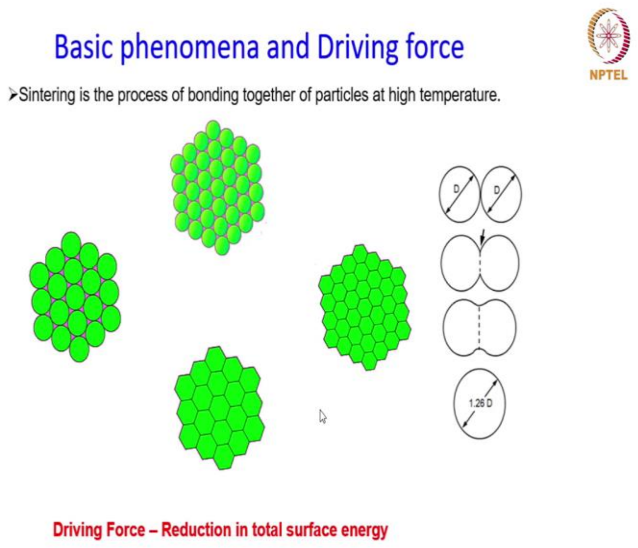
Powder Metallurgy
Prof. Ranjit Bauri
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Madras

Lecture – 42
Sintering – 2

Hello and welcome back. So, in the previous class we have started this topic Sintering which is the final and one of the most important steps of the Powder Metallurgy process, we started discussing about the basic fundamentals of the sintering process.

(Refer Slide Time: 00:32)



Basic phenomena and Driving force

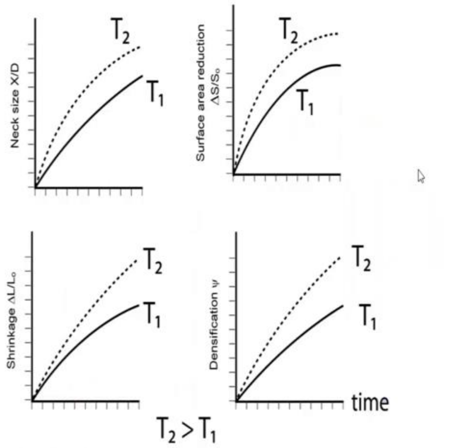
- Sintering is the process of bonding together of particles at high temperature.

Driving Force – Reduction in total surface energy

First we had seen the driving force behind the sintering process and we have seen that the driving force is the reduction in the total surface energy which ultimately leads to the reduction in the total energy of the system. So, the sintering process basically starts with the formation of a neck at the contact points between the particles as we discussed and as this neck grows densification happens in the compact.

(Refer Slide Time: 01:08)

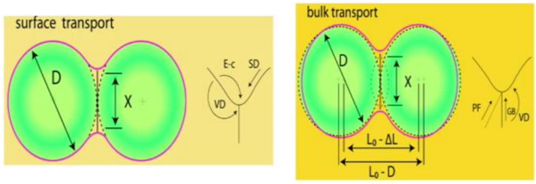
Sintering



(Refer Slide Time: 01:11)

Mass Transfer Mechanisms

- **Surface Transport** – Mass flow originating and terminating at particle surface.
  - Neck growth without change in particle spacing.
  - Surface diffusion – dominates low temperature sintering of metals.
  - Evaporation condensation – not as important, dominates in low-stability metals like Pb.
- **Bulk Transport** – Mass flow from particle interior to the neck . High temp process.
  - Volume diffusion
  - Grain boundary diffusion
  - Plastic flow

