Hydrogen Energy: Production, Storage, Transportation and Safety
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Lecture - 54
Novel Materials and Overall Storage

We have been studying solid state hydrogen storage and the different materials which can be used for storage, among those we have studied the adsorption based materials and absorption based materials. So, we have seen the metal hydrides as a representative example for absorption based materials and there are many other materials which can also be used for solid state hydrogen storage.

However, the entire field of solid state hydrogen storage is very vast and it is not possible to cover all the materials. So, as such we have gone in depth on the metal hydrides rest of the materials which can be used for solid state hydrogen storage, we will today very briefly touch upon.

Now, one class of hydrogen storage materials which have recently received a lot of attention globally is the high entropy alloys.

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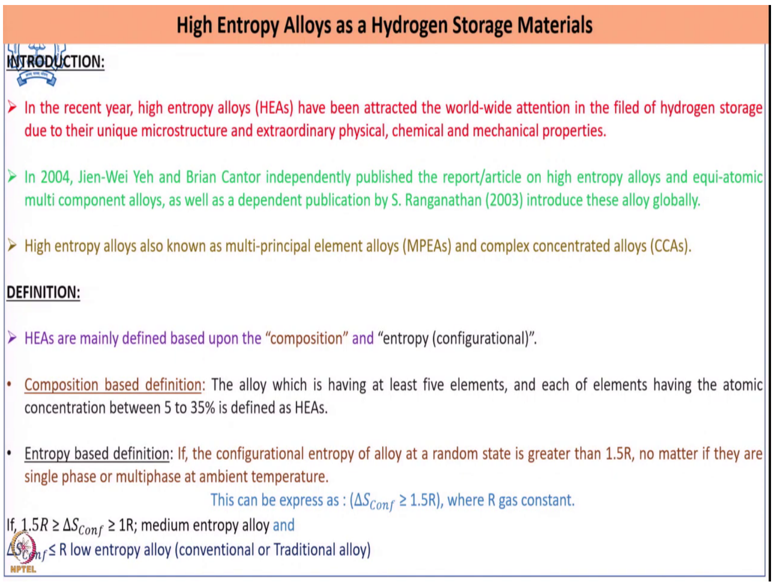

Now, when we consider alloying it is a method a process to prepare materials in such a way so that we can get alloys of desired properties as well as the improved performance.

Now, in this case generally a small amount of another material which is a secondary metal is added to a primary material. But in case of high entropy alloys in last 15 years it has received entirely new strategy of hydrogen alloying has been come up wherein, we can have multiple elements all in high concentration acting as a principal element. And in that case, the materials which are synthesized are known as high entropy alloys.

Now, this new strategy of alloying has given a multi dimensional compositional space to tackle with a wide variety of opportunities and thus much has to be studied in this particular class of materials. Now, it was by JW Yeh that he proposed that when multiple elements either 5 or more than 5 they are combined in such a way that they have higher concentrations they are combined in that case the configurational entropy of mixing it can overcome the enthalpies of formation for the compounds.

And that can deter the formation of intermetallic. However, there are several exceptions to the class of high entropy alloys, wherein the number of elements could be less than 5 or there could be several phases which are being formed or there could be alloys which rather than entropy stabilized they could be enthalpy stabilized. So, there are different exceptions existing through the, this particular class of definition.

Now, if we broadly look at the definition of these high entropy alloys, these can be defined based on composition as well as its configurational entropy. Now, if we look at the composition which is based on definition these alloys should have at least 5 elements such that each of these elements have an atomic concentration lying between 5 to 35 percent; then they are called high entropy alloys.

If we look at the another definition which is based on the entropy, then it states that if the configurational entropy of the alloy at a random state it is higher than 1.5R, it independent of whether it is a single phase or multi phase at ambient temperature in that case the alloy formed is known as a high entropy alloy.

It can be expressed as that the configurational entropy of mixing is greater than or equal to 1.5R where R is the gas constant for such alloys; however, if this configurational entropy, it lies in a range of 1.5R to 1R then the alloys are known as medium entropy alloys. And when this value is less than or equal to R, then the alloys are low entropy alloys or the conventional or traditional alloys.

