Advanced Materials and Processes
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Lecture – 60
Advanced Functional Alloys (Contd.)

Welcome to NPTEL, myself Doctor Jayanta Das from Department of Metallurgical and Materials Engineering, IIT Kharagpur. I will be teaching you, Advanced Materials and Processes. Last couple of classes, we have discussed about the advanced functional alloys and today, we will continue that discussion and a new advanced functional alloy today we will briefly discuss that is high entropy alloys. You may have heard about the terminology entropy, while reading in thermodynamics also on the mixing entropy, you have heard.

So, in case of several alloy system, we can increase this entropy value or mixing entropy value and these are the major aspect of a high entropy alloy.

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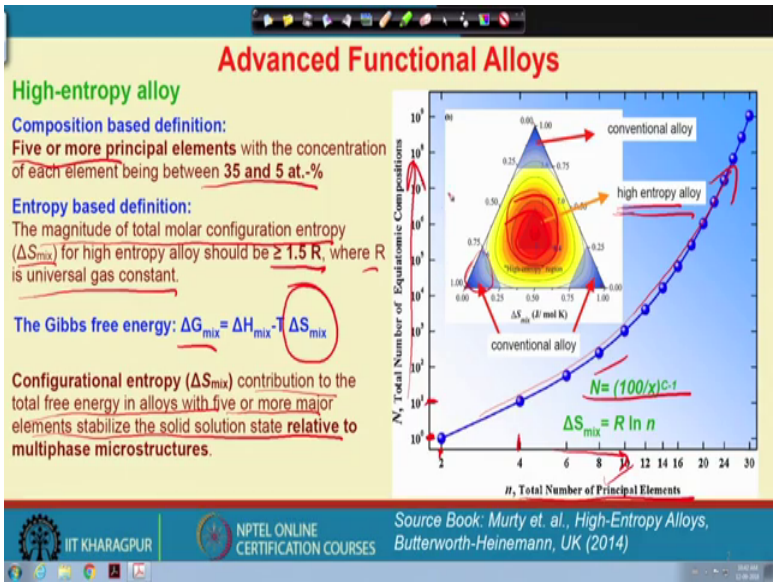

So, this high entropy alloy are the composition based definition, it says that 5 or more principal elements with concentration of each element being 35 to 5 atomic percent.

Now, the entropy based definition said that, the mixing entropy or the magnitude of total molar configuration entropy should be greater than equal to 1.5 R, where R is basically,

the universal gas constant. Now let us try to understand, by looking at a very simple ternary phase diagram. Here, you see a ternary phase diagram a schematic diagram.

So, whenever we develop some alloys let us say, a aluminium alloy, aluminium copper alloys ok. So, mostly we took the help of one of these terminal, solid solution and maybe it is mixed with some intermetallic phases, in order to improve the strength solid solution, may have a lower strength right and now if we go far away from these terminal solid solutions and then reach to some of the central alloy space then we can get a larger value of this entropy.

So, here the existence of high entropy alloy actually evolve; however, one should remember that there should be 5 or more multi principle element. A multi principle element means that all of them has almost equal composition ok. Now if I take a AB as an example even though, it is not an high entropy alloy. So, let us say, 50 50 ok. Now for a 3 component system, it is all are 100 divided by 3 right.

Now, in case of 5 element system means all of them has 20 atomic percentage. So, A has 20, B has 20, C has 20, D has 20 and E has 20. Now, in such a case, we can simply estimate the total number of such equaiatomic composition and let us say, with the total number of principal element. In case of 2, we have only 1 possibility A 50, B 50. So, there is only 1. So, 10 to the power 1 number of equi automatic composition, you can generate, but in case of 4, it is 10 ok.

So, in this way, if we keep on increasing the number of multi principle element, it basically follows that N is equal to 100 by x to the power c minus 1. So, you can keep on increasing the number of such compositions. So, that is a enormous possibility of getting such huge number of composition in this central space.

So, usually the Gibbs free energy are represented with delta G mix is equal to H mix minus T into delta S mix. And so, the configurational entropy that is the delta S mix, that is the contribution of the total free energy in alloy with 5 or more major element, that stabilizes the solid solution state relative to a multi fringe microstructure. Since here, we are talking about evolution of 1 or phases by due to the presence of multi principle element. So, that is basically, the uniqueness in case of a high entropy alloy.

