Non - Metallic Materials

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Module - 07
Processing of non - metallic materials, sintering and microstructure development
Lecture - 35
Introduction to Sintering, Sintering Mechanism

Welcome to my course Non-Metallic Materials and today, we are in module number 7 that describes Processing of non-metallic materials, sintering and microstructure development. And, we are in lecture number 35, where I will introduce the concept of Sintering and various Sintering Mechanisms.

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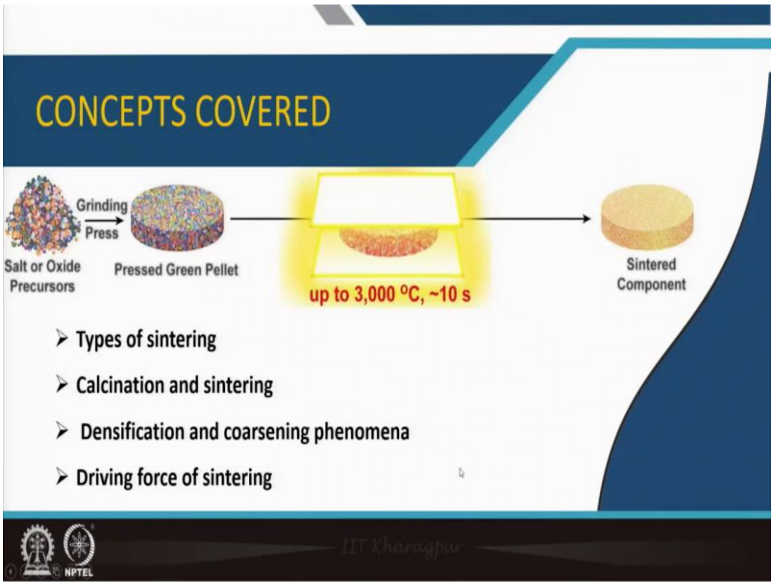

CONCEPTS COVERED

Salt or Oxide Precursors → Grinding Press → Pressed Green Pellet → up to 3,000 °C, ~10 s → Sintered Component

- Types of sintering
- Calcination and sintering
- Densification and coarsening phenomena
- Driving force of sintering

So, to start with this is a special operation particularly for oxide ceramics and also other types of ceramics glass materials and also powder metallurgy. So, we will talk about the various types of sintering, then we will differentiate the concept of calcination and sintering and followed by densification and coarsening phenomena of the particles and finally the driving force of sintering.

So, as you can see that the powders ceramic powder initially is grind to form finer particles to increases surface area, then with a binder it is pressed. So, this is a green pellet and the green pellet is finally, sintered at high temperature. We can go as high as 3

3,000 degree Celsius in certain occasions. And, we can vary the sintering time, we can vary the ambient of the sintering they have their effect in microstructure development and finally, we get the sintered product, which is a dense ceramic material.

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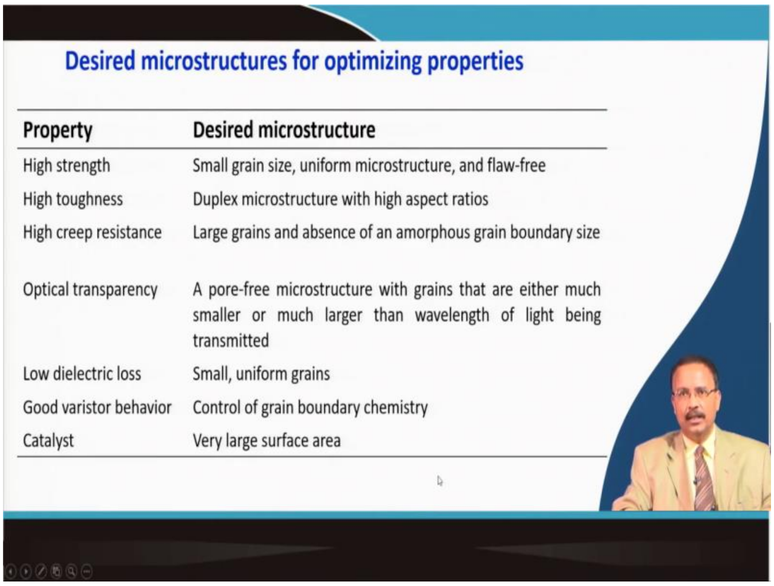

Desired microstructures for optimizing properties

Property	Desired microstructure
High strength	Small grain size, uniform microstructure, and flaw-free
High toughness	Duplex microstructure with high aspect ratios
High creep resistance	Large grains and absence of an amorphous grain boundary size
Optical transparency	A pore-free microstructure with grains that are either much smaller or much larger than wavelength of light being transmitted
Low dielectric loss	Small, uniform grains
Good varistor behavior	Control of grain boundary chemistry
Catalyst	Very large surface area

So, the sintering it has immense importance in controlling the various properties of ceramic material. And you are now familiar with the strength of the oxide non-metallic materials and usually smaller grain size uniform microstructure, where the grain size does not they are homogeneous.

They do not change much uniform microstructure, which is flaw free that will give high strength. Toughness is usually gotten with duplex microstructure where the aspect ratios are high. Then, creep resistance that is usually in order to have a good creep resistance we should have larger grains and any absence of amorphous phase along with the grain boundaries.

For optical transparency, very first slides I told that pore free microstructure with grains that is either much smaller or much larger than the wavelength of light is being transmitted. So, that is required. So, very high degree of sintering almost marginal porosity or no porosity is required for this.

For the dielectric material having low dielectric loss small and uniform grain size is one of the primary requirements. We will talk about the varistor behavior in certain ceramic material. So, there you will see that the grain boundary chemistry, the control of it is important. For catalyst very large surface area is required. So, for microstructure control we will adopt the sintering procedure. So, it is a very important procedure in case of ceramic processing.