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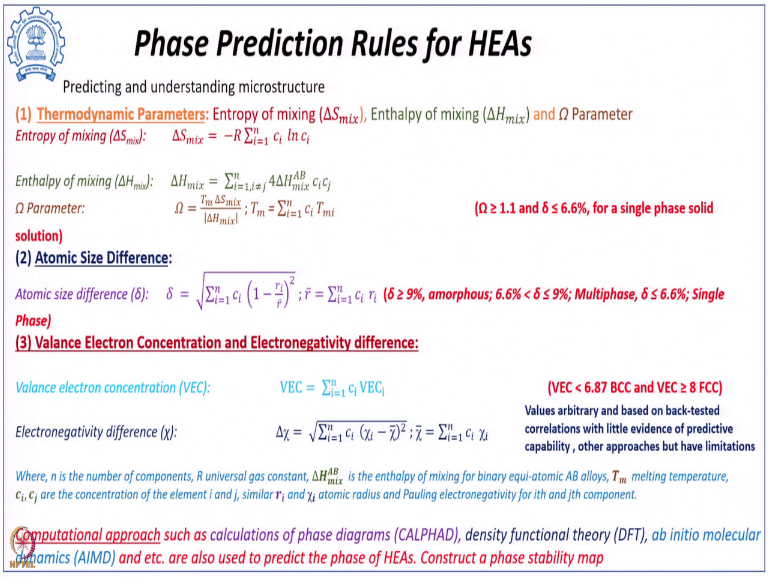

Now, predicting and understanding the micro structure of these high entropy alloy is very important and for that the phase stability of these alloys is being considered. And it is being calculated using different approaches like the computational approach where the phase diagrams are calculated using software’s CALPHAD either using density functional theory or ab initio molecular dynamic studies.

And then all these are used to predict the phases present in HEA or phase present in HEA. So, the approach that lies is a complete phase stability map is being drawn considering a series of parameters like thermodynamic parameters entropy of mixing, enthalpy of mixing or the ratio of these times temperature or the atomic size difference, valence electron concentration or the electronegativity these all these parameters are calculated.

So, a phase stability map is found using different parameters then a range of values is being defined for these parameters. And when the values lie above or below a certain range or value in that case a particular phase is stable. However, these are the parameters which have been well reported in literature, but these values have been find to be arbitrary. And these are based on the back tested correlations and there is a little evidence of their predictive capability. There are many other approaches to do that, but they have their own limitations.

So, there are conflicting literature studies which reports dependence on these parameters, at the same time, there are some studies which have also reported that there are little evidences of their predictive capabilities.

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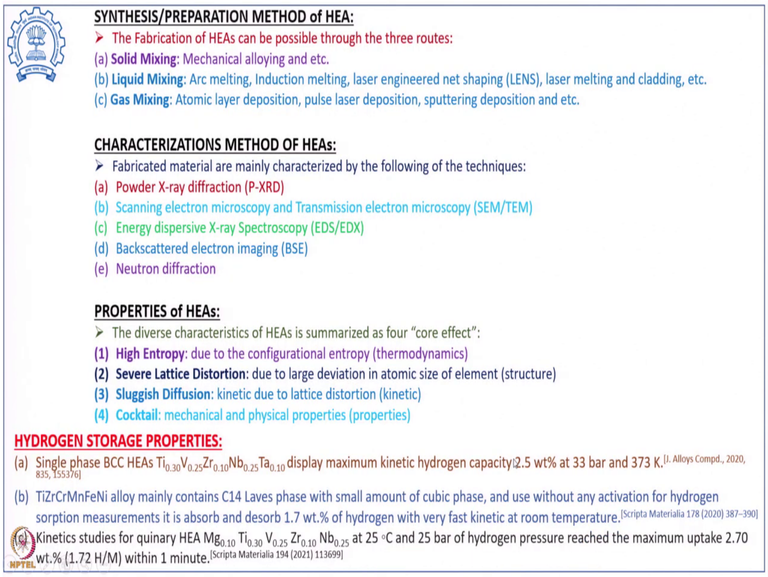

Now, there are different ways in which we can synthesize high entropy alloys, either it could be by means of solid state mixing using mechanical alloying or it could be by means of liquid state mixing, either they are melted through an arc melting route or using an induction melting furnace.

