Advanced Materials and Processes
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Lecture – 59
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. Last couple of classes we have discussed different categories of functional alloys which are very recently developed or advanced functional alloys due to their multi functional properties. And today we will continue that discussion and we will try to explore another new domain of functional alloys these are called as complex metallic alloys.

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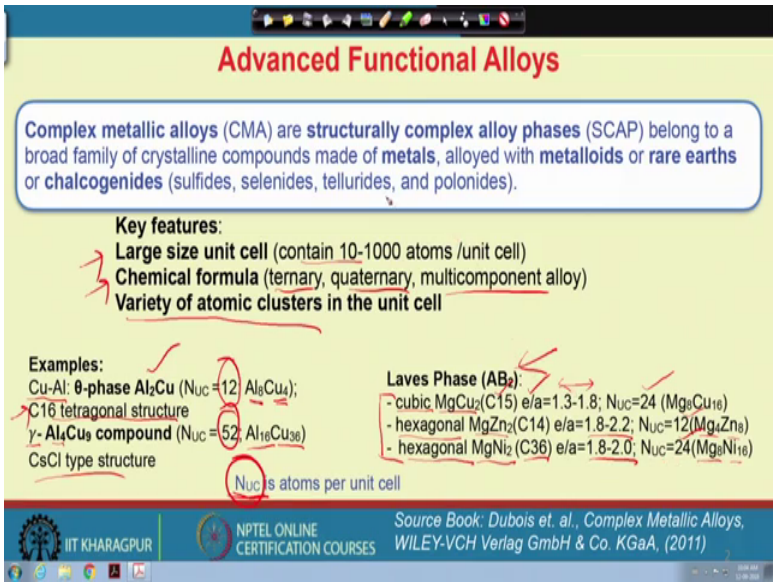

These complex metallic alloys are structurally complex alloy phases belong to a broad family of crystalline compound made of metals, alloyed with metalloids, rare earths and chalcogenides. So, chalcogenides means let us say tellurides, sulfides, selenides, polonides and so on. So, from this basic definition we can easily try to understand that these must be very close like inter metallics, but having very complex structures.

And so if we look at all these complex alloy phases there are some uniqueness or key features of all these CMS. All of them exhibit a large size of the unit cell, a large size of

unit cell is only possible when there is large number of atoms involve in a unit cell. Now, let us try to consider the very basic primitive cell of simple cubic what we know I have how many number of atoms per unit cell? Yes your guess is right it is only 1.

Now, in case of FCC we have phase sintering atoms, as well as we have corner atoms all together it will be total 4 is not it? Now, in case of complex metallic alloys or complex phases this unit cell contain more than 10 number of atoms per unit cell or even it can go beyond 1000 ok. So, you can understand how giant unit cells they have; now usually these complex phases have chemical formula which contain; let us say ternary quaternary or multicomponent elements.

Also they have variety of different atomic clusters that are present in a unit cell like how so you can how the structures may look like. Just as a imagination you have seen for a FCC structure; we know about there is one cornering atom, but it can also be possible that a cluster of atom present at those cornering positions right. So, those are called as association or a association of cluster of atoms are present here ok.

So, these are usually the key features of the complex metallic alloys. So, definitely we need to know some of the very examples very known examples that we have studied quite a long time ago; like aluminum copper age hard enable system. You already have heard about those age hard enable aluminum alloys what we have? We have gp zones where we have some coherent precipitate copper clusters.

And then if you prolong anneal it then from theta double prime, theta prime, theta phase will ultimately appear and theta phase if it precipitate at the grain boundary; they may not be very much useful for enhancing the mechanical properties so, that is already known to us.

Now, these theta phase which is available in a copper aluminum system; it has a chemical composition like Al 2 Cu; it simply says this is the inter metallic and it is a stoichiometric compound right. And if we look at the structure then it has a tetragonal type of structure with a strukturbericht; which we called structural classification C 16 and this number of atom per unit cell are represented by N UC. So, number of atom per unit cell, here we have total 12 number of atoms per unit cell so it is quite a giant cell.

And now, if we take this 12 atom then usually the number of copper atoms should be 8 and copper should be 4. Now, let us come to another example in the same copper aluminum system which we call at gamma Al 4 CU 9 compound ok. Here we have 52 number of atoms and aluminum 16 atoms are present in the unit cell and copper 36 atoms so, these are very large unit cell it has a CsCl type of structures.

