Advanced Materials and Processes
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Lecture - 26
In - Situ Composites Part – I

Today's class, this is basically a continuation of what we have been talking, in the last class in Situ Composites. We said some of the most advanced composites, particularly metal matters composites. We are dealing with are what are called in situ composites, which people call them as the new generation composites.

Basically because most of the composites made, so far till at least 5 years back are all ex situ composites, where you externally add a reinforcement. Whatever may be the type of reinforcement, whatever may be the morphology of the reinforcement. Whether their particulates or fibers, short fibers, long fibers, continuous or discontinuous fibers. All of them are usually externally added to a melt containing the alloy. That you are interested in, which is the matrix

So, the present trend is to come up with reinforcements, which are generated within the liquid. So, that one can avoid all the problems that we have with the ex situ composite. We have talked in the last class what are the various problems with ex situ composites, particularly the wettability problem. Second the formation of reactive compounds or the interface, which make the whole alloy whole composite very brittle. And the load bearing capacity of the composite comes down.

So, because which, the in situ composites have become very popular. So, yesterday's class are the last class we have started with aluminum T I B 2 composites. And aluminum T I B 2 composites can be made by two roots. One you can because there is Ti and B involved. In this titanium and boron, which is there in the T I B 2. One can make a aluminum titanium alloy and aluminum boron alloy separately. And then add them together re mail that two together to make a T I B 2. And we have shown in the last class that thermodynamically T I B 2 is more stable than Al3Ti and AlB2.

So, because of which if you take a aluminum titanium master alloy, which will contain Al3Ti particles and aluminum matrix. And aluminum boron master alloy, which will contain AlB2 particles and aluminum matrix. You take these two and re melt both the casting together at high temperatures of the order of about one thousand or more than that.

Then you will see both the castings melt. And in the liquid you have now Al3Ti particles and T I B 2 particle suspended. I mean AlB2 particles, which are suspended which have a tendency to react with each other to give you T I B 2. And that is how you end up in aluminum T I B 2 composites. And that is what this picture shows you here, this is what we call the master alloy route. In the master alloy route what we have is…

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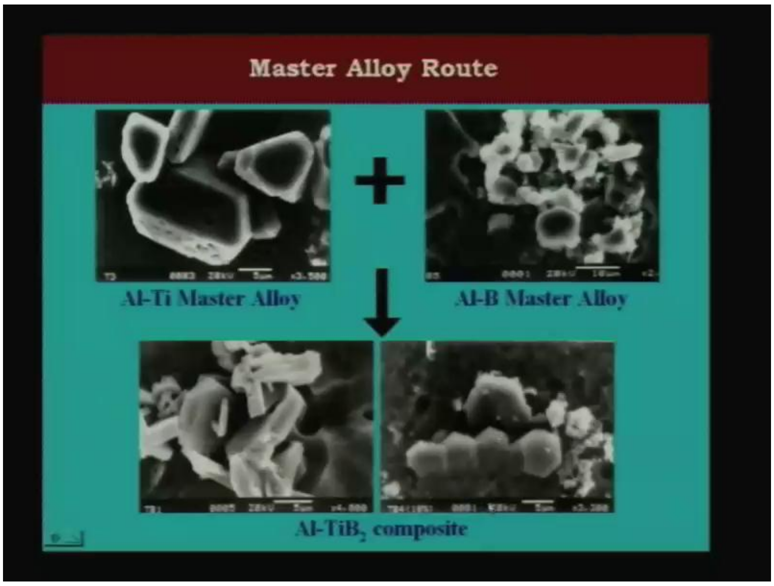

Master Alloy Route

Al-Ti Master Alloy

Al-B Master Alloy

Al-TiB_2 composite

You take a aluminum titanium master alloy with Al3Ti particles shown here. And AlB master alloy aluminum boron master alloy containing the AlB2 particles. Put them together and react them together to get T I B 2 particles. And this T I B 2 particles are hexagonal in structure. And give you very high strengths. And that is what is what is called the master alloy route.

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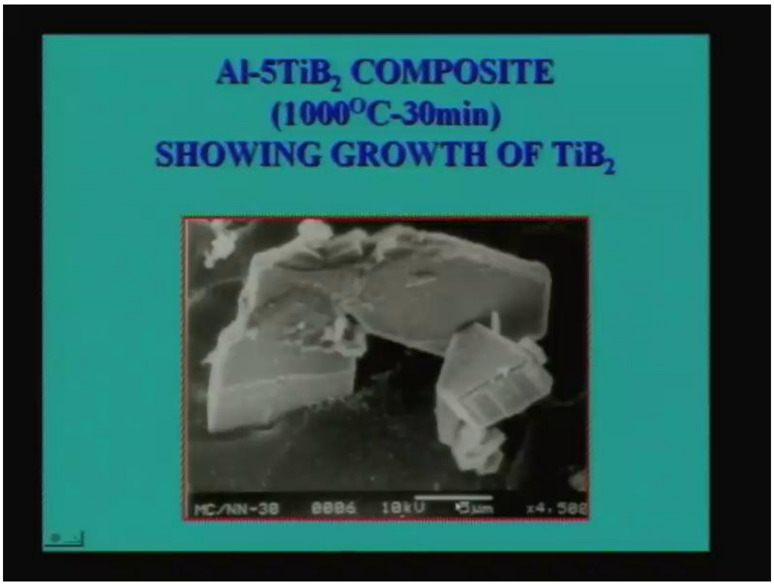

Al-5TiB$_2$ COMPOSITE
(1000°C-30min)
SHOWING GROWTH OF TiB$_2$

And the growth morphology we have talked about it basically the growth occurs on the basal planes of T I B 2. Because, T I B 2 has hexagonal structure and basal plane is the most close pack plain. So, the growth occurs in the c direction on the Basel plain. Once unit cell has formed are the once nucleus has formed the growth occurs in the c direction.

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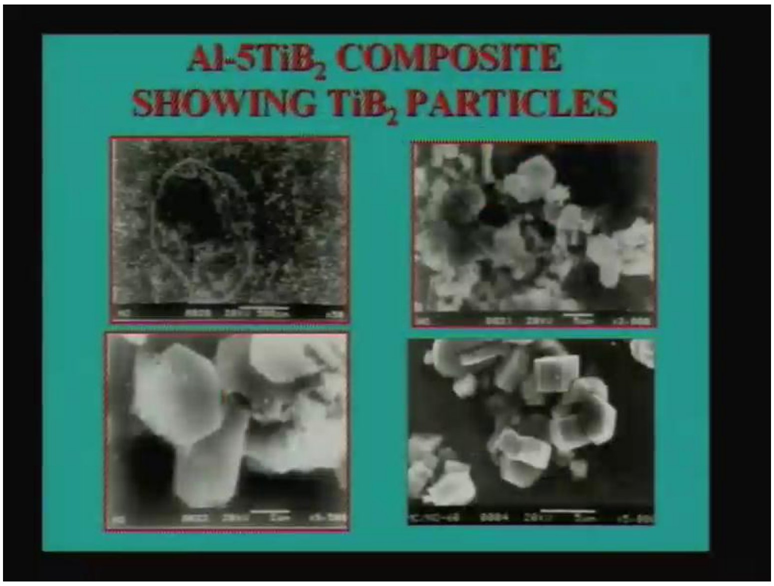

Al-5TiB$_2$ COMPOSITE
SHOWING TiB$_2$ PARTICLES

And one can also make these composites at either with different volume fractions. This is for 5 percent T I B 2 will also come to 10 percent Ti B two a little latter. And this is the extraction of particles we have talked about. That means, one can dissolve all the aluminum matrix and show what is the morphology of this Al T I B 2 particles three dimensional morphology.

So, can have a look at the three dimensional morphology. Once the whole aluminum has been dissolve, and you have this powder particles of T I B 2 which you can see it under the SEM. And one can also take them to an X-ray diffraction and conform that it has only T I B 2 one nothing else.

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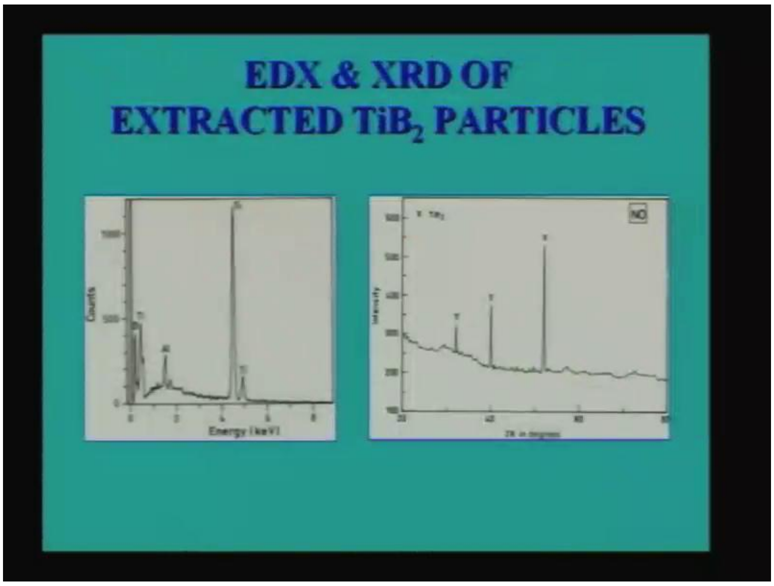

EDX & XRD OF EXTRACTED TiB_2 PARTICLES

So, if you take this powder particles which have come because of the extraction T I B 2 from the aluminum T I B 2 composite, where you dissolve all the aluminum. And whatever residue that is left out, you collect the residue. And that residue if you subject it to XRD what you see is this kind of peaks, which are completely T I B 2 peaks.

So, you, so that this confirms that no Al three Ti is forming, because that is one of the problems that I told you in the last class, that whenever you are making a T I B 2 composite with aluminum matrix. There is always a chance for Al three Ti also to from. So, one has to really control. So, that is one way we control it.

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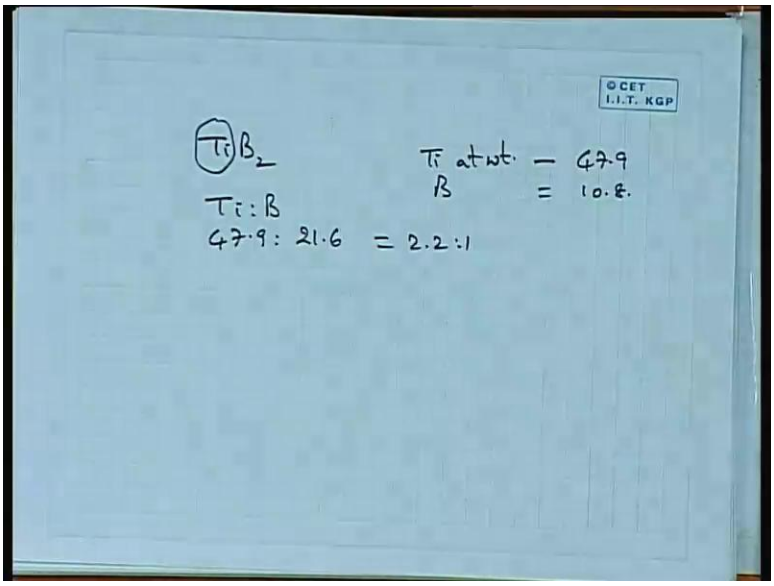

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TiB_2 — Ti at wt. — 47.9
B = 10.8

Ti : B
47.9 : 21.6 = 2.2 : 1

One of the basic ways of controlling is the composition, as you now T I B 2 when you say T I B 2. If you look at it, what is the ratio of titanium is to boron in a T I B 2, how do you now that?

Student: ((Refer Time: 06:22))

Weight ratio, obviously when I say titanium is to boron weight ratio.

Student: ((Refer Time: 06:29))

From the stoichiometry, one can find out, what is the atomic weight of titanium? Anybody remembers, atomic weight of titanium is 47.8 it is close to 48 and boron atomic weight is 10.8. So, you have two atoms of boron. So, the weight ratio will become 47.9 is to 21.6, 10.8 multiplied by 2.

