Powder Metallurgy
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Lecture – 57
Full Density Processing - 2

Hi everyone. In the previous lecture, we started on Full Density Processing.

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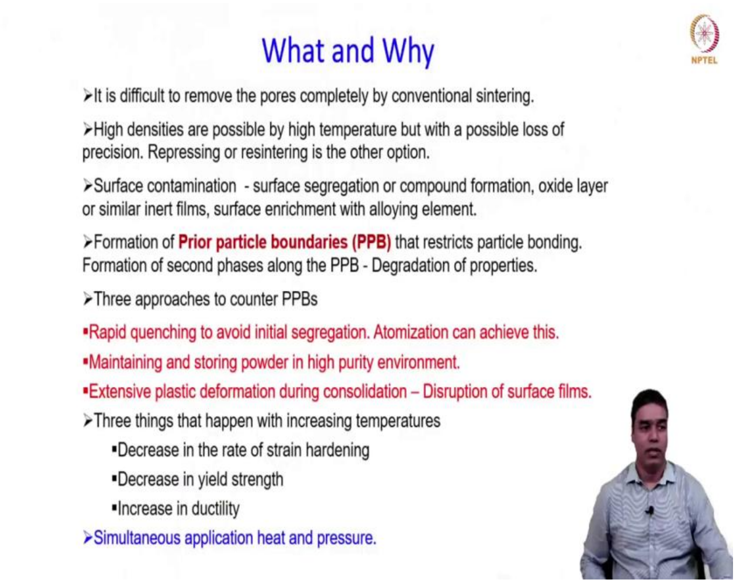

What and Why

- It is difficult to remove the pores completely by conventional sintering.
- High densities are possible by high temperature but with a possible loss of precision. Repressing or resintering is the other option.
- Surface contamination - surface segregation or compound formation, oxide layer or similar inert films, surface enrichment with alloying element.
- Formation of **Prior particle boundaries (PPB)** that restricts particle bonding. Formation of second phases along the PPB - Degradation of properties.
- Three approaches to counter PPBs
- Rapid quenching to avoid initial segregation. Atomization can achieve this.
- Maintaining and storing powder in high purity environment.
- Extensive plastic deformation during consolidation – Disruption of surface films.
- Three things that happen with increasing temperatures
    - Decrease in the rate of strain hardening
    - Decrease in yield strength
    - Increase in ductility
- Simultaneous application heat and pressure.

And we have seen that this is all about application of heat and pressure simultaneously during the sintering process. This is to overcome the limitations of the conventional solid state sintering, where only heat is applied and there is no external pressure.

And in the previous class we have seen the effect of pressure and how it brings in additional driving force for the densification.

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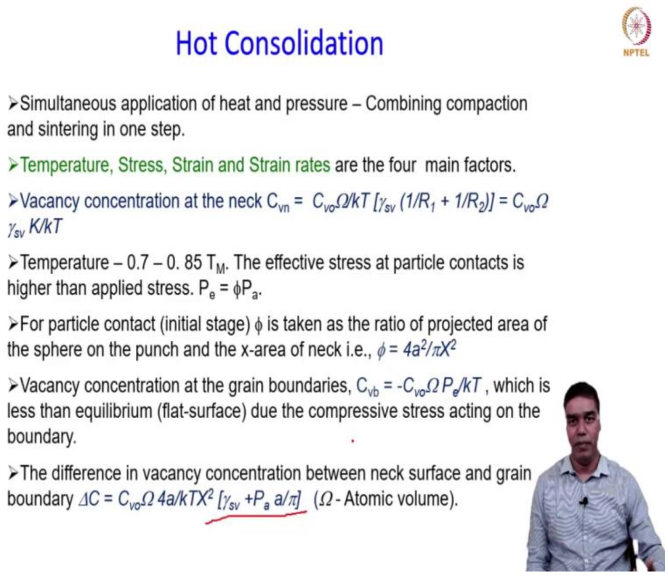