Laser engineered net shaping or laser melting and cladding or it could be gas phase mixing where it is deposited using atomic layer deposition or pulse layer deposition or sputtering deposition or there could be other ways as well. These are well characterized, if we try to categorize their properties then the diverse characteristics of the high entropy alloys some of the high entropy alloys they have proven to have a very good properties chemical, mechanical properties as against the even the conventional alloys.

However, they are diverse characteristics because of the variation in the compositions that could be achieved the different phases that could be achieved this can be summarized in terms of 4 core effects; like high entropy and this is because of the high configurational entropy of mixing.

Severe lattice distortion that arises due to large deviation in the atomic size of the element. Sluggish diffusion or this could be a cocktail effect that results into varied mechanical and physical properties. Now, if we look at some of the examples of such high entropy alloys which have been studied for hydrogen storage applications for their hydrogen storage properties.

The example could be like the single phase BCC high entropy alloy Ti0.3V0.25Zr0.1Nb0.25Ta0.1 and this alloy has been studied to display and it displayed maximum kinetic hydrogen capacity of 2.5 weight percent at 33 bar pressure and 373 kelvin it has shown very good kinetics.

Another high entropy alloy that has been studied is Ti-Zr-Cr-Mn-Fe-Ni and this alloy was found to contain both C14 phase and a small amount of cubic phase as well. And this alloy can be used without any requirement of activation. It was found that the absorption desorption studies when it was carried out that it can take up 1.7 weight percent of hydrogen and that too at very fast kinetics at room temperature.

Kinetic studies were also performed for a quinary high entropy alloy Mg0.1Ti0.3V0.25Zr0.1Nb0.25 at 25 degree centigrade and 25 bar of hydrogen pressure and that could show a maximum uptake of 2.7 weight percent which is 1.72 H/M and that was very fast it was measured in a duration of 1 minute. So, these are some of the examples of such alloys high entropy alloys.

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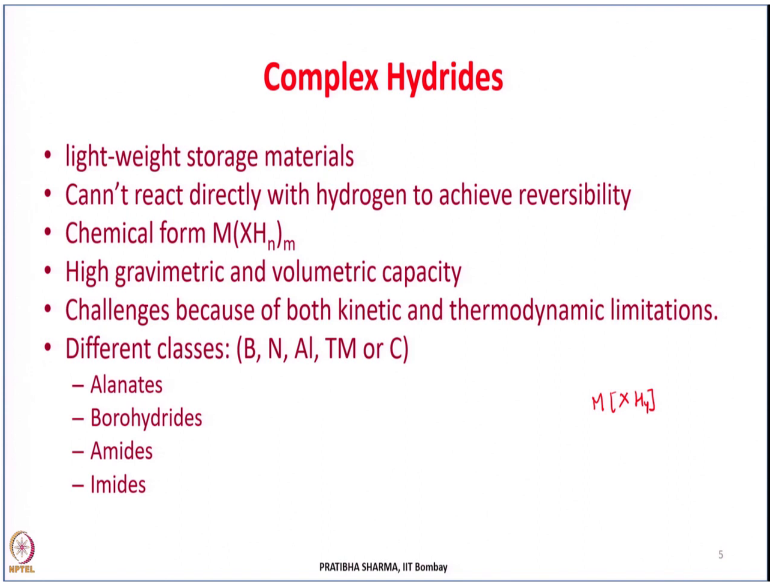

Now, the another class of such materials which can be used for hydrogen storage are the complex hydrides. Now, in the complex hydrides the hydrogen it is covalently bonded with another metal or non metal and this forms an anion and then it is bonded with a metal cation.

So, these class of materials complex hydrides, so the difference between complex hydrides and metal hydrides is metal hydrides they can be directly regenerated back or charged again after discharging by exposing it to hydrogen at a certain temperature pressure conditions. But complex hydrides they do not directly react with hydrogen to achieve reversibility.

At the same time complex hydrides they are formed up of lightweight elements, the major disadvantage as we have seen in the metal hydrides was their poor gravimetric capacity. And this was because, the elements that were used like the transition metals or other elements that were used to form the metal hydrides or their alloys or solid solutions they were heavy; as such that reduce the gravimetric capacity.

