

Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 49
Different Types of Hydrides for Hydrogen Storage

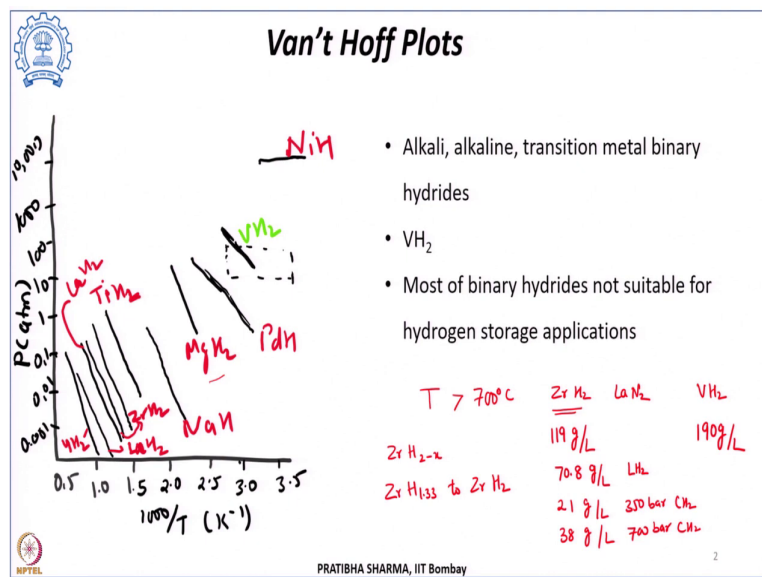
In the previous class we have seen the pressure composition temperature isotherms as it says isotherm; that means, these are drawn at a particular temperature. We have also seen the Van't Hoff Plots now we have seen how to draw the Van't Hoff plot like when the pressure composition isotherms they are drawn at different series of temperatures and from these when the equilibrium pressure is extracted and that is plotted with respect to $1/T$ we get a Van't Hoff plot.

Now this Van't Hoff plot that gives very important information about the metal hydride reaction about the metal hydride materials itself. That slope of the curve we have seen in the previous class that tells the ΔH value or the enthalpy of reaction or enthalpy of formation. It not only tells about the stability of the material, but it also tells like how much amount of heat will be released in the charging process during the hydrogen uptake.

And how much amount of hydrogen need to be supplied during the discharging process or during the release of hydrogen and that helps in designing such systems. In metal hydrides which operate under optimum conditions it is even possible to get the required heat of desorption from waste heat of either fuel cell or IC engine.

So, it is usually required that the operational temperature or the working temperature and pressure should be such that the temperature could be say at max 100 degrees centigrade or lower than 100 degrees centigrade, and pressure required should be close to ambient. But depending upon the what sort of applications we are at which we are looking at that may be say in the range of 1 to 100 bar maximum. Now if we look at the Van't Hoff plot for various binary hydrides.

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Now, then we can see from this particular curve that most of the binary hydrides they are actually not having desired thermodynamic properties; that means, the binary hydrides if we see the Van't Hoff plot pressure versus $1/T$ curve then these binary hydrides they are having higher thermodynamic stability. Like if we consider an equilibrium pressure of one bar, then they may have a temperature of desorption which is higher than 300 degrees centigrade.

For example, for magnesium hydride like it desorbs above 300 degrees centigrade at the same time the heat of reaction that even could be higher like for magnesium hydride it is 75 kilo joule per mole. Now the typical examples of such hydrides are alkali hydrides alkaline hydrides or transition metal hydrides like the scandium, titanium or vanadium groups.

Now the more electropositive hydrides the elements they react with hydrogen to form ionic hydrides while this magnesium hydride is a sort of intermediate. Intermediate in the sense between the ionic hydrides and the covalent hydrides of the other elements in the first two periods. If we look at the high temperature hydrides like the hydrides which at an equilibrium pressure of say one bar they desorb at temperature higher than 700 degree centigrade, then the typical examples could be like the zirconium hydride or the lanthanum hydride.


Now, this zirconium hydride this has a very high desorption temperature although the volumetric capacity of hydrogen storage in zirconium hydride this is high like about 119 grams per litre of hydrogen being stored. But as compared to say liquid state storage where the volumetric density 70.8 grams per litre that is in the liquid hydrogen storage or in case of

compressed hydrogen storage that is 21 grams per litre for 350 bar compressed hydrogen storage, or 38 grams per liter for 700 bar compressed hydrogen storage.

This zirconium hydride like many other hydrides it forms different hydride phases like it could be ZrH_{2-x} and this composition can be something between say 1.33 to it can be ZrH_2 . The another binary hydride is like vanadium hydride. Now this vanadium hydride again has a very high volumetric capacity; vanadium hydride has a high volumetric capacity of 190 grams per litre.

But the major problem that lies is if we see this box this is the alone hydride which lies in the range of optimal conditions of temperature and pressure, rest either they have high desorption temperature. So, most of the hydrides if we see they have higher desorption temperature or higher stability.

