

Advanced Ceramics (MM 652, IITB)

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Problem: Agglomeration. Typical properties of nano-sized powders-

- Enhanced tendency

. Two forms of pores: intra and inter crystal. Usual powder compaction is not good enough to break agglomerates. When the agglomerates are not broken, two widely different sizes need to be addressed. Higher porosity. Finer inter particle pores tend to get removed during sintering compared to the inter agglomerate size. What is the problem?

- eventually the inter agglomerate pores should get filled (thermodynamically feasible) but time required may be too high. Once agglomerate forms, inter agglomerate pore size can't be controlled. Sintering time increases, so microstructural coarsening takes place.
- Because intercrystallite pores are gone: density high, Uneven density.
- There is no porosity to pin the grain growth so coarsening keeps going on. Regions in which inter agglomerate pores are present then not much coarsening. Not only non-uniform porosity but also microstructural length scales will be different in different regions. Mechanical properties, optical

Most oxide materials are transparent but defects : porosity, better to remove porosity to get transparent. Polycrystalline will be translucent.

Physical breaking of agglomerates. Ball milling can be used to break agglomerates and we get non-agglomerates. What's the problem then? Re-agglomeration: When does re-agglomeration happen? not during compaction but when evaporating the aqueous medium. Ceramics can't be dry milled, always need an aqueous medium. In milling, we don't have control on temperature. Regions near the surface can reach very high temperature. Non-uniform agglomeration happens during drying of the aqueous medium after milling. Natural process: surface tension will pull agglomerates together. Hence, use surfactants to give steric hindrance. Adding end groups to side walls and provide steric hindrance. When making a composite with Carbon fibre (main problem is dispersion- just provide steric hindrance), But for ceramics not that helpful. Instead of electrostatic repulsion, Adding Bulky groups for steric hindrance. Same problem even with ultrasonication. So what to do? **Freeze drying**: Phase diagram of water (later). On evaporating, problem occurs when crossing liquid-vapour interface, go to the other side and freeze it. Then it will cross the liquid solid interface: immobile as ice. Particles dispersed in ice: lower

the pressure and cross the solid vapor interface.

Aerogels are also prepared based on this kind of phase diagram. Its light because of porosity inside it. If removing liquid medium from aerosol to make aerogel, again porosity will be lost. Hence not to do evaporation. But freeze drying also not good because structure will get damaged (doesn't matter for powders but affects products in final form) due to expansion. So it goes other way towards critical point. **Supercritical drying**: Goes over the critical point.

Next time (wednesday) **Prof. Sanjay Sampad (Stony Brook)** who is a world leader in ceramic coating, will be taking a lecture. Recall Zirconia phase diagram and phase transformations from Ceramics and Powder Metallurgy course.

Recap of **sintering**, and a few points for advanced sintering. High temperature treatment of the cold compact (green compact, already compacted into required shape) to remove pores.

Primary driving force is reduction in overall free energy due to reduction of net surface area. Driven by:

- Surface energy of powder particles
- external pressure : will see explicitly in pressure applied sintering, flash sintering.
- chemical reaction : if the removal of pores is made thermodynamically more favorable. Died out because of difficulty in controlling reactions at high temperature.

Types of sintering:

- Solid state
- liquid
- vitrification

Sintering mechanisms: insert diagram three particle from Sintering of ceramic, taylor and francis group (later)

- Surface diffusion: It also takes material from points of higher chemical potentials to points of lower chemical potentials. Some material transport towards the pores but major transport from points of higher chemical potentials to points of lower chemical potentials. Radius lower: regions of higher chemical potential, Radius higher/ flat regions: regions of lower chemical potential. Movement along the surface.
- Lattice diffusion (from the surface): similar to above. Some densification but a lot of coarsening.
- Vapor transport: similar to above. Some densification but a lot of coarsening.
- Grain boundary
- Lattice diffusion (from the grain boundary)
- Plastic Flow