Now, there are also very known example we already heard about laves phase right. So, laves phase usually have a composition of AB 2. So, A is one element B is another element it has a stoichiometry of 2 so AB 2 and there are 3 very basic structure and of laves phases are possible; definitely there are many super structures also and more complex. But these 3 are the very basic structure available in all the different laves phases.

So, usually they are magnesium copper 2 type or magnesium zinc 2 type, magnesium nickel 2 type. And these structures here are cubic system these follow hexagonal and magnesium nickel 2 also has a hexagonal, but not the hexagonal that we have read in the textbook these are hexagonal base structures. And from the strukturbericht it has C 15 structure of magnesium copper 2; magnesium zinc 2 it has C 14 structure and here it is C 36. The electron atom ratio in these cubic type of structure in between it varies between 1.3 to 1.8; in the second case it is 1.8 to 2.2 and here also 1.8 to 2.0.

Now, how many number of atoms are present in those basic structures of 3 different major types of laves phases? Here we have 24, here we have 12 and here we have 24 also and accordingly I have shown you here the ratio of the different 2 different types of element or atoms. And therefore, these structurally complex alloy phases are really unique and here you see that mostly I have talked about aluminum copper.

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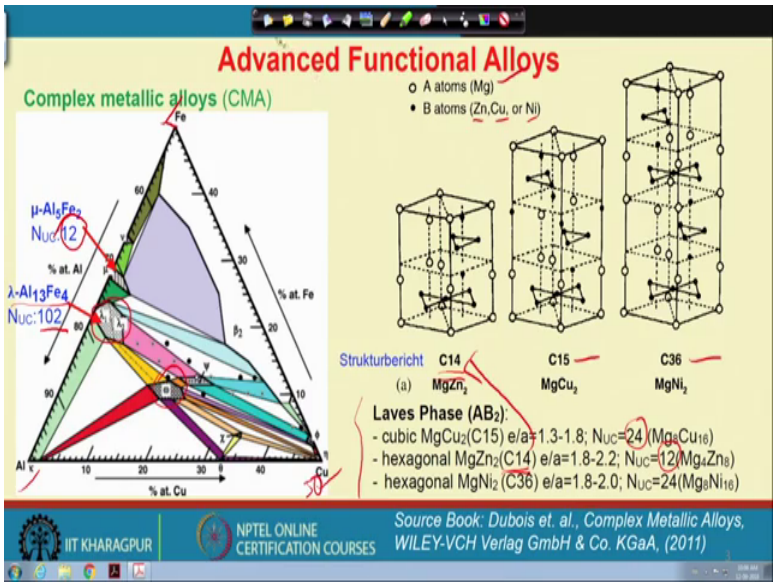

Because, aluminum copper or copper zinc these systems are very much well developed and when these phases has been classified or identified these systems are where investigated quite a lot. So, that is why we must start with looking at the diagram of aluminum copper with iron ok.

So, this is a ternary diagram not the full diagram is shown here; you can see here copper is up to 50 percent 50 atom percent; here this is shown from 100 to 50 ok so, aluminum up to 50 percent is shown here. Now, there are many of such complex phases alloy phases appear here these are lambda phases. So, lambda aluminum 13, iron 4 it has 100 to 100 to number of atoms per unit cell here we have a mu phase where we have 12 number of atoms and we have also omega phases and so on.

And so, if you look at these very basic laves phases structures so, the first one is basically shown here the C 14 structure which is shown here. So, it has a hexagonal type of structure even though you see here just one part of that structure hexagonal base structures are shown here. So, these solid field atoms are representing let us say the B type of atom where we may have zinc copper or nickel and A type of atoms which are the unfilled one and similarly here also C 15 structure or C 36 structures are shown here.

So, in all these cases these are the field atoms are the nickel atoms and here the unfilled atoms are the magnesium atoms. And by looking at those structures you can easily calculate how many numbers of atoms are present here and you will definitely get these

numbers of such large numbers of atoms present in the unit cell. Because, here this is the C 14 structure where we have only 12 atoms and here we have 24 number of atoms.

