Hydrogen Energy: Production, Storage, Transportation and Safety

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Lecture - 50
Tailoring Metal Hydrides for Practical Applications: Nanostructure Part 1

The next two lectures will be by Professor Jacques Huot. He is Professor in the Department of Chemistry, Biochemistry and Physics at the university of Quebec Trio Rivieres this is in Quebec Canada. Professor Jacques he is well known for his work. He is a renowned scientist working in the field of metal hydrides.

Hello, everybody. My name is Jacque Huot. I am a professor at the Universite Du Quebec a Trios Rivieres and also member of the Hydrogen Research Institute. Today we will talk about tailoring metal hydride for practical application. This is in two part – the first part will be nanostructure in general and the second part will be on the effect of nanocrystalline structure on the capacity of metal hydride and also some other method to get nanostructure materials.

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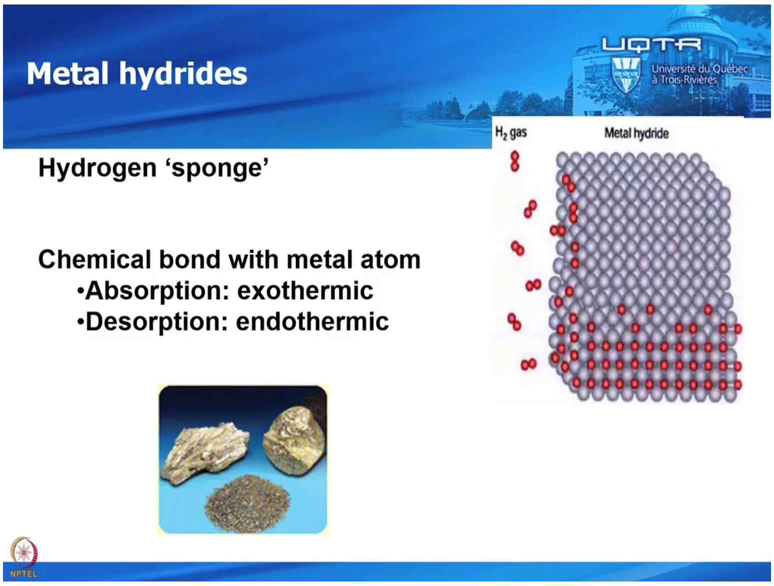

Metal hydrides

Hydrogen 'sponge'

Chemical bond with metal atom
- Absorption: exothermic
- Desorption: endothermic

So, just a quick recap on what our metal hydride. You could consider metal hydride to be like a kind of hydrogen sponge. So, in the metal hydride you have a chemical bond with the metal atom and the absorption is an exothermic reaction and the desorption is an endothermic reaction.

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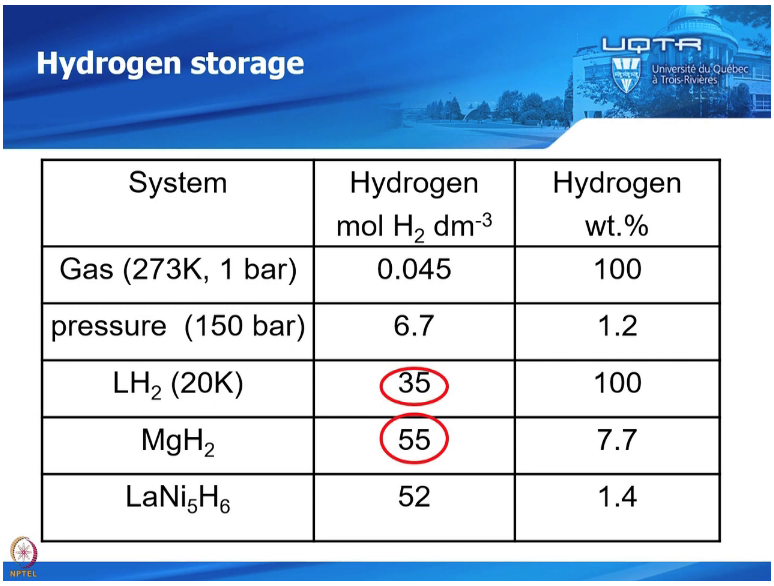

Hydrogen storage

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System	Hydrogen mol H_2 dm^{-3}	Hydrogen wt.%
Gas (273K, 1 bar)	0.045	100
pressure (150 bar)	6.7	1.2
LH_2 (20K)	35	100
MgH_2	55	7.7
$LaNi_5H_6$	52	1.4

So, to give you some idea of the difference about metal hydride with respect to the other ways to store hydrogen. So, if you store hydrogen as a gaseous form at one bar at room temperature you see that the volumetric capacity is quite low. In order to increase that, you have to increase the pressure. So, if you go to 150 bar you have a much better volumetric capacity and if you are using liquid hydrogen.

So, usually if you want to transport a huge quantity of liquid hydrogen in my opinion liquid hydrogen is the best way of course, it is at low temperature at 20K, but you see that the volumetric capacity is quite good. But, you see for metal hydride here you have high temperature metal hydride and you have a low temperature metal hydride. So, this metal hydride is working at room temperature, this one is working at least 200 degree to 250 degree C.

And, you see that actually it is an it is a little bit counterintuitive, but you see that the volumetric capacity of hydrogen is higher in a metal hydride than in a liquid. So, the hydrogen atoms are more compact in a metal hydride than in a liquid its counterintuitive, but this makes this is one of the best advantage of metal hydride is that hydrogen is compact.

So, your tank will be very small, but the disadvantage as you see here is that the gravimetric density is quite low. So, here this means that you only have 7.7 weight percent of hydrogen in a metal hydride tank made of magnesium hydride, and the rest is just the weight of magnesium. And, for LaNi5, it is even worse. It is only 1.48 percent. So, that is one of the big disadvantage of metal hydride.

