Friction and Wear of Materials: Principles and Case Studies
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Lecture - 34
Wear of TiB2 Ceramic Composites

So welcome back to this NPTEL lectures on and this lecture as well as the next lecture I will be discussing that wear of friction and wear of ultra-high-temperature ceramics or high temperature ceramics mostly on the titanium diboride and another one is that niobium boride.

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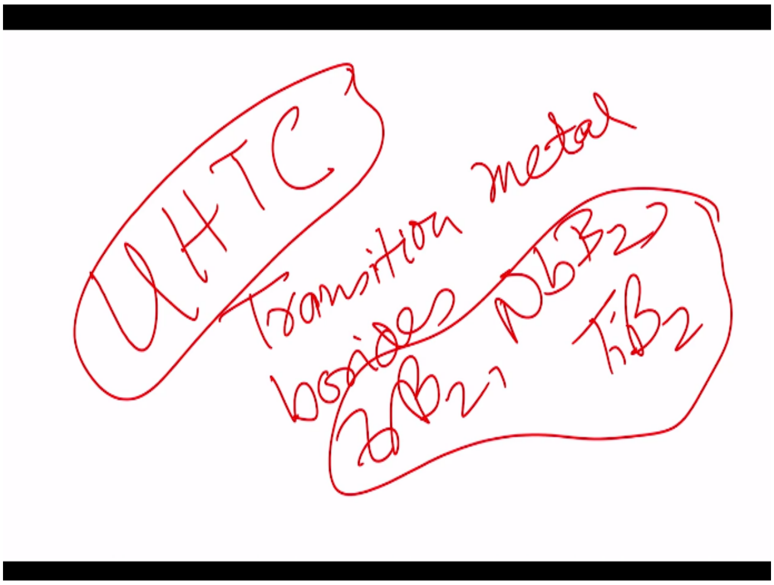

Although, we are not discussing this in more details which I will be doing in the next slide is this transition metal borides like zirconium boride, niobium boride and to some extent titanium boride. So these are the transition metal borides, they belong to a generic class of materials which we call as UHTC. UHTC stands for ultra-high-temperature ceramics. Since this is not a course in ceramics but this is a course on tribology.

But as I mentioned to you multiple times that this course is unique because here our focus is to understand the wear mechanisms of a broad range of ceramics as well as metals and these understandings of our wear mechanism would be useful to develop next generation materials for better and better wear resistance properties.

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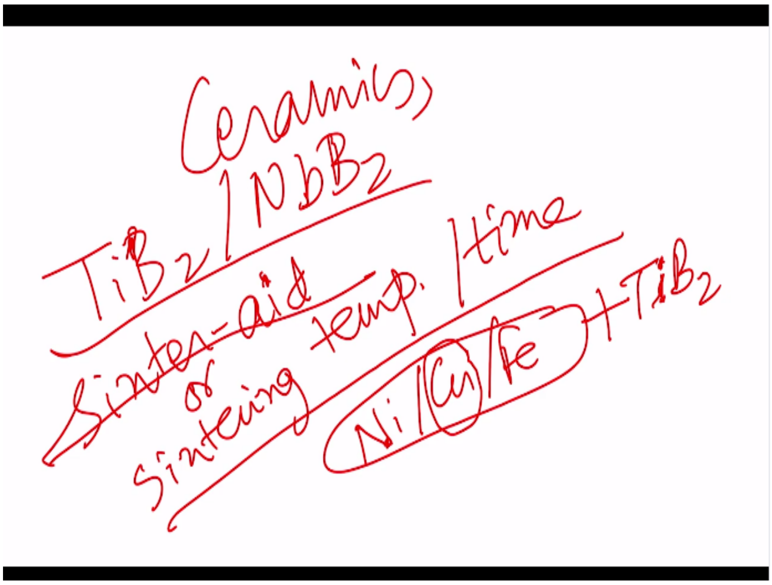

Now this particular ceramics so like titanium diboride and zirconium diboride these kind of materials that consolidation or densification of these materials is fairly important and which is not a very easy task. So some of the things that which are important it is sinter-aid like what is the addition of the sinter-aid and sintering temperature or sintering conditions, sintering temperature, sintering time, etc.

