

Hydrogen Energy: Production, Storage, Transportation and Safety

Prof. Pratibha Sharma

Prof. J. Huot

Department of Energy Science and Engineering

Indian Institute of Technology, Bombay

Lecture - 51

Tailoring Metal Hydrides for Practical Applications: Nanostructure Part 2

Hello everybody. So, this is the part 2 of our talk on Tailoring Metal Hydride for Practical Application.

(Refer Slide Time: 00:29)

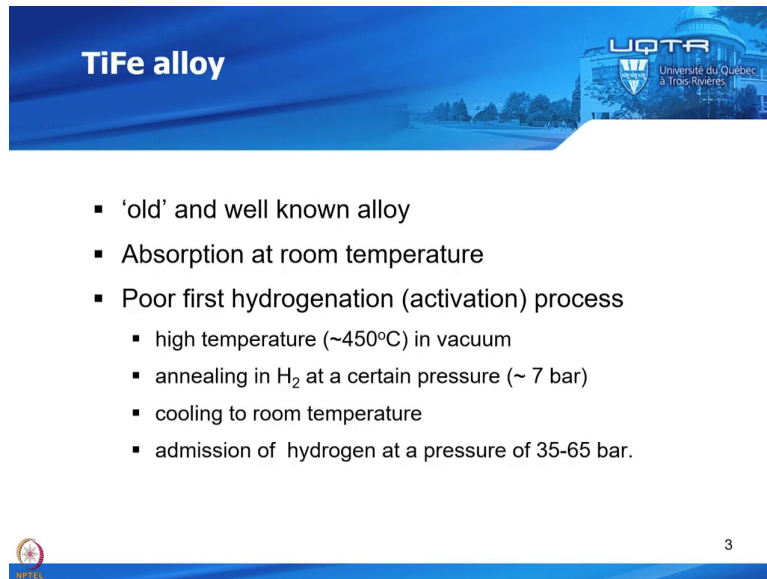


- Effect of reducing the crystallite size on the hydrogen storage capacity
- Other techniques to obtain a nanostructure



In this talk, we will see the effect of reducing the crystallite size on the hydrogen storage capacity. And, also we will see the use of other technique to obtain nanostructure.

(Refer Slide Time: 00:50)



TiFe alloy

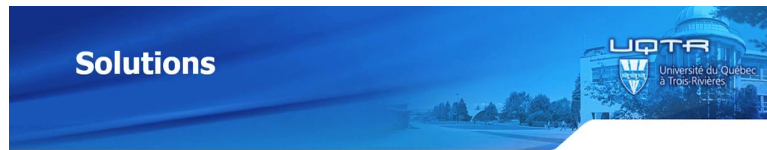
- 'old' and well known alloy
- Absorption at room temperature
- Poor first hydrogenation (activation) process
 - high temperature (~450°C) in vacuum
 - annealing in H₂ at a certain pressure (~ 7 bar)
 - cooling to room temperature
 - admission of hydrogen at a pressure of 35-65 bar.

3

So, first let me talk about iron titanium alloy. This is an old and a well known alloy. This was discovered as metal hydride in the 1970s. It could absorb temperature hydrogen at room temperature, but the first hydrogenation what we call activation is very difficult. So, you even if the alloy could store at absorb hydrogen at room temperature, usually the first act the first hydrogenation you have to go to high temperature like there 450-degree C in vacuum.


After that you anneal at a certain pressure like 7 bar, you cool to room temperature and then you go at high pressure and you do that a couple of times. So, it is a lengthy and a complicated process. So, what will be ideal will be to be able to do the activation, the first hydrogenation directly at room temperature under low pressure.

(Refer Slide Time: 02:03)



Solutions

- Element substitution for Fe in TiFe with transition elements
 - Could change thermodynamics and capacity
- Adding another element/alloy
- Getting a nanostructure

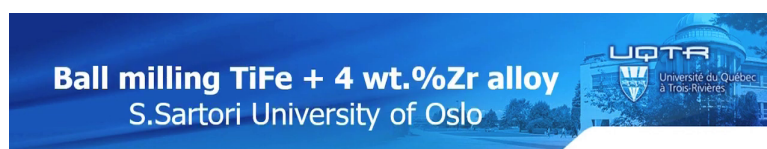


4

So, how you could do that? Well, you could substitute some element, usually people are substituting on iron. So, they replace iron by other and a transition element for example, manganese and then you could add the first hydrogenation that is quite quick.


But the with the when you do that, you could change the thermodynamics and the capacity. So, that is not the ideal way or you could add some other element or add an alloy, another alloy and have like a nano composite or you could get a nano structure. So, this is what we will see in this talk.