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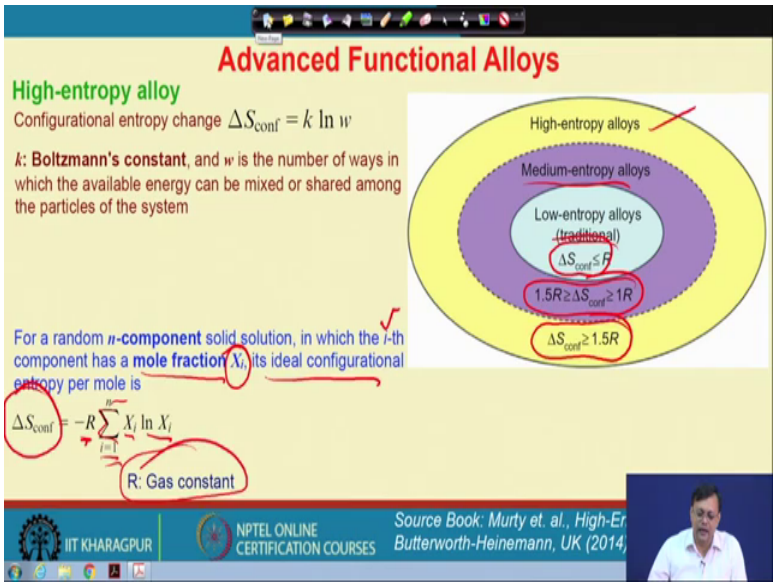

So, the configurational entropy, which came from this thermodynamic third principle third law, you know that is delta S is equal to k l n w ok. So, w is a measure of the randomness ok. So, w is basically, the number ways, in which the available energy can be mixed or shared with the particles in the system. So, that is a typical definition of the third law.

Now, in case of n number of element system in a random solid solution, in which case let us say, I have the i-th a component, I may have a i-th component, which has a mole fraction of a Xi. So, the ideal configurational entropy per mole is basically Xi into ln Xi ok. Now I a multiplied with R and the summation of let us say, i is equal to 1 to n will give me basically, the net configurational entropy, where R is basically presented with the gas constant. So, this is the basic understanding of this high entropy alloy.

Now, let us have a look at the different alloys that people have developed so far and we first need to look at let us say, the mild steel and then the super alloys, we have discussed right and stainless steel, we have discussed. And if you look at the very traditional engineering alloys, most of them has a configurational entropy less than R and for medium entropy, it is in between basically 1.5 R to 1 R.

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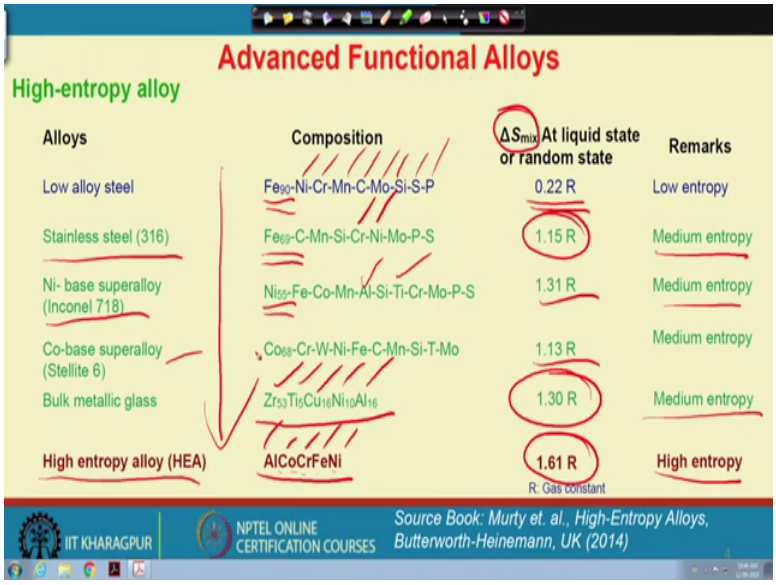

Now in case of high entropy alloy, this should be greater than 1.5 R ok. So, in such a unique cases, we can simply look at how we have reached to these values and we must need to calculate and let us take a low alloy steel. In case of a low alloy steel almost, we have 90 percent of iron and then we may add little amount of nickel, chromium, manganese, carbon, molybdenum, silicon, sulfur, phosphorus and so on. So, we consider all the presence of different very little amount of element present in a steel and then we measure basically, the value of the delta S mix and this value will be somewhat, in the range of 0.22 R ok.

Now, in case of stainless steel, let us say, 316 stainless steel, where we have a less iron content however, we may have some high amount of chromium and nickel, which are one of the very major alloying elements and the values are 1.15 R. So, these are let us say, medium entropy alloys as for the definition.

Nickel based superalloys 718 here also, we have nickel and then we have we also need aluminum, some amount of titanium. So, the values lie let us say, 1.31 and you can see cobalt, the super alloy also the values is 1.13 or let us say, a typical bulk metallic glass, which has zirconium, titanium, copper, nickel, aluminum here also, we have multi principle element, but these are let us say, the amount of other element is less and you can calculate, it is somewhat in the range of 1.3.

