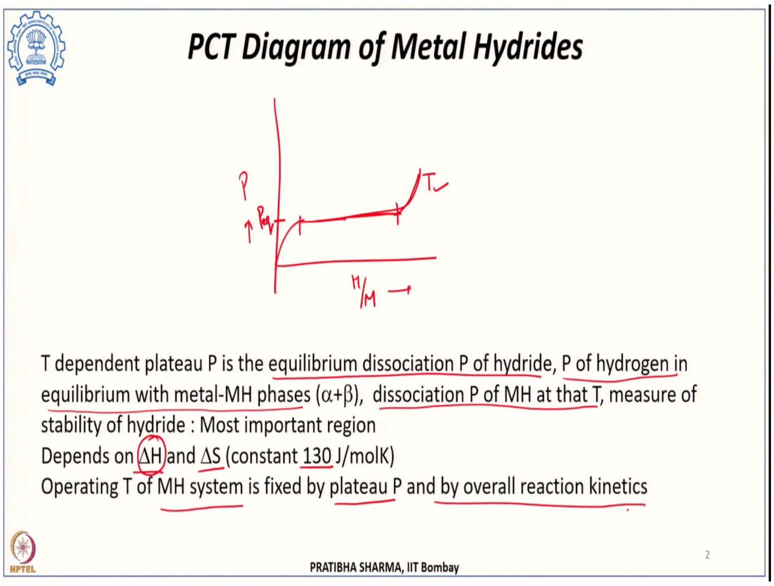
Hydrogen Energy: Production, Storage, Transportation and Safety

Prof. Pratibha Sharma
Department of Energy Science and Engineering
Indian Institute of Technology, Bombay

Lecture - 48
Fundamentals of Metal hydrides for Solid State Hydrogen Storage Part - 2

In the previous class we have seen the thermodynamics associated with the metal hydrides; we have also seen the different regions in the pressure composition temperature isotherm. Now the existence of this flat plateau is under ideal condition and true holds true for some of the metal hydrides. But in many of the hydrides this is not the case. So, now let us see the other exceptions as well as other cases which occurs in the real metal hydride and some of the terminologies we are going to learn in this particular class.

(Refer Slide Time: 00:51)



PCT Diagram of Metal Hydrides

T dependent plateau P is the equilibrium dissociation P of hydride, P of hydrogen in equilibrium with metal-MH phases (α+β), dissociation P of MH at that T, measure of stability of hydride : Most important region

Depends on ΔH and ΔS (constant 130 J/molK)

Operating T of MH system is fixed by plateau P and by overall reaction kinetics

PRATIBHA SHARMA, IIT Bombay

Now, we have seen in the earlier class the pressure composition isotherm and the 3 regions that exist. Now here this plateau region that has it is own importance, this flat plateau that we have seen when we have plotted the pressure with the concentration this is temperature dependent. So, this is drawn at a particular temperature. If we change the temperature this equilibrium pressure, this plateau pressure will also change.

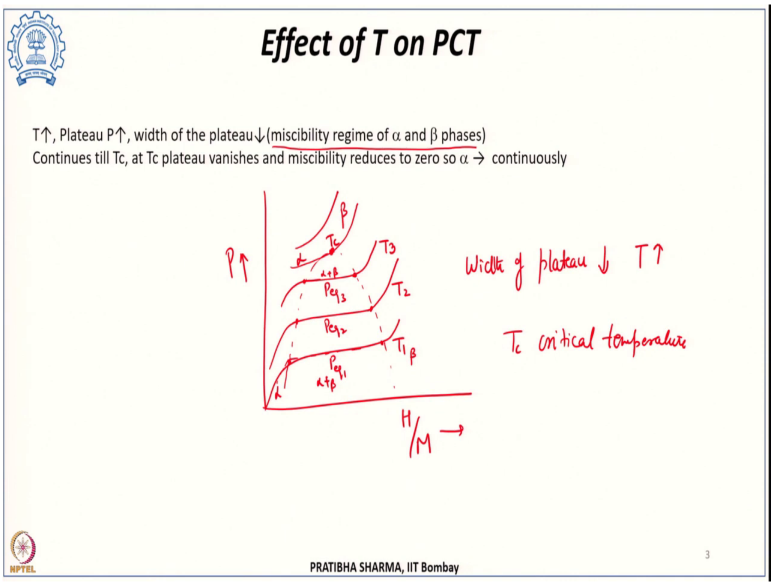
Now, this is a temperature dependent plateau pressure it is also known as equilibrium pressure. So, this has a great importance when designing the metal hydride based systems or while selecting the metal hydrides for various applications. This is known as the equilibrium dissociation pressure of hydride; this is the pressure of hydrogen in the equilibrium with metal-metal hydride phases or α + β phases.

