

Advanced Ceramics
MM 652 IITB
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<https://somphene.github.io/notes/>

Notes
by
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1 Lecture Jan 10

First class intro and logistics.

2 Lecture Jan 17

§2.1 Agglomeration in Nano Powders

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.

§2.1.i Physical breaking of agglomerates

Ball milling can be used to break agglomerates and we get non-agglomerates.

Question 2.1.1. What's the problem if we can ball mill to break down agglomerates?

Re-agglomeration. When does re-agglomeration happen? not during compactification 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.

Question 2.1.2. So what to do to avoid the above problems?

Freeze drying: Phase diagram of water as seen in [fig. 2.1](#). On evaporating, problem occurs when crossing liquid-vapour interface, go to the other side and freeze it. Then it

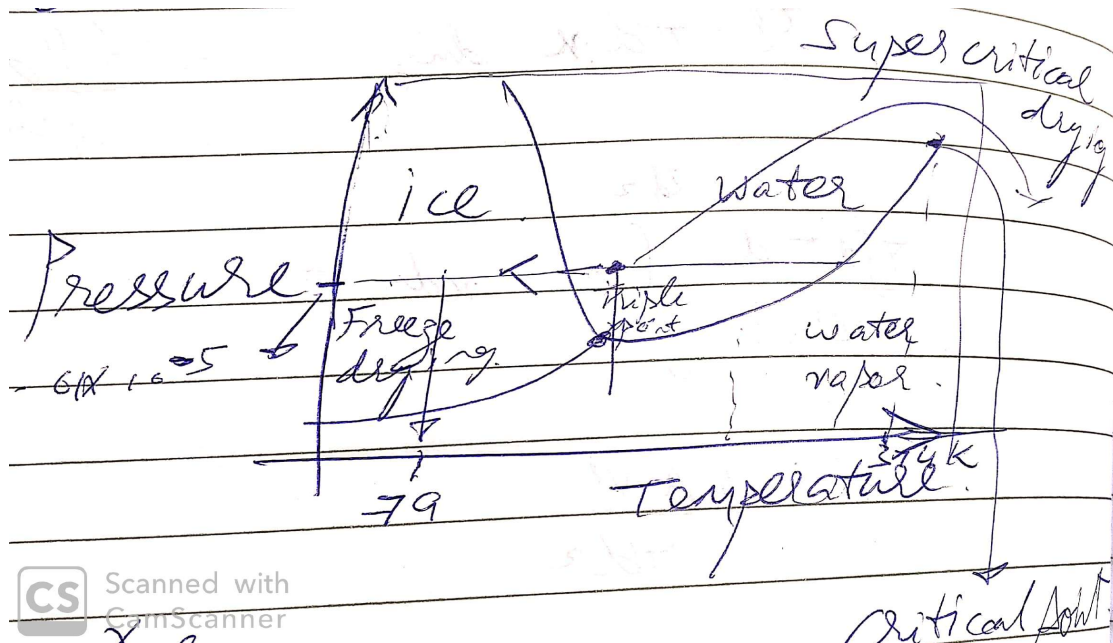


Figure 2.1: Phase diagram trajectory during freeze or supercritical drying

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.

§2.2 Sintering

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.

§2.3 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 2.3.1. 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).

§2.4 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 $600^{\circ}\text{C} - 700^{\circ}\text{C}$. 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 100MPa . To even get cold compact: need 600MPa 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.

§2.5 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 cant be removed. Non-oxides are suitable for ultra-high temperatures $2000^{\circ}C$. TiB_2 with Fe cant be used at $1000^{\circ}C$ 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 $2000^{\circ}C$. However react with TiB_2 to get $TiB_2 - MoSi_2$ which melts at $1700^{\circ}C$, product can be used upto $1250^{\circ}C$. Diborides potential to be used at ultra-high temperature applications hasn't been used.

Question 2.5.1. 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.

3

Lecture Jan 22

§3.1 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.

§3.1.i 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.

§3.1.ii Semiconductors

Pervades most of society.

