Advanced Materials and Processes
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Lecture - 19
Advanced Al Alloys Part-II

We start with this today's class and the objective of this particular part up to work is to look at the Advanced Aluminum Alloys, particularly those with high strengths.

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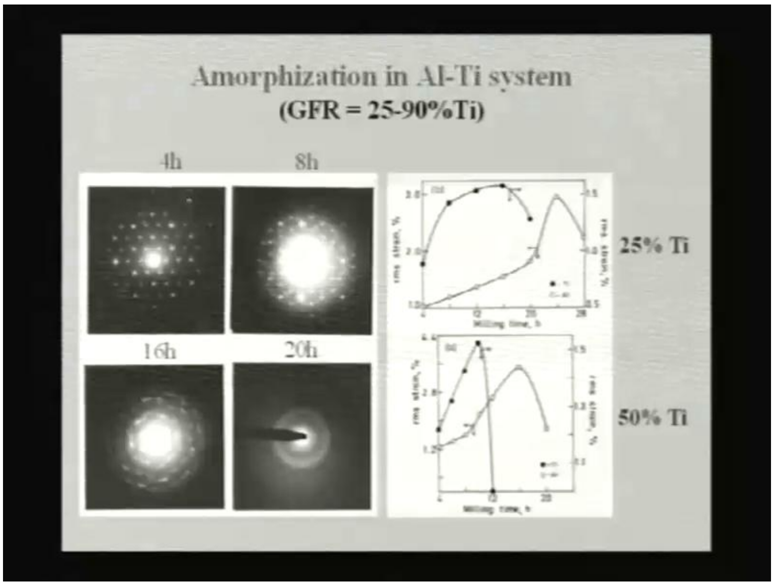

Amorphization in Al-Ti system
(GFR = 25-90%Ti)

So, when, we look at high strength alloys, most of the alloys, with high strength aluminum alloys or basically nothing but those nano crystalline alloys or nano quasicrystal alloys or amorphous alloys or composites of alloys. So, let us, try to look at some of the work, that has happened in the world, so far on this kind of alloys. So, if you look at the first transparency, this is basically nothing but how amorphization occurs in a simple binary system.

Though, usually in a binary system, we all know that, the glass forming ability is very poor. Particularly, aluminum based binaries; it is very difficult to make glass. But, there are a few systems, where people could successfully make it. This is one of those systems aluminum titanium, where you can see with increasing time of ball milling; you have a destruction of the crystalline structure. And then finally the development of the amorphous phase, beyond a certain strain.

And if you can look at the range of glass forming compositions, what is called that glass forming range, GFR, people usually call it. That means the composition range over, which one can get a glass. It is very wide in this system, 25 to 90 percent of titanium. Whereas, if you look at the same system, aluminum titanium system by rapid solidification processing.

If any one of have looked at this phase diagram of aluminum titanium. Aluminum titanium is basically peritectics. There are number of peritectics titanium phase diagram and there are no eutectics. And because of which you know that, if a system does not have eutectics, it is very difficult to form a glass. We know, we have considered; all the various criteria of glass formation. And we know by now that it is only deep eutectics, which are amenable for glass formation, when a liquid is being cooled.

So, if you want to have good glass forming ability, you need to have deep eutectics. Whereas, if you do not have eutectics at all, then it is very difficult to form a glass, I would not say, it is impossible. Because, we know, but because of the kinetic constrains, if one can cool it very rapidly and somehow, suppress the formation of the crystal, he can always get a glass. But, those cooling rates are very high and difficult to be achieving in a normal practical circumstances.

So, as a result, this system is one example, where you can easily get a glass by high energy ball milling, when compare to rapid solidification. And shows the kind of an advantage, that we have, by this solid state processing root, when compare to the liquid state processing root, such as rapid solidification.

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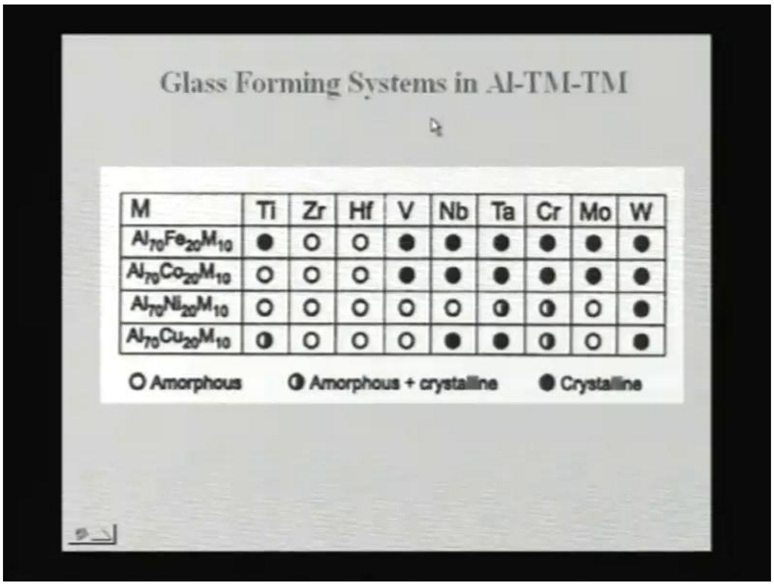

Glass Forming Systems in Al-TM-TM

M	Ti	Zr	Hf	V	Nb	Ta	Cr	Mo	W
$Al_{70}Fe_{20}M_{10}$	●	○	○	●	●	●	●	●	●
$Al_{70}Co_{20}M_{10}$	○	○	○	●	●	●	●	●	●
$Al_{70}Ni_{20}M_{10}$	○	○	○	○	○	◑	◑	○	●
$Al_{70}Cu_{20}M_{10}$	◑	○	○	○	●	●	◑	○	●

○ Amorphous ◑ Amorphous + crystalline ● Crystalline

This is the binary, as I told you before, when you add more number of elements, the glass formation becomes easy and aluminum is not an exception. So, in aluminum systems, also if you can add a turnery element, the glass formation becomes very easy. This gives you an idea of in aluminum transition metal transition metal systems, how the glass formation occurs. In what kind of systems, you can easily get a glass, in what kind of system, you can get, it is more difficult to get a glass.

If you look at any of these aluminum transition metals system, such as aluminum iron, aluminum cobalt or aluminum nickel or aluminum copper. If you add some zirconium or titanium or hafnium, these are the three, which can easily give you a glass. Because, these are the elements, which are much bigger atoms, when compare to aluminum and that gives you very easy glass formation.

As I told you before, you always for good glass ability, you need big atom as small atom and an intermediate atom. Aluminum is basically that kind of an atom, with about 1.47 or so as the atomic size. And copper, nickel, these are all about 1.28, 1.27 as the atomic size in angstroms and zirconium is much bigger. So, as a result, if you look at these kinds of systems, it is very easy to form the glass.

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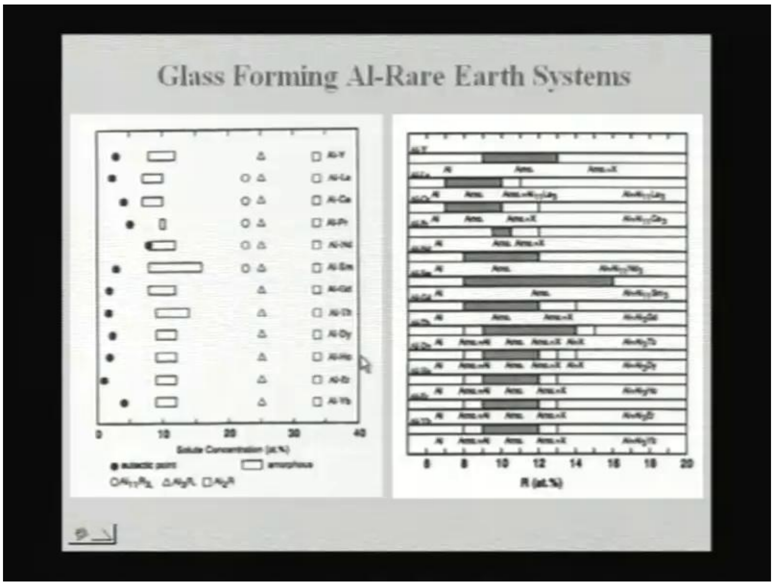
Glass Forming Al-Rare Earth Systems

And there are rare earth systems, aluminum based rare earth systems, where glass formation is very easy. Most of the aluminum rare earth systems glass formation is very easy. But, the composition ranges are very rarer. If you look at these systems, there are number of binary aluminum rare earth system shown here, aluminum yttrium, aluminum lanthanum, aluminum cerium, aluminum niodium, aluminum samarium, gadolinium and so on.

And if you look at all of them, in all the cases, you can get a glass. And this box, tells you the composition range in which you can get a glass. It is usually in the range of around 10, which is close to the actual deep eutectic compositions. The eutectic compositions, I would not say, deep eutectics, there are not really very deep eutectics, in this systems.

So, these compositions are close to the eutectic compositions and this is also shows you, that there are intermetallic compositions, intermetallic compound forming compositions, which are shown here. So, the glass formation occurs, away from these intermetallic forming compositions. So, and this second figure, gives you in a wider composition range, slightly magnified view of this, to show you, what is the glass forming range in all the systems. You can see aluminum samarium, shows the almost the highest glass forming range, when compare to all of them. So, but in all cases, you can get glass.

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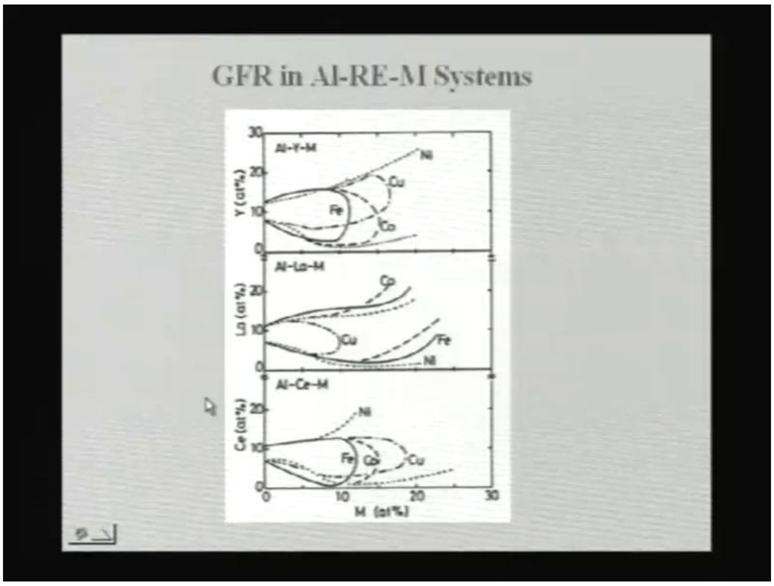

GFR in Al-RE-M Systems

And one if you add some turnery elements again into aluminum rare earths, then you can enhance the glass forming ability, which we have talked about it before also. So, you can see this is aluminum yttrium, various metals, transition metals, for example iron, copper, cobalt nickel. So, this domain, tells you, what is called the glass forming domain on one side yttrium, on the other side the metal percentage is plotted. So, you can see, this particular domain, gives you, what is the glass forming range.

And for various yttrium, lanthanum, cerium, type of rare earths, if you put various transition metals, how the glass forming domain can be expanded, can be seen in this kind of a figure. So, one can really expand, you can see in that in the binary, if you do not put any turnery element, the binary the glass forming range is very small. You can it is around 10 percent, may be 8 to 12.

In most of the cases, it is something like around 8 to 12 or 10 to 12 or 10 to 11, this is the small range. Whereas, if you put certain turnery element, it can be made, much wider as you can see here or you can see in case of cobalt or copper or nickel is much more wider. So, like that, one can widen the glass forming ability range.