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Intermetallic Hydrides

- Libowitz et al. in 1958, IMC $ZrNiH_3$, thermodynamic stability between ZrH_2 and NiH
- Zr-Ni bond had a strong destabilizing effect on the Zr-H bond, at 1 bar P_{eq} T_{des} decreased
- completely new research field
- Miedema's Rule


$$\Delta H(A_n B_m H_{x+y}) = \Delta H(A_n H_x) + \Delta H(B_m H_y) - \Delta H(A_n B_m)$$

- In 1974, $LaNi_5$ (T_{des}), $FeTi$ and Mg_2Ni
- In 1984, Griessen and Drissen, semi-empirical band structure model:

$$\Delta H = \alpha \Delta E + \beta$$

$\Delta E = E_F - E_s$ (E_F is Fermi energy and E_s is center of lowest band of host metal),
 $\alpha = 59.24 \text{ kJ(eVmolH}_2\text{)}^{-1}$ and $\beta = -270 \text{ kJ(mol H}_2\text{)}^{-1}$

- several hundreds of other intermetallic hydrides were reported
- stoichiometric compounds from two metallic components A and B
- relationship between lattice parameter or unit cell volume and respective plateau P in different materials



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Now, it was in the year 1958 that Libowitz et al they came up with a completely new class of materials. So, that was a major breakthrough in the hydrogen storage materials. So, prior to that as we have seen in binary hydrides they are not suitable for hydrogen storage, but then when they came up with this class of materials which is known as intermetallic compounds.

They observed that these compounds they reversibly react with hydrogen storing hydrogen. At the same time, they have a thermodynamic stability which is intermediate between the two compounds and this opened up a completely new field of research. So, in 1958 they came up

with the intermetallic compound that was zirconium nickel and they mentioned that this zirconium nickel they observed that forms a ternary hydride.

And that ternary hydride the interesting thing that they found was that was having a thermodynamic stability between the highly stable zirconium hydride that has an enthalpy ΔH of formation of 169 kilo joule per mole and an unstable hydride of nickel hydride that had an enthalpy of formation of 8.8 kilo joule per mole. So, the interesting finding from this particular work was that the zirconium nickel bond which is being formed in this ternary hydride that had a strong destabilizing effect on the metal hydride that is the stable hydride zirconium hydride.

And it was observed that if we consider the equilibrium pressure of one bar the desorption temperature highly reduces. It reduces from 900 degrees to 300 degrees centigrade and that opened up a completely new research field of hydrogen storage materials and hundreds of more intermetallic compounds were developed and were studied.

But most of them they were found to follow the well-known Miedema rule and that was in fact, a relationship that connected the ΔH value of these intermetallic compounds with their individual hydrides and the intermetallic compounds itself. So, as per the Miedema rule if A and B these are the two elements in such that the $\Delta H(\text{AnBmH}_{x+y})$ is equal to $\Delta H(\text{AnH}_x)$ hydride of A plus $\Delta H(\text{BmH}_y)$ minus $\Delta H(\text{AnBm})$.

Now this rule we are able to explain or we are able to find out the ΔH enthalpy of reaction for most of the hydrides. Another breakthrough was when in 1974 the low enthalpy of formation metal hydrides was found. So, the two well-known metal hydrides we know today are LaNi_5 and FeTi . So, these were developed these were discovered in the year 1974 and it was observed that lanthanum nickel 5 which forms LaNi_5H_6 it has at say two bar of equilibrium pressure when it desorbs at 1300 degree centigrade.

However, it was observed that lanthanum hydride LaH_2 at an equilibrium pressure of say 2 bar it desorbs hydrogen at 1300 degree centigrade. However, the compound which was found intermetallic compound LaNi_5H_6 that desorbs hydrogen at 2 bar equilibrium pressure and at a temperature of 20 degree centigrade. Another interesting compound was iron titanium and also magnesium nickel Mg_2Ni .


So, in late in 1984, Griessen and Drissen they came up with a more accurate formula compared to the Miedema rule correlating the enthalpy of reaction with the characteristic energy of the electronic structure of the host metal. So, they came up with a semi empirical band structure model which has showed that there is a linear relationship between the ΔH and ΔE .

So, ΔH is equal to α times ΔE plus β where α and β these are constant having these values while the ΔE is the difference of Fermi energy E_F and E_S where E_S is the centre of the lowest band of host metal. Now, after this there were wide number of intermetallic compounds that were reported it was found that the host of these intermetallic compounds they generally are ordered stoichiometric compounds and these are being formed from two species two metallic components A and B.

So, these origin is there are two intermetallic compounds in various compositions forming nearly or stoichiometric compounds and also we have seen in the previous class that interstitial hydrides when hydrogen enters into the interstitial sites there occurs an expansion of the lattice. So, it was also found that the lattice parameter or the unit cell volume, it is related to even the plateau pressure in the different materials.

Now, coming up to these intermetallic compounds as we mentioned that the intermetallic compound it refers to a combined phase or an integrated phase between two metallic species A and B.

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Intermetallic Compounds (IMC)

IMC refers to an intermediate phase between A and B
Alloying 2 elements increases the degrees of freedom in the material formed and leads to various changes


A

Transition Metal or Rare Earth with a strong affinity for hydrogen and thus high thermal stability
Y, La, Ti, Zr etc.

B

Transition Metal forming unstable hydride e.g. Cr, Mn, Fe, Co and Ni etc. absorbing hydrogen only at high P

e.g. $\text{LaNi}_2 \Delta H = -32 \text{ kJ/mol H}_2$, $\text{LaH}_2 \Delta H = -208 \text{ kJ/mol H}_2$ and $\text{NiH} \Delta H = -8.8 \text{ kJ/mol H}_2$


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Now, alloying of these two species together, it increases the degrees of freedom of the final product in the product material like that may change several properties of the material its hydrogen storage properties will change. So, when we alloy these together it increases the degrees of freedom in terms of the change in the structure.

There may be a change in there would be defects or anti phase boundaries which are created and that may help in improving on to the hydrogen storage properties of these materials. Now among the intermetallic compounds between this A and B. So, these are A and B making an intermetallic compound the metal element A is such that it is a transition metal or a rare earth and that element A has a stronger affinity towards hydrogen.