(Refer Slide Time: 02:53)



Ball milling TiFe + 4 wt.%Zr alloy
S.Sartori University of Oslo

- 'old' and well known alloy
- Addition of 4wt.% of Zr makes the alloy easy to activate
- What is the effect of ball milling?
- Experimental details
 - Alloy cast by arc melting
 - Milling on SPEX 8000
 - B/P = 10
 - Milled for 5, 15, 30 and 60 minutes
 - Cryomilled on Retsch CryoMill at 77K in air

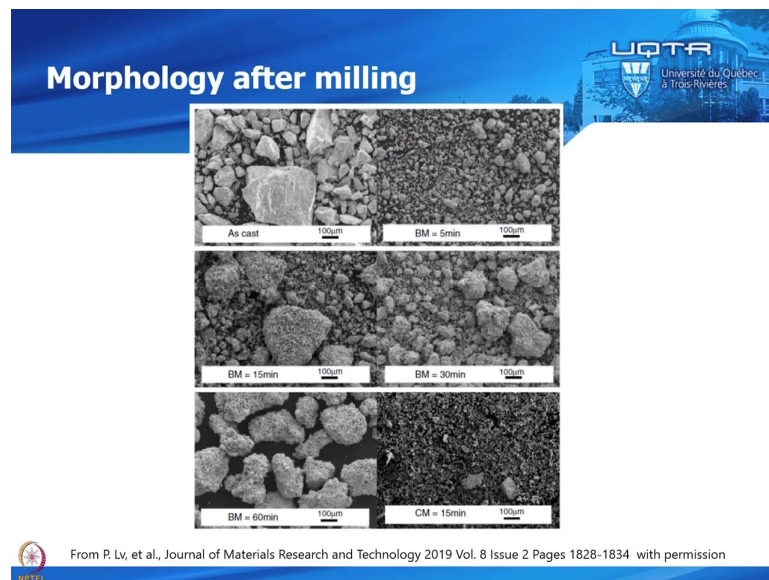


5

So, the word that I am showing you is the ball milling of iron titanium with some addition of zirconium and that work was done in collaboration with Sabrina Sartori of the University of Oslo. So, again here we add 4 weight percent of zirconium to make the alloy easy to activate we know that, but we would like to know what is the effect of ball milling.

So, all this compare with ball milling. So, we cast the alloy by arc melting and then we mill it on a SPEX machine, a high energy milling machine and we melt for 5, 15, 30 and 60 minutes and also we try cryo-milling. So, milling at low temperature, but this time it was in air. All this milling here was done in argon. But, the milling at low temperature was done in air and we will see that this made some problem.

(Refer Slide Time: 04:05)

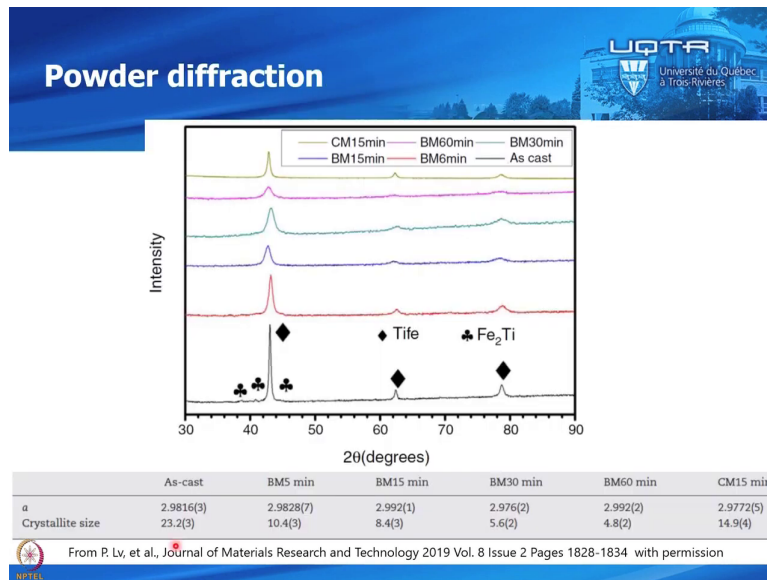


So, this is a morphology of our powder after ball milling. So, this is as cast. So, we cast the sample and then we just crush it with a mortar and a pestle. And, you have this big chunk of iron titanium and then we ball mill it for 5 minutes, 15 minutes, 30 minutes, 60 minutes and this is CryoMill.

So, you see that after just 5 minutes of ball milling, you have a huge reduction of particle size. But, after if you continue to mill for 15 minutes, you see that you have agglomeration of smaller particle and this agglomeration will continue for 30 minutes and even 60 minutes. And, now you see that all these particles are agglomeration of the small particle that you see here.

And so, you do not see any small particle anymore because you have an agglomeration of all of that. And, for CryoMill you see that the particle is very small, but we think it is because it was mill in air and you have a lot of formation of oxide and it prevent agglomeration and that it makes the part the decrepitaion of the particle.

