation energy could result from a contribution of grain boundary diffusion to the total creep. The as-deposited nanobinder would introduce a significant amount of grain boundary area. This area would increase the diffusional transport via grain boundaries, which has a much lower activation energy (40 kJ/mol) [15] than lattice diffusion. Kolobov et al. [4] showed that creep activation energy of nanostructured materials can approach that of grain boundary diffusion even when no
porosity is present. As the particles sinter, and the grain sizes grow, the total transport via grain boundaries decreases because there is less grain boundary area. The significance of grain boundary creep during the deflection measurements depends on how much residual porosity remains and the size of the grains.

Gas adsorption tests of the powder of dried deposits without a substrate showed continued nanoscale porosity after heating to 1100 C. SEM images of deposits on substrates showed that densification seems to proceed more rapidly on a substrate where the carbon in the deposits can diffuse into the substrate converting the deposited material from iron carbide into iron. Still, SEM images of broken interparticle bonds created by nanobinder treatment show pores on the 100 nm and larger scale in the substrates. SEM images of fractured bonds also show micron scale pores in the bond as seen in Figure 5-15. The ferrofluid treated bar seemed to have even more pores than the nanoiron parts. Interestingly, the activation energy for these bars was also lower than for the nanoiron bars.

Figure 5-15 Pores in broken bonds created from magnet dried nanoiron. Bonds broken after completing the deflection cycle. Pores are clearly visible as circular inclusions in the broken bond.
Creep of Porous Parts

These pores provide surface area for fast diffusion. They may also restrict grain growth so that the grains remain small—further increasing the grain boundary area and the contribution of grain boundary deformation to diffusional creep. Both effects would reduce the effective activation energy for creep deformation.

Grain boundary diffusion is also a likely cause of the reduced activation energy of the specimen treated with iron oxide. Due to the volume change on reduction of the oxide to metal, the sintering shrinkage of this suspension would be much larger than for the nanoiron treated parts. Given the constraints of the powder particles, it is likely that the residual porosity increased—reducing the grain size in the stressed regions and increasing the importance of grain boundary diffusion.

The small grains remaining from the nanobinder particles may grow significantly during heating and deflection. The grain growth would reduce the grain boundary contribution to the creep deformation with time. This would be another kinetic effect that might reduce the calculated activation energy.

The nanoiron treated parts consistently show low creep deflection and lower creep rates than the untreated parts despite a lower measured activation energy. In order to achieve lower total creep rates, the diffusional creep mechanisms must also be attenuated. Otherwise, the increased grain boundary creep would augment the lattice diffusion processes in the untreated parts and increase the total deflection rate. The attenuation of creep in the lattice could be a function of reduced stress or changes in composition such as through increases in the carbon content.

5.5 Deviations of Creep Deformation from Idealized Assumptions

The methods used here have shown that the creep of the treated and untreated bars can be modeled as an equivalent isotropic material with a stress exponent of one and an activation energy similar to but lower than activation energies for diffusion in similar alloys. At the local level, these assumptions are not fully met. While the modeling factors above describe the observed tip deflection behavior, an accurate understanding of the local
deformation mechanisms is necessary to understand how the work may apply under other conditions. Some evidence for the deviations from ideal behavior is presented below followed by a discussion of implications for the modeling and testing that might be done to better characterize these responses.

Two deviations from ideal behavior will be considered. The first deviation is the possibility of tensile strain by particle rearrangement rather than elongation of bonds and/or particles as hypothesized. This would be particularly likely at low initial densities or high strains where the tension-loaded bonds may begin to fail—reducing the constraints on the particles.

The second is differing creep strength in tension and compression. As creep strain progresses, the compressive bond diameter will increase while the tensile bond size will decrease. The increase in the compressive bond size will be particularly dramatic as the adjacent spherical particles deform at the contact points in a process analogous to Hertzian contact.

5.5.1 EXAMINATION OF DEFORMED POWDER STRUCTURE

A sintered powder structure was created and deformed via creep to permit examination of the structure and local strains. Two cantilever beam specimens were prepared from 63-90 μm diameter spherical 410 SS powder. An alumina mold was filled with the powder and sintered to 1000 C for 30 minutes in an atmosphere of argon with 5% hydrogen according to the method described in Chapter 4.