So, this is as per definition, we call it as a medium entropy alloy. But a in case of a high entropy alloy like aluminum, cobalt, chromium, iron nickel this 5 element, they are

present almost let us say, equiatomic composition and that is why, the compositions are not written. So, the estimated value is of delta S is 1.16 R. So, this is a high entropy alloy.

So, from a low alloy steel to stainless steel to nickel base super alloy and cobalt base super alloy, bulk metallic glass, we have discussed all of them actually in this course and with increasing, we reached let us say to a high entropy alloy system, where the configurational entropy is very high.

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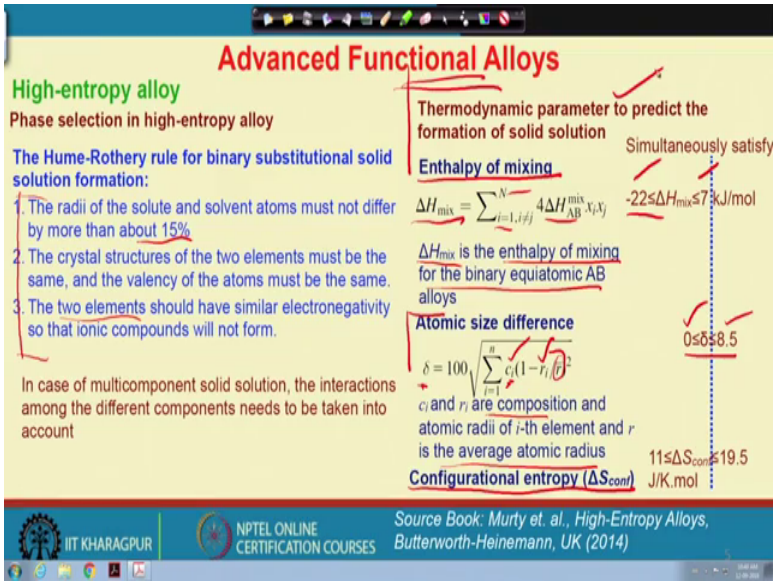

Now, if we look at again, the humeral theories rule for formation of such a solid solution or substitutional solid solution, it has been told that the radii of the solute and the solvent atoms should not differ more than 15 percent. So, they should be less than that ok. The crystal structure of 2 elements must be very much similar and the valence electron atom, must be very similar otherwise, if that is differ too much then, we will get basically intermediate phases or as the 2 element should have very similar electronegativity otherwise, ionic compound will form.

So, this is one of the very basic rule of formation of solid solution that we have learnt earlier. However, in case of these high entropy system or high entropy alloys, people find out that, there are some thermodynamic parameter that can predict the formation of such solid solution phases. So like one is the enthalpy of mixing. So, enthalpy of mixing, we can calculate that is delta H mix is equal to the summation of i-th to N and we have

basically delta H mix A B compound, where the delta H mix is the enthalpy of mixing for the binary equiatomic AB alloy.

Whereas the atomic size difference is delta which is the ci and ri are the composition of the atomic radii of the i-th element and r is basically the average atomic radius. We are talking about, these r is the average atomic radius and ri is the is basically, the atomic radii of the i-th element and c is the concentration.

So, the net atomic size difference, we can estimate and these value basically lie with 0 to 8.5 ok. So, in case of the enthalpy, it lies in between let us say, minus 22 to 7 kilo joule per mole. Whereas, the configurational entropy value is also important, in order to get such kind of formation of solid solution in case of high entropy alloy, the value lie is in between 11 to 9.5 joule per Kelvin into mole here, basically, we have multiplied with R.

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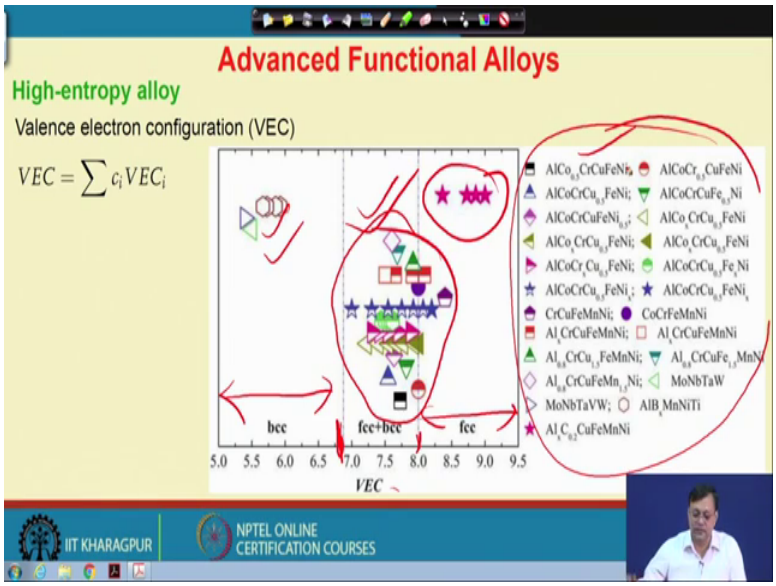

So, some of these important parameters that can assist us to understand, these high entropy alloy. At the same time valence electron configuration, so far also shows such kind of interesting behavior, because in some of the high entropy alloy, it has been observed that bcc phase solid solution has formed whereas, in some cases we get fcc phase.