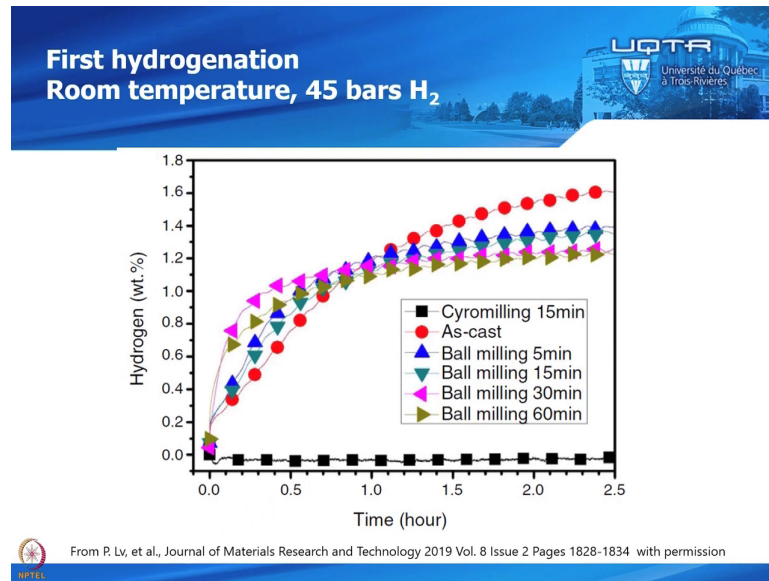
(Refer Slide Time: 05:33)



So, this is the X-ray diffraction pattern. So, this is the as cast, you have FeTi and also a little bit of Fe₂Ti. And, when you mill you see the peak are getting broadened because, it is getting nano crystalline structure, but we do not have formation of any new phase. So, you see the crystallite size as cast this 23 and ball mill 5 minutes were already reduced by a factor of 2 and it continued to be reduced.

And, here for 15 minutes of CryoMill, we have about 15 nanometers. This is bigger than this because this milling machine is not as energetic as the SPEX machine, the machine that we use for milling at room temperature. So, that is why this crystallite size is bigger than this one, because they are taking on different machine.

(Refer Slide Time: 06:43)

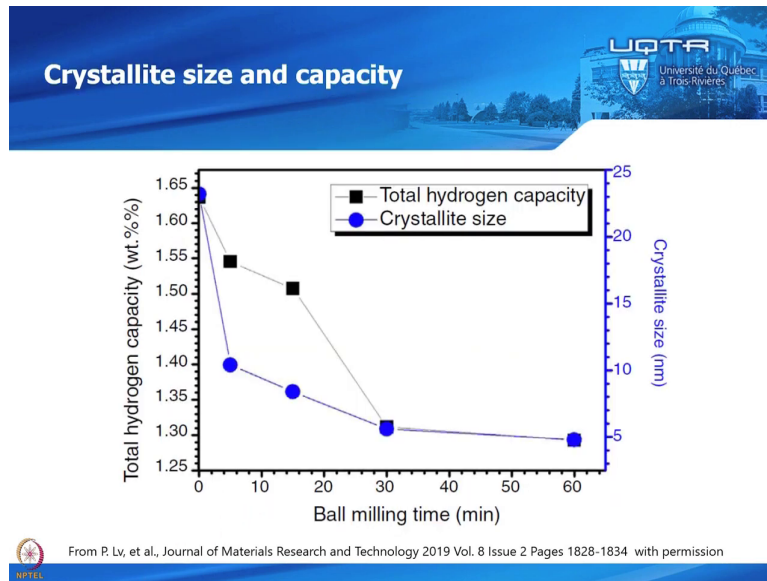


So, this is the first hydrogenation at room temperature and under 45 bar of hydrogen. So, you see this is the as cast here and you see it activate and takes about 2 hours and a half to fully absorb hydrogen. If we try our mill for 15 minutes, you will see that the sample is totally dead. It is because we mill under our on in air and then we have formation of oxide and as you as we saw in part 1 in order to hydrogenate the hydrogen as to go through the oxide layer.

And, here the oxide was probably too thick and it was impossible. So, in the future we will do this experiment again, but under argon and then were confident that the sample will then absorb hydrogen. But, for milling in at room temperature, you see that this is 5 minutes and 15 minutes, 30 minutes and 60 minutes. And, you see that as the milling time is getting bigger, the kinetic is getting faster.

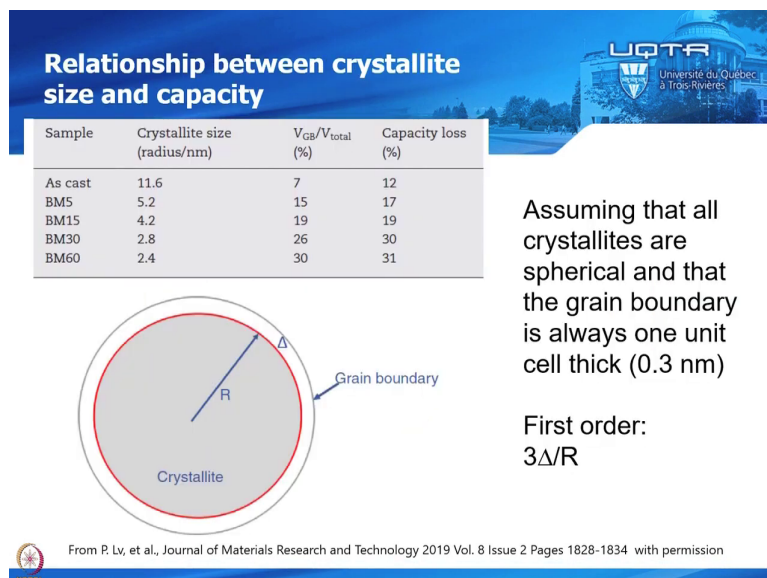
So, you have a faster kinetic, longer milling time give you faster kinetic, but you see that the capacity is getting down. So, genetic is getting better, but capacity is getting ah worst. So, how could you explain that?

