Powder Metallurgy
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Lecture – 43
Sintering – 3

Hello and welcome back. So, right now, we are on this topic sintering and in the past couple of classes, we have discussed about the basic fundamentals of the sintering process and we have seen that the sintering process is actually driven by atomic diffusion. So, we have also discussed little bit about the diffusion process as such as to what is diffusion, what are the mechanisms of diffusion and so on in the last class.

So, today, we are going to continue on this topic. So, one thing that you would have seen as I just now said is the fact that diffusion plays a major role in the sintering process in the sense that the matter which is to be transported to the neck for it to grow happens by this process and we have also seen that there are well defined paths for the diffusion process to happen during the densification.

So, apart from those parts, there is one more thing which plays a role in this densification process and that is the curvature of the surface of the particles ok. So, that is what we are going to discuss today and then again, we will come back to this sintering process and we will see how the curvature is correlated with the densification that happens in sintering.

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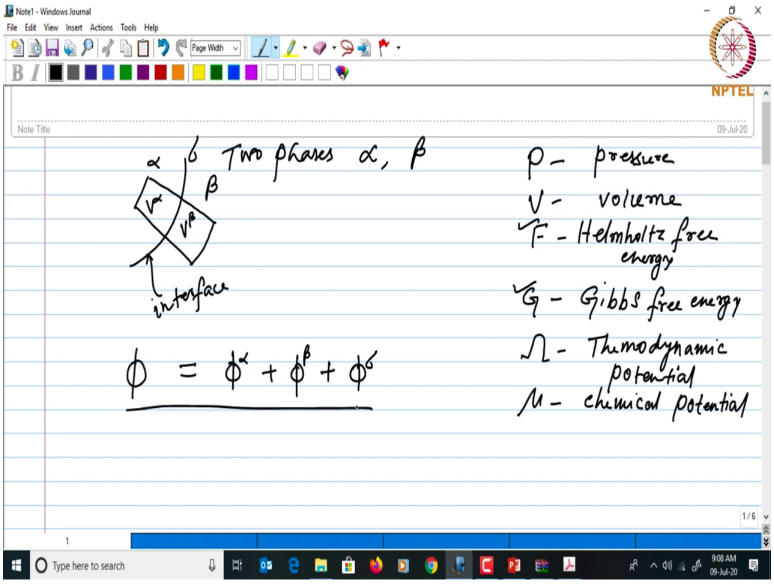

Two phases α, β

P - pressure
V - volume
F - Helmholtz free energy
G - Gibbs free energy
Ω - Thermodynamic potential
μ - chemical potential

$$\underline{\phi = \phi^{\alpha} + \phi^{\beta} + \phi^{\sigma}}$$

So, let us say we have two phases alpha and beta separated by a curved interface like this. This side is alpha, this side is beta, and this is the interface which separates these two phases . Let the volume of the phase alpha is v_{α} and that of phase beta is v_{β} .

We are also going to use a set of terms. So, let me first define those terms before we proceed. We are going to use P as pressure and V as volume and then we have some thermodynamic terms such as F which is the Helmholtz free energy, G which is Gibbs free energy, Ω is thermodynamic potential, μ is chemical potential. So, these are the terms that we are going to use and if there is any more, I will define that.

So, let us come back to this. So, these are the two phases that we have here α and β separated by a curved interface. So, now, when you have an interface like this between any two phases, any thermodynamic property can be represented as the sum of the bulk; that means, the property of this two phases α and β and that of the interface.

So, let us say any thermodynamic property such as let us say we call that as Φ which could be any of the thermodynamic properties that could be represented as the sum of the thermodynamic properties of this two phases and that of the interface. Let us call that interface as σ . So, therefore, this will be given as phi for alpha, for beta and that for the interface sigma .

$$\Phi = \Phi^{\alpha} + \Phi^{\beta} + \Phi^{\sigma}$$

Now, this two terms that we have here Gibbs free energy and Helmholtz free energy.

