MSE 160 class page: bowmanlab.eng.uci.edu/class

Lab reports

Experimental methods section should be specific to your experiment, not a copy/paste from the manual
Lecture outline

Outline

• Ceramic synthesis
  • Sol-gel synthesis
  • Powder processing

Sol-gel (Solution-Gelation) Synthesis of Materials

Outline

Introduction

Liquid phase synthesis of nanoparticles

Sol-gel chemistry for ceramics

Application of sol-gel process
Liquid phase synthesis of nanoparticles

Major categories
1. Colloidal methods
2. Sol-gel processing
3. water-oil microemulsions
4. hydrothermal syntheses
5. polyol method

Solution precipitation relies on the precipitation of nanometer-sized particles within a continuous fluid solvent.

An inorganic metal salt, such as chloride, nitride and so on, is dissolved in water. Metal cations exist in the form of metal hydrate species, for example, Al(H₂O)₃⁺ or Fe(H₂O)₆³⁺. These hydrates are added with basic solutions, such as NaOH or Na₂OH. The hydrolyzed species condense and are then washed, filtered, dried and calcined in order to obtain the final product.

Colloidal methods

Wet chemistry processes where different ions are mixed to form insoluble precipitates

Used to produce metals, metal oxides, organics, and pharmaceuticals.

Basic principles of colloidal preparation were known since antiquity. E.g. gold colloids used for high quality red and purple stained glass from medieval times to date. However, proper scientific investigations of colloidal preparation methods started only in 1857 when Faraday has published results of his experiments with gold.
Sol-gel (Solution-Gelation) technique

“Sol”
colloidal solution made of solid particles few hundred nm in diameter, suspended in a liquid phase.

“Gel”
a solid macromolecule immersed in a solvent, formed by cross linking.

Simple process and at relatively low process cost.

Transformation of a liquid into a gel state, with post-treatment and transition into solid oxide material

High purity and uniform nanostructure achievable at low temperatures.
Sol-gel for ceramics

Synthesis of ceramic materials of **high purity and homogeneity** without fusion of oxides (solid state synthesis).

**Process occurs in liquid solution. Hydrolysis and condensation reactions create a new phase (the sol).**

Metal alkoxide: $M-O-R + H_2O \rightarrow M-OH + R-OH \text{ (hydrolysis)}$

What is “R”?

$R = \text{alkyl group (e.g. } (CH_3)^-, (C_2H_5)^-, (CF_3)^-, \text{ etc.)}$

$(M = \text{Si, Zr, Ti})$
Synthesis of ceramic materials of **high purity and homogeneity** without fusion of oxides (solid state synthesis).

**Process occurs in liquid solution. Hydrolysis and condensation** reactions create a new phase (the sol).

\[
\begin{align*}
\text{M-O-R} + \text{H}_2\text{O} &\rightarrow \text{M-OH} + \text{R-OH} \text{ (hydrolysis)} \\
\text{M-OH} + \text{HO-M} \text{ (condensation)} &\rightarrow \text{M-O-M} + \text{H}_2\text{O} \text{ (water)} \end{align*}
\]

\[(M = \text{Si, Zr, Ti})\]
Sol-gel for ceramics – controlling the product

Hydrolysis of the alkoxide precursor strongly influences the structure of the M-O-M network (e.g. Si - O - Si).

Because **OH is a marginally better leaving group than -OR**, the condensation process can be tailored to favor the formation of dimers, chains, or 3-D agglomerates.

**DIMERS:**

\[
2 \text{RO-Si-OH} \rightarrow \text{RO-Si-O-Si-OR}
\]

\( f = 1 \)

1-DIMENSIONAL CHAINS:

\[
\text{nHO-Si-OH} \rightarrow \text{HO-Si-O-Si-OH}
\]

\( f = 2 \)

2-DIMENSIONAL RINGS:

\[
n \text{HO-Si-OH} \rightarrow \text{HO-Si-O-Si-OH}
\]

\( f = n \)

3-DIMENSIONAL FRAC'TALS:

\[
\text{HO-Si-OH} \rightarrow \text{HO-Si-O-Si-OH}
\]

\( f = 4 \)
Sol-gel process

Metal Alkoxide Solution → Coating → Xerogel film → Heat → Dense film

Hydrolysis Condensation → Cooling → Wet gel → Evaporation → Xerogel → Heat → Dense ceramics

Gelation → Extraction of solvent → Uniform particles → Aerogel

Dense ceramic
Aerogel – solvent replaced by gas

Possible to generate ceramic precursors at low temperature

Gel glass processing sequence

- Mixing
- Casting
- Gelation
- Aging
- Drying
- Stabilization
- Densification

Temperature (°C)

Relative time

Sol | Gel | Aged | Dried | Porous Gel | Dense Gel
Common application - fabrication of coatings and films

Dip coating process

What parameters influence the final film?

19

20
Dip coating process
Substrate is immersed in a sol and withdrawn with well-defined speed under controlled temperature and atmospheric conditions. The sol forms a film with thickness mainly defined by the withdrawal speed, the solid content and the viscosity of the liquid. Gelation (densification) of the layer occurs by solvent evaporation, and finally annealing (heating) yields the oxide coating.