This also represents the dissociation pressure of metal hydride at that particular temperature. This is a very important parameter to measure the stability of hydride, because we have seen that it is also related to ΔH and this is the most important region in the pressure composition isotherm. So, this equilibrium pressure through Van't Hoff relation in the previous class we have seen that it depends upon ΔH and ΔS.

But delta S we know that remains constant. So, this equilibrium pressure it is related to ΔH which in turn is related to the thermochemical stability of the metal hydride. So, thus at the operating temperature of metal hydride, when we are considering a metal hydride system design then at an operating temperature that is fixed by this equilibrium plateau pressure and that also decides the overall reaction kinetics.

So, and that plays an important role, so this equilibrium pressure at a particular temperature is used while designing a metal hydride based system along with the reaction kinetics needs to be considered.

(Refer Slide Time: 03:07)



Effect of T on PCT

T↑, Plateau P↑, width of the plateau↓(miscibility regime of α and β phases)
Continues till Tc, at Tc plateau vanishes and miscibility reduces to zero so α → continuously

PRATIBHA SHARMA, IIT Bombay

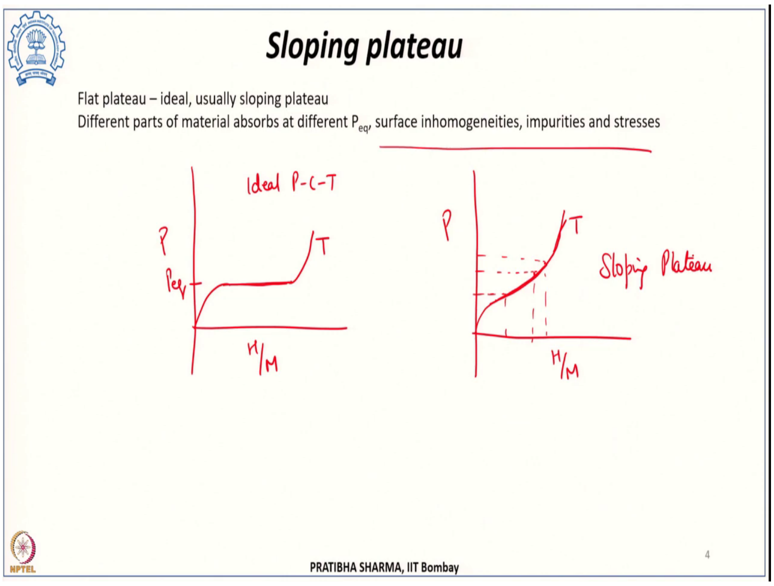
So, this was a pressure composition temperature isotherm which was drawn at a particular temperature. Now, what happens is if we change the temperature of the system this also changes. So, this is at a particular temperature at another temperature we can get another PCT curve. So, this is let us say at temperature T_1, T_2, T_3 and this is at critical temperature. So, this is when the pressure is plotted versus a concentration. Now we can see that, as the temperature increases this equilibrium pressure this also increases.

And we are getting the width of the plateau which is also reducing. So, this width of plateau region also decreases as the temperature increases. Now the important thing to be noted here is this plateau tells about the miscibility regime of the 2 phases which is alpha and beta. So, as the temperature increases and the plateau pressure increases or the plateau width decreases, the miscibility region of alpha and beta phase also decreases.

And this continues till a temperature which is the critical temperature. So, T_C being the critical temperature and this continues. So, the width continues to decrease until it diminishes to 0. So, the plateau width become 0 and the miscibility also reduces to 0 and after that what happens is earlier we have seen there is an alpha region, alpha plus beta region and finally a beta region.

So, alpha in between we were getting an alpha plus beta region, but beyond this critical point there is no 2 phase region alpha plus beta or alpha is directly converting into beta continuously. So, that is the impact of change in temperature on the PCT curves.

(Refer Slide Time: 05:28)



Sloping plateau

Flat plateau – ideal, usually sloping plateau
Different parts of material absorbs at different P_{eq}, surface inhomogeneities, impurities and stresses