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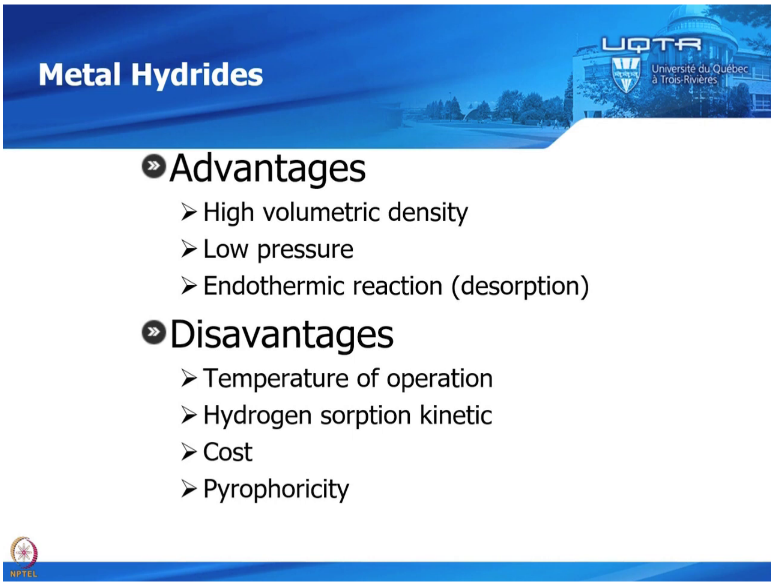

Metal Hydrides

- Advantages
  - High volumetric density
  - Low pressure
  - Endothermic reaction (desorption)
- Disavantages
  - Temperature of operation
  - Hydrogen sorption kinetic
  - Cost
  - Pyrophoricity

So, the advantage and the disadvantage well you see that for metal hydride the advantage that we said its high volumetric density it could work at low pressure, but and the reaction of desorption is endothermic. So, why I listed as an advantage is because if you have hydrogen metal hydride tank in your car and you have an accident and the tank is ruptured and you have hydrogen getting out and hydrogen is taking fire. So, then it will heat up the tank.

But, as the tank is heating up it will desorb hydrogen, but as a desorb hydrogen because the reaction is endothermic it will have a tendency to cool itself. So, it will kill the reaction by itself. So, this is inherently safe the disadvantage is you have a usually you have a high temperature of operation if you want to have a good capacity for example, with magnesium hydride. You have to work at high temperature more than 300 degrees C usually the hydrogen sorption kinetic, hydrogenation dehydrogenation is relatively slow.

The cost depending on the material it could be expensive and again you have to consider not only the cost of the raw material, the cost of the alloy, but also you have to consider the cost of you know loading the alloy with hydrogen and putting that in the tank and so on. So, the process cost could be quite expensive. So, you have to take that into account and pyrophoricity because metal hydride after many cycle of hydrogenation dehydrogenation they will turn into the very small powder and small any powder that is very small could be pyrophoric.

And, also for metal hydride because they react with hydrogen. So, it means that they could react with oxygen also. So, you could have problem of pyrophoricity.

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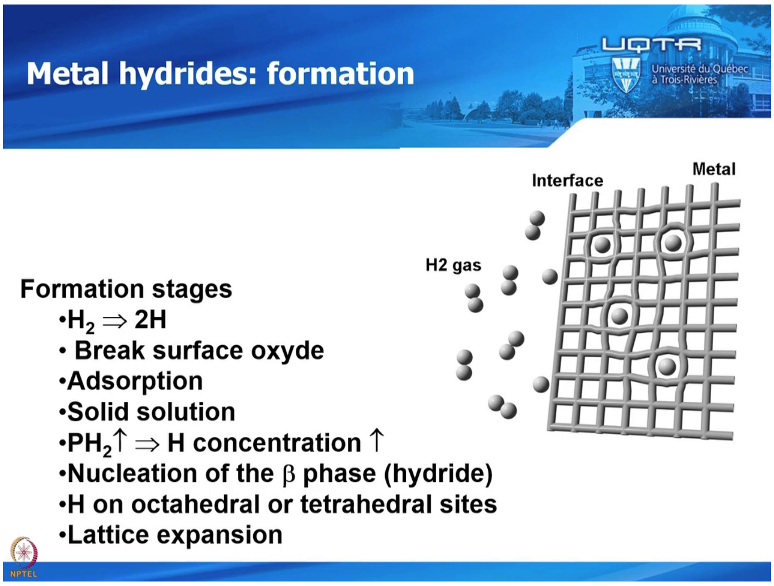

Metal hydrides: formation

Formation stages

- $H_2 \Rightarrow 2H$
- Break surface oxyde
- Adsorption
- Solid solution
- $PH_2\uparrow \Rightarrow$ H concentration $\uparrow$
- Nucleation of the β phase (hydride)
- H on octahedral or tetrahedral sites
- Lattice expansion

So, very quickly just the step for forming metal hydride. So, first you have hydrogen in gas phase and this hydrogen has to be split into proton to hydrogen before entering because on a metal hydride what is store is not a molecule H_2, but its a proton.

It is the it is the hydrogen atom. So, first you have to break this molecule, after that the hydrogen has to break, usually you have a small oxide layer on the surface of your alloy. So, it has to break this oxide layer and for hydrogen first you have to be an adsorption. So, you adsorb on the surface and then it split into and it and then the proton will enter the hydrogen the metal.

And, first it will form in solid solution. So, it will just go into the metal structure, but as the pressure of the gas is increasing, then the concentration of hydrogen in your metal will increase up until your nucleate the metal hydride phase and in that phase then the hydrogen will go on specific site depending on the crystal structure it could be on the octahedral or tetrahedral site.

And, you have a lattice expansion it could be up to 30 percent of expansion of your lattice of your metal.

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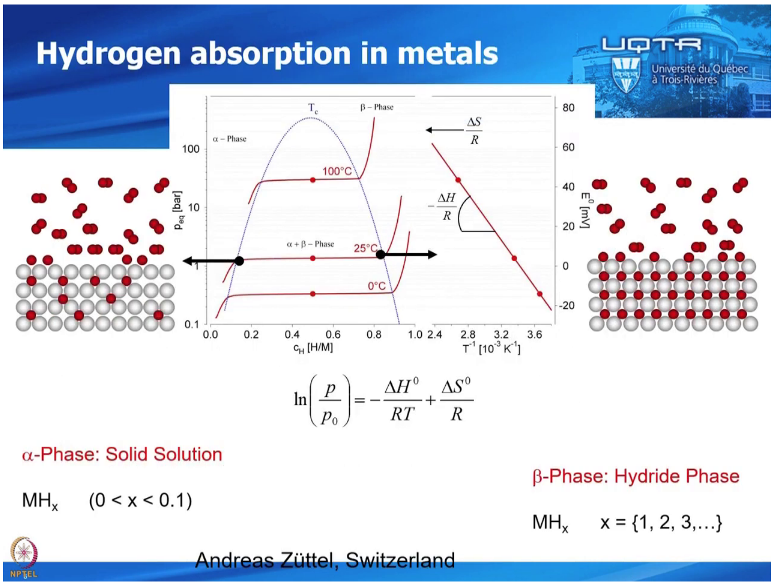

Hydrogen absorption in metals

$$\ln\left(\frac{p}{p_0}\right) = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$$

α-Phase: Solid Solution

MH_x $(0 < x < 0.1)$

β-Phase: Hydride Phase

MH_x $x = \{1, 2, 3, \ldots\}$

Andreas Züttel, Switzerland

So, that is a thermodynamic. So, you have your metal and this is the pressure of hydrogen this is the capacity of hydrogen. So, it is the number of hydrogen atom over the number of metallic atom and as you start you increase the pressure, hydrogen will enter in solid solution in your metal until you reach that point at that point you start to nucleate the metal hydride phase.