One specimen was directly heated through a deflection heating cycle as described in Chapter 4 and allowed to deflect under the self weight of the unsupported beam. The sample was not sintered before deflecting so that very high strains could be obtained. The sample was then fractured along a vertical plane through the base of the cantilever such that the dominant compressive and tensile stresses applied to the beam during deflection ran parallel to the sample. The powder particles were then imaged in the SEM to compare the morphology of the particles in the tensile and compressive regions.
Creep of Porous Parts

The strain in the outer surface in the tensile region of the specimen was approximately 20%. Such large strains should be visible as elongated bonds between the particles and/or elliptical particles. Figure 5-16 shows some images from the tensile region. Given that the average particle size is 75 μm, the separation between the particles would be approximately 15 microns if all of the strain occurred by elongation of the neck region. Very little neck strain is visible in the images. Alternatively, if all the strain was in the particles, the particles should be clearly elliptical with a 20% elongation along the stress axis and contraction along the orthogonal axes. Figure 5-16 shows that on average the particles still appear very spherical.

These observations suggest that a significant portion of the tensile strain is accommodated by particle motion through bending of the interparticle bonds, effectively reducing the density of the tensile region of the sample. This deformation mechanism should be very sensitive to the number of bonds between the particles. Increasing the number of bonds restrains the particle motion. They must be deformed or broken for particle motion to proceed.

![Figure 5-16 Fracture surface of a deflected porous skeleton in a region with 20% tensile elongations. Neither the bonds nor the particles show sign of such large strains. This suggests that strain could occur by rearrangement of the particles. Scale bars are 200 μm.](image)

Images of the particles under compressive stress show clear signs of deformation of the skeleton particles. Many of the particles are indented to a significant degree as seen in Figure 5-17. These indentations would increase the contact area and increase the contact
stiffness accordingly. If the part is indeed stiffer in compression than tension, then the neutral axis of the beam would move closer to the compressive side. This can be understood by considering the balance of moments across the beam cross-section. Equilibrium requires that the integration of moments arising from the stress across the section balance the applied moment on the section.

Figure 5-17 Fracture surface of a deflected porous skeleton in a region of compressive strain. Many particles have indentations from compression against neighboring particles. In many particles, the strain is primarily local with the spherical particle shape generally maintained.

Strain compatibility requires that the strain vary linearly through the height of the beam to satisfy the basic assumption that plane sections remain plane during deformation. However, if the stiffness of the compressive section is higher than the tensile section, less compressive area is required to balance the moment. This effect would result in higher tensile strains than compressive strains at highly strained locations in the beam. This hypothesis was tested with the second specimen.
Creep of Porous Parts

The specimen was prepared by sintering in a mold as before. Fiducial marks were then cut along the sides of the bar with a slitting saw. The marks were spaced 2.54 mm apart and were approximately 0.1 mm deep and 0.4 mm wide. The specimen was then heated through deflection temperatures as before but with a modified heating cycle. In the first step, the bar was heated to 750 C in 30 minutes and then at 2 C/min to 1000 C. The furnace power was then turned off and the sample cooled. The bar was photographed and then the process was repeated. This time the bar was heated to 1000 C in 50 minutes and heated at 2 C/min to 1100 C. The furnace power was turned off and the sample cooled to room temperature.

![Initial Geometry](image)

**Figure 5-18 Photos of porous metal skeleton before and after deflection.** Fiducial marks on the skeleton permit measurement of the average strain after each deflection increment.

**Figure 5-18** shows the sample before deflection and after each heating cycle. The strain is clearly observed near the base by the difference in angle between adjacent bars. The distance between adjacent marks was measured and the strain in each section was calculated. The strain distribution by segment at both the top and the bottom is shown in **Figure 5-19.** The tensile strains are clearly larger than the compressive strains as anticipated.
Comparing the measurements after the two heating cycles shows that the compressive and tensile strain in the second heating cycle occurred in different locations. The tensile strain was predominately in the regions of peak strain. The compressive strain occurred in the center region of the bar where the applied load on the bar is lower than at the base. On the compressive side, the skeleton seems to reach a maximum strain level of about 6%.

![Graph showing average strains at the top and bottom of the bar at different locations along the bar length.](image)

Figure 5-19 Average strains at the top and bottom of the bar at different locations along the bar length. The locations are measured from the original x-position where the origin is at the base of the cantilever. The tensile strains are much larger than the compressive strains after both heating cycles. With additional heating, the peak tensile strains increased while the peak compressive strain remained constant.