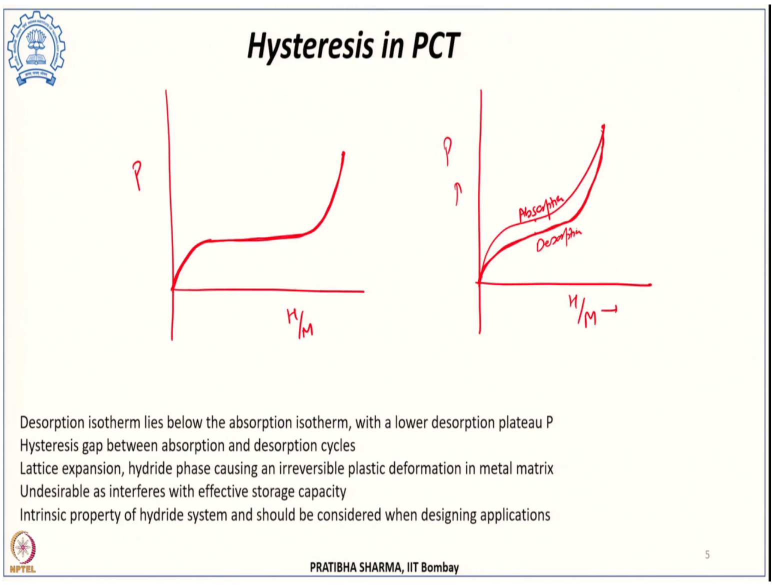
PRATIBHA SHARMA, IIT Bombay

Now, ideally what we should get is that a pressure composition isotherm with a flat plateau. So, this is how we get the ideal pressure composition temperature isotherms at a particular temperature. Some of the hydrides they still show this flat plateau, but most of the hydrides there is a sloping plateau that is being observed and this continues to change, when we plot pressure with the concentration.

So, this instead of getting a flat plateau we are getting a slope plateau and that tells us and this is again at a particular temperature, this is in case of most of the hydrides or this is in the real case we get a sloping plateau. Now this tells us that the equilibrium pressure is different here it also changes. So, instead of getting a particular equilibrium pressure, here different regions of the material that is having a different equilibrium pressure. Now the significance of this sloping plateau is that tells us that the different part of the metal or the material or the host matrix that absorbs at different equilibrium pressure.

The reason for this sloping plateau is the presence of different in homogeneities into the metal or the presence of different impurities or the presence of different stress. So, these are the reasons, which gives rise to a sloping plateau and we have to remember that while designing a metal hydride based system, we have to consider that, what is the actual plateau in the case of the metal hydride being selected for that particular application. Now, the another deviation from the ideal case is the presence of hysteresis.

(Refer Slide Time: 07:36)



Hysteresis in PCT

Desorption isotherm lies below the absorption isotherm, with a lower desorption plateau P
Hysteresis gap between absorption and desorption cycles
Lattice expansion, hydride phase causing an irreversible plastic deformation in metal matrix
Undesirable as interferes with effective storage capacity
Intrinsic property of hydride system and should be considered when designing applications

PRATIBHA SHARMA, IIT Bombay

Now, in ideal case what happens is like if we plot the pressure with the concentration during the absorption as we go along the curve and when we reach to the maximum pressure or the maximum absorption occurs, if we want to now release hydrogen from the system or if the hydrogen is to be withdrawn from the system.

Then we should be able to trace back the same curve or we should move on to the same curve getting back that hydrogen, the same curve is expected to be retraced back during the desorption process. That means, the equilibrium pressure for absorption and desorption is expected to be the same, but in actual practice what happens is for the actual hydrides this is the absorption curve while during desorption the same curve is not retraced back, rather the desorption curve it lies below the absorption curve.

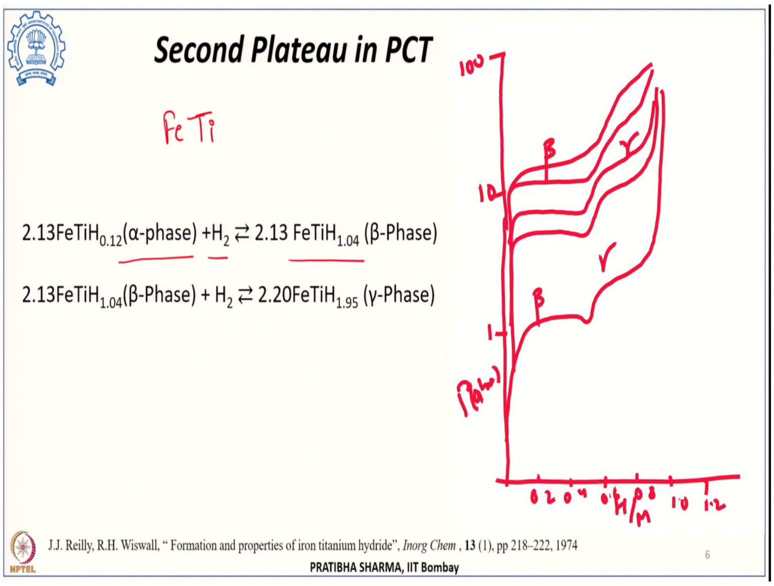
So, pressure and concentrations if these are plotted this is let us say absorption curve, then after reaching the maximum point or the maximum capacity here. If we want to the hydrogen to be released the curve that is obtained during the desorption is different or lower below the absorption curve. So, this is the desorption curve or the equilibrium pressure for absorption is not equal to the equilibrium pressure for the desorption here.