So, usually it has a different crystal structure and now that you have a new phase in your system by the law of Gibb's. So, if you have a new phase it means that you are losing a degree of liberty. So, if you are losing a degree of liberty it means that the capacity could increase even if the pressure does not increase because as the pressure try to go up you have more hydrogen that will go into the metal hydride that will form the metal hydride.

So, on this plateau you go from 100 percent metal and 0 percent hydride up to here where you have 100 percent metal hydride and 0 percent metal and here it is 50 – 50. So, you have the transformation along that plateau, you have the transformation from the metallic state to the metal hydride state and once all the, your material all your alloy is on a metal hydride state, then you are losing one phase you are losing the metal phase.

So, you are gaining one degree of liberty and then to increase the capacity, the pressure has to increase and here hydrogen will enter in solid solution and the metal hydride. So, and of course, this is a standard phase transition. So, depending on the temperature the plateau pressure will change. So, you could plot the logarithm of the plateau pressure as a function of 1/T, and the slope will give you the enthalpy of the reaction and the ordinate at the origin will give you the entropy of your reaction.

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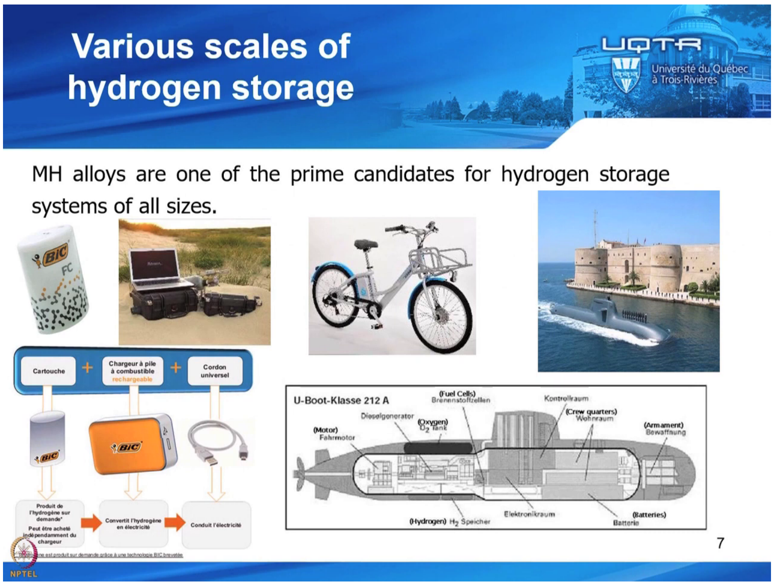

Various scales of hydrogen storage

MH alloys are one of the prime candidates for hydrogen storage systems of all sizes.

ne est produit sur demande grâce à une technologie BIC brevetée

So, one advantage of the metal hydride is that you it could spend a large range of application from portable and mobile up to something as big as the fuel cell submarine. So, I do not think if you have like a few micro fuel cell with a smartphone you could not store hydrogen in a liquid phase. It does not make sense you could not have a reservoir at 20 K in your pocket and the same thing with pressure you could not have a small tank at high pressure because the amount of hydrogen that you need for this is very very small.

So, the tank will be almost as big and as heavy as the device itself. So, it does not make sense. So, and the same thing up to up to the submarine for. So, the for the submarine well what is important for them is space they do not have a lot of space. So, they need something that will store hydrogen that will not take space and for them weight is not a problem. It could be heavy it does not matter for submarine.

So, this is why that the choice of storing hydrogen for a fuel cell submarine is metal hydride.

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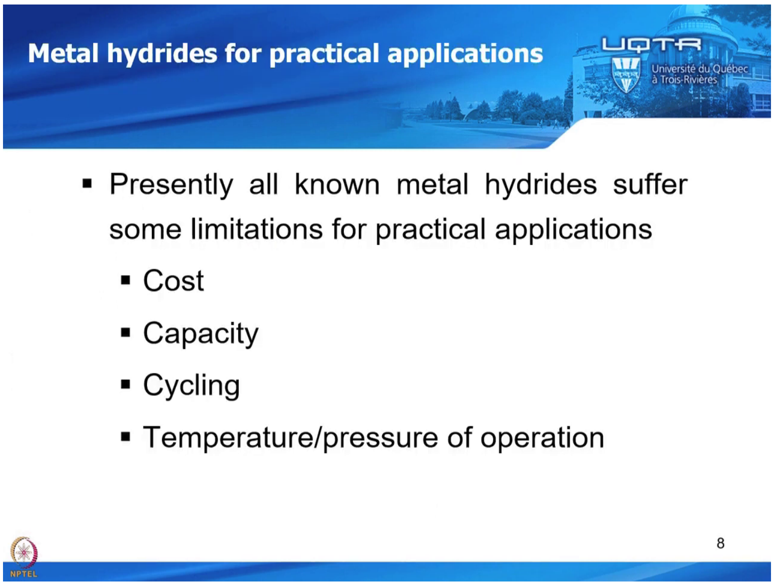

Metal hydrides for practical applications

- Presently all known metal hydrides suffer some limitations for practical applications
  - Cost
  - Capacity
  - Cycling
  - Temperature/pressure of operation

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So, metal hydride for practical applications. So, presently all known metal hydride suffer some limitation for practical application either they are too expensive or the capacity is too low or they lose capacity during cycling or the temperature and the pressure of operation is not right for your application.

So, most of the time the metal hydride is not ideally suited for practical application right now. So, the goal is to multiply this and to try to find metal hydride that will really meet the specification for practical application.

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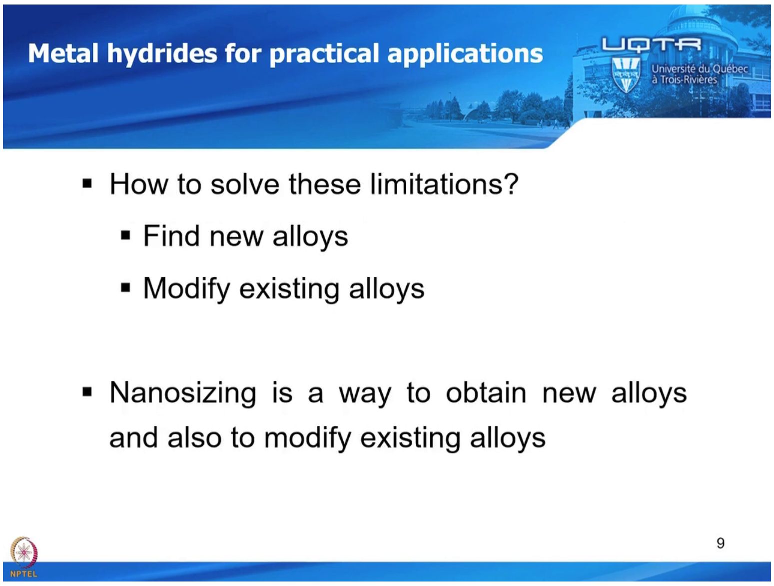

Metal hydrides for practical applications

- How to solve these limitations?
  - Find new alloys
  - Modify existing alloys

- Nanosizing is a way to obtain new alloys and also to modify existing alloys

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So, how to solve this limitation well we are trying to find new alloy or we could modify existing alloy. And, nanosizing is a way to obtain new alloy and also to modify the existing alloy.