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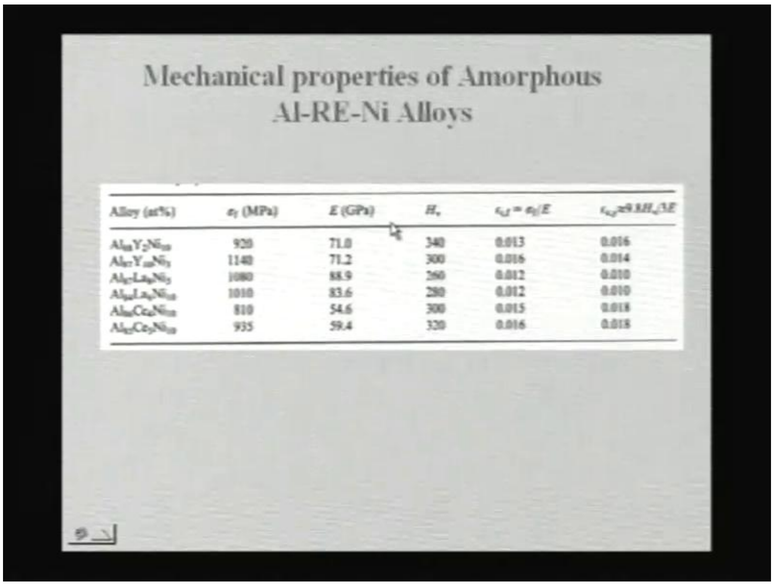

Mechanical properties of Amorphous Al-RE-Ni Alloys

Alloy (at%)	σ_f (MPa)	E (GPa)	H_v	$\varepsilon_{t,f} = \sigma_f/E$	$\varepsilon_{t,f} \approx 9.8H_v/3E$
$Al_{88}Y_2Ni_{10}$	920	71.0	340	0.013	0.016
$Al_{87}Y_{10}Ni_3$	1140	71.2	300	0.016	0.014
$Al_{87}La_8Ni_5$	1080	88.9	260	0.012	0.010
$Al_{84}La_6Ni_{10}$	1010	83.6	280	0.012	0.010
$Al_{86}Ce_4Ni_{10}$	810	54.6	300	0.015	0.018
$Al_{87}Ce_3Ni_{10}$	935	59.4	320	0.016	0.018

The question is, why do you want to do that? You want to do that, because there are a number of advantages; that you get in these amorphous alloys. The strengths that you can achieve are very high. You can see in some of this aluminum transition metal, rare earth systems, it is shown here, particularly, aluminum nickel rarer earth metals, with various rare earths, yttrium, lanthanum and cerium.

And for different compositions, you can see, the fracture strength is of the order of almost 1 Giga Pascal, which is much higher than any of the commercial aluminum alloys. I will also show you, some more comparisons, with the commercial alloys, where you can see, very easily the difference between these alloys. But, one problem is, you can see, the ductility is still not very good, about 1.5 percent, 1.6 percent 1 to about 2 percent is the ductility. So, that is one of the I would say the draw backs. So, one cannot use them really in a tensile conditions. Wherever, you need a good compressive strength, probably, you can easily use it, but that uniaxial elongation is not very high.

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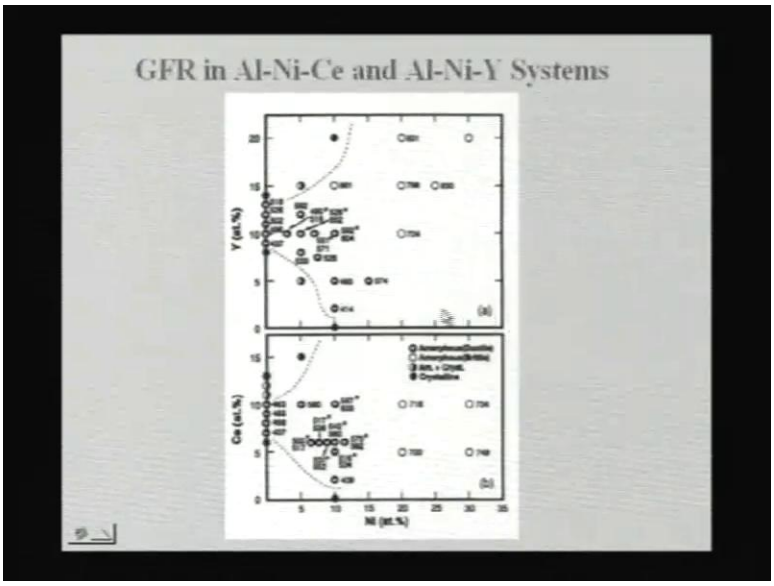

GFR in Al-Ni-Ce and Al-Ni-Y Systems

You can also see here, another system aluminum nickel cerium, aluminum nickel yttrium, the glass forming ranges, yttrium and nickel shown here. And here, we also show, which are the compositions were you can possibly get a ductile amorphous. It is not that always amorphous phase is very brittle. If you can control the composition in such a way, particularly, keep the rare earth element to very low. If you add large amount of rare earths, it is become very brittle.

And similarly, if add a large amount of transition metal, also it becomes brittle. For example, you can see, all these open circles, these are all brittle amorphous materials. Whereas, wherever you see the thick circles shown here, these are all ductile amorphous. So, you can see, if you go to large amount of transition metals, you get a brittle amorphous phase. Otherwise, one can vary the composition and can still get ductile amorphous.

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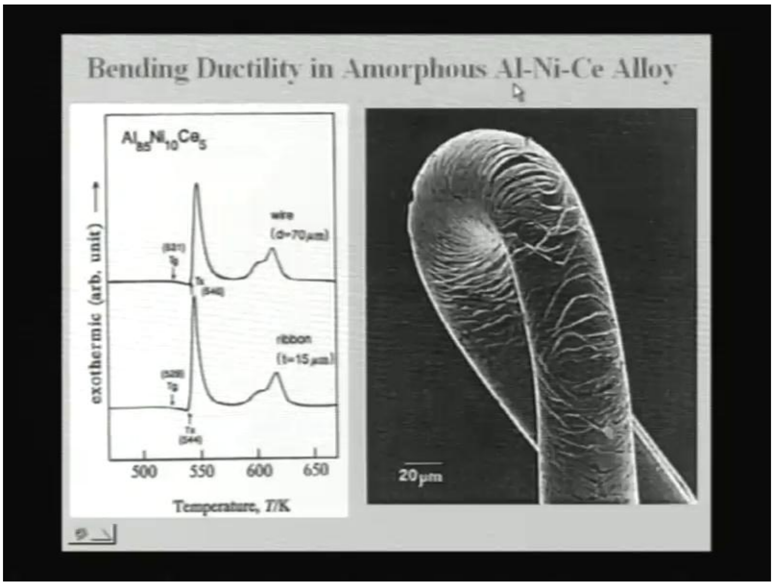

Bending Ductility in Amorphous Al-Ni-Ce Alloy

And this is, here is an example, that you have really a ductile amorphous. That you can make a wire, out of this aluminum, nickel, cerium, amorphous wire. And can bend it, 180 degrees, without any really breaking it. So, most of the amorphous alloys, if you try to bend like that, the immediately break. So, one can have good bending ductility and this is in case of wire and this in case of melt span ribbons.

The D S C curve to show that basically the nature is the same, weather you make a wire or you make a melt span ribbon. So, more or less you get similar D S C plots. And you can easily show that some amount of ductility is there. And there is a lot of shearing, which occurs, you can see, all shearing in these wires.

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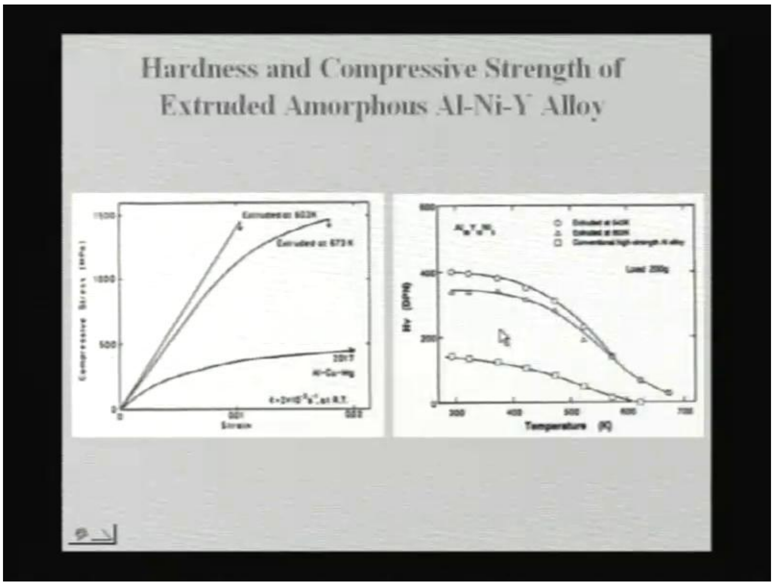

Hardness and Compressive Strength of Extruded Amorphous Al-Ni-Y Alloy

And you can also take these amorphous alloys, made by either melt spinning or by ball milling. And exclude them, make into rods and look at their mechanical properties and if you compare the mechanical properties here with a conventional aluminum copper magnesium alloy. You can see, these aluminum nickel yttrium alloys have much higher strengths of the order of almost 1.5 Giga Pascal's.

Though, this is compressive strength, you have to remember. We are talking of compressive strength and not really tensile strength. So, you can get very high the strengths, but aluminum nickel yttrium alloys or not really good for ductility. But, if you replace yttrium with cerium, what you can see here, aluminum nickel cerium gives you sufficient amount of ductility.

So, you have to control the composition in such a way, that one can have a good combination of strengthen ductility. Similarly, you can also look at high temperature strength. A conventional aluminum alloy, high strength alloy, loses it is strength very rapidly more or less. And you cannot really use them, beyond about 300 degree centigrade, I told you and this is sown in terms of Calvin.

So, almost around 573 Calvin, beyond that you lose the strength, very rapidly. Whereas, this excluded aluminum nickel yttrium amorphous alloys, show you much higher strength, even at higher temperature. So, this is one of the advantages of going for such a, so to say exotic alloys, which are meta stable though, definitely they are all meta stable alloys.

So, we know that at very high temperatures, they tend to crystallize. But, we are going to talk about those things also that one can crystallize them and get nano crystals out of it and then use them forever advantage. So, we will go to those alloys also a little later.

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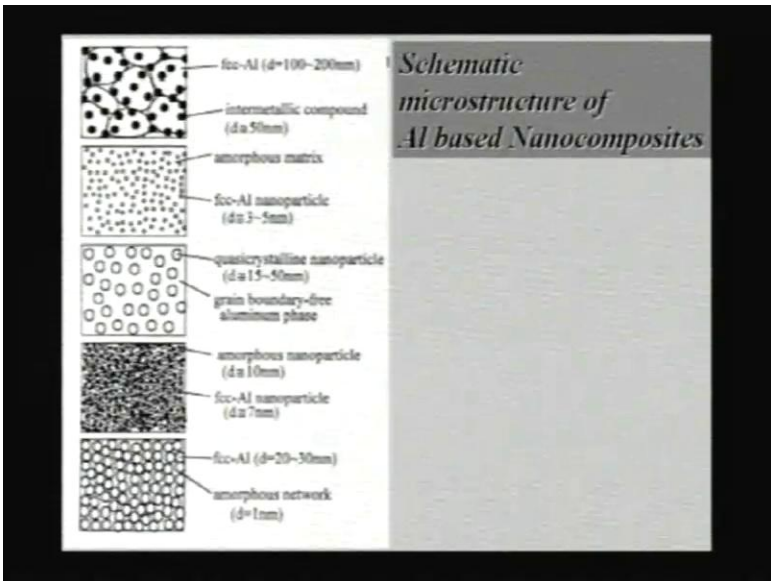

Schematic microstructure of Al based Nanocomposites

And that is, where you came across, what are the various possibilities. We talked about it in the last class, that one can have various combinations, when we are talking of nano composites. You can have an amorphous with alpha aluminum nano particles; you can have aluminum with intermetallic nano particles. You can have amorphous and quasicrystalline inter metallic particles or you can have aluminum grains with quasicrystalline nano particles or you can have another combinations also.

So, a various varieties of combination are possible and one can really realize all these things by choosing of proper composition and proper temperature and time of heat treatment. So, that, you can end up in all these type of micro structures and look at their mechanical properties. We are going to look at some of such micro structures and their mechanical properties.

This is one such system, aluminum nickel cerium iron. So, take aluminum nickel cerium, put a small amount of iron in it. You have seen earlier, aluminum nickel cerium is basically an amorphous alloy.