(Refer Slide Time: 08:29)



So, here we took with plot. So, this is the hydrogen capacity as was measured as a function of milling time and you see that the capacity is going down. And, here this is crystallite size, again as a function of milling time and you see the crystallite size is also decreasing and it looks similar. So, probably these two are related. So, this is what we will see in the next slide.

(Refer Slide Time: 09:07)



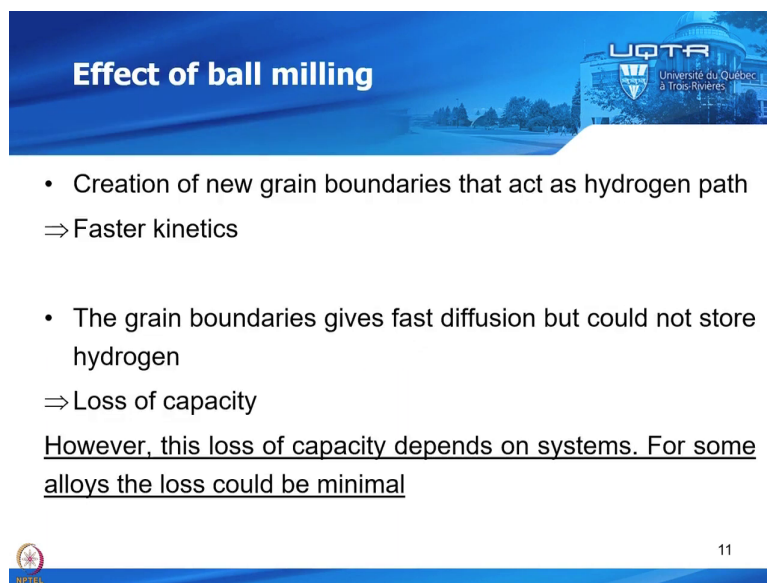
So, if you consider that the crystallite again from the first part, we saw that the crystallite is the current domain, the crystallographic current domain. And so, in order to break that that coherency, all you need is one-unit cell that is not coherent with the unit cell that is beside it.

So, that is more or less the smaller the thinner grain boundary you could have is to have one-unit cell, that does not match you know the unit cell beside it. So, in the in for iron titanium the unit cell is a 3 angstrom. So, we assume that the grain boundary is 0.3 nanometers. And, then if we assume that the crystallite is spherical and of course, a crystallite that we measure by $\times 3$ is an average.

But, we assume that all the particles are at this average and we assume that all of them as have the same grain boundary thickness. And, then we could calculate the volume of that grain boundary compared to the total volume of the particle; so, this is a very simple equation. So, on first order this is 3 times that is the thickness of the grain boundary and that is the radius of the crystallite.

So, if you do that, you see that if you express the volume of the grain boundary over the total volume; these are with respect to the crystallite size. So, these are the number and that is the capacity, the hydrogen capacity loss that we measured and you see that these numbers are very close to these numbers. So, it looks like the loss of capacity is scaling exactly as the volume, the total volume of the grain boundary.

(Refer Slide Time: 11:39)



Effect of ball milling

- Creation of new grain boundaries that act as hydrogen path
⇒ Faster kinetics
- The grain boundaries gives fast diffusion but could not store hydrogen
⇒ Loss of capacity

However, this loss of capacity depends on systems. For some alloys the loss could be minimal

NPTEL 11

So, then we could explain the loss of capacity. So, when you create a new boundary, new grain boundary this act as an hydrogen path as we saw in the first part. So, this means that its fast kinetics because now you have more grain boundary. So, you have more path for

hydrogen to go into your crystallite, but the grain boundary gives a fast diffusion, but it could not store hydrogen.

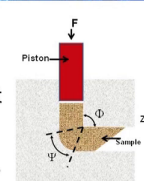
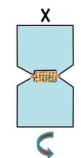
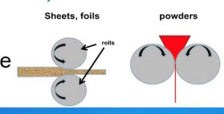
So, hydrogen is going through the grain boundary, but does not stay there. So, you have a loss of capacity and of course, the more grain boundary you have, the less capacity you will have. So, and you see that for iron titanium the scale perfectly well, but I have to tell that this loss of capacity depends on the system. So, for some alloy this loss could be minimal because, when you hydrogenate, dehydrogenate you may recreate a coherency.