So these are the parameters which needs to be optimized while consolidating these materials. Now people in the past has used some of the metallic sintering aid like nickel or copper or iron to consolidate titanium diboride. Now what happens when you add these metallic materials, these metals depending on the sintering temperature these metals can melt and giving rise to liquid phase sintering.

But because of the liquid phase sintering your grain morphology also would change like microstructure would change but the point that is more important that if we use these materials at high temperature then what happens at high temperature this metallic phase again will be molten and therefore you cannot use these materials at high temperature. So the use of metals will severely restrict the application temperature of these classes of ceramics.

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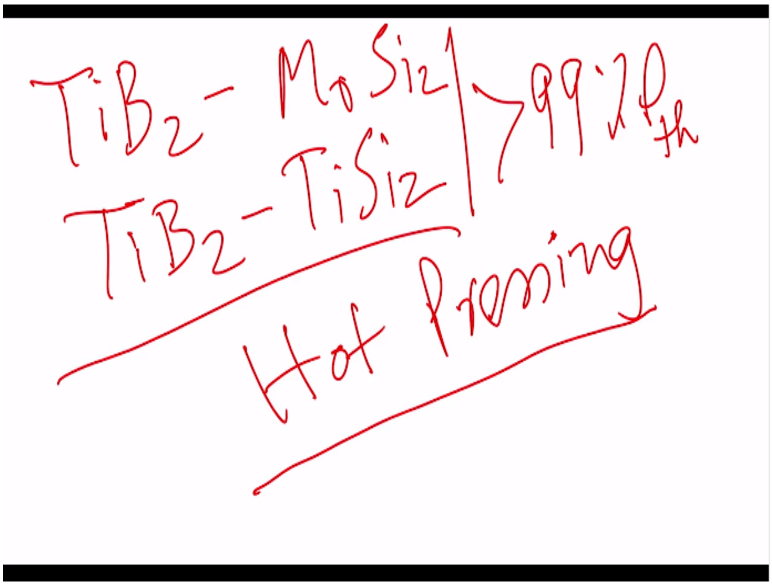

Now keeping this in mind what we have used and what you will see in next 25 minutes or so we have used the different type of sinterate one is molysilicide because molysilicide also is one of the materials for high temperature applications because some of the high temperature furnaces you will have this molysilicide as a heating element and while analyzing that microstructure and phase composition of TiB2 molysilicide composites what we have noticed that.

Because of the sintering reactions TiB2 reacts with molysilicide to form TiSi2 or Ti5Si3 so at the next level what we have done, we are trying to understand whether we can use the TiSi directly to TiB2 in order to develop another classes of materials that TiB2 TiSi2 ceramics. So these are the two classes of ceramic materials mostly based on TiB2 but with different sinter-aid ate one is molysilicide, one is titanium disilicide.

And we have used that hot pressing as a technique to consolidate these materials, so depending on what is the sinter-aid right we have used the sintering temperature and we have tailored the sintering temperature but hot pressing is the major consolidation route that we have utilized to densify this particular ceramic materials for more than 99% theoretical density, so 99% rho th that is the theoretical density of this sintered materials.

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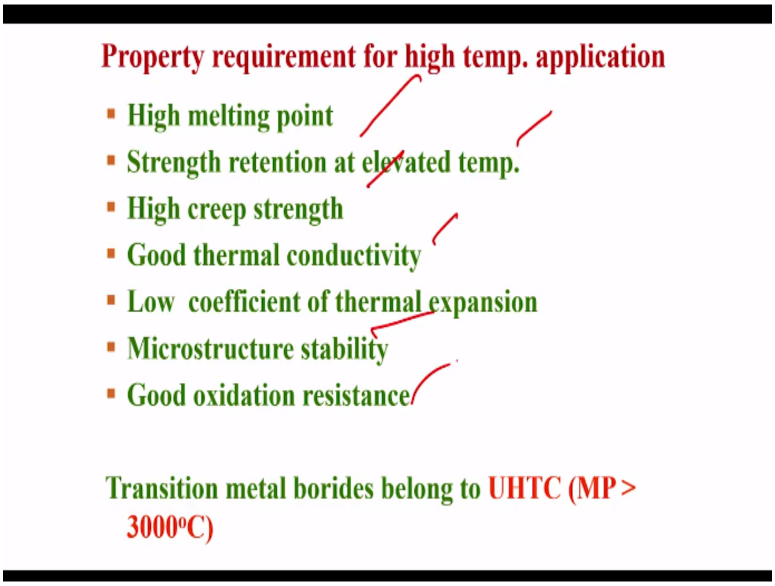

So what is this property requirement for high temperature applications, this material should have high melting point, there should be strength retention at high temperature, high creep strength, good thermal conductivity, microstructure stability and good oxidation resistance.