Hot Consolidation

- Simultaneous application of heat and pressure – Combining compaction and sintering in one step.
- Temperature, Stress, Strain and Strain rates are the four main factors.
- Vacancy concentration at the neck $C_{vn} = C_{vo}\Omega/kT\ [\gamma_{sv}\ (1/R_1 + 1/R_2)] = C_{vo}\Omega\ \gamma_{sv}\ K/kT$
- Temperature – 0.7 – 0. 85 T_M. The effective stress at particle contacts is higher than applied stress. $P_e = \phi P_a$.
- For particle contact (initial stage) ϕ is taken as the ratio of projected area of the sphere on the punch and the x-area of neck i.e., $\phi = 4a^2/\pi X^2$
- Vacancy concentration at the grain boundaries, $C_{vb} = -C_{vo}\Omega P_e/kT$, which is less than equilibrium (flat-surface) due the compressive stress acting on the boundary.
- The difference in vacancy concentration between neck surface and grain boundary $\Delta C = C_{vo}\Omega\ 4a/kTX^2\ \underline{[\gamma_{sv} + P_a\ a/\pi]}$ (Ω - Atomic volume).

We have considered that with respect to the concentration of the vacancies. So, here if you see the parameter that we considered to demonstrate the effect of pressure is $(\gamma_{sv} + \frac{aP_a}{\pi})$. So, apart from the surface energy term which comes due to the surface curvature of the neck, there is an additional driving force which is the applied pressure.

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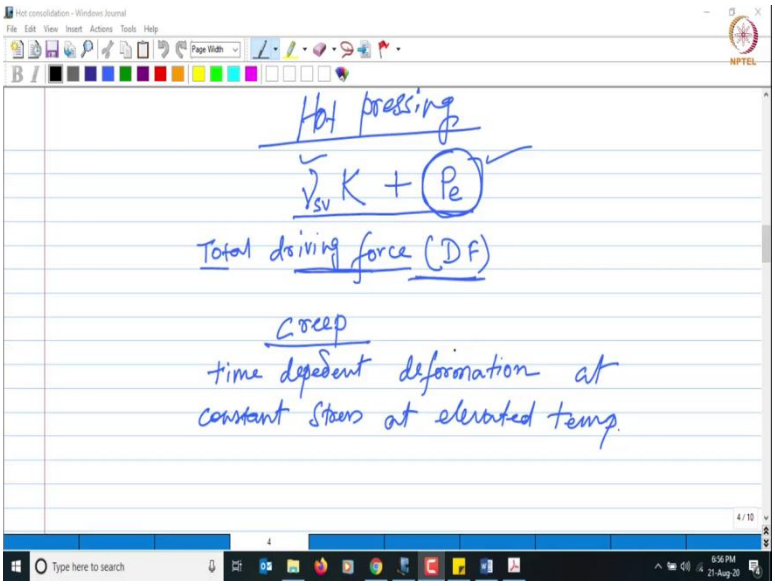

Hot pressing

$\gamma_{sv} K + \boxed{P_e}$

Total driving force (DF)

Creep

time dependent deformation at constant Stress at elevated temp.

So, if you see the driving force behind this hot pressing process, wherein we apply both pressure and heat simultaneously.

Apart from the curvature of the neck that is this contribution, where K is the curvature; there is additional contribution coming from the applied pressure or the effective pressure which is acting on the component. So, therefore, when you talk about the equations which describe the hot pressing mechanism; apart from this surface energy term, you will have to add the pressure term to derive those equations.

So, instead of simply using the curvature as the driving force, the total driving force here is a combination of the pressure due to the curvature as well as the applied pressure. So, therefore, we simply have to use this driving force instead of the surface energy and the curvature in the equations in order to derive the mechanisms for the hot pressing process. So, now, you might know that hot deformation occurs by a process called creep.

Creep is time dependent deformation at constant stress at a given temperature. So, in order to derive the equations for the hot pressing mechanism, we can simply look at the equations that describe the creep phenomena and we can suitably modify the creep equations by including this total driving force instead of only the stress. So, let us first look at the creep mechanisms. The deformation is all about the change in the dimension or the strain rate.