§3.1.iii Other Applications

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

§3.1.iv 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.

§3.2 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

§3.2.i Families of materials

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

§3.2.ii

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 stores. Implants: to replace hip, spine- metals are not biocompatible- ceramic calcium phosphate is bone-mimicking so body doesn't think of it as external.

§3.2.iii 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 3.2.1. Achieving specified density requires what parameters to be changed in the process?

Shall cover.

§3.3 Ceramic Coating Material

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

§3.4 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 upto 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 20-40 μm . 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.

Applications

Dental implants, pulp extracts.

TS offers a range of innovative spray devices

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

TS allows unprecedented tailoring of microstructures and properties

Don't want air to escape, need tight seals. Put ceramic coatings that abrades 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(abrasables), 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 3.4.1. 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 3.4.2. 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.

§3.4.i 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.

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.

Requires integrated consideration of system, design and materials and manufacturing

Performance requirements is

- ΔT barrier
- Durability
- BC oxidation

Never fight nature. Nature is not to be fought against. Yittria 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.

§3.4.ii Optimally designed layers

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

§3.4.iii 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.

4 Lecture Jan 24

§4.1 Liquid Phase Sintering

Wetting: Contact angle has to be lesser than 90° . For liquid phase sintering, angle which the two phases form depends on the ratio 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

$$\Psi = \text{Dihedral Angle} \quad (4.1)$$

$$\cos\left(\frac{\Psi}{2}\right) = \frac{\gamma_{gb}}{2\gamma_{sl}} \quad (4.2)$$

$\gamma_{gb} < \gamma_{sl}$ 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

§4.2 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

§4.2.i 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 reversed 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: [Ra07]

§4.2.ii 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.

§4.2.iii 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.

5 Lecture Jan 29

§5.1 Sintering Techniques

Without external pressure :

- Pressureless Sintering
- Microwave Sintering
- Reaction Sintering
- Flash Sintering

Spark Plasma sintering has been there for long but hasn't been understood completely. Restricting the grain size to a finer scale becomes difficult. One such example is **two-step sintering**. Hold at a lower temperature after peaking the Typically Al_2O_3 the sintering temperature is $1500^{\circ}C$. It needs much more time, say 20 hrs instead of 5hrs. Counter-intuitive thing is that even though the time is much , the grain size can be resolved much finer. Grain growth was preferentially suppressed compared to densification. For grain growth, going across the grain boundary requires activation energy. However, in densification, transport is along the grain boundary and hence at the low temperatures, it is preferred (refer to phase transformation notes linked: [MM 325 Som Phene Notes](#)).

Parameters to control grain coarsening:

- Slides
- Heating rate

§5.2 Hot Pressing

Enhanced driving force and kinetics. The way hot pressing chamber is, it allows more heat transfer to the powder. In normal sintering, mostly non-contact heating. In the case of hot pressing, conducting die material. Here contact heating by induction. In some ordinary hot press, instead of induction, can press it in a vertical furnace, but usually induction heating for efficient heat transfer. Heating rate varies from $1 - 15^{\circ}/C$. One can get $30 - 40^{\circ}C/min$ for isostatic hot press. But primarily, pressure action contributes significantly. Die has to be able to bear the pressure, conduct electricity and heat. Typical dies that are used goes out of question. Two possibilities: Diboride, but don't want to work with the same boride materials as by adhesion, the sample may get sintered to the die. High strength WC (tungsten carbide), with metallic additive otherwise the Die will crumble. Still not commercial yet. For high temperature processing, typically a graphite die is used. Pressure limit for graphite is up to 50MPa. It's the pressure activity during sintering that helps. With hot pressing, one can get a dense di-boride at $2100^{\circ}C$. Some of these are common with spark plasma sintering. Nearly impossible to measure the actual temperature of the sintering product. For Hot pressing, heating rate and then holding for one or two hours, then the temperature stabilize. Typically $50^{\circ}C$ off from the value at surface. However, if the heating rate is high and holding rate is lower,

then the temperature reading may be off by a larger margin. It can only be used for preparing standard simple shape as well as dimensions for time needed to equilibrate the temperature. Intricate shapes are difficult because extraction will require breaking it. Most ceramics are insulating at room temperature but at high temperatures, they start becoming conducting, this property is used in flash sintering.