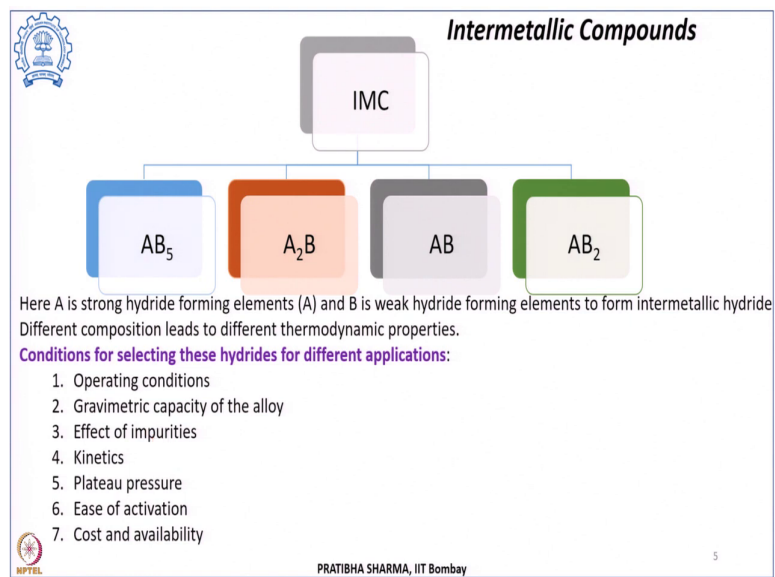
Once it has a stronger affinity with hydrogen that make; that means, it makes a stronger bond with hydrogen and that makes that hydride highly thermally stable. So, the examples of elements that appear at A side could be yttrium, lanthanum, titanium, zirconium or there could be more. Similarly, the other element B in these compounds it could be a transition metal, but that transition metal which forms an unstable hydride example chromium, manganese, iron, cobalt and nickel.

So, these are they form unstable hydride and they absorb hydrogen only at a higher pressure. So, a combination of one element which has a strong hydride forming tendency forms the stable hydride and another element which forms an unstable hydride gives rise to a intermetallic compound which will have intermediate between the two properties.

So, they will have different chemical and physical properties compared to both A and B. A typical example could be like at A site if it is lanthanum at B site if it is nickel. So, an example being LaNi_5 such that the ΔH value of LaNi_5 is 32 kilo joule per mole; however, lanthanum hydride we have already seen that this is a stable hydride having a ΔH value of 2008 kilo joule per mole, nickel forms an unstable hydride with a ΔH value of 8.8 kilo joule per mole.

But when an intermetallic compound is formed with La and Ni it forms LaNi_5 and having an enthalpy of formation of 32 kilo joule per mole which lies in between the two. Now depending upon the way these are combined. So, what are the different elements being used, what are the different combinations?

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These intermetallic compounds can be divided into different classes. So, there could be either an AB₅ type of compound, it could be A to B, it could be AB₂ type of compound AB, A₃B₇, AB₃ type of compounds. So, these are the different classes of intermetallic compounds. So, as we have seen in this A and B, A is a strong hydriding element, B is a weak hydriding element and that forms the intermetallic compound. The different compositions can lead to different thermodynamic properties.

Now, when we are selecting these intermetallic compounds for different hydrogen storage applications what we need to look at is, what are the operating conditions, what are the temperature and pressure, what is the capacity of that alloy? Is it affected by the presence of impurities in the material itself as well as in the gaseous hydrogen? How is the kinetics of that reaction of uptake as well as release whether it is a sluggish kinetics whether it is a faster kinetics usually the desirable is it should have a faster kinetics?

What is the plateau pressure or the equilibrium pressure for that particular intermetallic compound? How easily it can be activation activated? So, activation we have seen in the previous class and ease of activation also plays an important role. What is the cost of that material and how easily is that available? So, rare earth could be avoided.

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Metal Hydride						
Type of metal hydride	Most studied alloy	Reversible H ₂ storage capacity	ΔH kJ mol ⁻¹ H ₂	P _{eq} (bar)	T _{des}	Crystal structure
AB	TiFe	1.5	-28	5	RT	Cubic Pm3m
AB ₂	ZrMn ₂	0.9	53.2		440	Fd3m
A ₂ B	Mg ₂ Ni	3.3/3.6	-64.5	1	255	Cubic P6222
AB ₃	LaNi ₅	1.28	-30.8	2	285	Hexagonal P6/mmm
AB ₃	CeNi ₃	0.85	-35.36			Hexagonal
A ₂ B ₇	Nd ₂ Ni ₇	0.77	-34	10		
BCC compound	V ₂₂ Ti ₃₅ Cr ₄₃	2.5	-35	10		Cubic (Im-3m)
Saline hydrides	Mg	<7.0	-74.5	1	552	Hexagonal
High entropy alloy	TiVZrHfNb	Maximum=1.9H/M	-59			BCC (Im-3m)

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Now, these are the typical examples of the most widely studied class of these compounds like for AB FeTi has been widely studied, for AB₂ ZrMn₂, for A₂B Mg₂Ni, for AB₅ LaNi₅, for AB₃ CeNi₃, for A₂B₇ Nd₂Ni₇ and other compounds.

So, their reversible storage capacity may vary their ΔH value may be different their equilibrium pressure temperature and crystal structures may vary and these are quite important when we design a particular metal hydride based hydrogen storage system all these needs to be considered while selecting a appropriate material.