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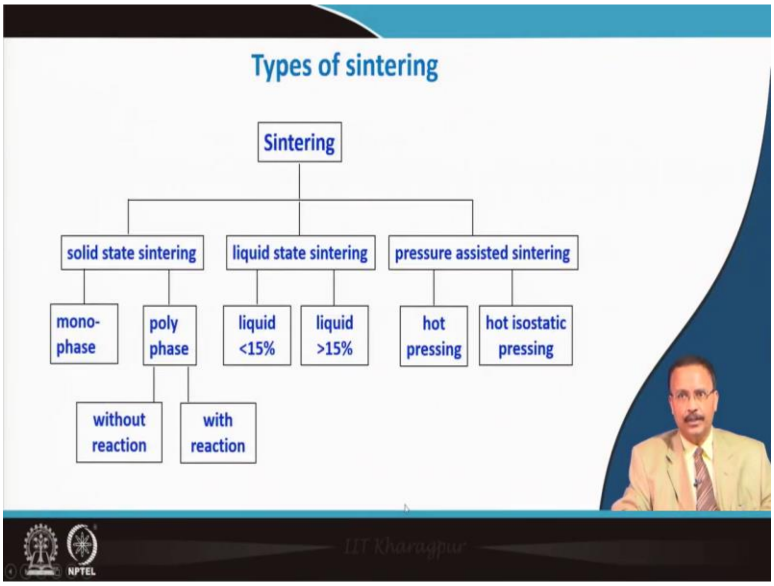

Types of sintering

- Sintering
  - solid state sintering
    - mono-phase
    - poly phase
      - without reaction
      - with reaction
  - liquid state sintering
    - liquid <15%
    - liquid >15%
  - pressure assisted sintering
    - hot pressing
    - hot isostatic pressing

So, we can categorize the sintering in different types of sintering. The first one I will be describing the solid state sintering which can have mono-phase only one type of material or polyphase different types of materials are sintered together. So, this polyphase material either can undergo reaction or without reaction during the sintering.

Another type of sintering mechanism is liquid phase sintering where a liquid forms while the sintering operation is carried out and usually the liquid content varies. So, in certain case it is less than typically 15 volume percent or in other case it is more than that. So, liquid phase sintering we will cover part of another lecture.

And, third one is a pressure assisted sintering – sometimes we apply pressure as well as along with the temperature. So, this is called hot pressing and sometimes this hot pressing is done uni-axially, sometimes it is bi-axially or sometimes it is a isostatic kind of thing pressure is applied from all direction. So, then we call it is a Hot Isostatic Pressing, which is abbreviated as HIP.

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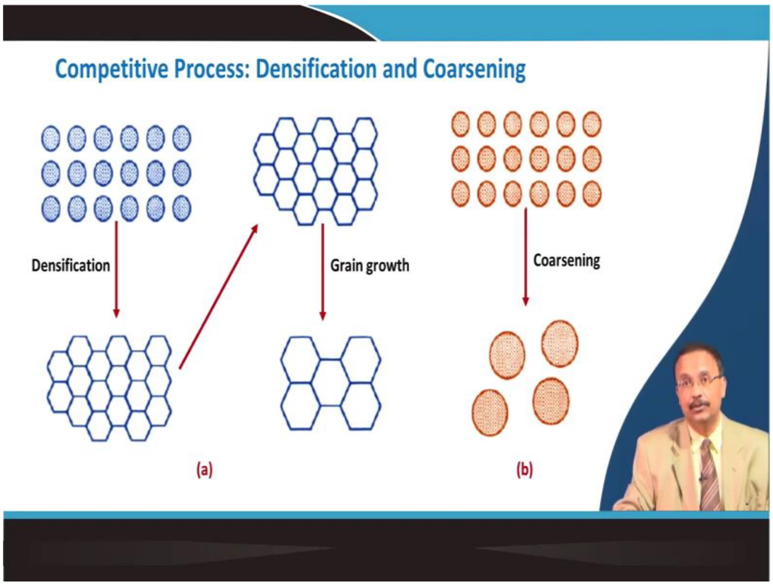

Competitive Process: Densification and Coarsening

So, sintering there are two competitive process and that is very interesting. You are starting with the normal particles I have taken it is a uniform particle size and it can be densified something like this. So, the curvature is gun of the particle, it is replaced by almost straight kind of boundary. So, from particle it is transforming into grain and there is no porosity in between the grains. So, this is called densification.

And, once the densification is completed then if the grain growth starts, so, this individual grains they grow then we call it is a grain growth and then finally, you see that the grain size has increased and it is very much different from the initial particle size. So, that is the pure densification. Sometimes what happen that this particle they do not undergo this kind of grain growth. So, this kind of microstructure it is not formed, but instead the individual particle they are fatter they grow.

So, we call this is a coarsening. Coarsening is not good for most of the applications; some of the applications probably coarsening is welcome, but very few, but mostly we need densification and not the coarsening. So, the particle size will grow, no grain formation will be there, porosity will not be affected or reduced or so, this kind of thing is not required. So, coarsening as such should be avoided.

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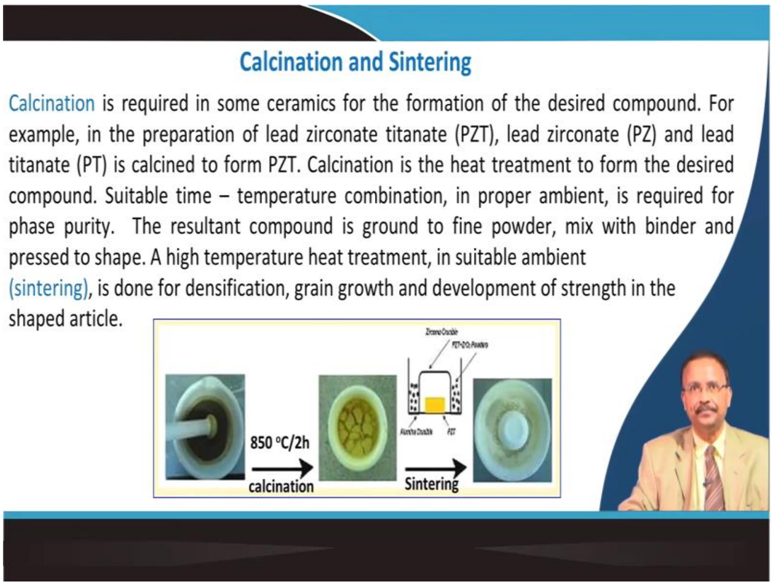

Calcination and Sintering

Calcination is required in some ceramics for the formation of the desired compound. For example, in the preparation of lead zirconate titanate (PZT), lead zirconate (PZ) and lead titanate (PT) is calcined to form PZT. Calcination is the heat treatment to form the desired compound. Suitable time – temperature combination, in proper ambient, is required for phase purity. The resultant compound is ground to fine powder, mix with binder and pressed to shape. A high temperature heat treatment, in suitable ambient (sintering), is done for densification, grain growth and development of strength in the shaped article.