So, this becomes equivalent to about 2.2 is to 1. That means, when you take the titanium and boron, when you are making aluminum titanium master alloy and aluminum boron master alloy separately. You have to make sure that the aluminum titanium master alloy the titanium content is 2.2 times the boron content of the aluminum boron master alloy.

That has to be controlled and in initial when you are making these master alloys. There are three is always some loss of boron. Particularly, I talk to you about the boron loss because of the Bf 3 formation, which is a gas at the temperature of around 750. So, one has to consider their losses of boron. And then make this kind of a ratio maintain. And one can if one can use the processing conditions. Such as that reaction temperature, reaction time all these carefully such that this ratio is maintained, if the ratio is not maintained. For example, if you have excess of titanium, what will happen, if you have excess of titanium.

Student; Sir Al3Ti

Al3Ti will form, then excess of titanium whatever is left out that will react with aluminum and form the Al3Ti. And if you have access of boron that excess of boron will form AlB2 So, our objective is not to have these two phases. But, to you have only T I B 2. And hence the process parameter control is very crucial. That is why this new composites the in situ composites are still I would say they are in there infancy. That people are still doing a lot of research. And they have not at still a become commercialized.

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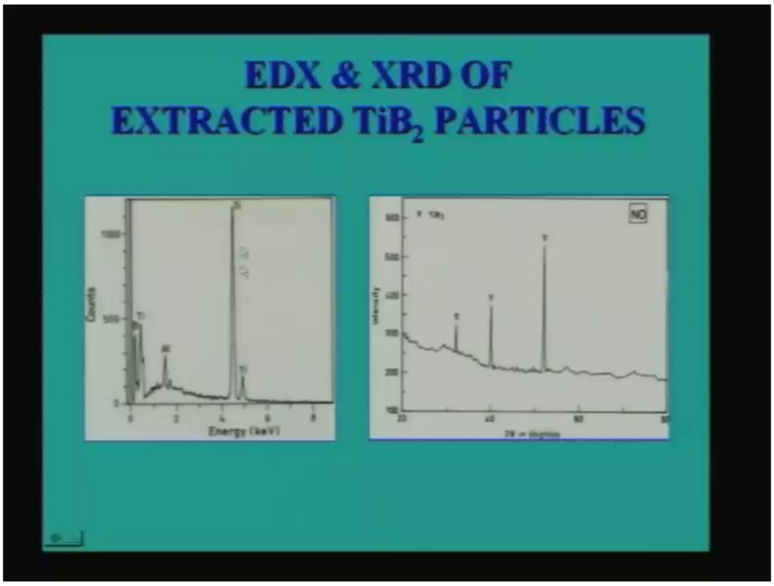

EDX & XRD OF
EXTRACTED TiB_2 PARTICLES

So, this is another SCM picture, I mean s SCM EDX to confirm this is from one of the extracted particles, which shows you the titanium and boron. If you carefully see there is also small amount of aluminum. This a small amount aluminum is possibly some of the. For example, when you extract these particles aluminum dissolves. But, at the same time some aluminum probably sticks to particles like this. And that kind of aluminum can give you a small amount of signal EDX signal as you can see here.

Otherwise it is mostly T I B 2, one can do quantitative analysis from these spectrum and confirm that it is T I B 2.

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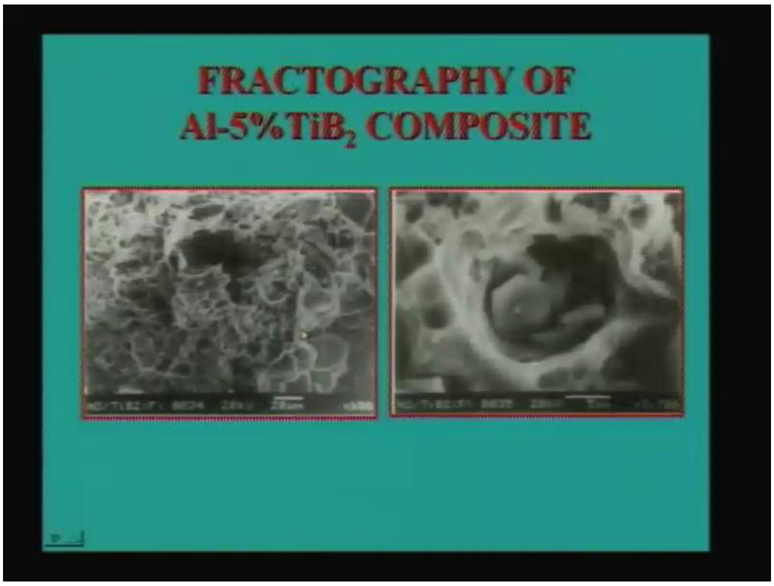

FRACTOGRAPHY OF
Al-5%TiB_2 COMPOSITE

So, this is the fractography to show that these are all ductile fracture. That means, though the strength is very high still they are a ductile.

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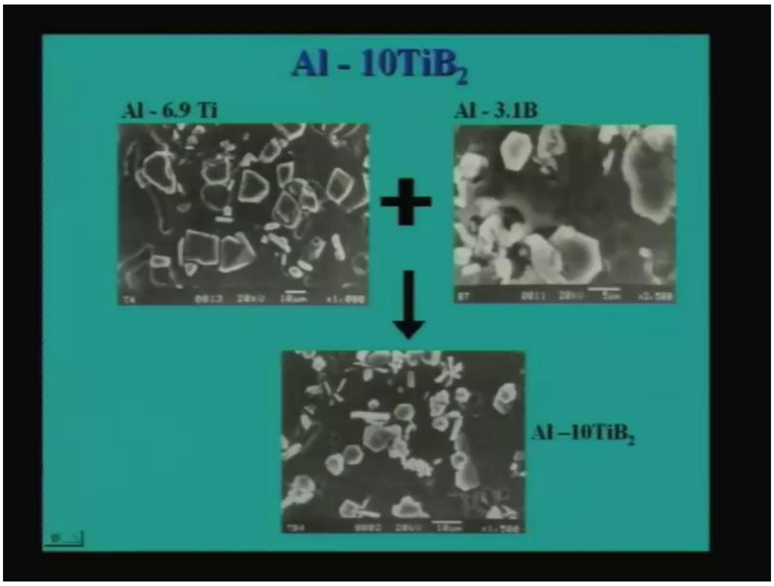
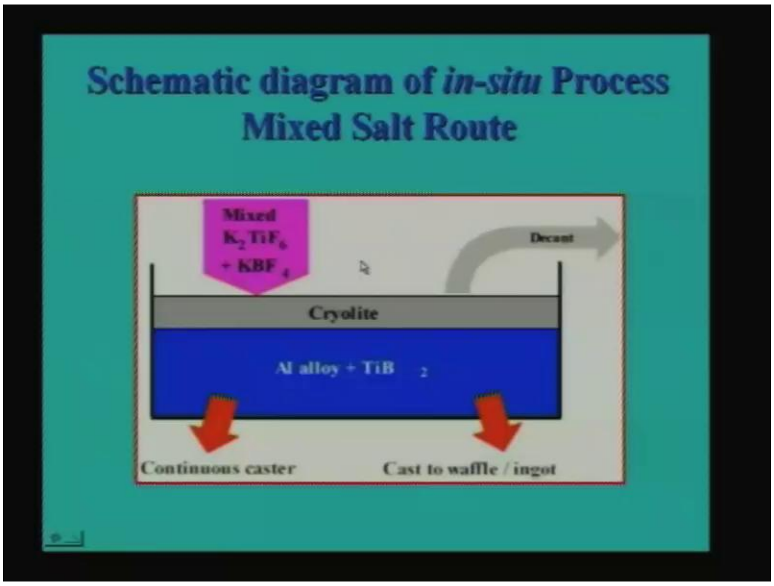


Al - 10TiB_2

And this is for 10 percent T I B 2. Similar thing one can do if you carefully observe the composition of titanium here. And the composition boron here it is 6.9 and 3.1 and the ratio is 2.2 is to 1 and that is what we maintain. So, if you do not maintain this ratio you will not end up with only T I B 2, because ultimately in the composite that you are getting you want only T I B 2 particles. So, there one has to control this composition. (Refer Slide Time: 10:14)



Schematic diagram of *in-situ* Process Mixed Salt Route

And this is the morphology. And the other route is what we just started in the last class to introduce. What is called mixed salt route? That means, instead of going by this separate master alloy making. One can directly add both the salts into the liquid aluminum at about 750 or 800 degrees centigrade and make these composites.

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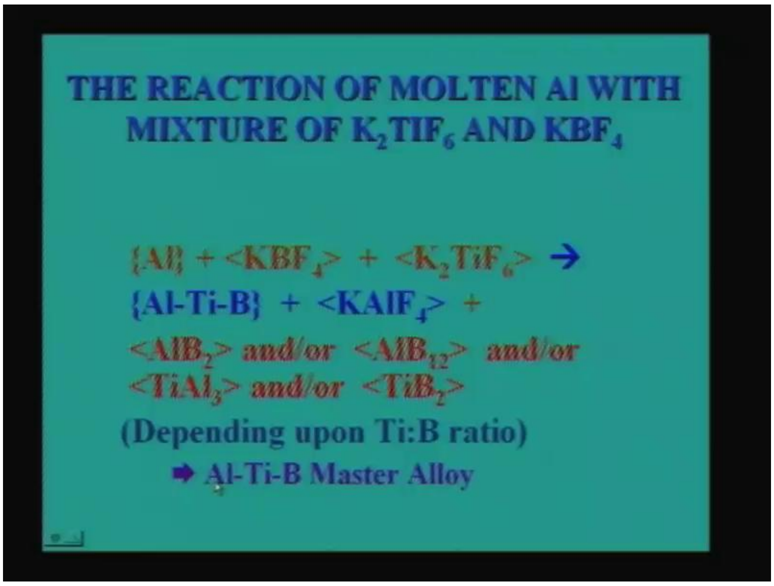

THE REACTION OF MOLTEN Al WITH MIXTURE OF K_2TIF_6 AND KBF_4

{Al} + <KBF_4> + <K_2TiF_6> →
{Al-Ti-B} + <$KAlF_4$> +
<AlB_2> and/or <AlB_{12}> and/or
<$TiAl_3$> and/or <TiB_2>
(Depending upon Ti:B ratio)
➡ Al-Ti-B Master Alloy

And this if you look at what are the reaction that are involved in this kind of a situation. If you take liquid aluminum add KBF4 plus K2TIF6 together. Then boron and titanium come out of these salts, and going to the liquid aluminum and make a liquid aluminum solution with titanium and boron.

So, this is a liquid solution. And from this liquid and in addition the KAlF4 will come out which is a braze, and from this titanium and boron containing a liquid aluminum. You can have all kinds of compounds that can come out you can have AlB2, AlB12, TiAl3 and TIB2. Now, the question is if you want only TIB2 to come out. One has to control various process parameters. One point is the Ti is to one Ti is to B ratio. Another the temperature, which is crucial and the time of reaction, which is crucial.

So, all these have to be controlled. So, that ultimately you end up in aluminum TIB2 composite. So, this is similar to making a grain refiner, aluminum, titanium, boron grain refiner, which we talked earlier. Only thing is in aluminum titanium boron grain refiner. We do not really bother whether you are getting only TIB2 or only Al3Ti or a combination of these two because both Al3Ti and TIB2 can act as nucleating sites for aluminum during solidification.

So, as a result, whether if, even if you have mixture of Al3Ti and TIB2 in a grain refiner, it is as a grain refiner. But, it is not really as a composite because as a composite Al3Ti is more brittle. So, as a result people do not want to have Al3Ti in aluminum TIB2 composite. So, one has to control that. So, the control that you need to exercise is much more than what you do in case of aluminum, titanium, boron, master alloy, which is made for the grain refinement of aluminum alloys.