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AB₅ type alloys

- Widely studied: electrochemical properties
- Vast range of compounds, ease of substitution
- Structure: CaCu₅ with space group P6/mmm
- In 1969, SmCo₅ first studied for magnetic properties leads to development of AB₅ type hydrogen storage alloys
- Plateau P, slope, hysteresis, tolerance to impurities and cycling can be controlled (one property improve)
- Most studied system is LaNi₅ - favorable PCT, low hysteresis, plateau P at RT is 20 bar (1.25wt%)

A

↓

Lanthanides
Calcium
Yttrium
Zirconium
Misch metal

B

↓

Nickel
Tin
Titanium
Aluminum
Cobalt
Iron
Copper

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Now, starting with AB₅ class of compounds, these AB₅ class of compounds these have been widely studied. This is because of their special applications like that was in the case of electrochemical applications. So, they have good electrochemical properties as such these have been studied and a vast range of such compounds they have been studied they have been developed. The reason being ease of substitution at the A and B sites their typical structures are of CaCu₅ type.

And the first material in this class which was studied was SmCo₅ and that was studied for their magnetic properties and thereafter the development of the AB₅ type of hydrogen storage materials started. Now in this AB₅ type of compounds the first element A here this it could be either lanthanide, it could be calcium, it could be yttrium, it could be zirconium or Misch metal. Now this Misch metal is in fact, a combination of different rare earths and that is in their naturally occurring composition.

So, it can have different composition depending upon the different source. Usually a general composition could be like 45 percent of lanthanum, 50 percent of cerium others could be neodymium or praseodymium. On the B side it could be nickel, tin, titanium, aluminium, cobalt, iron, copper, silicon. Now when this alloy class is being considered because of this alloy they have a different hydrogen storage characteristics and their stability of these compounds all that depends upon what is the plateau pressure.

So, the factors that govern stability will be what is the plateau pressure and their hydrogen storage properties as well. What is the slope of the plateau? What is hysteresis all these terms we have seen in the last class, does these compounds have hysteresis? Are they tolerant to the impurities present in the material itself as well as in the gas?

How good is the cyclic life of these materials and all these can be controlled by appropriate selection of elements onto the A and B sites and that makes these class of compounds very interesting in the sense that we can tailor the properties the required hydrogen storage properties by appropriate selection of A and B at the same time substitution of these elements.

But sometimes what happens is if we try to improve one property let us say for hydrogen storage property resorption temperature may be higher. So, if we try to improve one property that may deteriorate the other. So, that makes it little complex in that case. Among this class

of compound, the most widely studied one is the LaNi_5 . Now this is having several advantages because it has a favourable pressure composition temperature isotherm.

This has very low hysteresis at the same time if we see the plateau pressure at room temperature is 20 bar and both like the operational conditions if we see are very favourable room temperature and 20 bar both are quite favourable operational condition. So, the reversible capacity of these type of materials LaNi_5 materials this is 1.25 weight percent.

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AB_5 type alloys

	Wt%	ΔH (kJ mol^{-1})	P_d at 25 °C (atm)	Hysteresis	Slope
MmNi_5	1.46	21.1	23	1.65	0.54
LaNi_5	1.49	30.8	1.8	0.13	0.13
CaNi_5	1.05	31.9	0.5	0.16	0.19

} Significant disproportionation and can loss reversible capacity during cycling, partial substitution

Ni Substitution

	Wt%	ΔH (kJ mol^{-1})	P_d at 25 °C (atm)	Hysteresis	Slope
$\text{MmNi}_{4.15}\text{Fe}_{0.85}$	1.14	25.3	11.2	0.17	0.36
$\text{LaNi}_{4.8}\text{Sn}_{0.2}$	1.4	32.8	0.5	0.19	0.22
$\text{MmNi}_{3.5}\text{Co}_{0.7}\text{Al}_{0.8}$	1.24	39.8	0.11	0.2	1.2

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Now, if we consider some of the examples, like if this A side it is Misch metal or lanthanum or calcium these are substituted with Misch metal lanthanum or calcium, B side is Ni. So, MmNi_5 or LaNi_5 or CaNi_5 , we see that they will have different storage characteristics like MmNi_5 has a weight percent gravimetric capacity of 1.46 weight percent, LaNi_5 has 1.49 weight percent, CaNi_5 has 1.05 weight percent.

ΔH value we can see that it also with this substitution in this order it increases 21, 30, 31.9, the desorption pressure at a temperature of 25 degrees centigrade it is also decreasing. So, for Misch metal it was 23 atm, for LaNi_5 it is 1.8 atm, for CaNi_5 it is 0.5 atm at the same time on this substitution on the A side that reduces the hysteresis.

So, for 1.65 it has reduced to 0.13 and then it has slightly increased to 0.16. At the same time the slope of the plateau has also reduced and then increased in the CaNi_5 . Now this shows the effect of substitution on the A side. However, it has been found that these 2 LaNi_5 and CaNi_5


on repeated cycling we have seen that when hydrogen gets into the lattice there is an expansion and when it is released then there is a contraction.

So, because of that repeated cycling it is possible that significant disproportionation can result in these type of compounds like LaNi_5 and CaNi_5 and that disproportionate can cause the property changes can lead to loss in the reversible capacity during cycling and that could be taken care of by partial substitution on to the nickel side. So, a typical example of this partial substitution reducing this disproportionate is substitution by means of tin.

So, on nickel side if we substitute $\text{LaNi}_{4.8}\text{Sn}_{0.2}$ it was found that this has a better cyclic stability. It has weight percent 1.4 percent, ΔH is 32.8, plateau pressure reduces 0.5, hysteresis 0.19 and slope being 0.22. Similarly, if we consider other substitution on the nickel side for Misch metal like that of iron that again changes the characteristic like the weight percent; however, is found to reduce compared to MmNi_5 from 1.46 to 1.14, ΔH value has increased 25.3.

