Lecture - 25
Super alloys

We have been taking about Super Alloys last class. And super alloys we mention that the major high temperature strength in super alloys comes from two aspects. One is the precipitates, that you are putting in the gamma prime Ni3Al mostly, and some carbides of course. And secondly, the oxide dispersoids, that we are putting it we all know usually that any time you have a precipitate. A precipitate has an inherent problem the, what is inherent problem?

The problem is that it dissolves at high temperature. Because, the precipitate has come from the matrix as long as it has come from the matrix anything that comes out of something has to go back into it. So, provided you provide that temperature and pressure. That is necessary and the time that is necessary for it to dissolve back.

So, if you heat this precipitate, the alloy at higher temperatures for a long period. These precipitates either coarsen are dissolve. So, as a result most of the alloys, where precipitation hardening is used as a main strengthening mechanism, cannot be really used at higher temperature. That is where people tend to use, particularly for high temperature application particles, which do not dissolve back into the matrix. Those are what we call dispersoids. just to differentiate between precipitates, we call them as dispersoids.

But basically, the more or less strengthening mechanisms are similar. Accepting that dispersoids are never coherent or semi coherent, they are always incoherent. Because, they are something which has come from outside they are externally added is it not.

So, they have not been generated from the matrix. So, as a result they are usually incoherent. And incoherent precipitates do not give you high strengthening at the nominal temperature. At the low temperature or at ambient temperature I should say.

So, you use them for high temperature application only, but not really for low temperature application. And this kind of materials, where you add dispersoids intentionally, have been called from time memorial, that they are what are called composites.

We have a number of discomposites. We basically classify these composites as metal matrix the ceramic matrix. And the polymer matrix based on the matrix, one can also classify them, depending on their enforcement that we are using. There are different types of composites particulate composites, fiber reinforce composites, discontinuously, discontinuous reinforce.

Composites or continuous reinforce composites depending on whether the fibers that we are using are sharp fibers or long fibers. Whether they are continuous, from one end of the component to the other end or they are existing, as a randomly distributed fiber kind of reinforcements in a matrix.

So, depending on whether you are looking from the matrix point of view or the reinforce point of you, one can talk of a number of composites, but many of these composites. Particularly if you look at the metal matrix, which as a metallurgies we are more interested in. If you look at this metal matrix composites, most of the composites traditionally, which are made. Are those, where the reinforcement is added externally.

That means, we take a liquid metal or an alloy or the reinforcement particles or any other morphology. Whatever it is, whether it is the wires are the fibers of these or fine spherical particles. Or whatever may be the shape of the shape and morphology of this particles. We are usually we add them externally. And the most common example of that is the aluminum silicon carbide, which is very famous, most of the components now-a-days. Even for example, some of the engine blocks. People are trying to make these with aluminum silicon carbide composites, but there are problems with this; what are these problems if you try to understand.
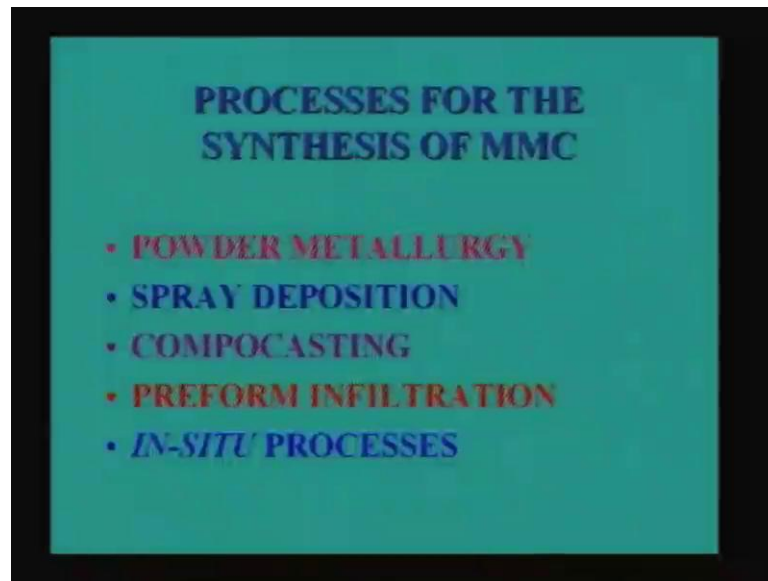
Before we go throw that let us see, how we make composites? Composites are made by a number of routes starting from, what is called powder metallurgy you can take the matrix powders of matrix. And the powders of the reinforcement, and them mix them together sinter them together and you have a composite. And now-a-day's people also do it in a finer scale. What are called nano composites, in a similar way. You make nano composites by mechanical alloying again compact them are sinter them either.

Whether you generates these particles in situ insert the matrix. During mechanical alloying or take a matrix powder. And the reinforcement powder ball mill them together to make them finer and then compact it and sinter them. This is all basically a solid state processing route. Broadly one can call it as solid straight processing route. Whether it is a conventional powder metallurgy root are the recently developed new technique such as high energy ball milling techniques.

So, in all these techniques basically it starts with powders. The other technique is what is called spray deposition. Here also you basically generate powders, but from the liquids. So, in a spray deposition, what you do is you melt the whole alloy, put these particles in that liquid metal. And then spray this liquid containing these reinforcement particles as droplets. And let this liquid droplets condense on some substrate. And then generate whatever component that you are interested in, this is what is called spray deposition.

The number of people are working on such things. And the other thing is call compo casting or this is also called stir casting. Stir casting techniques is basically you again

take the liquid metal, add these particles the reinforcement particles to it stir the liquid. So, that they are uniformly homogeneously distributed. And then pour the slurry into a mold. And then generate a casting out of it. And that casting would be a composite casting. So, this is what is called compo casting. That means you are casting a composite that is why it is called compo casting. Or people also usually call it as stir casting, because you need to stir for the uniform distribution of that.

We will come to it, what kind of problems that we face with this kind of methods. The other method which has become popular is called infiltration technique. The infiltration technique, basically comes, because of the disadvantages in this compocasting. What are the disadvantages? The basic disadvantage is the wettability of the particles with the liquid. Many times, when you have added externally these reinforcement particles to the liquid metal, not every particle has good wettability with the liquid; that means.

That surface energy the interfacial energy of the particle with the liquid is not compatible. In such a way that you do not get good wetting. If the wetting is not good the composite that you are making will have two problems. One is that if the particles are not wetted by the liquid all the particles get segregated. And then either they float or sink in the liquid depending on the densities or even if they are suspended in the liquid, they will gets aggregate to certain regions.

And then what you generate is a casting which will have inhomogeneous distribution of this particles, and then clustering or agglomeration of these reinforcement particles in some regions. So, that you do not have uniform distribution, that is one problem. Second problem is if the wetting is not good. The interface between the particle and the inter and the matrix is not going to be very good. And because of that the load transfer.