So, calcination is the terminology that is used that is also a heat treatment process and that is used when two compounds they are reacting with each other. One example I have cited say you know about the ferroelectric ceramics is which is lead zirconate titanate. So, their lead zirconate is reacted with lead titanate to form PZT at high temperature.

Typically, 850 degree Celsius for about 2 hours in air ambient that is that heat treatment is used to form the for the phase PZT lead zirconate titanate. And, then after that you take this powder out and then you ground it in a mortar pestle like this and then add the binder and press it in the form of a pellet and then you heat treat it. Here in this case since lead is lead oxide is volatile, so, we usually heat it in an ambient of lead zirconate and zirconium oxide mixture.

And, then you again heat treat it at higher temperature so that the densification and grain growth occurs coarsening is not required or not welcome for this process and eventually you get a sintered product. So, calcination is for compound formation and sintering is to develop the strength.

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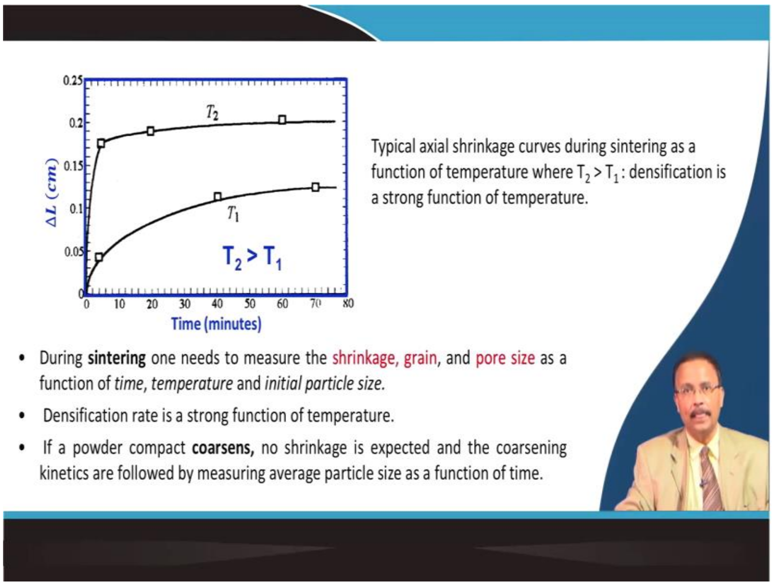

Typical axial shrinkage curves during sintering as a function of temperature where $T_2 > T_1$: densification is a strong function of temperature.

- During **sintering** one needs to measure the shrinkage, grain, and pore size as a function of *time, temperature* and *initial particle size.*
- Densification rate is a strong function of temperature.
- If a powder compact **coarsens,** no shrinkage is expected and the coarsening kinetics are followed by measuring average particle size as a function of time.

Now, the important part of sintering is that the shrinkage should take place. So, shrinkage is required so that the porosity inside the material they are driven out and grain growth takes place. So, the material the physical dimension of the pellet or any of the material, which you are pressing that material should have a considerable amount of shrinkage.

So, if I plot this shrinkage at two different temperature, one is relatively higher temperature as compared to the other one you will see that as the time elapse then the shrinkage is more and then finally, it saturates. So, if you go to high temperature you can see that your densification is more. So, there is more shrinkage here it is taking place as compared to the low temperature sintering.

So, therefore, sintering temperature is one of the important parameters and also time initially you see the shrinkage is more at lower time duration and after that it almost saturates it does not mean much if you keep this at relatively for higher duration. So, this is important that the temperature of sintering is important and as a thumb rule if the melting temperature say is T m about 70 percent of that melting temperature you will have to raise during sintering and then you can sinter the material.

So, during sintering one actually measure the shrinkage the grain as well as pore size as a function of time temperature and also initial particle size. And, as I said densification is a strong function of temperature and if a powder coarsens then no shrinkage is expected and the coarsening kinetics are followed by measuring the average particle size as a function of time and usually it grows fat, so, that is not desirable.

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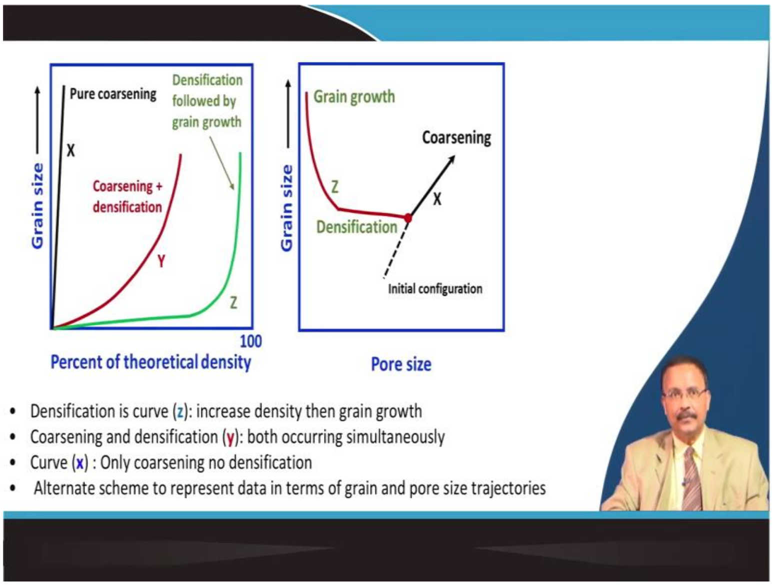

- Densification is curve (z): increase density then grain growth
- Coarsening and densification (y): both occurring simultaneously
- Curve (x) : Only coarsening no densification
- Alternate scheme to represent data in terms of grain and pore size trajectories

So, this concept if I pictographically show, then you see there are three types of graph the first one where only coarsening is taking place. So, grain size or I should say the particle size is abruptly grown here and the third one is initially the grain size is small and after that the grain growth takes place.