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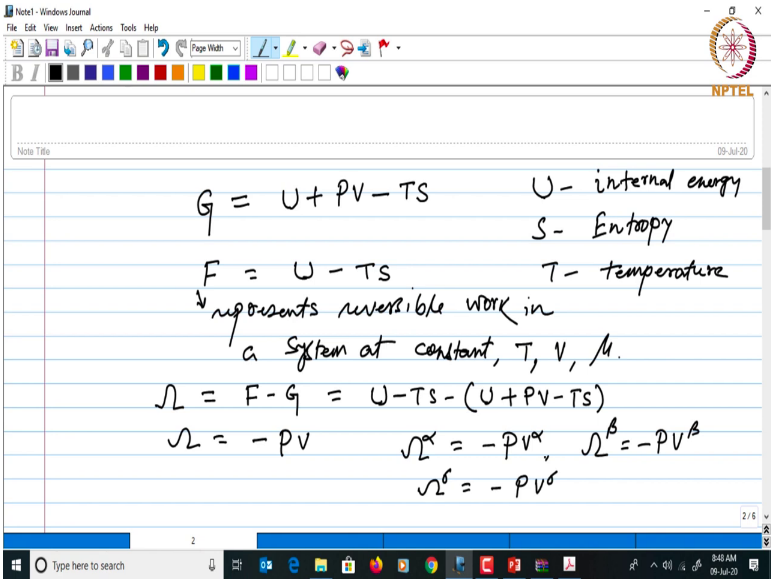

$G = U + PV - TS$

U - internal energy

S - Entropy

T - temperature

$F = U - TS$

↓ represents reversible work in a system at constant, T, V, μ.

$\Omega = F - G = U - TS - (U + PV - TS)$

$\Omega = -PV$

$\Omega^{\alpha} = -PV^{\alpha}$, $\Omega^{\beta} = -PV^{\beta}$

$\Omega^{\sigma} = -PV^{\sigma}$

Let us define this two terms and then, we will proceed to the curved interface. G is given as

$$G = U + PV - TS$$

where U is the internal energy and S is entropy, T is temperature and the Helmholtz free energy F is defined as

$$F = U - TS$$

F basically represents the reversible work in a system at constant temperature volume and chemical potential .

Now, let us consider a thermodynamic potential which is represented by this omega. So, this is given as

$$\Omega = F - G = U - TS - (U + PV - TS)$$

$$\Omega = -PV$$

and if you substitute G and F over here, you will get omega equals to minus PV right. So, therefore, for the three entities that we have alpha, beta and the interface sigma we can write this term for each of them.

$$\Omega^{\alpha} = -PV^{\alpha},\ \Omega^{\beta} = -PV^{\beta},\ \Omega^{\sigma} = -PV^{\sigma}$$

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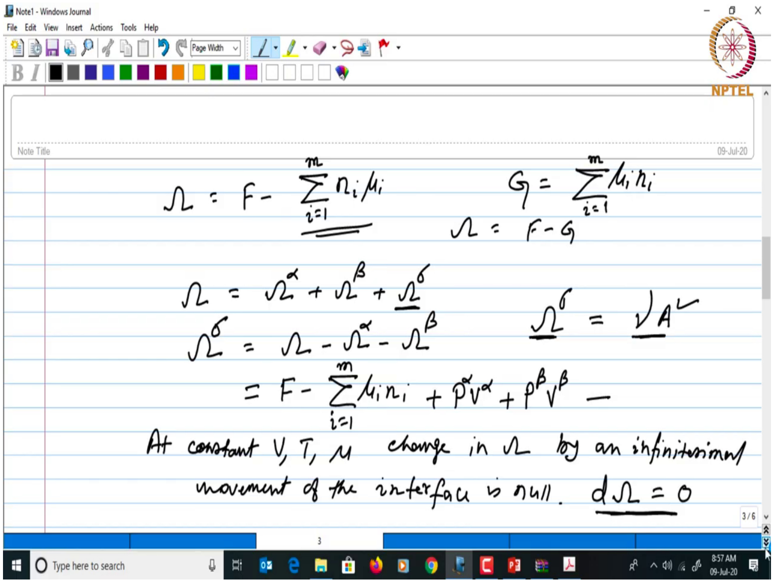