So, people have calculated, there valence electron configuration of very large number of alloys, you see these are the large number of alloys and people find out that for a

particular valence electron configuration range, we get bcc phases in some ranges, we get fcc phases and in between let us say around 7 to 8 valence electron configuration, we basically get the fcc, a mixture of 2 phase ok.

But all of them are high entropy alloy even though, the 2 phase is present here because, the entropy is high all in a greater than 1.56 R, in all these cases.

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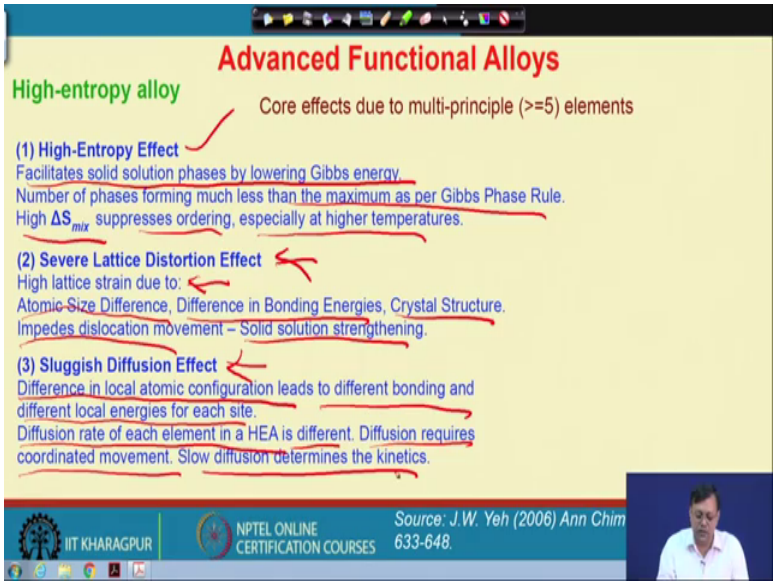

So, these are some of this interesting feature to explain, this high entropy alloy and people have proposed that, there are some core affect because of what a high entropy alloys has formed. Even though, it is words to mention that some of the bulk metallic glasses, may also has this kind of high entropy effect means, if you estimate the total entropy delta S configurational entropy that is greater than 1.5.

. So, the 3 very basic core effect is present, the high entropy effect here, we are talking about the mixing entropy, very high mixing entropy that suppress the ordering especially at higher temperature and it facilitate the formation of solid solution phases by lowering the Gibbs free energy. So, the higher the delta S mix, because there is a negative term minus T delta S. So, definitely the G will decrease, if we simply increase the entropy of the system and number of phases form must be less than then the maximum number of Gibbs phase rule actually.

Now, the second point here that the severe lattice distortion effect because once, we introduce multi principle element then, we have a high chance that we distort the lattice. So, here the high lattice distortion occurred due to the atomic size difference ok. So, I have A, B, C, D, 4, 5 different types of atom and they have different different atomic radii even though we can estimate delta, which is a atomic size mismatch, but differences in the bonding energy, crystal structure which basically, impede the dislocation motion, it can also provide us a good solid solution strengthening.

So, different atomic sizes will provide the solid solution in effect that is already understood from the very basic metallurgical principle. Now, on the other hand, if we have such very different types of atoms then, it is expected that the diffusion of atoms will be sluggish in nature because, we have to create some extra space, vacancy or some other side vacancy side so that, we can get a good diffusivity. So, because of such kind of differences in the sizes, the difference in the local atomic configuration or environment that also lead to the different bonding and different local energies of the each site and diffusion rate of each element is high entropy alloy is different.

So, diffusion require the coordinated movement and slow diffusion determine the kinetics ok. So, you can think about that in case of metallic glasses yes, we also have a lower diffusivity in the under cool melt; however, there is a effect of a cooling rate ok. So, we need to achieve certain cooling rate so, that we can get the metallic glasses and the TG should be higher in a system so, that we can get a glass.

But in this case, we are only talking about the diffusivity in a solid solution.