4, 5, 6, lead to densification majorly, minimal coarsening. 1,2,3 are non-densifying, 4,5,6 are classified as **Densifying mechanisms**. **Herrin's scaling law**: the coarser the particle, longer the time for scaling. Longer it takes for sintering, further coarsening. Time for sintering needs to be minimized.

$$\frac{\Delta t_2}{\Delta t_1} = \lambda^m = \left(\frac{a_2}{a_1}\right)^m$$

or $(Rate) \propto \lambda^{-m}$. $m = 4$ for grain boundary diffusion, $m = 3$ for lattice diffusion

At lower temperature, 1,2,3 dominate. At higher temp, 4,5,6 dominate. Faster the heating rate, lower time required at the final sintering temperature to achieve the same densification. Lesser time at final sintering temperature means lesser microstructural coarsening.

1.0.1 Stages of Solid state sintering

True density or **Sinter density**: density of bulk sintered body as a percentage of the theoretical density (no porosity body).

Definition 1.1. Sinter density: ρ_{th} : ratio of bulk density

- Instantaneous contact $\rho_{th} \sim 0.60$
- Interparticle neck growth $\rho_{th} \sim 0.65$
- (later)
- $\rho_{th} \sim 0.95$ Pores are isolated at disjoint locations.
- $\rho_{th} \sim 0.99$. Almost impossible to get rid of grains inside the grains.

$\rho_{th} = 1 - P$, where P is the fraction of porosity, using microstructural measurement of area fraction (stereochem: area fraction is same as volume fraction).

1.0.2 Processing challenges for ultra-fine/nano-sized powders

Atmosphere will provide contaminants: dust, carbon particles on the surface of the powder. In air atmosphere, amorphous carbon will go away at $600^\circ C - 700^\circ C$. Carbon at surface hinders sintering significantly. Excessive grain growth at area where contamination is less vs that where contamination is more. High temperature properties may be degraded because of silica contaminants.

- (later)
- later
- Getting a good cold compact will also be difficult. Typical cold compact pressure is $100 MPa$. To even get cold compact: need $600 MPa$ because of prevention of interparticle sliding. Excessive friction prevents sliding to come to a configuration where they geometrically fit and reduce pore size. We may start with ultra fine powder but high surface area means more coarsening. Advantage of using fine powder will be negated. Coarsening needs to be controlled.

- Inhomogeneous densification from edge to core: Most heating processes are from side to core. When we have ultra-fine sized surface gets sintered faster, transfer of heat from the surface to the core slows down. Convection of air from surface to the core will be slowed down as it is blocked by surface sintering. Need more time for sintering. Because of agglomeration as well there will be inhomogeneous densification
- Grain growth due to particle agglomeration: Inter agglomerate pores will need more time to be removed, Interparticle pores that have already been removed so that region will grow more.

Summary:

- Suppress the particle coarsening.
- Lowering of sintering time and temperature. But initial rate of heating should be high
- Activated sintering: faster heating rate and additional driving force.
- Some of the ceramics that are non-oxide such as borides, carbides, nitrides have melting points above 3000°C . Something like alumina can be done by solid state sintering or no additional pressure but for non-oxides can't get more than 95% density. Hence used pressure based or liquid phase sintering.

1.0.3 Liquid Phase sintering

Liquid phase aids in the sintering. Fe which melts during sintering at high temp can provide liquid phase. Given the combination, which factors favour:

- Don't react.
- Wets the particles.

Inherent increase in diffusivity in liquid phase. Liquid phase occupies more so area of transport channel is more.

Non-oxide ceramics sintered by metallic additives like Fe , Co etc. are called **Cermets**. Enhancement of fracture properties. Metal inherent in microstructure of cermet. It can't be removed. Non-oxides are suitable for ultra-high temperatures 2000°C . TiB_2 with Fe can't be used at 1000°C because of creep. Lot of work being done to replace metallic sinter additives by non-metallic sinter additives. MoSi_2 can be used at a high temperature but for melting, need to go to 2000°C . However react with TiB_2 to get $\text{TiB}_2 - \text{MoSi}_2$ which melts at 1700°C , product can be used up to 1250°C . Diborides potential to be used at ultra-high temperature applications hasn't been used.

