Advanced Materials and Processes

Prof. Jayanta Das
Department of Metallurgical and Materials Science Engineering
Indian Institute of Technology, Kharagpur

Lecture – 58
Advanced Functional Alloys (Contd.)

Welcome to NPTEL, myself Dr. Jayanta Das from Department of Metallurgical and Materials Engineering, IIT Kharagpur. I will be teaching you Advanced Materials and Processes. This week, we are discussing about many advanced functional alloys, which shows multifunctional properties. Among them two of the very important properties like ferromagnetic shape memory alloys and Heusler alloys are already discussed. Today, we are going to discuss the effect of magnetic field on the entropy change in material and that basically finally, lead to for any refrigeration purpose means temperature change in material that occur due to the application of magnetic field.

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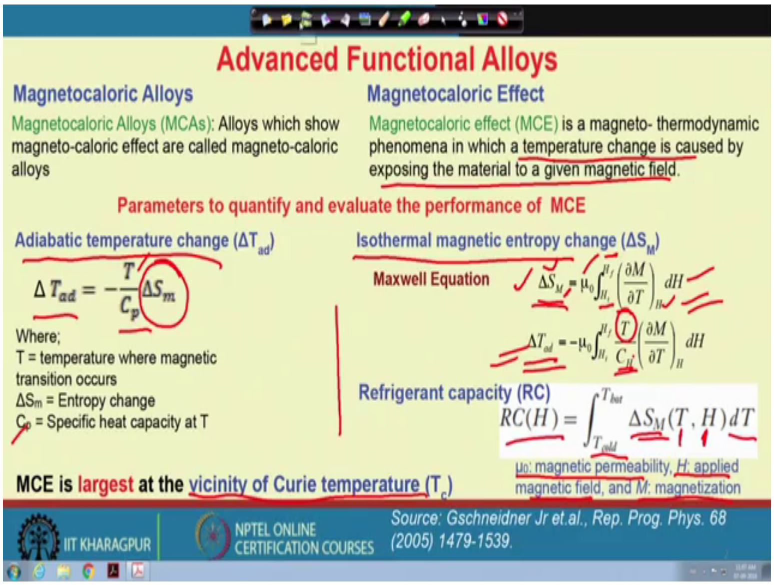

So, let us start today's discussion about those functional alloys, which are called as a Magnetocaloric alloys. Magnetocaloric this is a effect, where this is the thermo magneto a magneto thermodynamic effect or phenomena in which the temperature change is caused by exposing the material with an magnetic field. So, this particular behavior has been observed in case of metals alloys as well as some of the ceramics, but in case of ceramics those change of temperature is very very low; whereas, some of the alloys which are called as magnetocaloric alloys, showing magnetocaloric effect is quite high.

Now, to assess a material whether, they could be performed as a magnetocaloric materials or not there are 3 basic parameter that can help us to assess this effect, the first one is the adiabatic temperature change. The adiabatic temperature change is measured by the temperature by C p, C p is the specific heat capacity of the material multiplied by the entropy change in the material ok. Now these magnetic entropy change we actually measure by using the Maxwell equation.

The Maxwell equation says that the delta S M; delta S means the entropy change, the magnetic entropy change stands for the M here is equal to mu 0 into integration of from initial magnetic field to the final magnetic field and d l dM by dT means the change of the magnetic moment with temperature at a given magnetic field and dH. So, this integration gives us a value of this particular delta SM value. And from there, we can also calculate the adiabatic temperature change, which is basically estimation of a delta SM divided by the CH here, C is the specific heat at a given field yes and the temperature at which it is measured ok.

So, this has a same equation, we apply here actually with the delta SM value. Now, um we also need to estimate the refrigerant capacity of the material and RC, which is a refrigerant capacity at a given field is the integration between the hot and cold junction and delta SM, which is basically function of temperature and field into dT. So, mu 0 here is the magnetic permeability and H is the applied magnetic field and M is the magnetization.