Similarly, the desorption pressure has reduced to 11, hysteresis also was found to reduce 0.17 on iron substitution, slope was also found to reduce to 0.36. Similarly, if we substitute on the Misch metal side on the nickel side in the Misch metal alloy of MmNi_5 if we substitute to the nickel 3.5, cobalt 0.7, Al 0.8. So, this we can see that the weight percent has; however, reduced the ΔH value has increased the desorption pressure it reduces to 0.11 hysteresis as well as slope. We can see that these are also changed when it is substituted on the nickel side.

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AB_5 type alloys

Advantages:

- Good kinetics
- Good cyclibility
- Low hysteresis
- Good tolerance to impurities

Disadvantages:

- Low hydrogen storage capacity (1.2 wt%)
- High Cost of raw material




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Now, the advantages of AB₅ type of alloys is they have good kinetics they show good cyclicability, they have a low hysteresis that is very important they are tolerant towards impurities. But the disadvantages of these class of compounds is they have a low hydrogen storage capacity of 1.28 percent. At the same time the cost of the raw material is also high, but Misch metal is could be used for large scale production because the cost of Misch metal is lower.

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AB₂

- Laves phase - C14 Hexagonal (MgZn₂), C15 cubic (MgCu₂) and C36 Hexagonal (MgNi₂) structure
- Largest group IMC, factors: geometry, packing density, valence e⁻ conc or electronegativity difference
- Very attractive – high capacity, good kinetics, long cycle life but too stable at RT and sensitive to impurities
- Structure: Laves phase alloys (first reported in 1960)
- TiCr₂ and ZrCr₂ most studied system
- More hydrogen storage capacity than AB₅ alloys : 1.9 wt% for TiMn_{1.5}
- Wider temperature range of hydrogen possible
- Sub or super stoichiometric e.g. ZrMn_{2-x} (eg reduces & capacity reduces)
- Desired properties, multicomponent systems e.g. Zr_{1-x}T_x(Mn, Cr)_{2-y}M_y, where T = Ti, Y, Hf, Sc, Nb and M = V, Mo, Mn, Cr, Fe, Co, Ni, Cu etc

A


↓

Ti, Zr, Hf or
Lanthanides

B

↓

TM or non-
TM : V, Cr,
Mn, Fe



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"A panoramic overview of hydrogen storage alloys from a gas reaction point of view", *Journal of Alloys and Compounds* 877, 293–295, 1999

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Now the another class of compounds is AB₂ type of compounds and these are usually the laves phase type of compounds wherein the crystal structure they have three different type of crystal structures they show different phases like the C14 phase which has a typical structure of hexagonal structure of MgZn₂, a C15 phase which is cubic which is structure of MgCu₂ and a C36 phase hexagonal with MgNi₂ type of structure.

Among the different class of intermetallic compounds this is the compound which are most widely being studied and being developed. So, this is the largest group of intermetallic compounds and it is observed that the stability of these type of compounds it depends upon their geometry what is the packing density, what is the valence electron concentration and the electron negativity difference between the A and B sites. These are being studied a lot the reason being they are very attractive.

Because of their high capacity they show good kinetics, they have a longer cycle life, but the major disadvantages associated are that they form stable hydrides at room temperature. So,

they are too stable at room temperature, at the same time they can get poisoned to the impurity. So, they are sensitive to impurities present in the gas or in the solid as well. So, the first such structure Laves phase was reported in 1960 and the typical most studied structures are TiCr_2 and ZrCr_2 .

Now, among this AB_2 type of compounds usually this A site could be either titanium, zirconium, hafnium, or lanthanides and the B could be either a transition metal or it can be a non transition metal including vanadium, chromium, manganese or iron. Now these materials can be instead of being ordered stoichiometric this could be slightly sub or super stoichiometric example that of ZrMn_{2-x} . Now when this $2-x$ if we consider that x is positive.

So, when we are considering it to be $2-x$ what happens is the equilibrium plateau pressure that reduces compared to ZrMn_2 . So, equilibrium plateau pressure reduces at the same time capacity also reduces, when x is positive or the structure is or the composition is ZrMn_{2-x} . However, and it is $2-x$, then the equilibrium pressure rises and capacity is a very small reduction negligibly small reduction as against ZrMn_2 .

So, we can tune the desired properties like plateau pressure can be either increased or it can be decreased by changing the composition here. We can also get the required properties with such compounds by having multi component system. A typical example of such multi component system is like $\text{Zr}_{1-x}\text{T}_x\text{MnCr}$ it is either Mn or $\text{Cr}_{2-y}\text{M}_y$ where this T could be either titanium, yttrium, hafnium, scandium, niobium or M could be this M could be vanadium, molybdenum, manganese, chromium, iron, cobalt, nickel, copper or anything else as well.

So, we can have multi component such systems so, as to get the required hydrogen storage properties.

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AB_2 type alloys

	Wt%	ΔH (kJ mol^{-1})	P_d at 25 $^{\circ}\text{C}$ (atm)	Hysteresis	Slope
TiCr _{1.8}	2.43	20.2	182	0.11	0.12
TiMn _{1.5}	1.86	28.7	8.4	0.93	0.57
ZrMn ₂	1.77	53.2	0.001	0.99	0.74

Ternary alloys

	Wt %	ΔH (kJ mol^{-1})	P_d at 25 $^{\circ}\text{C}$ (atm)	Hysteresis	Slope
ZrFe _{1.5} Cr _{0.5}	1.5	25.6	4	0.34	1.26
TiMn _{1.4} V _{0.62}	2.15	28.6	3.6		1.4


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Now if we see certain examples of this type of material we can say that titanium chromium 1.8 and if chromium this is B site if it is Mn or on A site if it is zirconium. So, we can see that if it is titanium chromium 1.8, the weight percent which could be achieved is 2.43 weight percent this is reasonably good. We see that with such change the plateau pressures the desorption pressure at 25 degrees centigrade that changes significantly.