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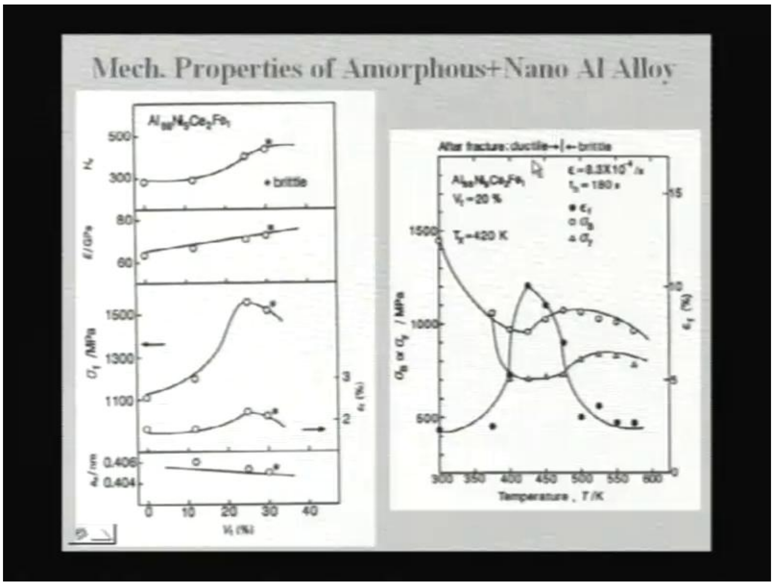

Mech. Properties of Amorphous+Nano Al Alloy

If you put a small amount of iron into it, it leads to the formation of easy crystallization and gives you nano crystalline aluminum particles, embedded in an amorphous matrix. And that shows you, that if you increase the volume fraction of those embedded nano particles of aluminum. That the strength increases, the hardness increases, young’s modulus increases and one can achieve very good strength levels here. And one can talk in terms about, almost 1.5 Giga Pascal’s fracture strength in all these alloys.

That one can vary the volume fraction and you see that there is a volume fraction beyond, which if you go to much higher levels. You are not going to get any additional advantage. Basically, because you need these nano particles to be separated by an amorphous matrix, the moment there you start seeing that these nano particle start joining with each other. Then, you will see the crack propagation occurs at the grain boundaries of these nano particles.

So, you need to have always an amorphous kind of a region, which is engulf, the whole nano particles. So, you need have a matrix of amorphous and then in which these nano particles are embedded. And similarly, if you have a look at the high temperature strength, you can also achieve much higher strengths at even higher temperature. But, there is a temperature beyond which, they show some kind of brittle nature.

So, one has to consider this aspect also. This is basically because of the precipitation of crystalline phases at high temperatures, which make them brittle, because most of these crystalline phases, are intermetallic, brittle intermetallic. So, because of which, high temperature, you lose their ductility to a large extant.

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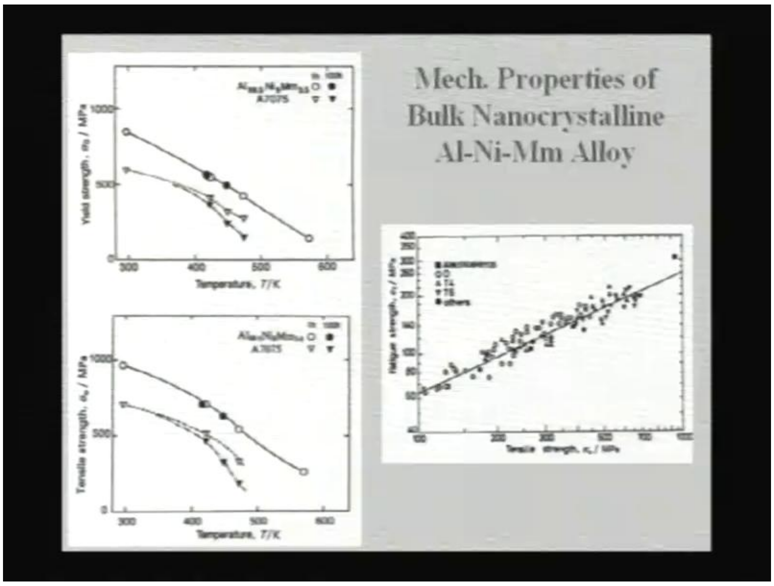
Mech. Properties of
Bulk Nanocrystalline
Al-Ni-Mm Alloy

One can also make, bulk nano crystalline alloys. This is one such example of aluminum nickel mischmetal type of alloys. Mischmetal, have you heard of what is a mischmetal, mischmetal is basically an alloys consisting of rare earths. For example, if you have an alloy of lanthanum, samarium and cerium alloy of all these, because whenever you are trying to extract these rare earths. Most of these rare earths in the earth crust, they are all together.

So, when we try to extract individual extraction of the rare earth elements is very difficult. So, most of the time, what people do is, they generate a kind of an alloy, during the extraction process, which consist of a combination of these rare earths. And you people call them, as mischmetal. And wherever, you are not particularly looking at any one of the rare earth element, one can use this kind of a mischmetal, which is a combination of various rare earths.

You have lanthanum about 40 percent of lanthanum is there, about 30 percent of cerium is there and some amount of samarium and things like that, some amount of gadolinium. So, if you take aluminum nickel mischmetal type of alloy, and then look at the creep properties or stressed as a function of temperature. You can see, you get much higher strength, when compare to conventional aluminum 7075, what is a 7075 alloy, aluminum zinc magnesium alloy very good.

So, if you compare with a standard aluminum zinc magnesium alloy, you get a much higher strength in these alloys, at any temperature of your consideration. So, you can even talk in terms of up to around 600 Calvin and you get much higher strength. And similarly, look at the fatigue strength of this alloy and compare with any of the conventional alloys. All the conventional alloys fall here and this aluminum mischmetal alloy is much higher.

So, it has good combination of tensile strength of almost around 1 Giga Pascal and a good amount of fatigue strength. So, these have a good combination of both strength and high temperature properties. So, you can have a good creep strength, a creep resistance and fatigues resistance and in edition a good tensile strength. So, that way, this kind of bulk nano crystalline alloys, produced by the crystallization of the amorphous alloy.

As I told you, there are two ways of doing this. One way we talked about it in the last class. One way is to get a glass, by rapidly cooling the alloy or by making, going through the process of mechanical alloying, high energy ball milling. And once you get the amorphous alloy, then crystallize it, at temperatures and timings, which can give you is nano crystals. That is one possibility. Other possibility is that use a cooling rate, during rapid solidification. In such a way, that you get a combination of amorphous plus the aluminum as I showed you in the last class.

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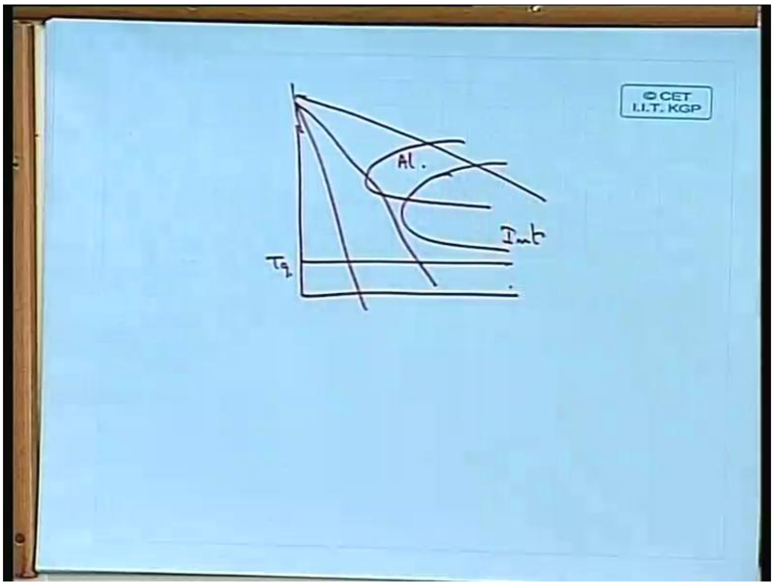

If you look at the TTT diagram, if this is aluminum and this is intermetallics, basically and you have a T G here. If you try to cool it, very rapidly, you get a glass. If you try to cool it, at an intermediate rate, you get amorphous and whatever is left out, will give you a glass. And if you cool it very slowly, you get a crystalline aluminum plus some intermetallic compound, whatever, crystalline intermetallic compounds.

So, similarly, you can see inertmetallics, always are below and to the right in the TTT diagram. Why is that they are to the right and below in the TTT diagram. What does that mean in TTT diagram, we have gone throw all this?

Student: ((Refer Time: 20:13))

Why, because, the nucleation of these intermetallics is more difficult, when compare to nucleation of aluminum. You can see aluminum is simple FCC. So, it can easily nucleate and grow. Whereas, intermetallics are mostly ordered and also have certain tachometry, so because of that, the nucleation and growth are such intermetallic is more difficult. As a result, you always need more time, the incubation period is longer.

And that the same time, you need a higher under cooling. If you do not give higher under cooling, you cannot get, you need a higher driving force. Unless, you provide a large driving force you cannot nucleate. So, that is why, you will see this kind of intermetallic compounds are there. So, if you still cool it very slowly, you get a combination of aluminum plus intermetallic compounds.

But, otherwise you can get and in case, you have a quasicrystal in a system, having a frank as per phases. You will have, let say a quasicrystals somewhere here or may be somewhere here, depending on the type of system. So, that, you can have a combination of amorphous plus quasicrystal or amorphous plus aluminum plus quasicrystal, all kind of combinations are possible. So, this is the bulk nano crystalline alloys.

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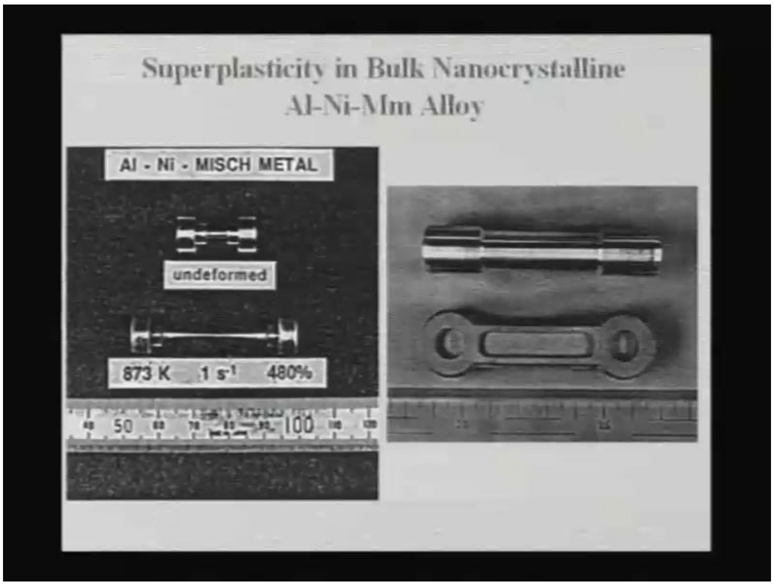

Superplasticity in Bulk Nanocrystalline
Al-Ni-Mm Alloy

And one can show in some of these nano crystalline alloys, that they can even be super plastic. This is one aluminum nickel mischmetal alloy, which is, you can see the un deformed sample. And after deformation, you can almost have about 480 percent deformation. So, you can just elongate it by almost 480 percent. But, provided you use a proper temperature.

This is one important point; that you should also know that, have you ever heard of, what are called deformation maps? You have all gone throw deformation course. Suppose, every material, can be deformed in an easy fashion, if you choose the proper strain rate and the temperature. Each metal, for example, if you take a metal, deform it at very high strain rates, it becomes brittle and it breaks very easily. Similarly, if you take the material and deform it at a very low temperature, again it behaves a brittle fashion.