So, this is all about the 3 major important parameter in order to characterize a magnetocaloric material, whether it could be metal, it could be alloy or it could be ceramic; however, since I said that in case of a metals and alloys, this effect has been observed quite a large. So, these magnetocaloric effect, we will focusing mostly on the alloys. However, this effect of entropy change has been observed to be maximum at the vicinity of the curie temperature.

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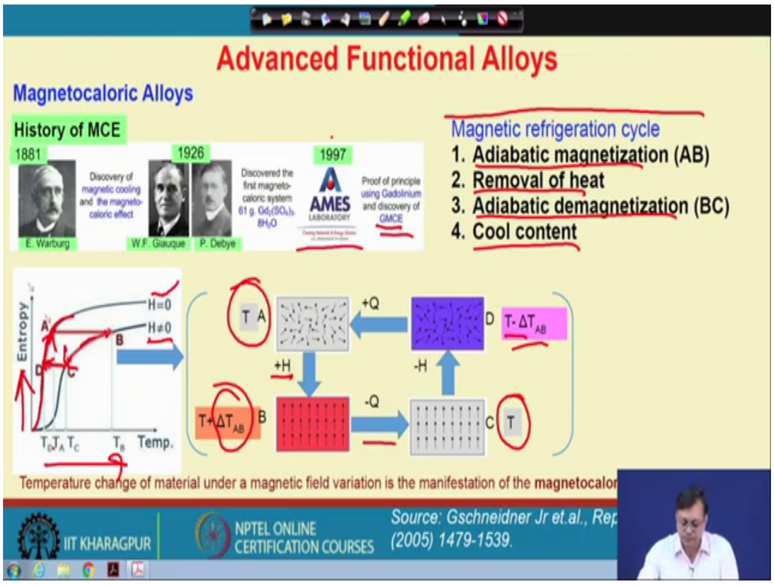

So, curie temperature, we know at the temperature, where ferromagnetic to paramagnetic transition magnetic transition occur by the application of a temperature. The effect of magnetocaloric effect that is told quite a long time ago that was around 1881 by Warburg and he shows basically, this magnetocaloric effect could be produced and later on in 1926 the magnetocaloric system like Gadolinium and the processing of such compound Gadolinium based compound was shown.

Now, in 1997 AMES laboratory was prove the principle of gadolinium gadolinium and the discovery of the giant magnetocaloric effect. So, since then there is a large number of researchers, who are developing these alloys for the commercial application and practical application; now these magnetic refrigeration cycle, if we need to think about, we have to see these plot and carefully understand the matter.

So, here is the entropy versus temperature and let us say at 0 applied field, if we increase the temperature this is the entropy. And let us say, we start with point A and if we immediately apply at a given temperature, if we apply let us say a magnetic field that is H, which is a nonzero then, immediately there will be a change in the temperature value. So, you can see from A to B, then if we simply extract the heat and reduce the temperature then we will come here.

And if we withdraw the magnetic field then, it will go to point D and then the material will be will be heated and so on. And so we have a close cycle of this Carnot type of cycle actually or otherwise, we can think about let us say, we start with a differently oriented magnetic domain inside a material, which has a higher entropy and then we apply a field. So now, the magnetic domains are aligned and that basically increases the temperature of the system. So, delta T will increase.

Now, we extract the heat from the system. So now, material gets cooler. So, we kept at temperature T and so, after that if we simply remove the magnetic field then again the material will come back and T minus delta T adiabatic will occur. So, this is basically cooling of the material. So, adiabatic magnetization then removal of the heat adiabatic demagnetization and the cool content; or like these are the 4 major steps. So, in that case first the magnetization and then we remove the heat and so then we have adiabatic demagnetization and then we again basically, apply those 2 to 2 cooling purpose.