However, the elements which are used for making complex hydrides for synthesizing complex hydrides or the elements which are present in the chemical formula of complex hydrides these are lightweight. As such the gravimetric capacity of complex hydrides is higher as well as the volumetric capacity.

So, when we talk about the gravimetric or volumetric capacities there are some of the complex hydrides which can even give 13 weight percent or 16 weight percent and even 18 weight percent of hydrogen storage capacity and a higher volumetric capacity of even 150 kg per meter cube.

So, their chemical formula in general can be represented as $M(XH_n)_m$. Now, here M is a metal, X can be a metal or non metal and depending upon that whether it is a metal or non-metal the bonding with hydrogen can be covalent or ionic covalent bonding. So, this class of materials they have several advantages when it comes to capacity of storage of hydrogen, but then there are several challenges as well.

So, the challenges are in terms of both kinetics and thermodynamic limitation they have a sluggish kinetics at the same time the temperature at which they desorb hydrogen are appreciably higher. The reversibility of these complex hydride is another major challenge. So, most of these chemical hydrides are found to be irreversible.

So, the classes of complex hydrides that could be categorized into alanates, borohydrides, amides or imides. Now, here in the element could be either boron this X could be either here it could be Al, it could be boron, it could be nitrogen or even now the compounds which having transition metal or carbon are known.

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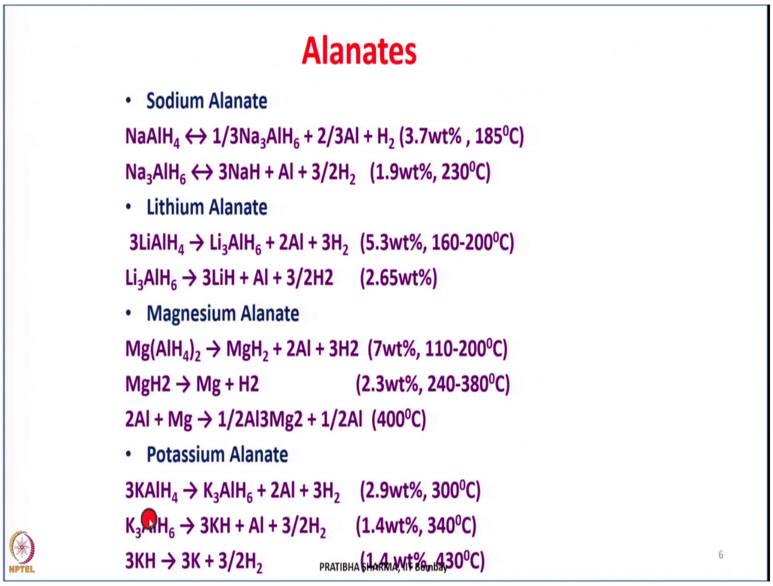

Now, these alanates, borohydrides, amides, imides they desorb hydrogen in sequence of steps. In each step they release a certain amount of hydrogen. Now, let us take some of the examples for example, sodium alanate, NaAlH6, it can it can give hydrogen at a temperature of 185 degree centigrade releasing 1 mole of hydrogen and producing Na3AlH6 + 2/3 Al.

Now, this compound which is formed at 185 degree centigrade, Na3AlH6 can further give another mole 3/2 mole of hydrogen producing NaH at 230 degree centigrade which is approximately giving 1.9 weight percent.

However, if we want to get another hydrogen out of the NaH that will require very high temperatures. Now, this particular class of complex hydride that is alanates has received a lot of attention specially because, in 1974 Bogdanovic Et al, they found that sodium alanate it can reversibly store hydrogen and it is reversible under milder conditions at when it is being reacted with titanium salts.

So, that was the time when lot of interest was drawn in this particular class of compounds. Now, the other example could be lithium alanate. So, lithium alanate, 3LiAlH4 can give Li3AlH6 + 2 Al + 3H2 and this reaction occurs at a temperature of 160 to 200 degree centigrade releasing 5.3 weight percent of hydrogen. This Li3AlH6 can further give 3/2 H2, giving another 2.65 weight percent at a further higher temperature.