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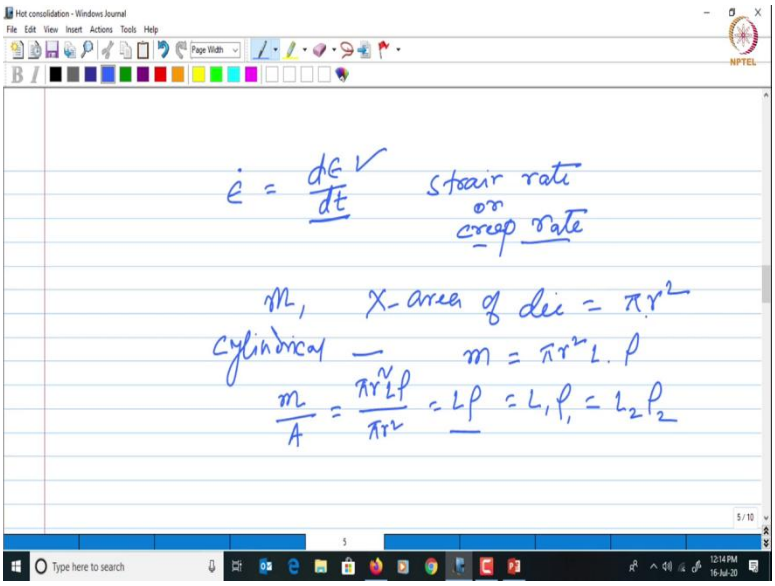

$\dot{\epsilon} = \underline{\frac{d\epsilon}{dt}}$ ✓ strain rate or $\underline{\text{creep}}$ $\underline{\text{rate}}$

m, X-area of die $= \pi r^2$

cylindrical — $m = \pi r^2 L . \rho$

$\frac{m}{A} = \frac{\pi r^2 L \rho}{\pi r^2} = \underline{L\rho} = L_1\rho_1 = L_2\rho_2$

When you talk about the deformation with respect to time; this parameter that is rate of change of strain with respect to time, $\dot{\varepsilon} = \frac{d\varepsilon}{dt}$, will define the deformation. And when you talk about the creep deformation, $\dot{\varepsilon}$ is the creep rate which will define the deformation happening at high temperature.

So, this is basically the rate of deformation and this can be related to the densification rate as well. So, let us say we are talking about in the hot pressing process and a cylindrical die is being used to press the powder. So, in that case, the mass of the powder m and the cross sectional area of the die remains constant during this operation.

So, considering a cylindrical shape, the cross sectional area is $A = \pi r^2$, if r is the radius of the die and the mass m will be given as the volume which is $\pi r^2 L$, where L is the length multiplied by the density ρ. That is $m = \pi r^2 L\rho$. So, if you take this ratio $\frac{m}{A} = L\rho$ is a constant.

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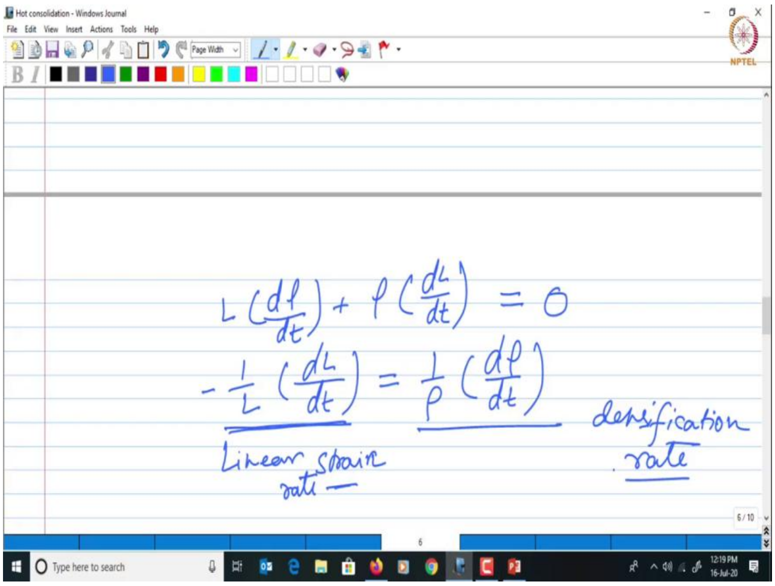

$$L\left(\frac{d\rho}{dt}\right) + \rho\left(\frac{dL}{dt}\right) = 0$$

$$-\frac{1}{L}\left(\frac{dL}{dt}\right) = \frac{1}{\rho}\left(\frac{d\rho}{dt}\right)$$

And now if we differentiate this with respect to time; then we will get the following equation,

$$L\left(\frac{d\rho}{dt}\right) + \rho\left(\frac{dL}{dt}\right) = 0$$

This will be equal to 0; because Lρ is constant and therefore by rearranging, we can write this in terms of the following equation.

$$-L\left(\frac{d\rho}{dt}\right) = \rho\left(\frac{dL}{dt}\right)$$

So, the left hand side term is the linear strain rate of the compact during the hot deformation process and the right hand side term is the densification rate. So, you can see that, the densification rate is associated with the deformation rate. So, therefore, we need to see the deformation rate and derive it in order to derive the densification equations for the hot pressing process.