So, you could the existing alloy as we will see if you have a conventional alloy, but you make it in a nanocrystalline dimension, then the characteristic will change a little bit. So, it could make your alloy attractive for practical application.

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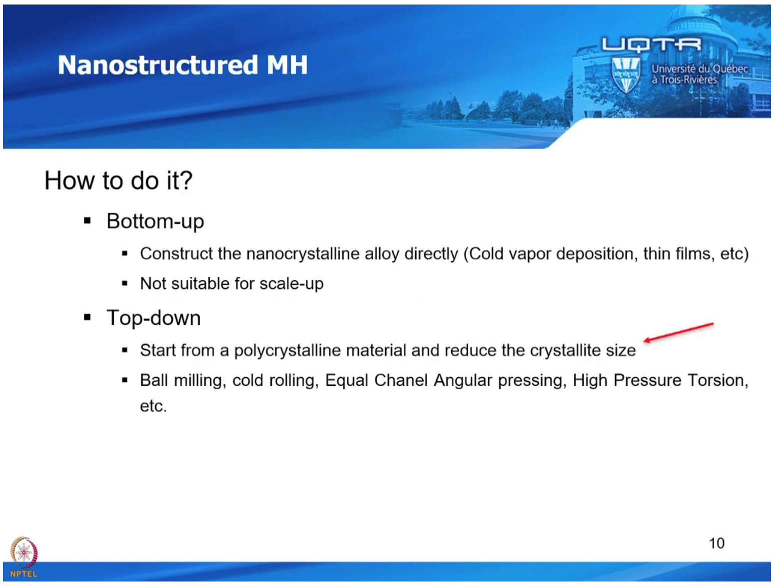

Nanostructured MH

How to do it?

- Bottom-up
  - Construct the nanocrystalline alloy directly (Cold vapor deposition, thin films, etc)
  - Not suitable for scale-up
- Top-down
  - Start from a polycrystalline material and reduce the crystallite size
  - Ball milling, cold rolling, Equal Chanel Angular pressing, High Pressure Torsion, etc.

So, how to do nanostructure in metal hydride? Well, there is two ways as for name metal. So, it’s either bottom up or top down. So, bottom up is that you construct a nanocrystalline alloy directly. So, you could do that by cold vapor deposition and film and so on. So, you start and you more or less you assemble atom per atom until you get your nano crystal but in my opinion this is not so suitable for scaling up. You could not produce tone of material with this.

But, these are technique that are very interesting from a fundamental point of view because you could really control the size of your material and also the chemistry and so on. So, you have more control on your sample and it makes the understanding and it makes the study much easier. So, these are interesting technique, but we will not discuss them in this course.

So, what we will discuss is the top down. So, you start from a poly crystalline material and you reduce its crystallite size. So, this is what we will study in this course. So, there are many ways to do that. You could do that by ball milling, cold rolling, equal channel angular pressing, high pressure torsion and so on. So, we will discuss some of them in this course.

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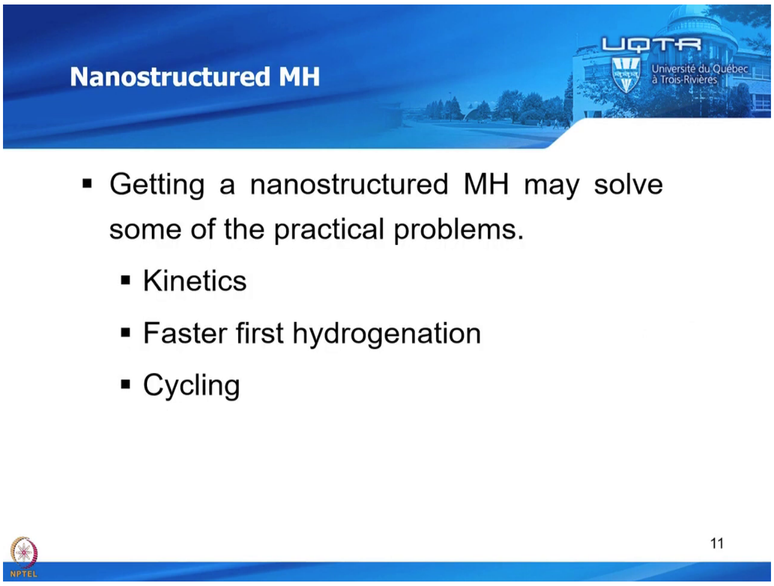

Nanostructured MH

- Getting a nanostructured MH may solve some of the practical problems.
  - Kinetics
  - Faster first hydrogenation
  - Cycling

So, nanostructure metal hydride. So, getting nanostructure metal hydride could solve some of the practical problem. For example, the kinetics or the first hydrogenation. So, we could make the first hydrogenation much faster and you could make the alloy much easier to cycle. So, after many cycle of hydrogenation dehydrogenation you will not lose so much capacity.

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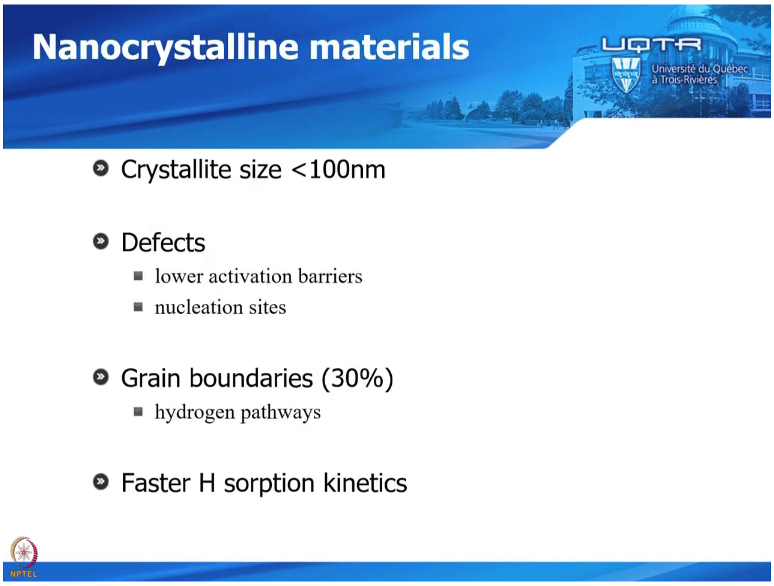

Nanocrystalline materials

- Crystallite size <100nm
- Defects
  - lower activation barriers
  - nucleation sites
- Grain boundaries (30%)
  - hydrogen pathways
- Faster H sorption kinetics

So, what is the definition of a nanocrystalline material well the classical definition is that your crystalline size should be less than 100 nanometers. So, the crystallite size is the coherent domain of your crystal and in an nanocrystalline material you have a lot of defect. So, these defect could act as activation nucleation site. So, they will lower the activation barrier.