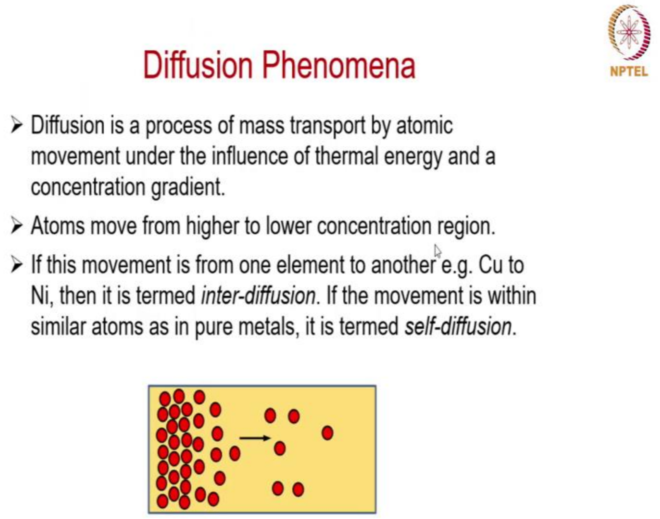


SD – Surface diffusion, VD – Volume diffusion, EC – Evaporation condensation, PF – Plastic flow

So, for the neck to grow, the material has to be transported towards the neck and there are well defined paths through which the matter is transported from the particles towards the neck for it to grow and the densification to occur. So, this mass transport or the atomic diffusion process is a very important phenomena with regard to the densification process and that is why it calls for a little bit of discussion at this point.

So, that we have a better understanding as to what exactly is happening during this densification as it happens in the sintering process . Now, let us have some discussion on the basics of diffusion and then we will come back to this sintering process again .

(Refer Slide Time: 02:01)



Diffusion Phenomena

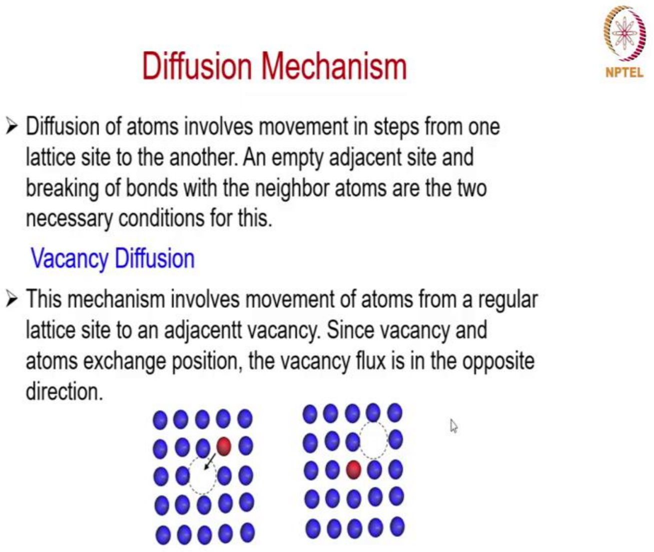
- Diffusion is a process of mass transport by atomic movement under the influence of thermal energy and a concentration gradient.
- Atoms move from higher to lower concentration region.
- If this movement is from one element to another e.g. Cu to Ni, then it is termed *inter-diffusion*. If the movement is within similar atoms as in pure metals, it is termed *self-diffusion*.

So, diffusion is a process of mass transport by atomic movement under the influence of thermal energy and concentration gradient. So, the matter moves from the higher concentration to the lower concentration region and if this movement is from one element to another for example, copper to nickel, then it is called inter - diffusion and if the matter transport is within similar atoms as in pure metals, then it is termed as self - diffusion.

So, there is a pictorial over here that you can see- you know this red dots indicate the atoms which in turn indicate the concentration of the matter at a particular region. So, on the left hand side here you can see there are more number of atoms. So, this is the high concentration region and here you have less number.

So, this is the low concentration region. So, therefore, this arrow indicates the direction of the mass transport right. So, as I said it will move from higher to lower concentration region as indicated by this arrow over here.

(Refer Slide Time: 03:23)



Diffusion Mechanism

- Diffusion of atoms involves movement in steps from one lattice site to the another. An empty adjacent site and breaking of bonds with the neighbor atoms are the two necessary conditions for this.

Vacancy Diffusion

- This mechanism involves movement of atoms from a regular lattice site to an adjacentt vacancy. Since vacancy and atoms exchange position, the vacancy flux is in the opposite direction.