So, from A site if it is ZrMn₂ it is 0.001 atmosphere; however, when it is B side it is Mn, TiMn_{1.5} it is 8.4 atmosphere, for TiCr_{1.8} it is 182 atmosphere, similarly there is a change in the hysteresis and the plateau slope. Now, multi component systems also can be seen like the ternary compound where this is ZrFe_{1.5}Cr_{0.5} this gives a weight percent of 1.58 percent, ΔH value of 25.6.

Desorption pressure of 4 atmosphere, hysteresis 0.34 and a slope of 1.26, titanium manganese vanadium compound. So, TiMn_{1.4}V_{0.62} it has a capacity of 2.15 weight percent, ΔH value of 28.6 kilo joule per mole, desorption pressure of 3.6 atmosphere and a slope of 1.4.


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AB_2 type alloys

- Low hysteresis in TiCr1.8
- Maximum hydrogen storage capacity is 1.86 for TiMn1.5
- Reversible hydrogen capacity 1.15 wt%

Advantages:	Disadvantages:
<input type="checkbox"/> Higher capacity than AB_5	<input type="checkbox"/> Difficulty in activation
<input type="checkbox"/> Low cost	
<input type="checkbox"/> Work at room temperature	




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So, among these compounds we see that there is a low hysteresis for the compound TiCr1.8, the maximum hydrogen storage capacity is 1.86, for TiMn1.5 and reversible hydrogen storage capacity that could be achieved could be even 1.15 percent or even higher. Now the advantages of these compounds is we can get a higher capacity compared to the AB_5 type of compounds.


Correspondingly they have a lower cost they can operate at temperatures closer to room temperature, but the biggest challenge which these class of compounds is there is a problem in activation. So, the first hydrogenation requires high temperature and pressures.

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AB type alloys

- First study in 1958 on ZrNi, showed higher desorption temperature at 300 °C
- Structure: ordered BCC, $Pm-3m$
- Most studied system TiFe system (in 1970 by Reilly & Wiswall)
 - Absorb and desorb at room temperature
 - Maximum HSC is 1.9 wt% at H/M 0.975, reversible capacity of 1.5wt%
 - Difficulty in activation: need high temperature >400 °C
 - Two step absorption, Two plateau
 - Large hysteresis
 - Partial substitution can modify hydrogen absorption



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Another class of compound is AB type of compound. Now compare to AB₅ and AB₂ type of compound the different compositions studied in AB class are very less. So, the first study was in 1958 on zirconium nickel and that we have seen that shows a desorption temperature of 300 degrees centigrade.

They have structure ordered BCC and the most widely studied structure in AB type of compounds is iron titanium compound and this was for the first time studied by Reilly and Wiswall and that was in 1970. The biggest advantage of this class of material FeTi is that they absorb and desorb at room temperature and that is what is highly desirable when we select a material for hydrogen storage. It can give maximum hydrogen storage capacity of 1.98 percent at H/M ratio of 0.975 with a reversible capacity of 1.58 percent.

But the major challenge that lies is the problem in activation and it requires a high temperature for activation greater than 400 degrees centigrade. At the same time, it shows two plateaus that we have seen in the previous class there is two step absorption and there are two plateaus there are two different hydrides which are formed beta gamma phases and there is large hysteresis in these type of systems.

However, we can address these problems by partial substitution and that if we do a partial substitution then that will change the hydrogen absorption characteristics.

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AB type alloys

Partial substitution modifies sorption behaviour

	Wt%	ΔH (kJ mol ⁻¹)	P_d at 25 °C (atm)	Hysteresis	Slope	
TiFe (L)	1.86	28.1	4.1	0.64	0	
TiFe _{0.85} Mn _{0.15} (L)	1.9	29.5	2.6	0.62	0.92	Good cyclic stability
TiFe _{0.8} Ni _{0.2} (L)	1.3	41.2	0.1	0.05	0.36	

AB shows two plateau
L: values for lower plateau



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Examples like if we consider the parent iron titanium, now as I mentioned that there are two plateaus if we only consider the lower plateau, like if we consider the only the lower plateau then the desorption pressure corresponding to 25 degrees centigrade is 4.1 atmosphere for FeTi, but if we substitute on the iron side by manganese 0.85 is iron and 0.15 is manganese.

Then the desorption pressure reduces to 2.6 atmosphere, but the capacity increases to 1.98 percent if we substitute it by nickel. So, TiFe_{0.8}Ni_{0.2}. So, the lower plateau for the lower plateau we see that the desorption pressure further decreases to 0.1. In this process like we can see that the maximum weight percent is obtained for manganese substitution, the maximum ΔH value is for nickel substitution and the lowest desorption pressure is for nickel substitution.


So, the desorption pressure decreases as we move from iron titanium to its substitution to manganese and nickel and this particular alloy TiFe_{0.85}Mn_{0.15} is known to have good cyclic stability.

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AB type alloys

Advantages: <ul style="list-style-type: none"><input type="checkbox"/> Good hydrogen storage capacity<input type="checkbox"/> Low cost<input type="checkbox"/> Operate at room temperature	Disadvantages: <ul style="list-style-type: none"><input type="checkbox"/> Need of activation step before hydrogenation - very high temperature and pressure<input type="checkbox"/> Sensitive to gaseous impurities<input type="checkbox"/> Upper plateau instabilities
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So, this particular class of compounds they have advantage that they have very good hydrogen storage capacity they have low cost they operate at room temperature, but the major challenge remains is there is a requirement for activation step before the hydrogenation. And that activation step involves high temperature and pressure conditions at the same time these compounds are sensitive to the presence of impurities in the gas and there lies the upper plateau instabilities.