§5.3 Hot Isostatic Pressing

Enclosed in fluid and the fluid is pressurized. Cold isostatic pressing in which at room temperature, the green body is put inside a fluid chamber and pressure is applied. Done to make the green density more uniform across the body. Any gaseous medium that doesn't interact with the body. It needs to be pre-sintered and then subjected to hot isostatic pressing.

Question 5.3.1. Till what sinter density should we pre-sinter?

One has to get rid of open porosity because the pressurized gas will go into the pores. After 90% sintering only isolated pores remain. Hence go at least up to 90%.

§5.4 Spark Plasma Sintering

Modification to hot pressing. In addition to uniaxial pressure as in Hot Pressing, a pulsed direct current is applied. Heating rate can go up to $1000^{\circ}\text{C}/\text{min}$ heating rate. Measured sinter temperature is found to be typically one or two hundred degrees lower than hot pressing. Fast process, not equilibrated. The temp measurements are off. Heating is done by a pulsed direct current. Total processing time is 30min. Cooling is also fast. Common die is Graphite. In UC Davis, high strength ceramic dies which allow them to go to higher temperatures. They are able to go to 5GPa. Goes up to 99.99%.

There is no evidence of spark or plasma. Theoretically, spark and plasma cannot be generated. Named after a company. Field assisted sintering (FAST) or Pulsed electric current sintering (PECS). The graphite die will get heated, more effectively. When the ceramic is conductive, it will also get heated. Ultra-high temperature borides are actually conductive. If non-oxides are non-conductive, at high temp, under SPS they get conductive and heated by electrical resistance heating. Dielectric breakdown for Air requires 10^6 V/m but here hardly 50V drop. Hence there's no strong support for this argument. The grain boundaries which form SPS are very clean and perfect. If one does pressureless sintering, hot pressing, one is bound to find some impurity. If silica based, carbonaceous it is found. There is a spark discharge at the gap between the powder particles, the voltage is sufficiently large to cause spark cleaning. Reasons of high heating rate:

- Cleaning and surface activation of particles
- (later)

These are the five methods that lead to high densification. Pulsing optimizes the grain structure as direct current can lead to uncontrolled grain coarsening. With hot pressing hold time 2h, SPS only 3min. WC grain boundary which is nearly perfect and clean after SPS.

§5.4.i Inhomogeneous densification

Multi-stage Spark Plasma Sintering (MSS): hold the sample at intermediate temperatures before reaching the final sintering temperature. Decide the temperatures using a dilatometer, record densification changes. One can get a much more uniform microstructure from surface to the core. The mechanical properties change accordingly.

6 Lecture Jan 31

§6.1 Recap

Last time we talked about SPS and problems with inhomogeneous densification.

§6.2 Microwave Sintering

Metals reflect the microwaves, which can concentrate the energy to cause sparks. Tap water gets heated faster than distilled water in the microwave. Need ions and mobility (conductivity). Silica suspension in Water will be heated non-uniformly. Water gets heated, silica hardly gets heated. Microwave sintering is pressureless sintering. Dimension restriction due to power generation.

§6.3 Microwave and material-microwave interaction

Microwave allowed spectrum of frequencies : 0.915GHz and 2.45 GHz. Other frequencies are used extensively for communication, especially in radar, television and satellite applications.

§6.4 Microwave Heating

Primarily caused by following processes:

- Orientation polarization: caused by influence of electric field to rotate the dipoles and cause electromagnetic repulsion.
- Ionic Conduction: Movement of ions and collisions.

§6.5 Material-Microwave Interaction

With respect to microwave interaction, classification is:

- Transparent or Low Loss materials, where microwaves pass through without any losses.
- Conductors and reflectors (or opaque) which reflect microwaves without any penetration (again no self heating, but excessive reflection can be disastrous).
- Absorbing or high loss materials: which absorb microwaves and dissipate the electromagnetic energy.