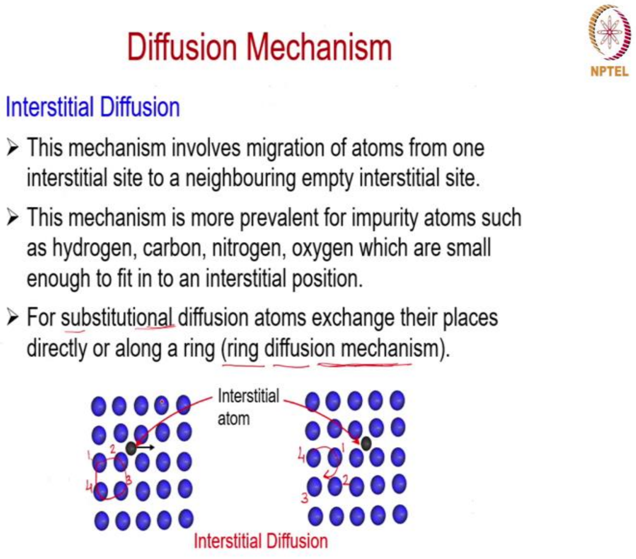
Now, there are certain mechanisms by which these atomic transport happens and some models are proposed with regard to that. First of all the atoms move in steps from one lattice site to another. An empty adjacent site and breaking of bonds with the neighbouring atoms are the two necessary conditions for this to happen right.

So, how these atoms actually move from one lattice site to another lattice site for that certain models have been proposed. So, we are going to discuss those models just to understand and you know try and get a picture of this atomic movement inside a material during the diffusion process.

The vacancy diffusion mechanism involves movement of atoms from a regular lattice site to an adjacent vacancy right. So, vacancy is kind of a lattice defect when there is a missing atom that creates vacancy in the lattice. So, if there is a vacant space or there is a vacancy, one adjacent atom can move into that and that is how it moves from one place to another as indicated by this arrow over here. So, this red atom over here moves to this vacancy and that is how it goes in this direction.

So, in the process what happens the vacancy moves to the other direction as you could see from the second image over here right. So, as the atom moves to this place where the vacancy was before the vacancy switches its position to the atoms position. So, the vacancy moves in the opposite direction. The vacancy flux is therefore, is in the opposite direction of the atomic flux in this vacancy diffusion mechanism. Then, there is one more model called interstitial diffusion.

(Refer Slide Time: 05:27)



Diffusion Mechanism

Interstitial Diffusion

- This mechanism involves migration of atoms from one interstitial site to a neighbouring empty interstitial site.
- This mechanism is more prevalent for impurity atoms such as hydrogen, carbon, nitrogen, oxygen which are small enough to fit in to an interstitial position.
- For substitutional diffusion atoms exchange their places directly or along a ring (ring diffusion mechanism).

This mechanism involves migration of atoms from one interstitial site to a neighbouring empty interstitial site. Interstitial sites are nothing, but the spaces in between the regular lattice sites. So, this space for example, here that you see between these lattice positions that is an interstitial site .

So, if the atom is small enough to fit into this gap or in this void, then it will be called as an interstitial atom. So, therefore, this mechanism is more prevalent for atoms such as hydrogen, carbon, nitrogen, oxygen which are small enough to fit into an interstitial position right.

So, it simply moves from one interstitial site to another interstitial site as we can see from here, this black circle this black atom that you have this is an interstitial atom. So, this moves into a neighbouring interstitial site as shown by this second picture and that is how the atomic transport happens through this interstitial site in this particular model.

