

## **PROTOCOL FOR DEVELOPING SINTERING CYCLES FOR DIFFICULT MATERIALS**

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### **ABSTRACT**

Powder metallurgy (P/M), sintered materials (S/M), and powder injection molding (PIM) are all graduating to the fabrication of materials that prove difficult to sinter. This is generally to expand the product offering while differentiating the P/M, S/M, and PIM concepts from competitive technologies. A goal is to sustain product value added in contrast with the global, low-cost sintering production of common oxide ceramics and ferrous alloys. However, the moves to some of the advanced materials often meet with processing frustrations. What are the difficulties with many of the “advanced” materials? Is there some protocol for solving these problems? What are the new developments? These questions are addressed in this paper, and a case is made that the difficulties are usually sintering problems associated with contamination, decomposition, or densification. Accordingly, a solution outline is provided that includes the most fruitful responses. Examples are offered based on success with aluminum alloys, titanium, cobalt-chromium, bronze, sendust, FeCrAlY, tool steels, silicon nitride, silicon carbide, aluminum nitride, FeAl, superalloys, and other materials new to S/M.

### **INTRODUCTION**

As sintered materials moves to higher value applications, there is a corresponding shift in the materials we must sinter. Often great difficulty is encountered. In a sense the powder production skills have now exceeded the sintering skills. The powders are available, but the sintering technology is lagging. Accordingly, first efforts are in place at Penn State to create a sintering cycle advisor, a knowledge system for first help in solving sintering problems ▪ sort of how to deal with difficulty materials.

This is a quick overview of the situation, looking at the materials, processes, process alternatives, and capturing some of the logic anticipated in the eventual sintering cycle design advisor.

## EXAMPLES

What are some examples of difficult to sinter materials? Nickel-base superalloys are a good example. The production of fuel and exhaust parts for jet engines, actuators, pistons, hinges, and other components associated with warm and high stress components is nearly the exclusive realm of casting and machining. However, powder injection molding has been successful in demonstrating a much lower cost option. A good example is IN 7 18 and many papers have detailed the opportunities, property goals, and scale of the need. However, IN 718 and related alloys are designed to have high strength at high temperature. This of course makes sintering densification difficult, since the material is intentionally designed to hold shape (high temperature strength) at the temperatures associated with sintering. The cure is to anneal out the gamma prime precipitates and dissolve them into the matrix, thereby weakening the powder in the sintering cycle. Accordingly, the sintering stress eventually exceeds the *in situ* strength, leading to delayed sintering densification. When properly executed, the mechanical properties are exceptional.

Other examples encountered at Penn State over the past few years include ■

- titanium surgical tools
- sendust magnetic card reading sensors
- aluminum selective laser sintered freeform prototypes
- FeCrAlY catalytic substrates
- FeAl fuel injector nozzles
- boron nuclear reactor components
- tool steel powder injection molded bodies with high dimensional precision
- TiC-based cermets for diesel engine fuel systems
- 15-5 PH stainless steel high strength fuel system components
- indium oxide ■ tin oxide sputtering targets
- porous niobium capacitors
- large (20 kg) bronze porous tool bodies with high dimensional precision
- tungsten-titanium alloy sputtering targets
- rhenium rocket nozzles
- titanium-tantalum-cobalt biomedical implants with controlled porosity gradients
- aluminum nitride computer heat sinks
- silicon carbide spray nozzles for high temperature polymer dispersion
- cobalt chromium alloys for saw teeth
- NiTi (nitinol) shape memory eyeglass frames
- silicon nitride sliding components for heavy duty earthmoving equipment
- WC-TiN composite wire drawing dies
- diamond bonded with bronze-steel mixtures at low sintering temperatures
- tungsten carbide and chromium carbide cermets for cutting tools
- double composite cemented carbide oil well drilling tips
- aluminum-oxy-nitride optically transparent materials
- sterling silver injection molded jewelry sintered to a pore-free condition
- invar-silver composites for heat dissipation applications
- tungsten-copper heat sinks for computer chip mounts.

## CATEGORIZATION OF PROBLEMS

The problems in general can be categorized as follows:

- the material is thermodynamically unstable at the sintering temperature
- the material is too strong at the sintering temperature and will not densify
- the material sinter bonds, strengthens, but will not densify
- the component fails to hold shape
- the process is not repeatable, everything is too sensitive
- the material decomposes during sintering
- the material reacts and will not densify.