So, your crystallite size may increase a little bit because, the hydrogen will force you know the unit cell that is on the grain boundary to adopt the same to get coherent with the unit cell beside it. So, this loss of capacity with the grain boundary is not true for all system, but for some system we see that it scale very well.

(Refer Slide Time: 13:39)

Other mechanical methods to obtain a nanostructure

- Equal Channel Angular pressing (ECAP)
 - Advantage: Could induce deformation in different planes.
 - Disadvantage: bulk sample that has to be filed. May be difficult to scale-up
- High Pressure Torsion (HPT)
 - Advantage: Very high strain
 - Disadvantage: small sample
- Cold Rolling (CR)
 - Advantage: Well known, scalable
 - Disadvantage: usually plates

So, the other aspect that I would like to see in this talk is the other method to obtain a nanostructure. So, in the field of metal hydride right, we have a couple of methods that are widely used by the researcher; maybe the one that is mainly used as equal channel angular pressing. So, I will not go into detail, but here you have the piston, you have a dye and there is an angle in the dye.

So, you take your sample. So, this is your sample and you push it through the dye. So, it has to go through this angle and then by going through this angle, it will sustain a lot of strain.

And so, you could get a highly strain material and also you could get nano crystalline structure. The other advantage is that depending on because, you could do that, you could repeat that many time and depending on how you push back the sample.

If you rotate it a 90 degree or 180 degree, you could induce the formation in different plane. So, this is interesting because like according to the crystal structure of your material you could say, well I would like to induce deformation mainly in that plane and not in that other plane. So, from a fundamental point of view, this is quite interesting. The disadvantage is that the bulk sample has to be filed.

So, after you process that you have so, typically this dimension is maybe 1 centimeter. So, you have a block of 1 centimeter by 1 centimeter by maybe a couple of centimeter long and you have to file this block. So, you more or less you modify your sample by doing that. So, you went use some other deformation by just filing you by reducing in powder. And, also this could be difficult to scale up. The other technique that is more and more used now is high pressure torsion.

So, here your sample is a thin disk that you put between two mandrels and you rotate it, you rotate the mandrels and you press on it very hard. So, the advantage is you have a very high strain. So, maybe this is the technique that you have the highest strain, but the disadvantage is you have a very small sample. So, maybe it is 1 centimeter of diameter by maybe 1 millimeter of thickness.

So, your sample is very very small and finally, we have a cold rolling. So, the advantage of that its a well known technique and I think it is very easy to scale, because the industry is doing a lot of cold rolling. The disadvantage is usually you have to use a plate, but in our case we solve this problem because we took the cold rolling machine and we rotated 90 degrees. So, then we could process powder because, usually our material our metal hydride is in form of powder and not plate.

(Refer Slide Time: 17:25)

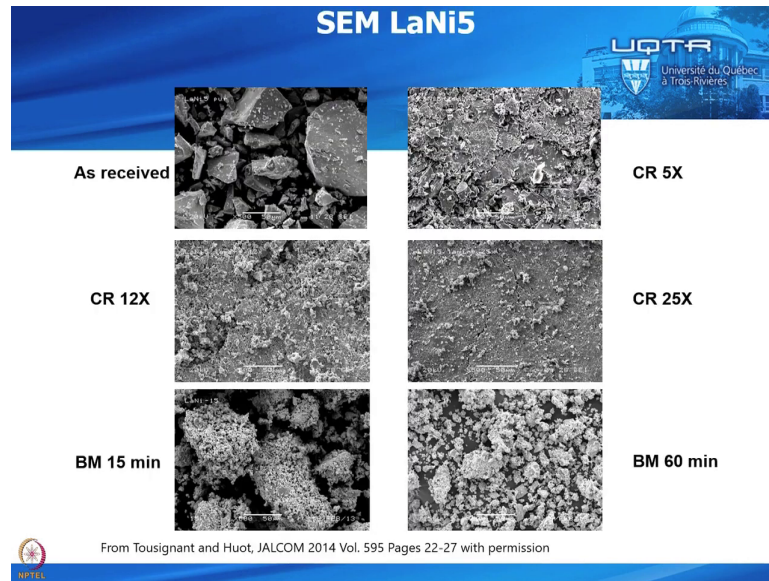
Experimental details LaNi₅

- Commercial LaNi₅ :
 - Rolled in air
 - Activation at 50°C, 1500 kPa
 - Desorption at 50°C, 5 kPa
 - Theoretical capacity ≈ 1.5wt.%
- Cold rolling performed in air
- Comparison with ball milling
 - Spex 8000
 - Balls/Powder 10
 - Milled atmosphere argon
 - Milled for 15 and 60 minutes

So, the example that I will show you today is LaNi₅. So, cold rolling of LaNi₅. So, we took commercial lanthanum nickel 5, we roll it in air and after rolling without the first hydrogenation, the activation at 50 degree and 15 bar. And, that desorption was also done at 50 degree and 5 kilopascal and the theoretical capacity of LaNi₅ is about 1.5 weight percent.