So, as I was mentioning, the hot deformation occurs by a process called creep and the creep equations can be suitably modified by taking into account the porosity in order to get the equations for the hot pressing mechanisms.

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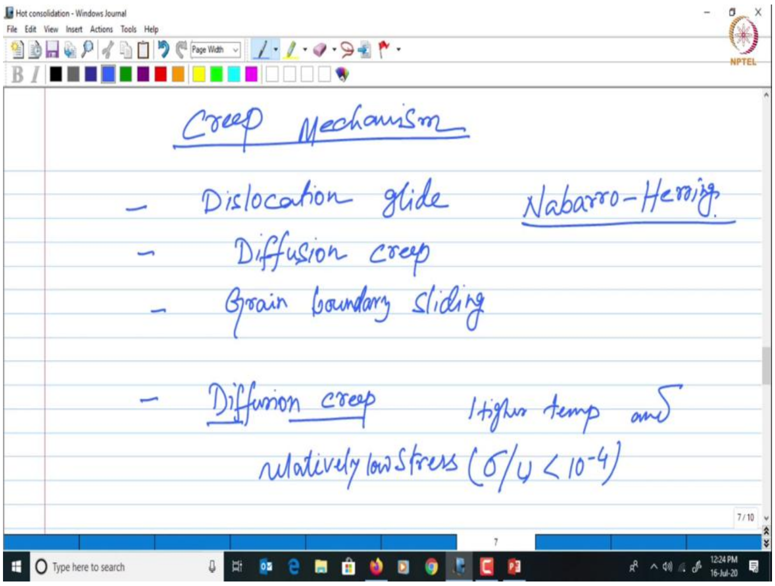

Creep Mechanism

- Dislocation glide   Nabarro-Herring
- Diffusion creep
- Grain boundary sliding

- Diffusion creep   Higher temp and relatively low stress ($\sigma/U < 10^{-4}$)

So, if you look at the creep mechanisms, primarily there are three mechanisms of creep; dislocation glide, diffusion creep, and grain boundary sliding. In the temperature and stress which are generally encountered during the hot deformation or the hot pressing process, diffusional creep is the more prevalent mechanism.

So, when the temperatures are on the higher side and the stress is relatively low, which is in the range, $\frac{\sigma}{U} < 10^{-4}$, where σ is the applied stress and U is the shear modulus. Then under these conditions, a creep mechanism called Nabarro Herring creep will take place. Here the stress changes the chemical potential of the atoms on the surface of the grains in a poly crystalline material.

And therefore, the vacancies will flow from grain boundaries which experience tensile stresses to those having compressive stresses. And therefore, due to this atomic flow, there will be a deformation or elongation happening. And this mechanism of creep is known as Nabarro Herring creep, according to the name of the people who proposed this theory.

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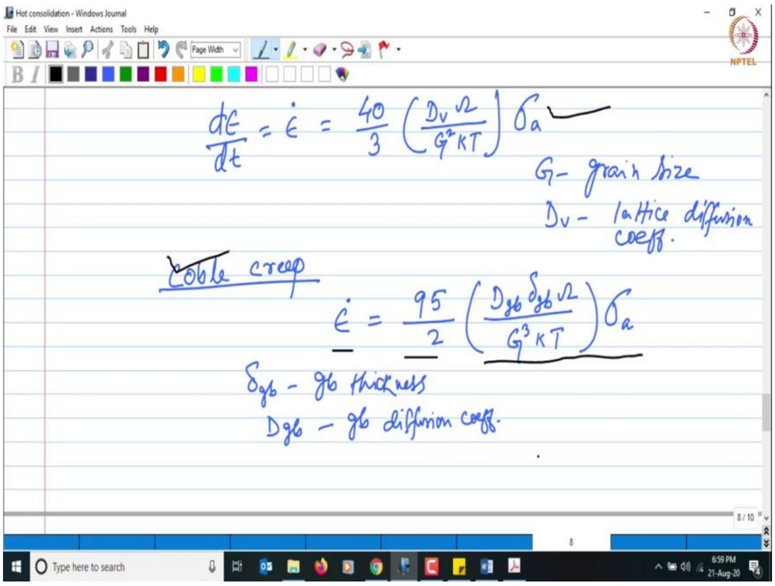

$$\frac{d\varepsilon}{dt} = \dot{\varepsilon} = \frac{40}{3}\left(\frac{D_v \Omega}{G^2 kT}\right)\sigma_a$$

G - grain size

D_v - lattice diffusion coeff.