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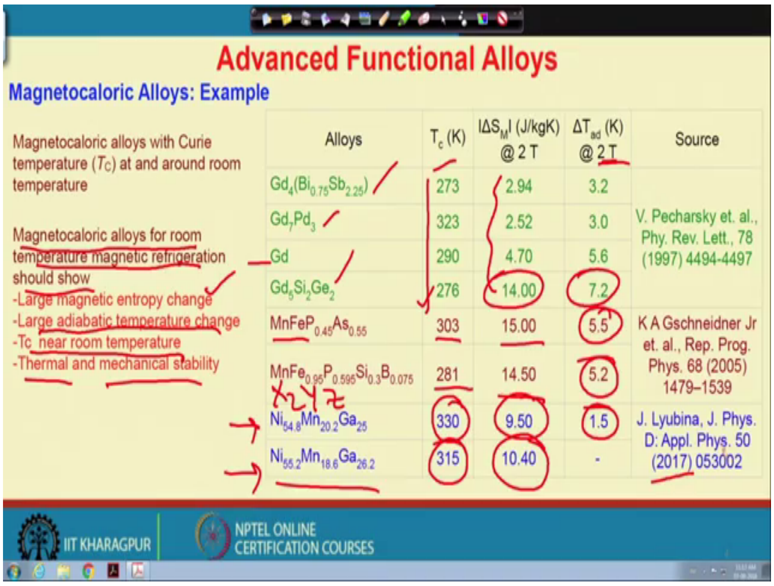

So, this is a typical a magnetic refrigeration cycle and there are a several alloys and metals also have shown the first metal that shows these was basically, gadolinium this is a pure metal that shows such a effect um. Now they have a some other compound, gadolinium based compound and interesting thing is that the curie temperature is very close to a room temperature and gadolinium is a very expensive material; however, the entropy change varies from 2 to 14.

So, this is a very quiet high value even though the applied field is also high, the temperature change is also high. So, this is around a 2 Tesla. So, magnetic magnetocaloric alloys with curie temperature and around room temperature is required for refrigeration purpose at room temperature. So, these alloys from room temperature magnetic refrigeration should show a large magnetic entropy, change a large adiabatic temperature, change the curie temperature is expected to be near room temperature. The material should have very good thermal and mechanical stability that is also very much important it should not be very brittle.

Um and on the other hand, some of these compounds containing iron and phosphorus arsenic with manganese have shown such very good magnetocaloric effect, where the adiabatic temperature change has been observed in the range of 5.5 to 5.2. So, the total entropy change is also very high and you can now recognize these alloys system, which are full Heusler type of compound, where X 2 Y and Z. So, like a P type element and then we have nickel and manganese, these alloys nickel manganese gallium alloys also have shown such near room temperature, a curie temperature and we get a quite large a delta SM at 2 Tesla and even though the temperature adiabatic temperature is not, so high like 1.5 um K.

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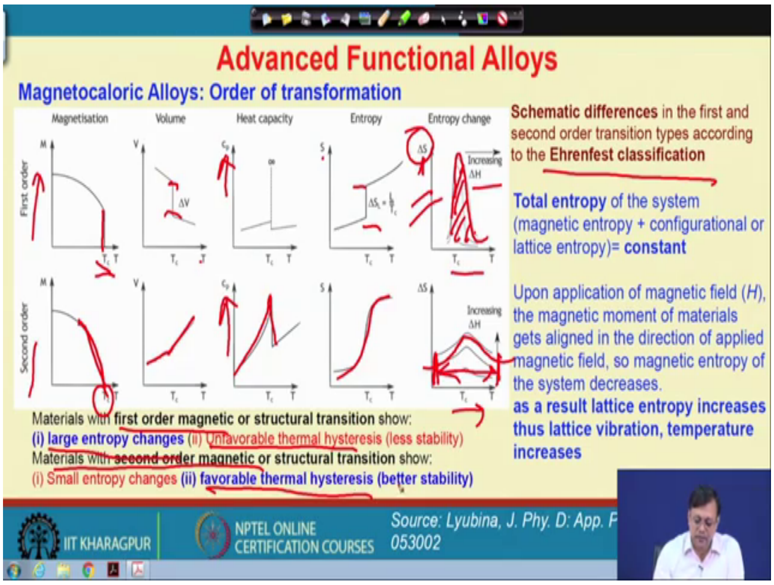

So, these are a very recent trend of the literature that shows such a magnetocaloric effect in alloys. But, before going to all these detail once again, we must look at the order of the phase transformation, what is desired and what is not? Means, if we think about a first order transformation, whether these transformation could be magnetic in nature or it could be a structural phase transition; now, in any of the case if the order of the transformation is a first order, then for a first order transformation the typical characteristic that M the magnetic moment that basically changes very sharp.