And, again I have to stress that the cold rolling was done in air and we compare that with ball milling, because ball milling is used by everybody and everybody knows what this ball milling is doing to mill to metal hydride. So, we use a high energy mill and the milling was done in argon, contrary to here that was done in air and we mill for 15 and 60 minutes.

(Refer Slide Time: 18:33)

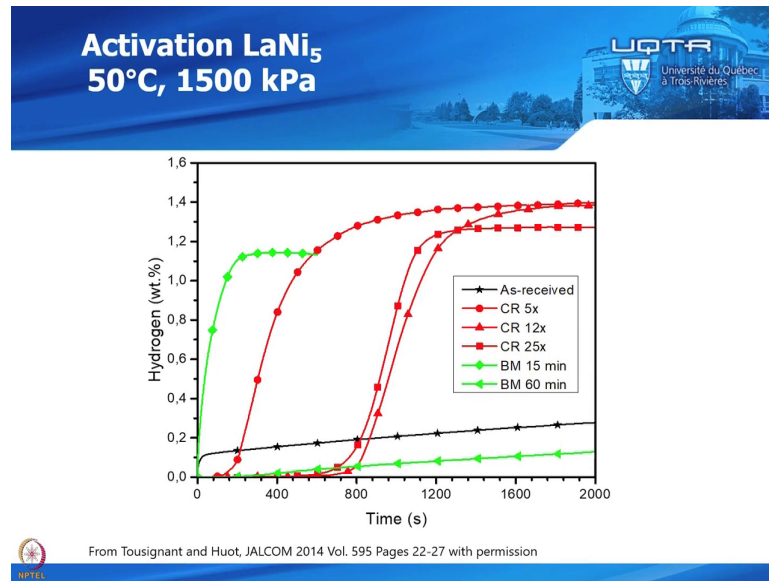


So, this is a morphology. So, after so, the as received one is a like big block. So, this is 50 micron. So, this is almost 150 micron. So, you have big particle and when you cold roll basically what you do, you take all these particle and you make a small plate with it ok.

So, you see that the and then we took this plate after rolling once, we take the plate, we fold it in 2 and we roll again. So, at after each rolling, we have a reduction of 50 percent of our plate. So, this is after 5, 12 and 25 roll and you see the morphology of the plate do not change so much. But of course, we will have reduction of crystallite size and strain the because, we are every time after every roll we reduce the thickness of that plate by 50 percent.

And, this is ball mill 15 minutes. So, you see as we saw previously, you have agglomeration of smaller particle here and after 60 minutes you more or less you take this particle and you break them again. So, you see the particle are smaller and you have even smaller particle here.

(Refer Slide Time: 20:07)

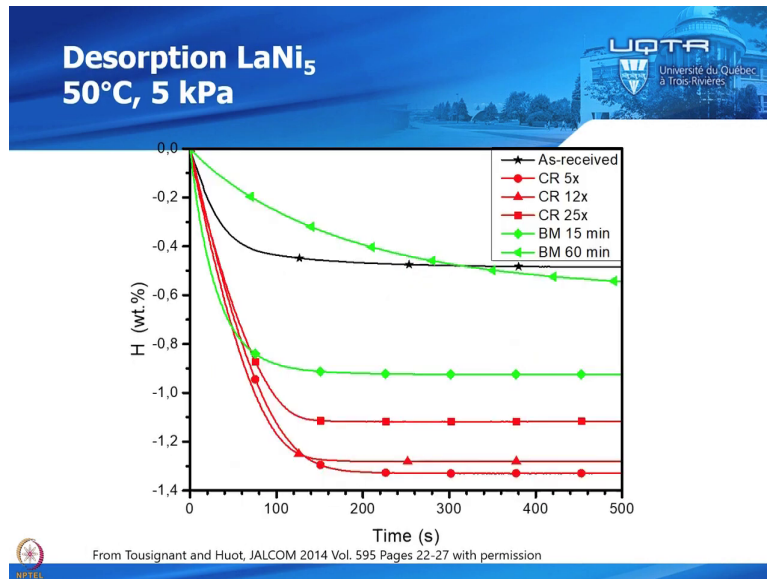


So, this is the first hydrogenation, activation at 50 degree and 15 bar. So, this is the as received. So, you see the as received, it is very difficult, its it takes forever to activate. And, if you ball mill 15 minutes, you see that its very fast. You know its that, the sample is taking hydrogen right away, but you have a loss of capacity here.

But, if you ball mill more, if your ball mill 60 minutes, you see that you have the reduction of capacity and the sample is almost dead again. It is even worse than the as cast. But, if you do cold rolling, you see 5 times cold rolling. It is quite fast, not as fast as ball milling, but you see we have almost full capacity.