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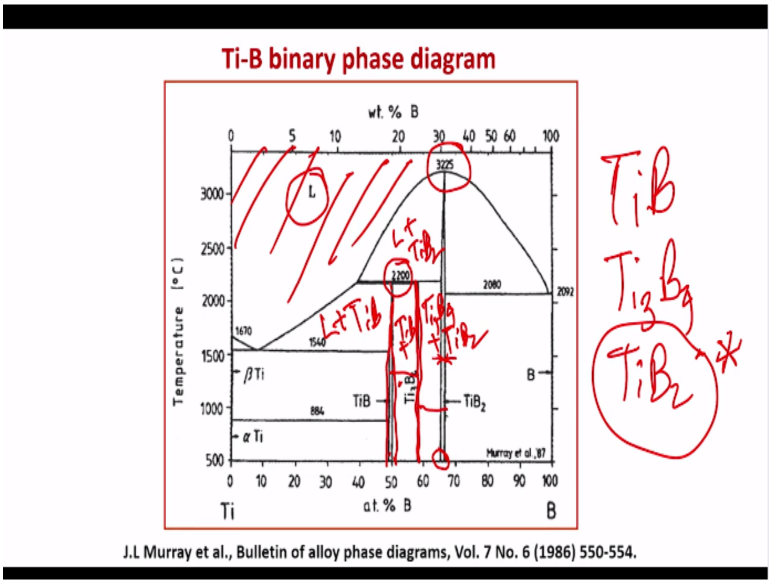

Now this is the titanium boride binary phase diagram. So those who are not from metallurgy background essentially the phase diagram is a 2-dimensional space which describes the stability of different phases in temperature, composition, space. So that is how typically undergraduate students in metallurgy learn in the university that essentially a phase diagram to any metallurgist essentially means temperature versus compositional variation.

Here if you see along the x-axis it is atomic percent boron which is varied from 0 to 100%. Now how to find out that which are the phases that are present. For example, this L stands for liquid that means this entire region, this shaded region this material exists in the liquid state. Now this is your line compound that is Ti3B4, line compound means it does not have any off-stoichiometric range, it is essentially has a fixed composition.

But TiB2 is not in strictest sense, it is a line compound because TiB2 has a smaller window, has a smaller window of the off-stoichiometric composition. So TiB2 is essentially around 65 to 67% boron content so that is the range of the boron in the TiB2 and TiB2 has a melting point in 3225 degree Celsius. So as far as the melting point wise, TiB2 certainly can be classified as ultra-high-temperature ceramics.

But one of the additional requirement for ultra-high-temperature ceramics is that these materials must be used without ant property degradation at extremely high temperature so where zirconium diboride or niobium diboride that actually qualifies so other things that are important is that it is not only the line compound or the covalent compound like TiB or Ti3B4 that is important.

TiB also some of the TiB goes to so this is the region is liquid+TiB2 okay, so if you increase the temperature to above 2200 degree Celsius at this particular composition, so TiB will melt and it will enter into phase domain of liquid+TiB2 phase okay. So therefore the maximum temperature stability of all these 3 compounds in the TiB system, these 3 compounds means TiB, Ti3B4 and TiB2.

The TiB2 is the base, so I put a star here because TiB2 has a large melting point of 3225 degree Celsius okay. So other things is that you know that if you look at this particular phase diagram it is this region is the liquid+TiB so this would be TiB+Ti3B4 and this is the Ti3B4+TiB2 okay. So like that one can find out that what are the phases that present so you can take a horizontal line.

And then you can see that which are the phases that are present at two ends of the horizontal line and that will be used as a guideline to say that what are the two phases that are stable in this particular temperature composition space.