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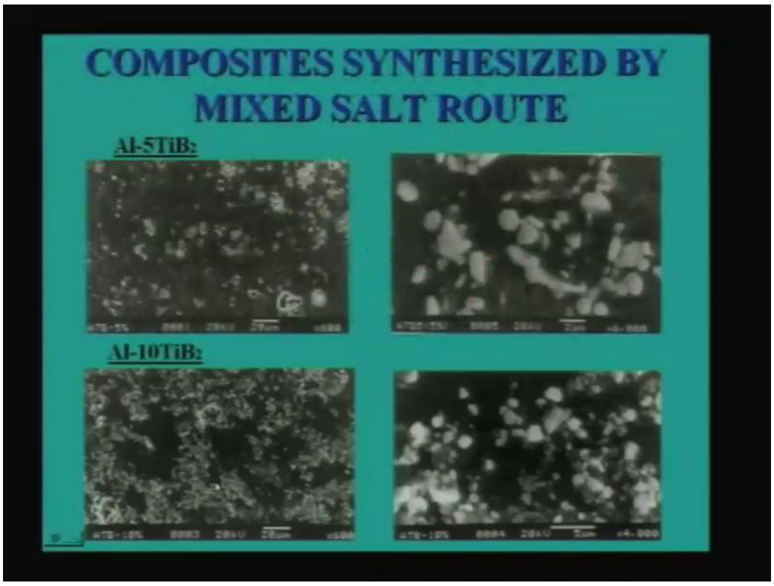

COMPOSITES SYNTHESIZED BY MIXED SALT ROUTE

Al-5TiB_2

Al-10TiB_2

So, if you do that you end up in the TIB2 particles. Definitely, but one has to control these are all ha after controlling various process parameters. This is for 5 percent TIB2 this is for 10 percent TIB2. As you can see in a 10 percent TIB2 you will have more volume fraction TIB2, which is what is expected.

What whatever percentage that we are talking here is weight percent. And one has convert it into the volume percent. How do we convert? Weight percent to volume percent, whenever you are talking of a composite. We usually refer to as only volume fraction, whenever I say aluminum 20 percent silicon carbide composite. We are not talking about weight percent of silicon carbide. We are talking of volume percent of Ti carbide. So, how do we converted it by

Student: ((Refer Time: 13:36))

By considering the densities of the two phases. So, once we know the density of the two phases, one can calculate the volume fraction.

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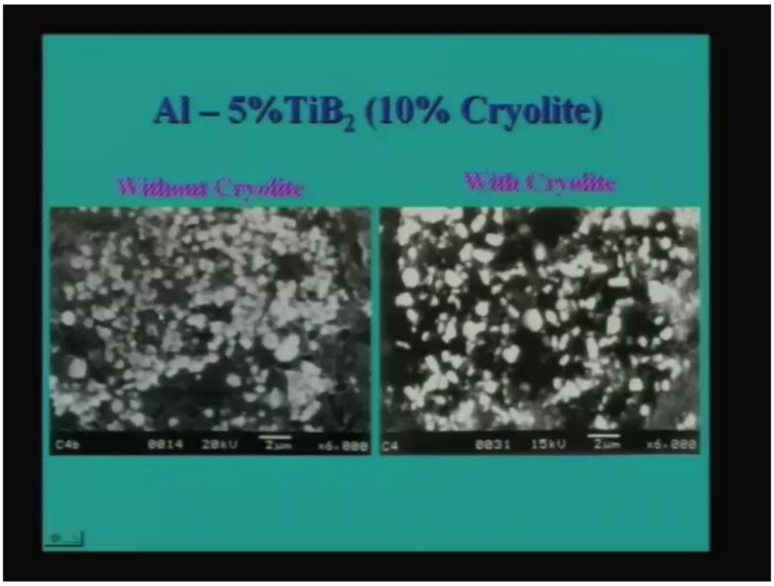

Al – 5%TiB_2 (10% Cryolite)

Without Cryolite

With Cryolite

So, and one can also see that if you add a surface active kind of a salt, which is called cryolite, which has a tendency to make the TIB2 form. Basically, the problem with TIB2 formation is that. This K2TIF6 when you add together with KBF4, K2TIF6 reacts with aluminum much faster than KBF4. Because, it has a much stronger exothermic nature of the reaction

So, the reaction is much vigorous and K2TIF6 is also has a tendency to from what is called emulsification. That means, the K2TIF6 in an aluminum matrix. If you add it gets uniformly distributed and it emulsifies the liquid. That means, it makes the liquid into droplets. Because, of which there is a rigorous reaction. And that is what will lead you to the formation of the Al3Ti more than the TIB2, because aluminum is reacting with K2TIF6 first before the KBF4 starts reacting.

So, you have to control this reaction in such way that both of them the reactivity is more or less controlled. So, cryolite is one such a agent, which we add which can reduce the reactivity of the K2TIF6 with aluminum. So, that the reaction of both simultaneously occurs. Otherwise you end up with only Al3Ti and not the TTIB2. So, one has to control that.

So, people have done that in a number of cases with. If you do not have cryolite addition you get agglomeration of particles which contain both Al3Ti and TIB2. And if you add cryolite you have more or less uniform distribution of only TIB2. This particles which you from have also sum Al3Ti. If you do EDX an individual particles, you will also fine some Al3Ti in them.

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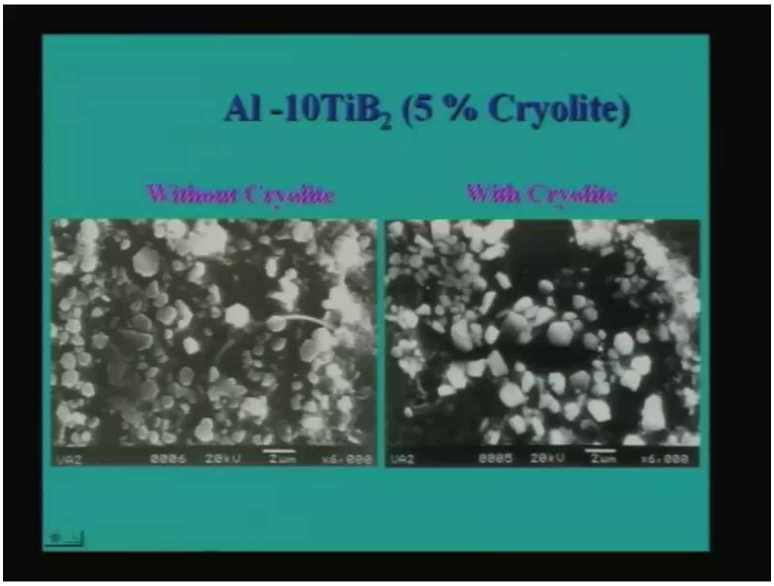

Al -10TiB$_2$ (5 % Cryolite)

Without Cryolite

With Cryolite

Similarly, one can also do for 10 percent T I B 2 in case of 10 percent T I B 2 also one can get similar nature.

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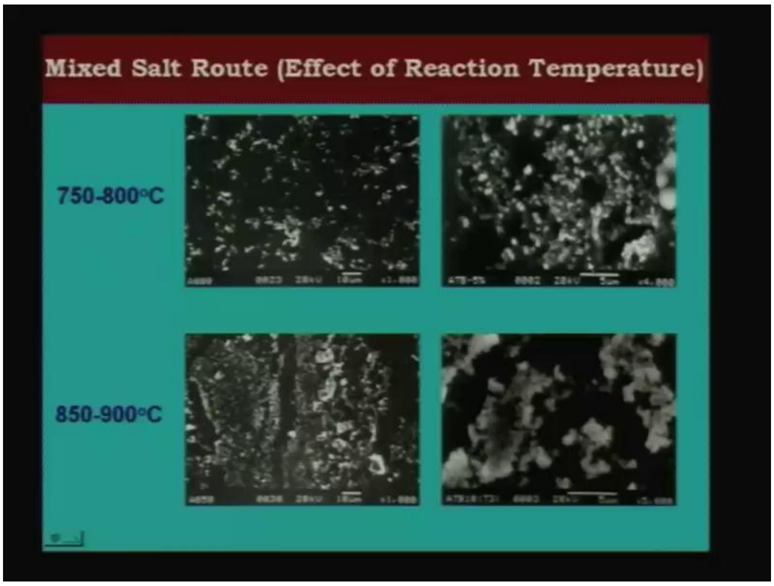

Mixed Salt Route (Effect of Reaction Temperature)

750-800°C

850-900°C

So, one can also study the effect of temperatures. At higher temperature there is a problem. The problem is as I told you before KBF4 has a tendency to dissociate and form Bf3 gas, and this tendency to dissociate increases with increasing temperature.

So, as a result if you go to higher temperature 850 to 900 degree centigrade you end up in less number of particles. And most of those particles will be Al3Ti particles because boron has already vanished most of the boron has already vanished. So, because of which you do not have the boron left out to react with the liquid metal to give you the TIB2 particles. So, as a result one has to control the temperature and keep the temperature down. So, that you have the formation of TIB2 particles alone.

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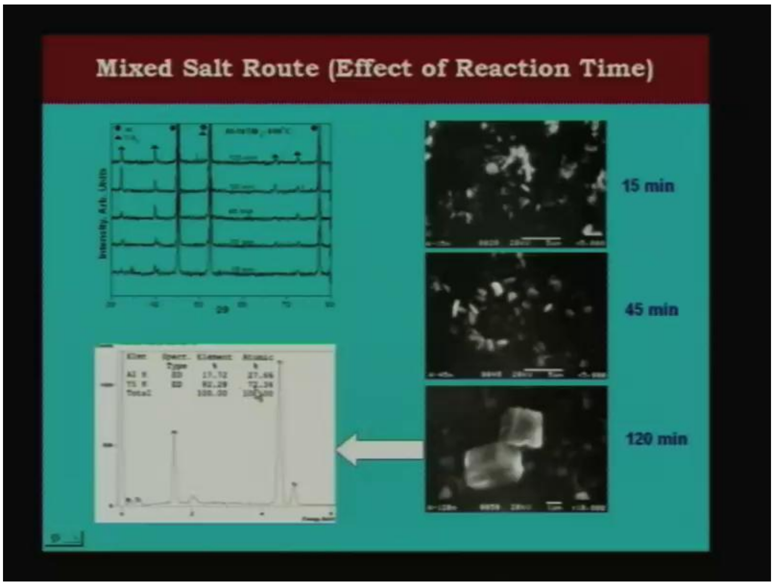

Mixed Salt Route (Effect of Reaction Time)

And one can also study the effect of reaction time, because there is a minimum time. That is required for the reaction to complete. If you do not allow sufficient time then what you see is that the reaction is the incomplete So, you will have un reacted slats left out in the liquid metal, which will go into the dross and you lose a lot of titanium and boron.

So, as a result there is minimum amount of time and we have seen that almost about 45 to 60 minutes of reaction time is required, for the formation of TIB2 particles. And one can also study, how the XRD patterns change as you keep on increasing, the reaction time. That with you with increasing reaction time the TIB2 peaks start becoming bigger and bigger that indicates the volume fraction the TIB2 is increasing.

So, this is again the EDX to show what is the volume fraction of this is on one of the Al3Ti particles.

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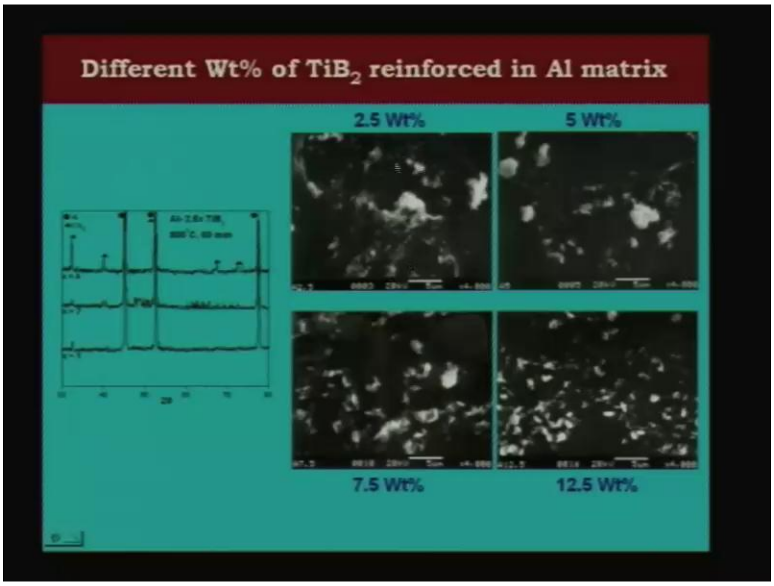

Different Wt% of TiB_2 reinforced in Al matrix

And one can also vary the percentage of TIB2 the 2.5 percent, 5 percent, 7.5 percent and 12.5 percent shown here. Just give you an idea that one can vary the volume fraction of these particles. So, that one can have improvements in the strength. As we know that with higher reinforcement amount will have better strength.