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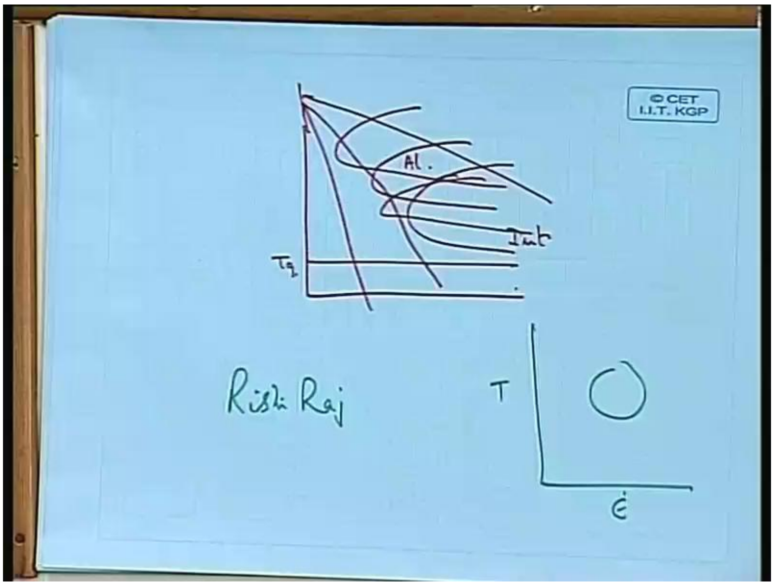

So, there is a particular domain are particular window of temperature and strain rate. If you plot a domain of temperature and strain rate, you can identify a domain, where dynamic re crystallization easily occurs and deformation becomes very easy. And such domains, these are called, have been identify by a number of people. And the person, who started this, is a person by name is Rishi Raj, these are called Rishi Raj maps.

And a number of people have worked on this particularly in IAC Bangalore in India, professor, Y.V.R.K. Prasad. If some of you have heard. So, he has done a lot of work on various alloys, titanium base alloys, super alloys, aluminum based alloys, aluminum lithium alloys. In all these alloys, people have worked and identified what kind of domain is this.

So, because, it is very important, when you want to commercially make alloys with various shapes. You need to identify this temperature entirely. Particularly, when you are developing newer alloys, such as, let us say a nickel base super alloys or alloys like that. Unless, you really identify this domain, it becomes very difficult for you, to process it over a very large amount of deformations.

And particularly, in case of bulk nano crystalline alloys, because you have a fine crystal size, some of these alloys can behave in a super plastic manner. And that is where, you can see here, at about 873 Calvin; that means, about 600 degrees centigrade. If this alloy is deformed, at a strain rate of 1 per second, one can achieve almost 480 percent. And these have been also deformed by super plastic manner, forged into various shapes. And a number of shapes have been made in alloys like this without much problem.

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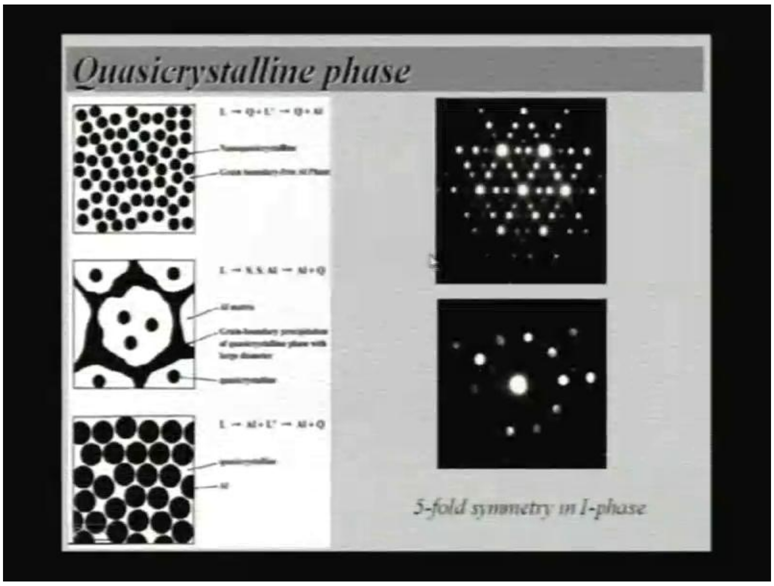

Quasicrystalline phase

5-fold symmetry in I-phase

Let us now, come to the aluminum based quasicrystalline and nano quasicrystalline alloys. As I told you before, quasicrystalline phases can be obtained in a number of systems and aluminum base systems are the starting point. What was the first alloy, where people have observed by quasicrystalline phase, do you remember?

Student: ((Refer Time: 25:15))

What was the first alloy were aluminum manganese, aluminum 14 percent manganese is the first alloy, were people have observed in 1984, ((Refer Time: 25:30)) the quasicrystalline phase. So, after that, a number of aluminum alloys people have observed quasicrystalline phase. And now, people do not want to use, this kind of quasicrystalline phase as a single quasicrystalline phase. If it can be obtained in the nano quasicrystalline fashion, one can have much better properties.

So, people are looking at, such a nano quasicrystalline phases and these nano quasicrystalline phases can be obtained in a number of configurations, a in number of micro structures. For example, you can have an aluminum matrix in which you can have nano quasicrystalline particles. You can also have some grain boundary precipitation of quasicrystalline phase in an aluminum alloy. Or you can also have quasicrystalline alloy in which aluminum nano particles have been precipitated by choosing a proper composition.

So, in all such cases, one can achieve very good mechanical properties and will try to see some of those mechanical properties. And these diffraction patterns show you in some of these alloys, that these are quasicrystalline in nature. For example, the tenfold pattern that you can see and the three fold pattern with a quasi periodic arrangement of atoms arrangement of diffraction spots. I should not say atoms, these are diffraction spots and one can get an idea, that these are basically quasicrystalline.

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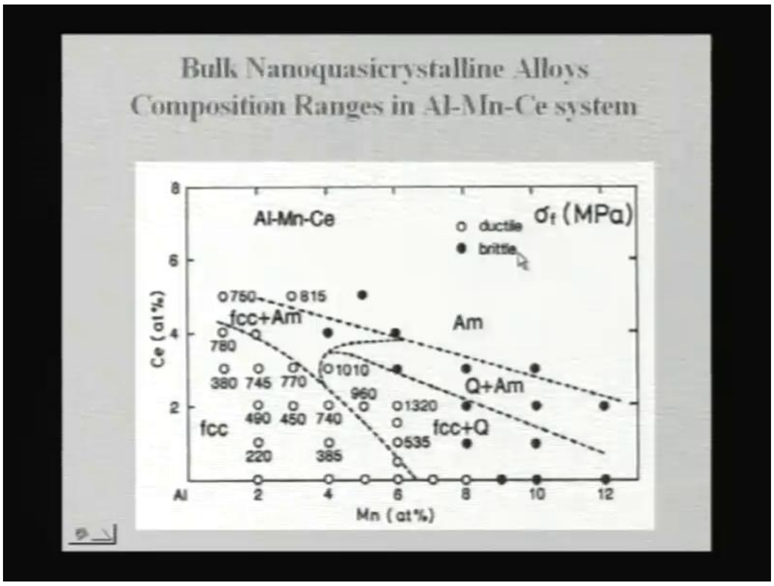

Bulk Nanoquasicrystalline Alloys
Composition Ranges in Al-Mn-Ce system

And look at some of these systems, this is aluminum manganese cerium. We talked about earlier aluminum nickel cerium, where you can get a completely single phase amorphous alloy. Whereas, if you replace that nickel with manganese, if you take a aluminum manganese cerium, we already know that in aluminum, you got a quasicrystal. But, if you add cerium to it, you can get a nano quasicrystalline phase and a bulk nano crystalline alloy.

And this gives you an idea of the composition ranges of cerium and manganese, to get various phases. For example here, if you have high amount of cerium and manganese, you get completely amorphous phase. That means, beyond this dotted line, you get amorphous phase. You can have a quasicrystal plus amorphous combination. You can have FCC aluminum plus quasicrystal combination or you can have FCC aluminum plus amorphous combination by choosing a proper composition.

So, depending on the choice of the composition one can achieve various micro structures like this. And the strength levels are also shown here, for example, that you can have strengths of the order 1.3 Giga Pascal's, 1300 mega Pascal's. And you can also see here that some of the compositions are brittle, some of the compositions are ductile. And particularly, those compositions with low amount of manganese and cerium, they are all ductile.

And if you add more amount of manganese and more amount of cerium, they become very brittle. So, one can control the ductile brittle nature of this alloys, also by choosing the proper composition.

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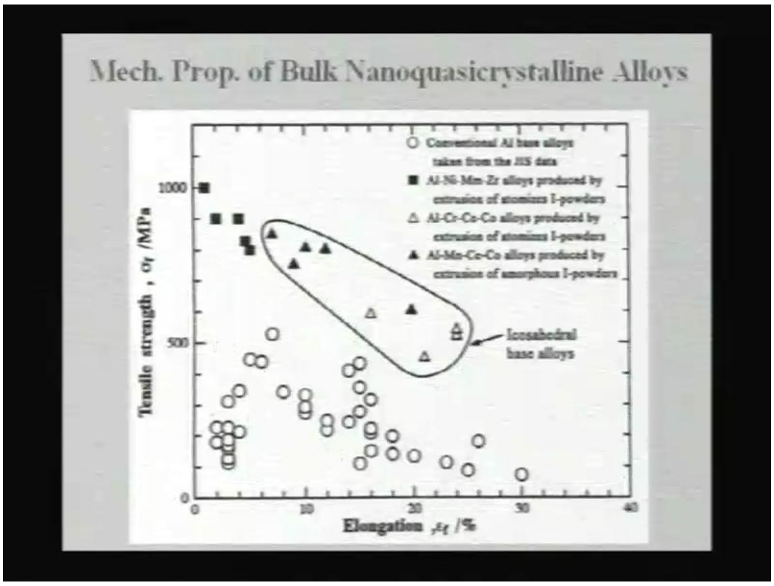

Mech. Prop. of Bulk Nanoquasicrystalline Alloys

And this is another example, where aluminum nickels mischmetal with some zirconium or aluminum chromium cerium with cobalt, various nano quasicrystalline alloys. And if try to compare with conventional alloys, all these circles or all conventional aluminum alloys, conventional aluminum alloys. If you look at their strength elongation combinations, they are all very low strength alloys. And if you can make these the nano icosahedral alloys, you can achieve much higher strength. So, you can have a good combination of strength and ductility, by choosing the proper compositions, will be these alloys.

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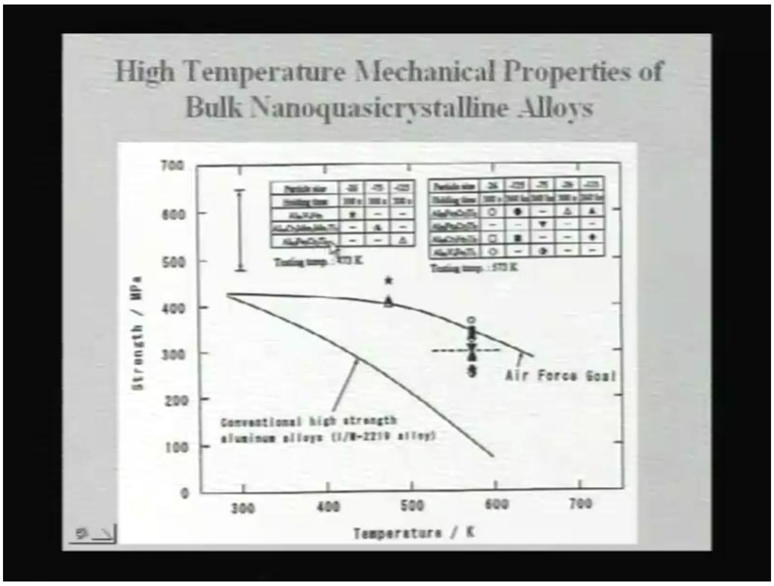

High Temperature Mechanical Properties of Bulk Nanoquasicrystalline Alloys

And this is another example of bulk nano quasicrystalline alloys, where aluminum iron chromium titanium, this is an entirely a different root. There are no rare earths here; we do not use any rare earths here, only aluminum and transition metals. You can put, iron, chromium, titanium, some of these elements, have a tendency to give you nano quasicrystalline phase. So, if you can properly choose the composition and make an alloy like that, you can make these alloys with very high strengths.