The inability to densify is a common problem. To densify any material in sintering requires heating to a temperature where it is thermally softened.

## GENERAL SOLUTIONS

Various routes are known for inducing densification in a powder that responds poorly to sintering. For example, if decomposition or other thermodynamic problems occur at the typical temperatures needed for sintering densification, then lower temperatures can be used with an external pressure. Such external pressure assisted sintering is seen in hot pressing, pressure-assisted sintering, or hot isostatic pressing. This is the common protocol in tungsten carbide and diamond sintering, where the materials decompose at the temperatures needed to induce full-density sintering.

An alternative is to induce sintering densification using a bulk transport process with suppression of surface transport controlled processes. Grain boundary diffusion is most effective in giving densification, so grain boundary segregants that promote faster diffusion are termed activate sintering. On the other hand, agents that poison surface diffusion are equally effective. An example of the former is in the nickel activate sintering of tungsten and for the latter the most famous example is seen in magnesia doped alumina. Both cases give optimal behavior with just 0.1% additive.

## SOME SPECIFIC EXAMPLES

### **Lower *In Situ* Strength**

The best example of lowering the strength of the material at the sintering temperature is seen in sintering nickel-base superalloys. The inter-metallic gamma-prime phase provides high temperature precipitation strengthening, thus the use in high temperature components. However, that same phase makes the particles too stiff to undergo sintering plastic flow and sintering densification. To circumvent this problem requires a long sintering hold, about 16 h, mostly to redissolve the gamma-prime precipitates. Once the strengthening phase is dissolved, then sintering will occur from the combination of capillary forces and low material strength, just as most other powder sinter densify at high temperatures. In situations where the upper temperature is limited (by equipment or thermodynamic instability) the protocol is to apply pressure to supplement the

normal sintering stress. For most materials the sintering stress is on the order of 1 to 10 MPa at the sintering temperature. If the material is substantially stronger, then very slow sintering densification takes place. Higher temperatures induce thermal softening, and formation of a liquid phase is often very useful. But in some cases the material decomposes or evaporates - this is the problem with W-Cu, WC-Co, indium oxide, and even brass. The alternative is to apply pressure or use a smaller powder. To be effective, the applied stress must exceed the material strength at the sintering temperature. Since most materials are stronger at lower temperatures, this means higher stresses. Since the sintering stress is relatively low, often just 20 atmospheres pressure (2 MPa) might be effective. To be successful, the sintering compact must have closed pores, an external container, or the pressure must be applied via a medium that will not penetrate into the pores. Thus, there are several variants to densification and the higher the temperature and smaller the powders size, then the higher the density possible with low pressures.

### **Increase Bulk Transport**

The need to increase bulk transport is usually coupled to a very sluggish system, where higher and higher temperatures give gains, but the activation energy is so high that very high temperatures are required to densify the material. Mass transport in sintering is possible via many mechanisms - volume diffusion, grain boundary diffusion, dislocation climb, plastic flow (dislocation slip), viscous flow, surface diffusion, evaporation-condensation, and such. Only some of these give densification, namely when the source of the mass is at the interparticle neck. Promotion of mass transport via bulk diffusion processes helps attain densification. Grain boundary diffusion is most useful in this effort, and faster grain boundary diffusion is possible by small composition shifts. A key means for faster grain boundary diffusion is by adding a species that has a low solubility in the material and yet lowers the liquid and solidus temperatures with alloying. Such species segregate to grain boundaries and lower the activation energy for grain boundary diffusion. Concentrations of just 40 to 100 ppm are often sufficient to induce dramatic changes in densification, as evident by boron additions to stainless steels and nickel additions to titanium carbide. In some cases, even faster sintering occurs when a liquid is formed on the grain boundaries, but the concept is similar.

### **Suppress Surface Transport**

The need to suppress surface transport is seen by the evolution of strength, loss of surface area, but lack of densification. Just as mass transport along grain boundaries assists in sintering densification, mass transport on pore surfaces consume the system energy without delivering densification. These surface transport processes, such as surface diffusion and evaporation-condensation, retard densification. Effectively, they consume energy but do not deliver densification. If surface transport can be suppressed, then the remaining surface area shifts to drive bulk transport, giving densification. Means to do this shift go to species that effectively change the surface energy, and the most famous example is magnesia additions to alumina as first isolated in the 1950's. This process is still the mainstay for sintering transparent alumina, and similar ideas have been employed in sintering silicon carbide and other covalent ceramics. It is also important to the sintering of ice, lead containing compounds, and some thermoelectric ceramics and intermetallics.