§6.6 Microwave heating of Absorbers

Power absorbed per unit volume, $P = \sigma |E|^2 = 2\pi f \epsilon \epsilon' \tan \delta |E|^2$ where E is the magnitude of electric field

σ is the total effective conductivity (via molecular displacements and ionic current)

f is the microwave frequency

ϵ_0 is the permittivity of free space ($\sim 8.85 \times 10^{-12} Fm^{-1}$)

Industrially lower frequency is preferred because penetration depth is more (penetration depth is inversely proportional to frequency).

Once the sintering is at 90% densification, similar rate as compared to usual sintering. If there is too much heating, leads to vapour transport which is not preferred for densification. Heating is in the other direction.

§6.7 Flash Sintering

“Magic Process”

Flash sintering occurs when an electric potential difference is applied across a ceramic powder and is characterized by an electrical power surge at a specific temperature.

§6.8 Methodology

The process is described as :

- A constant DC voltage V (between 10-1000V/cm) is applied across the specimen by means of the wires and the furnace is programmed to heat at a constant rate. On reaching a critical furnace temperature (T_{onset}), the current, I , and concomitantly the electrical power dissipation (VI) occurs rapidly (b/w 10 – 1000mW/mm³)
- The main flash event happens in 15s and most of the sintering itself takes 5s.

A lot of mobile species get lost ($Li_7O_X \rightarrow O_x$ by movement of ions to the surface and the vaporization), close to the high temperatures it may even melt.

§6.9 Typical Setups

Due to problems with melting of wires, Plasma or SPS set up have been used. In addition to high power surge, creation of Frenkel defects, then ionization to form neutral electron-hole pairs. Few researchers have used AC power supplies operating in the low to mid-range of 50-1000Hz and high frequency range of 1MHz.

§6.10 Mechanisms

One of the possible mechanisms: **Thermal Runaway due to Joule heating**: electrical power dissipated V^2/R increases because R decreases with temperature, which leads in turn to an increased Joule heating rate.

This is all for 1st quiz syllabus.

§6.11 Mechanical Behaviour

§6.11.i Fracture Toughness

Griffith's Criteria:

Fracture toughness based on stress intensity factor : $K_{IC} = Y\sigma_C\sqrt{\pi a_c}$

Gives critical(c) mode I fracture.

Question 6.11.1. Do ceramics show plastic deformation?

Of course! Vicker's Indentation is an important characterization technique in which the indent is a plastic deformation.

If defect free, they deform.

Question 6.11.2. What causes deformation? For polycrystals, it is harder to deform?

Dislocation Movement. There have to be at least 5 independent slip systems to be active. Hence easier to deform single crystals. Dislocation movement more difficult in presence of cationic and anionic charges. They raise the stress requirement for the operation of slip systems. In most polycrystalline ceramic materials, there will be less than 5 slip systems that are active at room temperature. At high temperatures, there will be 5 slip systems that are active at strain below the fracture strain. Primary slip system $\{110\} < 1\bar{1}0 >$

- When Vicker's indentation is happening, what causes the deformation at room temperature?

Tip has very high stress concentration which causes both fracture and deformation. Fracture can be suppressed so that energy is not lost in cracking and we get accurate hardness value. Most ceramics have size dependent indentation hardness. The lower the normal load used for indentation, the more the hardness. For the same material, nano-indentation gives smaller indentation than micro-indentation. Need to take many measurements for nano-indent and then take average.