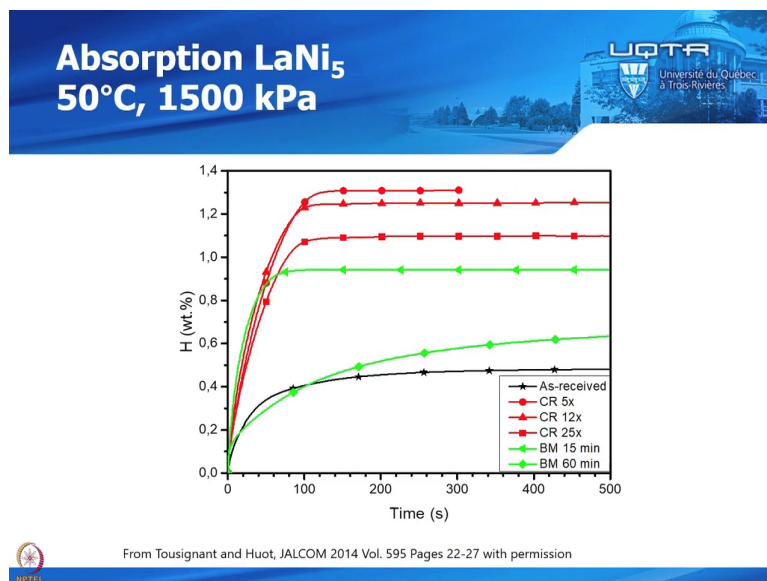
And, if we roll 12 times or 25 times, you see that 12 times actually its getting a little bit slower, the incubation time is longer, but we are we have almost no loss of capacity. But, if we keep cold rolling, we have a loss of capacity because again we do have all of that in the air. So, as we roll we will start to produce oxide and to make oxide and then it will reduce the capacity.

(Refer Slide Time: 21:44)



So, this is the desorption. So, you see that this is the desorption of the as receive and this is the ball mill 15 minutes. So, it is quite fast and that is the ball mill of 60 minutes its slow. But, what is interesting is that all of them, the ball mill 15 minutes and all the cold rolling there are all of them have more or less the same kinetic. They just the only difference is the capacity, but they all have the same kinetic.

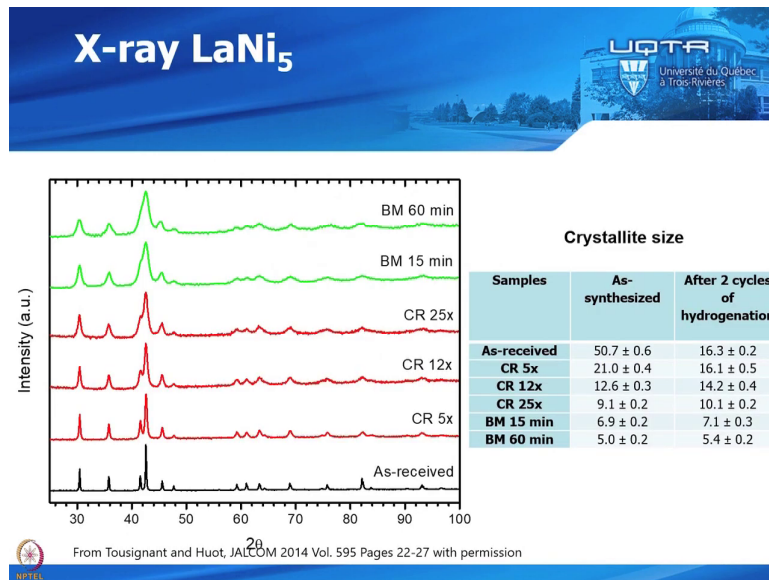
(Refer Slide Time: 22:34)



So, the point is after 1 cycle, they almost have all the same capacity, the same kinetics and this is what you see on the second absorption. So, on the second absorption you see that all of

them are absorbing at the same rate. So, the difficulty is the first hydrogenation. Then, you have a difference of kinetic between all of the all of them. But, after the first hydrogenation and this is a common example for many metal hydride after the activation, then the kinetic is the same. The only thing that the that is different is the capacity.

(Refer Slide Time: 23:18)

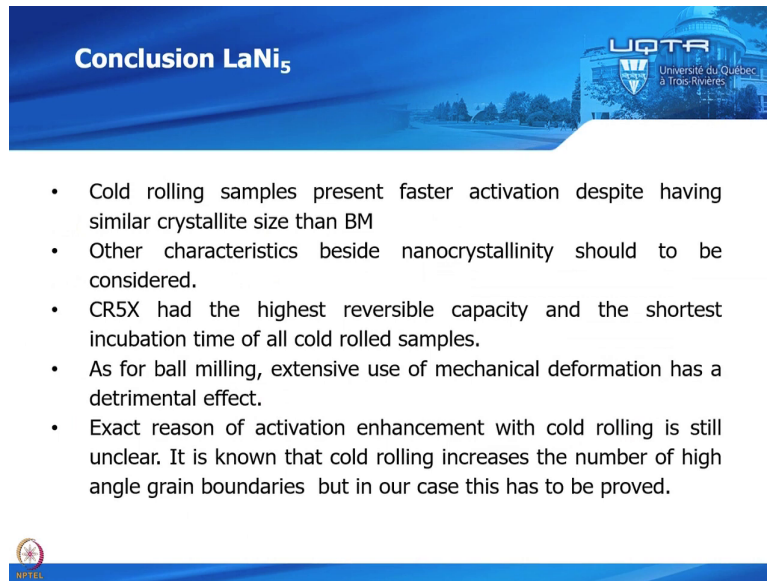


So, this is the diffraction pattern. So, as receive cold roll 5 time, 12 time, 25 and ball mill and you see that 15 minutes of ball mill, the peak are already quite broad compared to 5 cold roll the peak are broader, but not so much ok. So, nano the ball milling is much more efficient to reduce and to nano crystalline structure and you see it here. So, as synthesized.