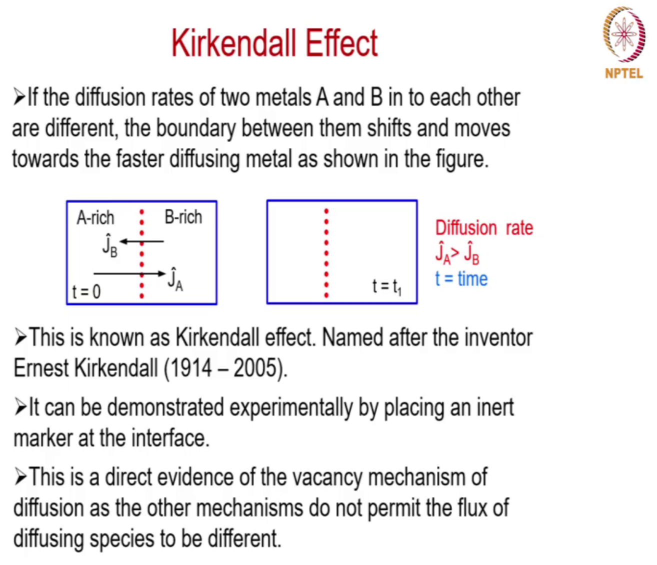
Now, in this case you can see that no defect is involved in the previous case, vacancy defect was involved for the atomic transport to happen, but here there is no defect it is simply the atom moving from one position to the neighbouring position. So, this was for an interstitial position, but if this has to happen for this substitutional site; that means, from one regular site to another regular site. So, for that kind of substitutional diffusions atoms have to exchange their places directly.

For example; this atom and the neighbouring atom these two atoms can switch their places for the transport to happen. So, this kind of substitutional transportation can happen either by a pair of atoms switching their positions as I said or a group of atoms can form a ring and the transport can happen through a rotation among those atoms .

For example; if you consider these four atoms over here let us say this one 1 2 3 4. So, these four atoms can form a ring and the diffusional process will then happen by a rotation among these atoms. So, if you consider a clockwise rotation for example, then 3 will come to 4, 4 will go to 1, 1 will go to 2 and 2 will come to the position of 3 .

So, this is how through a clockwise rotation in this ring which is formed by this four atoms the atomic diffusion will take place . So, that is why this is known as the ring diffusion mechanism which is for substitutional diffusion when the atoms move between the regular lattice sites.

(Refer Slide Time: 09:33)



Kirkendall Effect

- If the diffusion rates of two metals A and B in to each other are different, the boundary between them shifts and moves towards the faster diffusing metal as shown in the figure.

Diffusion rate
$\hat{J}_A > \hat{J}_B$
t = time

- This is known as Kirkendall effect. Named after the inventor Ernest Kirkendall (1914 – 2005).
- It can be demonstrated experimentally by placing an inert marker at the interface.
- This is a direct evidence of the vacancy mechanism of diffusion as the other mechanisms do not permit the flux of diffusing species to be different.

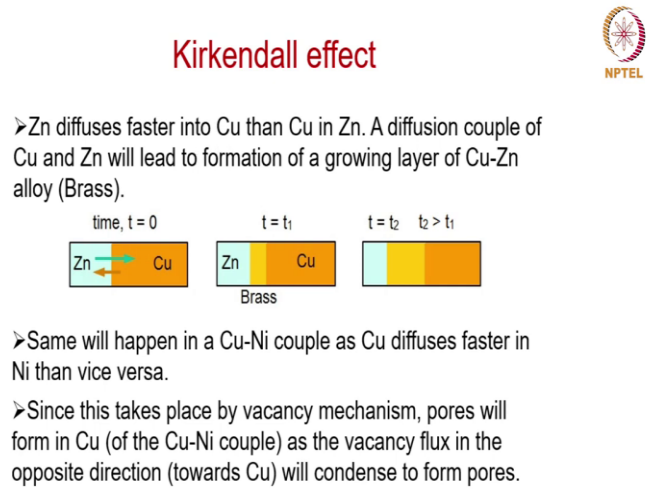
And, there is a phenomenon called Kirkendall Effect which is actually a direct evidence of the vacancy mechanism. For example, if you keep two metals A and B the boundary between them will shift and move towards the faster diffusion metal as shown in the figure .

So, this is known as the Kirkendall effect named after its inventor Ernest Kirkendall. In fact, this can be demonstrated experimentally by placing an inert marker at the interface and you can actually monitor the movement of the marker and that will indicate in which direction the atoms are moving .