So, TC you can get almost comes to 0 at a very definite temperature and so, this is a typical characteristic of a first order, and the volume change also occurred at a very sharp is a discontinuity in the volume versus temperature plot. And where the CP change occur like a like a infinities goes to infinity and discontinuity here and the similar type of effect occur, if we think about only entropy. And if we plot entropy change delta S versus T then near this TC, we will see sharp relatively sharper change of entropy change with increasing the let us say, the delta H and so on.

Now, these particular schematic differences are classified, according to Ehrenfest classification of first order and second order whereas, if the transition is a second order transition even though, we get the same TC, but the transition occurred quite a wide range of temperature whereas, the volume change does not have any discontinuity rather the slope only changes, in case of a second order transformation and very similar like, in case of a specific heat capacity change and it goes higher and then again like typical a glass transition type of feature, you can see actually right.

So, that was a typical second order type of transformation and then the slope changes in the entropy curve and so it shows a little bit broader entropy change plot with temperature ok. So, in this case the temperature or we can create actually larger delta T adiabatic in this case whereas, the value of delta S for a first order transformation the area under the curve is quite high because delta T the T into delta S gives you, the net caloric changes in the material.

So, for the first order transformation magnetic or structural there is a unfavorable thermal hysteresis or less stability, but the large entropy can be changed here in a first order. Whereas, in case of second order magnetic or structural transition the favorable thermal hysteresis, they are have a better stability, but a smaller entropy change. So, a combination of these 2 different types could be could be could be better means, what I am talking about that a combination of both magnetic as well as the structural transformation could be a better chance for us to develop a newer alloys along this direction.

So, the total entropy change is in a system is a magnetic entropy change plus the configurational entropy change, which is constant if the system is in adiabatic in condition. Now you we can think about let us say, if I have these magnetic domains, which are randomly oriented and differently oriented, if I apply now a magnetic field H. So, they will be oriented along the direction of the applied field right. So, a magnetic entropy will decrease if the total entropy is constant. So, configurational or lattice entropy will increase and if lattice entropy increases then, what is going to happen if lattice entropy increases? The temperature of the material will increase ok. So, we can easily understand that in any material it should be possible, but how much change of the lattice entropy will occur or not that depends on the material and so we can easily get this magnetocaloric effect. So, upon application of a magnetic field or magnetic moment in the material that align the direction of the applied magnetic field.

So, magnetic entropy of the system basically decreases because, once the spins are aligned then a magnetic entropy should decrease whereas, the lattice entropy should increase and it increases the lattice vibration as well as the temperature. So, this is one of the very interesting phenomena, in case of a magnetocaloric material and that is a very fundamental understanding that, we really need to see.

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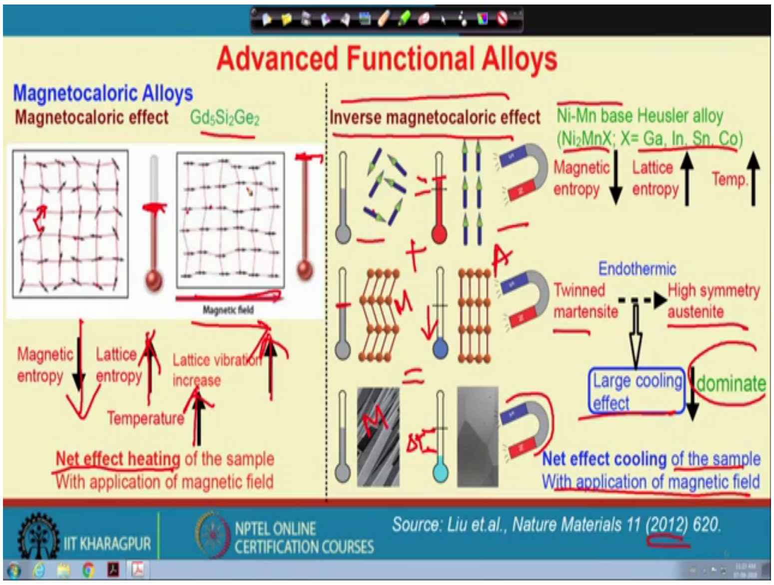

Now, in case of a conventional magnetocaloric effect with an example like gadolinium based compound silicon germanium containing compound.