So, if you have more nucleation site your kinetic will be faster and also depending on the size of your grain boundary and the size of your nanocrystalline you could have grain boundaries could make up to 30 percent of your material. And, this grain boundary could serve as a hydrogen pathway. So, hydrogen could go through these grain boundaries to reach your nanocrystalline material.

And, all of this will make the kinetic will be much faster in a nanocrystalline material compared to a poly crystalline material.

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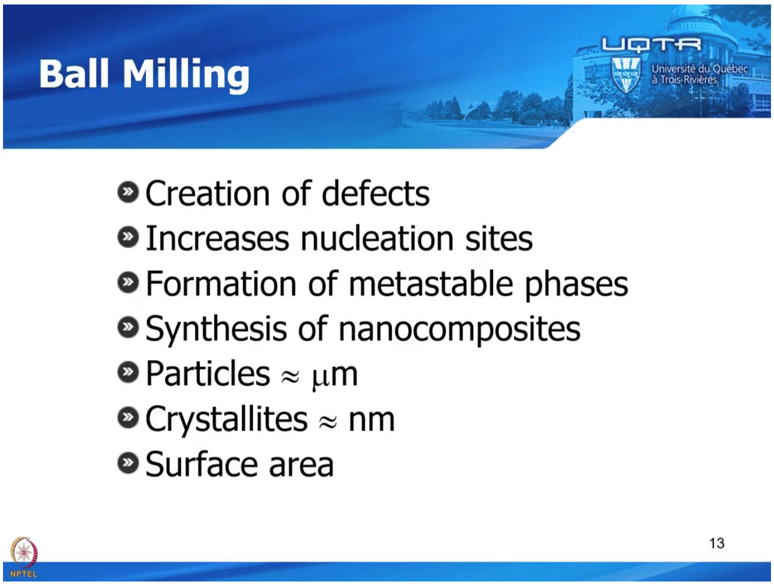

Ball Milling

- Creation of defects
- Increases nucleation sites
- Formation of metastable phases
- Synthesis of nanocomposites
- Particles ≈ μm
- Crystallites ≈ nm
- Surface area

So, today we will look mainly at ball milling to prepare metal hydride. This is the, this is the technique that is used by most of the researcher in the field of metal hydride. So, almost all of them are using ball milling to get a nanocrystalline structure and as we saw by ball milling you could have defect you will. So, that will increase the nucleation site.

You could have formation of the metastable phase. This is a common feature of ball milling. So, not only in metal hydride, but also in other type of material usually you could get a metastable phase a high pressure, high temperature phase just by ball milling at room temperature.

Of course, you could synthesize nano composite. So, you could mix two alloy and you could get a nanocomposite usually when you do ball milling the particle are of the order of the micron, but the crystallite is order of nanometer. So, you have to be careful when we talk about nanocrystalline material. It does not necessarily mean that the particle or nanocrystalline size it is the crystallite that are nanosize.

And, sometime in the literature you see people are talking about grain size, but I do not like to use this word because for some people grain may means particle and for some other people grain may means crystallite. So, I prefer to talk about particle and crystallite and then it is clear for everybody. So, we should talk about particle that is a particle. So, that particle could be of the order of micron, but it is made of many smaller crystal small crystallite of the order of nanometer.

And of course, by ball milling you could increase the specific surface area.

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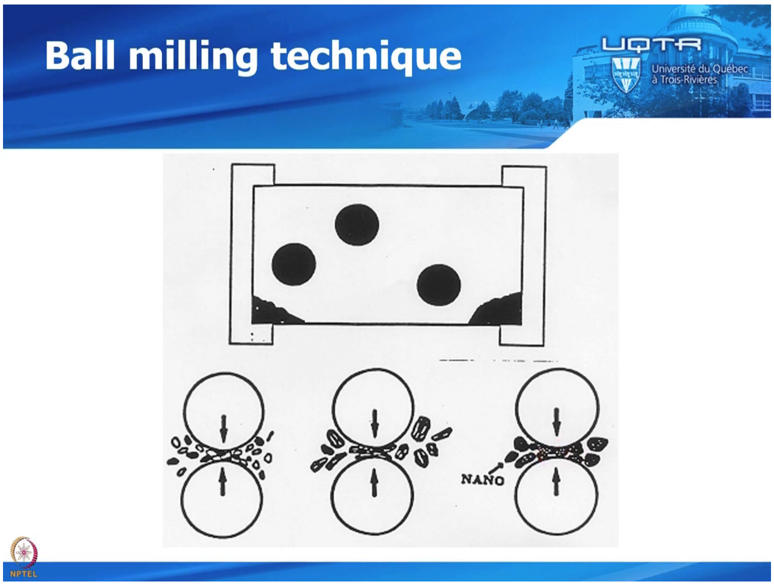

Ball milling technique

So, ball milling varies schematically. So, in ball milling you have a crucible and you put your raw material in form of powder and you have balls that are made of stainless steel, argon stainless steel or tungsten carbide or some other material you select the material depending on what you want to ball mill and you shake this crucible, and then you will have a collision between two particle or between the particle and the wall of your crucible.

And, of course, if you have powder in your crucible then you will have powder that is trapped between two balls or between a ball and a wall. So, when the two ball collide you have your powder that was here will be broken, ok. So, you will have or they could be cold weld together, the two particle could be cold weld with the force of the impact of the two balls.

So, it is a repetition of fracture cold welding fracture cold welding and so on and after you repeat that many times you will have a nanostructure material.