Coble creep

$$\dot{\varepsilon} = \frac{95}{2}\left(\frac{D_{gb}\delta_{gb}\Omega}{G^3 kT}\right)\sigma_a$$

δ_{gb} - gb thickness

D_{gb} - gb diffusion coeff.

For the Nabarro Herring creep, the steady state creep rate is given by the following equation,

$$\frac{d\varepsilon}{dt} = \dot{\varepsilon} = \frac{40}{3}\left(\frac{D_v \Omega}{G^2 kT}\right)\sigma_a$$

where G is the grain size and D_v is the lattice or bulk diffusion coefficient. And the other terms have their own meaning, which we have already defined before.

And at lower temperatures, the creep occurs predominantly through the grain boundary diffusion and this kind of creep is known as coble creep. And the creep rate for the coble creep is given as follows.

$$\dot{\varepsilon} = \frac{95}{2}\left(\frac{D_{gb}\delta_{gb}\Omega}{G^3 kT}\right)\sigma_a$$

So, here δ_{gb} is the grain boundary thickness and D_{gb} is the grain boundary diffusion coefficient; σ_a of course is the applied stress.

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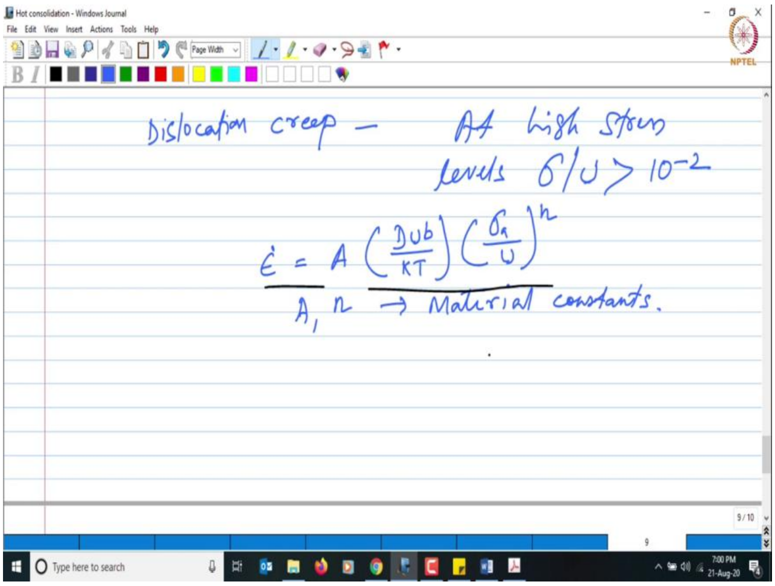

Dislocation creep — At high stress levels $\sigma/U > 10^{-2}$

$$\dot{\epsilon} = A\left(\frac{DUb}{kT}\right)\left(\frac{\sigma_a}{U}\right)^n$$

A, n → Material constants.

Dislocation creep can occur at high stress level, in the range when$\frac{\sigma}{U} > 10^{-2}$. So, this kind of stress is much higher compared to what is generally encountered during creep deformation.

Dislocation creep basically involves thermally activated movement of dislocations leading to deformation. So, here the dislocations overcome obstacles like precipitates, solute atoms and other dislocations by thermal activation and the creep rate is established by the ease with which the dislocations can overcome such obstacles.

And the creep rate in this case is given as follows,

$$\dot{\varepsilon} = A(\frac{DUb}{kT})\ (\frac{\sigma_a}{U})^n$$

where b is the burgers vector of the dislocations and A and n are material constant and D is the diffusion coefficient. Now, if you see the hot deformation equations which are derived from these creep equations by including the corresponding term to take into account the porosity, that is this effective stress that we talked about before.

So, now, if we include this effective stress or the total driving force into the creep equation, we can actually derive the equations for the hot pressing mechanisms. So, this is how they will look like (table below) when you include this total driving force instead of the applied stress.