$$\Omega = F - \underline{\underline{\sum_{i=1}^{m} n_i \mu_i}} \qquad G = \sum_{i=1}^{m} \mu_i n_i$$

$$\Omega = F - G$$

$$\Omega = \Omega^{\alpha} + \Omega^{\beta} + \underline{\Omega^{\sigma}}$$

$$\Omega^{\sigma} = \Omega - \Omega^{\alpha} - \Omega^{\beta} \qquad \underline{\Omega^{\sigma}} = \underline{\gamma A} \checkmark$$

$$= F - \sum_{i=1}^{m} \mu_i n_i + p^{\alpha} V^{\alpha} + p^{\beta} V^{\beta} -$$

At constant V, T, μ change in Ω by an infinitesimal movement of the interface is null. $\underline{d\Omega = 0}$

And omega is also expressed as

$$\Omega = F - \sum_{i=1}^{m} n^{i} \mu^{i}$$

F minus sum of the chemical potentials when you have a number of components in a system. So,μ is the chemical potential of the ith component and n is the number of moles of that particular component. So, this one is basically the Gibbs free energy . So, that is how you have omega equals to F minus G right.

So, let us come back to this when we say that any thermodynamic property is the sum of the properties of the phases and the interface. So, here, you can write for the thermodynamic potential as the sum of those three quantities that is the thermodynamic potentials of alpha, beta and the interface . So, therefore, this quantity, the interfacial quantity can be written as this.

$$\Omega = \Omega^{\alpha} + \Omega^{\beta} + \Omega^{\sigma}$$

So, to create this interface, you need the surface energy because a surface is created now, the interface is basically a surface. So, this thermodynamic potential will be actually given by that surface energy

$$\Omega^{\alpha} = \gamma A$$

if we call that as gamma and A, the area of the interface. So, here gamma is the specific surface energy that is surface energy per unit area and A is the area.

So, this is the total energy which is actually needed to create the interface right. So, Ω^{α} that is the omega for the interface is basically the surface axis; that means, to create that interface between two phases and γ is the energy or the work required to create a unit area of that surface.

So, now, if we come back to this, this can be re written as.

$$\Omega^{\sigma} = \Omega - \Omega^{\alpha} - \Omega^{\beta}$$

$$= F - \sum_{i=1}^{m} n^{i} \mu^{i} + P^{\alpha} V^{\alpha} + P^{\beta} V^{\beta}$$

Now, at constant V, T and mu constant volume, temperature and chemical potential the change in omega by an infinitesimal movement of the interface is null. What it basically means is $d\,\Omega = 0$.

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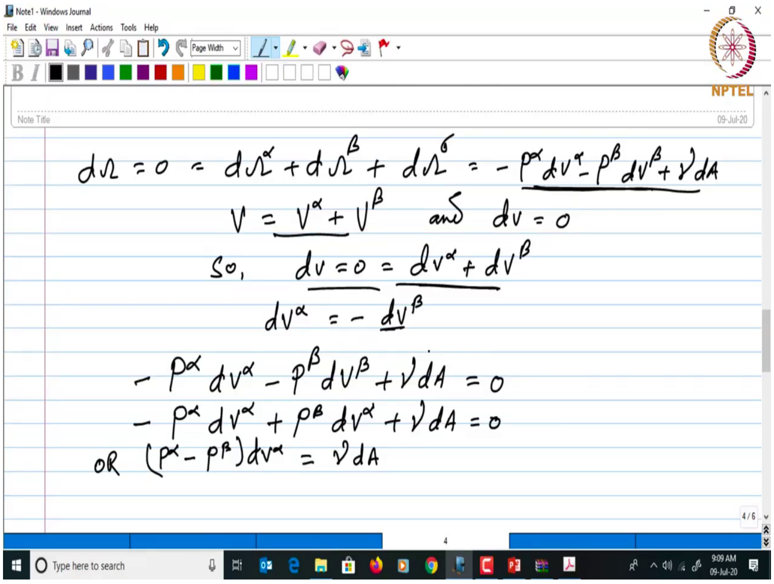