Question 1.2. Why do we need cermets at ultra-high temp? Instead work with porous TiB_2 ?

Porous react more with atmosphere to give oxides. Usually passive layers are formed but for high porosity large amount of materials will be lost. These materials have application in aerospace which might have more gases that can react other than oxygen.

Lecture Jan 22

2 Materials are crucial components of systems

Solar energy cheaper in Dubai than oil. Need to scale up. Even in wind. Next revolution in batteries- storage. China has done tremendous work already in this field.

2.1 Fibre Optics

Fibres needed for communicating across bandwidth. Solid state lighting: Red LED 1960s, then green and finally blue after 50 years of effort that led to Nobel Prize a few years ago.

2.2 Semiconductors

Pervades most of society.

2.3 Other Applications

Microwaves, energy storage, IOT: internet if things-all human actions into analogue.

2.4 Bio-sensor

Sensor to measure the blood sugar. Bluetooth transmitter to the phone. Relatively cheap, works without breaking the hand. Need materials to hold together, sustains even while taking a bath.

3 Overlay Ceramic Coatings

Ceramics are brittle materials. They don't accommodate dislocation plasticity. On the other hand if metal is overlaid with ceramic then we get duality- metals allow ductility. Don't want to put metals at high temperatures hence expose ceramic surface to prevent heat transfer. Ceramics resistant to wear protective applications

- corrosion resistance
- Contact damage prevention
- etch resistance
- sliding surfaces
- TBCs, EBCs, Abradables, SOFC interconnects

Ceramics as insulating

- Functional dielectrics
- respond very well to gases.
- Luminescence: phosphor
- Bone mimicking
- Ceramics are best way to make fuel cells.
- Thermoelectrics heat generates

3.1 Families of materials

Stabilized zirconias, oxides (naturally found, others need to be extracted).

3.2

Refractory kilns with ceramics are not for engineering applications: no continuous mechanical stress, fatigue. In engineering situations, would like to use a metal with a protective coating. Fly an aircraft then most of the surface is ceramic coated, semiconductor chips have ceramic coatings for insulating. Printing paper, create patterns in which the ink gets stored. Implants: to replace hip, spine- metals are not biocompatible- ceramic calcium phosphate is bone-mimicking so body doesn't think of it as external.

3.3 Functional Ceramic coatings

- Ceramic exhaust gas filters
- Microwave, luminescence devices

Pouring a metal needs a ceramic mould. Melting ceramics is at very high temp, difficult to fuse ceramics. Manufacturing Coating needs some work. Two classes- protective are thick $50\mu\text{m}$ to 1mm . Functional films 10 to $100\mu\text{m}$. Electron beam PVD. Precursors and react them CVD. Sputter the dispersed phase- Pulsed Laser Deposition. Cooking: Cut and Paste (Screen printing) used in thick film coatings on the phones. Ceramics are brittle- can't use deformation to manufacture. Only in Aerosol some impacting makes it plastic.

Question 3.1. Achieving specified density requires what parameters to be changed in the process?

Shall cover.

4 Ceramic Coating Material

Transparency market research data "High-performance Ceramic Coatings": Market of the entire technology in billions.