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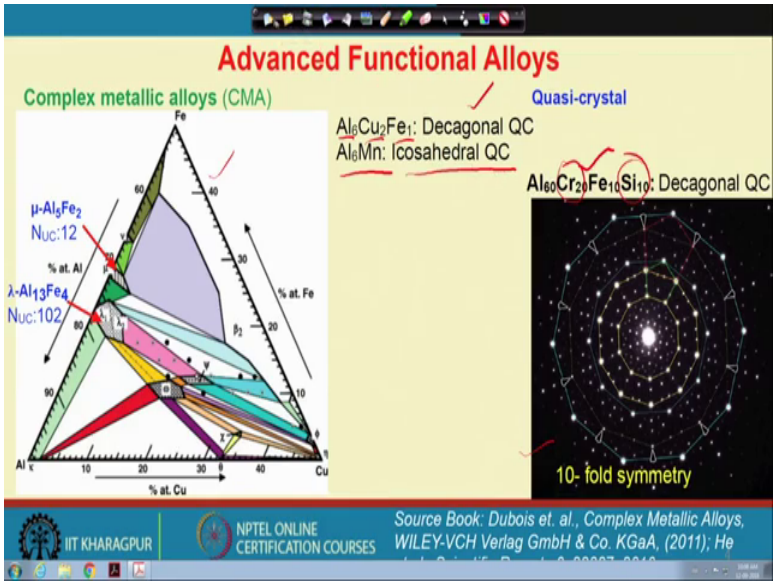

And these are somewhat interesting, but do we have some other kind of clusters present also? Yes we have discussed briefly about quasi crystalline structures when in the very beginning of this course and you may recall that quasi crystalline structure shows quasi periodicity which follows those fignosis series. And since there is no such Bravais lattice present usually quasi crystal structures are represented in terms of the cluster ok.

So, in quasi crystal you can think about infinite array of atoms which are arranged in a quasi periodicity. And definitely the Penrose styling structures matches with the similarity of those quasi crystalline periodicity and there are couple of nice example available in similar system like aluminum copper iron; the system that I have talked about, here aluminum 6 copper 2 iron 1 we have decagonal quasi crystal.

So, another example of such decagonal quasi crystal with some silicon and chromium in aluminum iron system. I have shown you here a 10 fold symmetry selected area diffraction pattern. So, these are also very very giant number of cells giant number of atoms are present and since we do not have any concept of a unit cell so, we can think about a infinite array of atoms, so number of atoms are infinite ok. So, let us say aluminum 6 manganese here we have icosahedral cluster of quasi crystals.

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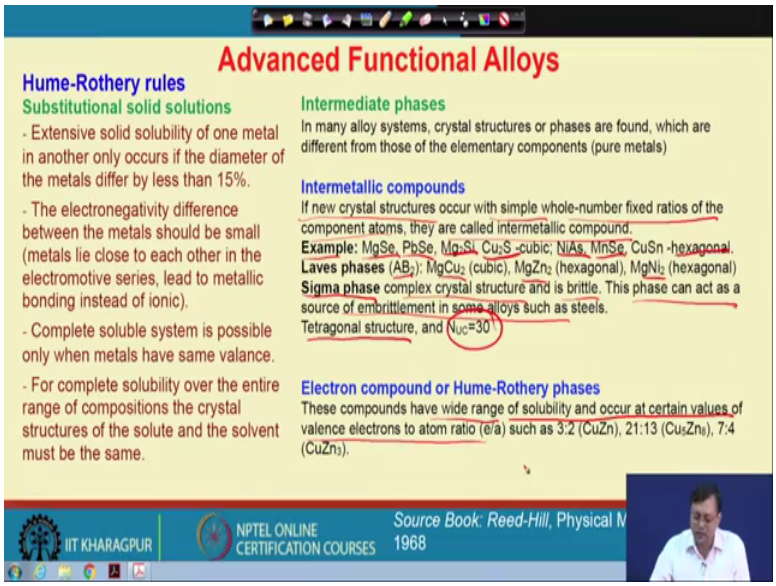

And so people usually think about these issues and try to look at that whether to how it is correlated with those Hume Rothery rules. We have discussed very detail of this Hume Rothery rule on solid solution formation while we have talked about metallic glasses. However, here in case of complex alloy phases we need to again recapitulate another part of this Hume Rothery rule which are the intermediate phases; right. In many of the alloy system crystal structure or phases that are found which are different, than the elementary component means I can take about aluminum I add 2 percent copper; I get an FCC aluminum alloy with a structure that is basically FCC.

But, here I have pure metal I have an alloy, but if these same type of aluminum copper is alloyed and we may also get for certain composition a intermediate phase or inter metallic phase. So, in those kind of cases what are the possibilities and we must look at the rules. So, here a new crystal structure of such may form with simple whole number fixed ratios component and they are usually called as inter metallic compound.

As an example like magnesium AC and led selenide and let us say we have magnesium silicon with 2 1 and also some sulfide with copper 2 sulfur cubic type of structure; also we may have some hexagonal type of structure like nickel arsenide and copper tin and so on.