When you use this, components in service is not going to be good. And because of which you do not get whatever strength level that you are expecting. Usually whenever we add a reinforcement to the matrix, we except the strength to increase. And we usually use a formula something like this.
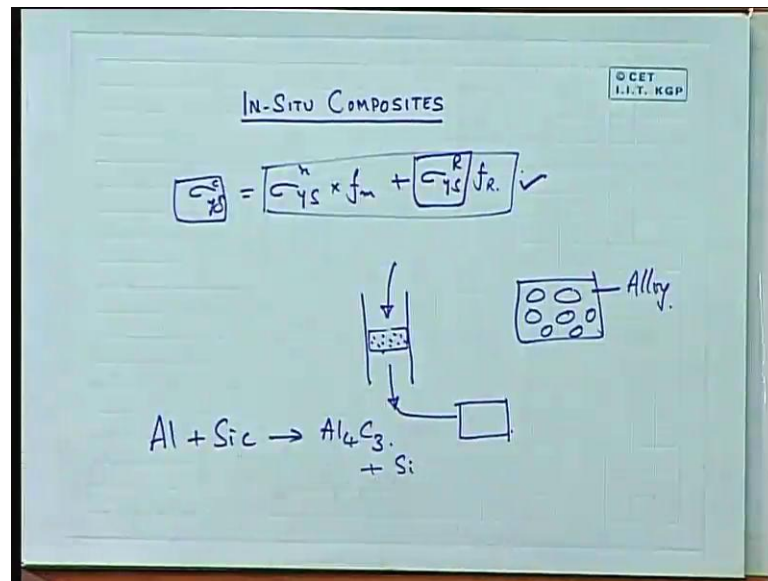
Sigma heal strength of a composite is given by sigma heal stress of the matrix multiplied by the volume fraction of the matrix. Plus the sigma heal stress of the reinforcement multiplied by the volume fraction of the reinforcement. This is what is called role of mixtures, which is not valid in all cases. Under ideal conditions one can use this kind of a thing. And there can be possibilities. And in fact, in reality many times the composite strength does not exactly confirm to this particular equation.

But, is a either higher or lower depending on again the interface strength, if the interface is good if there is a compatibility between the reinforcement particle. And the matrix at the interface, then more or less the load transfer is very smooth across the interface. And hence one can use this kind of an expression very easily. And hence as you can see that when compared to a normal pure metal. When you added reinforcement particle, because the heal strength of a reinforcement particles are much higher.

Because, they are all ceramics their strength level s are very high. So, as a result the strength of the composite is going to be higher. So, this is what we except. So, but that is possible only, when you have a good cohesion at the interface.

And most of the time the particles that, we add do not have good cohesion at the interface. And if that is the case then the stir casting technique is not a good answer to make such composite, because when you try to stir to have a uniform distribution. Still if the particle does not get wetted by the liquid, whatever starring that we you do is of not much of a use.

So, that is why the infiltration has an advantage. Basically, here what you do is you take the reinforcement particles in a tube like this. In the form of a perform all that reinforcement particles inside this. And then pour the liquid from top and try to suck this liquid throw this pre form, using some vacuum pumps. Let us say, there are different types of infiltration pressure infiltration pressure less infiltration.

For example, if you just pour liquid metal on top of this, because of the gravity also the liquid tries to go through this pre form. So, called pre form and if you have the pre form basically containing. These silicon carbonate particles, there are certain pores in the perform. And the liquid goes through that pours. And finally, what you end up is a composite, where all the pours in the preform are field with the liquid metal.

So, you will have the liquid metal engulfing all these particles. So, that you have ultimately a microstructure like this. You have particles and the matrix alloy surrounds the all those particles. This kind of a composite you can achieve more or less uniform distribution of this particles, because here the liquid is passing through the whole pre form. If within your perform if the particles are uniformly distributed, which anyway is guaranteed. Because, you have take an powder particles, compacted the powder particles made a perform.

Only problem is here the volume fraction of the reinforcement particles is going to be much higher than a typical composite. In a normal aluminum silicon carbonate composite. The usual volume fraction of the reinforcement that we add is of the order of 20 to 30 percent, nobody adds more than that, whereas here if you can imagine, you imagine a kind of a close pack spears.

If you imagine close packs pears of these particles, silicon carbide particles. If you assume them to be spherical balls if they are closely packed, and if you have perform which is close pack. What is the extent of porosity that is left out

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26 percent to be exact, because close packing the packing factor 74 percent. We know it from our 2nd year B Tech level. So, 26 percent is our, so you will have 26 percent of matrix and 74 percent of reinforcement in principle, if it is a close packing.

So, how do we solve this problem. And if it is going to be like that, you have more volume fraction of the reinforcement. Definitely the composite that you are going to

make is going to be brittle. So, you are not going to get the advantage of having a metal matrix composite, why do you make a metal matrix composite. So, that we can gain the advantage of the metal matrix, which is a ductile.

So, we want the composite to be both strong and ductile. And that is why we going for metal matrix composites and not for ceramic matrix composites are ceramic. So, the advantage of having metal is lost, if we have that kind of volume fraction. So, there are techniques. Where people try to reduce this volume fraction, can you suggest some ways. How one can reduce this, volume fraction of silicon carbide. By using this kind of a technique, do not change the technique of a infiltration.

If you want to use infiltration techniques and still have lower volume fraction of the reinforcement what you do.

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How do you separate the distance between the particles

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Electro lighting charging, yes any other techniques.

Student: ((Refer Time: 6:48))

Isostatic processing, no if you do isostatic processing they will come closer.

Student: ((Refer Time: 16:52))

Loose powder sintering. There are also methods by which you add some binding agents, which have a tendency to evaporate the movement the liquid metal comes in contact, which have a lower boiling point.

So, you add such volatile matter while compacting or while mixing the powders, and then compacting. So, that you fill up the whole thing with some of those low I mean low boiling volatile maters. So, that the moment liquid metal comes in contact it is lost. So, that those voids, that are left out are field by the liquid metal, there are also methods like that.

So, the basic advantage with this is, yes with this kind of methods. One can control the volume fraction, but more important is, one can achieve uniform distribution of particles without any segregation. But, there are limitation with this also, one cannot produce very

intricate castings. Usually infiltration is feasible, if you are the shape of your casting or shape of the in perform, which is being infiltrated. If it is very simple such as a cylinder or something like that. If it is very intricate a casting, then infiltration becomes more difficult.

So, but one can produce, let us say rods. And further deformed them for any shape of our interest, if you want to achieve various shapes on that. Let us say rods or I know are even people are interesting in slabs, plates, if you are interesting like that. So, this is one possibility. So, there are limitation with this technique, but at that same time one can achieve the more uniformed distribution.

Another problem that come with stir casting is that. The liquid metal has a tendency to react with these particles in a number of cases. For example, if you take aluminum and put silicon carbide into it. There is tendency for the silicon carbide to react with aluminum and form Al4C3 compound plus some silicon comes out.

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This is the problem in stir casting, which can be controlled in infiltration, because in infiltration that time of contact is very short. What we are doing is just pouring the liquid metal, and then sucking it using some vacuum pumps. Let us say if you want to in decrease the time of contact, the best thing is to use a vacuum sucking; rather than gravity infiltration. If you use gravity infiltration the time required for infiltration is very long. So, instead of that if one can use a pressure gradients, to suck the liquid metal, through the perform, one can achieve it very fast.

So, because of this I do not see the, this problem does not existing the infiltration. But, it can be controlled because the time of contact is very short. In a normal a stir casting route root one has to hold the liquid metal for a long period along with the particles, because of which you can have more reaction. So, that is why one goes for infiltration, but as I told you infiltration itself has limitations. And because of which a new technique have come up, which are called in-situ technique.

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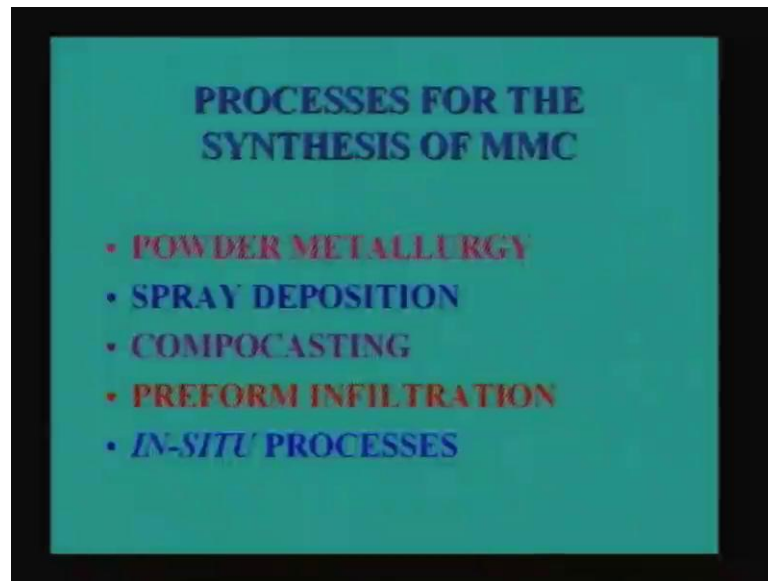
So, in in-situ processes, what we do is we generate these particles in-situ. We will go in detail about this, before that let us look at once again what are the problems of normal MMC's is conventional MMC's.