So, one can have all these, but the problem with this kind of method. Is I should also tell you what are the difficulties with this kind of method. That one cannot have very large volume fractions in case of ex situ composites. One can even imagine 30 percent, 40 percent of volume fractions. Because, you are externally adding the silicon carbide particles let us say. But, here what you are doing is that you are adding a salt, which is reacting with aluminum. And then giving you these particles TIB2 particles

So, because of that if want more volume fraction, you have to add more amount of salt. And for example, if you want some 10 percent of TIB2; that means, if you take about 1 kg of liquid metal. And you want 10 percent of TIB2 in that; that means, how much about 100 grams of TIB2 in that if you want to 100 grams of TIB2 in a 1 kg of liquid metal. You need to add almost 1 kg of a salt. Because, K2TIF6 if you look at it, if you want to make a 10 percent of TIB2 you need to make add 6.9 percent of titanium is it not. That is what we have seen before 6.9 percent of titanium plus 3.1 percent of boron will give you 10 percent of TIB2.

So, if you want 6.9 percent of titanium; that means, 69 grams of titanium. So, you can calculate how much of K2TIF6 has to be added to get 69 grams of K 2 of titanium into it, because potassium and fluorine also has to be considered because. So, the molecular white of that K 2 T I F 6 is going to decide how much of weight of K 2 T I F 6 is going to give you how much of titanium.

So, as a result one has to add excess of this salt, and if you want to add a lot of salt to liquid aluminum. The whole liquid is going to become very viscous. And if you want to overcome this viscosity, you have go to higher temperature. And you go to higher temperature you have a problem of boron loss. So, one has to have a limitation. So, it is very difficult to make more than about 15 percent of salt 15 percent of T I B 2 15 to 20 percent is more or less. The limit it is almost next to impossible to get more than 20 percent. But, the advantage here is that you are getting much finer particles, the particles which are very compatible with the liquid metal.

So, that the strengthening that you can achieve is going to be much better than what you get even with a 20 or 30 percent of silicon carbide ultimately that is important. So, when you are comparing you have to see that unless this new generation composite. If it cannot guaranty, you better mechanical properties. Even with whatever limitations of volume fraction that you have. So, if you have a limitation of the volume fraction ,even with a lower volume fraction. If it is able to promise you a higher mechanical properties, that particular process or that particular composite is going to see the light of the day, at the end towards commercialization. Otherwise this particular new composite are going to die out. So, that is what we will show at least some of the mechanical properties a little later, yes.

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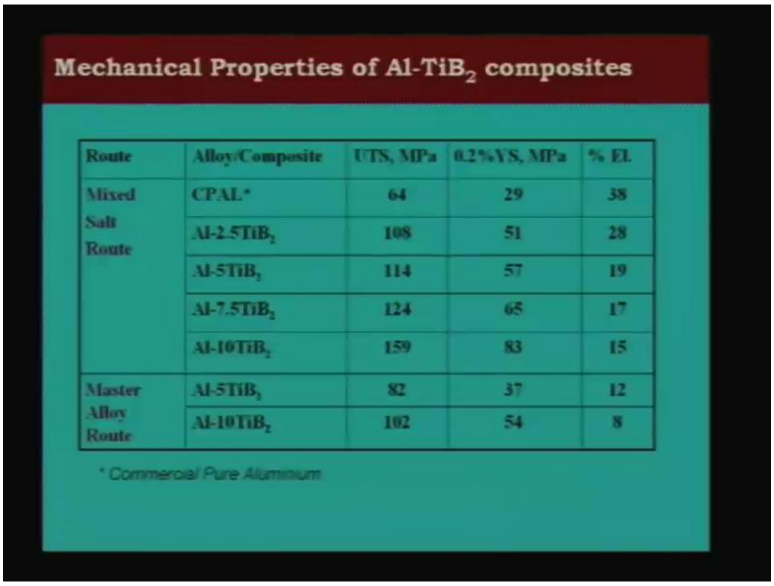

Mechanical Properties of Al-TiB_2 composites

Route	Alloy/Composite	UTS, MPa	0.2%YS, MPa	% EL
Mixed Salt Route	CPAL*	64	29	38
	Al-2.5TiB_2	108	51	28
	Al-5TiB_2	114	57	19
	Al-7.5TiB_2	124	65	17
	Al-10TiB_2	159	83	15
Master Alloy Route	Al-5TiB_2	82	37	12
	Al-10TiB_2	102	54	8

* Commercial Pure Aluminium

Here it is that if you try to compare take aluminum alone. Frankly speaking I will tell you nobody wants to make aluminum TIB2 composites alone with aluminum as a matrix. The reason is aluminum is very ductile. Whenever somebody wants to commercially make a composite, nobody wants to take the matrix as pure aluminum.

So, people usually take aluminum alloys such as aluminum copper, aluminum silicon kind of alloys. So, but before you try to understand what kind of strengthening, that you get with aluminum silicon alloys as matrix or aluminum copper alloys as the matrix. We should understand what you get with aluminum alone.

So, this is what you get with aluminum. If you take a pure aluminum you get a UTS of only 64 MPa. And if you add about 10 percent of TIB2 you can go from there to here. Almost three times increase in the or more than 2.5 times increase in the strength that one can achieve with this. And carefully see the elongation has not really gone down, it is not really become brittle. 15 percent elongation is a great elongation for a composite aluminum silicon carbide composite do not give more than even 5 percent elongation.

So, this is one of the important thing. The reason is again the comfort ability of the particles with the reinforcement. If you do not have comfort ability to the particles with the reinforcement, then at the interface what you have is some kind of a void.

So, immediately this void will act as a nucleating sites for the crack. And the crack will and what we say de-lamination of the particles are you now the particle pull out people say. Or the in a reinforcement pull out will take place when you subject it to the stresses during the service. So, whenever the particle is not coherent with the matrix or compatible with matrix. So, that is why you can see that in most of the composites. Particularly those ex situ composite the ductility levels are very low that is because of that.

Here you can see the ductility levels are still higher. But, one thing is that master alloy route does not promise you that much high strengths. Basically, because the temperature set which these are made are very high. At those high temperatures thousand degrees or so you have to go. So, the both these master alloys when you try to re-melt; they melt together and give you the reaction.

At those high temperatures there is always possibility of gas absorption. Aluminum strongly absorbs hydrogen. So, that is another problem one has to control. So, how to control gas absorption by this aluminum. high temperatures lead to that and because of which the elongation comes down and the strength also comes down to some extent. So, that is why the mixed salt route is commercially also more viable. Because, you are not really going through a three step process of making two master alloys first, and then re-melting them together. And also at the same time one can achieve much better strengthening.

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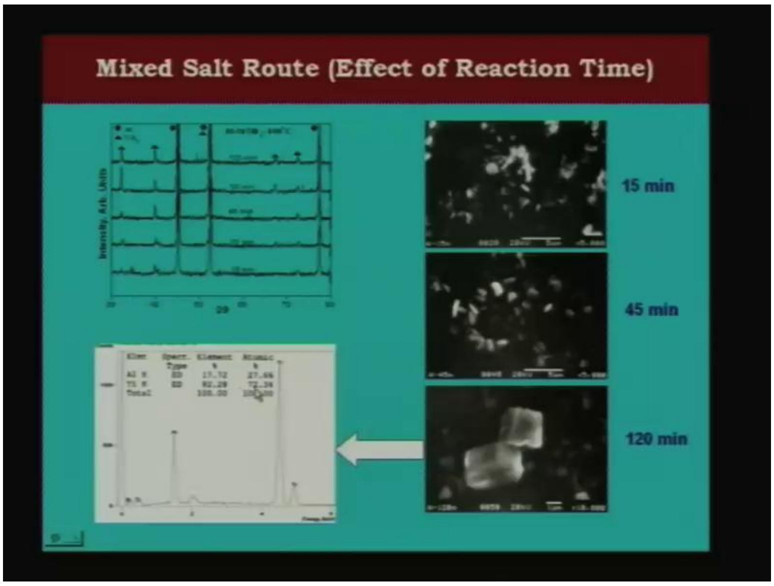

Mixed Salt Route (Effect of Reaction Time)

Elem	Spect. Type	Element %	Atomic %
Al K	ED	17.72	27.66
Ti K	ED	82.28	72.34
Total		100.00	100.00

And this is about aluminum copper. As I told you usually people prefer to and TIB2 are any reinforcement for that matter to aluminum alloy rather than pure aluminum. So, when you particularly aluminum copper has an advantage, because it is a age hardening system is it not. So, one can also have what is called precipitation hardening, formation of the theta double prime or theta prime end of precipitates. So, that you can have additional strengthening coming, because of the precipitates, in addition to the reinforcements that you have already added.

So, if you take this kind of aluminum copper alloy and add different amounts of precipitates. Different amounts of not precipitates reinforcement 2.5 percent, 5 percent, 7.5 percent, 10 percent. As you can see here different volume fractions of precipitates have been added to an aluminum copper alloy base alloy. And then look at all these you can see with increasing percentage of TIB2 you can see the peaks of TIB2 become bigger and bigger.

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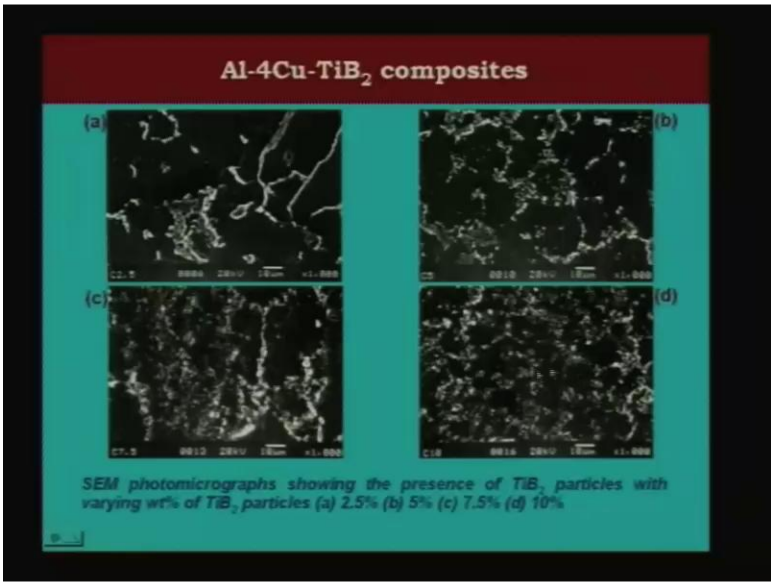

Al-4Cu-TiB$_2$ composites

SEM photomicrographs showing the presence of TiB$_2$ particles with varying wt% of TiB$_2$ particles (a) 2.5% (b) 5% (c) 7.5% (d) 10%

And this is the SEM photograph showing higher volume fraction of these TIB2 particles the magnification is very low. So, that is why you can see very fine particles of TIB2 which are uniformly distributed in the matrix.