Now, in case of laves phase we already heard that these are AB 2 type of compound and there are 3 major type of such possibilities which has been discussed just few minutes

ago. Now, like another example of sigma phase which also have such complex crystal structure and these are very very brittle material. And these phases presence of such phases in a micro structure causes embrittlement and they have some tetragonal structure with 30 number of atoms per unit cell.

Now, Hume Rothery also said that there could be possibility that depending on the valence electron and atom ratio some compound may form which are also called as Hume Rothery compound or electron compound. So, in this particular case we have wide range of solubility that may occur in certain values of some typical valence electron mostly in case of copper zinc system; it was told like 3 is to 2 which basically means 1.5; this is a electron atom ratio or 21 is to 13 or 7 is to 4 ok so, like copper zinc 3 compound.

So, they also have some wide range of solubility; so, even though it looks like 1 is to 3, but they have some mutual solubility or solid solubility range and they that composition is not so fixed like other inter metallics and that is basically the message he wished to convey.

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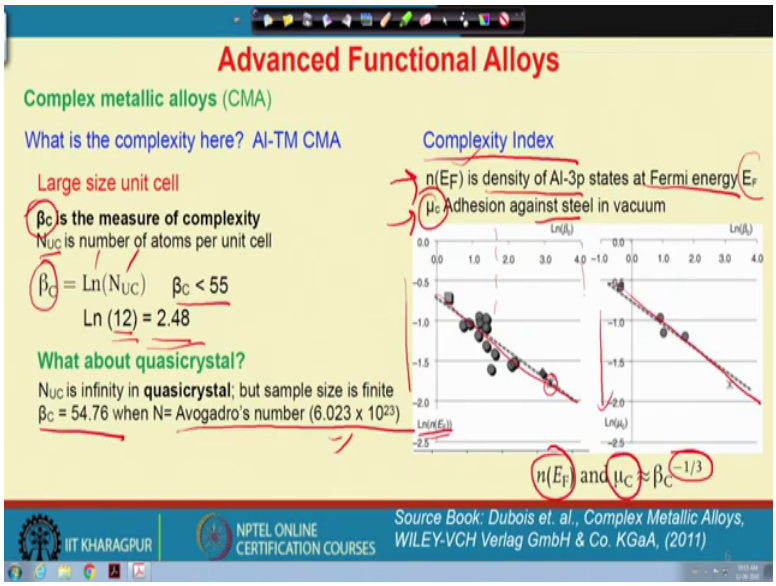

Now, seems we are talking about these complex alloy phases we must need to think about classification or how one can classify; how complexity is present in an intermediate phase or in a complex alloy phases.

And so people came out with an idea that beta C would be a measure of the complexity. So, here number of atom present in a unit cell like N UC that is the number of atom per unit cell and beta C is the logarithmic of N UC. So, let us think about one of the laves phase which has 12 number of atoms. So, how much is the value? Logarithmic of it is 2.48 right and now what about quasi crystal since I said that quasi crystal has a infinite a number of atom present. Because, this is a cluster and we do not have such a concrete definition of a unit cell here concept here.

So, we can think about 1 mole of atom ok; in 1 mole how many number of atoms are present? That is represented by the Avogadro's number; we already know about it. So, Avogadro's number is 6.023 into 10 to the power 23 and now if I put these digits here then the value of beta C comes like 54.76. So, usually people consider we have some beta C in a limit of something in the range up to 55 so from logarithmic of 10 2 to logarithmic of Avogadro's number.

So, here this complexity index is also another index which basically says the complexity in that a represent in a intermediate phase is represented by the density of aluminum 3 p state at the Fermi level of energy; so, E F is the Fermi level of energy. So, this is one of the parameter to measure the complexity index and second is the friction here basically the adhesion against a steel in vacuum ok. So, that is also represented by such kind of density of aluminum 3 p states of the Fermi energy level.

So, I have plotted here logarithmic of beta C; so here you can see from somewhat in the range of 2 to let us say of beta C which has a value of logarithmic of beta C. So, here it will come something like here up to 4 is shown here so, in the y axis we shown here the logarithmic of this n of E F so, these are the density of states of aluminum 3 p states. Also here the same mu C adhesion against steel in vacuum is also presented.

And one can look at the plot these are linear in nature; these are in linear in nature and both these 2 complexity index scales with one third minus one third of the power. So, must be there must be some similarity between the density of the aluminum 3 p states with the adhesion of a particular complex alloy phases against a steel in vacuum.