§6.11.ii Indentation Toughness (short Crack Method)

One can use the cracking that happens during vicker's indentation. But then cracking can be used to estimate a parameter for fracture toughness. However, not to denote it as K_{1C} , because this is not truly in mode 1 loading.

$$K_{1C} = 0.018 \cdot H \cdot a^{1/2} \cdot (E/H)^{0.4} \cdot (c/a - 1)^{-0.5} \quad \text{Palmqvist crack model for } c/a < 3$$

$$K_{1C} = 0.016 \cdot H \cdot (E/H)^{1/2} \cdot (P/c)^{3/2} \quad \text{Anstis crack model for } c/a > 3$$

H is the hardness in GPa

2a length of indent diagonal

2c total length of crack

E composite elastic

P indentation load

§6.11.iii Indentation induced cracking

Commonly used are radial and Median. Radial is believed to happen upwards: half-penny kind of shape. Primarily happens when stress is generated. Median is straight down during indentation. Lateral cracking for brittle materials. Radial is parallel to the surface vs Lateral gives chips off all material around indentation. Lateral cracks also grow parallel to the surface (see image later).

7

Lecture Feb 5

§7.1 Processing and Mechanical Behaviour

We completed processing: looked at microwave sintering and flash sintering. Microwave: internal heating due to rotation of dipoles and translation of ions causing loss of energy by resistance. Microwave radiation is lost quickly, penetration depth is low for higher frequency. For smaller components, higher frequency may be faster. Flash Sintering is magic- not understood completely. Sudden surge in the power which leads to sintering. Resistivity decreases rapidly at some given temperature, onset temperature from which rapid decrease. Hence at certain combination of thermal runaway. We also looked at mechanical behaviour based on Griffith's criterion (from energy balance considerations). For sharp indentation test like Berkovich or Vickers, stress intensity causes cracking, loss of energy. If we apply less indent load, better as maximum energy is used for plastic deformation and minimum loss in forming crack. Lateral cracking leads to chipping of materials which is harmful.

§7.2 Bending Mode

Compressive testing can be done but its usually on the higher side. Most reliable way to measure hardness is by bending- either three point or four point (preferred). The entire specimen is not under tensile or compressive stress. Uniaxial compression load is applied from the top. There are two regions : bottom in tensile mode and top in compressive stress. Three point mode can have misalignment hence not preferred. Bottom is where the crack will be initiated hence need to be polished. The vertical faces also need to be polished as its lower part is in tensile. This is more close to Mode 1 failure.

$$\text{Flexural Strength}(\sigma_f) = \frac{3 \times F_{max} \times a}{W \times t^2}$$

where F_{max} is the maximum load, W is the beam width, t is the specimen thickness, a is the distance between two points of balls.

Definition 7.2.1. Fracture toughness is resistance to propagation of a pre-existing crack.

Crack initiation may take place at some other point than the notch we make for measurement.

Most ceramics are made by sintering, which means porosity ($\sim 0.01\%$) will stay. This has an important effect on the fracture toughness. Especially, if the crystal structure has anisotropic (alumina has HCP/ corundum structure), there is a prominent effect during cooling from sintering or operation temperature, there is differential contraction on either side of the grain boundary. This leads to strain mismatch which induces a stress at the grain boundary.

§7.3 Effect of Residual Strain across grain boundaries

Strain build up is dependent on the CTE mismatch and temperature range and provided there is no plastic deformation. Plastic deformation can nullify the residual stress at the

grain boundary. If there is an impurity, it is primarily present at the grain boundary. There is a propensity that the stress may propagate into a crack. For crack to propagate, surfaces to be formed which requires energy. Strain energy is localized in a volumetric region around the grain boundary. Volume over which the energy is available is varying as cube of the grain boundary length (since the strain energy per unit volume is staying constant). Whereas energy required to create new surface is varying as square of the grain boundary length.

$$\epsilon_{gb} = \Delta\alpha\Delta T(1 - \nu)$$

Rate of release of internal strain (U_i) with growth of crack of length C :

$$\frac{dU_i}{dC} = \frac{\sigma_{gb}^2(l_b - C)}{12E(1 - \nu^2)}$$

Where σ_{gb} is the grain boundary stress energy, E is the elastic modulus and l_b , is the length of the common interface between the two phases.

Critical elastic strain (ϵ_{gbc}), resulting in spontaneous fracture along the boundary is given by $\epsilon_{gbc} = \left(\frac{24\gamma}{l_b}\right)$ (later).