Similarly, the other compounds alanates like magnesium alanate, it can decompose to give hydrogen in different steps, like it forms Mg(AlH4)2, it forms magnesium hydride at 110 to 200 degree centigrade that gives 7 weight percent. Similarly, this magnesium hydride can further give hydrogen at 240 to 380 degree centigrade, 2.3 weight percent.

Similarly, potassium alanate, KAlH4 it can give hydrogen forming K3AlH6 releasing 2.9 weight percent of hydrogen at 300 degrees centigrade, the next step can give further hydrogen 1.4 weight percent at 340 degrees centigrade.

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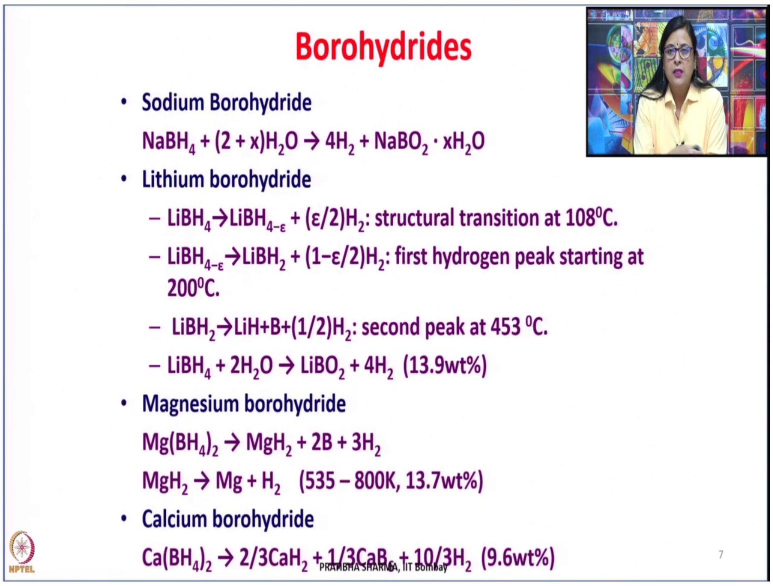

So, as we have seen that these complex hydrides release hydrogen in several steps and the temperature of these options are usually higher. Similarly, the other well-known class of complex hydrides is borohydrides. So, sodium borohydride it can either on thermolysis it can give hydrogen or it can even react with water by hydrolysis root giving hydrogen and forming borate. But this during hydrolysis the formation of borate this is a stable compound and the reversibility is the major challenge.

Similarly, lithium borohydride can still give hydrogen at a higher temperature like 200 degrees centigrade or 453 degrees centigrade, this release of hydrogen in steps. Finally, it can give 13.9 weight percent of hydrogen, but all these decompositions take place at a higher temperature.

Similarly, magnesium borohydride it can give hydrogen 13.7 weight percent, but the there are different steps involved and then the temperatures are like lying between 535 to 800 kelvin. And calcium borohydride can give hydrogen approximately 9.6 weight percent.

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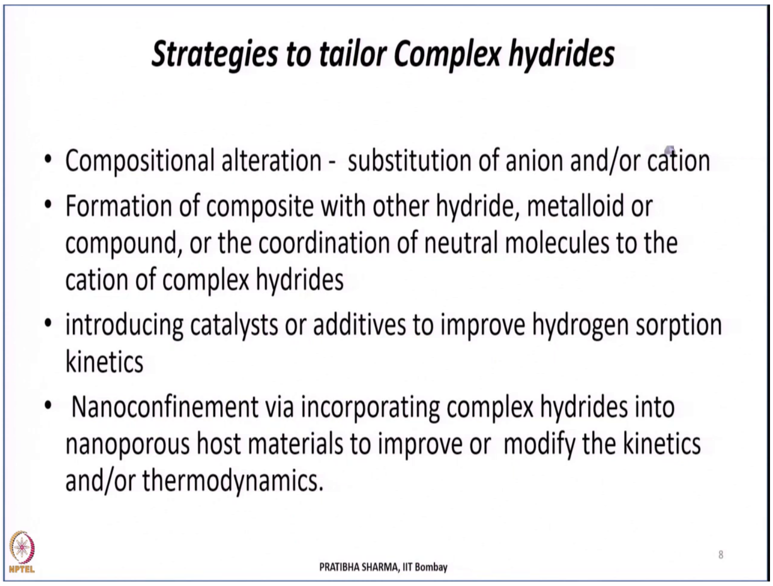

Now, as we have seen that this particular class of compounds they have higher desorption temperatures, they have sluggish kinetics reversibility is a challenge.