Angle-dependent dip coating
Coating thickness depends on the angle between the substrate and the liquid surface.

Spin coating
Used to make a thin coating on relatively flat substrates.
Cathode
Porous perovskite oxide

Electrolyte
Dense fluorite oxide

Anode
Porous ceramic-metal composite

C. Ding et al.,
Flow coating

**Coating thickness depends on the angle of inclination** of the substrate, the liquid viscosity and the solvent evaporation rate.

The advantage of the flow-coating process is that non-planar large substrates can be coated rather easily.

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**Powder processing**

Outline

- Applications
- Synthesis
- Processing
- Sintering

References

*Ceramic Materials Science and Engineering* by C.B. Carter & M.G. Norton *Springer*
Research activities

Synthesis of nanoscale oxide materials

Co-precipitation of rare earth carbonates

Video by Hasti Vahidi

Pulsed laser deposition

Processing bulk oxide ceramics

Powder sintering
What is powder?

Fine, dry particles produced by chemical processes, grinding, crushing, etc.

“No limitation is imposed on the size of the particles, which may range from nanometer scale, as in pigments or aerosols, to that of mined or quarried materials.”

- Journal of Powder Technology
What are some applications for powders?

Pharmaceuticals, chemicals, foods, pigments, structural and functional materials, environmental and energy related materials.
Powder applications – Powder metallurgy

Powder Metallurgy Process

- Base powder, lubricants and alloying elements
- Mixing
- Compacting
- Machining
- Secondary operations
- Tumbling
- Impregnating (resin/oil)
- Second compaction
- Joining
- Sintering
- Finished Product

Powder applications – Li-ion battery

Geometric Architecture
- Light Microscopy
- Scanning (Electron) Microscopy

Large-Scale Package Inspection
- X-Ray Microscopy

Quantification of Particles, Pore, Sizes, Tortuosity
- X-Ray Microscopy
- Multimodal Workflows
- Focused Ion Beam SEM

Chemical Composition, Reactivity
- Field Emission SEM
- Analytics
- Focused Ion Beam SEM

Zeiss.com
Powder synthesis – Mechanical attrition milling

Nanoparticles are formed in a mill where energy is used to transform course-grained materials into nanostructured powders.

size distribution of 1-100 nm with high crystallinity

Powder processing – Tableting

Method for pressing powder into solids (e.g. drugs, candy, biomaterial)

Dye mold is filled, and then the mixture is compressed and ejected

What are important variables?
Powder processing – Tableting

Method for pressing powder into solids (e.g. drugs, candy, biomaterial)

Dye mold is filled, and then the mixture is compressed and ejected

What are important variables?

particle size, flow properties of powder, pressure (powder polymorph)

Powder processing – Additive manufacturing

Three-dimensional objects iterative addition of thin layers of material
produce metals, ceramics, polymers and composites using photopolymerization, jetting, extrusion, directed energy deposition, and lamination

What pros and cons of additive manufacturing can you think of?
Selective laser melting

Powder processing – Additive manufacturing

Julie Schoenung Research Group, UC Irvine
Sintering – Overview

Sintering is the process of transforming a powder into a solid body using heat.

The most important process in making bulk dense and porous ceramics, but also needed for powder metallurgy.
Sintering – Overview

how best to pack particles (that are usually modeled as spheres), movement of grain boundaries (GBs), and knowing how the packing geometry and GB migration is affected by the need to balance surface tensions (interface energies).

Sintering is driven by the tendency to reduce the total energy of the system. This is especially true for nanoparticles. Why?

Sintering – Surface area and energy

Driven by tendency to reduce the total energy of the system by increasing radius of curvature of surface and by minimizing surface area.

A curved surface wants to be flat.
Sintering – Surface area and energy

Sintering is driven by the tendency to reduce the total energy of the system by increasing radius of curvature of surface and by minimizing surface area.

The extra energy of a surface with a radius of curvature, \( R \), may be calculated as a stress (\( \sigma \)) in a Laplace equation:

\[
\sigma = \frac{\gamma}{R}
\]

where \( \gamma \) is the surface energy.

In nanomaterials, this sintering stress may reach very high values.

**Example:**
the sintering stress may be as large as 300 MPa in 10 nm particles compared to only 3 MPa for 1 \( \mu \)m particles, if \( \gamma \) has a typical value of 1.5 J/m².

Which has less circumference, A or D?

Which has more surface (energy), left or right? Right

At some critical radius, the particle will continue to grow to minimize surface area.
Sintering – Mass transfer

Material must transfer from one part of the structure to another. **Solid phase sintering.** **Liquid phase sintering** achieved by phase transition.

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**FIGURE 24.13** Liquid at surfaces.