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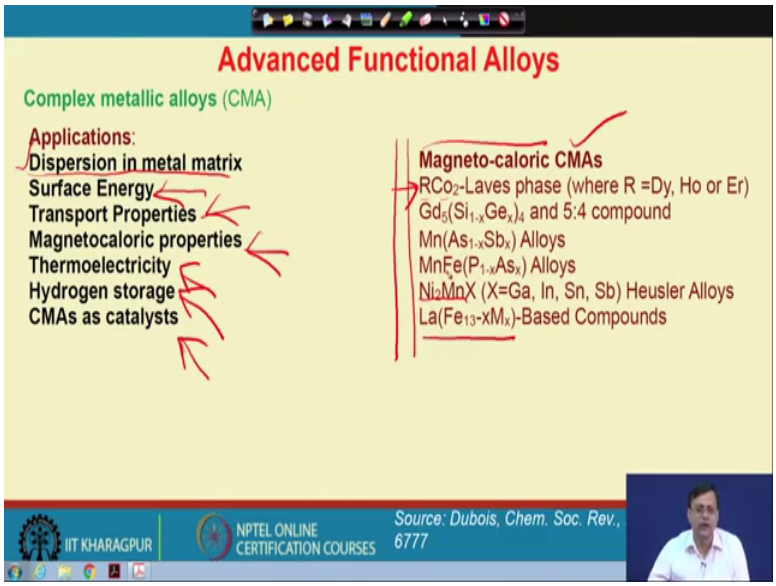

And therefore, people find out many different application areas of these CMA or Complex Metallic Alloys; since we already know about aluminum copper system of theta phase. And so we can use those complex alloy phases to make a dispersion strength in metal matrix. We can simply reinforce them in a to in a metal matrix; also we have interesting surface energy because we have already represented that with mu C that is the adhesion against steel in vacuum.

We may have some interesting transport properties, magnetocaloric properties, thermoelectricity also such kind of large number of atom present in the unit cell also give us some hydrogen storage and catalytic properties. If you have a look at the magnetocaloric alloy we have discussed in the last classes here the one of the very interesting example of such a magnetocaloric CMA or caloric alloys all have these RC o 2; basically this is a cobalt to laves phase. So, these are also laves phase and these are also the complex alloy phases.

So, the magnetocaloric alloy that we have talked about like the full heusler or half heusler compounds and lanthanum based compounds these are also the CMA complex metallic alloy and all of them also show magnetocaloric properties. So, we will not go into detail of these magnetocaloric properties, but we can now discuss about dispersion in a metal matrix. Usually all these magnetocaloric alloys or let us say the compounds has large number of atoms present in the unit cell.

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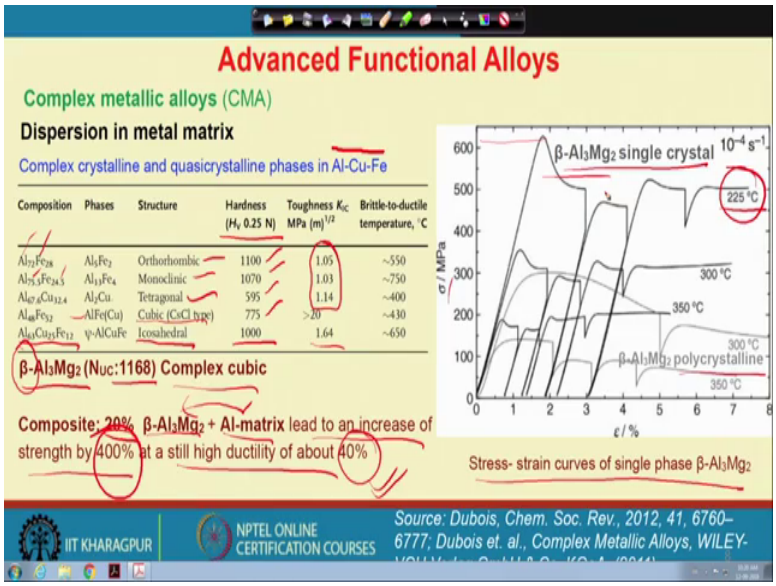

Now, dispersion in a metal matrix this complex crystalline or quasi crystalline phases as an example I show you here in case of aluminum copper iron system which is very well studied system. So, we have aluminum iron with 72 to 28 stoichiometry or 75, 24.5 and these have phases of 5 2 phase or 13 4 phase or 2 1 phase; these one we already have discussed. And it has orthorhombic monoclinic or tetragonal type of structures and almost 1 ratio with aluminum iron which has a CsCl type of cubic structure. If you look at the Vickers hardness the hardness values are very high and much higher almost 3 to 4 times higher than any of the high strength steels.