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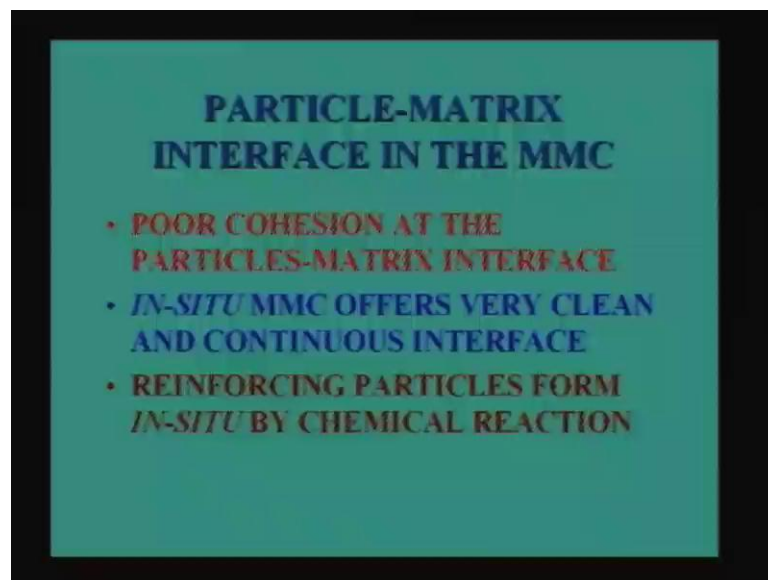
One is the poor cohesion at the particles matrix interface, which we have talked about. And the in case of in-situ MMC's, we have a much better clean interface. Why because, here the particle is coming out of the liquid. The particle is not externally added this is where we differentiate between these composites. One is called ex-situ composites, another is called the in-situ composites. Ex-situ composites are those, where the

reinforcement is externally added. In-situ components are those where reinforcement is generated in-situ.

Then you can say even precipitation hardening is also something like a in-situ composite. Why do not we call that as an in-situ composite, the only difference here is that. In precipitation hardening, the precipitates form in the solid state. From a super saturated solid solution. Whereas, here in the in-situ composites, the particles are coming from the liquid, because of the reaction of this liquid with something else. It is not that liquid is a super saturated solid solution from which it is coming.

So, the liquid is allow to react with certain materials. And the reaction product are these reinforcement particles, which get uniformly distributed in the liquid. And now if you take this liquid containing these reinforcement particles. And then pour it into a mold you generate the required casting and that is what is a in-situ MMC. So, in-situ MMC is are basically generated in the liquid state, whereas the normal precipitation hardening is usually in a solid state. And these are formed by chemical reaction as I told you.

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And a number of applications, where people have already started using these in-situ composites. Such as automobile and we also have helicopter blade sleeves. These are just a few examples I do not say that this is the complete list. And the cylinder liners in the automobiles the seat tracks. Wherever you need high wear resistance and a high strength combination is where we use these in-situ composites.
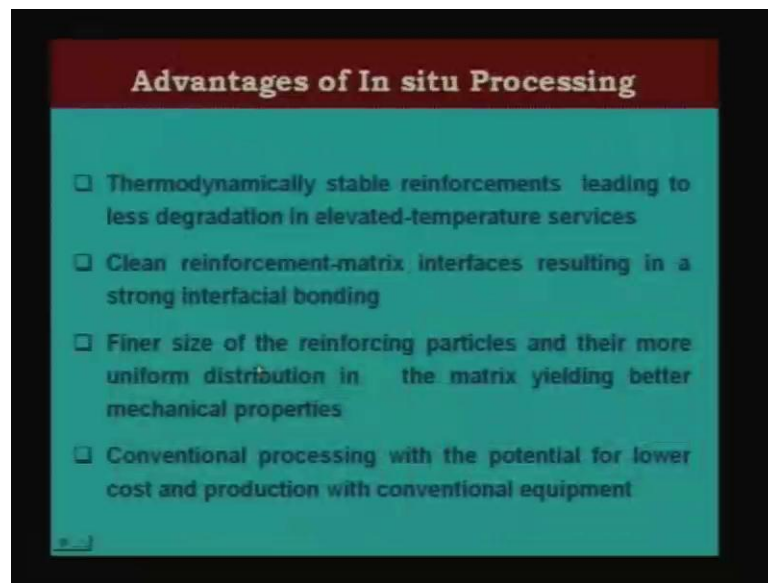
And what kind of advantages you have. A number of them, first of all these particles are stable, because they are coming from the liquid state. So, unless you take the whole composite up to the liquid state. They do not dissolve back. Unlike precipitation hardening, the particles do not dissolve back into the matrix.

So, they are thermodynamically stable reinforcement. And as a result is less coarsening. The tendency for coarsening of these particle are dissolution at high temperatures is very low. Because of which, one can use these composites at high temperature very easily. In addition the reinforcement matrix interface is very clean. And because of which you have a strong interfacial bonding.

You have a strong bonding, because of the clean interface, because there is no what is called the reaction products formation in this cases, because the particle are themselves coming from the liquid metal. As a result there is no reaction between the particle and the matrix itself. So, as a result, you have a clean interface. And one can control the finest of the reinforcement particles, by controlling the time and temperature at which these particles are coming out

Because in a case of ex-situ composites, the size is only controlled by the external particle size, whatever particle size, that you are adding. And in fact, there is a problem when you come to infiltration one cannot use very fine particles. If you use very fine particles then you can see that the pour size become. So, fine then the infiltration becomes very difficult. So, some of the techniques such as infiltration as suitable only

when you want to use larger size of particles. Otherwise if you want to use very fine size if is difficult.

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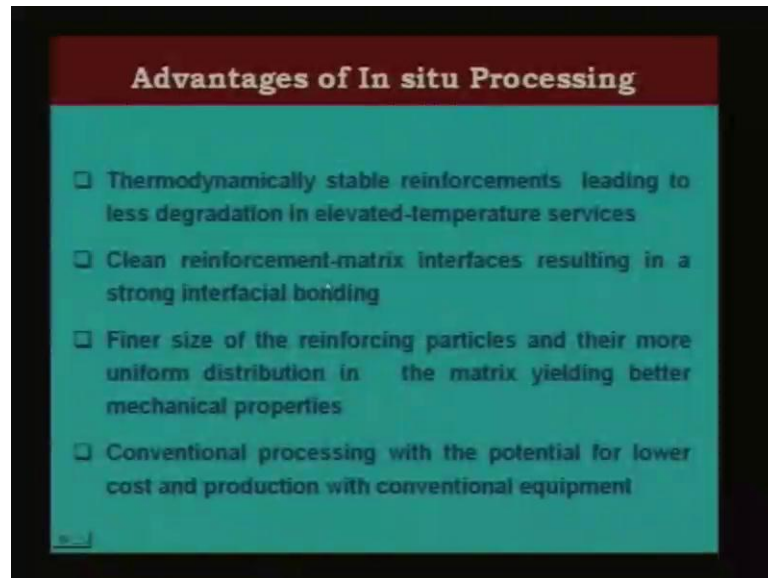
So, fines can be really controlled in this case and one can achieve uniformed distributions. And once you have uniformed distribution you can have uniform mechanical properties. This is one very important think in case of composites if you do not have uniform properties. Then the crack can initiate at any particular place. Where there is a lot of agglomerates of these reinforcement particles, and then the crack can propagate.