5.5.2 IMPLICATIONS FOR NANOBINDER MODELING

The observations of the deflecting particles show that there is substantial deviation from the basic assumption used in developing the model for strain reduction from applying the nanobinder. These factors include greater compressive than tensile strength in the structure and a lack of visible elongation of either particles or bonds in the tensile regions.
If tensile strain is accommodated by particle rearrangement, the performance of the nanobinder could be much higher than predicted by consideration of average stresses alone. Particle rearrangement will be very sensitive to the number of bonds between particles. If the nanobinder acts to increase the number of bonds per particle, this strain mechanism will be greatly reduced. This could increase the performance of the nanobinder over the predictions made above and may help to explain the large improvements in nanobinder performance relative to the bond size measurements as considered in Chapter 4.

Thus the simple area-based model for the nanobinder deflection reduction is inadequate to describe the test data, but it provides a useful understanding of the nanobinder impact at the level of a single bond.

Both of these deviations from the idealized performance would affect measurements of the creep parameters. The increasing compressive strength with increasing strain would act to reduce the measured activation energy. Each increment of strain would strengthen the compressive side of the bar so that strain in the following time segment would be decreased. Beruto et al. [18] showed how particle rearrangement could significantly reduce the measured stress exponent for uniaxial loading of low-density compacts. Similar phenomena could be observed in the higher density compacts loaded under tension, particularly at large strains.

These effects must be considered in order to relate the creep deformation of the sintered structures to the basic material properties of the materials. Both of these effects could be better understood through a series of isothermal, uniaxial tensile and compressive creep measurements. These tests would permit easy measurement of the actual activation energies with corrections for rates that change with time. The differences between tensile and compressive strengths and their variation with total strain would be clear.

The effective tensile and creep properties can also be determined form a series of bending tests. Chuang [19] proposed a method for extracting separate tension and compression properties from four-point bending tests. However, the current case may require the extension of the methods to characterize properties that vary with total strain.
5.5.3 GEOMETRICAL FEATURE FOR REDUCING CREEP DEFORMATION

The observed differences in tensile and compressive strength of the porous metal parts may permit a simple geometric modification to the parts to provide increased structural strength during infiltration. An I-beam structure is generally ideal for bending loads such as in unsupported overhangs. However, the high compressive strength and the observed plateau in strain would permit the bottom web to be removed and still have high bending strength. Thus, a small supporting structure as illustrated in Figure **** might dramatically reduce the creep with little additional effort. The feature could be easily removed during finish machining.

As the compressive strength increases significantly with increasing strain, the goal of the added feature is to maximize the compressive strain in the added feature while adding as little material as possible so that removal of the part feature during post-processing is simplified. The large distance from the tension side of the beam would allow the added feature to reach the observed plateau in compressive stress with minimal deformation of the supported structure. Once the plateau in compressive stress was reached in the feature, the deformation rate of the overhang should decrease substantially.

Figure 5-20 Simple support feature for reducing creep deformation of unsupported overhangs. Due to the high compressive strength of the porous metal skeletons, a very deep support structure that maximizes the compressive strain is desired. However, the higher compressive strength may make a large compressive area unnecessary. This makes the support structure easier to remove during finishing operations.
5.6 Conclusions

The primary metrics of creep deformation, stress exponent and activation energy were measured for the porous metal skeletons by measuring the deflection of cantilever tips and the final shape of the deformed cantilever bars.

The stress exponents measured for both treated and untreated specimens was one. This corresponds to a diffusional creep mechanism. This result agrees with the data from deformation mechanism maps of similar materials.

Creep activation energies of untreated bars showed significant deviation from reported values for the self-diffusion of iron in steels of similar composition. These differences are likely due to changes in the skeleton strength with time that are complicated by temperatures changes with time. These time dependent effects include sintering of the particles and primary creep.

Creep activation energy of the untreated bars is reduced much more. Some of this reduction is related to the increase in carbon from the nanobinder treatment. However, this difference is small relative to the 80 kJ/mol average difference between treated and untreated parts. The remaining difference is likely due to increased grain boundary diffusion from residual porosity and smaller grains in the nanobinder treated regions. Images of broken bonds do show some porosity.