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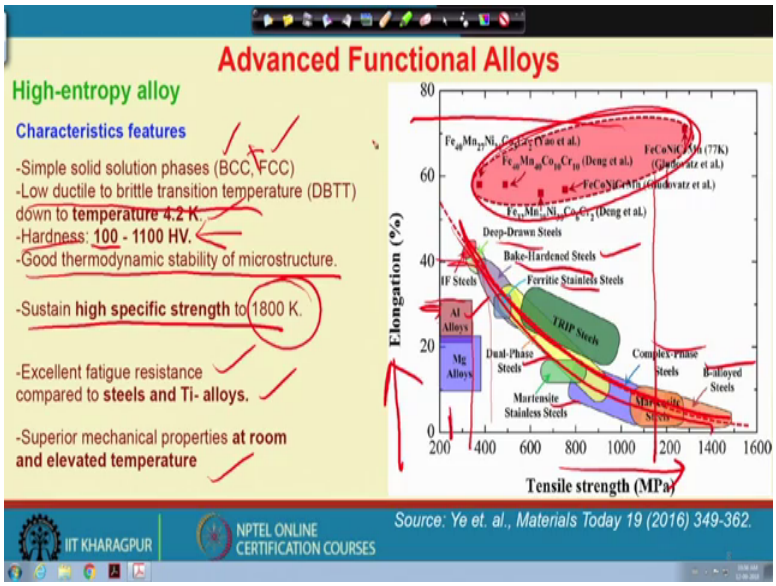

So, in this case these are the 3 or 4 very major core effect, that people think about and there are very basic characteristic of such high entropy alloys like, we get a very simple solid solution phases like, what we have talked about like, formation of bcc or fcc phases or a mixture of bcc plus fcc; however, if we go away from those composition, we can also get some laves phases and there are some specific utility of it. I will discuss within a minute.

Now, the ductile brittle transition temperature could be as low as to 4.2 Kelvin, this is a uniqueness all high entropy alloy shows such effect, but some of the high end of alloy has shown such. Hardness of solid solution is usually less; however, by making the microstructure finer by incorporating some second phases, we can also get a very improved hardness like complex alloy phases.

However, there is a good thermodynamic stability of the microstructure because, if delta S configuration is very high thermodynamically delta G e could be very low and so, we can get a better thermodynamic stability of the microstructure. Now it can also sustain a very high strength of 1800 Kelvin ok. So, excellent fatigue resistance compared to steel and titanium alloys superior mechanical properties at room temperature and elevated temperature.

Let us first, try to see at some of the unique properties in terms of tensile strength with let us say, the elongation. You all around heard about the aluminum alloys, aluminum alloys

has a very very low strength. Let us say 70 or maximum 100, 200, it can reach and magnesium alloys so, after certain precipitation hardening of aluminum alloys, we can reach within this strength level with a moderate a plasticity.

However in case of dual phase steel, martensitic steel, complex phase steels, boron alloy at steels, feretic stainless steel, bake harden steel. This bake harden steels are used for car manufacturing deep drawn steels ok. So, they have a relatively lower strength with a large ductility and so mostly, these steels follow a such kind of area or domain ok. Whereas, the high entropy alloys, you see are almost sitting at the top of any of the conventional steels. So, they have some unique domain of very high tensile strength as well as very high elongation level.

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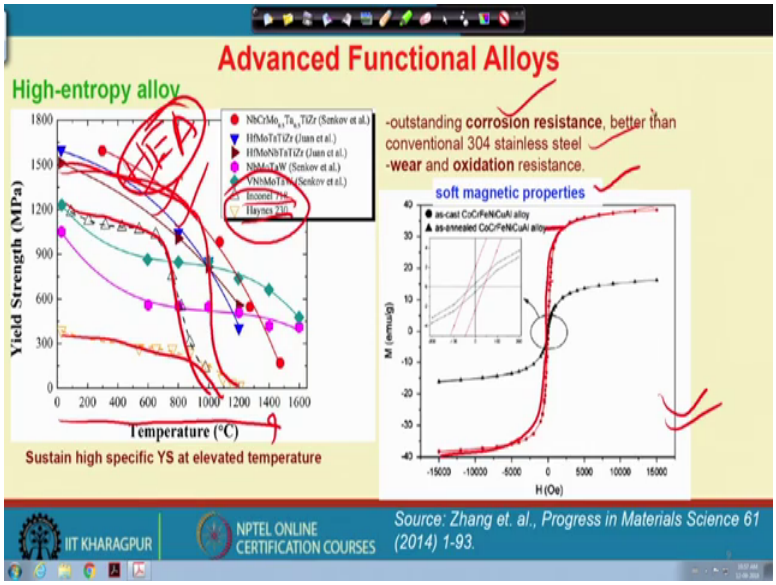

So, they are much superior than any of the conventional engineering alloys.

And now, if we look at the temperature of different refractory metal base high entropy alloy, they also shows a very high strength in a wide range of temperature than the conventional inconel or heynes alloy, these are typical super alloy that we have discussed earlier.