So, as result we do not want any agglomeration of particles or segregation of particles at some region. We want a uniformed distribution. So, that the material can achieve high strengths.

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If there is a segregation in the liquid state. That is the segregation, see this reaction once there is a reaction of we will come to know those things. Once there is a reaction of certain chemical with the liquid, there the some particles come out because of the reaction the reaction product. And some of this reaction product get dispersed in the liquid. And some of them because of their low density get floated and go into what is call that draws or the slag.

So, we will talk about those thing, whenever we talk about the reactions. So, defiantly you will have much more uniform distribution, then what you achieve in the executive composites. And another thing is, so this conventional processing with the potential for lower cost and production with a conventional equipment. That means, one can use the normal conventional equipment itself, you do not need any specials tools.

For example, in situ composites can be just melted in a normal furnace. And then pour into any mold of any particular intricate shape. And then generate the casting of a particular shape and that you are interested. So, you do not need to have any additional capital cost, then what you have in case of the typical conventional stir casting route.

In facts, in case of stir casting you need to have a stirrer in this case of in situ composites. Most of this reaction are exothermic in nature be cause of which you do not need any stirring. Automatically there is a lot of stirring that goes on because of these exothermic reaction. So, these are some of the advantages of these in situ composites.

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And we will today look at two types of in situ composites. One is aluminum TiB2 in situ composites, another is aluminum TiC in situ composites. There is a lot of work going on now-a-days on aluminum base in situ composites, because people want some alternative for aluminum silicon carbide.

Because aluminum silicon carbide, we know that there are problems. Because, of two things, one is a reaction that we have talked about the formation of Al4C3. Second is the

lack of compatibility of the particle with the liquid, because of which you do not have good cohesion at the interface.

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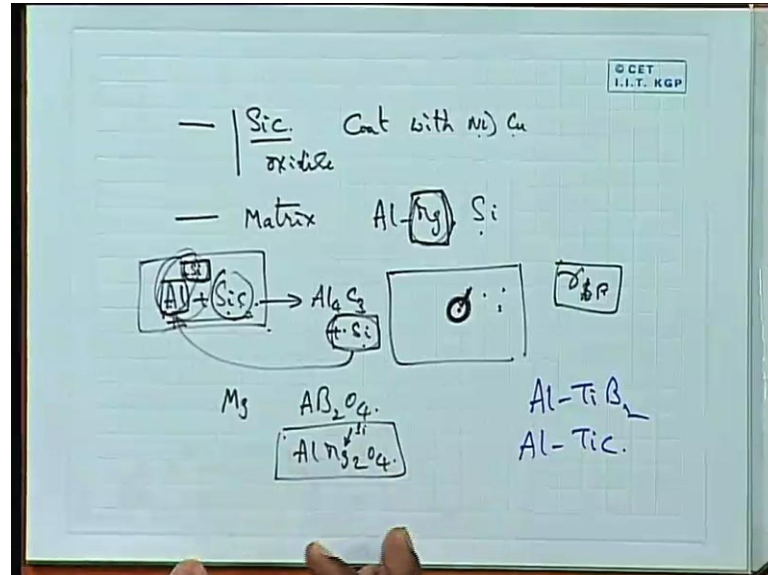
People try to overcome this by two ways, one is to modify the particle. For example, if you take silicon carbide particle. And then coat it with various metals, such as nickel copper by electroless coating or electro plating kind of techniques. We cannot use normal electro plating, because the particles themselves are not conducting in nature.

So, as a result you have to use other methods such as electro less coating techniques. Where people coat nickel copper and other elements. And now once you take this coated silicon carbide particles and put it into an aluminum matrix. Aluminum liquid matrix comes in contact not directly with the silicon carbide particle, but with this coating.

So, as result the metal, metal bonding is much stronger. So, as a result there can be a better cohesion between the particle and the matrix. So, this is one possibility, where the reinforcement particles is modified. Other possibility also is to oxidize silicon carbide, a number of people have taken silicon carbide particles. And oxidized the silicon carbide particles. And once you oxidize it you develop a surface oxide coating. And an oxides silicon oxide has a better wetting with aluminum then silicon carbide itself.

So, as a result you can have slightly better cohesion at the interface. So, this is another route people have tried. These both of these are basically manipulating the particles. People also try to manipulating the matrix, how do you manipulating the matrix by adding certain alloying elements, which can improve the cohesion.

So, when every we talk of a cohesive. Basically it is a interfacial energies that are important, when you think of a liquid and particle inside. What is important is the interfacial energy between the particle and the matrix. So, gamma l p or gamma L p gamma liquid particle interfacial energy.

And this gamma liquid particle interfacial energy depends on. What is the composition of the liquid; obviously, and also what is the nature of this particle. So, as a result if either one can modify this particle or modify the matrix. So, that one can have a better interfacial energy and have a better cohesion at the interface. So, people for example, people know that, if you can take aluminum add some magnesium to it or add some silicon to it. Silicon carbide is more coherent or more compatible with aluminum, silicon matrix or aluminum magnesium matrix, then the pure aluminum itself. This is one of the experimental observations a lot of people have made. And so know a day's people try to not make aluminum silicon carbide composites with pure aluminum itself. And the that instead of that people try to make aluminum magnesium, aluminum silicon alloys. And then add silicon carbide this is one reason.

Second reason is that the reaction of aluminum, which silicon carbide this decreases, if you have silicon already inside in the aluminum. If you take a aluminum silicon alloy melt. And then put silicon carbide particles into it. The reactivity of silicon carbide with aluminum silicon matrix, is going to be much lower than the reactivity of silicon carbide with aluminum.

So, that is another reason way. So, the reaction between these two particles, particles and matrix is also decreased when you add silicon to this.

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The reason basically is that when you take a pure aluminum. So, the reaction of this two basically depends on the activity. When you have silicon in a in the aluminum already there is some activity of silicon inside the aluminum. So, as a result this reaction progressing in this direction gets reduced. So, because you see, there this fraud the reaction generate silicon. So, if you already have a silicon here. So, the kinetics is of this reaction gets hampered.

So, as a result this reaction will not occur, so fast the way it occurs in pure aluminum. Because in a pure aluminum silicon comes outs the this back goes back in the silicon. So,

already there is silicon in this aluminum. So, as a result you can see that this reaction does not progress.

So, similarly the magnesium another thing people have observed is that, there is magnesium it forms what is called as a spinal. Do you know what is the spinal, what it is composition.

Student: ((Refer Time: 34:41))

AB2O4 fantastic, it is a AB2O4 type of structure and what is this A, and what is this B? It is AlMg2O4 with some silicon in it. So, what happens is this a magnesium this compound forms at the interface between the silicon carbide and the matrix. And then prevents the reaction of the silicon carbide with the matrix. And the formation of the brittle Al4C3 phase can be avoided.

So, as a result. So, magnesium helps in improving the vet ability of the liquid with a the silicon carbide. In addition magnesium also has a tendency to change the surface tension of the liquid aluminum. So, that, the wettability can be further improved. So, there are two advantages of adding magnesium, one the formation of the spinal, another the change of the surface tension.
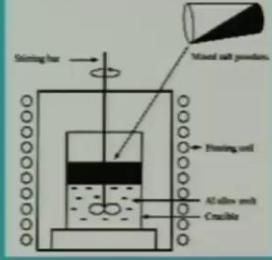
So, because of this aluminum silicon carbide composites are still being worked out by making this kind of modifications of either the matrix or the reinforcement particles. So, that one can generate still aluminum silicon carbide composites. But, there is a lot of tendency to develop newer composites, which are called the new generation composites.