So, in this case between A and B the diffusion rate of A is greater than that of B and therefore, the boundary will move towards the metal A right because that is what this effect talks about the boundary moving towards the faster diffusion metals. So, in this case A is the faster diffusing and therefore, this boundary will move towards A.

And you can see the boundary after a certain time is shifted towards the left hand side which is the a rich side. This can only happen if diffusion occurs by the vacancy mechanism as the exchange mechanism does not permit the fluxes to be different.

(Refer Slide Time: 11:21)



Kirkendall effect

- Zn diffuses faster into Cu than Cu in Zn. A diffusion couple of Cu and Zn will lead to formation of a growing layer of Cu-Zn alloy (Brass).

- Same will happen in a Cu-Ni couple as Cu diffuses faster in Ni than vice versa.
- Since this takes place by vacancy mechanism, pores will form in Cu (of the Cu-Ni couple) as the vacancy flux in the opposite direction (towards Cu) will condense to form pores.

This is an example of that where two metals copper and zinc are used to make a diffusion couple. Zinc diffuses faster into copper than the vice versa right. So, here zinc represents the A metal and copper represents the slower diffusing B metal .

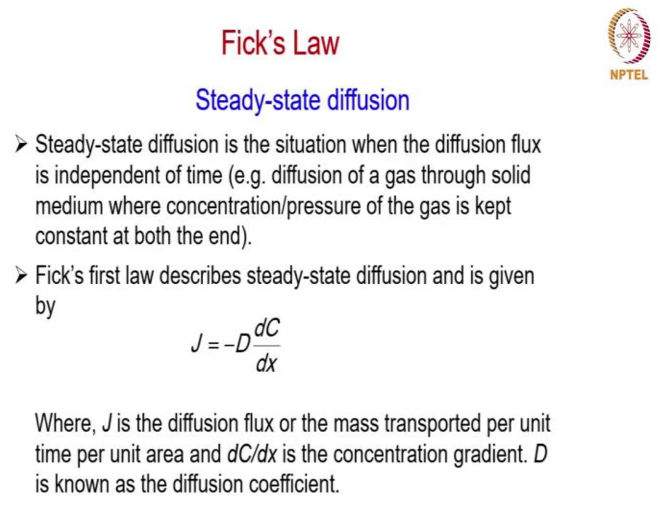
So, therefore, in this particular diffusion couple of copper and zinc as zinc atoms diffuse towards copper a growing layer of copper zinc alloy which is known as brass will form which is indicated by a different colour over here and as it progresses, this copper zinc alloy layer will grow into the zinc because zinc is the faster diffusing right.

Same phenomena will happen if there is a diffusion couple between copper and nickel in that case copper diffuses faster unlike here where copper is slower and therefore, when the atoms of the copper diffuse towards the nickel the vacancies will move in the other direction as we have discussed before.

So, therefore, you will find the vacancy flux in the opposite direction that is towards copper in this case of copper nickel diffusion couple and these vacancies will condense to form force right.

So, if you look at the copper after the diffusion has happened, you will actually find a lot of vacancies or force into the copper side of this diffusion couple. So, that is indicative enough that the vacancies actually have moved towards the copper as the copper atoms moved in the opposite direction towards nickel . So, this is how experimentally this can be shown as an evidence of the vacancy mechanism that we discussed.

(Refer Slide Time: 13:40)



Fick's Law

Steady-state diffusion

- Steady-state diffusion is the situation when the diffusion flux is independent of time (e.g. diffusion of a gas through solid medium where concentration/pressure of the gas is kept constant at both the end).
- Fick's first law describes steady-state diffusion and is given by