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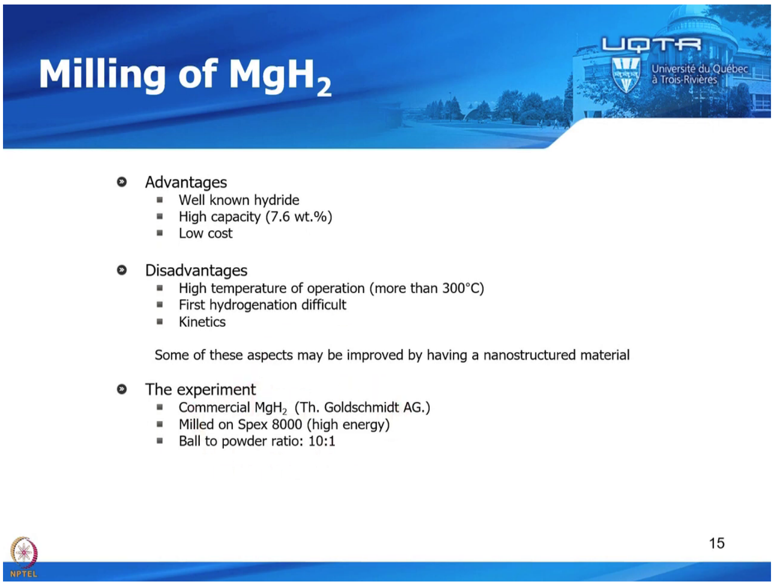

Milling of MgH_2

- Advantages
  - Well known hydride
  - High capacity (7.6 wt.%)
  - Low cost
- Disadvantages
  - High temperature of operation (more than 300°C)
  - First hydrogenation difficult
  - Kinetics

Some of these aspects may be improved by having a nanostructured material

- The experiment
  - Commercial MgH_2 (Th. Goldschmidt AG.)
  - Milled on Spex 8000 (high energy)
  - Ball to powder ratio: 10:1

So, today I will show you milling of magnesium hydride. Magnesium hydride well it is a well known hydride. It has a high capacity 7.6 weight percent and it is relatively low cost because it is abundant in the earth crust. The disadvantage is that the it has a high temperature of operation more than 200 degrees C usually the first hydrogenation is very difficult and also the kinetics is relatively slow.

So, what I will show you today is that the ball milling of commercial magnesium hydride that we ball mill in a high energy milling machine.

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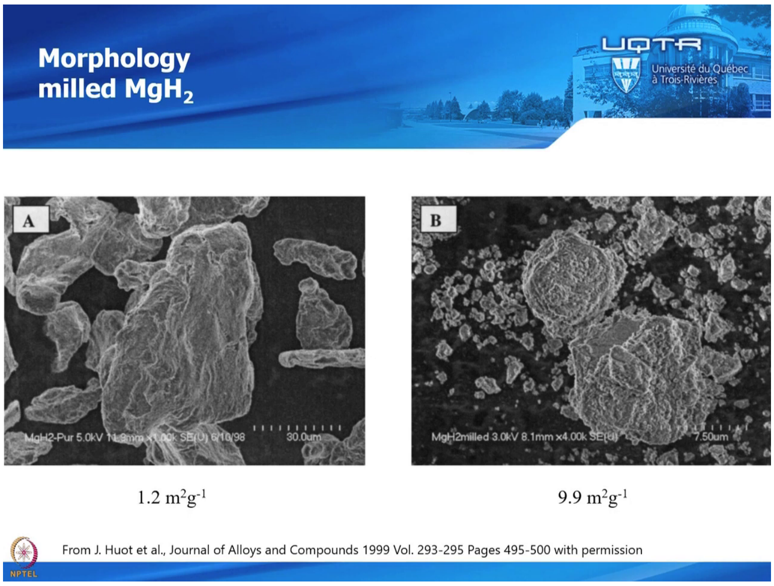

Morphology milled MgH_2

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1.2 m^2g^{-1}

9.9 m^2g^{-1}

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So, this is the powder before milling and after milling 20 hours. So, you see and the scale is not the same here. This is 30 micron, here it is a 7.5 micron. So, you see that before milling the particle are like a smooth, the surface is smooth, but you see here after milling the particle are smaller because this is only 7.5, but these are the big one, I have smaller one here.

So, you have a strong reduction of particle size and also you see that for example, this particle is an agglomeration of smaller particle. So, sometime by ball milling you will break particle, but also you will tend to fuse particle together. And, you see that the specific surface area was only 1.2 square meter per gram and by ball milling we increased it almost by a factor of 10, but it is still not a very high specific surface area.

So, you increase a specific surface area, but a by an order of magnitude, but it is still not very very high like you see in carbon nanotube or you know graphite or so on where you have a 100 and 1000 square meter per gram.

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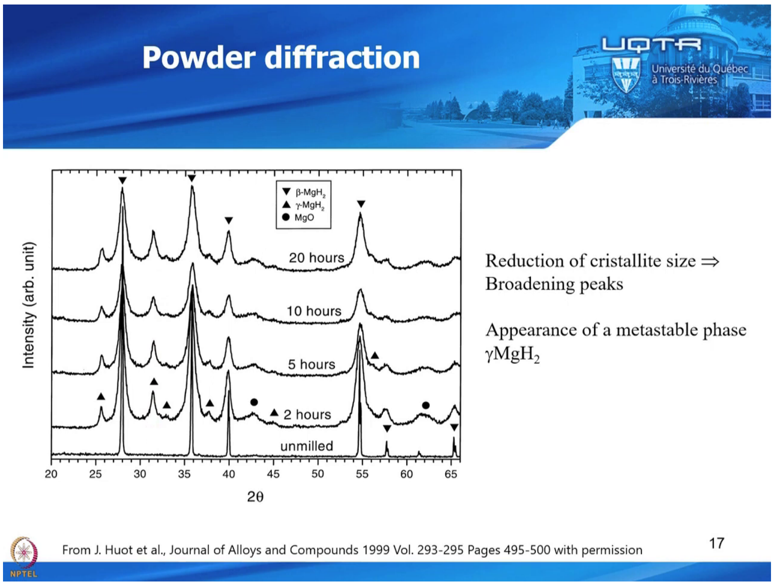

Powder diffraction

Reduction of cristallite size ⇒ Broadening peaks

Appearance of a metastable phase γMgH_2

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So, this is the powder diffraction of the unmill is here and after two hours you see that the Bragg peak are getting broad. So, that means, that it is a nanocrystalline structure and you see that these peak are appearing that we did not have these peak in the unmill and the mill one you have this peak well these peak actually are this phase. So, this is a metastable phase of magnesium hydride.

So, the normal phase is the better phase that the room temperature phase, but the gamma phase is the high temperature, high pressure phase and you see that you could synthesize it just by ball milling at room temperature.