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Solid Solution alloys

- Dissolving one or more minor element into hydrogen absorbing element (solvent)
- Unlike IMC which are stoichiometric or near, SS can be non-stoichiometric compositions
- Can be formed with Pd, Ti, Zr and V
- Pd- low capacity and high cost, Zr & Ti – too stable, V-several advantages
- High capacity e.g. Ti-Fe-V and Ti-V-Cr-Mn, 2 plateau, higher plateau considered 2.5wt% reversible
- Ti-Cr-V reversible 2.3 wt%, high cycle life
- Many compositional variation of SS alloys, the one with laves phase related BCC solid solution e.g. Ti-V-Mn, Ti-V-Cr, Ti-V-Cr-Mn



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Now, another class of compounds are solid solutions. Solid solutions these are formed by dissolving one or more minor element in smaller quantities which is solute here into another major compound which is solvent that is the hydrogen absorbing element. So, if one or more elements of solute, they are dissolved into a solvent that is the hydrogen absorbing element that are known as solid solution alloys.


Now in case of intermetallic compounds it was those used to be either stoichiometric or nearly stoichiometric now these it is not essential that these may follow the same. So, solid solutions can be either non stoichiometric as well. Usually the solvent that is used here could be either palladium or titanium or zirconium or vanadium.

If palladium is used, then problem is we get a low capacity and the cost is high with zirconium and titanium, they form two stable hydrides and for vanadium it has several advantages for hydrogen storage like they have ideal PCT, the required PCT the capacities are also higher. So, we can form such solid solutions high capacity solid solutions like we can even get 4 weight percent with Ti-Fe-V, Ti-V-Cr-Mn.

So, for them like we can get a 4 weight percent capacity. But then they have two plateaus and then if we consider higher plateau because the higher plateau could be considered for hydrogen storage then it reduces the reversible storage capacity that we will get is 2.58 percent. Similarly, for Ti-Cr-V the reversible capacity is 2.38 percent and the important is that they have a very good cycle life like this is capacity is 2 weight percent even after 1000 cycles. We can have several composition variations in the solid solution alloys.


And one possible variation could be we can have laves phase related BCC solid solution like the example of such compounds is Ti-V-Mn or Ti-V-Cr or Ti-Cr-V-Mn.

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BCC Solid Solution

- First studied in 1980
- Vanadium based BCC alloys most studied
- Maximum hydrogen storage capacity: 3.6 wt%
- **Laves phase related BCC solid solution** are show better hydrogen storage performance
- Both phases contribute to hydrogenation and have same P_{eq}
- $Zr_{0.5}Ti_{0.5}VMn$ showed three phases: C14, BCC and oxide
- Ti-V-Cr 2wt%, small hysteresis and only one activation
- Formation of two hydride phase, Monohydride (stable) and Di-hydride(responsible for capacity)
- Challenges are – destabilize monohydride, or to improve the reversible capacity of dihydride



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Hu, C. Ma, and Q. Chen, "Mechanism and microstructural evolution of TiCrVFe hydrogen storage alloys upon de/hydrogenation," *J. Alloys Compd.*, vol. 877, p. 160315, 2021.

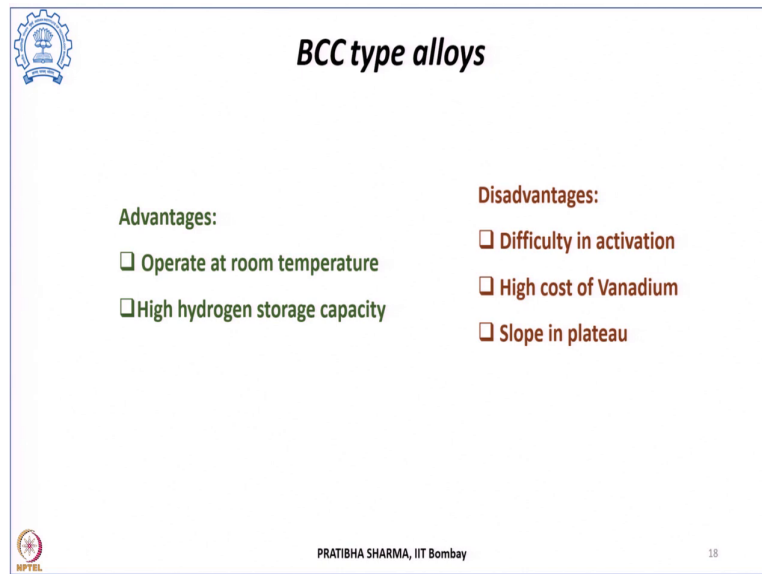
Now, in these type of compounds which are Laves phase related BCC solid solutions, the advantage is they show better hydrogen storage performance. These were first identified in 1980 and usually the most studied ones are the vanadium based BCC solid solutions. They can even give a maximum hydrogen storage capacity of 3.68 weight percent which is appreciably higher.

So, the thing is that they have both Laves phase at the same time they have BCC phase as well and both of these phases contribute towards hydrogenation and they have almost similar equilibrium pressure. Now example $Zr_{0.5}Ti_{0.5}VMn$ that shows three phases it is C14, BCC and a ZrO_2 oxide phase.

Another example Ti-V-Cr, they can give 2 weight percent of reversible capacity has smaller hysteresis and only one activation cycle is required. But the major disadvantage with these type of solid solution alloys is that they form two different hydride phase there is a monohydride phase which is much more stable and then there is a dihydride phase which is the one which is responsible for giving the required hydrogen storage capacity.

So, the major challenge which remains is to destabilize this monohydride phase and to improve the capacity or the reversible capacity of this dihydride phase.