So, the super alloy stresses are here and heynes, alloy is here and so, these are the high entropy alloy. So, we can get a much higher strength level with a much higher temperature level. Very similar way, many of such high entropy alloys have shown soft

magnetic properties, you can see that they have very high level of magnetization value and they have a very low hysteresis level a very low corrosivity level.

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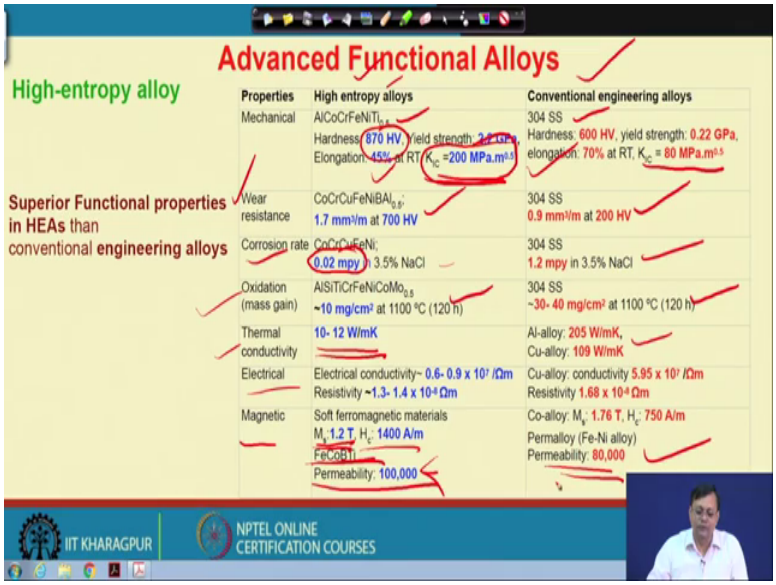

So, we can use these high entropy alloy, also for soft magnetic properties corrosion rate is also outstanding compared to our conventional stainless steels.

So, these are some of the very interesting properties that we have seen. So, if I compare with these the benchmark values of high entropy allies benchmark values means in terms of engineering or functional properties. So, this compared to the conventional engineering alloys, they are much superior so far, it has been reported.

So, let us have a look like, these are the high entropy alloys and these are the conventional engineering alloys. We look at the mechanical properties compared to some stainless steel; it has 870 Vickers hardness with 45 percent elongation, a toughness fracture toughness of 200 megapascal ok compared to any conventional steels with 80 mega pascal root meter. So, they are much superior than any of them.

Now, the wear resistance of high entropy alloy is also superior compared to these conventional engineering alloys. The corrosion rate of 0.2 mpy, which is much superior than any of the stainless steel. Oxidation resistance is also comparable with the stainless steel. The thermal conductivity, you can see that they have very good thermal conductivity, which is relatively less compared to the engineering alloys whereas; the

electrical and magnetic properties are much superior than any of these conventional engineering alloys.

So, here we have a saturation magnetization of 1.2 Tesla and Hc is 1400 ampere per meter, which is comparable with a cobalt base alloys and here, this is also another interesting high entropy alloy, which has a permeability level of 100,000, which is much higher than the perm alloy.

So, we can achieve much much higher level of good functional properties compared to these, all these conventional engineering alloys. So, we have looked at. So, they have a bright at prospect and we have large opportunities for future application.

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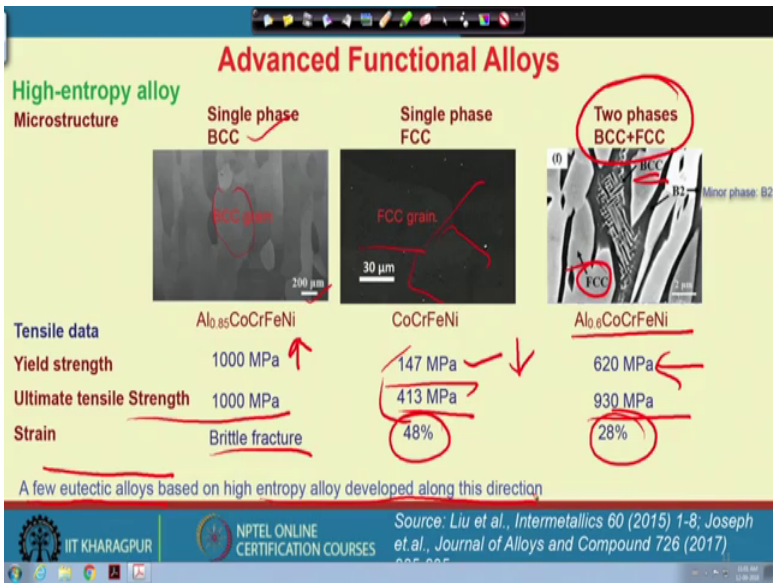

Now, if we look at the microstructure as we said, that it may contain single phase BCC, single phase FCC or maybe 2 phase microstructure is also possible, people have discovered these days, these are very recent literature, I have collected for you from 2017.