So, this is densification initially take is taking place followed by the grain growth and usually it is in the intermediate curve which is actually achieved where both densification and grain growth are simultaneously occurred. So, the same kind of thing in this view graph you can see the same phenomena.

So, your starting point is somewhere here. So, if only coarsening is taking place then you see the pore size is increased, grain size is also increased, but pore size is not reduced. So, there is no sintering taking place. If you go by this curve z you see there the pore size is reduces followed by the grain growth.

So, here densification is taking place followed by the grain growth. So, it is the same kind of thing is plotted into different manner. So, this three types of curve is very important in case of the ceramics and x the curve x is not desirable and we will see that how it can be controlled.

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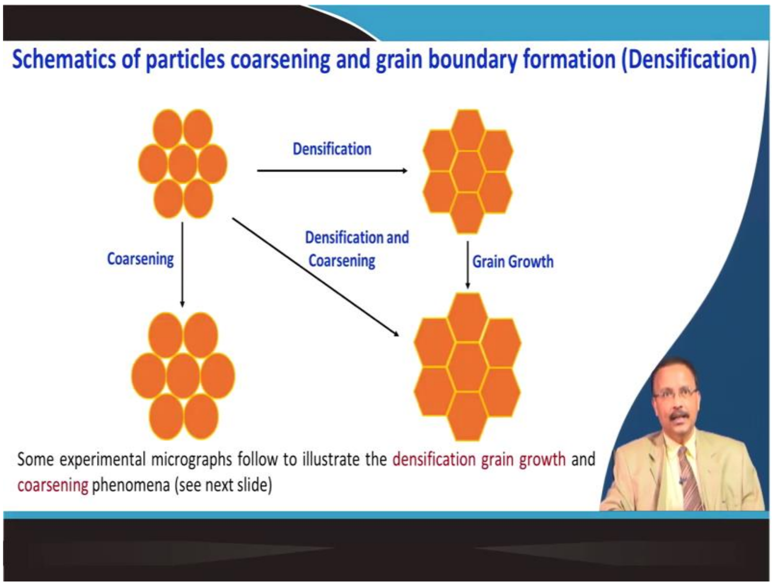

Schematics of particles coarsening and grain boundary formation (Densification)

Densification

Coarsening

Densification and Coarsening

Grain Growth

Some experimental micrographs follow to illustrate the densification grain growth and coarsening phenomena (see next slide)

So, if I show you the schematically you see that it is coarsening taking place, here it is densification that is taking place followed by the grain growth and for the y curve densification and grain growth they are simultaneously occurring.

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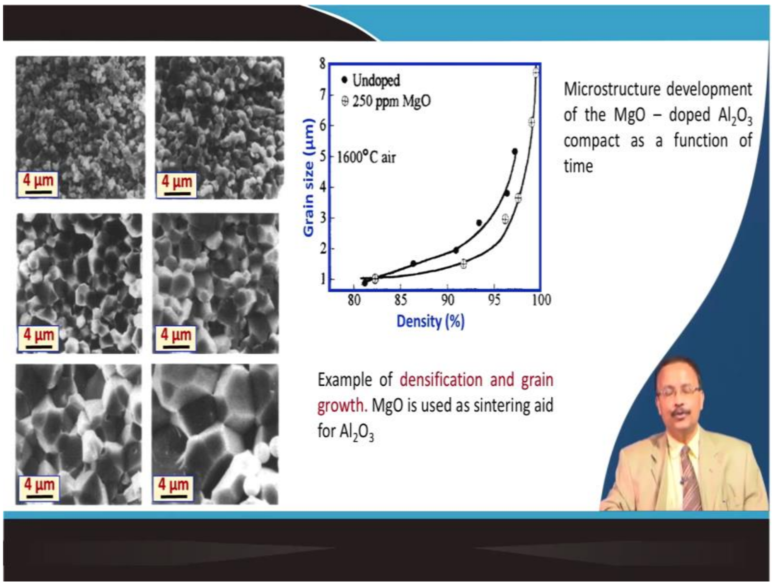

Microstructure development of the MgO – doped Al_2O_3 compact as a function of time

Example of densification and grain growth. MgO is used as sintering aid for Al_2O_3

So, if you see the microstructure typically, you know that magnesium oxide dopant we have used for aluminum dioxide to make for example, the cover for the sodium vapour lamp, which is almost translucent in nature. So, the light can pass and here the densification is very much important.

As you can see the starting particle something like this, then it is progressively sintered. So, the porosity they are gone and then the grain growth is taking place as a function of temperature as well as time. And finally, you get this pore free kind of microstructure nice faceted growth. So, if you have a undoped material which is pure alumina you see here densification is taking place along with the grain size increment.

So, this is here, but you cannot densify it more because it will be taken up by the grain growth, but if you see the same kind of material sintered in same type of temperature here you can see that densification is quite good and then it is followed by the grain growth. So, dopant really helps in case of the sintering and we therefore, term is a sintering aid.