Let us assume initially, that the spins are aligned randomly ok. So here, all the spins are aligned randomly and we so, here is the temperature of the system let us assume, this is a thermometer, this is a temperature just as a schematic. Now, we are applying a magnetic field here, what is going to happen? All the spins, they are aligned along the direction of the magnetic field. So, magnetic entropy decreases because now, we have all the spins that are aligned ok.

So, entropy of the system decreases since the net entropy is constant. So, the lattice entropy will increase if such a thing occur then, we have a lattice vibration that will increase and so temperature of the system will increase. So, a temperature from here it will increase up to here. So, temperature of the material will increase. So, the net effect of heating will observe in a sample. So now, if I take a magnetocaloric material and put it in a magnetic field then the temperature of the material will increase.

So, that is a conventional magnetocaloric effect, but in case of nickel manganese based Heusler alloy, we have enough discuss about these Heusler alloys compound and this is a full Heusler compound nickel 2 manganese X X is the P type of element. So, a inverse magnetocaloric effect has been observed, what is inverse magnetocaloric effect? Please have a look.

So, this is a conventional type of magnetocaloric effect is shown with a magnet schematic and here these are the randomly oriented magnetic spins and if we align the spins then temperature of the system will increase. So, here the system increases this temperature. Now, if we introduce a phase transformation into the system, what is going to happen? We have a martensite, it has a temperature right. And so, I apply a magnetic field the transformation temperature has increased due to the application of the magnetic field like, magnetic a magnetic phase transformation and magnetic induce structural phase transition.

So here, martensite transformed into austenite and therefore, there is a net decrease of the temperature ok. So, this is a endothermic reaction and so, the temperature of the material has decreased on the other hand, due to magnetic spin alignment the temperature has increased. So, the net we will get basically, a decreasing effect of the temperature. So, this is delta I. So now, I had a martensite by application, this is just a summation of these 2 is equal to these 2.

So, one is the magnetic entropy change and twin martensite transform into a high symmetry austenite there is a large effect of cooling that basically dominate. And so, the net temperature decreases of the net effect of cooling in the sample that occur with application of the magnetic field and this is called as a inverse magnetocaloric effect. And this is also a very recent published work by you. And so, we can understand that not only we get a heating, but depending on our choices, whether we want a inverse magnetocaloric effect or a conventional magnetocaloric effect, we can design alloy accordingly. So, that the structural transformation as well as the curie transformation means, and lots let us say, the alignment should occur in a very close by temperature and their effect on the on the net entropy changing of the system and net adiabatic temperature change in a system.

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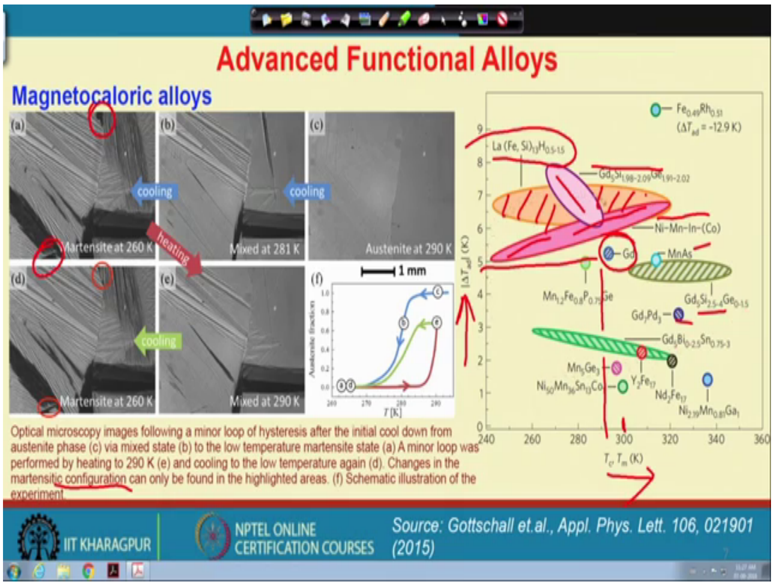