And two examples of that is aluminum TiB2 and aluminum TiC. We will try to see some results of this work people have been doing in this particular direction. If you look at aluminum TiB2 people have try to make composites with pure aluminum, as the matrix. Aluminum copper as a matrix or aluminum silicon as a matrix.

The advantage of taking aluminum copper as a matrix is because you can have precipitation strengthening also in addition to the reinforcement particles, that you are adding. So, one can have a combined effect of both the precipitates and the reinforcement.

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So, as a result aluminum copper alloys particularly aluminum 4 copper alloy. If you take it and add the TiB2 particles, one can have much better strengthening that one can achieve, when compared to pure aluminum. Similarly, aluminum 7 silicon in aluminum 7 silicon. We already know that silicon gives you strengthening. So, as a result one can have additional strengthening, because of that. And how do people make it, they again take a liquid aluminum in a crucible. Add certain salts which react with this liquid aluminum and then generated the TiB2 particles.

And if you want to improve the reaction one can use steering, but this is not essential, because this reaction itself generates a lot of heat, because of the exothermic nature of this reaction.

Routes to incorporate *in situ* TiB$_2$ particles

Mixed Salt Route:

Employs the addition of mixed salts into the melt at the reaction temperature to form the in situ particles

$$Al + K_2TiF_6 + KBF_4 \longrightarrow Al + TiB_2 + KAlF_4$$

Master Alloy Route:

Employs the addition of Al-Ti and Al-B Master Alloys prepared separately to form the in situ particles

Al-Ti Master Alloy $\quad Al + K_2TiF_6 \longrightarrow Al_3Ti + KAlF_4$
Al-B Master Alloy $\quad Al + KBF_4 \longrightarrow AlB_2 + KAlF_4$

Final Composite $\quad Al_3Ti + AlB_2 \longrightarrow Al + TiB_2$

What are these reactions? The reactions are like this, the salt that are usually use are two types are salts. One is called K2TiF6 and another is KBF4. If you careful see one has titanium unit, another has boron unit. So, you are adding two salts, two liquid aluminum one containing titanium another containing boron. And when you add to these two salts to aluminum the reaction of this two salts.

With aluminum is vigorous and exothermic in a nature. And that leads to the formation of TiB2. And gives some kind of a slag or draws which is nothing but KALF4 and which can be separated from the liquid metal very easily. And this is one of the techniques which people use, which is called mixed salt route. That means, by adding the two salts together to the aluminum.

Another possibility is what is called master alloy route. That means, you separately make aluminum titanium and aluminum boron master alloys, how take aluminum plus K2TiF6. When you take these two and react them together. The titanium that comes out of the reaction reacts with the liquid aluminum an forms Al3Ti and the KAlF4 comes out.

Similarly, when you react aluminum with the KBF4 the boron will react with aluminum and forms AlB2. And if you take these two master alloys and them re-melt them together. What you see is that this Al2Ti reacts with the AlB2 at high temperatures and you ultimately end up in TiB2.

So, one can either use this technique or this technique only thing is a commercially this technique is more viable then this. Obviously, you can see here you have to melt it three

times to master alloy have to be made and the two master alloy have to be re-melted together to get this. So, as a result this is much better alternative.

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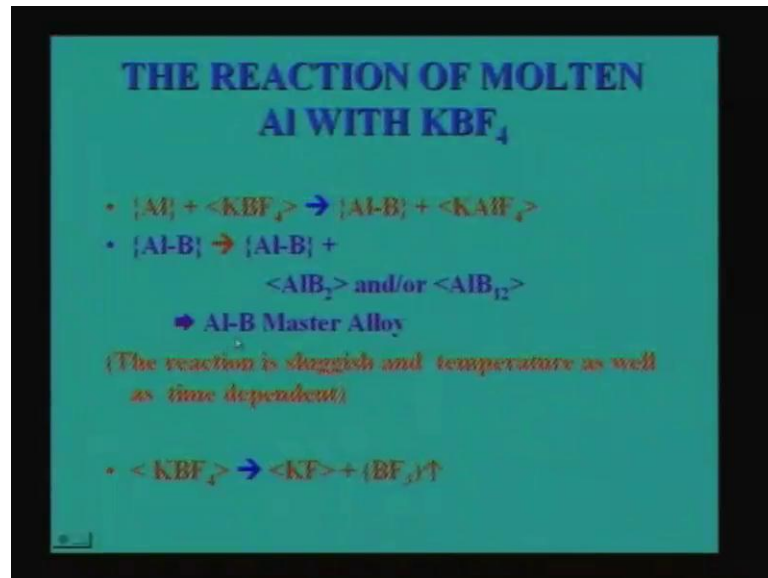
And the reactions are like this, if you look at it carefully. Aluminum when it reacts with KBF4. First thing that happens is the boron is rejected out of the KBF4 and goes and dissolves into liquid aluminum. And are the boron keeps on dissolving into liquid aluminum. Once it crosses the solubility limit, in a liquid aluminum boron is soluble up to certain extent. It cannot dissolve to whatever extend that you want.

So, there is a certain solubility. Once the solubility is reached at that temperature the AlB2 or AlB12 comes out the depending on the temperature. At high temperature AlB12 comes out, at low temperature AlB2 comes out.

So, that is how you can make a aluminum boron master alloy. Another problem with this technique is that the KBF4 has a tendency to dissociate into KF plus BF 3, where the BF3 is a gas. And this gas can escape out of the crucible. If it is escape the outs of crucible. Then all the boron is lost, because you can see here KF does not contain any boron. So, only BF3 contains boron.

So, as a result before this gas escape out of the crucible, it has to react with the aluminum. If it does not react with the aluminum before it escapes. So, you lose lot of boron. So, one has to control the process carefully. So, that you do not have loss of boron this is one problem with the aluminum KBF4, then the second reaction, if you look at it aluminum K2TiF6x.