So, the desorption plateau pressure here we can see it is lower than the absorption plateau pressure and this effect is known as hysteresis. When the absorption cycle absorption curve is not matching with the desorption curve in the desorption cycle. So, this hysteresis gap occurs between the absorption and desorption cycle, the reason for occurrence of this hysteresis is considered to be the plastic deformations, which are not reversible.

Because of the lattice expansion that occurs when hydrogen incorporates into the host metal matrix, because of the irreversible plastic deformation in the metal matrix and this is highly undesirable when metal hydrides are to be used for various applications. The reason being this interferes with the effective storage capacity, but this is not an error this is the intrinsic property of the hydride system.

And if we do that several times this will be retraced back or this hysteresis will be every time observed and this it is essential that while designing a hydrogen storage system we should consider the presence of this terraces. That the desorption pressure will be different from the absorption pressure and also there will be a difference in the capacities as well.

(Refer Slide Time: 10:52)



Second Plateau in PCT

Fe Ti

$2.13FeTiH_{0.12}$(α-phase) $+H_2 \rightleftarrows 2.13\ FeTiH_{1.04}$ (β-Phase)

$2.13FeTiH_{1.04}$(β-Phase) $+ H_2 \rightleftarrows 2.20FeTiH_{1.95}$ (γ-Phase)

J.J. Reilly, R.H. Wiswall, " Formation and properties of iron titanium hydride", *Inorg Chem* , **13** (1), pp 218–222, 1974

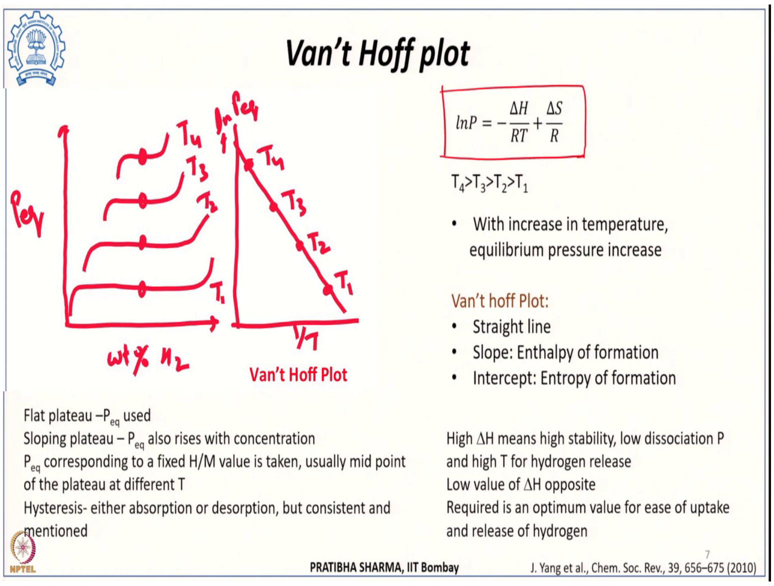
PRATIBHA SHARMA, IIT Bombay

6

One more deviation could be that instead of or in certain metal hydrides like in iron titanium type of metal hydride it is observed that instead of having 1 plateau, there are 2 plateaus which are observed. So, there is a plateau which is at a lower pressure, 1 plateau at a lower pressure and then there is another plateau that could also be there, which is at a higher pressure or at a higher concentration. Now for example, for FeTiH we can say that there is an alpha phase which gets hydrated to form a beta phase, so that is the beta phase and this beta phase further hydrides to give one more phase which is the gamma phase.

And thus there are 2 different plateaus existing. So, there are 2 different types of hydrides these could be mono hydride and dihydride and these results into 2 different plateau regions, so while designing any system that also needs to be considered. Usually the mono hydrides, so we will see later that the there may be difference in the stability of these hydrides as well and that has to be considered in a hydrogen storage system.

(Refer Slide Time: 12:09)



Van't Hoff plot

$$lnP = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$

$T_4 > T_3 > T_2 > T_1$

- With increase in temperature, equilibrium pressure increase

Van't hoff Plot:

- Straight line
- Slope: Enthalpy of formation
- Intercept: Entropy of formation

Flat plateau $-P_{eq}$ used
Sloping plateau – P_{eq} also rises with concentration
P_{eq} corresponding to a fixed H/M value is taken, usually mid point of the plateau at different T
Hysteresis- either absorption or desorption, but consistent and mentioned

High ΔH means high stability, low dissociation P and high T for hydrogen release
Low value of ΔH opposite
Required is an optimum value for ease of uptake and release of hydrogen

PRATIBHA SHARMA, IIT Bombay

J. Yang et al., Chem. Soc. Rev., 39, 656–675 (2010)

Now, we have seen that the Van't Hoff plot or the Van't Hoff equation in the previous class where the lnP the pressure it is related to the ΔH value. Now this ΔH the first term that if we plot lnP with 1/T the first term will give us the ΔH/R value, which is the slope of the curve. If we draw a straight line of log P with 1/T the slope will give us -ΔH/R while the intercept will be given by ΔS/R.