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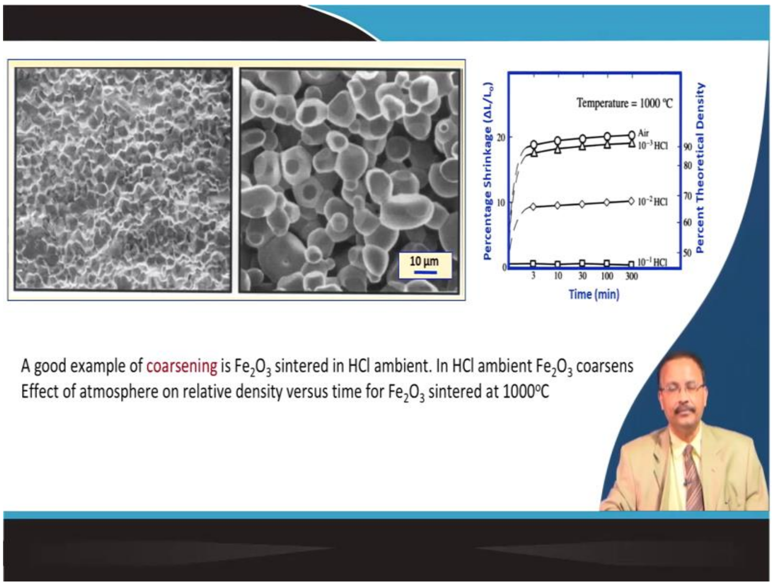

A good example of coarsening is Fe_2O_3 sintered in HCl ambient. In HCl ambient Fe_2O_3 coarsens
Effect of atmosphere on relative density versus time for Fe_2O_3 sintered at 1000°C

In certain case the ambient of sintering is important. Here one example I have shown that is iron oxide which is sintered in HCl ambient, acidic ambient. So, in acidic ambient it just coarsens and you will see that only the particle growth has taken place, but this black portions of porosity.

So, lot of pores are there. So, if you sinter it in air, then the shrinkage is more about 20 percent shrinkage is taking place. But, you progressively increase the HCl concentration, then percent shrinkage is actually this is quite less and you will not get sintering as such in this type of material.

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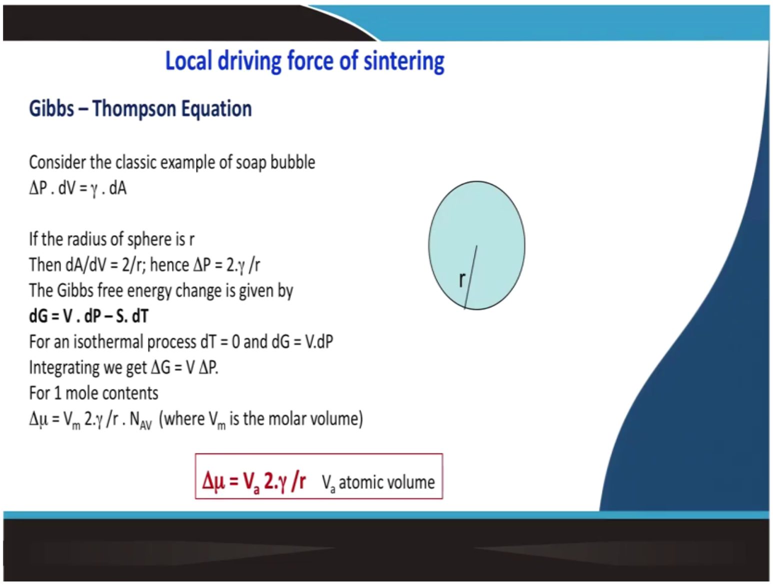

Local driving force of sintering

Gibbs – Thompson Equation

Consider the classic example of soap bubble
$\Delta P \, . \, dV = \gamma \, . \, dA$

If the radius of sphere is r
Then $dA/dV = 2/r$; hence $\Delta P = 2.\gamma / r$
The Gibbs free energy change is given by
$dG = V \, . \, dP - S. \, dT$
For an isothermal process $dT = 0$ and $dG = V.dP$
Integrating we get $\Delta G = V \, \Delta P$.
For 1 mole contents
$\Delta \mu = V_m \, 2.\gamma / r \, . \, N_{AV}$ (where V_m is the molar volume)

$\boxed{\Delta \mu = V_a \, 2.\gamma / r \quad V_a \text{ atomic volume}}$

So, now we will have to understand what is the local driving force for the sintering and we will take help of the well known Gibbs-Thompson equation. So, if I consider a classic example of a soap bubble, then the pressure change and the volume that is equated with the surface tension and the increase in the area.

So, I have considered the radius of that soap bubble is r, then we have differentiated the area and the volume dA by dV. So, you know that for spherical it is 4 by r square and for the volume it is 4 by 3 pi r cube. So, if you do dA by dV you will get 2 by r. So, pressure difference you will get this dA by dV. So, that comes to be around 2 gamma by r for a perfect spherical particle.

Now, if you calculate the Gibbs free energy change we know that fundamental equation dG equal to V dP minus S dT. So, if I consider is a isothermal process then dT is 0. So, dG is equal to V dP. So, if you integrate it you get del G equal to V del P. So, for 1 mole of the contents, you know that this free energy is transferred to or denoted as the chemical potential difference.

So, I will put it back and you get the molar volume into this del P term and the Avogadro number. So, this is the molar volume. So, we get this the change in the chemical potential is this atomic volume and the surface energy and it is dependent on the radius of the particle, we will be using this relation.

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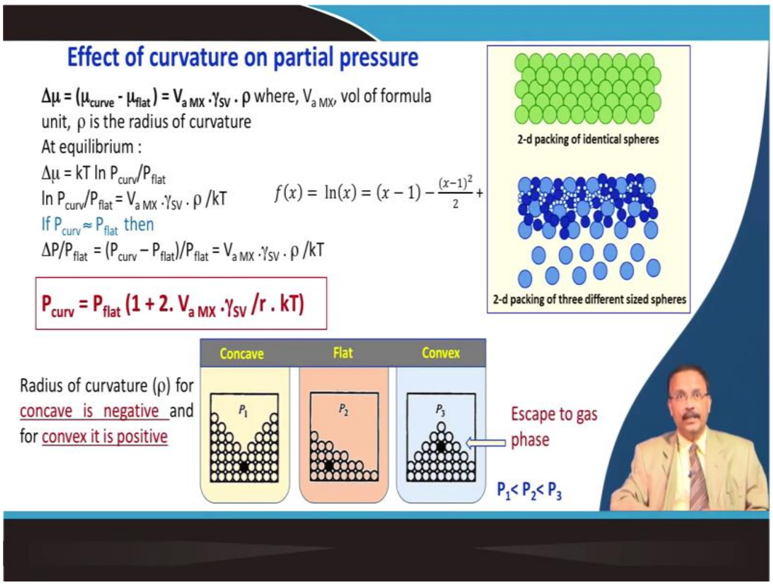