For example, conventional aluminum alloys, 20 series has strength levels like this, as a function of temperature. And usual air force limit, air force goals are also shown here. Particularly, the defense, aircrafts, wants to have very high strengths at high temperatures. Why do, they want high strength at high temperature?

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Efficiency becomes higher, anything else, raise, if not that

Student: ((Refer Time: 30:27))

Speeds, particularly that is I aspect, so most of the air force, aircrafts, nowadays, people wants to go to higher and higher speeds. If you want to go to higher, because you want to go and hit the target, before anybody you now notice you. So, for that, you need to really go at high speeds, Mac 2, Mac 3. So, these are the kind speeds everybody wants to achieve. And if you want to go to high speeds, you always have a friction, from the air, surrounding air.

And the friction results in a lot of temperature raise, so you need to use alloys which have high strength at high temperatures. So, as a result, one puts a goal like this and there are number of these aluminum, iron, chromium, titanium alloys, which can achieve all those goals. And people are still working on this and some of the achieved goals, for example, aluminum, vanadium, iron; I am going to show more results of that.

And aluminum, vanadium, iron has much higher strength and then what is the objective that is set as the goal. So, people have been able to achieve these goals of very high strength at high temperatures by making these nano quasicrystalline alloys.

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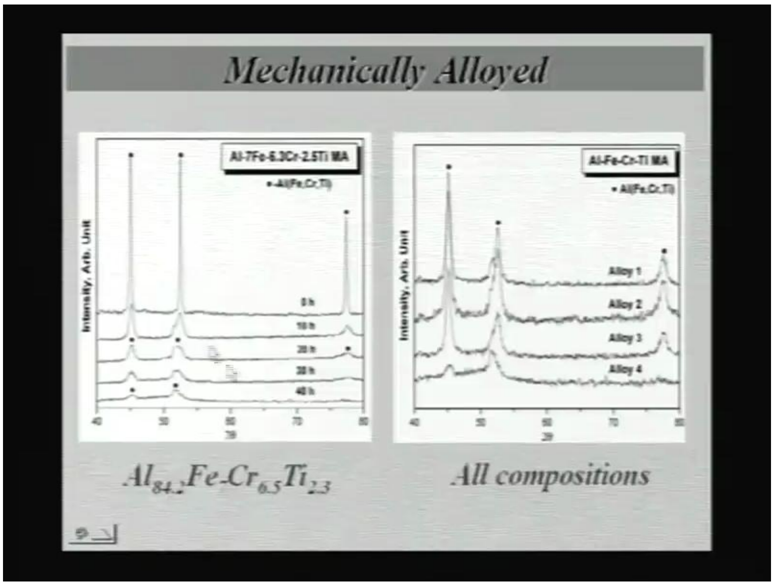

Mechanically Alloyed

$Al_{84.2}Fe\text{-}Cr_{6.5}Ti_{2.3}$

All compositions

One can also make these by the ball milling root and these are some of the examples of that. For example, if you take aluminum, iron, chromium, titanium alloy, some particular composition. And go throw by mechanical alloying root, what you ultimately end up is a solid solution. Because, all these alloying elements will dissolve into aluminum, when start taking these elemental blends.

That means, you take pure metals mix them together, put it in a ball mill and continue ball milling. After some time, all these alloying elements dissolve, and then if you look at, this is for various alloys with different compositions. In all cases, you basically get a solid solution.

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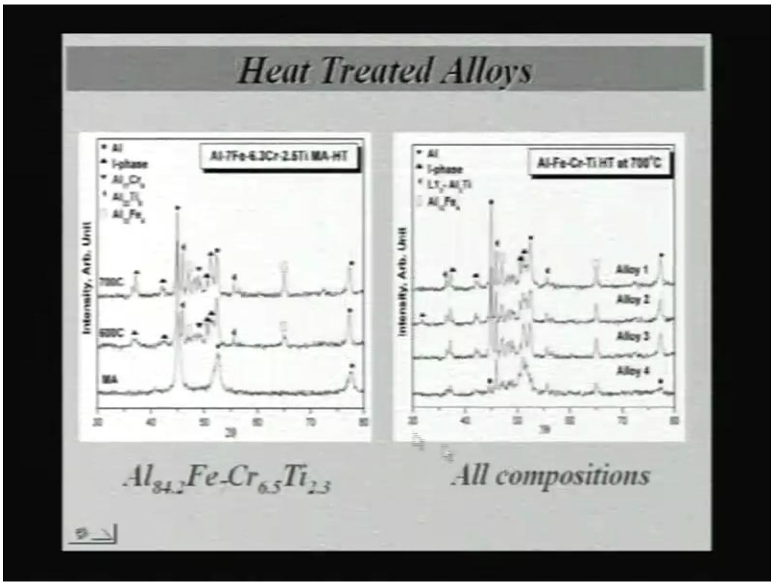

Heat Treated Alloys

$Al_{84.2}Fe_7Cr_{6.5}Ti_{2.3}$

All compositions

And if you a take the solid solution, and then crystallize it, you can get the formation of icosahedral phase. But, one has to control the temperature; otherwise you also end up in some crystalline phases like this. So, one can control, if one can have a proper control on the temperature and time, one can only get the nano quasicrystalline phase and generate the strength levels, that we have talk, just a while ago.

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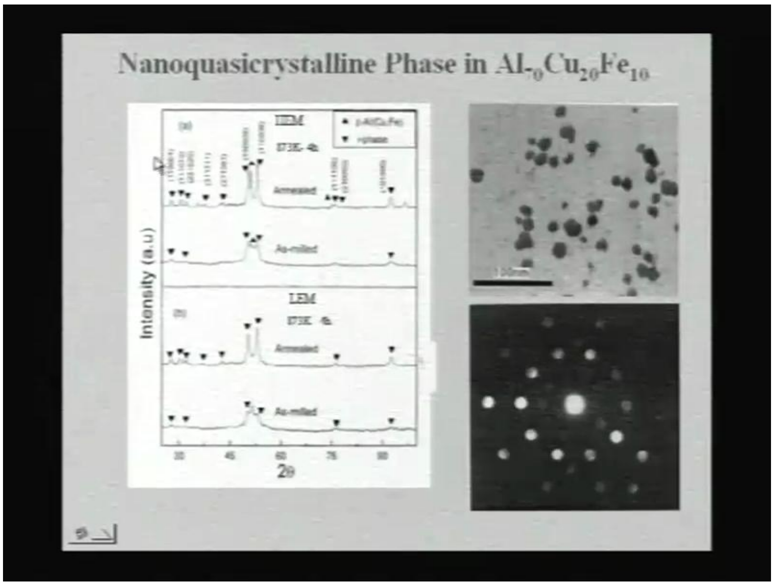

Nanoquasicrystalline Phase in $Al_{70}Cu_{20}Fe_{10}$

And one can also make bulk nano quasicrystalline alloys, in simple system such as, aluminum copper iron. This is a standard composition, lot of people have worked on it, for example, aluminum, copper, iron is known to be a stable quasicrystalline composition. Stable, what do you mean by that? Stable means, you take a liquid, cool it slowly, by a normal casting process, you get a quasicrystalline.

You do not need to do any fast cooling, just take a like any aluminum, normal aluminum, you melt it and cast it. So, similarly, you melt this aluminum copper iron alloy, the composition is 65, 20, 50, 65 aluminum, 20 copper, 50 iron. This particular composition is called the stable quasicrystalline composition. So, if you can, choose that composition, and then melt aluminum, those that alloy, all the three elements together. And then if you can cool it slowly, you can generate quasicrystalline alloy.

But, the problem is, if you get an alloy by that casting root, the quasicrystals that you are going to get, is going to have large grains and that is not going to give you very good properties. So, if you can generate them in a nano crystalline form, as you can see here, one can have much higher properties. So, that is the advantage of going to either rapid solidification or ball milling roots like that. That you can generate the same nano quasicrystalline phases in a nano form, and then achieve much better mechanical properties.

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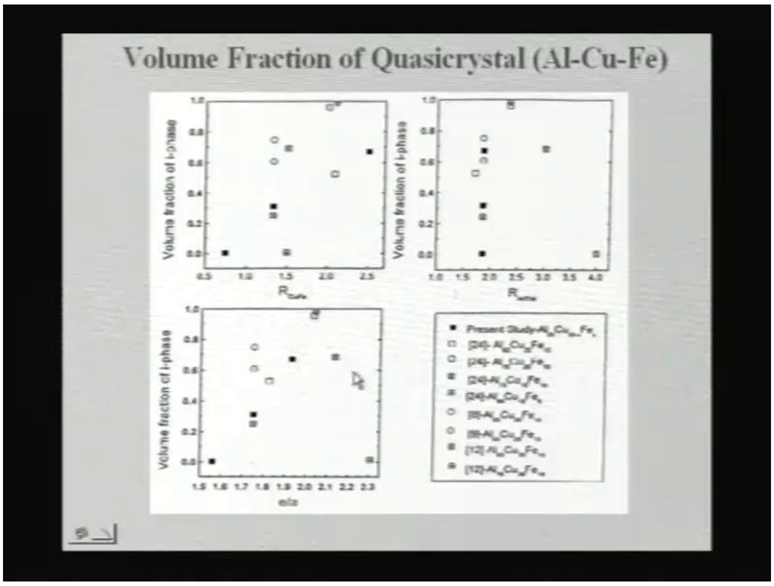

Volume Fraction of Quasicrystal (Al-Cu-Fe)

And one can also identifies, which are the best compositions for making this. For example, as a function of e by a ratio, if you look at it, there is a certain e by a ratio of about 2 to 2.1. Where, you get the stable quasicrystalline phase with 10 percent volume fraction of I phase. Otherwise, if you are either on the both the sides, you get only a small amount of icosahedral phase and nano quasicrystalline phase, but not 100 percent.

If one wants to get bulk nano crystalline alloy, with 100 percent icosahedral phase, one has to choose the composition properly, this is very crucial. So, and for choosing the composition, what is crucial parameter is not really the composition, but it is the e by a ration. Because, we as we have seen earlier also, that the quasicrystalline phases are basically, what are called the Hume Rothery phases. Like, as we know in case of copper zinc alloys, you get a bit of at when the e by a ratio is 1.5.

Like that, you get various phases at various e by a ratios. The quasicrystals also form at certain e by a ratio, they form at certain composition, they have fixed e by a ratios. So, similarly, you can this particular aluminum copper iron also. If you can fix the e by a ratio properly, you can get a 100 percent quasicrystalline.

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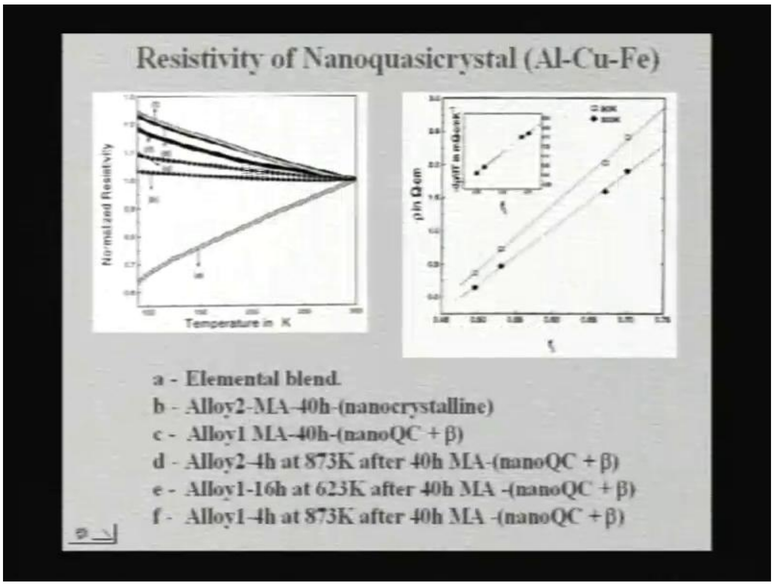
Resistivity of Nanoquasicrystal (Al-Cu-Fe)

a - Elemental blend.
b - Alloy2-MA-40h-(nanocrystalline)
c - Alloy1 MA-40h-(nanoQC + β)
d - Alloy2-4h at 873K after 40h MA-(nanoQC + β)
e - Alloy1-16h at 623K after 40h MA -(nanoQC + β)
f - Alloy1-4h at 873K after 40h MA -(nanoQC + β)

And some other interesting properties other than mechanical properties of these nano quasicrystalline phases are there, what is called semi conducting nature? Usually, most of the crystals are have a metallic nature. For example, if I take aluminum copper iron, all the three elements together, make an alloy and this alloy; I look at it is electrical resistivity as a function of temperature, you see that the electrical resistivity increases in temperature, this is the bottom curve.