So, this is as received its 50, this is in nanometer. So, 50 nanometer and ball milling 15 minutes you reduce that by a factor almost a factor of 10. So, its 6.9 and 60 minutes, you go down to 5 nanometer. While, for the cold roll, you see its 21 nanometer and then 12 and then 9. So, you have a reduction of crystallite size, but not as important as for the ball milling ok and this is after 2 cycle of hydrogenation.

So, you see that even for the as receive, the crystallite size will reduce in this case because of the decrepitation of your material, but you see here you go from 21 to 16. So, you have a reduction, but here you have an increase and here its more or less constant, but it does not absorb hydrogen so much. But so, you see that it looks like you have like a natural size of crystallite, after cycling it will tend to have like a certain size of crystalline.

(Refer Slide Time: 25:20)



Conclusion LaNi₅

- Cold rolling samples present faster activation despite having similar crystallite size than BM
- Other characteristics beside nanocrystallinity should to be considered.
- CR5X had the highest reversible capacity and the shortest incubation time of all cold rolled samples.
- As for ball milling, extensive use of mechanical deformation has a detrimental effect.
- Exact reason of activation enhancement with cold rolling is still unclear. It is known that cold rolling increases the number of high angle grain boundaries but in our case this has to be proved.

UQTR Université du Québec à Trois-Rivières

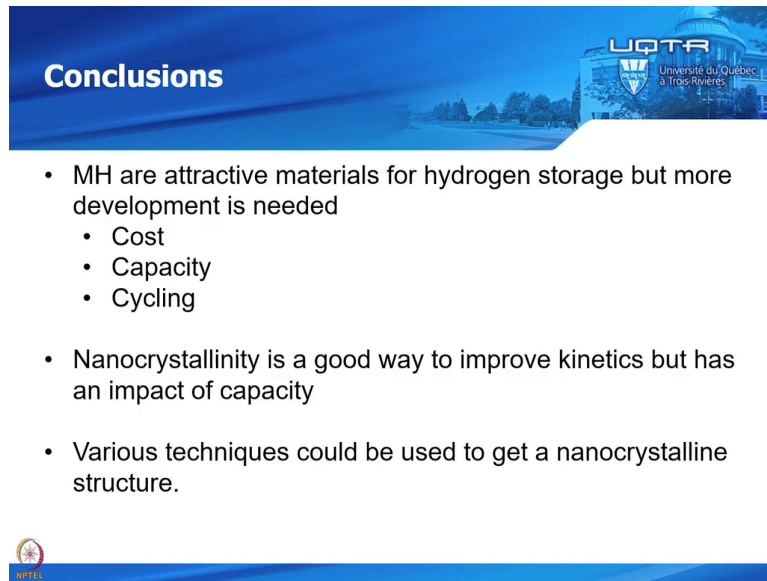
NPTC

So, the conclusion for the LaNi₅ is that cold rolling sample present a faster activation despite having similar crystallite size than ball milling. So, the point that I want to give you here is that nano crystalline is important for kinetics and for activation, but it is not the only parameter. Some other characteristic also have an effect on the hydrogenation kinetics.

So, cold rolling 5 time had the highest reversible capacity and the shortest incubation time of all the cold roll sample. For ball milling, if you ball mill for too long it has a detrimental effect. So, it is not good to ball mill for too long and to try to reduce the crystallite size at a very small, sometimes it is better to have a crystallite size that is a little bit bigger, but you will still have faster kinetic.

Up to now the exact reason for activation and enhancement with cold rolling is still unclear to us. But, it is known that cold rolling increase the number of high angle grain boundary, but in our case it still has to be proved. We still have to do some experiment about that.

(Refer Slide Time: 26:50)



Conclusions

- MH are attractive materials for hydrogen storage but more development is needed
 - Cost
 - Capacity
 - Cycling
- Nanocrystallinity is a good way to improve kinetics but has an impact of capacity
- Various techniques could be used to get a nanocrystalline structure.

So, in conclusion of that course, I hope I show you that metal hydride attractive material for hydrogen storage, but we need more development. We need to reduce the cost to get better capacity and also to improve the cycling. Nano crystallinity is a good way to improve the kinetic, but it has an impact on capacity. And, we saw that many techniques could be used to get a nano crystalline structure.

So, with this I will end my course. I would like to thank you for your attention and I hope, I hope you will have a better understanding of metal hydride now.

Thank you very much. Bye, bye.