5 Thermal Spray is Complex

Most combustion processes with oxy-fuels have max temp of 3000°C . Moreover, diffuse, Many ceramics don't melt. To generate a heat source at such high temp- generate a thermal plasma (as found in the Sun). Fourth state of matter: plasma has unstable ions. If we can succeed in fission, then self sustaining. Plasma-welding: anode and cathode. Cathode emits electrons and anode absorbs them. In the gap b/w the cathode and anode, inert gases are broken apart if the potential difference is high. Energy released when ionization is going back. The temperatures can go up to 10000°C . Want to create a discharge. Open circuit will be completed by ionizing the gas. Gas is ionized by bombardment of electrons. Argon ionized, then goes back to gas phase. Very high energy. Just like Spray painting using robotic manipulation of weld to get curved welds. Droplets impact the surface and get a shock. Surface is relatively much colder so the droplet freezes. Length scales are $20\text{-}40\mu\text{m}$. Should be able to manipulate the porosity-

40 years of work and still don't understand it. Robotic arm manipulation takes huge investment and time. Many car cylinders have such sprayed coatings. Can't scale up because need very high source for ionization and low conductivity of ceramics.

5.0.1 Applications

Denatl implants, pulp extracts.

5.0.2 TS offers a range of innovative spray devices

APS, Triplex. Like a restaurant that have a variety of dishes.

5.0.3 TS allows unprecedented tailoring of microstructures and properties

Don't want air to escape, need tight seals. Put ceramic coatings that abrade by itself. Want to prevent heat from going through. Pockets of air in materials: pores that prevent heat from going through. Tiny gaps scatter phonons that prevent heat from going through. (high porosity (abradables), layered porosity (TBC's))

Heating issues: ceramics and metals expand at different rates. If we make cracks in ceramics we can use them as Dense, Vertically cracked (DVC) for strain tolerance.

Question 5.1. Thermal fluctuations in high temperatures may diffuse the cracks. How to handle that?

Sand and dust can go into the cracks- huge problem. Volcanic ash and sand. Major airlines stopped flying to Delhi because of the same problem. Small crack sucks up soil. Try to put up thin skin layer. Dense electrolyte (SOFC's).

Question 5.2. Why do we need ceramic coatings?

Metal-ceramic duality. Metal for mech, ceramic for environment resistance. Expensive materials don't want to expose. Integration of high value addition. Enhancing performance: Hot air hits metal then it will get destroyed, ceramic coating doesn't let the heat go through.

5.0.4 Gas Turbine Technology

Runs on reciprocating action. Connecting rod is used. Typical automobiles are not efficient. In aircrafts, we can use expensive, more efficient turbines. Every blade gets a puff of hot air, rotates, pulls in more air. The fan rotates and blows most of the air around the engine. Very high temperatures. Car engines are relatively cold- we can use Al. While flying, can't stop to check or refill for a long time. Most of the technology in India was to rotate at the same speed. Nobody knew how to make geared engines for aircraft. Indigo customer to some company that came up with a way but needed highly efficient gear. (Slide courtesy: Prof. C.G. Levi, UCSB). The hotter the environment, more the efficiency. If heat is increased too high, metals will melt away. Use ceramic coatings. Gas turbines are incredibly efficient, extremely reliable. GE revolutionary: using oxide CMC (get rid of metal). Every kilo of weight reduced saves huge cost. Gas turbines

run their entire university for 6 months or so straight.
 To just put a ceramic coating on a metal surface is not easy.
 Topcoat, Bondcoat, superalloy. Bondcoat needed for protection at high temperatures. Science but also an artform.

5.0.5 Hot section coatings

Graph showing temperature with years. Temperature capabilities is 20°C per decade. 100°C over 5 decades. TBC, CMC add to efficiency and make it nearly 50%. GE offering 10%, Pratt promising 15%. They will trade technology to give 25% efficiency.

Plasma spray PVD or Electron beam PVD for making feathers.
 Evolution of TBC materials and thermal spray manufacturing. Zirconia has low conductivity, relatively cheap- beach sand. Yttrium stabilized zirconia also available.

5.1 Requires integrated consideration of system, design and materials and manufacturing

Performance requires is

- ΔT barrier
- Durability
- BC oxidation

Never fight nature. Nature is not to be fought against. Yttria stab Zirconia, is God's gift to gas turbines. Unique metastable phase- tetragonal structure, has unusually high toughness which makes it durable. Low conductivity- can be kept thin.