This theory that grain boundary diffusion contributes to the creep in the nanoparticle treated specimens is supported by measurements of a cantilever bar treated with a suspension of iron oxide particles similar to the nanoiron particles. The oxide particles reduced the carbon in the skeleton to nearly zero, but the activation energy was reduced much more than in the nanoiron treated bars. These iron oxide deposits are likely to be more porous than the iron deposits due to the large volume change of the iron oxide particles on reduction to metal. These volume changes would substantially increase the total shrinkage. This would be expected to reduce the density of these deposits and increase the contribution of grain boundary diffusion to the creep process with its much lower activation energy.
Creep of Porous Parts

Some deviations of the powder deformation from the model assumptions were noted based on observations of highly strained specimens. These factors may be an additional source of deviation between the measured parameters for the deformation of the cantilever bar and parameters that represent the local physical creep processes. However, the measurements made in this chapter are adequate to describe the global response of the cantilever bars.
Creep of Porous Parts

5.7 References


6 Conclusions

This thesis has shown how a suspension of nanoparticles can be applied to a porous metal skeleton to reinforce it at low temperatures. This can be used to strengthen porous metal skeletons that are heated to high temperatures so that creep deformations and shrinkage are reduced. This chapter first restates the motivation for this work. It then reviews what has been learned in this work in two sections. First, the basic properties of the nanoparticles and their response to sintering are summarized. Secondly, the response of porous metal skeletons to applied nanoparticles is reviewed. The chapter concludes with recommendations for implementation into solid freeform fabrication processes and future work.

6.1 Motivation and Goal of the Work

The goal of this work is to increase the final dimensional accuracy of metal parts produced by three-dimensional printing (3DP). In the 3DP process, micron-scale powder is bound together by printing a liquid binder into the powder. While the as-printed accuracy of these parts is good, they are very porous. Material properties of metal parts are usually improved by infiltrating the pore space with liquid metal. During the infiltration process, the dimensional accuracy of the part decreases due to sintering shrinkage and creep deformations. Creep deformation of unsupported sections can be especially severe (Figure 1-7). Other processes such as selective laser sintering (SLS) that produce porous parts that are densified by liquid-metal infiltration have similar problems.
6.2 Proposed Nanobinder

This work proposed and tested a “nanobinder” to strengthen the skeletons and reduce the dimensional changes due to both shrinkage and creep. The proposed “nanobinder” is a suspension of metal nanoparticles. This binder can be applied to the skeletons as a 3DP binder or by infiltration after forming the geometry. Once the solvent in the binder is dry, the metal particles in the binder are deposited in the skeleton. On heating, these nanoparticles quickly sinter to form strong bonds between the larger micron-scale skeleton particles. These bonds reduce the rate of creep in the skeleton and the sintering shrinkage to improve the final dimensional accuracy. (See Section 2.2)

6.3 Densification of Nanoparticles

This concept is demonstrated using a suspension of iron nanoparticles of 8-10 nm diameter dispersed in an organic solvent. (Section 3.2) This suspension is referred to as “nanoiron”. The sintering characteristics of this suspension were studied by TEM imaging, gas adsorption, and X-ray diffraction. These studies show that the nanoparticles can pack into ordered close-packed arrays (Section 3.5, Figures 3-4, 3-5, 3-6), but that the density of iron in the structure can be very low due to the coating ligands that separate adjacent particles by 1-3 nm (Section 3.5.1). If the particles are exposed to oxygen at room temperature, they readily oxidize. (Section 3.2)

On heating, the ligands decompose leaving a carbonaceous residue. When heating above 500 C, the carbon residue will react with oxygen present in the atmosphere or iron oxides to form carbon monoxide and carbon dioxide. This reduces the volume and the weight of the deposits. If no oxygen is present, the carbon reacts with the iron to form iron carbides. The total carbon content of an oxidized suspension is less than 1% after heating to 700 C compared to approximately 10% in the unoxidized case. (Section 4.6.2) Both compositions densify on heating as observed by measuring the pore size distribution through gas adsorption after successive heating cycles. (Section 3.6) However, the oxidized particles with lower carbon residues densify at lower temperatures and shorter times than the unoxidized particles with the higher final carbon content. The high carbon
deposits densify more rapidly when they are sintered on a substrate that can act as a sink for the carbon. (Section 3.7, Figure 3-16)

These results show that it is possible to densify the nanoparticles at reduced temperatures (700-900 C) relative to micron-scale particles. This should allow the nanobinder to be printed into the powder and sintered while unprinted powder remains unbound. The oxidation state of the nanoparticles strongly influences the final carbon composition of the deposits. High carbon deposits may change the material properties of the final part.