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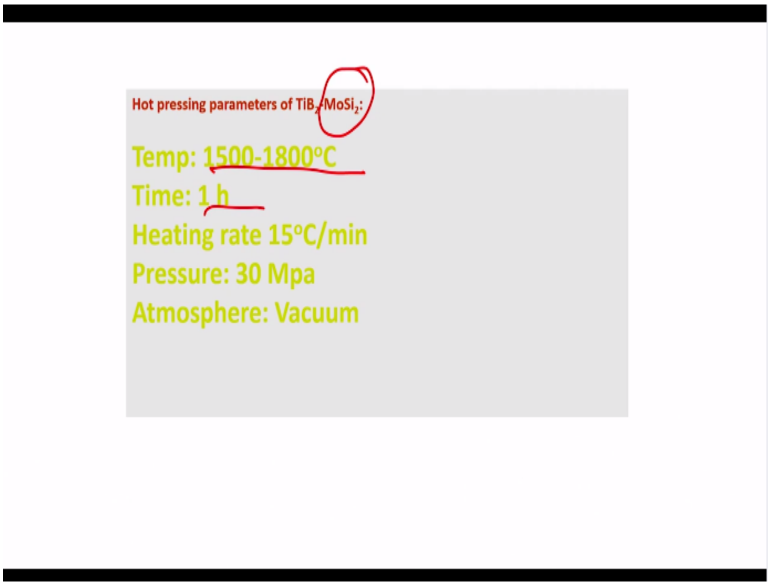

So as I said before that we have used two different types of sintered-aid one is the molysilicide so that is the first set of experiments. So in order to optimize the hot pressing conditions we have varied the temperature from 1500 to 1800 degree Celsius, time is around 1 hour so this is the heating rate and then hot pressing was conduction in vacuum.

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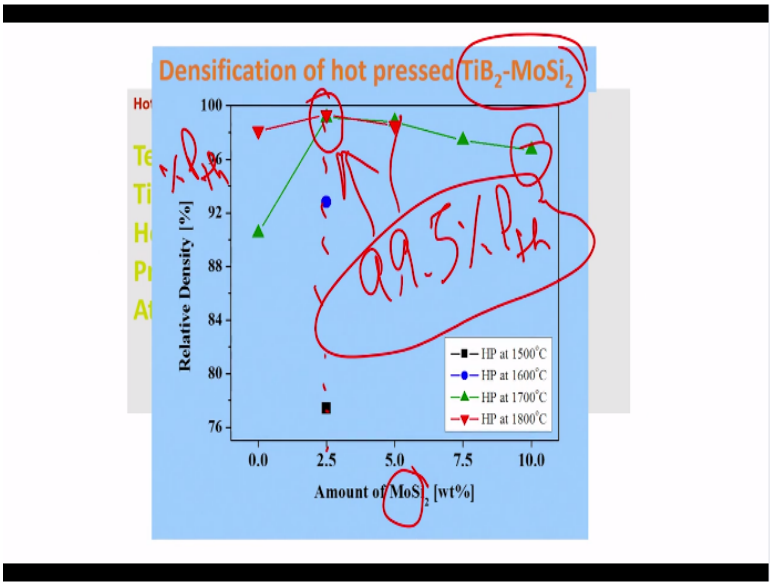

Now here goes the typical data that we have obtained of the relative density that is percentage rho th, rho th stands for theoretical density. So when you add molysilicide as the sintering-aid and when you sinter them at 1700 degree Celsius black one or 1800 degree Celsius what you have seen at 2.5 molysilicide content addition that you are getting close to 99.5% theoretical density, so 99.5% theoretical density is the maximum theoretical density that one can get in the hot pressed TiB2 molysilicide content at low amount of sintered-aid.

The second thing it is important for you to realize that while developing this wear resistance ceramics while you need to use the sintered-aid to densify the ceramics but one has to use the sintered-aid to as low amount as possible so that the base line properties of the major ceramic phase is not compromised. Let me substantiate my statement in reference to TiB2 molysilicide.

So what I am saying for example if you do not do these experiments if you suddenly started using with the intuition that if you add 5% or 10% anyway the material would be sintered to full density or more than 98% sintered density. So if you add this 10% molysilicide what would happen, your base ceramic base ceramic phase is lesser right TiB2 would be 90% but then your baseline properties like in terms of hardness and other strength properties would be compromised simply because of the presence of unnecessarily higher amount of sintered-aid.

So one has to use simply more amount of sintered-aid while achieving higher sintered density in the hot pressed ceramics so that is the major message that I wanted to send across.