That you can see here, but the moment, you make it into a quasicrystalline phase. Then immediately, you see a negative temperature coefficient of electrical resistivity, which indicates that, from a metallic nature, we are converting into a semi conducting nature. People are trying to exploit this nature of these nano quasicrystals also; a lot of work is going on these alloys. But, as melt, just we are more concerned about the mechanical properties. So, we will discuss a little more on those.

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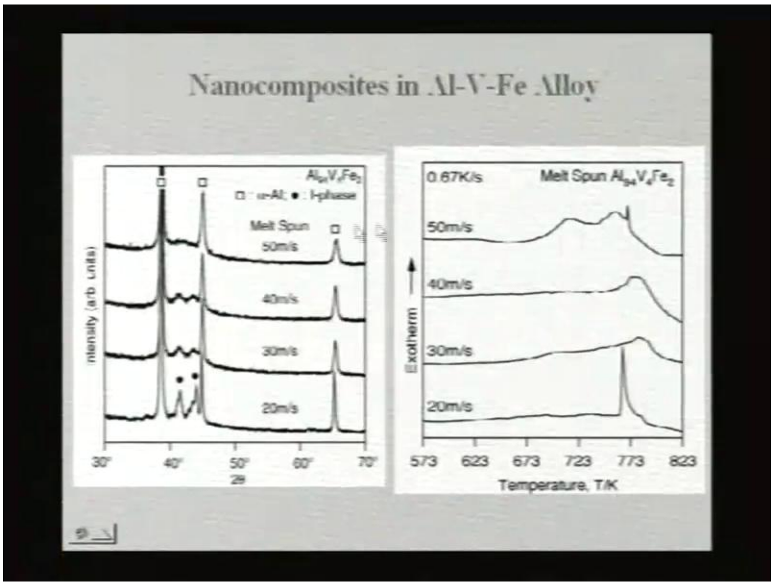

Nanocomposites in Al-V-Fe Alloy

One more alloy system is aluminum iron vanadium, where you can again generate this nano quasicrystalline phases, either in an amorphous matrix or in an aluminum matrix. For example, you can see here, if you take a composition such as aluminum 94, vanadium 4 and iron 2, just a small amount of vanadium and iron only 6 percent of it. Mostly, it is aluminum, if you take that and heat it, I mean cool it by melt spinning at different cooling rates, 20 meters per second, 30 meters per second.

These meters per second, basically mean the linear velocity of the melt spinning wheel. And we already know, that this velocity is related to the cooling rate, the higher the velocity the higher the cooling rate. So, as a result, you can see that at low velocity, what you end up is aluminum peaks plus a quasicrystalline peak. So, you get a mixture of aluminum plus nano quasicrystal here.

If you use a low cooling rate, if you use a high cooling rate, you have amorphous, you get a, you see a broad peak there and aluminum. So, it very difficult to avoid aluminum here, because as you can see, this particular alloy is such that.

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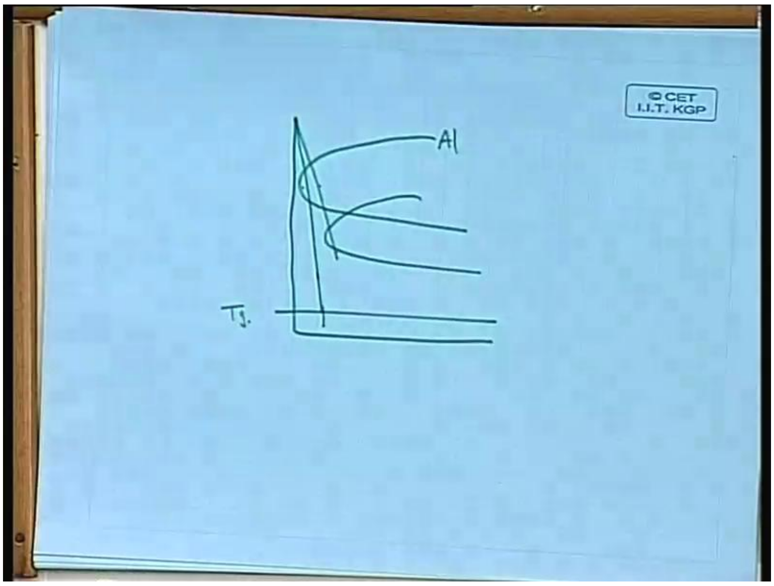

Probably, the aluminum, if I look at this, the aluminum, if it is like this, that it TTT curve for the aluminum. So, whatever cooling rate, you add off, you will always hit this aluminum. And if you choose a cooling rate in such a way, that you get a quasicrystalline phase, you will end up in aluminum plus quasicrystal. If you use a cooling rate, where you do not touch the quasicrystalline phase and go up to the T G.

You will get some aluminum and the remaining aluminum, a remaining liquid transforms into an amorphous phase. And that is what exactly you see here, if you go to high cooling rates, that you will end up in aluminum plus amorphous. If you use a slow cooling rate, you will end in aluminum plus the quasicrystal. If you still use much slower cooling rate like conventional cooling rate, you may not end up in any quasicrystal.

But, ultimately only aluminum plus some inter metallic compounds, which are corresponding to that particular phase diagram equilibrium phase diagram. So, that is what, ultimately you get, so whereas under non equilibrium processing, you end up in these novel micro structures. Such as either a combination of nano crystalline aluminum plus amorphous or nano crystalline aluminum plus quasicrystalline.

And if you look at the D S C, if you use go to higher cooling rates, you get a two peaks basically. The first peak is, where amorphous phase become quasicrystal and the second peak was the quasicrystal becomes crystal. So, you have this kind of, in this, at low cooling rate, you get only one peak, were the quasicrystal, which is there, will give you crystals, so because, there is no amorphous phase there.

So, like that, one can see depending on the cooling rate, one can also get an idea from the D S C, what kind of phases are there.

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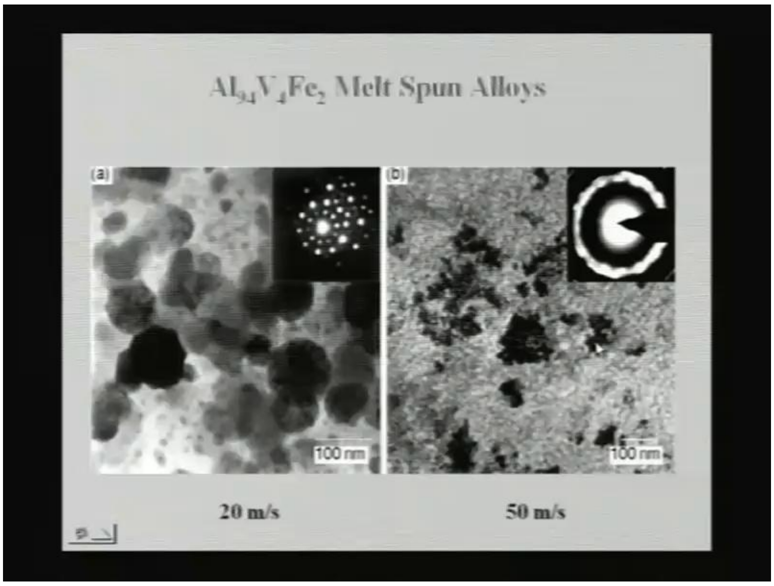

$Al_{94}V_4Fe_2$ Melt Spun Alloys

And look at the TEM images, you can see when you have low cooling rates you have spherical particles of quasicrystal in an aluminum matrix. You have an aluminum matrix with a very fine particles ranging from almost about 5 nano meters, very fine particles up to almost about 70, 80 nano meters. And these are all quasicrystalline, you can see from the diffraction patterns, very easily.

And if you go to very high cooling rates, what you have is an amorphous matrix in which some aluminum grains are there. You can see the amorphous broad ring, with some sharp spots, coming from this aluminum. So, you have amorphous matrix, with those black regions are all aluminum grains.

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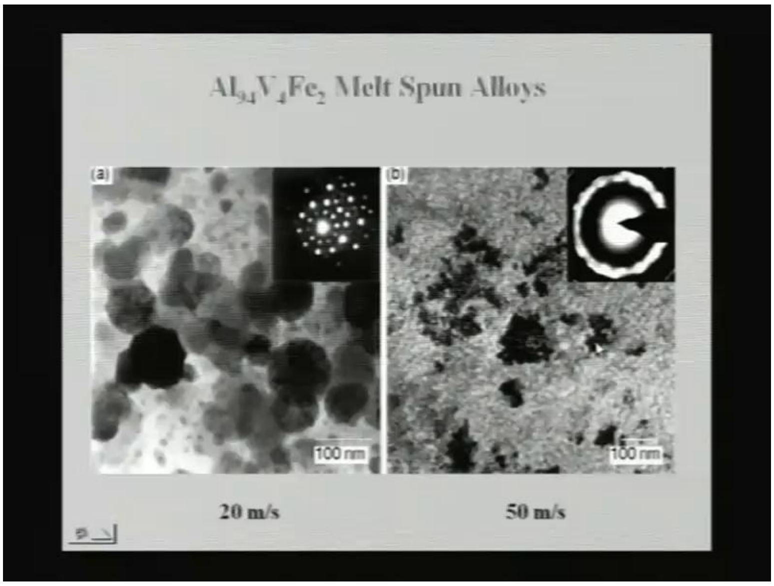
$Al_{94}V_4Fe_2$ Melt Spun Alloys

And if you use different cooling rates, one can get different grain sizes, as you increase the cooling rate, the grain size of aluminum keeps on decreasing. You get much bigger grains here; you get much finer grains here. So, one can achieve finer and finer grains of aluminum at higher cooling rates.

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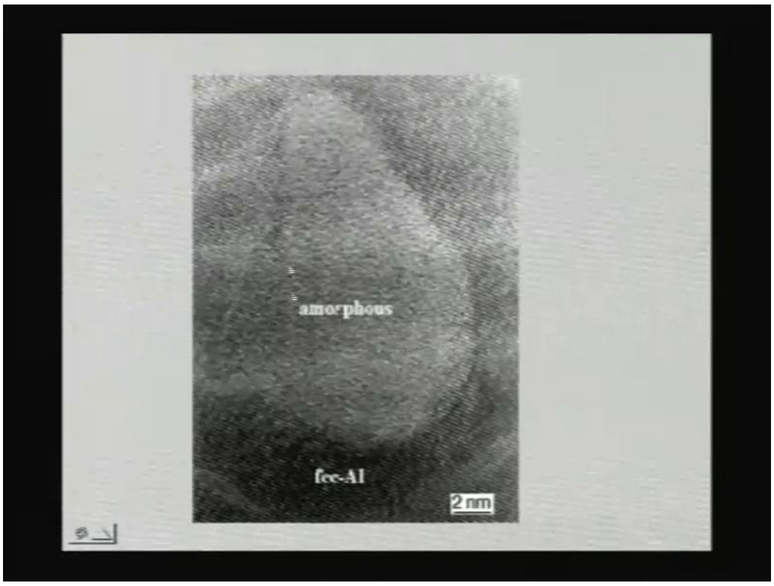

And one can also generate this kind of micro structure, which I told you before. That you can have aluminum inside that a kind of nano particle of amorphous, how do, you get this. As I told you, when the dendrites of aluminum are growing, the liquid is trapped between this dendrites. And when the liquid, which is trapped, reaches the T G, that liquid under goes a glass transition and you get an amorphous phase.

So, you can see nice droplets of amorphous phase in a matrix of aluminum FCC aluminum, one can generate. You can see clearly these are high resolution images and these lattice fringes, those lines that you are seeing, they are all nothing but atomic plains, each of those are atomic plains. And inside the amorphous, you cannot see any of those atomic plains, because there is no regular arrangement of atoms in an amorphous phase. So, everything is random. So, you see a random arrangement of atoms.