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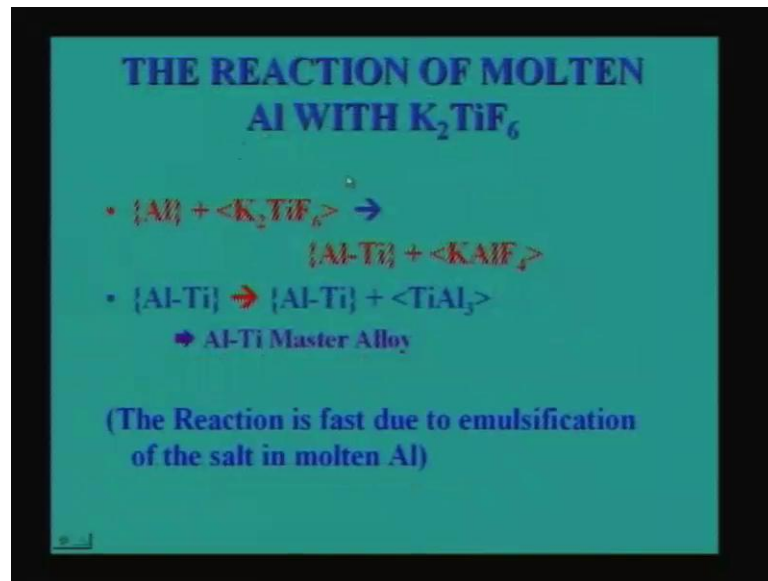
Here again the same process, first the reaction occurs and the titanium is released. And this titanium dissolves into aluminum. And once the solubility is crossed you get the Al3Ti or TiAl3. And that is what is called an aluminum titanium master alloy, where you will alpha aluminum which is the matrix and the Al3Ti particles. And this reactions is very vigorous and highly exothermic in nature and very fast reaction this occurs.
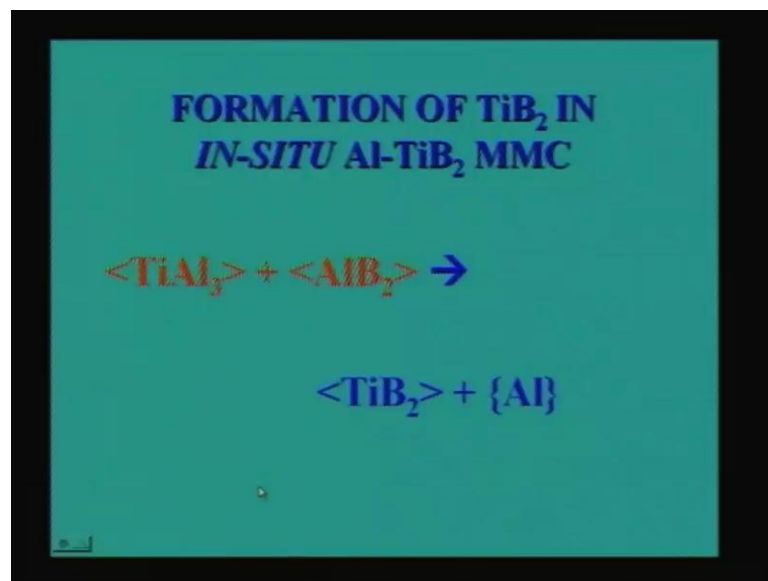
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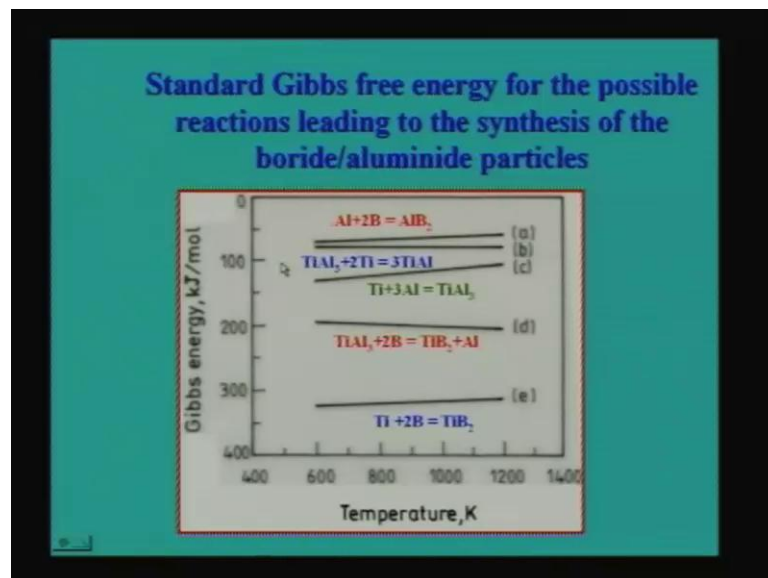
And if you look at the thermodynamics, according to thermodynamics the TiB2 is most stable phase. When compared to AlB2 are TiAl3, this TiB2 is the most stable phase; that means, if you have Al3Ti and AlB2 together. At any given temperature there is a

possibility of these two reacting together and forming TiB2, because you can see the Ellingham diagram, which shows clearly that this TiB2 much below, then all these reactions. This is the top one is for the aluminum reacting with the boron giving you AlB2. The next one is TiAl3 giving to TiAl. This happens at high titanium contain, because we do not add that much titanium. So, we do not go into this regime at all, then the titanium plus aluminum giving TiAl3 and TiAl3 reacting with the boron and given TiB2. And this is titanium reacting with boron giving you TiB2. So, if you look at that TiB2 is the lower free energy.

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So, as a result if you put this together, you can definitely get TiB. That is what thermodynamics tells you.

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Al-3.45Ti (800°C-60 min)
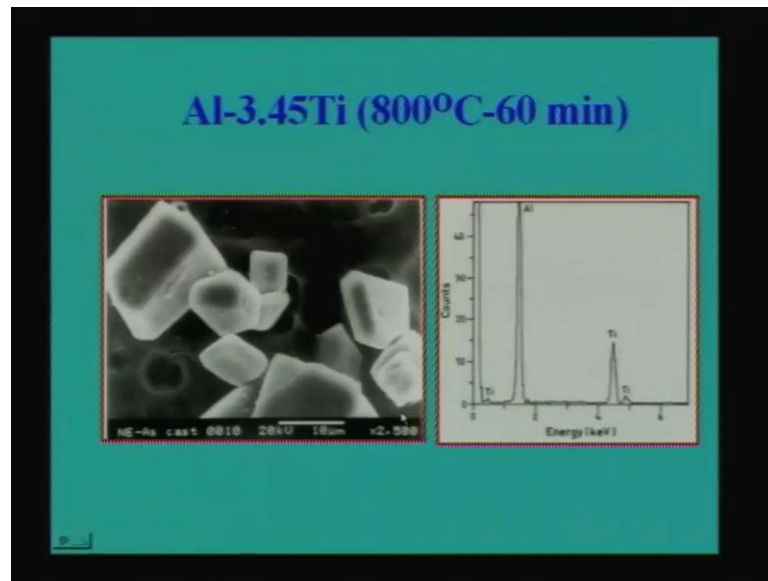
So, this is what people have done. What they done is, they made an aluminum titanium master alloy by reacting aluminum with K2F6 at certain temperature, this is 800 degree for 60 minutes. And you end up in a composite like this, you can call it as a composite, you can call it as a master alloy, whatever you want to call it.

It has a matrix aluminum plus particles. What are these particles TiAl3 particles because this is aluminum titanium alloy. And one can do X-ray diffraction and one can do edact this an example of the edacts taken from one of this particles and it shows aluminum plus Ti. And if you do quantitative analysis of this you will see that it has 75 percent aluminum and 25 percent titanium. So, these are all TiAl3 particles one can conformed this.
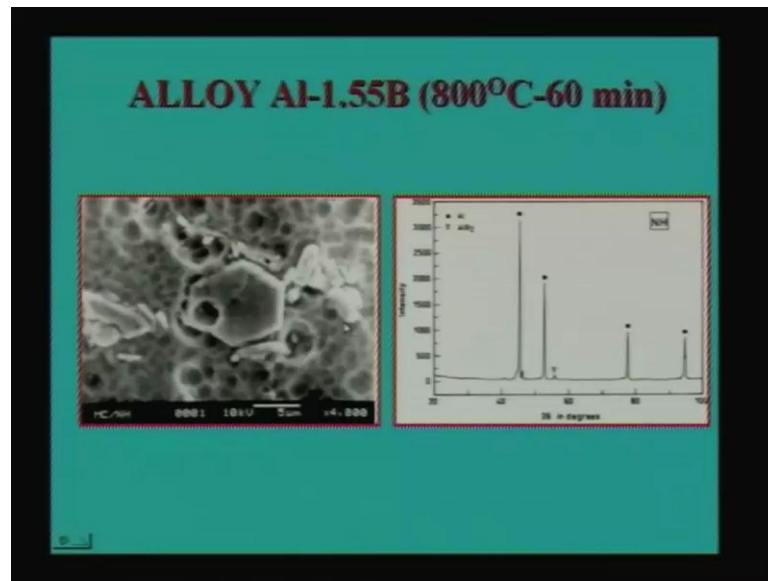
And similarly one can take aluminum and the react it with KBF4 and one make aluminum boron. And these particles are AlB2 and one can do an X-ray and you can see these is an X-ray of such a composites are master alloy, showing aluminum peaks. And AlB2 peaks saying that yes this alloy has AlB2 plus aluminum.
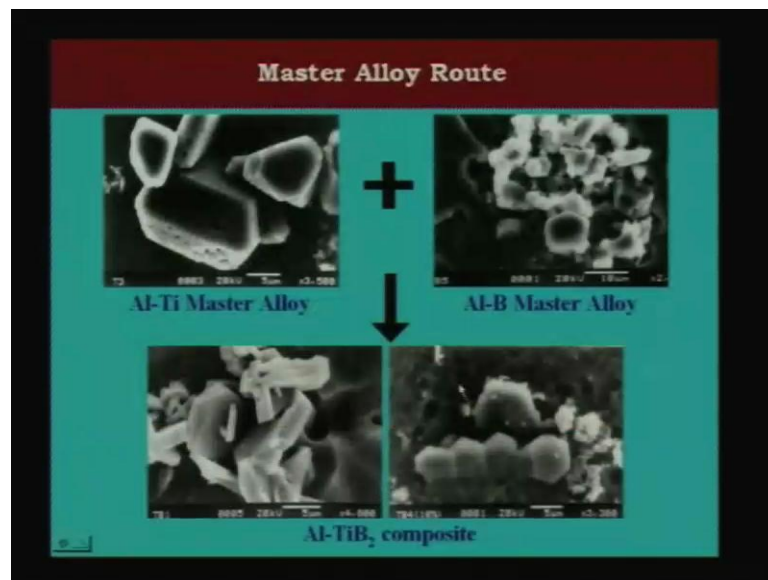
And now what we do you take a mixture of these two fellows. The two master alloys, one is an aluminum master alloy, aluminum boron master alloy react them together, at about 1200 degrees centigrade or 1000 degree hundred centigrade. A minimum of 1000 degree is enough is a required for such reaction and you end up in TiB2 particles.