$$J = -D\frac{dC}{dx}$$

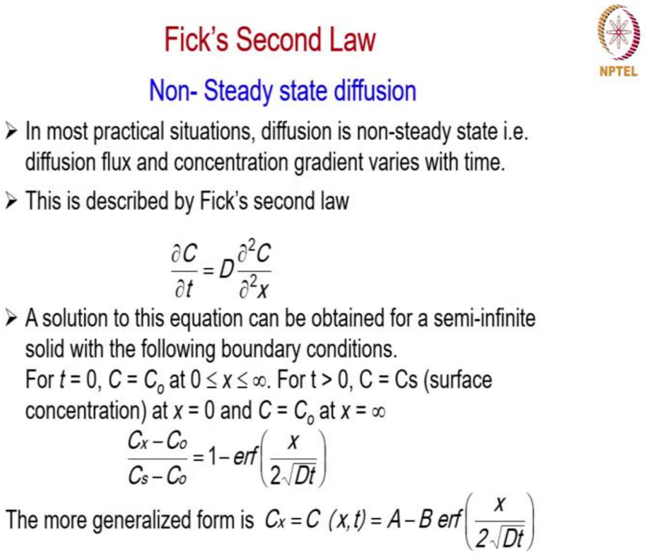
Where, J is the diffusion flux or the mass transported per unit time per unit area and dC/dx is the concentration gradient. D is known as the diffusion coefficient.

Now, this diffusion phenomena is described by Fick's law; Flick's first law and Flick's second law. Fick's first law describes the steady state diffusion where it is not dependent on time and the diffusion primarily takes place basis the concentration gradient.

$$\mathbf{J = - D\ (dC/\ dX)}$$

So, here dC by dx that you see is the concentration gradient, where C represents concentration and x is the distance and J is the diffusion flux or the mass transported per unit time per unit area . So, that is how flux is defined mass per unit area per unit time and D is known as the diffusion coefficient. The negative sign that you see over here indicates that the mass transport happens from higher concentration to lower concentration; that means, dC/ dx is negative.

(Refer Slide Time: 14:50)



Fick's Second Law

Non- Steady state diffusion

- In most practical situations, diffusion is non-steady state i.e. diffusion flux and concentration gradient varies with time.
- This is described by Fick's second law

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial^2 x}$$

- A solution to this equation can be obtained for a semi-infinite solid with the following boundary conditions. For $t = 0$, $C = C_0$ at $0 \le x \le \infty$. For $t > 0$, $C = Cs$ (surface concentration) at $x = 0$ and $C = C_0$ at $x = \infty$

$$\frac{C_x - C_0}{C_s - C_0} = 1 - erf\left(\frac{x}{2\sqrt{Dt}}\right)$$

The more generalized form is $C_x = C\ (x,t) = A - B\ erf\left(\frac{x}{2\sqrt{Dt}}\right)$

Fick's second law talks about non-steady state diffusion which happens in most practical situations and in this case the flux and the concentration gradient are dependent on time unlike the first law where they are independent of time. The Fick's law is given by this equation over here which shows the variation of the concentration with respect to time.

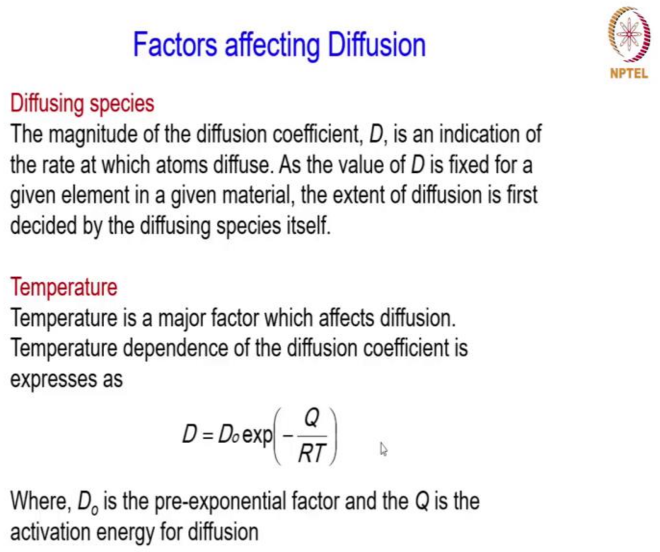
$$\partial C / \partial t = D\ (\partial^2 C / \partial x^2)$$

With this left hand side term $\partial C / \partial t$ **,** a solution to this equation can be obtained for a semi - infinite solid with the following boundary conditions at t equals to 0, C is equal to C_0, the initial concentration for x greater than equal to 0 and less than equal to infinity and when t is greater than 0, then C becomes Cs which is the surface concentration at x equal to 0 and C becomes equal to C_0 at x equal to infinity.