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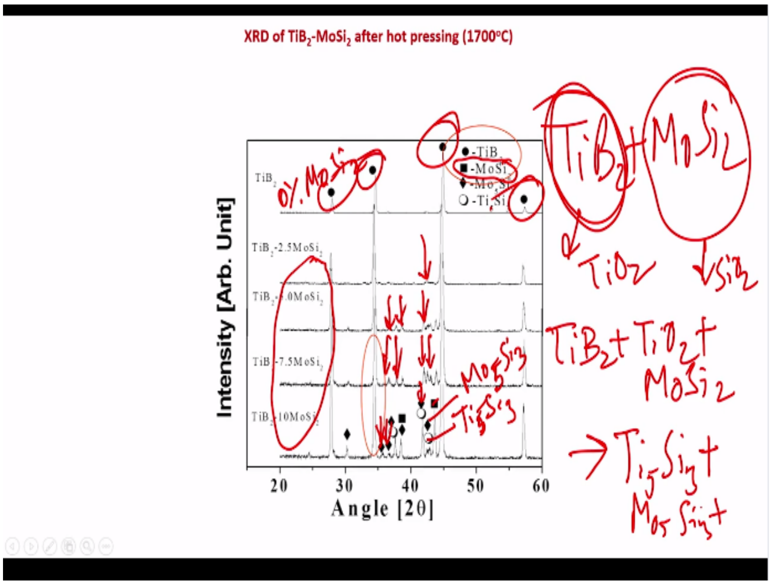

Now these are the XRD traces of this TiB2 based materials so this is the 0% molysilicide that is the top most one, so you get all the TiB2 phase that is what you expect in the hot pressed ceramics. In the TiB2 molysilicide 2.5 and 5% you see something is popping up, something is coming up okay and this phase is getting more and more pronounced when you add these 7.5% molysilicide.

Now if you look at the symbols very carefully filled and square it is molysilicide and that is certainly that should be certainly present when the molysilicide content is 5% and more. Now what are the other symbols? Diamond symbols, these are Mo5Si3 so diamond symbols are Mo5Si3 which are also discernible and this circle unfilled circle that is this one is Ti5Si3. So these are the two phases that are formed presumably because of the reaction between TiB2 and molysilicide.

So what are those reactions that can possibly take place between these things? So one of the reaction that can take place TiB2 so essentially TiB2 and molysilicide that will react to Mo5Si3 and Ti5Si3 right. So what happens, we have to consider the two things here. Each of the TiB2 particles it has a surface oxide layer of TiO2 okay. Similarly, molysilicide also can have a surface oxide layer as a SiO2.

So when you use these reactions TiB2 then one has to also find out that what is the reaction like MoSi2 TiB2 and you can find out that how these sintering reaction product Ti5Si3 and Mo5Si3 this kind of phases are formed and there will be certainly some boron oxide or silica that would be the third phase that is forming.

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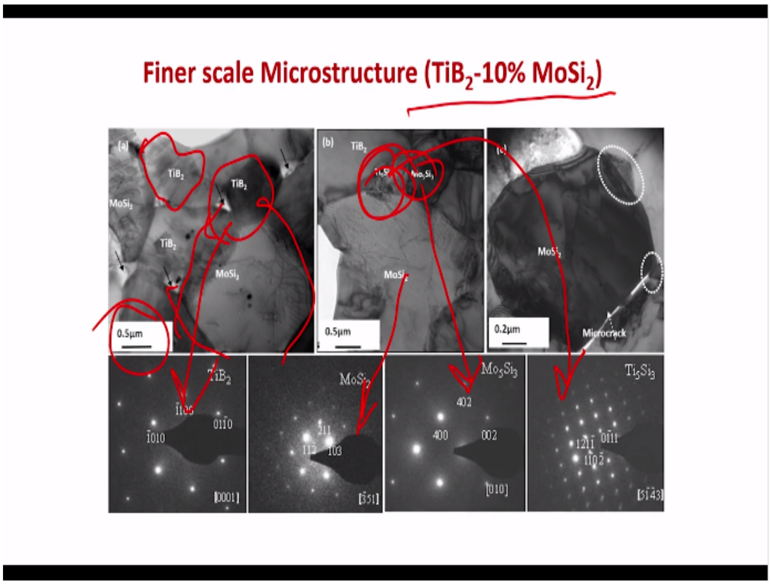

Now this is the transmission electron microscope images for one of the composition that is with the high molysilicide content is TiB2 molysilicide and then each of this grains are also marked on this TEM images whether it is TiB2 or molysilicide and Mo5Si3 and then corresponding selected area diffraction pattern has been shown here. For example, this is for

Mo5Si3, this is for molysilicide and this is for Ti5 there is also Ti5Si3 phases these are formed right, so this is for Ti5Si3 and this is for TiB2.