Now, this term remains constant and from there we can even get the value of delta H. How is that obtained? Like, these are the pressure composition isotherms which are being drawn for different temperature T1, T2, T3, T4. Now when we get an equilibrium pressure so this is a case of a flat plateau it becomes easier because the equilibrium pressure remains constant throughout the plateau region and we have also seen that as the temperature increases the plateau pressure also increases the plateau width decreases.

So, equilibrium pressure here is increasing as the temperature is increasing. Now this equilibrium pressure in the middle of the plateau could be used, these series of points of equilibrium pressure at different temperatures can be used to plot log of equilibrium pressure with 1/T.

And this according to this equation will be given by a straight line. So, this equilibrium points pressure points when plotted with 1/T at different temperatures T1, T2, T3, T4 we get a straight line having a slope of -ΔH/R and an intercept of ΔS/R. So, this slope is going to tell us what is the ΔH value for that particular material and the intercept will tell us what is the ΔS value enthalpy and entropy of formation.

Now this it becomes very easy when it is flat plateau; however, if we have also seen that for in actual practice or for most of the hydrides this we get is a sloping plateau. Now how to find the equilibrium pressure corresponding to that which can be used for the Van't Hoff plot?

What is being done is when it is a sloping plateau we get a P equilibrium that also changes with the concentration. So, instead of being constant it also changes with the concentration. So, a particular value of H/M, a particular value of H/M is selected for that particular sloping plateau condition and usually this is taken to be the middle point of the plateau region at different temperatures.

Like here it has been shown for the flat plateau we have taken to it to be the middle point same can be taken when it is a sloping plateau. So, the middle point is taken as a P equilibrium at different temperature even if it is a sloping plateau. Now, what if there is a hysteresis. So, in that case we will have a different P equilibrium for absorption and a different P equilibrium for the desorption case.

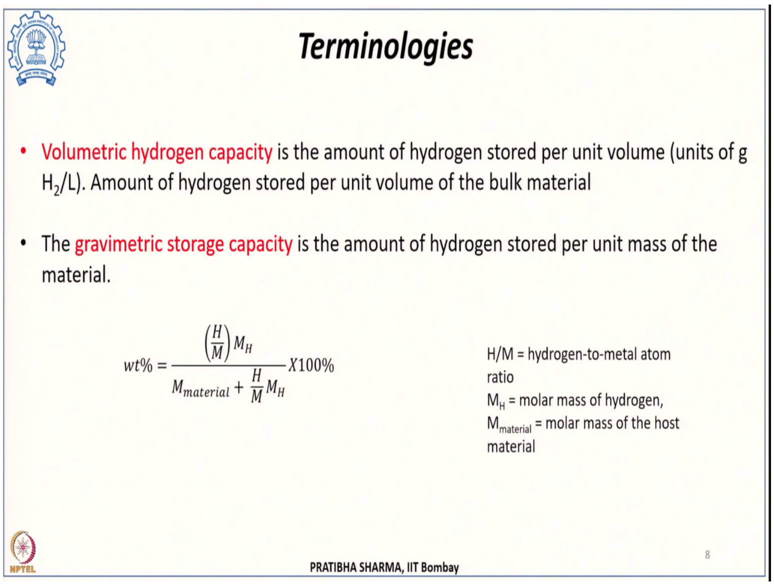
So, in that case if there is a hysteresis either we can consider absorption P equilibrium or desorption, but for that we have to be consistent. Like if for a particular temperature we have taken absorption equilibrium pressure then for the other temperatures also we will have to take the same absorption equilibrium pressure only. That means, absorption equilibrium pressure only not the, we cannot take for other desorption plateau pressure or the equilibrium pressure.

And that has to be mentioned while reporting the ΔH value. So, in this way drawing a Van't Hoff plot we can get the value of ΔH and ΔS. Now this ΔH as we have mentioned this is related to the stability of the metal hydride, if the ΔH value is high that means that material or the metal hydride has a higher stability. If it has a higher stability; that means, we will require low dissociation pressure or high temperature in order to get the hydrogen from the metal hydride system or for the hydrogen release.

So, as the ΔH value is higher that means, higher stability and a higher temperature or low dissociation pressure is required for the release of hydrogen. However, reverse occurs if like it is ΔH value is low; that means, the system is less stable and we will require higher dissociation pressure or low temperature for the hydrogen release. Now in actual case what is required is neither ΔH should be very high nor it should be very low.

An optimum or a medium or an intermediate value is required for getting for having an ease of uptake and release of hydrogen from these metal hydrides based systems. Now let us understand some of the terminologies, which are commonly used in metal hydrides or solid state hydrogen storage systems, like the term volumetric hydrogen capacity.