So, if you consider these boundary conditions the solution to this equation can be given by this particular equation that you see over here and more generalised form of this solution is given by this expression over here alright.

$$C_x - C_0 / C_s - C_0 = 1 - \mathrm{erf}(x / 2\sqrt{(Dt)})$$

(Refer Slide Time: 16:40)



Factors affecting Diffusion

Diffusing species

The magnitude of the diffusion coefficient, *D*, is an indication of the rate at which atoms diffuse. As the value of *D* is fixed for a given element in a given material, the extent of diffusion is first decided by the diffusing species itself.

Temperature

Temperature is a major factor which affects diffusion. Temperature dependence of the diffusion coefficient is expresses as

$$D = D_0 \exp\left(-\frac{Q}{RT}\right)$$

Where, D_o is the pre-exponential factor and the Q is the activation energy for diffusion

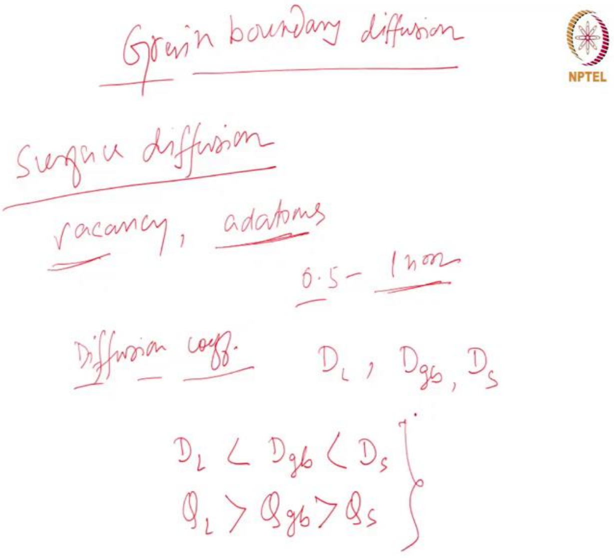
So, there are certain factors on which the diffusion is dependent on and temperature is one of them because here we are talking about the movement of atoms and when you increase the temperature it is obvious that this movement is also going to increase and that can be expressed with an equation like this where D is the diffusion coefficient and D naught is the pre-exponential factor.

$$D = D_0 \exp(-Q / RT)$$

So, here you can see that the diffusion coefficient increases exponentially with the temperature T which means that the diffusion process is thermally activated. R is the gas constant and Q is known as the activation energy for diffusion. So, this is the activism barrier that the atoms have to overcome for their movement to happen right and this whole thing is dependent on temperature.

So, you can see as the temperature increases the diffusion coefficient also increases which means that the diffusion process is thermally activated. So, this diffusion that we talked about it was all about lattice diffusion, but as we have seen while discussing about the sintering there could be other paths of diffusion also for example, the grain boundary and the surface diffusion.

(Refer Slide Time: 18:32)



Grain boundary diffusion

Surface diffusion

vacancy, adatoms

0.5 - 1 nm

Diffusion coeff. D_L, D_{gb}, D_s

$D_L < D_{gb} < D_s$

$Q_L > Q_{gb} > Q_s$

So, let us talk a little bit about those also, Grain boundary diffusion happens in polycrystalline material where a large number of grain boundaries are present. Grain boundary basically is a region of defect which is very different from the grain interiors and it also has a very small width which is typically in the range of 0.5 to 1 nanometer though the exact size is not known, but it is typically in that range.