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**TABLE 24.1** Mechanisms and Transport in Sintering (Diffusion to the Neck)

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Transport Path</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD</td>
<td>Surface diffusion</td>
<td>Surface</td>
</tr>
<tr>
<td>VD</td>
<td>Volume diffusion</td>
<td>Surface</td>
</tr>
<tr>
<td>E-C</td>
<td>Evaporation-condensation</td>
<td>Surface</td>
</tr>
<tr>
<td>GB</td>
<td>Grain boundary diffusion</td>
<td>GB</td>
</tr>
<tr>
<td>VG</td>
<td>Volume diffusion</td>
<td>GB</td>
</tr>
<tr>
<td>PI</td>
<td>Plastic flow</td>
<td>Dendrites</td>
</tr>
</tbody>
</table>

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Oxide annealing: 900 °C, in situ TEM
Sintering – Compaction

A compact (a.k.a. green body) is formed by pressing the powder

Sintering defects may be related to the microstructure of green body. Inhomogeneities in density, packing, and particle size in green compact will limit the final sintered density.

Alumina particles during compaction

Sintering – Densification

Sintering starts when compact is heated to temperatures about \( \frac{2}{3} * T_{\text{melt}} \), when diffusion becomes significant. Elimination of large pores originating from the green compact requires high sintering temperatures which promotes grain growth.

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle size, nm</th>
<th>Temperature, K</th>
<th>Percentage of densification</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>140–170</td>
<td>1900</td>
<td>91</td>
</tr>
<tr>
<td>TiC</td>
<td>5000</td>
<td>3070</td>
<td>91</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>nano sized</td>
<td>1745</td>
<td>100</td>
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<tr>
<td>ZrO₂</td>
<td>conventional</td>
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<td>100</td>
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<td>&gt; 1630</td>
<td>100</td>
</tr>
<tr>
<td>TiN</td>
<td>1823</td>
<td>1823</td>
<td>63</td>
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<tr>
<td>TiN</td>
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<td>63</td>
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What is the relative particle size?

Higher temperature may be needed for larger particles
Sintering – Densification

Sintering starts when compact is heated to temperatures about $2/3 \times T_{melt}$, when *diffusion becomes significant*. Elimination of large pores originating from the green compact requires high sintering temperatures which promotes grain growth.

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Sintering – Densification

Sintering starts when compact is heated to temperatures about $2/3 \times T_{melt}$, when *diffusion becomes significant*. Elimination of large pores originating from the green compact requires high sintering temperatures which promotes grain growth.

Pores may persist as grains grow

*FIGURE 24.11* Atomistic model for GB migration.

BowmanLab

UC Irvine

EngrMSE 160, 2020 Winter

2/4/2020
The general relationship between sintering parameters $n$ is a constant, $p$ is the density, $Q$ is the activation energy for sintering and $d$ is the mean powder particle diameter. The $n$ is usually about 3 and $Q$ is considered to be equal to the activation energy for grain boundary diffusion.

Which has the lowest sintering temperature?

<table>
<thead>
<tr>
<th>Material</th>
<th>Particle Size (nm)</th>
<th>$T$, K</th>
<th>$T/T_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$</td>
<td>40</td>
<td>950</td>
<td>0.46</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>13</td>
<td>823</td>
<td>0.4</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>70</td>
<td>1370</td>
<td>~0.5</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>8--9</td>
<td>870--920</td>
<td>~0.3</td>
</tr>
<tr>
<td>Fe</td>
<td>2000</td>
<td>~900</td>
<td>0.5</td>
</tr>
<tr>
<td>Fe</td>
<td>30</td>
<td>393</td>
<td>0.21</td>
</tr>
</tbody>
</table>

Which has the lowest sintering temperature?
Sintering methods – Conventional & microwave furnace

Microwave sintering has **rapid processing time**, two to 50 times faster than conventional heating.

There is also an acceleration of sintering and diffusion in the material because of high electrical fields; thus densification can occur at lower temperatures.


Sintering methods – Hot isostatic press (HIP)

Process to densify powders or cast and sintered parts in a furnace at high pressure (100-200 MPa) and at temperatures from 900 to 1250°C for example for steels and superalloys.

Gas pressure acts uniformly in all directions to provide isotropic properties and 100% densification.

High performance alternative to conventional processes such as forging, casting and machining.
Sintering methods – Field assisted “spark plasma” sintering

Plasma state is achieved by pulsed current
Surface temperature of particles rises rapidly by self heating, so particle growth is controlled.

(I) The electrons are withdrawn from one power (the cathode) and accelerate toward the anode.
(II) The electrons collides the gas atoms in the powder gap, then the gas is ionized.
(III) The accelerated electrons hit to the anode, the ions of the sintered materials are evaporated like a sputtering process.

Initial activation through the application of a pulsed voltage; subsequent heating and densification by DC current. Typically less than 10 minutes for the full densification of both conductive and non-conductive materials.

Sintering methods – Field-assisted “flash sintering”

A newer densification technology for ceramics allowing a dramatic reduction of processing time and temperature.

Reduce energetic costs associated with firing. Develop out-of-equilibrium microstructures.

“Flash sintering of ceramics” M. Biesuz V.M.Sglavo
References (see Class page)

Given throughout