The interesting part of this microstructure of such material one can see, I will start from this c diagram, where I have austenite ok. So, this is austenite kept at 289 K 289 K, means very close to our room temperature, and now I cool the sample. So, I expect that martensite should form and yes martensite has started forming. So, these are the martensite. So, martensite has covered all over the microstructure by cooling and this is a martensite at 260 K and now I heated these martensite and so martensite again, start forming at 290 K at austenite.

So, part of the martensite already transformed into austenite and here that some part of martensite is given. Now again, if I cool it then we will see that again the martensite has form. So, this is a, with interplay with temperature and the austenite fraction, which is shown in this particular diagram, where c is represented here as c. So, I cool it then I transform austenite just below in close to 281 martensite started forming. So, part of the microstructure is martensite part of them are austenite.

So, I have austenite plus martensite here, here I have fully austenite and here I have martensite ok. So now, I continuously increasing the martensite fraction austenite fraction goes to 0 to a and then again, I have heated it, I have heated it up to e this is the e microstructure where I have again some austenite and martensite and again I am cooling it. So, again I am getting this martensite. So, these are the typical optical microscopy images and what I like to mention that these are the points, where the martensite configuration are changes.

So, there is a change of the martensite configuration, if you clearly look at these the micros the places of here and here. So, there are some a configurational changes that that actually occur martensite configuration during heating and cooling cycle actually and these are typical metallurgical effect that one should expect during heating and cooling effect of martensite and austenitic transformation and this is a structural transformation, sometimes scientist believe is required for getting a larger adiabatic change.

So, you can have a look at the typical 2 temperature versus adiabatic temperature change in different materials. So, far has been discovered. So, we must first look at the gadolinium actually. So, gadolinium has such a value of temperature change and the TC and these all these curie temperature are close to room temperature, you can see this is 300 k, a manganese arsenide and gadolinium based compounds. They all align here and the largest values are these gadolinium silicon germanium, which are conventional magnetocaloric.

And let us say, the inverse magnetocaloric alloys and so, on also some rear earth base lanthanum based compounds has been discovered, which are also dominating in these areas even though, the lanthanum based compounds are quite corrosives because, the corrosion resistance are not so high because we also need some liquid to carry the heat and that should not react with the these material. If we really need to apply at for commercial purpose whereas, nickel based compound or Heusler compounds also cover a large region.

So, these are so far, different material has been discussed for this particular aspect.

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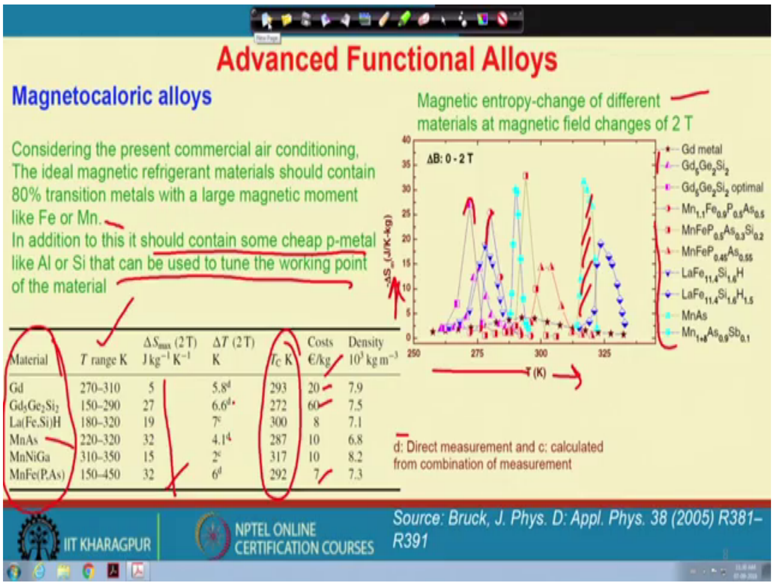

Now, considering the present commercial of air conditioning, the ideal magnetic refrigerant material should contain 80 percent of the transition metals with a large magnetic moment like iron or manganese. And in addition to this it should contain some cheaper P metal like aluminum, silicon or it can be used to tune the working point of the material.