And TiB2 is hexagonal crystal structure. So, one can easily see these particles with the growing on their basal particles. If you carefully see all of them will have hexagonal morphology.

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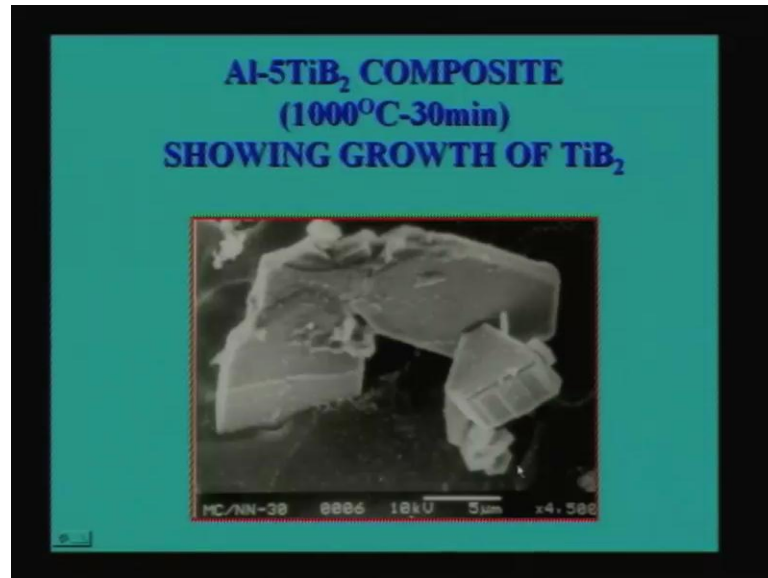
And this is how they grow depending on the direction at which you crack the particular plate. The growth morphology is almost like this. And one can generate the TIB two particles of different morphology is depending on the temperature at which you make.

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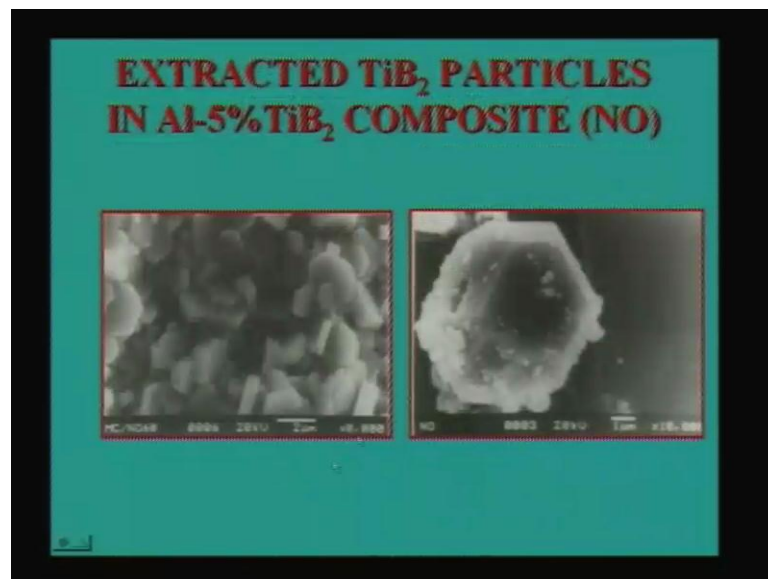
And one can also do one thing, the take this composite and extract the particles out of the composites. how do you extract the particles out of the composites. If you want to extract a particles reinforcement particles out of the composite what will you do.

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If you heat it, will they come out.

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Anybody who has been working to some extent on composites should know this. In any composites, if you want to a extract the reinforcement particles. You have to dissolve the matrix. For example, in aluminum matrix composites, you can easily dissolve in aluminum in a sodium hydroxide solution.

So, take a sodium hydroxide solution, put this composite into it, immediately aluminum dissolves and the particle will remain. And take all those particles and look at them in you can see clearly all this disk shaped particles. And this is the external morphology of these particles.
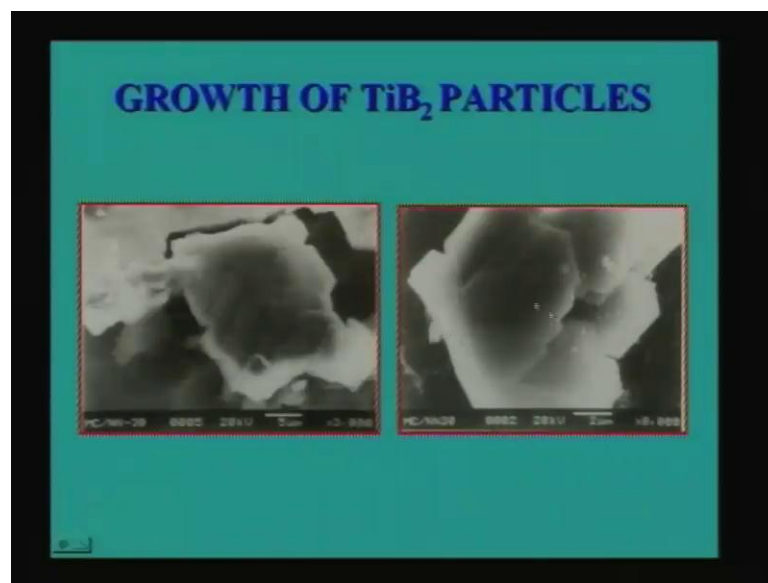
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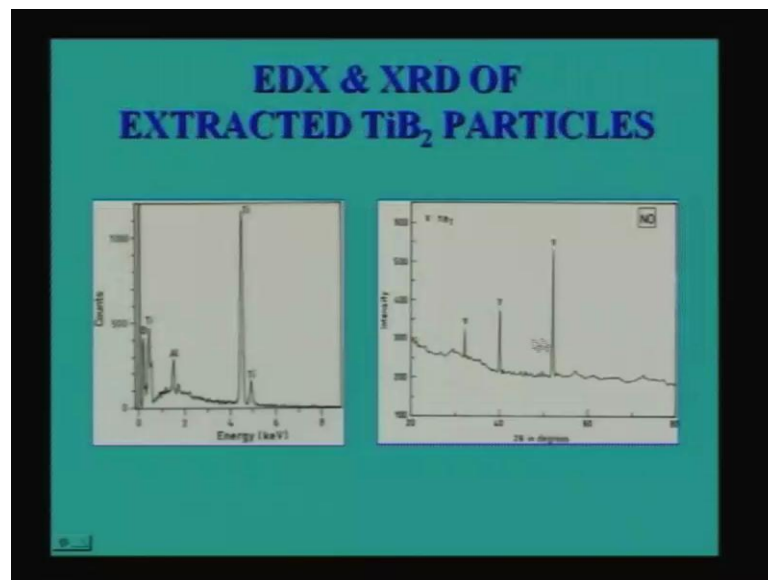
And one can do an X-ray of these two particles and show that these are only TiB2 nothing else. Because now will not get matrix peaks. Earlier if you take the composite and do an x-ray you will have the matrix peaks. And also the particles peaks, here you are doing only the particles. So, you can see the particles peaks only will appear.