(Refer Slide Time: 17:37)



Terminologies

- Volumetric hydrogen capacity is the amount of hydrogen stored per unit volume (units of g H_2/L). Amount of hydrogen stored per unit volume of the bulk material
- The gravimetric storage capacity is the amount of hydrogen stored per unit mass of the material.

$$wt\% = \frac{\left(\frac{H}{M}\right) M_H}{M_{material} + \frac{H}{M} M_H} X100\%$$

H/M = hydrogen-to-metal atom ratio
M_H = molar mass of hydrogen,
$M_{material}$ = molar mass of the host material

PRATIBHA SHARMA, IIT Bombay

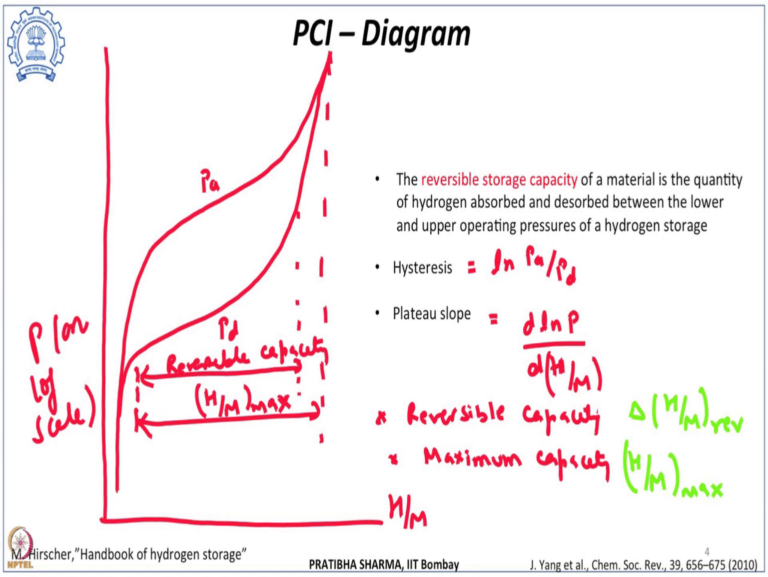
So, volumetric hydrogen capacity it represents the amount of hydrogen which is being stored in that system or in that material per unit volume, that is gram of hydrogen per liter. Now, if it is systems based then it will be system volume, if it is for we are reporting for material then it will be considered to be material volume.

Now the amount of hydrogen that is being stored per unit volume of the bulk material is being considered when we are talking about the material based volumetric hydrogen storage capacity. Similarly, we can use another term which is known as the gravimetric storage capacity and this is the amount of hydrogen which is stored per unit mass of the material.

Now, it can be expressed in 2 ways either H/M that is the hydrogen to metal atoms ratio or it can also be expressed in terms of weight percent. So, weight percent here the amount of hydrogen or the mass of hydrogen divided by the mass of the material and along with the mass of the hydrogen as well, where H/M is the hydrogen to metal atom ratio and correspondingly the molar mass of hydrogen as well as the material being considered.

So, the mass or the weight of hydrogen being stored divided by the weight of the material plus weight of hydrogen being stored times 100 that will give into weight percent.

(Refer Slide Time: 19:07)



PCI – Diagram

- The reversible storage capacity of a material is the quantity of hydrogen absorbed and desorbed between the lower and upper operating pressures of a hydrogen storage
- Hysteresis $= \ln P_a/P_d$
- Plateau slope $= \dfrac{d\ln P}{d(H/M)}$

* Reversible capacity $\Delta(H/M)_{rev}$

* Maximum capacity $(H/M)_{max}$

M. Hirscher,"Handbook of hydrogen storage"

PRATIBHA SHARMA, IIT Bombay

J. Yang et al., Chem. Soc. Rev., 39, 656–675 (2010)

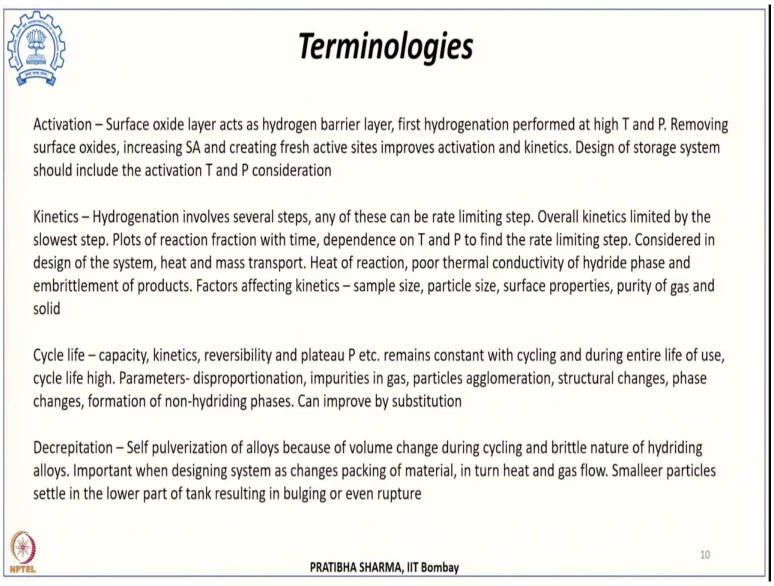
So, if we consider now consider PCT curve or PCT diagram, we can see that this is the typical pressure composition isotherm which is having a sloping plateau and then there is a hysteresis as well. So, this is let us say the absorption curve and then this is the desorption curve. So, there exist a plateau slope, there is a hysteresis and then we can identify the different terms in this PCI diagram.