However, the toughness values of these inter metallic or intermediate phases are very less. So, also if you look at one of such a quasi crystalline compound which has a shown a icosahedral structures and the hardness also very high. So, there is definitely some interesting property besides the toughness values are very less. So, one of such complex cubic structure has been formed in case of aluminum 3 magnesium 2 which is also a very well known complex alloy; it has a number of atom per unit cell 11168.

And this beta phase is a complex cubic and people have tried to reinforce it in aluminum matrix and it has been shown that 20 percent of such complex phase present in a aluminum matrix lead to an increase of strength by 400 percent and without losing the ductility.

So, still it has shows some ductility of 40 percent. So, even though the single phase complex phases has very poor ductility, but in case of a composite it show some unique properties. So, as a comparison I show you the high temperature properties of a single phase beta aluminum 3 magnesium. Here these are the single crystal the solid black color line and the grey color line these are the poly crystalline single phase; beta phase.

You see that the strength value reaches at 225 degree centigrade around 600; so, this is not possible for any aluminum alloy to show such a high strength at such a high temperature so, it is for sure that these complex phases are unique in nature.

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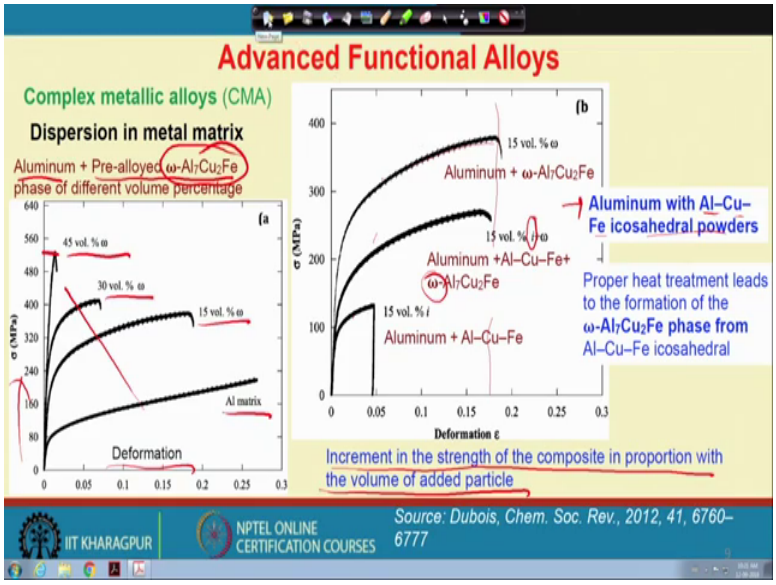

Very similar way another example of such dispersion in metal matrix I show you here in case of aluminum and pre alloyed omega phase. So, this is also a complex phase which has been reinforced in a aluminum matrix, this is the strength versus ductility you can see with increase of the omega phase the ductility decreases whereas, the strength is increases.

Whereas, if we take the same omega phase along with some i phases; i is the icosahedral phases in case of aluminum with aluminum copper iron icosahedral powder that is mixed with pure aluminum; here both the strength level increases as well as the plastic strain also increases. So, in both way can be benefited by appropriate a portion of such complex alloy phases along with icosahedral complex phases, if they are reinforced in a aluminum matrix.

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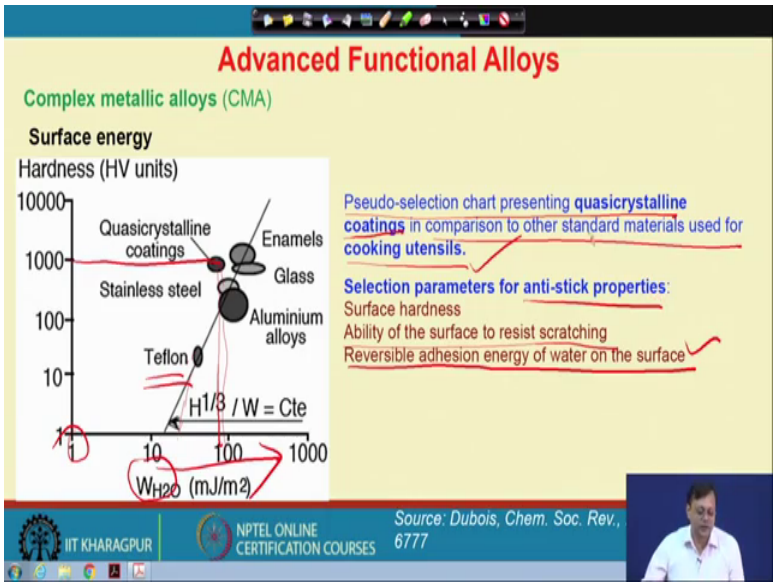