So, all the peaks will be TiB2, this is how one can confirm whether there are also TiAl3. The problem with this kind of composite making is that there is always tendency for the formation of Al3Ti. Because whenever you are making a composite, there is also aluminum liquid and titanium there. So, titanium and aluminum can react together and from Al3Ti.

If you do not control your temperature and composition and time properly. So, as a result you might end up in composites, which contain both Al3Ti and TiB2. And Al3Ti is a more brittle phase because it has a body centered tetragonal kind of structure. So, as a result people want avoid Al3Ti and Al3Ti is much bigger particles usually about 20 to 30 micron size where as the TiB2 particles you can look at this. This is a two micron bar. So, the particles are of the ordered of the one to microns. So, very fine particles. So, one was to achieve this kind of microstructure.

So, which is possible only if you can suppress TiAl3 formation. So, how to show TiAl3 has been suppressed by extracting this particles and doing an X-ray and show at only TiB2 is there and there is no Al3Ti. If the particle also contain Al3Ti, then the X-ray will show the present of those Al3Ti peaks. So, one can do like that.

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And one can show that these particles, basically grow on basal plane in a lead structure.

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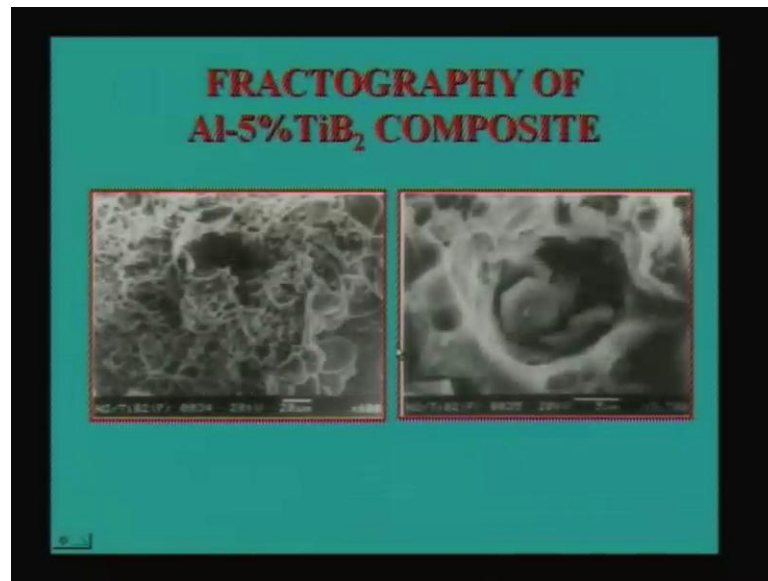
And what is important to know is that these composites are more or less ductile. We can see the dimpled fracture that you see. That indicates they are not only strong, but also ductile. And you can see those TiB2 particles in those dimples.

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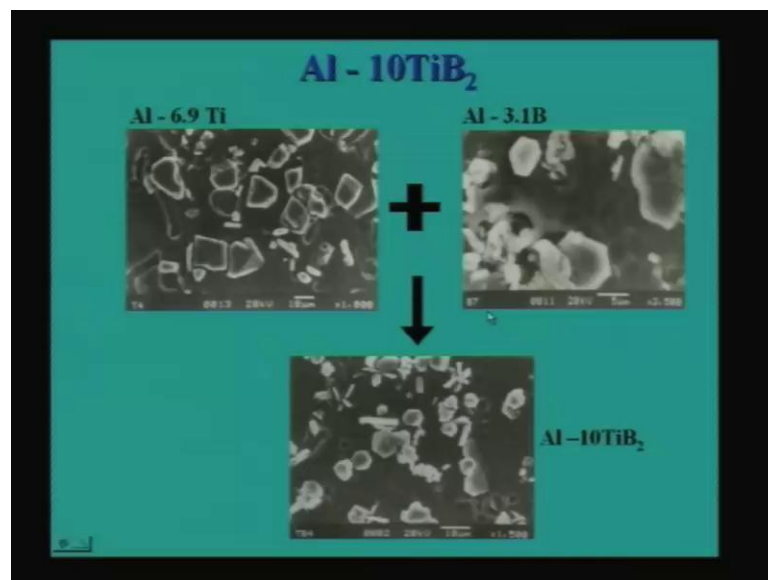
So, which clearly show that yes one can have these composites, which sufficient strength. We will talk about the strength a little later and the ductility. And one can also make higher volume fraction of this particles. This is whatever I have shown you earlier the 5 percent this is with 10 percent volume fraction people can also try higher up to 20 percent or so.
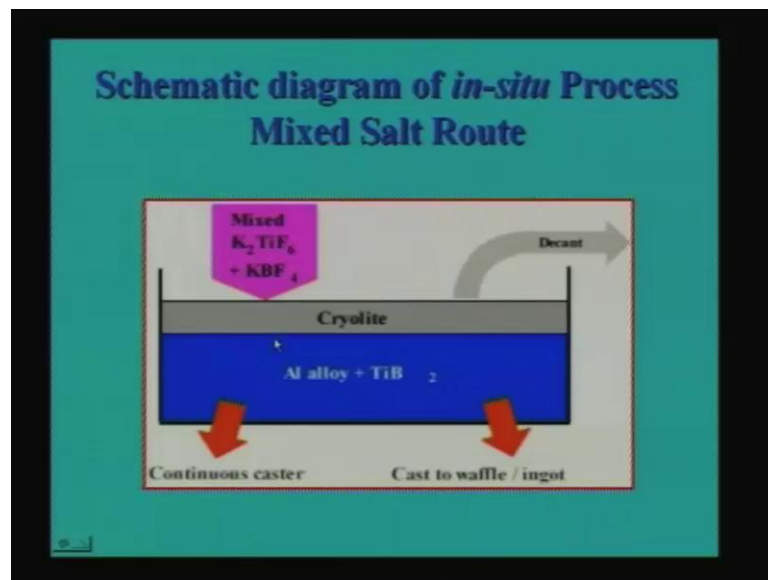
And again for this also one can make aluminum titanium, aluminum boron mixed them together and make aluminum 10TIB2 kind of composite.

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And this is the composites again.

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And this is a other route, which what is called mixed salt route, where the people add the a mixture of the two salts. Whatever we have talked, so far this is what is call master alloy route; where you separately make the aluminum titanium and aluminum boron mixed them together and make the final composites.

Here what you can do is take liquid aluminum and add the K2TiF six and KBF4 salt. And finally, get TiB2 particle out if it one can also study this. We will take about this in detail in the next class.