Now there are 2 terms which are related to the capacity here one is the maximum capacity, which we can find out if we consider the absorption curve. So, this is the maximum that it can take, so this the entire this value will give us the maximum storage capacity so H/M maximum.

However, the reversible storage capacity will be lower than this maximum storage capacity and this is the capacity of hydrogen being absorbed and desorbed between the lower and the upper operating pressures of hydrogen storage. So, reversible storage capacity is usually the width of the plateau pressure which is being considered. So, this is in that case the reversible storage capacity given by $\Delta(H/M)_r$.

The slope of the plateau is given by d(ln(P))/d(H/M) the concentration ratio while the hysteresis between the absorption and desorption curves is given by ln (pressure of absorption/pressure of desorption). So, here in a single curve we have shown the different terms and their representation in the PCT diagram.

(Refer Slide Time: 20:58)



Terminologies

Activation – Surface oxide layer acts as hydrogen barrier layer, first hydrogenation performed at high T and P. Removing surface oxides, increasing SA and creating fresh active sites improves activation and kinetics. Design of storage system should include the activation T and P consideration

Kinetics – Hydrogenation involves several steps, any of these can be rate limiting step. Overall kinetics limited by the slowest step. Plots of reaction fraction with time, dependence on T and P to find the rate limiting step. Considered in design of the system, heat and mass transport. Heat of reaction, poor thermal conductivity of hydride phase and embrittlement of products. Factors affecting kinetics – sample size, particle size, surface properties, purity of gas and solid

Cycle life – capacity, kinetics, reversibility and plateau P etc. remains constant with cycling and during entire life of use, cycle life high. Parameters- disproportionation, impurities in gas, particles agglomeration, structural changes, phase changes, formation of non-hydriding phases. Can improve by substitution

Decrepitation – Self pulverization of alloys because of volume change during cycling and brittle nature of hydriding alloys. Important when designing system as changes packing of material, in turn heat and gas flow. Smalleer particles settle in the lower part of tank resulting in bulging or even rupture

PRATIBHA SHARMA, IIT Bombay

Along with that there are many more terminologies, which becomes important when we consider the design of hydrogen storage system, when we consider different metal hydrides. Like one of the most important process when metal hydrides are used for storage is the activation.

Now usually these metal surfaces they are covered by oxide layers and these oxide layers are of different thickness that depends upon the synthesis method. Now presence of the surface oxide layer that blocks the hydrogen entering into the metal or it acts as a hydrogen barrier layer and does not allow the hydrogen to get into the metal to form metal hydride.

So, that needs to be broken for that activation is being performed this is also known as first hydrogenation. So, activation or first hydrogenation is usually performed at a higher temperature and pressure. So, that hydrogen can penetrate inside this oxide layer could go through this oxide layer. So, what happens is when hydrogen enters into this into the metal lattice there is an expansion and when hydrogen is released there is a contraction.

When there are several cycles of expansion and contraction occurs the metal it breaks up into the or fine particles metal particles are obtained and that the process of removing the surface oxide increasing the specific surface area creating fresh surfaces or active sites that improves both the activation and kinetics of the process; so, when we are considering the design of a storage system the temperature and pressure which are required for activation.

The high temperature and pressure that we mentioned required for activation that has to be considered or included while we are considering the designing of such system. So, the system should be able to bear those temperatures and pressure should be able to handle. Now another terminology that we use is the kinetics and that we study in several other courses as well.

We have seen in the previous class that hydrogenation of metal hydrides is a complex process and it involves several steps that we have seen before and out of these several steps, any of the steps could be a slower step. So, that slowest step will be the rate determining step or the rate limiting step and the overall kinetics will be limited by that slowest step. So, we can plot the kinetics of a system or a metal hydride by plotting the reaction fraction against time.

And the dependence of this plot on different temperatures and pressures that will be helpful in finding out the rate limiting step and that has to be considered when we are designing the system. That is important because we will see when we will learn about the designing of the system that heat and mass transfer that plays an important role.

And metal hydride that plays an important role, because one of the reaction that is the forward reaction of formation of metal hydride it is an exothermic process and the reverse reaction is an endothermic reaction. So that means, heat is required for the reverse reaction and heat is released for the forward reaction. So, there involves the heat of reaction at the same time the thermal conductivity of the hydride phase is poor.