Now, there have been several strategies to tailor the properties of these complex hydrides like either the compositions can be varied and that can be done either by substitution of the anion or cation or it can be at both the places anion and cation or formation of composites with different hydrides can be considered or metalloid or it could be coordination with neutral molecules to the cation in the complex hydrides.

There is a possibility of tailoring the properties by introducing catalysts or additives, so as to improve the hydrogen absorption and desorption characteristics or kinetics. Another strategy could be confinement of these incorporation of these complex hydride into nanostructures into nanoporous host materials and that has also been found to improve or modify the kinetics or thermodynamics or both for these complex hydrides; class of materials called complex hydrides.

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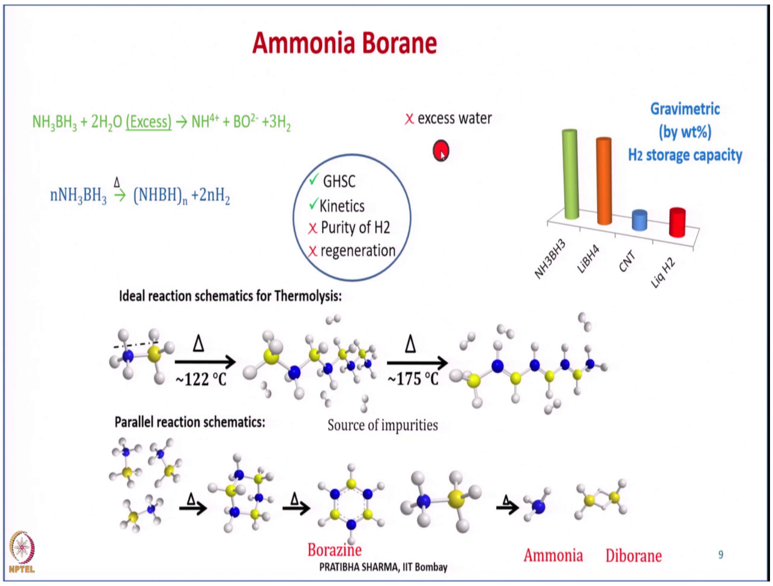

Now, another class of compounds these are known as chemical hydrides like one of the example being ammonia borane. Ammonia borane like complex hydrides can also react with water producing hydrogen, here in again on reacting with water. It will give borates which are more stable and it gets difficult to regenerate back and will require excess amount of water.

Now, if we compare the gravimetric capacity of these compounds like say for example, ammonia borane as against the borohydrides, lithium borohydride or carbon nanotube or liquid hydrogen, then the capacity is significantly higher for hydrogen storage when it is considered in the compound ammonia borane; as compared to even liquid hydrogen.

So, there are two ways one we have seen is hydrolysis, another way could be that this material undergoes thermolysis to produce hydrogen. Now, there are 3 hydrogen molecules we can see 3 protic hydrogen, 3 hydridic hydrogen and in every step of decomposition it will give rise to 1 mole of hydrogen.

So, the ideally the reaction scheme for thermolysis of hydrogen, heating the hydrogen heating to get hydrogen-thermolysis is where ammonia borane, it is heated at temperatures of around 120 to 125 degree centigrade and it produces an oligomeric species that is poly aminoborane and releasing 1 mole of hydrogen.

Further when it is heated to 175 degree centigrade, it will release another mole of hydrogen forming poly aminoborane. Now, this is under ideal characteristic such reactions occur.

However, in actual practice there are several parallel reactions that can occur like three ammonia borane molecules during thermolysis, they can react to form cyclic species like borazine it can also result into cleavage of the bond of nitrogen and boron resulting into ammonia and diborane formation and it is observed that the release of these borazine or ammonia or diborane these are not desired or these are undesirable species which are obtained along with hydrogen.