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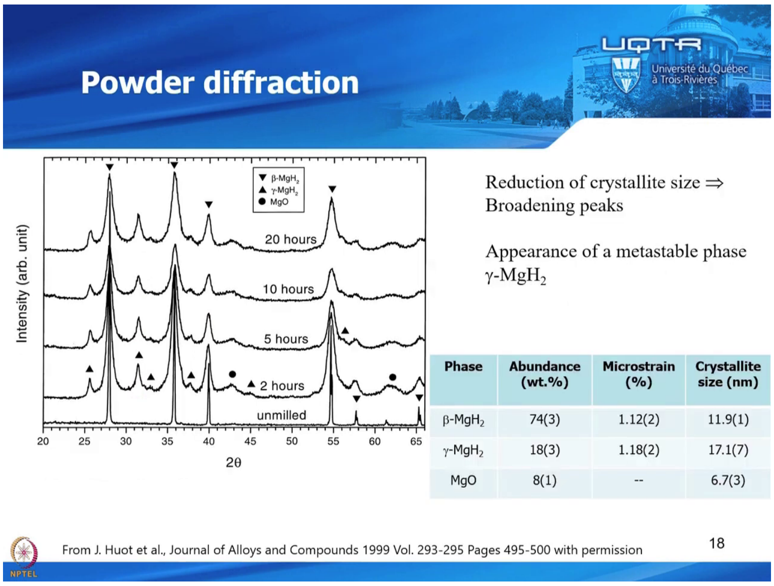

Powder diffraction

Reduction of crystallite size ⇒ Broadening peaks

Appearance of a metastable phase γ-MgH_2

Phase	Abundance (wt.%)	Microstrain (%)	Crystallite size (nm)
β-MgH_2	74(3)	1.12(2)	11.9(1)
γ-MgH_2	18(3)	1.18(2)	17.1(7)
MgO	8(1)	--	6.7(3)

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So, if you look at if you do a residual refinement, if you analyze these pattern then you see that after milling you have 74 percent of magnesium hydride and 18 percent of the of the metastable phase of magnesium hydride and you see a reduction of the crystallite size. So, now, it is only of the order of 10 nanometers. So, while before it was a polycrystalline. So, it was more than a 100 nano nanometer.

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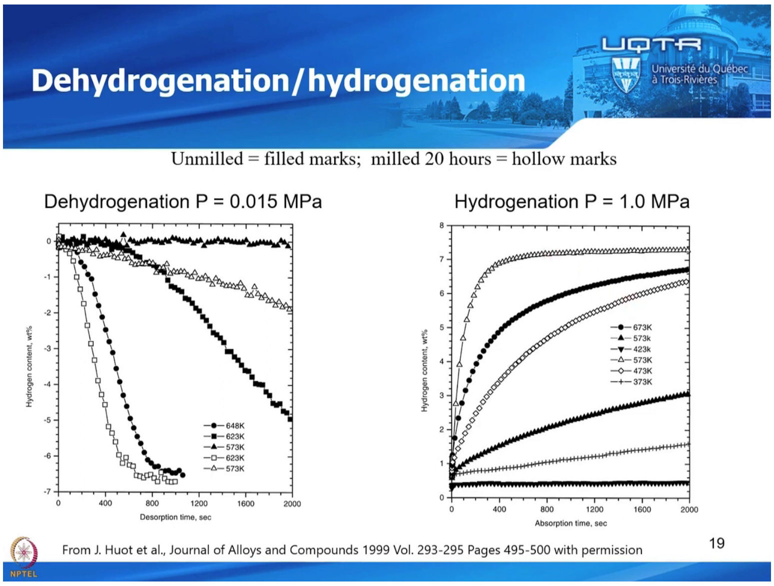

Dehydrogenation/hydrogenation

Unmilled = filled marks; milled 20 hours = hollow marks

Dehydrogenation P = 0.015 MPa

Hydrogenation P = 1.0 MPa

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So, if we look at the hydrogenation characteristic. So, you see so, this is un mill is the fill mark and mill is the hollow mark. So, this is the unmill this one, this one and this one and so, you see for example, at 573-degree K the unmill one is really not desorbing. It does not want to desorb, but at the same temperature for the mill 1, you see it started to desorb.

And, if we look at 623 K so, 350 degrees C, so, this is the desorption of the unmill 1 and you see the mill 1 is here its much faster its totally desorb and 800 seconds. So, about 12 minutes while here after half an hour it is still not fully desorb and you see even the unmill 1 at 648 it is still slower than the mill 1 at 623. So, you will see that ball milling just getting an nanocrystalline structure drastically improve the desorption kinetic and also the hydrogenation kinetic. So, you have the same thing here.

So, for example, at 573K so, this is the absorption and after half an hour it is not fully absorbed and you see that this one is fully absorbed about in a maybe 12 minutes, 800 second its fully fill. So, you see again that nanocrystalline makes the hydrogenation and dehydrogenation much faster.

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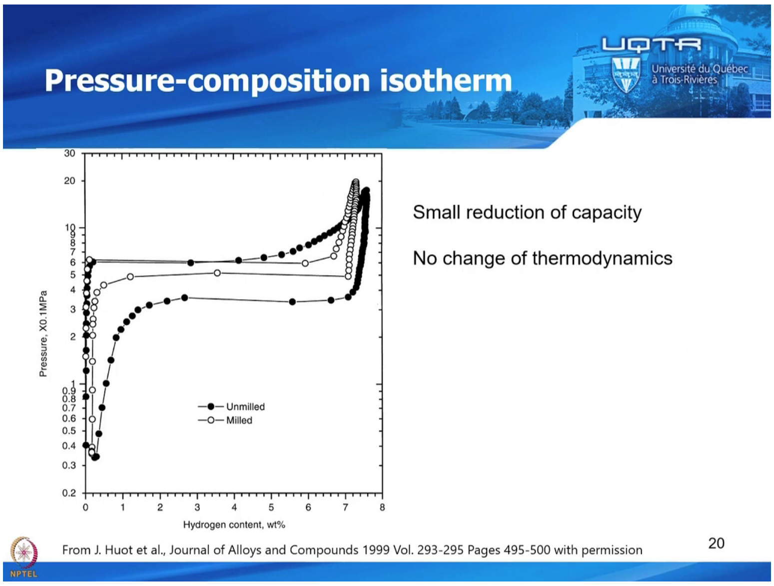

Pressure-composition isotherm

Small reduction of capacity

No change of thermodynamics

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But, this is the thermodynamic. So, this is the pressure composition isotherm as we saw in our one of the first slide. So, this is the unmill 1. So, the unmill 1 you have your plateau as we saw in the first slide and then you have. So, this is the absorption and after that you have the desorption and you have a plateau again. So, the plateau and absorption and desorption are usually not at the same position this is what we call hysteresis, but this is the resist depends on many factor, but also on the kinetic.