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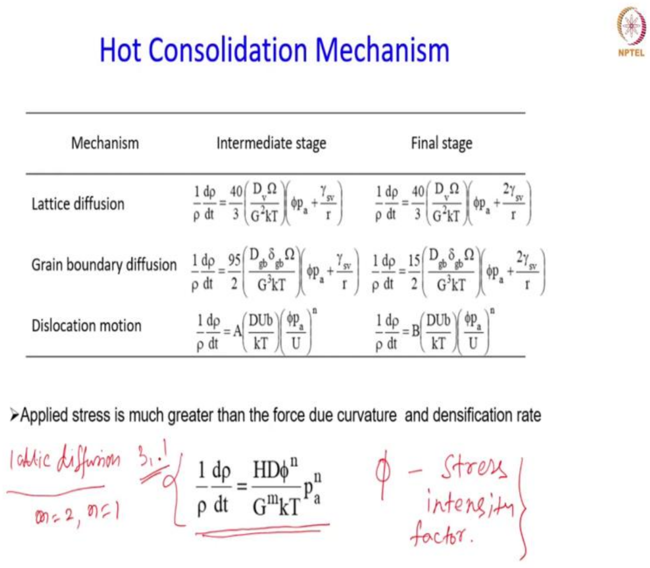

Hot Consolidation Mechanism

Mechanism	Intermediate stage	Final stage
Lattice diffusion	$\frac{1}{\rho}\frac{d\rho}{dt}=\frac{40}{3}\left(\frac{D_v\Omega}{G^2kT}\right)\left(\phi p_a+\frac{\gamma_{sv}}{r}\right)$	$\frac{1}{\rho}\frac{d\rho}{dt}=\frac{40}{3}\left(\frac{D_v\Omega}{G^2kT}\right)\left(\phi p_a+\frac{2\gamma_{sv}}{r}\right)$
Grain boundary diffusion	$\frac{1}{\rho}\frac{d\rho}{dt}=\frac{95}{2}\left(\frac{D_{gb}\delta_{gb}\Omega}{G^3kT}\right)\left(\phi p_a+\frac{\gamma_{sv}}{r}\right)$	$\frac{1}{\rho}\frac{d\rho}{dt}=\frac{15}{2}\left(\frac{D_{gb}\delta_{gb}\Omega}{G^3kT}\right)\left(\phi p_a+\frac{2\gamma_{sv}}{r}\right)$
Dislocation motion	$\frac{1}{\rho}\frac{d\rho}{dt}=A\left(\frac{DUb}{kT}\right)\left(\frac{\phi p_a}{U}\right)^n$	$\frac{1}{\rho}\frac{d\rho}{dt}=B\left(\frac{DUb}{kT}\right)\left(\frac{\phi p_a}{U}\right)^n$

- Applied stress is much greater than the force due curvature and densification rate

lattic diffusion 3,∴

m=2, n=1

$$\propto \left\{ \underline{\underline{\frac{1}{\rho}\frac{d\rho}{dt}=\frac{HD\phi^n}{G^mkT}p_a^n}} \right.$$

ϕ – Stress intensity factor.

The equations for the different mechanisms of hot pressing will be given as follows, what you can see from this particular table over here; for the lattice diffusion, we have already seen the creep equation. $\frac{1}{\rho}\frac{d\rho}{dt}=\frac{40}{3}\ (\frac{D_v\Omega}{G^2kT})(\Phi P_a+\frac{2\gamma_{sv}}{r})$

And here this term $(\Phi P_a+\frac{2\gamma_{sv}}{r})$ was only the stress (σ_a) in case of the creep, which is now replaced by the total driving force that includes the applied stress as well as the stress due to the curvature of the neck.

Similarly, in the grain boundary diffusion also the applied stress (σ_a) has been replaced by the total driving force$(\Phi P_a+\frac{2\gamma_{sv}}{r})$ to derive the hot pressing mechanism from the grain boundary diffusion mechanism of creep, $\frac{1}{\rho}\frac{d\rho}{dt}=\frac{15}{2}\ (\frac{D_{gb}\delta_{gb}\Omega}{G^3kT})(\Phi P_a+\frac{2\gamma_{sv}}{r})$. So, lattice diffusion as we have seen is nothing but that Nabarro Herring Creep, and grain boundary diffusion is the coble creep.