6.4 Reducing Shrinkage and Creep

The nanobinder was demonstrated by applying it to preformed porous steel skeletons with unsupported overhangs. These skeletons were heated through the temperature cycles typical of liquid metal infiltration. The total deflection of the bar tips was used as a measure of the relative creep rates. A deflection ratio was defined as the ratio of tip deflection of a nanoiron treated bar to the deflection of an untreated bar subject to the same heating cycles. This ratio is then used to compare various processing methods. Based on these results, several conclusions and recommendations can be made for optimal performance. (Section 4.1)

This work has shown that nanoparticles can be applied to the porous skeletons to substantially reduce the deflections and sintering shrinkage. In the best case, the creep deflection was reduced by over 95% while the shrinkage was reduced by 60% compared to untreated specimens. (Section 4.2)

6.4.1 PROCESSING CONDITIONS FOR MAXIMUM CREEP REDUCTION

6.4.1.1 Nanoparticle Selection

SEM imaging shows that interparticle bonds formed by the nanobinder fracture on heating due to sintering shrinkage. These cracks reduce the effectiveness of the nanobinder. The nanobinder can be improved by selecting nanoparticles that shrink less
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during sintering. The sintering shrinkage is a function of the initial packing density and
volume changes due to chemical reactions such as the reduction of metal oxides to metal.
The optimal nanoparticles and processing methods will produce high-density dried deposits
since particles with a higher initial density require less shrinkage to densify.

The upper limit on the dried density of the nanoparticles is a strong function of the
thickness of the coating ligand layer relative to the diameter of the particle. (Section 3.5.1) The smaller the coating thickness is, the higher the effective packing density of the nanoparticles will be. Increased packing density reduces the shrinkage and sintering so that the bonds are less likely to crack during drying. If a substantial improvement could be made in initial density, the number of applications required to create structurally sound bonds could be decreased. (Section 4.3.2) Unfortunately, larger particles may be less stable, reducing the maximum concentration and possibly increasing agglomeration.

Some improvement in the density could also be achieved by using a mixture of different sized particles. However, the density increase could be limited if the coating thickness is a significant fraction of the particle diameter.

The composition of the nanoparticles should be chosen to be compatible with the final alloy desired. Additionally, it should have a low creep rate or form an alloy with the micron-scale powder with a low creep rate. The easiest case is to use nanoparticles of the major alloy constituent. Under these conditions, the nanoparticles will have a relatively small impact on final alloy composition and local variation in deposition will have less effect on the material properties.

6.4.1.2 Application Method
Two methods were proposed for applying the nanobinder to the skeletons—direct
printing, and secondary infiltration. (Section 2.2.4) The most favorable for industrial application is directly printing the nanobinder in the 3DP process. This can eliminate one or more steps in the post-processing. However, it could be difficult to implement if the particles must be protected against oxidation during application. Measurements showed that the nanoiron oxidizes readily at room temperature (Section 3.3) but that the oxidized particles still provide significant benefit in reducing creep and shrinkage (Sections
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4.5.1, 4.7, 6.4.1.6). Additionally, these oxidized particles may be stable at higher concentrations than are metallic particles.

Alternatively, the nanobinder can be applied to parts by infiltration after the initial geometry is formed. This can easily be done for parts formed by 3DP or SLS. Drying can be done in a controlled environment to minimize oxidation if desired and the process repeated to increase the nanoparticle deposits and the benefits. This method provided the largest reduction in creep deformation and shrinkage in the current study (Sections 4.5.1, 4.7) although part of the difference may have been a result of the lower carbon residues in parts treated with oxidized nanoparticles (Section 4.6.2).