Now, another benefit of those complex alloy phases; I show you in case of quasi crystal each has a unique non sticky nature. So, we can compare such non sticky nature with a Teflon; Teflon has also a non sticky nature. So, both the hardness as well as the ability of the surface to resist the scratching and reversible adhesion energy of water on the surface is represented in the x axis. So, this is in case of water; it is actually 1 and in case of Teflon, it is somewhat just above 10 whereas, in case of quasi crystalline it is around 100.

So, the non sticky properties are very uniqueness of such a quasi crystalline alloys that can use as a coating compared to the standard material used for cooking utensils. So, anti sticky properties are also another uniqueness of such a complex alloy phases.

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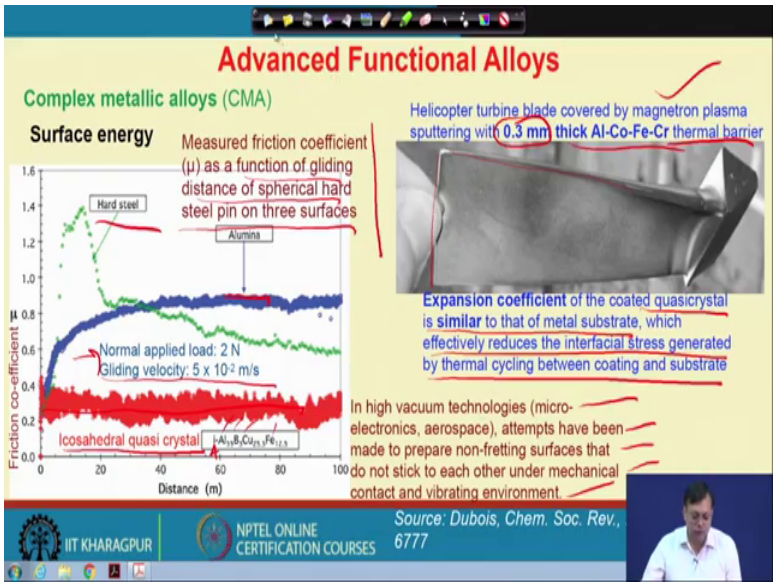

Now, due to such surface energy differences we think about the friction coefficient of such CMA. And I show you another example use of such icosahedral quasi crystal which is a i phase we call it as a aluminum and copper iron and boron phases; which has the lowest friction coefficient compared to alumina or hard steel. So, this is a stress that is applied at 2 Newton with a gliding velocity of 5 into 10 to the power minus 2 meter per second.

This is a friction coefficient measure as a gliding distance of a spherical hard steel pin on the surface ok. So, we took a surface and then we glide the pin and to measure this friction coefficient. So, we can use those CMA as a thermal barrier; so this is also another blade where quasi crystalline coating has been made which is similar to that of a metal substrate, but effectively reduce the interfacial stress generated during the thermal cycling which causes collation of any coating.

So, this is like a 0.3 micrometer thick thermal barrier coating by developed by magnetron plasma sputtering. So, we can use those technologies or material for making a newer technologies for a better purpose to solve and also it has a non sticky properties.

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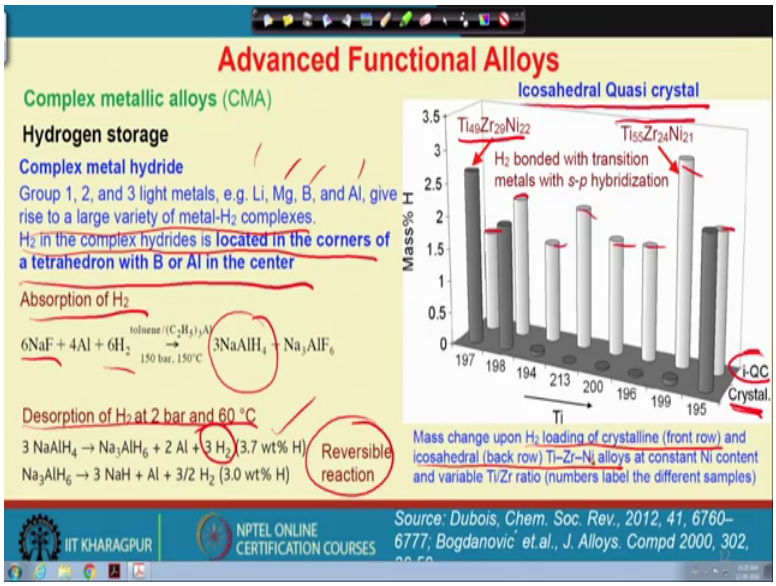