5.2 Optimally designed layers

Can design the layers to have structure that is optimal for the function desired.

5.3 Transition from Metallic to CMC hot section components

As use increases their problems will reduce like mobiles or cars. This technology needs time to mature. CMC can take-over metals if they can reduce cost.
 Waste heat to power conversion: All waste heat from cars etc. can be used.
 Thermoelectric effect: electron-hole pairs travel down. Titanium oxide is a dirty semiconductor: can make insulator (high seebeck coefficient) or more metallic type. APS TiO_{2-x} (Lee et al.). Can we apply materials on surfaces that can catch the heat back. Lecture Jan 24

6 Liquid Phase Sintering

Wetting: Contact angle has to be lesser than 90° . For liquid has sintering, angle which the two phases form depends on the ration between grain boundary surface

energy and liquid-solid interface energy. Greater the grain boundary surface energy, better the wettability. Ratio has to be at least 1. If

$$\Psi = \text{Dihedral Angle} \quad (1)$$

$$\cos\left(\frac{\Psi}{2}\right) = \frac{\gamma_{gb}}{2\gamma_{sl}} \quad (2)$$

$\gamma_{gb} <$ Insert diagram (later)

For wettability, gb should be the preferred interface. $\gamma_{gb} < \gamma_{sl}$, for wettability. (later)

$\frac{\gamma_{gb}}{\gamma_{sl}}$	Ψ	Microstructure
~ 2	0°	all grains separated

7 Stages of liquid stage sintering

Once the liquid forms, it reduces the interparticle friction considerably. Initial particle rearrangement itself reduces the porosity. This is followed by the Densification. Another requirement is that the solid material can dissolve in the liquid and then re-precipitate out when saturated. Dissolved transport is much faster. Transport in a suspension form is easier. Lower chemical potential regions are porosities (no material) and surfaces of higher curvature. Towards the end, when porosity is all removed, **Ostwald Ripening**. Once the porosity are gone, rapid coarsening of grains.

- Re-arrangement
- Densification
- Ostwald Ripening

7.1 Microstructure of liquid phase sintered materials

Previously, we saw the microstructure of solid sintering product. Here we compare with the microstructure of liquid sintering product. The corners are rounded in Liquid phase sintering product. Intentionally, solid state sintering at high temperature may still lead to rounded shape of microstructure, which means some impurity (silica) is dissolving the material to give a liquid sintered microstructure. Rounded edges are because of prominent Ostwald ripening, coarsening.

For ceramics with anisotropic cubic structures, the microstructure will have preferential growth along some planes. Non-oxides are sintered by liquid sintering. 3rd vs 4th : Greater liquid content, hence diffusion at all junctions so planes grow preferentially according to inherent anisotropy. In low liquid content, the situation is severed at boundaries where there is liquid content compared to those where there is not. Hence the growth is compounded in some direction. 4th has a lot of black regions which signify porosity. It is geometrically not feasible to fill up the pores when liquid content is
Typically for cermets (carbides, borides), liquid content is taken as greater than 5%. For oxides, one usually takes 1%.

Reference: Rahaman, Sintering of Ceramics

7.2 Problems in Liquid Phase Sintering

Some of the major problems in Liquid Phase Sintering are:

- Occurrence of abnormal grain growth
- Microstructure coarsening
- Presence of residual grain boundary phases: May result in degradation of mechanical properties by liquid phase sintering leading to rounded microstructure.

7.3 Driving Force

Free energy change due to removal of powder particles is $A_{sv}\gamma_{sv}$, where A_{sv} is the surface area of the powder particles, V_m is the surface area of the powder particles, V_m is the molar volume of the particles and a is the radius of each particle.

Assume $A_{sv} = 2A_{gb}$ since each grain boundary is formed from two surfaces.

$$\Delta E_d = -(A_{sv}\gamma_{sv} - A_{gb}\gamma_{gb})$$

Application of external pressure helps not only in increasing driving force but also in kinetics.