So, lot of thermal management is important and needs to be considered when we design a metal hydride based hydrogen storage system. At the same time, we have also seen that when hydrogen enters into the metal lattice, there is an expansion and when it comes out there is a contraction.

So, such expansion and contraction can even result into a sort of process which is could be even decrepitation or embrittlement could also be obtained. So, the factors that are very important when we consider the kinetics are like what is the sample size which we have selected, whether it is a lump whether it is a powder what is the particle size.

If we have selected even the powder what are their surface properties, whether the gas which we have used is pure or not, whether there are impurities present in the solid material which we have used the metal. So, all these play an important role while determining the kinetics of the process. One more term that we use is the cycle life, now what is expected when we design a system is that the material which is being used that should have a very high cycle life.

By cycle life we mean here that the hydrogen storage properties should be consistent over several cycles; that means, its capacity, its kinetics, reversibility, plateau pressure all should remain constant when we are considering repeated cycling or it should be same during the entire life of use of that material and that system. So, the desirable is that the cycle life of material should be high.

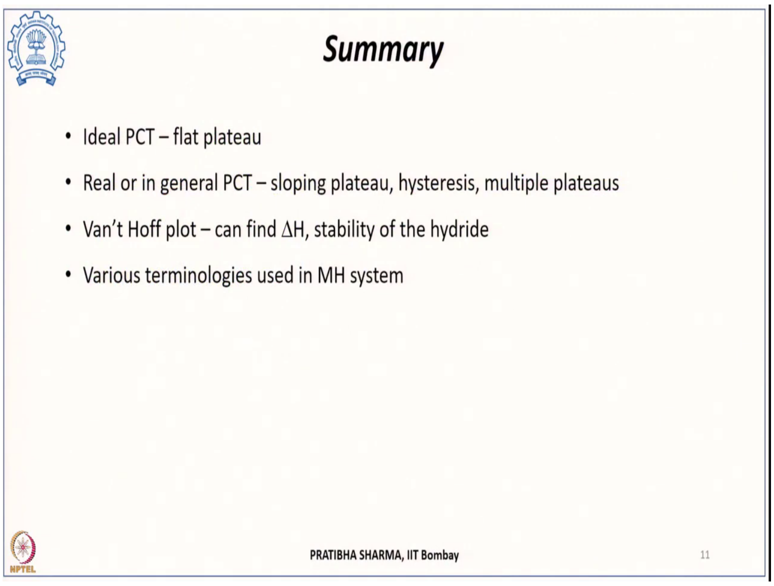
Now, again there are several parameters which govern the cycle life of these materials like disproportionation, again the expansion contraction of volume if there are any impurities present in the gas. If impurities are present, then some of the metal hydrides they get poisoned because of these impurities and then their cycle life reduces. Whether there is a particle agglomeration that has happened are there any structural changes or phase changes involved.

Sometimes there are non hydriding phases are formed or sometimes there are stable hydrides which are formed, which are very difficult to desorb under normal conditions. So, all that can not only reduce the capacity, but can also reduce the cycle life of the materials. So, what can be done is we can improve by several ways substitution is one of the way of improving the cycle life.

One more term that is being used is the decrepitation, this decrepitation means this is the self-pulverization of the alloy that happens because of the volume change during cycling process. It is also because of the brittle nature of these hydriding alloys and this is very important that needs to be considered while designing a storage system, because this decrepitation can change the way this material has been packed.

Now, with time what will happen is with repeated cycling the particles will break into smaller particles and that may affect that may change the porosity that may affect the gas and heat flow inside the metal hydride bed. These smaller particles they will tend to settle down into the tank or the lower part of the tank and in that case what will happen is when they settle down into the bottom part of the tank during hydrogenation. Again there will be an expansion of the lattice and that could even lead to after certain time bulging of the tank from the bottom or it can even lead to rupture of the tank.

(Refer Slide Time: 28:24)



Summary

- Ideal PCT – flat plateau
- Real or in general PCT – sloping plateau, hysteresis, multiple plateaus
- Van't Hoff plot – can find ΔH, stability of the hydride
- Various terminologies used in MH system

So, in this class we have seen that ideal PCT usually have a flat plateau, but a real or for most of the hydrides there is a PCT which shows sloping plateau hysteresis or there can be multiple plateaus. While designing a system we have to consider all these take into account all these while considering or selection of the metal hydride.

We have also seen how to plot Van't Hoff plot and using that we can find the delta H value which determines the stability of the hydride or the conditions at which the metal hydride will dissociate to release hydrogen. And we have also learned the different terminologies, which are used in a metal hydride based system. In the next class we will see what are the different metal hydrides, which could be used for solid state hydrogen storage.

Thank you.