So, gadolinium based compounds definitely, they are quite expensive, but we also need to develop some cheaper compounds and the temperature of the curie, temperature should be close to it and the temperature range is should be near room temperature with a large entropy change and these are the materials. So far, has been has been already developed and you can see the cost of the material for gadolinium is quite high or gadolinium based compounds are quite high compared to some arsenide or phosphide iron manganese compounds.

So, these are some of the directly measured or some of the calculated values are represented here and difference of these compounds are shown with the net entropy change curve. So, we ultimately get this delta S versus T by magnetic measurement and the area of the curve basically, gives us the net refrigeration or gives us the indication of the refrigeration values. So, magnetic entropy change this is a measured for various compounds, you can see with a different-different temperature range.

One a clever idea would be to prepare material with a very close or nearby TC or where the peak temperature peak of this entropy change can be achieved and to make a cascade of those different plates and pass the fluid. So, that to the cooling effect, the net cooling effect will be much larger means, I add on a delta T adiabatic for different-different material for at different-different TC ok.

So, that will be a very nice work for that.

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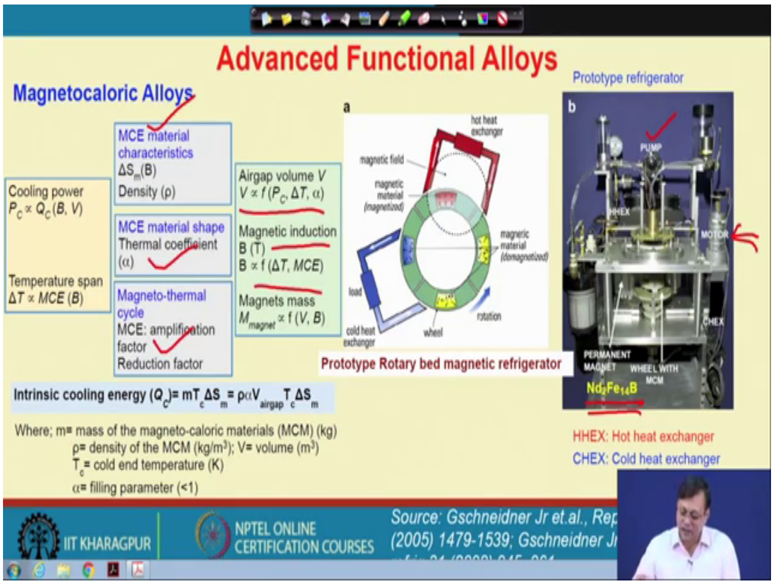

So, in this direction the net cooling power that is PC, which is basically has been observed to be proportional with the intrinsic cooling energy, which is the mass of the material Tc. Tc is the cold end temperature not the curie temperature, please remember this and delta Sm is the magnetic entropy change. So, which is the density and alpha is the filling parameter V is the air gap and TC that is also the cold end temperature and delta Sm. So, these are the intrinsic cooling energy for a given magnetic field and the volume of the material.

So, these are some of the important parameter for developing basically, the magnetic refrigerator already, there are prototype refrigerator that has been already developed in a various places of the world and a typical prototype refrigerator, I am showing you here that are so far published in different journals um. So, for such a prototype refrigerator, what we need? we need a wheel, where let us say, we keep this magnetocaloric a material with differently oriented magnetic domains. So, these are under the demagnetized state and we basically keep it in the magnetic in a magnetic field, where the spins are aligned ok.

Once it is aligned, if it is a conventional magnetocaloric alloy then, the temperature will increase. So now, the heat should be extracted ok. So, the hot heat exchanger which will extract the heat by the application of the magnetic field. And now we immediately demagnetize it or let us say, we take out the material out of the magnetic field and here the magnetic materials get demagnetized and feel basically, cool. So, we can again, take this cold heat exchanger and take out basically and use these as a cooling purpose actually.