Now, another example is the hydrogen storage. So, usually for hydrogen storage complex metal hydrides are often used and these are basically the group 1, 2 or 3 light elements like you have lithium or magnesium or boron aluminum that gives rise to a large variety of metal hydride complexes and this hydrogen is a complex hydride located at the corner of a tetrahedron with boron or aluminum at the centre.

So, it basically absorb hydrogen like here sodium aluminum and hydrogen; they from these compounds and there is a desorption process which evolve 3.7 weight percent of hydrogen so, this is by a reversible reaction. However, if we compare such thing with the icosahedral quasi crystal which is represented here with a icosahedral or let us say for a crystalline. So, a alloy which is crystalline and this one shows a icosahedral; you can see that the mass of hydrogen absorb in quasi crystal phases are much higher than the crystalline phases.

So, we can use those complex quasi crystalline structure in order to store hydrogen for as a hydrogen storage material. So, these are also some uniqueness or application areas of complex alloy phases.

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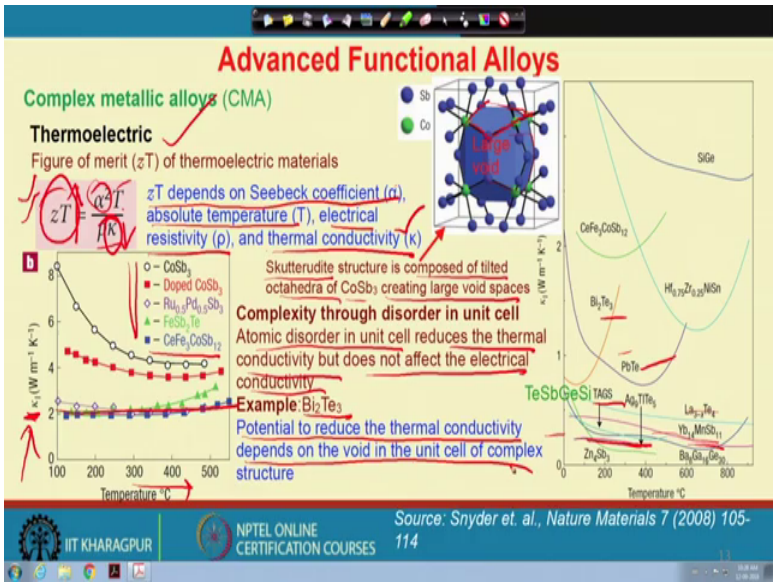

The other uniqueness of such complex alloy phases are the thermoelectric material. Usually for thermoelectric material a figure of merit that is represented by zT is the alpha square T by rho into K; here zT depends on the Seebeck coefficient alpha and absolute temperature T and electrical resistivity rho and the thermal conductivity.

So, thermal conductivity if it basically reduces then we can increase the figure of merit; so, K should be decrease as low as possible. So, here I show you that K versus different temperature of different such complex structures. You could clearly see that the K is very low in case of such one of these complex. In case of tellurides led telluride and bismuth telluride TAGS and there are so many different compounds which has a very very low thermal conductivity.

And this thermal conductivity is low because of presence of such kind of a structures which we call as skutterudite structure compose of octahedral cobalt and creating a large void spaces. So, because of the presence of such a large void in case of such a complexity in the disordered unit cell; the atomic disorder here reduces the thermal conductivity, but it does not affect on the electrical conductivity. And this is one of the unique properties that we need in order to enhance the thermoelectric properties by reducing the thermal conductivity, but it should not affect on the electrical conductivity electrical conductivity will remain as the same.

So, as an example here also one telluride is present like this material right so, potential to reduce the thermal conductivity that depends on the void of the unit cell of such a complex structure. So, in such cases of those kind of complex crystalline structure we can generate many of these interesting properties and complex metallic alloys are developing day by day and you can see so these are very recent literature which we have collected.

And this could be a well engineering application areas and more number of people need to devote their scientific research. With this we finish our discussion today, we will continue our discussion in the next class.

Thank you very much.