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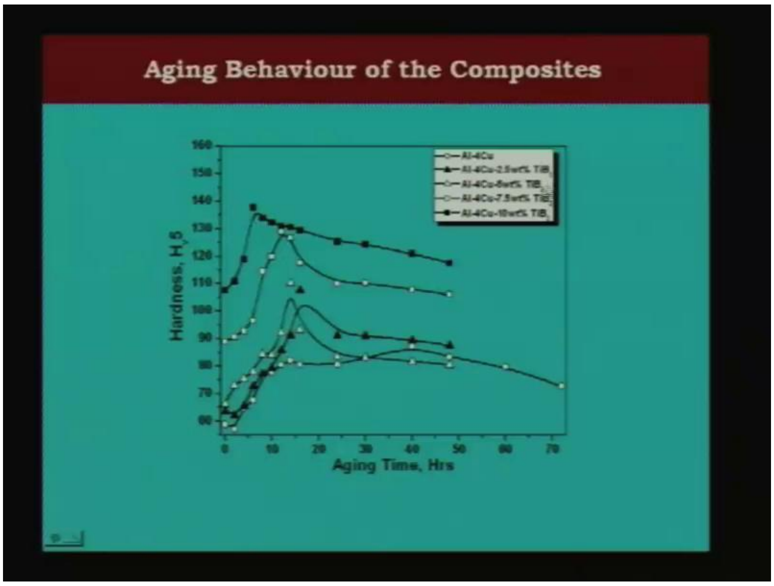

Aging Behaviour of the Composites

And if you look at the age hardening phenomena of this particular alloy. You can take the base alloy for example, which is nothing but this bottom curve with the open circles that you can see here.

So, that shows that the strengthening that you can achieve is lower than what you can achieve with all these particles. So, when you add different volume fractions are different weight TIB2. You can have much better strengthening because of the presence of TIB2 particles.

In addition another important thing, that you can see another important thing that you can see is that the peak hardness is achieved at a lower time. That means, aging process is hazel or the aging process becomes faster, why? Because the presence of these TIB2 particles act as nucleating sites, for the theta double prime or theta prime or the GP zones to form, and because of which the…

For example, if you take 10 percent of TIB2 the peak hardness is reached within almost about 6 hours. Whereas, this particular without any TIB2 the peak hardness takes almost about twelve hours or, so. In fact, it has a kind of very shallow peak and then more or less the higher highest peak is reached after about 40 hours.

So, you can see when you compare with this 40 hours within 6 hours. So, your aging time is drastically reduced. So, you have a double advantage here, not only that you can have higher strengthening, but also you can have much faster age aging treatment. And, you can see almost from about 80 Vickers hardness to almost 140. So, almost double the strengthening that we can achieve in this case.

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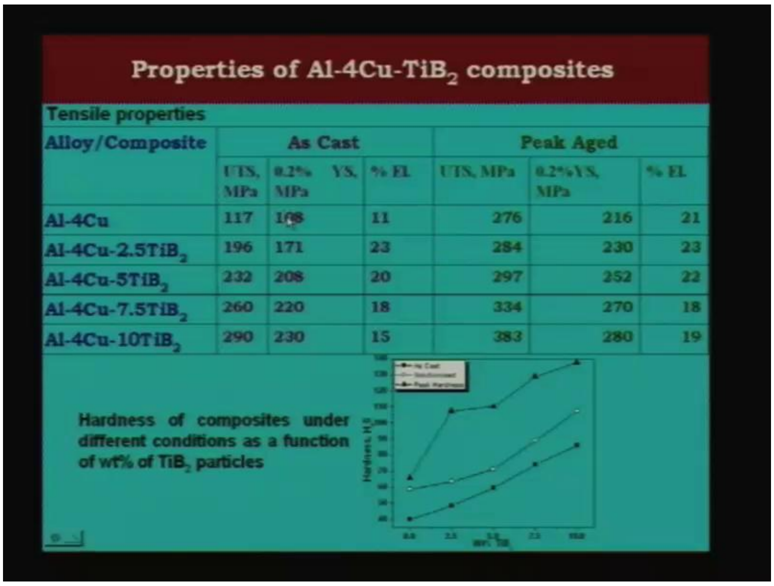

Properties of Al-4Cu-TiB_2 composites

Tensile properties

Alloy/Composite	As Cast			Peak Aged		
	UTS, MPa	0.2% YS, MPa	% El	UTS, MPa	0.2%YS, MPa	% El
Al-4Cu	117	108	11	276	216	21
Al-4Cu-2.5TiB_2	196	171	23	284	230	23
Al-4Cu-5TiB_2	232	208	20	297	252	22
Al-4Cu-7.5TiB_2	260	220	18	334	270	18
Al-4Cu-10TiB_2	290	230	15	383	280	19

Hardness of composites under different conditions as a function of wt% of TiB_2 particles

And that is as per as hardness is concerned, here we have the tensile properties. You can see aluminum copper as cast alloy has almost 117 UTS with about 11 percent elongation. And if you do peak aging you get about 276 UTS with about 21 percent elongation. And then if you take about 10 percent of TIB2 with increasing percentage of TIB2 the strengthening increases. With 10 percent T I B 2 you get about 290 even without aging itself.

In the as cast condition itself you reach about 290 and if you age it you get about 380 MPa which is much higher you can compare without any reinforcement. The highest that you can achieve even in the peak aging condition is only about 276 and almost about 100 MPa increase is possible with TIB2 and the ductility still remains.

Student: ((Refer Time: 29:22))

Almost 19 percent, yes

Student: ((Refer Time: 29:26))

This is only because of the fine TIB2, because this does not happen with if you do executive. If you take the same aluminum copper. If you add silicon carbide you will never see the strength may increase, but the ductility will never increase. In fact, the ductility will fall this is what happens with the TIB2 particles. Because, the TIB2 particles all also compatible with the matrix. That you have a good compatibility at the interface and there are no reaction products at the interface because…

Student: ((Refer Time: 30:03))

Aluminum copper also, because this is as cast also you can see about almost about 4 percent or so. But, the thing is if you carefully observe the increase is much higher at smaller volume fraction. If you go to higher volume fraction it is decreasing. And if you go to probably 20 percent volume fraction, then it further decreases. Because, whatever may be the compatibility TIB2 is any way a brittle inter metallic compound, it is a hard compound.

So, because of which if you keep on increasing the volume fraction of the hard phase. So, you cannot expect the elongation to keep on increasing.

So, if you carefully observe the elongation keeps on decreasing here. The small volume fraction you have much higher in elongation. But, as you keep on increasing the volume fraction the elongation decreases and 10 percent gives you only about 15 percent. But, what is important to see is that the elongation is good enough to give you a dimpled fracture. And which is what is important for any structural component. Any material which you want to use it for structural applications has to have certain amount of ductility.

If it does not have you cannot use it for any structural application, this is very important. And you can see here the hardness, which is plotted both in the as cast condition and in the solutionized condition. And the peak age condition, it increases with increasing volume fraction. This is expected as we know that higher amount of TIB2 will give you higher strengthening.

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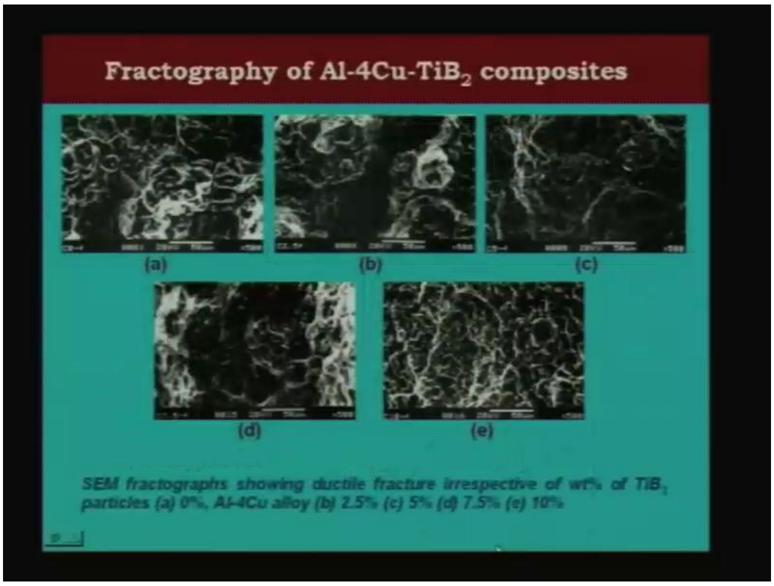

Fractography of Al-4Cu-TiB$_2$ composites

SEM fractographs showing ductile fracture irrespective of wt% of TiB$_2$ particles (a) 0%, Al-4Cu alloy (b) 2.5% (c) 5% (d) 7.5% (e) 10%

And this is as far as the fractographes are concerned. I can see that even with 10 percent you have some dimpled fracture, this is what I wanted to say.

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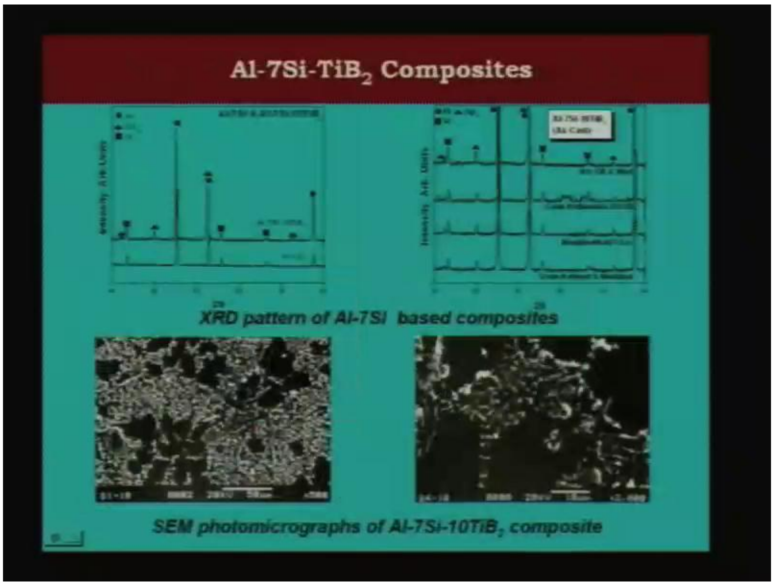

Al-7Si-TiB_2 Composites

XRD pattern of Al-7Si based composites

SEM photomicrographs of Al-7Si-10TiB_2 composite

And this is about silicon. If you take the silicon and you do the same thing with TIB2. And you can see the fine uniform distribution of the TIB2 particles in the matrix, with about 10 percent TIB2. And you can see that aluminum 7 silicon without any TIB2 will give you only aluminum plus silicon peaks. And the moment you add TIB2 you start getting the TIB2 peaks also, from the XRD pattern one can see. And one can have the this is another one can do the grain refinement of the aluminum 7 silicon alloy and do modifications. So, that one can have an improvement in the properties.

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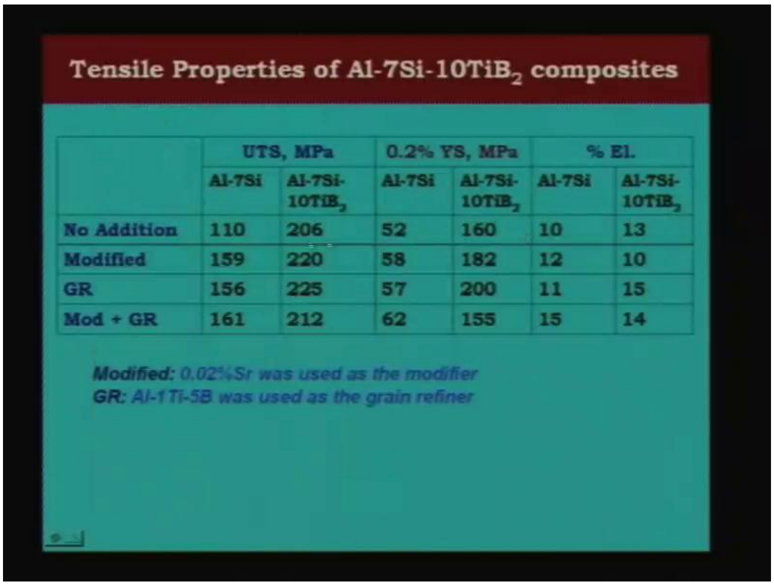

Tensile Properties of Al-7Si-10TiB_2 composites

	UTS, MPa		0.2% YS, MPa		% El.	
	Al-7Si	Al-7Si-10TiB_2	Al-7Si	Al-7Si-10TiB_2	Al-7Si	Al-7Si-10TiB_2
No Addition	110	206	52	160	10	13
Modified	159	220	58	182	12	10
GR	156	225	57	200	11	15
Mod + GR	161	212	62	155	15	14

Modified: 0.02%Sr was used as the modifier

GR: Al-1Ti-5B was used as the grain refiner

We will try to see what kind of improvements. The improvements are not really as dramatic as you can see in case of aluminum copper. Because, aluminum copper is a age hardening system one has to remember that. Whereas, aluminum silicon is not an age hardening system. So, one cannot achieve really very high strengthening here, but still you can see that. If you take this alloy aluminum 7 silicon alloy without any TIB2 you get about 110 UTS with TIB2 you get about 2 naught 6. So, almost double the strength and if you look at the elongation 10 percent and 13 percent.