So, in case of a single phase BCC, these are the larger, let us say BCC grain of somewhat in the range of 200 micrometer. We have also some FCC grains here and ah. So, they have yield strength level, FCC has a yield strength level, which is lower. Whereas, in case of BCC, the yield strength level is higher whereas, the ultimate strength is close to it. So, it is almost like a brittle like fracture whereas, in FCC we have seen, some of the

work hardening from 147 to 413. So, this is like a 48 percent, plastic strain people have observed.

And a better improve properties, when obtained, when people achieve such kind of 2 phase microstructure. So, like a BCC plus FCC microstructure, in such an alloy system, we have a relatively higher strength also we have a larger ultimate tensile strength with decent ductility.

So, along this direction people try to evolve that or people try to make micro structure with 2 phases and a new trend has been generated in these days to get basically, eutectic alloy based on these high entropy alloys.

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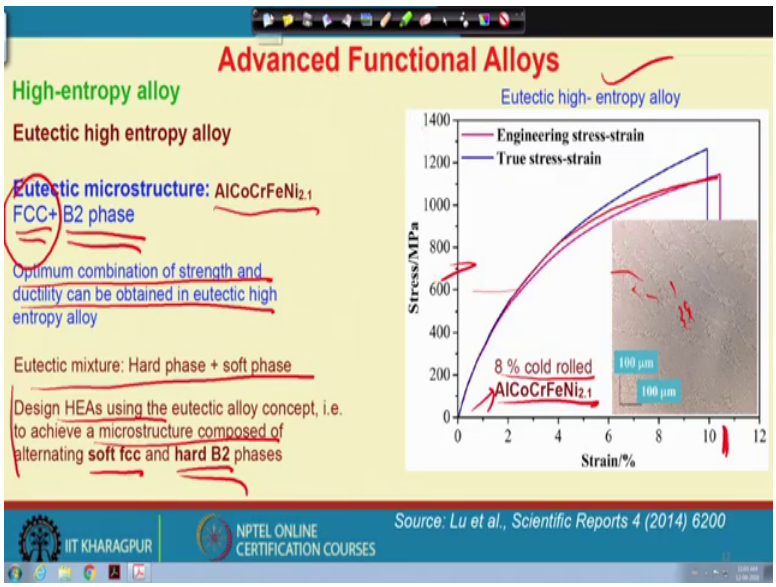

So, here the there is a large development has been done very decently within last 1 and 2 years.

People have seen, that in such a system like aluminum, cobalt iron and nickel system, where we get FCC plus a intermetallic B 2, which is also a ordered structure. So, such micro structure give a optimum combination of strength, ductility that can be obtained by making such a microstructure, which is a eutectic.

So, this is a eutectic alloy, which is partially cold rolled and you can see that the strength level is very high actually right and it has a very large plastic strain, which a usually, do not observe in most of the eutectic system. Eutectic system shows very high strength, but

not too much plastic strength. So, these eutectic high entropy alloy compared to conventional aluminum alloys are much superior and it is much easier to form and so we get basically a mixture of hard phase plus soft phases and design of such hue high entropy eutectic alloy, a concept is achieving a microstructure compose of soft FCC phase. So, the FCC phase gives us a softness of the matrix and we incorporate some lamellar B 2 phase inside those microstructure which gives us a to maintain such a high hardness values or high strength values.

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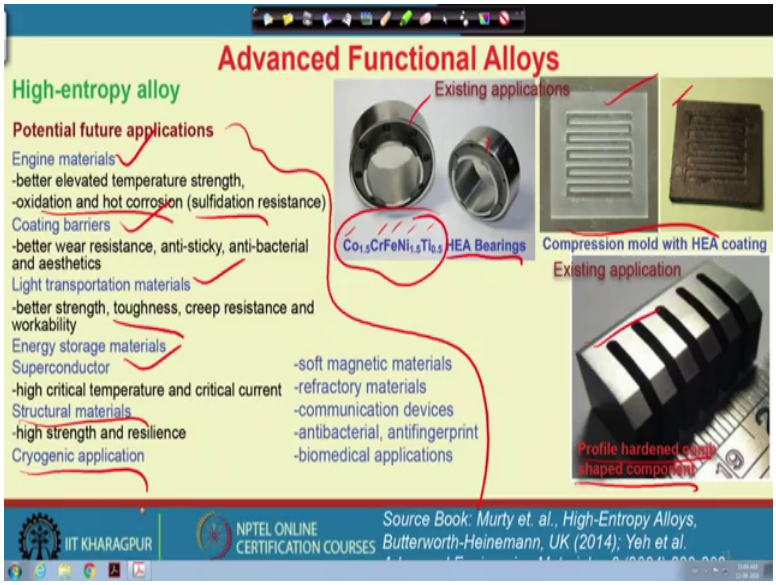