So, you see that this is not a flat plateau because here in principle at this point should be stable point. So, you should have equilibrium at this point, but how do you define equilibrium you define an equilibrium when the pressure does not change. So, you expose your material to that pressure and then you see that the material does not absorb hydrogen anymore. So, you say well, this is on equilibrium, but if the kinetic is very very slow.

Then the kinetic is. So, slow that your apparatus think that you reach equilibrium when actually it is not at equilibrium. So, this is due to the very slow kinetic, but as we saw when you do ball milling and you get a nanocrystalline structure the kinetic is much faster. And, you see that your plateau now is flat because the kinetic is faster and also this plateau move up to here.

So, hysteresis is much less because you could see here for the unmill 1 you see that it start to bend here, but the kinetic is so slow that it does not reach the equilibrium point. So, and so, this is why this plateau is lower. So, this is not due to thermodynamics this is due only to kinetic. So, but you see that you basically do not change the thermodynamics and you just change a kinetic. And, you see a small reduction of capacity after ball milling.

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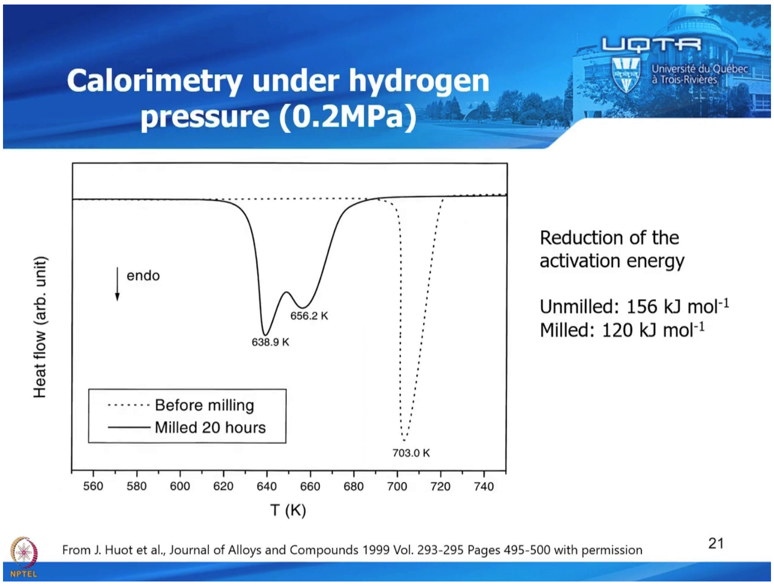

Calorimetry under hydrogen pressure (0.2MPa)

Reduction of the activation energy

Unmilled: 156 kJ mol^{-1}
Milled: 120 kJ mol^{-1}

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So, this is confirmed by a calorimetry. So, this is under hydrogen pressure. So, that was under two bar of hydrogen. So, if you put your magnesium hydride and you start to increase the temperature at one point it will desorb and that gives you that peak. And, that is the temperature of the peak, and if you ball mill then you reduce that temperature because the kinetic is faster and you notice that here I have only one peak and here I have two peaks.

But, you remember that in the ball mill material we had a two phase we had the gamma phase and the beta phase. So, that is why I have two peaks here now one of them is the desorption of the gamma phase and the other one is the desorption of the beta phase. Here I just have the beta phase, but you see a reduction of that temperature peak. So, it means that I have a reduction of the activation energy.

So, we could measure that and what we measured that for the unmill for this one the activation energy was 156 kilo joule per mole while for the milled one it was a 120. So, that is one of the reason why the kinetic is faster because the activation energy is lower.

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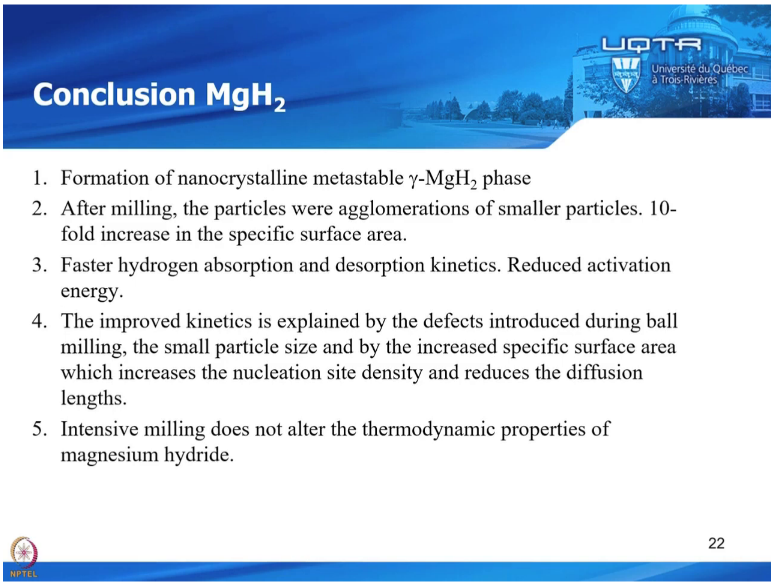

Conclusion MgH_2

1. Formation of nanocrystalline metastable γ-MgH_2 phase
2. After milling, the particles were agglomerations of smaller particles. 10-fold increase in the specific surface area.
3. Faster hydrogen absorption and desorption kinetics. Reduced activation energy.
4. The improved kinetics is explained by the defects introduced during ball milling, the small particle size and by the increased specific surface area which increases the nucleation site density and reduces the diffusion lengths.
5. Intensive milling does not alter the thermodynamic properties of magnesium hydride.

So, the conclusion for the magnesium hydride so, by ball milling we found that the you could have nanocrystalline material with a metastable phase. And, after a ball milling the particle were still of the order of micron, but much smaller than before milling and you have a tenfold increase in the specific surface area.

You have a faster hydrogenation and dehydrogenation and a reduction of the activation energy. So, this improved the kinetics and also because we have defect and the small particle size and the increase of the specific surface area. So, these are all features that will make your kinetic faster. So, reduction of activation energy, smaller size, defect and so on.

So, but we also saw that intensive milling does not alter the thermodynamic properties of magnesium hydride and this is a common feature in nanocrystalline material usually you do not change a thermodynamic unless you are going to very low very small crystallite size.

So, for example, for magnesium hydride you have to go to the thermodynamic stats to change at about 7 nanometers and just a little bit in order to have a good change of thermodynamics you have to reach like two or three nanometer. And, this is not the type of size that we get by ball milling usually. So, it is much too small.

So, in principle by ball milling usually you do not change the thermodynamics. So, with this will conclude this Part 1 and in Part 2, we will see. So, here we mainly see the effect on kinetics, but in Part 2, we will see the effect on capacity and also well see some other ways to make nanocrystalline material metal hydride; so.

Thank you very much for your attention.