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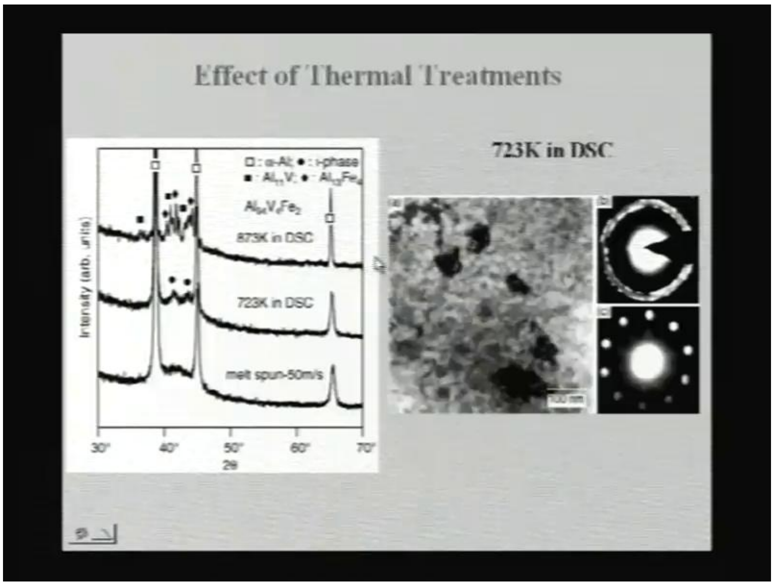

Effect of Thermal Treatments

723K in DSC

And one can also take an amorphous plus aluminum kind of sample, and then heat in a D S C and get a quasicrystal and heat it to still higher temperature, you can get a crystals and that is what you can see here take a sample. And can get very fine quasicrystals precipitated in it and one can get a diffraction pattern. This is called micro diffraction pattern from those particles and can show, yes you can get a quasicrystal in an aluminum matrix.

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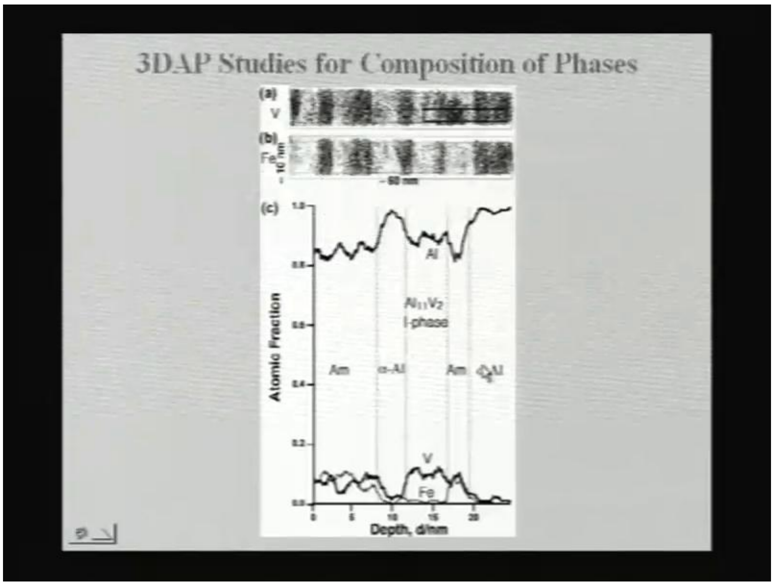

3DAP Studies for Composition of Phases

And one can also find out, what are the compositions of this, this is what is called three dimension atom studies, I have talk to you earlier about this technique, where you really see atoms and whatever dots that you are seeing here, each dot represents an atom. Because, this is an aluminum iron vanadium alloy, here only iron and vanadium map, composition mappings are shown.

Because, if you show aluminum, aluminum will be 94 percent, so everything looks black, because all these parts will completely fill that volume. So, if you look at this and see, there are different domains there. Some regions were the iron is reach, some regions where the iron is pour. Again, another region where iron is reach and if you look at this small box and try to enlarge that box and plot, what is called compositional profiles as a function of depth.

And you can see there is small region, were this is aluminum, this is vanadium, this is iron. There is the small region, where the aluminum is slightly low and another region there, it is aluminum reach. Aluminum reach region is nothing but the alpha aluminum, the low aluminum region is the amorphous region. Because, you will always get amorphous, when there is more amount of alloying elements in it. If you have small amount of alloying element, you will never get amorphous.

In order to get an amorphous phase, you have to keep on pumping it, with large amount of alloying elements. So, usually amorphous phase is that, where you have large amount of both iron and vanadium. And alpha aluminum is that, where you have more aluminum and small amount of iron and vanadium. And you have an icosahedral phase here, which has low amount of aluminum, but large amount of vanadium here, which has a composition equal ant to Al 11 V 2.

This is the phase in this system, which is like a sphere phase. So, it is composition is very close to that, and then you have amorphous and again alpha aluminum. So, you can see there is kind of banded type of micro structures, where some region of amorphous, some region of quasicrystals and some region of alpha aluminum. And such a composite, this is all a nano composite.

Because, the whole thing is in a small domain, for example, if you look at icosahedral phase, it is size; it is of the order of around 5 nano meters. So, we are talking of such a fine nano composite, consisting of amorphous phase and nano quasicrystalline phase and nano aluminum grains. And such a mixture, gives you much higher properties and that is what to see here.

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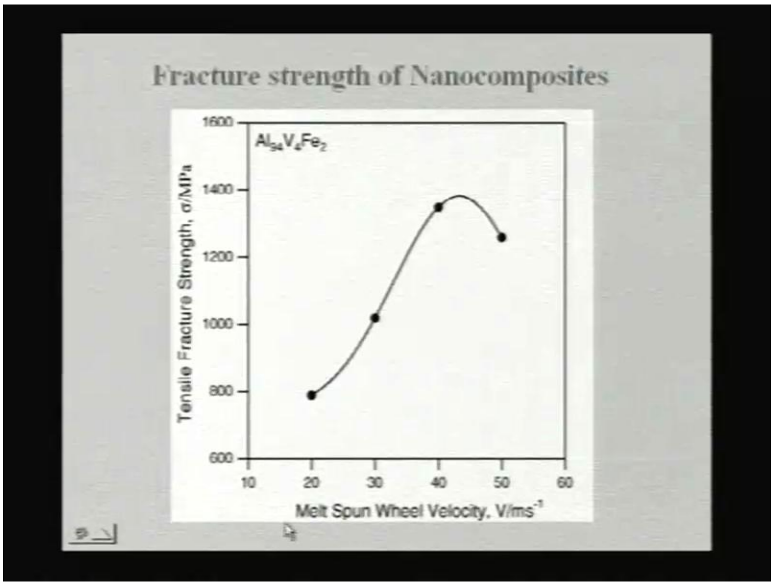

Fracture strength of Nanocomposites

You see here and the tensile fracture strength as a function of speed of milling. You see at low speeds, you get lower strength. Basically, because you have only aluminum plus quasicrystal here, as you keep on increasing aluminum grain sizes decreasing. If you go to higher and higher velocity, you get a lower grain size, because of which the strength goes up.

And if you go to much higher strength, then you get amorphous phase. And once, you get amorphous phase again the strength goes down a little bit. So, as long as you have a combination of fine aluminum grains and nano quasicrystalline phase, you get a much higher strength and that can be shown from the micro structures, what we have seen before.

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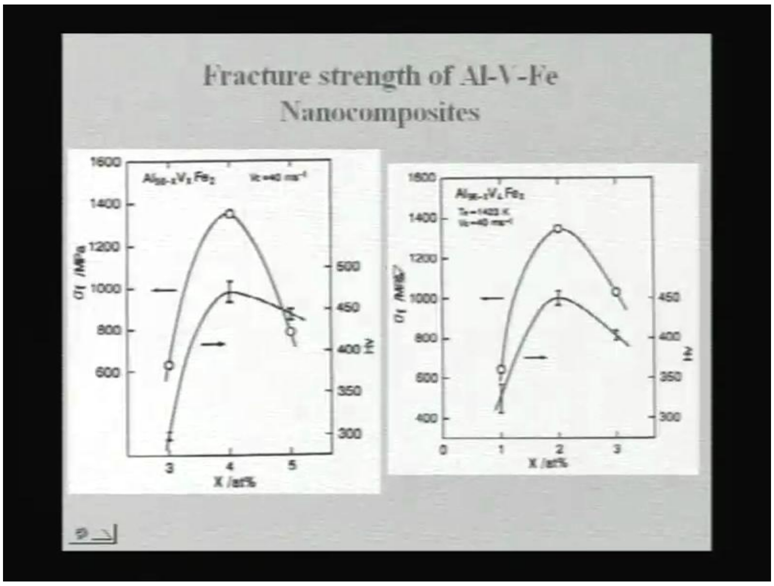

Fracture strength of Al-V-Fe Nanocomposites

One can also study, what happens, if you vary the composition, what we have seen so far is, for one composition, 94 percent aluminum, 4 percent vanadium and 2 percent iron. If you vary the composition, you can see the strength reaches a maximum at 4 percent vanadium. If you fix the iron content and vary the vanadium percentage, you can see, when you reach about 4 percent vanadium, you get the maximum.

Similarly, if you fix the vanadium and vary the iron, again you see, when you have 2 percent iron, you get the maximum. So, aluminum 4 percent vanadium and 2 percent iron is the best, as per as the mechanical properties are concerned. And that is what, we have seen before, whatever micro structures we seen are all for this particular composition.

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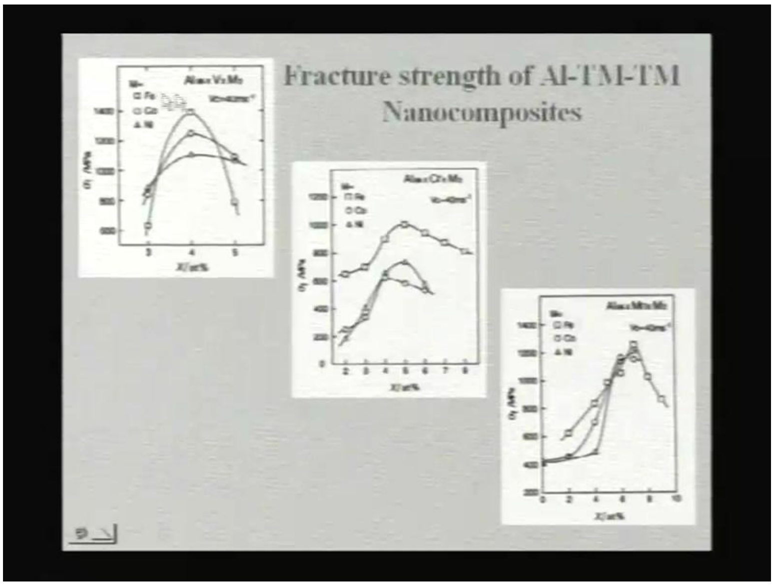

Fracture strength of Al-TM-TM Nanocomposites

One can also study, different other elements, vanadium we have seen. We can also study the presence of chromium, presence of manganese. In all the cases at certain particular compositions, one can achieve highest strength and in all this cases, the strength levels or of the order of around 1 Giga Pascal or even, more than that. So, one can achieve high strength nano composites in all these alloys.

So, you have a aluminum plus transition metal, two transition metals. If you use only one transition metal, you will not end up in this kind of a micro structure. So, at least two transition metals are crucial.