6.4.1.3 Multiple Nanobinder Applications
As discussed above, the nanoparticle deposits shrink on heating. SEM observations showed that this leads to cracked bonds between particles (Figure 4-10). If the nanobinder is reapplied one or more times, the bonds are at least partially repaired and the performance improves significantly. Thus, it is advisable to apply the nanobinder at least two times to repair sintering cracks formed after the initial application. The parts should be heated between applications to permit sintering. The parts tested in this work were heated to 700°C for 10 minutes between applications. Samples with multiple applications had much better performance (40-45% reduction in deflection) than those with the same amount of material applied in a single application (12-18% reduction). (Section 4.3.1, Figure 4-9)

6.4.1.4 Drying Rate
The drying rate can have a strong impact on the deposition locations of the nanoparticles. As the solvent evaporates, the concentration of nanoparticles at the surface increases. If the drying rate is rapid, the particles will accumulate near the surface and increase the size of deposits near the surface. Nanoiron deposits were higher at the surface than the interior in all of the drying conditions studied, but faster drying rates increase the non-uniformity of the deposits. (Section 4.3.2, Figures 4-12, 4-13, 4-14)

Unsupported structures loaded by self-weight have peak stresses on the part surface. High surface loadings concentrate the nanoiron deposits where the stresses are higher and thus increase the effectiveness of a deposit. Thus, fast drying rates can reduce...
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the creep deflection of unsupported sections. (Figure 4-9) However, this effect is only significant when the nanobinder is applied by infiltration after geometry formation. If the nanobinder is applied during printing, the deposits should be more uniform.

If creep deformation is only a problem in a small area, the nanobinder could be applied selectively to these areas. Such a process might be more difficult to execute repeatedly, but nearly the same benefit might be achieved with much less nanobinder. This may reduce the costs substantially.

6.4.1.5 Drying in a Magnetic Field

Drying the iron nanoparticles under a magnet field substantially increased the uniformity of the deposit and the size of the bonds that were created. The bond size increases because the magnetic field concentrates the nanoparticle deposits at the necks between the micron-scale particles. (Section 4.4, Figures 4-15, 4-16) Nanoiron-treated samples dried in a magnetic field consistently deflect less at high temperatures than samples with a similar amount of nanoiron that were dried without a magnetic field. In one case the sample dried under a magnetic field deflected 40% less than a comparable sample dried without a magnetic field. (Figure 4-17) Under the magnetic field, a larger fraction of the nanoparticles is deposited in the high stress regions at the contacts between particles where they are most effective at reducing dimensional changes.

Drying in a magnet field may be difficult to implement to variable geometries and would not be helpful when skeleton powder or nanoparticles are not ferromagnetic. Fortunately, drying without a magnetic field was also effective, if somewhat less so. In those cases in which drying in a magnetic field is helpful, the magnetic field might be applied locally using coils of high temperature wire around areas of specific interest. Drying must be done below the curie temperature of the materials or the magnetic field will have no effect.

6.4.1.6 Oxidation State of the Nanobinder

Test specimens were treated with both oxidized and unoxidized nanoparticles. The oxidized particles reduced the creep deflection of the test specimens, but creep deflection was 40% higher than in a similar bar treated with unoxidized nanoparticles. (Section 4.5.1)
Measurements of similar specimens show that the unoxidized particles are 10\% carbon by weight while the oxidized nanoparticles are only 1\% carbon after heating to 700 C. (Section 4.5.2) One of the detrimental affects of nanoparticle oxidation is probably the carbon reduction on heating. The carbon deposition will affect the final material properties of the part as discussed in Section 6.6 below.

Sintering shrinkage is also higher in oxidized particles than in unoxidized particles due to the volume change when the iron oxide particles are reduced to iron. (Section 3.7.1) The oxidized and unoxidized particles pack to similar densities on drying. However, on heating, the oxidized particles are reduced to metal. The volume of the remaining iron is half the volume of the initial iron oxide particles.

Thus, unoxidized particles are preferred for optimal performance. However, it can be difficult to avoid particle oxidation and the oxidized particles did still provide significant benefit. It may be possible to achieve good creep reduction with oxidized particles by increasing the quantity of deposited particles. Extra carbon might also be added to the deposits to offset carbon lost through reaction with the iron oxide.

6.4.1.7 Nonferrous Applications
There is substantial interest in applying SFF techniques to direct production of nonferrous metal parts. Materials of interest include nickel-based superalloys and precious metals. In these parts, the carbon deposited with the nanoparticles would not be helpful, and maybe very detrimental in some applications. (Section 2.2.1) Applications to these areas would require alternative processing methods that eliminate or reduce the carbon deposition. In the case of a precious metal nanoparticle deposited into a precious metal matrix of similar composition, the carbon could be removed by oxidation if the samples were heated in air.