So, this is one of the very important example of such functional alloys. Now in case of this high entropy alloys, there are already some existing application, which other alloys cannot replace. So, if you have very high wear resistance, we can use these high entropy bearings ok. So, like cobalt, chromium, iron, nickel, titanium, this is also a high entropy alloy bearing, you can see the outer loop or let us say, some of the compression mold, where the conventional mold does not perform well after some times of use. So, they have a less life than the high entropy alloy also some of the profile hardened comp shaped component, you can see the outer features and they must look superior than the conventional stainless steels.

So, the scientists basically, think about some of this potential future application, in case of engine material like better elevated temperature strength, oxidation and hot corrosion resistance due to a good sulfidation resistance, coating barrier and light transport material

with a very high toughness, you have seen 200 mega pascal root meter toughness, we can achieve.

So, energy storage material structural material and also for cryogenic application because, they have a very the ductile between transition temperature can also reach to let us say, 10 K.

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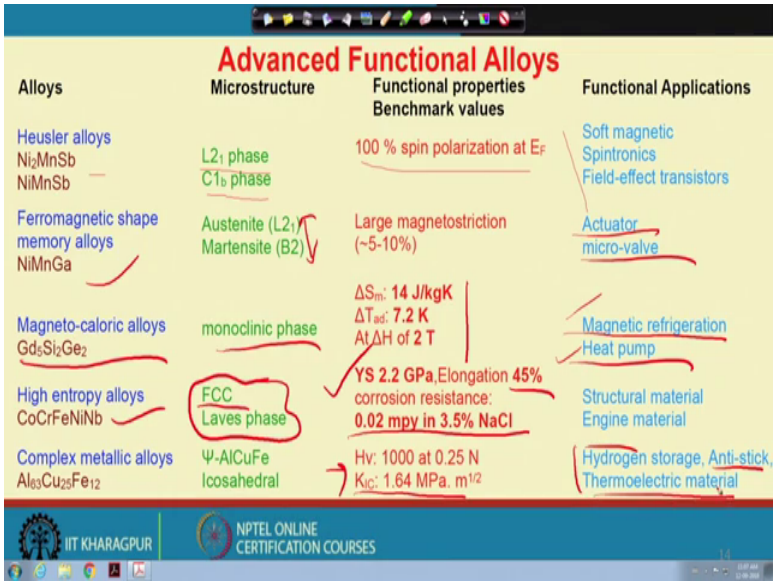

So, in that case, we can apply those material, for cryogenic application. So, there are enormous possibilities to use these, high entropy alloy.

And one has to devote those different engineering aspect and keeping all these things in mind one can develop such large number of high entropy alloys. And you can see the number of possible, if we increase the number of component, we can also increase the number of possibilities of getting a new alloy actually.

Now if we look at so far, whatever has been we discussed in these advanced functional alloys like Heusler alloys, which are one of the very important system, we have discussed. So, in this case in case of these Heusler alloys, we have basically nickel manganese and antimony system. So, we have L 2 1 structure C 1 v structure even though, I told them that these are also complex alloy phases, we have 100 percent spin polarization, we have larger number of these functional properties and so on. Also, we have such ferromagnetic shape memory alloy, where there is a austenite to martensite

transformation depending on the application of the magnetic field, which we use as actuator or micro valve.

We have discussed about large number of magneto caloric alloys, which has also a complex structures and monoclinic phases and they have some unique properties of a large magnetic entropy change and we can use them as a magnetic refrigeration or heat pump, because depending on the carnot cycle and which portion, we choose whether to use it as a heat extraction or a magnetic refrigeration as well as the high entropy alloy, we have discussed where we have enormous number of possibilities to achieve a very high strength and high elongation and very good corrosion resistance. These are some of the unique functional properties that we have achieved and people tried to achieve such kind of 2 phase microstructure in high entropy alloy by mixing let us say, the FCC plus laves phases.

At the same time, all of them fall in the category of these complex alloy phases and also the quasi crystals, which a cluster is represent the overall structure of a quasi crystal, whether it is (Refer Time: 30:02) quasi crystal or icosahedral quasi crystals, which also have very high hardness values and relatively low let us say, the toughness values, which could be used for hydrogen storage or anti sticky properties or maybe thermoelectric material.

So, these are some of the very unique properties that one can derive out of those advanced functional alloys. So, with this, we complete the discussion on advanced functional alloy and we hope that within next 20 out of 50 years, there are more number of such functional alloys will be developed. So, with this I express my sincerest thanks to all of you for your active participation and joining in this course with this.

Thank you very much.