$$d\Omega = 0 = d\Omega^{\alpha} + d\Omega^{\beta} + d\Omega^{\sigma} = \underline{-P^{\alpha} dV^{\alpha} - P^{\beta} dV^{\beta}} + \gamma dA$$

$$V = \underline{V^{\alpha} + V^{\beta}} \quad \text{and} \quad dV = 0$$

$$\text{So,} \quad \underline{dV = 0} = \underline{dV^{\alpha} + dV^{\beta}}$$

$$dV^{\alpha} = -\underline{dV^{\beta}}$$

$$-P^{\alpha} dV^{\alpha} - P^{\beta} dV^{\beta} + \gamma dA = 0$$

$$-P^{\alpha} dV^{\alpha} + P^{\beta} dV^{\alpha} + \gamma dA = 0$$

$$\text{OR} \quad (P^{\alpha} - P^{\beta}) dV^{\alpha} = \gamma dA$$

So, if we differentiate this equation on both the sides and use this condition, then we will have this equation

$$d\Omega = d\Omega^{\alpha} + d\Omega^{\beta} + d\Omega^{\sigma} = -P^{\alpha} dV^{\alpha} - P^{\beta} dV^{\beta} + \gamma dA$$

and now, here v is constant so, you can say that $V = V^{\alpha} + V^{\beta}$ and V is constant so, dv=0 .

So, you can write from here, we can write this and therefore, we can say that

$$dV^{\alpha} = - dV^{\beta}$$

and now, we take this equation and here, we replace dV^{β} in terms of dV^{α} and if we do that, we will get this one.

$$(P^{\alpha} - P^{\beta}) dV^{\alpha} = \gamma dA$$

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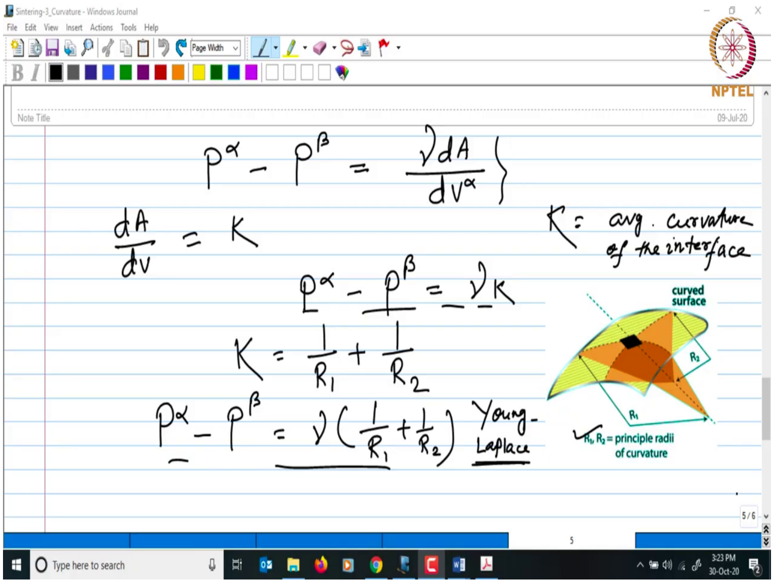

$$P^{\alpha} - P^{\beta} = \frac{\gamma\, dA}{dV^{\alpha}} \}$$

$$\frac{dA}{dV} = K$$

K = avg. curvature of the interface

$$\underline{P^{\alpha}} - \underline{P^{\beta}} = \underline{\gamma}K$$

$$K = \frac{1}{R_1} + \frac{1}{R_2}$$

$$\underline{P^{\alpha}} - P^{\beta} = \underline{\gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)}$$ Young-Laplace

And from here, we can write that

$$(P^{\alpha} - P^{\beta}) = \gamma\, dA / dV^{\alpha}$$

So, this dA / dv is nothing but the curvature of the surface and if we call that curvature as k, we can simply write dA/ dv = k where k is the average curvature of the interface right. So, from here, if we replace k over here in this equation, we will get this

$$P^{\alpha} - P^{\beta} = \gamma k$$

So, if you have a curved surface like this where R 1 and R 2 are the principle radii of curvature, then k is given as $1 / R_1 + 1 / R_2$. So, a generic form of this for any given curved surface with radii R_1 and R_2, this equation can be written as and this is the well-known Young-Laplace equation.

$$P^{\alpha} - P^{\beta} = \gamma\, (1 / R_1 + 1 / R_2)$$

It basically describes the stress on a curved surface.