6.4.2 SHRINKAGE REDUCTION
Nanoiron treatment reduced the sintering shrinkage of the treated parts by 40-60\%. The shrinkage reduction seems to increase with increasing levels of deposition. However, neither the oxidation state of the nanoiron particles nor the drying conditions (magnetic
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field, drying rate) had a significant impact on the shrinkage. Additional study is necessary to identify the mechanisms of this benefit. (Section 4.7, Figure 4-24)

6.5 Creep Property Measurements

The creep characteristics of porous metal structures were modeled using a power law relationship. (Section 5.1) The stress exponent and the effective activation energy were measured using cantilever specimens that represent the stress state likely to cause the most deflections during infiltration. (Section 5.2-5.4) These test methods proved effective at characterizing the deflection characteristics of the parts with few experiments. The tests measured a stress exponent of one in both treated and untreated specimens. (Section 5.3.1, 5.3.2) A linear stress-strain rate relationship is characteristic of diffusional creep.

The measured creep activation energy of untreated specimens (336 kJ/mole) is somewhat smaller than the measured activation energy for volume diffusion in similar alloys (350-380 kJ/mol). (Section 5.4.3) However, the activation energies for creep and diffusion are generally the same. The difference is likely due to deviations from the assumptions of the measurement method. The method used for measuring the activation energy assumes that the skeleton characteristics such as strength and local stress are constant with time. Strengthening of the skeleton during the test as by sintering would lower the measured activation energy. This is the likely source for the deviations from expected values. (Section 5.4.5)

These measurements show that there is a significant difference in activation energy between the treated (251 kJ/mol) and untreated parts (336 kJ/mol). The carbon added with the nanoiron would be expected to decrease the activation energy some. (Section 5.4.4) Increased grain boundary diffusion due to smaller grains and/or residual porosity in the deposits also plays a significant role in lowering the activation energy of nanobinder treated bars. (Section 5.4.6)
6.6 Mechanisms for Creep Reduction

Significant carbon deposition from the nanoiron was measured. (Table 4-4) The deposited carbon increases the room temperature hardness of treated skeletons and can play a significant role in decreasing deformation and shrinkage. The effect of carbon in reducing deformations was measured by adding carbon to the skeletons both by addition of polymer and by using a starting powder with higher carbon. Both methods were shown to reduce the creep of the skeletons. However, nanobinder treatment achieves greater reductions in deflection while adding less carbon. This confirms that there is a benefit from the deposited iron as well as the carbon. (Section 4.6.2, Figure 4-21)

The added iron was even more important in samples that were not sintered at 1300 C before deflection. Specimens with added carbon performed very well as long as they were sintered at 1300 C for an hour before deflection. However, if they were only sintered to 1000 C before deflection, the skeletons with added carbon performed similar to those with the base carbon composition. In contrast, the nanobinder deflection ratios followed a similar trend whether they were sintered at 1300 C or just 1000 C before deflection. This shows that the nanobinder plays an important role in creating larger bonds to lower the deflection as well as adding carbon. (Figure 4-21)

The sizes of the interparticle bonds were compared in samples with and without nanobinder treatment. A significant increase in bond size with nanobinder treatment was measured. However, the difference in bond sizes was insufficient to achieve the measured creep reduction by the increase in bond area alone. (Section 4.6.1, Table 4-3) Part of this difference is due to the effect of the carbon added with the nanobinder discussed above. Some of the difference is also related to deviation of the actual strain processes from the model assumptions. These differences include strain by bond bending and particle motion and differing strengths for compressive and tensile loaded regions. Measurements of tensile and compressive strain of an untreated specimen showed that the compressive strain seemed to reach a stable maximum at approximately 6% strain while tensile strains continuously increased during the test to over 15% (Section 5.5, Figure 5-19)
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6.7 Recommendations for Future Work

6.7.1 NANOBIINDER IN 3DP

6.7.1.1 Liquid-Metal Infiltration of Treated Skeletons
The nanobinder has been evaluated by heating treated metal skeletons to liquid-metal infiltration temperatures and comparing deflection rates to untreated parts. The process should now be tested with liquid-metal infiltration. The impact of deposited carbon on the infiltration process is of particular interest. Large surface deposits of nanobinder might hinder effective infiltration creating porosity or composition gradients near the surface. These effects should be examined.