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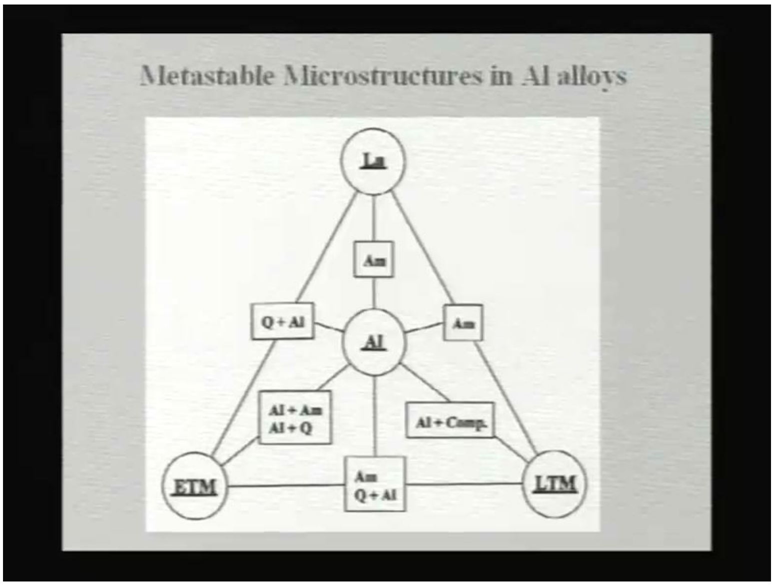

Metastable Microstructures in Al alloys

So, as a summary of this nano composite formation, you can see, what kind of combinations, give you what kind micro structures. If you take aluminum, which is kept at the center and you have lanthanides here, which are nothing but the rare earths. And early transition metals and lead transition metals, if you take the aluminum and combine it with lead transition metals.

If you have only a binary of these 2, you end up aluminum plus compounds. If you take aluminum plus lanthanides, you get an amorphous phase. Aluminum rare earths, I have shown you, a various rare earths, where glass formation can be obtained. If you take aluminum plus early transition metals, you can get aluminum plus amorphous or quasicrystal, depending on the type of alloying element that you choose.

If you choose manganese, you end up in quasicrystalline phase. If you choose iron are you now vanadium, you end up in amorphous phases, like that, if you choose a proper combination of these, you can get that. If you can have a combination of this aluminum plus early transition plus lead transition, you can have a nice combination of amorphous plus quasicrystal plus aluminum.

Similarly, if you can have aluminum plus early transition metal plus rare earths, you can have either quasicrystals plus aluminum combinations. Similarly, if you can take aluminum plus lead transition metal plus lanthanides, for example, I have shown you, the example of aluminum nickel cerium. Aluminum nickel cerium gives you an amorphous phase.

So, like that, one can have examples for all this combinations. We have seen most of these as example before and one can generate a variety of micro structures. And all of them are basically, those which give you high strength and strengths at high temperatures. That is advantage of this. So, you can see starting from aluminum copper duraluminum, we have made a long journey to all these, what you are called the exotic alloys.

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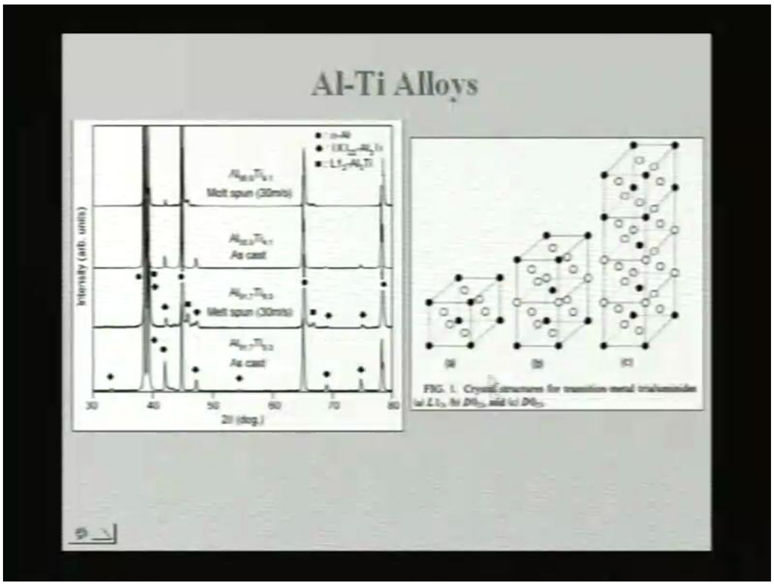

Al-Ti Alloys

So, we also go to other type of nano composites, where there are no amorphous phases, no quasicrystals, just simple aluminum plus nano intermetallics. This is one such example, which started talking about it in the last class, aluminum titanium alloys. I told you, the aluminum titanium alloys have one important aluminide, which is Al 3 Ti. The advantage of Al 3 Ti, when compare to all other aluminides is because, it has large amount of aluminum. It has 75 percent aluminum.

And because of which it has much lower density than any other aluminides and because it is titanium. For example, nickel aluminides, iron aluminides, titanium aluminides, if you look at it, among all these which aluminates have the lowest density, titanium aluminates. Obviously, because titanium is low density, among nickel, iron and titanium. So, titanium aluminum have the lowest density, among the titanium aluminides, you have three types of aluminides, that are possible told you, Al 3 Ti, Al Ti and Ti 3 Al.

So, if you compare these three, Al 3 Ti definitely has the lowest density, because it has highest aluminum amount. So, Al 3 Ti is the best intermetallic as per as the density is concerned, among all the aluminides. So, if one can produce them in a nano crystalline form and chase the crystal structure from the tetragonal structure to a cubic structure. Ordered cubic structure, one can really have a good combination of strengthen ductility and that was one of the objectives of making these alloys.

And you can see, if you do melt spinning of these alloys, one can generate in the normal cooling, if you take the alloy and cool it normally, you get aluminum plus D o 22 Al 3

Ti, Do 22 is the BCT type of structures. And if you rapidly cool it, you get these the L1 to structure. And if you take higher amount of titanium, you get more amount of these L1 to structure.

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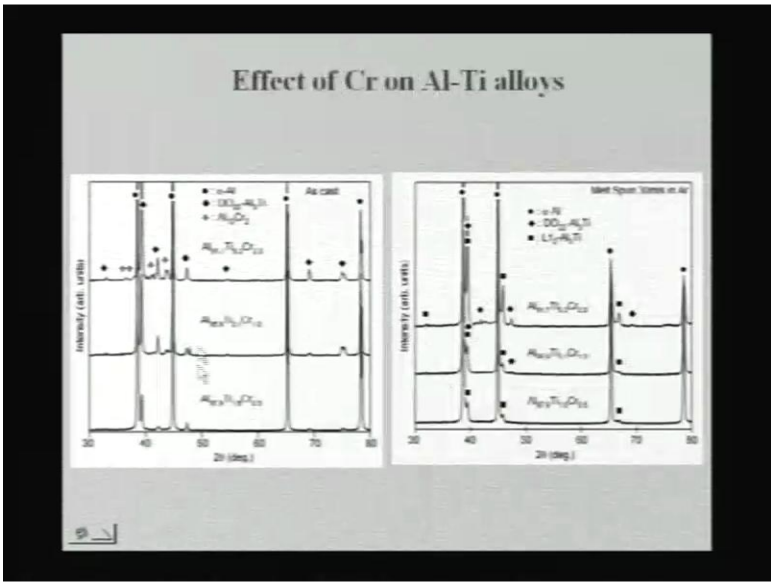

Effect of Cr on Al-Ti alloys

And one can add chromium, as I told you before and as you increase the titanium chromium content, one can produce more and more amount of these L1 to phase.

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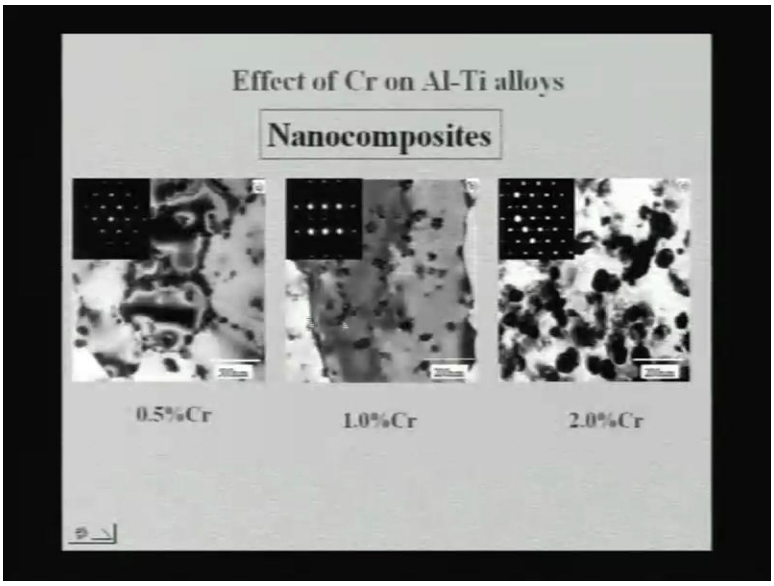

Effect of Cr on Al-Ti alloys

Nanocomposites

0.5%Cr

1.0%Cr

2.0%Cr

And look at these micro structures, you can see fine L1 to particles dispersed in a very sub micron, size of an aluminum grains. For example, you can see the grain size of aluminum is of the order of 500 nano meters; that means, 0.5 microns. It is very difficult to make this by any conventional root. Even, if you do grain refinement of aluminum alloys by inoculation, you never be able to achieve grain sizes less than about 30 microns are so... So, you can see here, one can achieve about 0.5 micron grain sizes and get fine particle here of L1 to Al 3 Ti.

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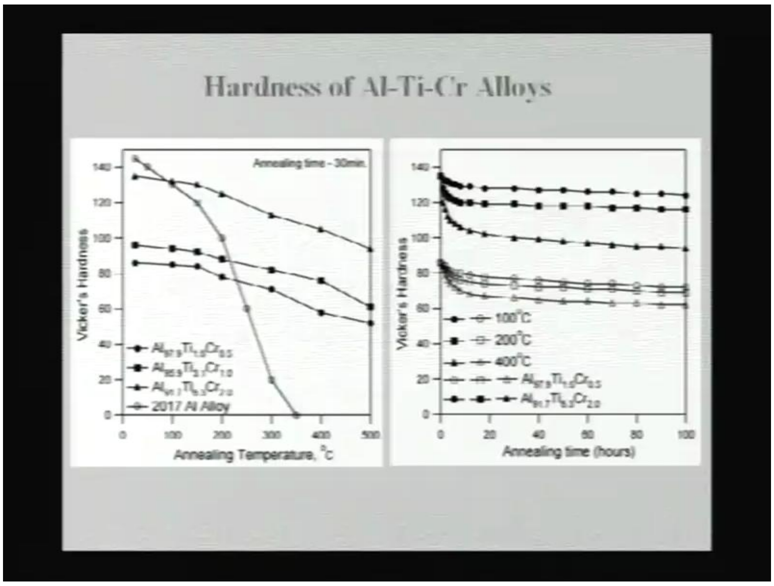

Hardness of Al-Ti-Cr Alloys

And as I told you, strengths can be retained up to high temperature in these alloys, when compare to conventional alloy, such as 2017.

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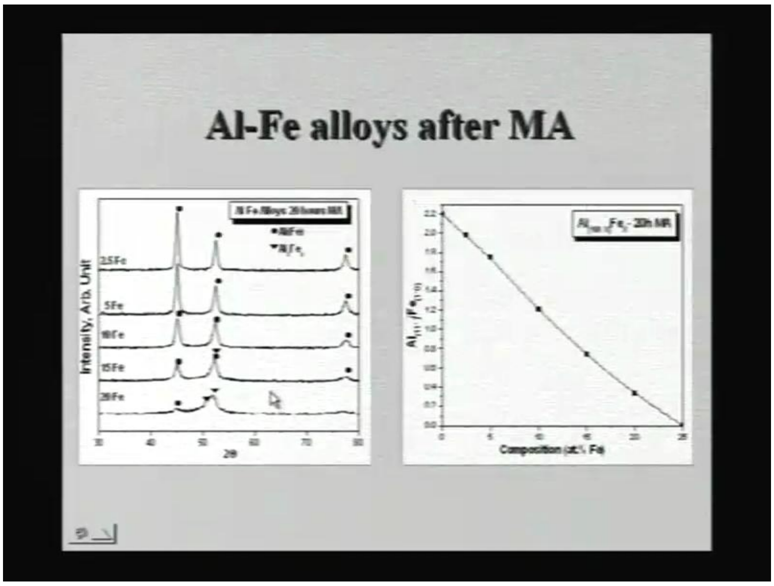

Al-Fe alloys after MA

I will talk about aluminum iron in the next class, will stop here.