So, you do not lose the elongation that is very important to note. And similarly when you modify it you get an improvement in the properties. And grain refinement also gives you improvement in the properties. And a combination of this also gives you an improvement in properties, but not really very high. And similarly if you have in presence of TIB2 also one can have an improvement in the properties. But, it is not as dramatic as in the case of copper.

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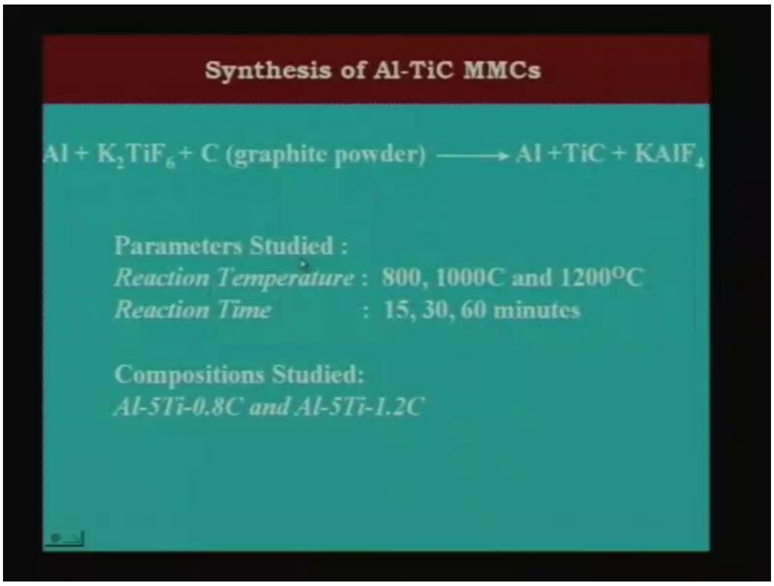

Synthesis of Al-TiC MMCs

$Al + K_2TiF_6 + C$ (graphite powder) $\longrightarrow Al + TiC + KAlF_4$

Parameters Studied :
Reaction Temperature : 800, 1000C and 1200°C
Reaction Time : 15, 30, 60 minutes

Compositions Studied:
Al-5Ti-0.8C and Al-5Ti-1.2C

So, this is as far as the aluminum TIB2 is concerned. Let us try to look at aluminum TiC composites. This is another class of new generation composites, where what we do is again similar situation. That you need titanium, you need carbon to form a TiC and what is the ratio here if you again look at TiC. Titanium atomic weight we have already seen 47.9 what is the atomic weight of carbon.

Student: ((Refer Time: 34:08))

Atomic weight of carbon is 12. So, the ratio of Ti is to C that we need here is of the order of around 4 is to 1 is it not. So, if one can have a ratio of about 4 is to 1. One can again control to give you only TiC particles; again TiC the interesting feature of TiC is TiC is a cubic phase.

It is like a, if you remember in case of aluminum nano composites. Earlier we have seen that we wanted to convert the Al3Ti, which is a body centered tetragonal type of a structure Do22 structure, to a cubic face by either ball milling or by adding certain alloying elements, which will stabilize the cubic phase.

So, that you have an aluminum matrix, which is a cubic structure face centered cubic structure. And inside that you have other cubic particles to give you composite there, where which we called it as a nano composite. Because, the phases are in the nano stage and you have a cubic nano particles, in a cubic matrix, which gives you much better strengthening. And also gives you sufficient amount of deformability. Because, the both the structures are cubic.

We know that cubic structures are more deformable. Similarly, here you have an aluminum matrix which is cubic and TiC, which is a cubic structure. So, that is why TiC composite we expect the strengthening to be very good here. So, and again the here titanium. One can have all kinds of sources, one can add directly pure titanium to the aluminum. And you can take carbon as graphite powder for example,. So, if you add titanium metal as titanium metal pieces. And carbon one can do that, but that process is going to be very costly process, because titanium metal is very costly.

So, instead the cheaper way to do it is adding a salt such as k2TiF6 as we have done before for TIB2 and add carbon as graphite powder. And this will give you this kind of a reaction aluminum plus TiC giving you KAL aluminum plus TiC plus KAlF4, which goes in to the ((Refer Time: 36:39)) and one has to control again.

Here also the composition has to be controlled the temperature and the reaction time both of them have to be controlled. So, that you end up only with this here, I show you an example of two such compositions. One where it is 5 titanium 1.2 carbons, if you carefully observe the ratio is again 4 is to 1.

Very close to 4 is to 1. In fact, if it is 4 is to 1 it has to be 4.8. So, very close to 4 is to 1. And in fact, this is the initial chosen composition after the alloy is made after the composite is made the actual titanium content is about 4.85, which is very close to what is expected and here you see the ratio is more than 4 is to 1. So, because of which you end up probably in some Al3Ti. So, that is what we want to see here.

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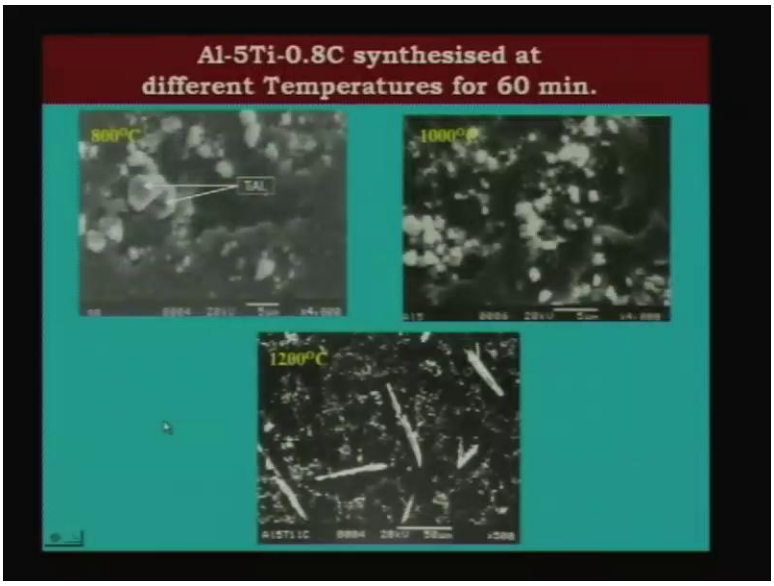

Al-5Ti-0.8C synthesised at
different Temperatures for 60 min.

So, when you look at this, this is 0.8c. When you take 0.8c and look at different temperatures. At low temperatures you get whatever may be the temperature frankly speaking. Whether it is low or high temperature in all the cases you end up with TAl three plus TiC both.

Basically because, you have an excess titanium, this excess titanium will react with aluminum to give you Tal3. The only difference as far as the temperature is concerned is at low temperature Tal3 forms in the form of a blocky type of particles; more or less ((Refer Time: 38:15)) type of particles at higher temperatures. Tal3 grows as needles or plates. Because, the Tal3 has a tendency at higher temperature to grow in one particular direction, which is a 001 type of direction to give you this kind of flake plate like or the needle like morphology. So, what is important to realize here is that you always end up with some TiC particles plus TAL3. So, this clearly shows you why we should control the composition.

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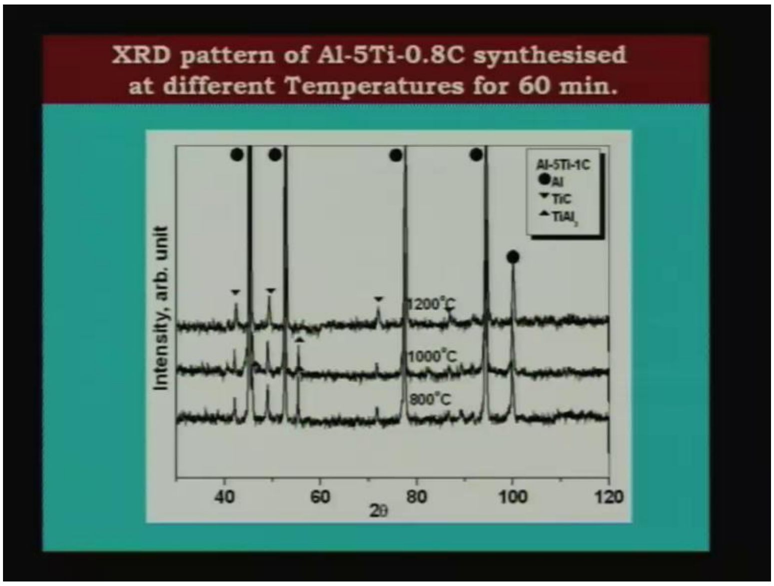

XRD pattern of Al-5Ti-0.8C synthesised at different Temperatures for 60 min.

Then go to the next one, we will come to that a little later. Here, you can see different temperatures the formation of both Tal3 and TiC can be seen here.

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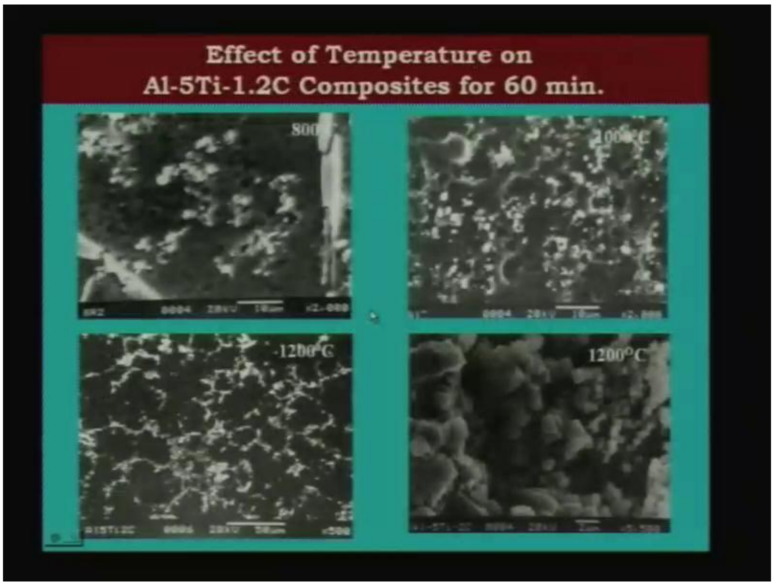

Effect of Temperature on Al-5Ti-1.2C Composites for 60 min.

And this is with 1.2 percent carbon. In 1.2 percent carbon you can see that only TAlC forms, how do you know that these are only TiC1 can do an X-ray of them. One can extract these particles and then study the X-ray of those particles or one can do EDX on those individual particles. And find out whether they are TiC particles or TAl3 particles.

If they are TiAL3 particles, you can easily see in the EDX that there will be no carbon coming peak coming out of. So, those particles one can easily say, yes these are not TiC particles. So, if you do that this is as a function of reaction time.

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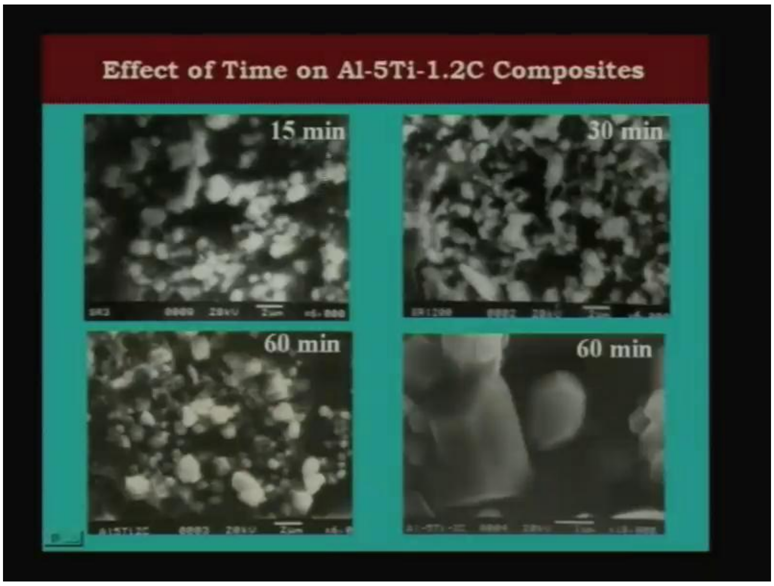

Effect of Time on Al-5Ti-1.2C Composites

Again here also you need a minimum of about 60 minutes for the reaction to give you, a more or less uniform distribution of particles. And these particles are of faceted nature. And this faceted nature is very useful when you want to use them as grain refiners also, because these phases. Because, TiC is cubic in nature TiC can also act not only as a aluminum TiC composites. But, also as a grain refiners one can use the aluminum TiC as a grain refiner for aluminum alloys. We will come to it a little later.