So, the research has been basically focused in this class of compounds towards suppressing the formation of these unwanted species using different supports, using different nano confinement methods, using different additives. So, that the release is basically hydrogen and the amount of these unwanted gaseous product release is reduced.

At the same time, lot of studies have been carried out so as to get reversibility of these type of materials and a certain percentage of reversibility has been achieved; however, that cycling is not being achieved for a larger number of cycles.

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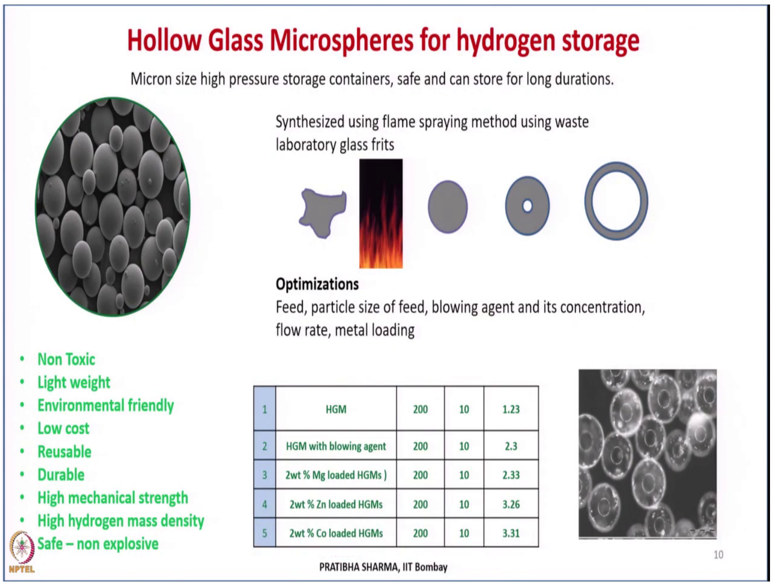

Another class of materials that could be used for hydrogen storage includes hollow glass microspheres.

Now, we have studied the compressed state hydrogen storage wherein hydrogen is stored in its molecular form inside the compressed pressurized vessels. Now, those were having a certain dimension and volume, herein these are micron sized high pressure containers again storing hydrogen in its molecular form such that it is safe to operate, it is safe to store and then in this mode of storage they can be carried over a longer distances and can be stored for a longer duration.

Now, these micron size hollow glass microspheres they can be synthesized through various routes one of the route that can be used for synthesis is flame spraying method and there in the different glass wares can be used of different compositions can be used so as to produce these hollow glass microspheres.

So, these are spheres hollow inside and have several pores on their periphery. And that could allow the hydrogen to get into subjected to a certain temperature and pressure condition. Now, when these materials are synthesized various optimizations are being done in terms of what will be the starting material, raw material what would be the particle size of the raw material?

What would be the blowing agent that will give rise to pores in the walls of these hollow glass microspheres? What would be the concentration of these the additional blowing agents? What would be the flow rate correspondingly, we can have different metal loading so as to improve the thermal conductivity of these hollow glass microspheres?

And these class of materials, they are interesting in the sense that they have been reported to store hydrogen under like say the charging could be carried out at 200 degrees centigrade, 10 bar pressure and it has been reported that these can store to a capacity of say 3.31 weight percent and this has been studied at IIT Bombay in our lab.

Since, these class of materials they are non-toxic, they are lighter in weight, they are environmental friendly, low cost, reusable, durable. They have good mechanical strength, high density of storage is possible and at the same time they are safe to operate with. So, as such this forms an interesting class of materials for hydrogen storage.