6.7.1.2 Impact of Carbon composition on creep and sintering rates of Steel
A chief benefit of the nanobinder may be the accompanying carbon deposition. Studies with higher carbon powder suggest that carbon substantially lowers creep and sintering rates. It may be possible to design the skeleton-infiltrant material system to increase the carbon in the skeleton. This could achieve a significant reduction in the creep rates of the material without incorporation of the nanobinder.

The intrinsic creep characteristics of these materials should be measured so that this effect can be better understood and the optimal carbon compositions determined. It is possible that the benefit is a result of a phase change in the material from a two-phase ferrite-austenite to single phase austenite. The austenite has a lower diffusivity than the ferrite and the single-phase field may reduce the grain boundary area for lower grain boundary transport. If this were the primary mechanism for improvement, other alloying elements could also be used to change the stable phase. Also, adding more carbon beyond what is required to shift the stable phases would be of little additional benefit. Alternatively, the carbon could be lowering the mobility of the iron in the matrix directly. In this case, the diffusivity and thus the creep rates might decrease continuously with additional carbon.
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With a better understanding of these mechanisms, the dimensional accuracy of the infiltration process could be optimized for all binder types. The applicability of these results to other material systems would also be clarified.

6.7.1.3 Metal-Oxide Nanobinder

As discussed, metal-oxide nanoparticles have been shown to reduce deformations when used as a nanobinder. These particles are also more readily available than metallic particles, at higher concentrations and lower cost. Additionally, they can be used without carefully controlling the atmosphere to reduce oxidation. The primary limitation of these particles is the reduced carbon deposition and the increased shrinkage of these particles. (Section 6.4.1.6)

Given the significant advantages of oxide particles, they should be studied further. Applying additional carbon either in the binder or as a secondary treatment could offset the carbon effect. Higher particle concentrations might compensate for higher shrinkage of the oxidized particles.

6.7.1.4 Nanoparticle Doping

Suspensions of nanoparticles could be applied to locally alter the composition of a material. This would be particularly effective for selectively treating the surface regions, as the nanoparticles applied by infiltration tend to migrate to these regions during drying. (Section 6.5.1.4, Section 4.3) A dopant of particular interest in steels would be carbides. These could be added as carbide particles or as metal particles coated with an organic that forms carbide on heating as was observed in the nanoiron. Surface concentration of carbides might increase the hardness and wear characteristics while maintaining a tough core for good impact toughness.

6.7.2 OTHER APPLICATIONS FOR NANOBINDER

The densification characteristics of the nanoiron were found to be very dependent on both the oxygen and carbon present. If oxygen exposure is limited, most of the carbon is retained on heating. The resulting nanoscaled structure sinters relatively slowly, probably due to the formation of iron carbide. Oxidized nanoparticles have very little
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residual carbon and so sinter at much lower temperatures but with increased shrinkage and porosity. This illustrates the importance of chemical effects on the properties of materials deposited from nanoparticles.

Much work has been done to explore the use of gold and silver nanoparticle suspensions for forming structures at low temperatures. These techniques rely on the reduced sintering/melting temperature of nanoparticles. Applications have include electrical interconnects, circuit elements, and MEMS devices. (Section 3.1.1.1) Frequently, the final properties such as resistivity have been much lower than bulk values. Some of these deviations are likely due to similar chemical effects and some to residual porosity.

These effects must be studied further in order to develop effective methods for depositing materials from nanoparticle suspensions. Studies of the processed structures of these materials similar to those conducted with the nanoiron in this work might yield significant insights into the limitations of these methods and the mechanisms through which their performance might be improved.

The gas adsorption tests showed that the nanoparticles could create very highly porous structures on drying and sintering. (Section 3.6, Figures 3-10, 3-11) Figure 6-1 illustrates micron-scale porous structures that were achieved by sintering oxidized nanoiron. When protected against oxidation, the iron carbide structures are remarkably stable up to temperatures of 700 C. (Figure 3-9) Such highly porous structures may be useful in both chemical and structural applications.
Figure 6-1 Porous structure created by sintering nanoiron. This highly porous structure was created by quick drying of an oxidized nanoiron suspension. On heating, the particles reduced to metal and sintered. Continued heating created these micron-scale pores. The same sample was heated to successively higher temperatures to illustrate the pore size evolution. Such porous structures may have low shrinkage and so would be have fewer problems with cracking.