Effect of curvature on partial pressure

$\Delta\mu = (\mu_{curve} - \mu_{flat}) = V_{a\,MX} \cdot \gamma_{SV} \cdot \rho$ where, $V_{a\,MX}$, vol of formula unit, ρ is the radius of curvature

At equilibrium :

$\Delta\mu = kT \ln P_{curv}/P_{flat}$

$\ln P_{curv}/P_{flat} = V_{a\,MX} \cdot \gamma_{SV} \cdot \rho /kT$

$f(x) = \ln(x) = (x-1) - \frac{(x-1)^2}{2} +$

If $P_{curv} \approx P_{flat}$ then

$\Delta P/P_{flat} = (P_{curv} - P_{flat})/P_{flat} = V_{a\,MX} \cdot \gamma_{SV} \cdot \rho /kT$

$$\boxed{P_{curv} = P_{flat}\,(1 + 2.\,V_{a\,MX} \cdot \gamma_{SV} /r\,.\,kT)}$$

Radius of curvature (ρ) for concave is negative and for convex it is positive

$P_1 < P_2 < P_3$

So, the initial particle size as you can see it is a curved surface and there are various types of particle inside a material when you are going to center it. So, there is a various types of curvature that is available. So, if you consider a 2D packing of identical sphere it is something like this the curvatures are almost same, but here you can see there are different types of curvature of the material before sintering.

So, if you see the change in chemical potential that is given by this relation just I showed you that V a MX is the volume of a formula unit of a typical ceramics, which are ionic in nature; MX is the formula of it NaCl kind of thing and rho is the radius of curvature. So, if I consider that it is of different types of curvatures are there so, radius of curvature will be different, but for a spherical this is 1 by r 1 plus 1 by r 2.

So, r 1 is equal to r 2, so, it will be 2r. So, I can have a relation of this change in chemical potential is kT into ln of partial pressure of the curve surface by partial pressure or pressure on the flat surface. So, that relation is valid. So, this ln of this relation I can relate it with the change in chemical potential. So, this is coming and you know the Taylor series of ln x.

So, if I consider that the curve pressure on the curve surface is almost equal to that of the flat surface then this relation is valid. So, this is x minus 1. So, this is P curve by P flat is x and x is very small. So, you can relate with this equation, which you do a small algebraic operation and you will get the pressure on a curve surface relation with the pressure on the flat surface.

So, here you see that if you have a curvature which is positive in nature then the second term is positive. So, for the convex surface you know that it is positive radius of curvature, for concave surface it is negative. So, partial pressure sorry pressure on the concave surface it is less than the pressure of the flat surface and that is again less from the pressure on the convex surface.

So, what does it tell you? That this pressure on top of this concave surface that is less than the pressure on this material which is convex in nature. So, if the pressure is high then this atom it has a tendency to go out, right. So, it can it will go out in this free space to increase the partial pressure and here the reverse is true. So, that is the implication of a curve surface on it is partial sorry, curve surface on the pressure on a curved surface.

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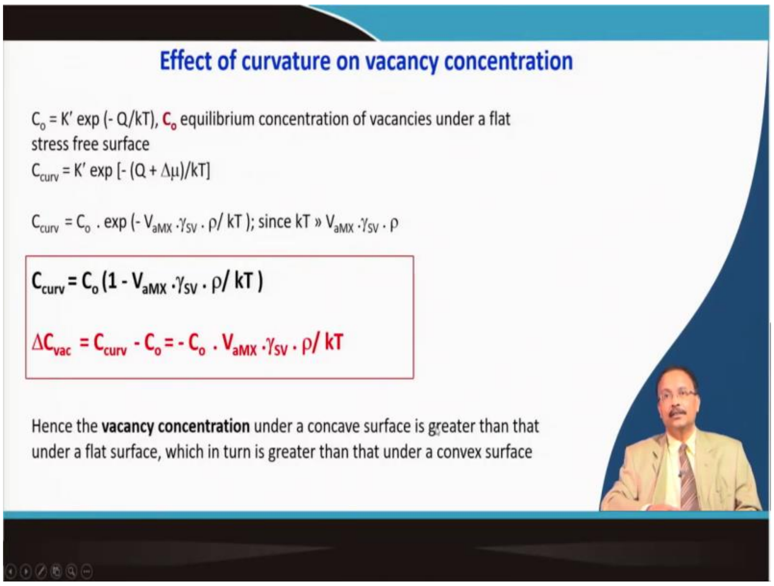

Effect of curvature on vacancy concentration

$C_o = K' \exp(-Q/kT)$, C_o equilibrium concentration of vacancies under a flat stress free surface

$C_{curv} = K' \exp[-(Q + \Delta\mu)/kT]$

$C_{curv} = C_o \cdot \exp(-V_{aMX} \cdot \gamma_{SV} \cdot \rho/kT)$; since $kT \gg V_{aMX} \cdot \gamma_{SV} \cdot \rho$

$$\mathbf{C_{curv} = C_o(1 - V_{aMX} \cdot \gamma_{SV} \cdot \rho/kT)}$$

$$\Delta C_{vac} = C_{curv} - C_o = -C_o \cdot V_{aMX} \cdot \gamma_{SV} \cdot \rho/kT$$

Hence the **vacancy concentration** under a concave surface is greater than that under a flat surface, which in turn is greater than that under a convex surface

Now, the vacancy is also depends on the curvature of the surface. So, I can treat the equilibrium vacancy concentration if I term it as C 0 that under a flat stress free surface this relation is valid, right. So, this Q is now it has an additional term of del mu, which is related energy the chemical potential for the otherwise flat surface if it is either flat sorry, either convex or concave then this additional energy term will come into picture.