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BCC type alloys

Advantages:

- Operate at room temperature
- High hydrogen storage capacity

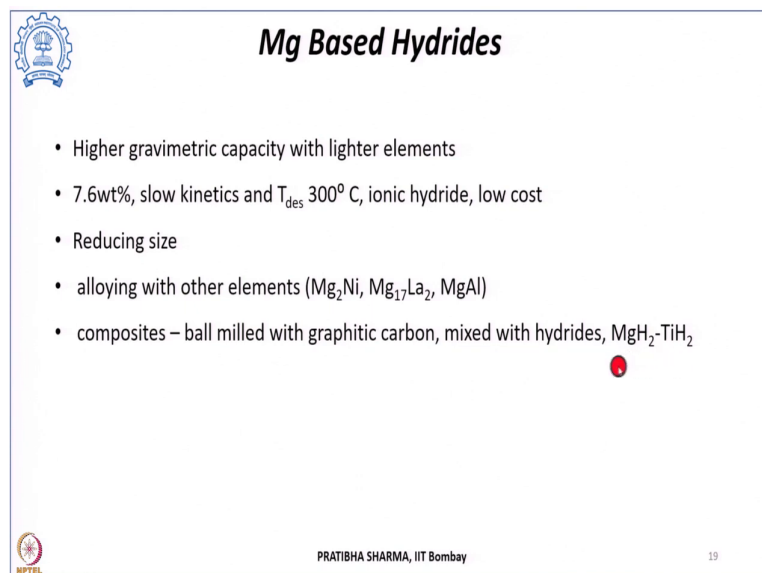
Disadvantages:

- Difficulty in activation
- High cost of Vanadium
- Slope in plateau

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So, the advantages of BCC solid solutions are they operate at room temperature, they have very good hydrogen storage capacity, but the problems are they are difficult to activate the vanadium is involved that has a higher cost and then the presence of slope in the plateau.

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Mg Based Hydrides

- Higher gravimetric capacity with lighter elements
- 7.6wt%, slow kinetics and T_{des} 300° C, ionic hydride, low cost
- Reducing size
- alloying with other elements (Mg_2Ni , $Mg_{17}La_2$, $MgAl$)
- composites – ball milled with graphitic carbon, mixed with hydrides, MgH_2-TiH_2

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Now, if we want to improve the gravimetric capacity of these materials, we have to consider lighter elements because that only can improve on to the gravimetric capacity one of the example is magnesium based hydride. So, the lighter elements could be considered could be calcium or magnesium. Magnesium hydride it has a very high storage capacity of 7.6 weight

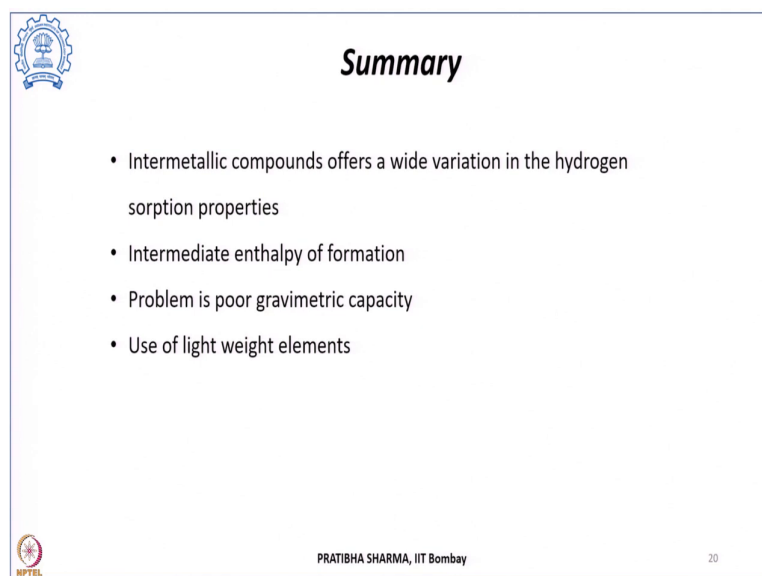
percent, but the problem is that of slow kinetics and the desorption temperature is very high that is 300 degree centigrade it forms an ionic hydride.

Another advantage of this class of material is that they have a lower cost other than the high gravimetric capacity. So, what we need to address is the sluggish kinetics, at the same time the high desorption temperature and that can several measures can be taken so, as to reduce the desorption temperature and improve on to the kinetics charging and discharging.

What has been reported in literature is to by reducing the particle size, by alloying them with other elements like forming Mg_2Ni , $Mg_{17}La_2$, $MgAl$ or by forming composites we can address these challenges to a certain extent. Like ball milling with graphic carbon, forming composites or mixed with different other hydrides like titanium hydride has shown to work well with magnesium hydride to reduce the desorption temperature.

However, still the desorption temperature achieved in this class of compounds are way higher. To summarize what we have seen today is we have learnt the different intermetallic compounds.

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Summary

- Intermetallic compounds offers a wide variation in the hydrogen sorption properties
- Intermediate enthalpy of formation
- Problem is poor gravimetric capacity
- Use of light weight elements

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We have seen that they offer a wide variation in the hydrogen absorption properties, variation in terms of the kinetics, variation in the terms of desorption temperature, pressure conditions, variation in terms of storage capacities. What is required is, an intermediate enthalpy of

formation which can be achieved by allowing two different metallic species in an intermetallic compound.

But the problem still lies is that they have a poor gravimetric capacity, what could be a solution is, use of lightweight elements to improve on to the gravimetric capacity. So, this can be achieved by certain noble metals; however, those noble metals also have their own disadvantages what are those noble metals? We will see in the next class.

Thank you.