And you might also know that as the grain size become finer and finer the grain boundary area increases and therefore, the fraction of solid that is occupied by the grain boundary will increase with decrease in grain size and therefore, the grain boundary diffusion rate is dependent on the grain size . So, that was about grain boundary diffusion.

Now, it can also happen through surface, as the surface of a crystalline solid is not really perfect there are certain defects which are present on the surface of the crystal. For example, there are vacancies, adatoms; adatoms are nothing, but atoms that lie on the surface and this can be considered as an entity which is opposite to vacancy.

So, here the migration of vacancies and the adatoms are the dominant mechanisms for the diffusion process and this diffusion process that happens in the surface considered to be confined in a thin surface layer having a thickness of around 0.5 to 1 nanometer.

If you talk about the diffusion coefficient for these three kinds of diffusion that we talked about the lattice diffusion, grain boundary diffusion and surface diffusion you would find that the lattice diffusion will be lowest and the surface diffusion coefficient will be highest.

This is because the atoms on the surface have less number of neighbours than those in the bulk of the material and also the atoms on the surface are less tightly bound compared to the atoms in the bulk and therefore, you can expect the activation energy for the movement of atoms on the surface to be lower compared to that in the lattice.

And therefore, the diffusion coefficient for surface diffusion will be significantly higher compared to that of the lattice diffusion and grain boundary is somewhere in between right.

So, if you talk about the trend of the diffusion coefficients D_L that stands for lattice diffusion, D_{gb} which stands for grain boundary diffusion and D_s which represent surface diffusion. Then, as I said Ds is the highest and D_{gb} ,grain boundary diffusion coefficient is in between and D_L is the lowest among these three and the activation barrier or the activation energy will then have just the opposite trend.

However, there can be conditions which might change these trends. So, these trends may not be always constant. So, now, that we have a good understanding about the diffusion process let us come back to this sintering phenomena.

So, as we discussed this basically happens through mass transport along well defined paths. There are number of such paths some of them fall under the category of surface transport and rest fall under the category of bulk transport.

In surface transport you primarily have the surface diffusion and evaporation condensation mechanisms as you can see. So, the surface diffusion happens by movement of atoms from the surface of the particles towards the neck region. Similarly, these vapours which are present around the particles can condense along the neck and lead to neck growth.

Volume diffusion on the other hand occurs through the lattice and grain boundary diffusion as the name suggests occurs through the grain boundaries and apart from them the plastic flow which is a dislocation controlled mechanism can also happen in metals.

So, before we finish this class let us quickly summarise it today we primarily talked about this diffusion phenomena which is a process of mass transport under the influence of a thermal energy and a concentration gradient and in this case the atoms always move from the higher to lower concentration region and this is also given by the Fick’s law as you can see from here from this particular equation.

This is the concentration gradient which is negative because as I said it is from higher to lower concentration. So, this defines the steady state diffusion which is not dependent on time .

And then there are certain models, which describes the mechanism of diffusion and we talked about these three models. First one was the vacancy diffusion which takes place with the help of the vacancies when the atoms move into the vacancy the vacancy moves towards the opposite direction and then there is this interstitial diffusion which is with regard to smaller atoms which fit into the interstitial sites of the lattice and here the diffusion happens as the atom moves from one interstitial site to the neighbouring one.

And then we also talked about this ring diffusion mechanism where a group of atoms form a ring and then through a rotation kind of mechanism the diffusion takes place and that is why this is known as the ring diffusion mechanism. Then we talked about this Kirkendall effect which is kind of experimental evidence for the vacancy mechanism.

We also talked about the dependence of the diffusion coefficient with temperature you can see that the diffusion coefficient increases exponentially with temperature and therefore, the diffusion process is thermally activated and then we also talked about great boundary diffusion and surface diffusion and we have seen that these two forms of diffusion are much faster compared to the lattice diffusion.

And therefore, the diffusion coefficient of surface diffusion and grain boundary diffusion are higher compared to that of the lattice diffusion if you talk about the trends grain boundary diffusion is in between lattice diffusion and surface diffusion

. And, with that we come to the end of this class.

Thank you for your attention.