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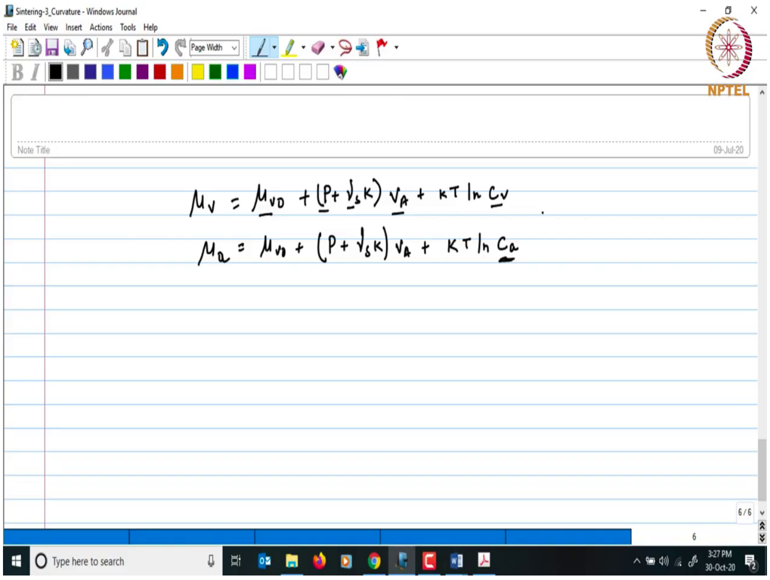

$$\mu_v = \mu_{vo} + (P + \gamma_s K) V_A + kT \ln C_v$$

$$\mu_a = \mu_{vo} + (P + \gamma_s K) V_A + kT \ln C_a$$

Now, the vacancies and atoms beneath curved surface will have their own chemical potentials and this chemical potential can be altered by the curvature of the surface and this change in the chemical potential can be shown to be as follows: for the vacancies, it can be given by this expression over here.

$$\mu_v = \mu_{vo} + (P + \gamma_s k) V_A + kT \ln Cv$$

Where μ_v is the chemical potential or vacancies, μ_{vo} is a reference value against which the chemical potential is generally measured, P is the main hydrostatic pressure in the crystal just beneath the surface, γ_s the specific surface energy, V_A is the atomic volume and Cv is the concentration of vacancies.

Similarly, the chemical potential of the atoms can also be given in a similar manner.

$$\mu_a = \mu_{vo} + (P + \gamma_s k) V_A + kT \ln Ca$$

Here, Ca is the fraction of lattice sites occupied by the atoms in the crystal. So, Cv and Ca are generally very small and therefore, you can see that the chemical potential primarily depends on the hydrostatic pressure in the solid and the curvature on the surface .

So, now, the powder particles which are being sintered also have their own curvature and that will lead to a change in the chemical potential which will drive the diffusional flux and as a result of that, the surface curvature also acts as a driving force for the sintering process.

So, this is something that is relevant for the sintering process also and in the next lecture, we are going to discuss as to how this is related and you know how the curvature is relevant for the sintering process or the densification that happens during the sintering process. But for today, this is all I have.

So, before we finish this, let us take a moment to summarize this lecture. So, to summarize, we can say that the curvature has a role to play in the densification process that happens during sintering. So, you can derive the pressure or the stress which is generated due to the curvature.

So that is what is going to play a role in the densification process and this we have done today with the help of diagram where we have considered two phases alpha and beta separated by a curved interface sigma and for scenario like this any thermodynamic property can be taken as the sum of the properties of the phases and that of the interface which you see over here and from that considering the thermodynamic property called thermodynamic potential we derive this relationship between the pressure and the curvature of the surface and from here, you can actually go to the Young-Laplace equation which basically talks about the stress on a curved surface due to the curvature ok. So, with that we come to the end of this class.

Thank you for your attention.