And, usually the term kT here, so, I have just replaced this with the value of del mu which I have derived earlier. So, usually this kT term is much much larger because you are doing the heat treatment at very high temperature. So, this is very much larger than this term.

So, then again the Taylor series you can apply and you can just simplify it with 1 minus this value. So, the curve surface the concentration of the vacancy in fact, the vacancy change is given by this relation. So, that tells you that under a concave surface it is greater. So, vacancy is more under a concave surface than under a flat surface, which in turn is greater than that under a convex surface.

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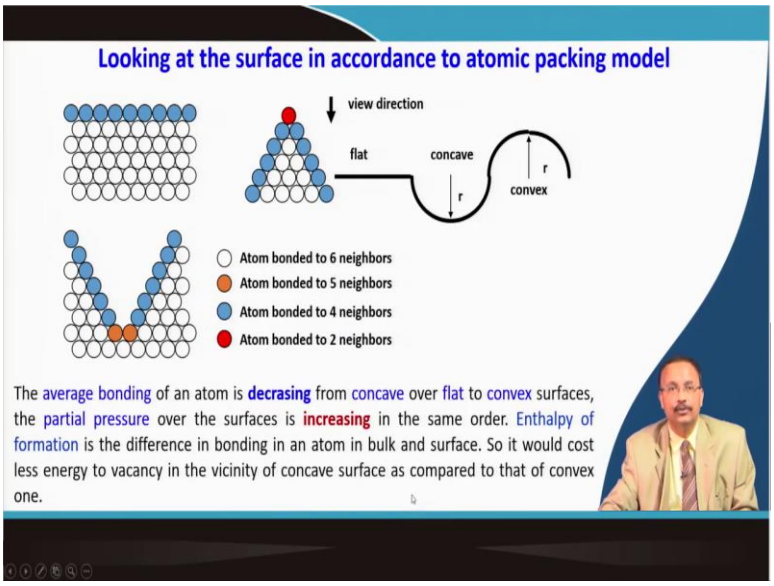

Looking at the surface in accordance to atomic packing model

- ○ Atom bonded to 6 neighbors
- ● Atom bonded to 5 neighbors
- ● Atom bonded to 4 neighbors
- ● Atom bonded to 2 neighbors

The average bonding of an atom is **decrasing** from concave over flat to convex surfaces, the partial pressure over the surfaces is **increasing** in the same order. Enthalpy of formation is the difference in bonding in an atom in bulk and surface. So it would cost less energy to vacancy in the vicinity of concave surface as compared to that of convex one.

So, that relation tells you that. So, I tried to explain it you see that this vacancy concentration that actually depends on the atomic packing under this three configuration the first one is a flat surface. So, here if you see a bulk atom it is bonded with 6 nearest neighbors. So, atom bonded to 6 neighbors.

Then if you consider an atom in the concave surface that is bonded to 5 such neighbor; if you consider atom on this surface on a flat kind of surface then it is bonded with four neighbors that is this one and if you consider it is on a convex surface it is bonded to two neighbors. So, progressively bulk, then concave, then flat and then finally, convex. So, it is going down like this.

So, the average bonding of an atom decreasing from concave over flat to convex surface, the partial pressure over the surfaces is increasing in the same order just we have seen. Now, enthalpy of formation of this defect the vacancy that is the difference in bonding in an atom in bulk and surface.

So, that you can see that it would cost less energy to vacancy in the vicinity of the convex, sorry, concave surface as compared to that of the convex one. Because the difference is progressively less; it is 5 and this one is 6. So, it is only 1; in case of convex it is 6 minus 2. So, that is 4. So, therefore, we can see that the vacancy concentration under a concave surface is more as compared to the convex one.

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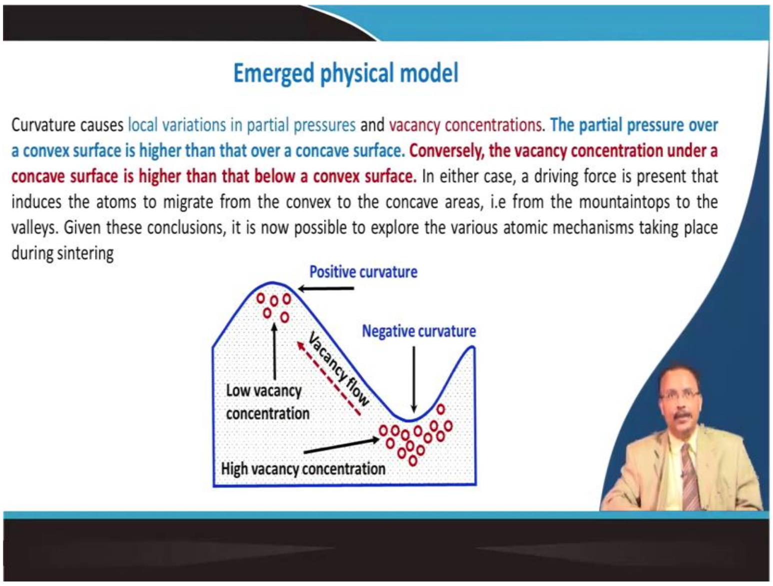

Emerged physical model

Curvature causes local variations in partial pressures and vacancy concentrations. **The partial pressure over a convex surface is higher than that over a concave surface. Conversely, the vacancy concentration under a concave surface is higher than that below a convex surface.** In either case, a driving force is present that induces the atoms to migrate from the convex to the concave areas, i.e from the mountaintops to the valleys. Given these conclusions, it is now possible to explore the various atomic mechanisms taking place during sintering

So, the physical model that is emerging out that is quite interesting you see that the curvature causes a local variation of the partial pressure and vacancy concentration first we have treated the partial pressure and second, we have treated the vacancy concentration.

Now, the partial pressure over a convex surface is higher than that over a concave surface. Conversely, the vacancy concentration under a concave surface is higher than that below a convex surface. So, that we have evaluated in the last couple of slides this concept.