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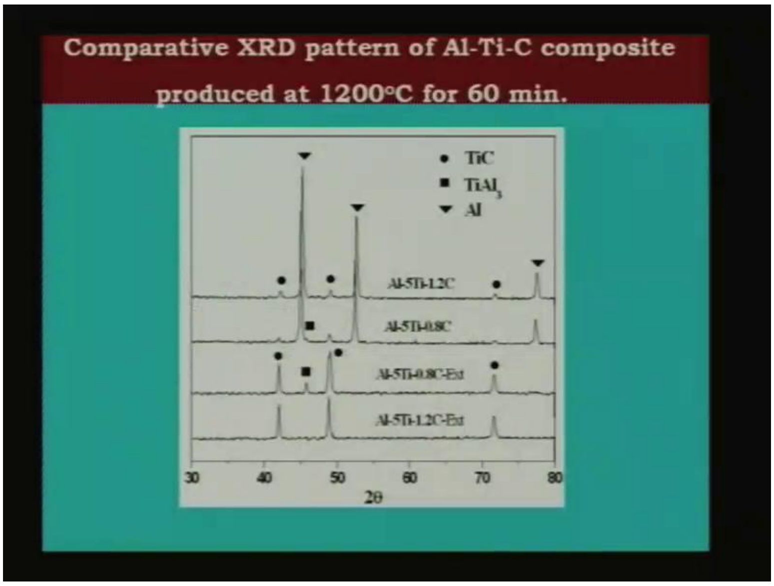

Comparative XRD pattern of Al-Ti-C composite produced at 1200°C for 60 min.

So, if you look at this aluminum TiC composites one with 0.8 percent carbon. Another with 1.2 percent carbon, you can see the presence of TiC particles very clearly, in the 1.2 percent. And if you try to take these two composites and dissolve all the aluminum matrix. And look at those extracted particles carefully. You will see in the extracted particles 0.8 percent carbon extracted particle shows you both TiC particles peaks and TAl3 peaks.

Here you cannot see those TAl3 peaks here because the volume fraction of TAl3 in this is very small. So, if you take the whole composite and subject it to the XRD, you can see the TiC itself is how much, you are taking a composite of aluminum 5 percent titanium and 1.2 percent carbon.

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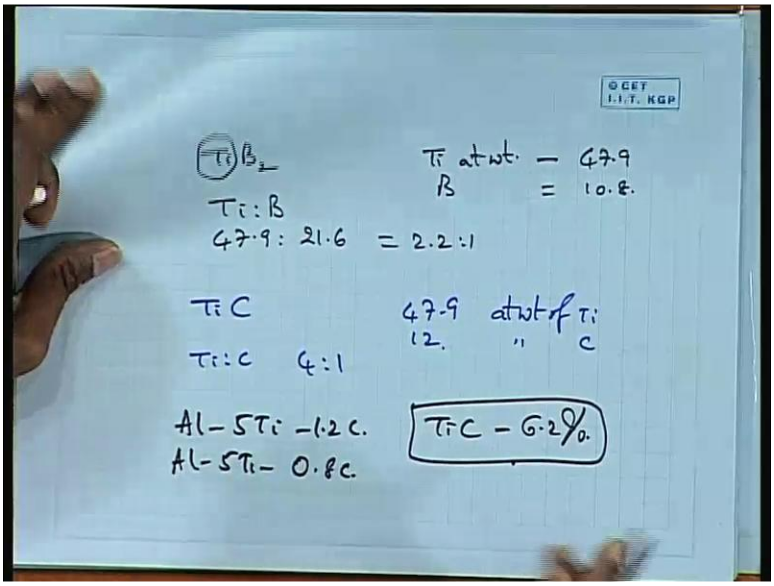

TiB_2 Ti at wt. — 47.9

B = 10.8.

Ti : B

47.9 : 21.6 = 2.2 : 1

TiC 47.9 at wt of Ti

12. " C

Ti : C 4 : 1

Al-5Ti-1.2C.

Al-5Ti-0.8C.

$\boxed{TiC - 6.2\%}$

So, how much is the TiC? TiC is 6.2 percent 5 plus 1.2 that is a TiC. So, 8 percent of TiC is 6.2 percent and we know X-ray has a limitation.

Whenever you have a volume fraction of phase, which is very low you cannot see those peaks. So, if at all there is some TAl3 also that has formed. In this composition or in that 0.8 percent carbon composition the TAl3 volume fraction will be, so small. Because, only after the titanium reacts with carbon. Whatever titanium that is left out that alone will react with aluminum and give you TAl3, because TiC again is much more stable than TAl3 thermodynamically.

So, as a result the first preference of titanium is to react with carbon. So, as a result you see that only excess carbon. For example, in this particular composition aluminum 5 titanium. One can easily calculate what is the volume fraction of TAl3 and TiB and the TiC.

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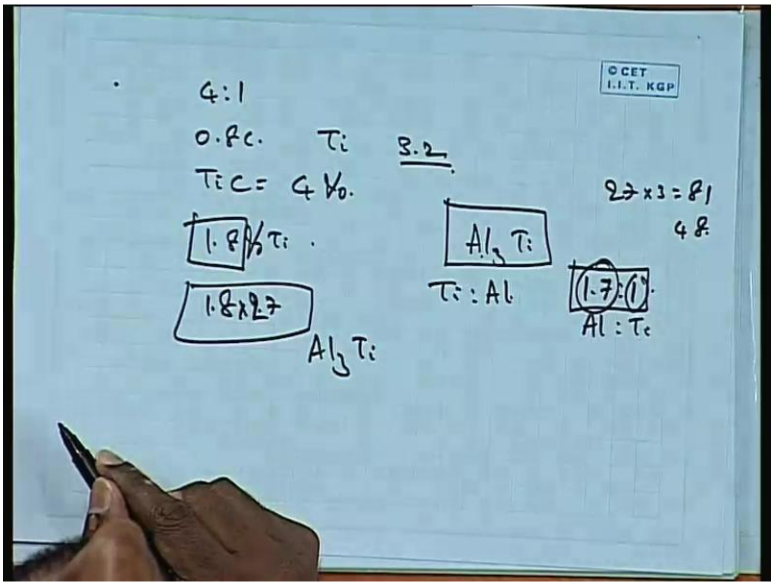

For example if you take 4 is to 1 is the ratio of titanium and carbon 4.8 percent of carbon how much of titanium you need.

Student: ((Refer Time: 42:39))

3.2 fine. So, what will be the volume weight fraction TiC 4 percent 4 percent of TiC will form. Now, what is the if I take 5 percent of titanium alloy. This is the alloy that I am talking about. In 5 percent titanium 3.2 of titanium has already gone and reacted with carbon.

So, what is left out 1.8 percent. So, that 1.8 percent titanium will react with the TAl3 aluminum to give you TAl3. So, as a result the volume fraction of TAl3 is going to be about 2 percent or 3 percent, because it is Al3Ti may be 3 percent or 4 percent again one has to calculate that.

Similarly, if you look at the ratio of titanium is to aluminum in a TAl3 one can find out what is the ratio of it. Because this is 27, 27 into 3 is 81. And titanium is how much 48. So, if you take the ratio of aluminum versus the titanium. You will get something like 1.7 is to 1, this is aluminum is to titanium.

So; that means, 1.8 percent multiplied by 1.7 will. In fact, 2.7 one should add. So, that this will give you the total weight fraction of Al3Ti, that one can get is it not. Because one of titanium 1.7 of aluminum. So, 2.7 is the total.

So, if you take titanium as 1.8 multiply with 2.7 you get something like about 4 percent or 5 percent or, so double of this 5 percent. So, that 5 percent is a again the volume fraction is small to see in an XRD. If you take the composite, but once you have extracted the particles out of the composite now aluminum has gone. So, whatever particles have been extracted. Now, in that particles you can see easily, whether there is TAl3 or TiC, if it is only TiC you will see this kind of a situation.

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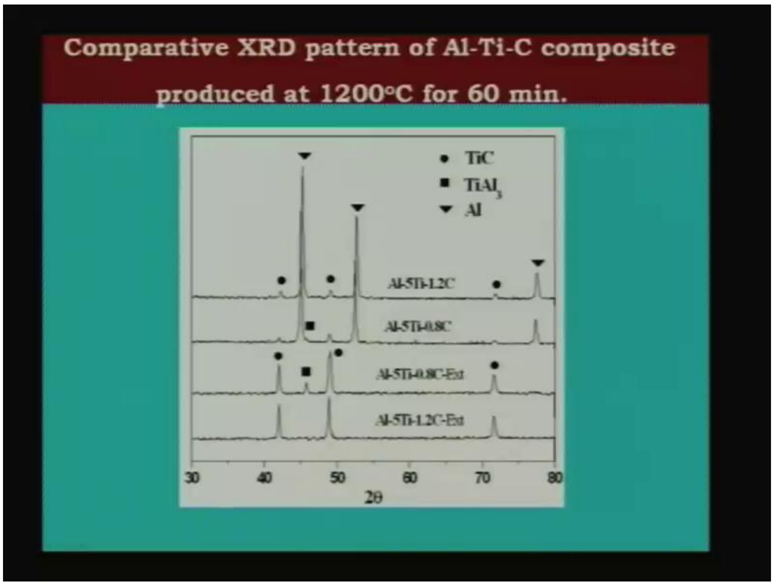
Comparative XRD pattern of Al-Ti-C composite produced at 1200°C for 60 min.

All the peaks will be only TiC peaks, from that you can clearly say that there is no TAl3 and if you go to 0.8 you can see this. And from the ratio of this peaks one can find out how much of TiC is there and how much of TAl3 is there. So, the weight fraction of TiC and TAl3 in the composite can be found out from this kind of extraction experiments. Whenever you are do working on composites, this is the best way to find out what is the volume fraction. Because, otherwise unless you do a large number of metallographic experiments, to find out what is the volume fraction. It is very difficult to find out the volume fraction. And mostly in a metallography, if you use what is called quantitative metallography. You will only get the area fraction, you will not get the volume fraction.

We usually assume the area fraction to be equivalent to volume fraction and then assume it and do it. But, that is not a correct assumption. So, as a result this is not a correct way of doing it. But, if you can dissolve the matrix very easily which is possible in aluminum makes alloy very easily. Then, you can get the weight fraction and once you know the densities one can calculate the volume fraction.

That means you take a known weight of aluminum, titanium, carbide composite and that known weight you try to dissolve into a let say sodium hydroxide solution. And take out all the particles that come out. And weigh those particles from that one can get an idea of what is the weight fraction of these particles.