### **Decomposition During Sintering**

Most of the materials that decompose during sintering show a concomitant weight loss. Suppression of decomposition largely comes from lower sintering temperatures, but there is difficulty in obtaining densification. Lower temperatures need to be accompanied by smaller powder sizes, but this is only realistic with a few materials. An overpressure during sintering can help suppress decomposition, and high (nitrogen) pressures are often used in sintering materials such as aluminum nitride and silicon nitride. In other cases, thermodynamic instability is a problem that can be adjusted via the sintering atmosphere, such as use of moisture in sintering tungsten heavy alloys or oxygen in sintering lead-zirconium-titanates.

### **Reactions During Sintering**

Reactions are usually characterized by a mass gain during sintering, in contrast with the mass loss seen with decomposition. When the reaction occurs such as the formation of a hydride or attach of the substrate, the sintering cycle is fighting basic thermodynamics. The cure is to shift the portion of the process that is providing the reaction species. For tantalum, niobium, zirconium, and other hydride formers this means use of vacuum. In reactions between the sintering material and substrate, the need is to move to more thermochemically stable substrates - WC reacts with alumina, so graphite is a better substrate. In other instances, lower temperatures are possible options. One often overlooked problem is with furnace contamination. Graphite heating elements or insulation in furnaces often contribute trace contaminants - carbon for sure, but often gases absorbed in the pores - that negatively impact the sintering material. The option is to move to more stable, cleaner furnaces, such as all-refractory metal hot zones.

Curiously, most of the materials that prove hard to sinter are manmade materials - TaC, IN 718, AlN, SiC, FeAl, and  $\text{In}_2\text{O}_3\text{-Sn}_2\text{O}$  as examples. Essentially we are fighting nature and a basic understanding of thermodynamics and kinetics are mandatory to find solutions.

### **ROADMAP TO SOLUTIONS**

Some simple concepts can help, and as the sintering cycle advisor concept advances these will be more involved and rigorous. As a first pass toward the solutions, consider the following principles:

**problem** - decomposition problems during sintering

**symptoms** - weight loss

**underlying problem** - fighting thermodynamics

**options** - lower sintering temperature, use smaller powders, shorter times at peak temperature, apply pressure, avoid vacuum

**problem** - densification incomplete

**symptoms** - component strengthens but will not densify

**underlying problem** - need for more thermal softening and faster grain boundary diffusion

**options** - reduce grain size (not particle size), look for low solubility grain boundary segregants that lower solidus and liquidus temperatures, use higher temperatures, heat faster to avoid low temperature surface transport, avoid use of inert gas atmosphere

**problem** ▪ contamination

**symptoms** ▪ weight gain or impurity increase

**underlying problem** - problems with unwanted reactions in sintering

**options** ▪ improve reduction potential of the atmosphere, move to more inert furnaces, use higher stability substrates, add getter to furnace or material

## **FUTURE VISION**

As knowledge and data are accumulated, some first efforts have taken place to find underlying principles. For example, is there a nondimensional sintering index that provides a measure of sintering or sinterability? Early research along these lines have evaluated a combination of particle size  $D$ , time  $t$ , temperature  $T$ , and material properties (especially the melting temperature  $T_M$ ). Sintered density then regresses to this sintering index with about a 65% correlation, based on the following equation:

$$\psi = At \exp(BT / T_M) / D^3$$

That is not very good, so the index needs more terms, but what factors? Unfortunately, most published sintering studies do not include sufficient data to fully account for the work performed in the cycle ▪ heating rates, cooling rates, and small particle content or surface area. Accordingly, the models are not working too well because the data base is incomplete on needed details. The goal of on-going Penn State research is to isolate more successes and to better define sintering cycles for the emerging, manmade, difficult to sinter materials that seem to make up our future. The emphasis will be on the powder injection molding route, largely since this is the more rapidly growing and sexy field of the future where good sintering is key to industrial success.

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## **REFERENCE**

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