So, in either case the driving force is present that induces the atoms to migrate from the convex to concave surface. So, you see that here the vacancy concentration is more; here the vacancy concentration is less. So, the vacancy will move from this side to that side. What does it tell you? It tells you that the atoms they will be moving from this side to that side and here the pressure is more.

So, it is pressing due to this positive curvature it is pressing the atom to move from this to here, right. So, from mountain tops to the valleys, so, atom moves from the mountain top to the valleys. Given this conclusions it is now possible to explore various atomic mechanism that takes part in sintering. So, this concept is utmost importance for you to understand it.

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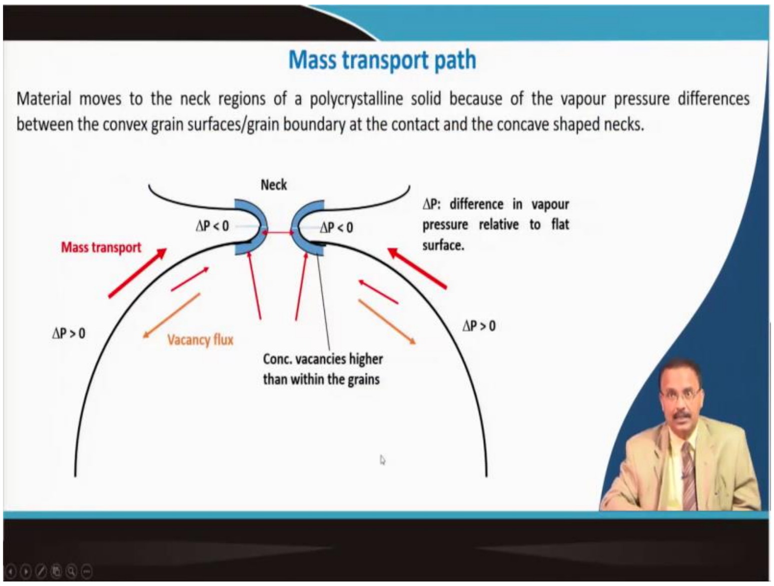

Mass transport path

Material moves to the neck regions of a polycrystalline solid because of the vapour pressure differences between the convex grain surfaces/grain boundary at the contact and the concave shaped necks.

ΔP: difference in vapour pressure relative to flat surface.

Conc. vacancies higher than within the grains

So, based on that we can adopt various types of mass transport path, which is occurring in case of sintering. So, the positive pressure surface there from here the mass will transport from here to the neck region where this pressure is negative. So, there will be a transport of atom from this region to this region.

So, it will be deposited here. It will act as a sink. The vacancy flask they will go to the opposite direction wherever atom is going it will consider the vacancy is moving into the opposite direction. So, concentration of the vacancy is higher here as compared to the other region. So, this difference will lead to the mass transport and in our next lecture, we will be introducing the solid state sintering mechanism where you will see that this concept we will be using it that where from this mass transport takes place.

And, depending on that we can assume whether the shrinkage will occur or not. It is possible that this mass transport is taking place, but the path is important where it is taking place, from where it is going to where, so, that is important. So, that will depend the sintering. We will see it in the next lecture.

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REFERENCES

- **M.W. Bersoum,** Fundamental of ceramics, Chapter – 10 Sintering and grain growth, 2nd Edition CRC press, 2020. (Study Material)
- **J. Reed,** Principles of ceramic processing, 2nd Edition, Wiley New York, 1990
- **D. Ganguli and S. Kumar,** Elements of Ceramic Science, Vol – II, Indian Institute of Ceramics, Chapter – 2 Densification of ceramics – Sintering and grain growth, A.R. Das, 1984

So, the reference for this part of lecture the study material is the book by Bersoum chapter number 10 additionally you can read the book by J. Reed and also a old book by edited by D. Ganguli and S. Kumar. So, that is in that book a chapter was written by my teacher professor A. R. Das from IIT Kanpur and that is a wonderful text to read to understand this basic concepts of sintering.

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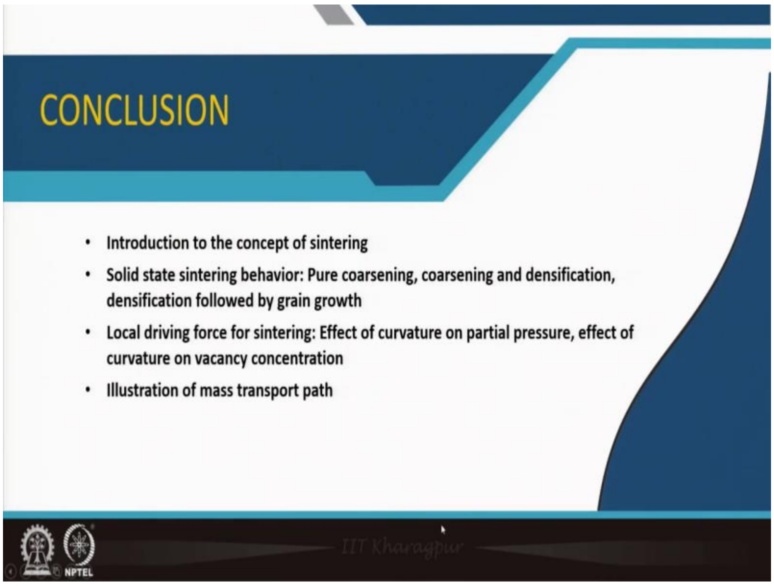

CONCLUSION

- Introduction to the concept of sintering
- Solid state sintering behavior: Pure coarsening, coarsening and densification, densification followed by grain growth
- Local driving force for sintering: Effect of curvature on partial pressure, effect of curvature on vacancy concentration
- Illustration of mass transport path

So, here in this lecture I have introduced the concept of sintering, then we have just started the solid state sintering behavior and I will just go into details, pure coarsening, coarsening and densification, densification followed by grain growth that concept was illustrated, local driving force of sintering, effect of curvature on partial pressure and effect of curvature on vacancy concentration and that is basically affecting the mass transport during sintering. And, we will continue with the next lecture.

Thank you for your attention.