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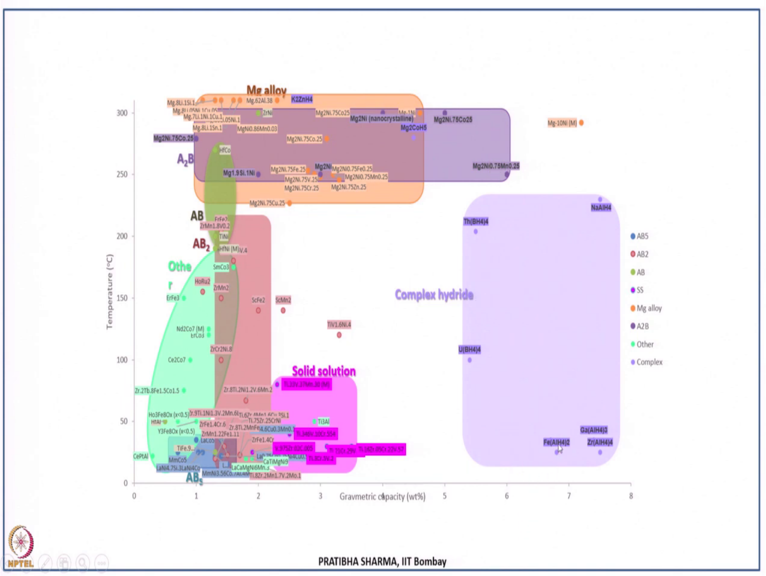

Now, in the solid state hydrogen storage part, we have seen a wide variety of materials which can be used. Now, among these if we try to plot what is the capacity of storage in these materials, against what is the desorption temperature at a pressure of say equilibrium pressure of 1 bar; in that case, we can see that the class of materials AB5 type of materials, they have a lower gravimetric capacity at the same time they have a lower desorption temperature.

AB2 type of materials, they have a wide window of desorption temperatures and a relatively lower gravimetric capacity compared to the magnesium based or complex hydrides; AB type of materials again they have a certain desorption range of temperatures, but a lower gravimetric capacity less than 2 weight percent.

Then we have class of compounds A2B type of compounds, we can see that they have although have higher desorption temperatures. But a wide range of gravimetric storage capacity can be obtained. Others among them comes A3B7 type of materials, magnesium based alloys they have a very high desorption temperature, but a good gravimetric capacity.

And lastly, solid solutions and complex hydrides. So, solid solutions they have compared to the other metal hydrides they have a higher gravimetric capacity and a lower desorption temperature and finally, the class of compounds which are known as complex hydrides, they have very high gravimetric capacity and a wide range of desorption temperatures.

So, this is all we have seen in the solid state hydrogen storage.

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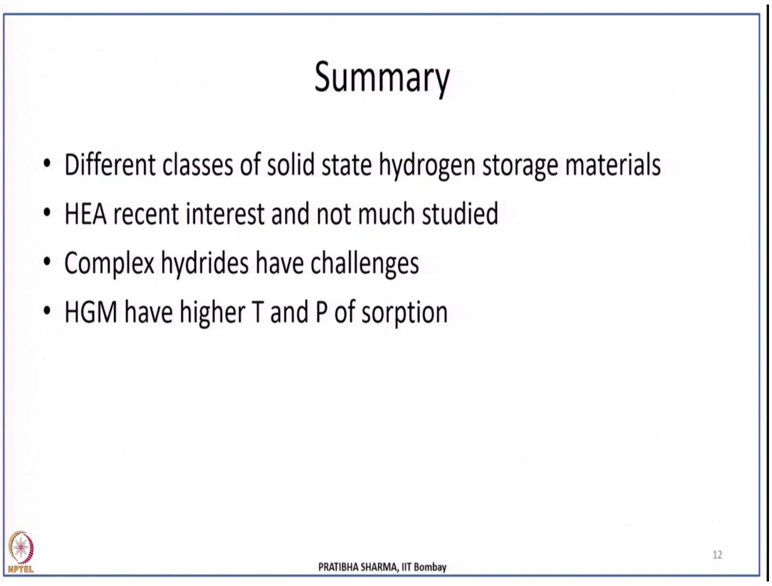

To summarize we have seen the different classes of materials that can be used for solid state hydrogen storage. We have seen a class of material today high entropy alloys that has been of recent interest, but has not been studied very well so far.

Then complex hydrides this have been studied for past 60 years, but then there are several challenges associated with their use for hydrogen storage like their unfavorable thermodynamics kinetics, irreversibility are the major challenges. Hollow glass microspheres they have sorption taking place at a higher temperature and pressure although they are very promising.

Thank you.