§7.3.i Fracture mode depending on the crystal structure

Monolithic Al_2O_3 , having hcp (anisotropic) showing intergranular fracture, monolithic MgO having cubic (isotropic) crystal structure, show intragranular fracture. In the image, fracture surface is being looked at from the top. Some valleys and protrusions will be seen in intergranular fracture. In transgranular (intragranular), there is less change in direction, there is smoother topography.

For anisotropic predominantly intergranular, isotropic it is through the grain (intragranular)

§7.4 Toughening Mechanisms

Presence of anisotropic grains helps by crack deflection.

§7.4.i Transformation Toughening in Yttria doped ZrO_2

There is hell lot of microcracks due to volume expansion during tetragonal to monoclinic structure on cooling down. Hence, people wanted to stabilize the metastable tetragonal phase. Why does oxygen vacancy help? Disorder or entropy becomes high which lowers the free energy and stabilizes the tetragonal phase. Tendency to transform to monoclinic. Doping is not the only way. Grain size has a major effect. Presence of dopant increases entropy but also finer grain size, which constraints the tetragonal phase from getting converted due to presence of excess surface energy of grain boundary.

Question 7.4.1. Why isn't Alumina used as the dopant?

Maybe because of size mismatch. Yttria is better.

Some remnant monoclinic phase leads to bad mechanical property. Spontaneous fracture is prevented. Then people discovered that there is advantage in fracture toughness due to transformation toughening. High stress surrounding the crack tip reduces the crack propagation. Yttria stabilized is known as TZP (tetragonal zirconia polycrystal).

Y-TZP means the dopant is Yttria. Partially doped for ionic conductivity. **Resistance curve effect** is the increase in the fracture toughness with increment in the fracture toughness. When there is an initial crack formation, not much of the material is under the stress field. After some time, it saturates. Transformation zone, partial zone and extended zone. End of mechanical properties.

§7.5 Tribology

§7.6 Introduction

Tribology is wear and tear of the surface.

Question 7.6.1. Is Tribology only based on surface properties?

Breaking of bonds means fracture. Fracture is a bulk property. Property at the surface can change and can be different than that of the bulk but underlying structure is the same as that of the bulk material. It is highly dependent on the conditions and environment. Tribological applications are one of the major avenues for structural ceramics. Metals are usually coated with ceramic materials.

Question 7.6.2. How does friction and wear get initiated?

It starts with interlocking. One surface may get interlocked with the other due to surface roughness.

One situation is two asperities directly in touch head on at the tips. There will be a normal load. Average pressure is not the same because local pressure at tips will be very large. Under high pressure, there is high probability of welding or adhering. This is more for materials with lower melting points. Softer the material, the adhesion at the contact between asperities, the greater the hardness. On movement of surface, there will be fracture to break away from the adhesion. For a very high melting ceramic material, there may be not much adhesion so not necessary to fracture.

Another possibility is two surfaces interlocked. In this case, either fracture or bending. Hence fracture resistance is a factor on which tribology depends.

It leads to removal of the material. Progresses deeper into the material with progress in time. Removal of the material can either lead to formation of debris or it can lead to sticking of surfaces. Or it may be a third body which remains at the tribo-contact or transfer of material from one surface to another surface.

§7.6.i Degree of Wear

Degree is classified as:

- Mild: worn away very little
- Severe: where the body surfaces are changes and the size of the worn particles/debris exceeds 100 microns.
- Catastrophic Wear: due to continued or very rapid severe wear Where the life expectancy of the material is reduced enormously

§7.6.ii Quantification of degree

Wear volume and wear rate

Wear volume is the amount of material removed during interactive relative motion.

Wear rate (in mm^3/Nm) does not denote the rate of material removal but the severity of wear damage with load and interactive distance. Two parameters which influence: Normal load (external parameter). Normalize with the magnitude of normal load. Similarly time hence normalize with the interactive distance. The wear rate depends now on the severity of wear damage and not the distance or overall material. Wear rate may actually come down even as wear volume is being increased.

Bibliography

[Ra07] Mohamed N Rahaman. *Sintering of ceramics*. CRC press, 2007.