So, these are the typical principle of that and one should keep it in mind, that the delta Sm, the density, the thermal coefficient, the amplification factor or reduction factor, these are all the important parameter for developing these refrigerator and air gap volume, magnetic induction, magnetic mass, all of these parameter is required for developing these kind of refrigeration facilities. So, let us say, we have a motor and we need a pump. So, these permanent magnets are kept here and we need like neudium, aron, boron permanent magnet, we have detailed discuss about this hard magnet.

So, we have a hot heat exchanger and cold heat exchanger to get this refrigeration effect.

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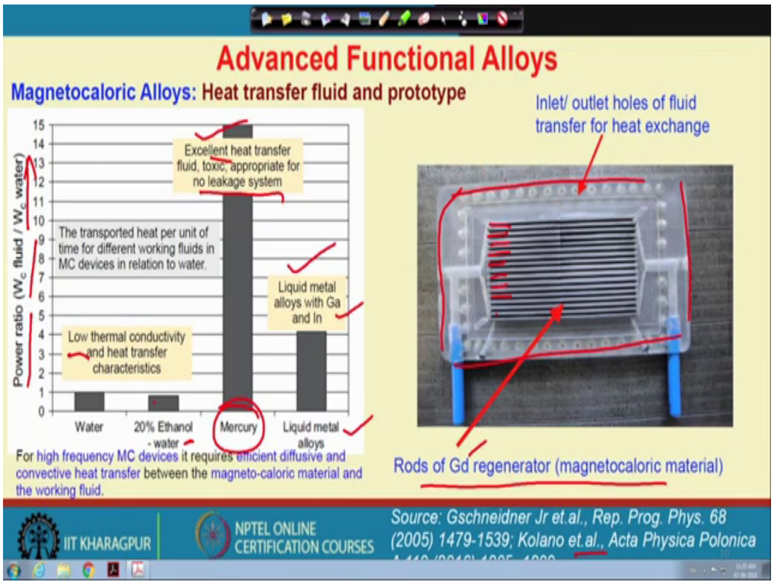

And we also need to think about the media, which extracts the heat or in the hot or cold junction and water, if it considered as a media of the fluid. So, different fluids like water plus ethanol can be compared with the water Wc, that is the power ratio, which is the Wc of the fluid and Wc of the water ratio of that. So, water has one value because, we are just comparing with water.

So, it the 20 percent ethanol and water they have a relatively low thermal conductivity, but the excellent one will be, let us say the mercury, some mercury is excellent heat transfer fluid, but the problem with that, it could be toxic and a appropriate system is required. So, that there should not be any kind of leakage. At the same time, a liquid metal alloy with gallium and indium that can also be used to transport the heat, you need either in the cooling junction or in the in the heating junction.

Here, I show you one of these, such regenerator, which made of pure gadolinium. So, a here there are a multiple gadolinium plates are stacked. So, that the fluid will flow through it and there is are more amount of contact area between the fluid so, that a proper heat transfer can occur. So, these are taken from some of the very recent literature and people are already developing for the commercial use of such magnetocaloric alloys for refrigeration purpose.

So, one has to keep it in mind, the heat transfer of the fluid for the prototype development. So, this magnetocaloric material will definitely, find suitable application and already in many parts of Europe and US national laboratories, they have developed in Situ, such kind of heat pump and the refrigeration facility, which you will expect it to be used for our benefit or human benefit. Because, we can avoid both the effect of a various type of gases in a conventional refrigerator at the same time, the Carnot Efficiency will increase from a very low value for our typical vapor compression refrigerator to a magnetic refrigerator to a value of Carnot Efficiency can reach up to 50 percent from 10 to 20 percent, we can increase further 40 percent. This is a high energy saving. So, we can save a large energy consumption of the around the globe.

So, with this we finish today's discussion on these advanced functional material alloys specifically, the magnetocaloric alloys. In the next class, we will continue some other functional alloys with some more interesting properties.

Thank you very much.