And if it is dislocation creep that happens with the thermally activated motion of dislocations; then the corresponding equation is, $\frac{1}{\rho}\frac{d\rho}{dt}=A(\frac{DUb}{kT})\ (\frac{\Phi P_a}{U})^n$ wherein b is the burger vector of the dislocations. A is a numerical constant and D of course is the diffusion coefficient.

Now, the applied stress is generally much higher than the stress due to the curvature and the densification rate can be accordingly given considering that with the following equation,

$$\frac{1}{\rho}\frac{d\rho}{dt} = \frac{HD\Phi^n}{G^m kT} P_a^n$$

where H is a constant and rest of the parameters have their usual meanings as already defined before. And Φ of course, is the stress intensity factor due to the presence of the pores. So, this is how the pores are accounted for in this densification rate which is derived from the equations of creep deformation. The values of the two exponents m and n will depend on the densification mechanism. For example, if it is lattice diffusion, the value of m is 2 and that of n is 1. And for grain boundary diffusion, the corresponding values are 3 and 1.

So, depending on which mechanism is operative, the values of m and n will change. So, that was all about the mechanisms of hot pressing. So, before we finish this lecture, let us take a moment to summarize it. So, today we talked about hot pressing in which pressure and heat are applied simultaneously for the sintering to occur. And therefore in this case, the driving force for the sintering not only comes from curvature of the neck, but also from the applied pressure.

So, this is basically a pressure assisted sintering; unlike the conventional solid state sintering, where there is no applied pressure and the driving force primarily comes from the curvature of the neck and the decrease in the surface energy. Now, the hot deformation that occurs during the hot pressing process, resembles creep which is a time dependent deformation which occurs at a constant stress at high temperature.

And therefore, the equations for the hot pressing mechanism can be derived from the creep equations by suitably modifying them, taking into account the pores which are present in the compact, right. So, while doing so, we first discussed about the different mechanisms of creep and saw the equations for those mechanisms.

The three main mechanisms of creep are as follows; dislocation glide or dislocation creep, diffusion creep, and grain boundary sliding. Diffusion creep occurs at higher temperature and relatively low stresses.

And depending on whether the diffusion is occurring through the lattice or through the grain boundaries, there are two forms of diffusion creep; if the diffusion occurs through the lattice, then it is known as Nabarro Herring Creep. And the creep equation or the equation for the creep rate for the Nabarro Herring Creep is given by this particular equation,

$$\frac{d\varepsilon}{dt} = \dot{\varepsilon} = \frac{40}{3}\left(\frac{D_v\Omega}{G^2kT}\right)\sigma_a$$

where G is the grain size and D_v is the lattice diffusion coefficient.

On the other hand at lower temperature, grain boundary diffusion becomes predominant and that form of creep when the diffusion occurs through the grain boundaries is known as coble creep. And the corresponding creep rate equation is given by this particular equation over here.

$$\dot{\varepsilon} = \frac{95}{2}\left(\frac{D_{gb}\delta_{gb}\Omega}{G^3kT}\right)\sigma_a$$

Then we also talked about dislocation creep, which basically occurs through thermally assisted movement of dislocations. And in this case, the corresponding creep rate is given by this particular equation.

$$\dot{\varepsilon} = A\left(\frac{DUb}{kT}\right)\left(\frac{\sigma_a}{U}\right)^n$$

And from these equations, we can derive the equations for the hot pressing mechanism by taking into account the porosity. So, we have derived the effective stress taking into account the porosity. And if we include that effective stress instead of this applied stress in the creep equations we can derive the hot pressing equations.

And that is what you see from this particular table in above slide; depending on the mechanism of diffusion you have different creep equations. And in that if we substitute the applied stress by the total driving force, which includes the effect of the porosity as well, we can easily derive the equations for the hot pressing mechanisms.

And then we have also seen that a generic form of the hot pressing mechanism equation,

$$\frac{1}{\rho}\frac{d\rho}{dt} = \frac{HD\Phi^n}{G^mkT}P_a^n$$

where the left hand side is the densification rate. And the exponents that you see over here m and n, the values of that will depend on the mechanism of diffusion; whether it is lattice diffusion or grain boundary diffusion, based upon that the values will m and n will change. So, that is how this generic form of equation can describe the hot consolidation or the hot pressing mechanisms through one single expression. And with that we come to the end of this particular lecture.