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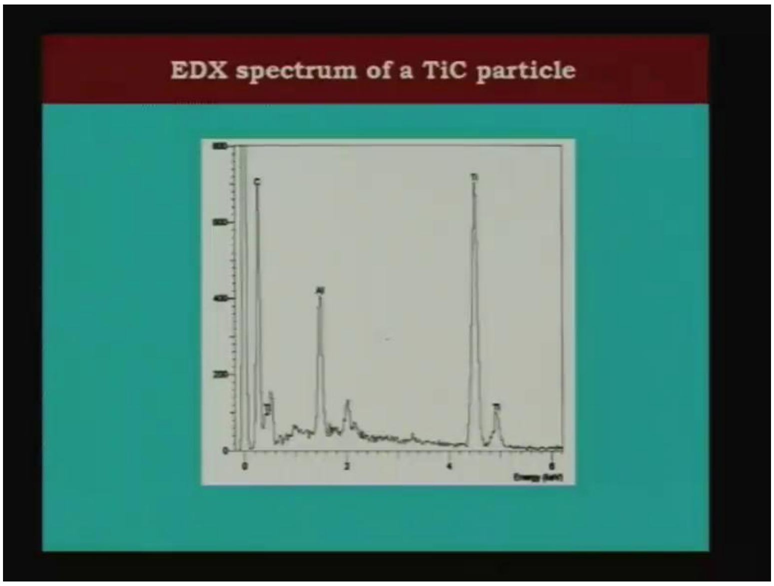

EDX spectrum of a TiC particle

And look at those particles in the EDX also confirm that they are only TiC particles.

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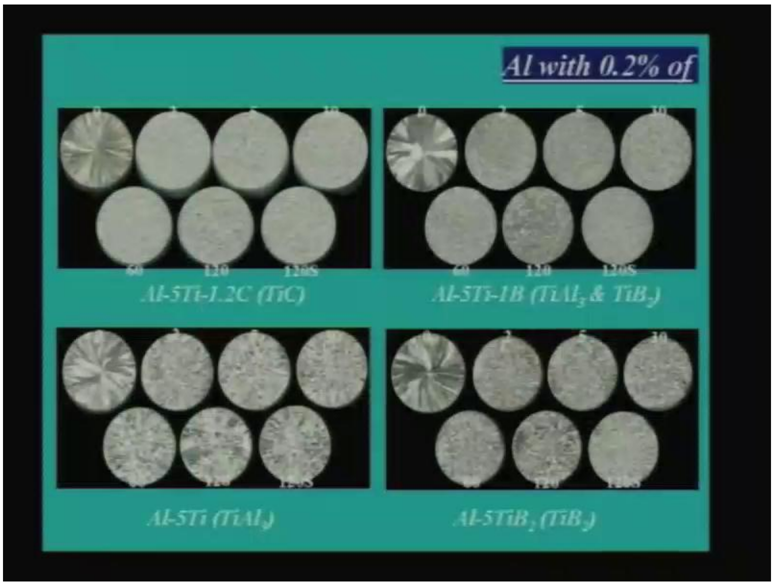

Al with 0.2% of

Al-5Ti-1.2C (TiC)

Al-5Ti-1B ($TiAl_3$ & TiB_2)

Al-5Ti ($TiAl_3$)

Al-5TiB$_2$ (TiB_2)

And here I am not showing you the mechanical properties, which are similar to that of the TIB2, but looking at the grain refinement behavior of this look at this alloy, which is added to pure aluminum and compared it with different type of grain refiners. One is a aluminum 5 titanium grain refiner aluminum 5 titanium grain refiner has only Ti3Al three particles.

So, here you have only Ti Al3 particles acting as nucleating sights. You can see the grain refinement is not very good. This is without any grain refinement you get a columnar grain structure, which is typical of any casting. And if you add the grain refiner you get some grain refinement, but not very good grain refinement. You add aluminum 5 TIB2 composite. Where only TIB2 is there again here also you get grain refinement. But, not as good grain refinement as you can get with TiC alone.

So, here you have only TiC here if you take aluminum 5 titanium one boron kind of master alloy, which is a conventional grain refiner. It will have both TAl3 and TIB2. So, if you compare all these this gives you an idea of grain refining potency or grain refining efficiency of individual particles. How does TAl3 act; that means, for example, whenever we are talking of heterogeneous nucleation, what is important is what is called contact angle.

You must have read about heterogeneous nucleation. In a heterogeneous nucleation the interfacial energies are going to decide, what is the wettability of the particle with the aluminum. And that is what is going to decide the contact angle. The lower the contact angle the better the wettability we say. So, that is what, one can indirectly get here that TAl3 is not very good T I B 2 also not very good. And a combination of these two also does not give you as good as what you get with TiC. So, this is one important thing with aluminum.

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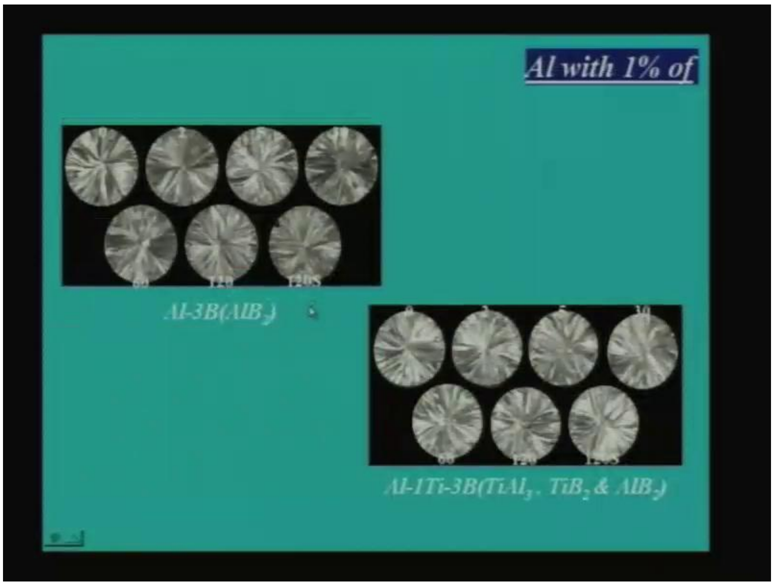

Al with 1% of

And e with aluminum boron where you have AlB2 you do not get any grain refinement at all. So, AlB2 does not give you any grain refinement with aluminum. You can see even after adding AlB2 you get the same columnar grain structure.

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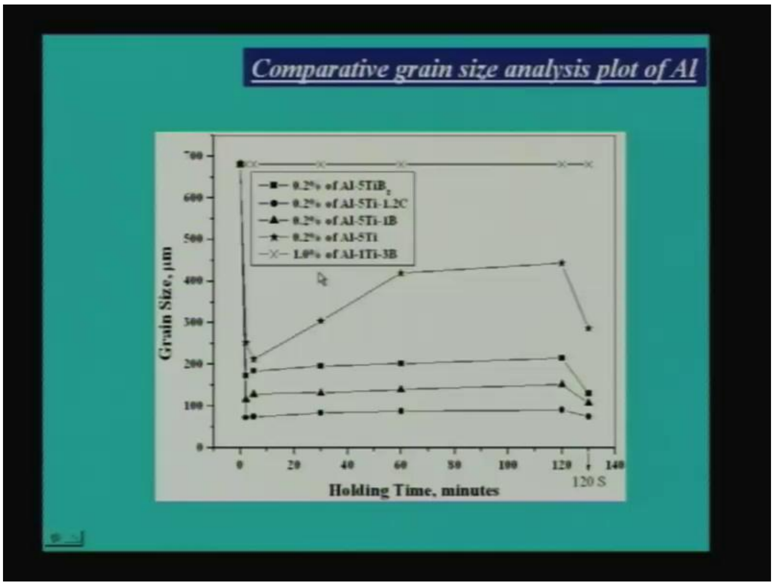

Comparative grain size analysis plot of Al

So, this is to give an idea of a grain sizes that you can get, yes. And you can see that with the TiC, you get the lowest grain size. And the AlB2 with boron alloy you get the highest grain size.

So, one can talk about the grain size analysis. And this is with silicon aluminum 7 silicon. Usually we know that most of the grain refiners. When you add to aluminum you get good grain refinement, but when you add to aluminum containing certain alloying elements, you do not get grain good grain refinement.

This is what people call it as poisoning effect; that means, the alloying elements present in the aluminum reacts with these particles, which are present, which you are adding for grain refinement. The heterogeneous nucleating sites and forms some kind of complex particles on the surface of these particles.

For example if I take a TiAl particle add it to aluminum silicon alloy. The silicon that you have will react with Al3Ti and form titanium silicon, because the titanium silicon has a stronger affinity. And because of that the silicon will react with TAl3 and form a titanium silicide coating on the TAl3. And this particle now which has a coating of titanium silicide cannot act as a nucleating site. Because, it is interfacial energies have completely changed. It is contact angle has completely changed because you have some other coating on the TAl3.

And this kind of a thing is observed in a number of aluminum alloys containing either silicon or for example, lithium aluminum lithium are also very bad for this. Aluminum chromium aluminum zirconium all these alloys are known to be poisoning alloys as for as grain refinement is concerned.

So, people want to study which kind of particle is very good as far as this kind of poisoning alloys are concerned. I cannot say you do not use that kind of an alloy, because aluminum silicon alloy have certain important applications.

We cannot say that do not use aluminum silicon alloy the only way to say is which either you do not grain refine it at all. That means, you do not grain refine means, you are not able to achieve an improve in the strength, because of the grain refinement which you could have achieved by doing grain refinement. Or add a grain refiner, where the particles do not get reacted by the silicon, where the particle of stronger, where the bounding between the two elements in the particle is much more stronger than with silicon one such as example his tic here again tic.

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Al-7Si with 0.2% of

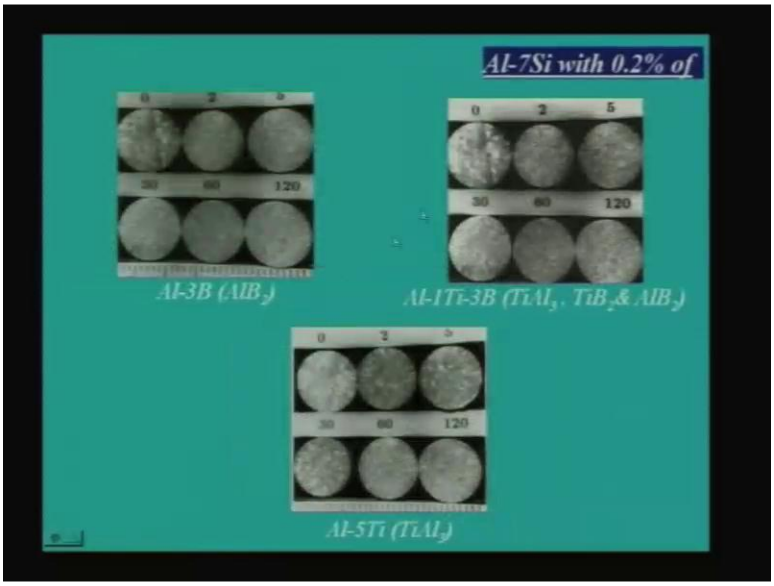
Al-5Ti-1.2C (TiC)

Al-5TiB$_2$ (TiB$_2$)

Al-5Ti-1B (TiAl$_3$ & TiB$_2$)

The titanium carbide is much more stronger than titanium silicide. The interaction parameter is much more stronger, because of which the affinity. Though if you hold very long period there is some reaction of silicon with TiC, but at particularly at short holding time you can see that here you get very grain refinement and you add and you add TiB alone you do not get that. And you add a conventional alloy which is 5 titanium one boron containing TiAl3 and TIB2 again you see you do not get as could grain refinement as you get here. So, this is one important thing, that this Ti is a good grain refiner not only for pure aluminum. But, also for aluminum alloys which have poisoning elements.

(Refer Slide Time: 52:30)


Al-7Si with 0.2% of

Al-3B (AlB$_2$)

Al-1Ti-3B (TiAl$_3$, TiB$_2$ & AlB$_2$)

Al-5Ti (TiAl$_3$)

This is with aluminum boron and this is with aluminum 1 titanium three boron containing different particles. This is with aluminum titanium alone containing TAl 3 particles all with aluminum 7 silicon to show these are all not as good as what you get with TiC.

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LM25 (Al-7Si-0.35Mg) with

0.1% Al-5Ti-1.2C (TiC)

1% Al-1Ti-3B ($TiAl_3$, TiB_2 & AlB_2)

1% Al-3B (AlB_2)

And this is with a commercial aluminum alloy called lm twenty-five containing small amount of magnesium in it. Again here also you see TiC gives you the best grain refinement, when compared to all other things. So, we will stop with this and continue in the next class.

Thank you very much.