So TiB2 is hexagonal structure and all other silicides are also their zone axes are also marked so this is the bright filled imaged, these top panels these images are bright filled images and you can clearly see this is a TiB2 grains and these are the larger coats are molysilicide grains are there. So if you look at this micron of 0.5 micron so certainly this molysilicide grains will have few microns like 3 to 4 microns.

And TiB2 phases fairly small and then some of the phases which are form the silicide phase molysilicide and Ti5Si3 which have essentially formed at the interface between the TiB2 and molysilicide.

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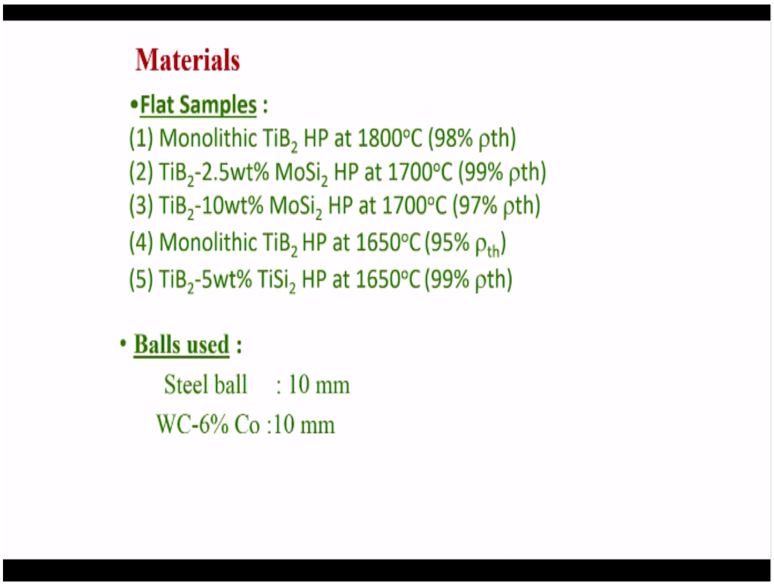

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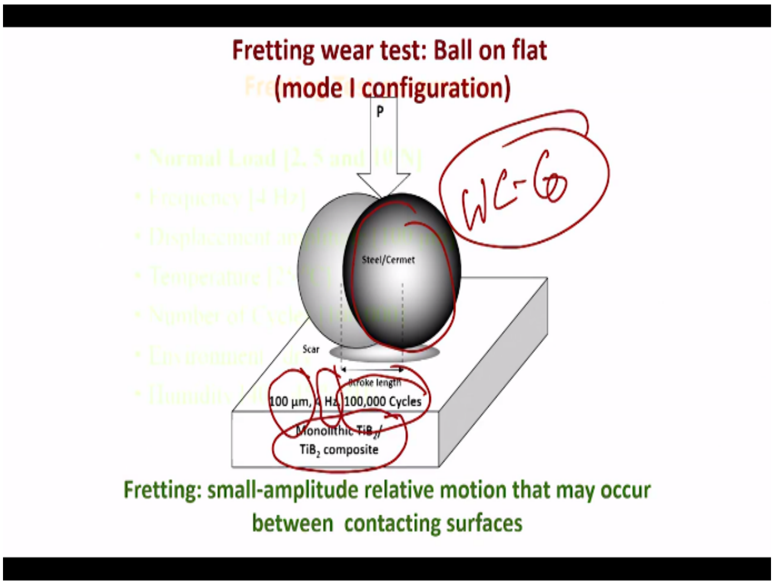

So we have done this friction and wear experiments particularly in the fretting mode, again TiB2 molysilicide is flat materials and steel wall or cermet tungsten carbide-cobalt is used as the matting material and then these are the fretting conditions like 100 micron sliding, 4 hertz is the frequency and 100,000 cycles.

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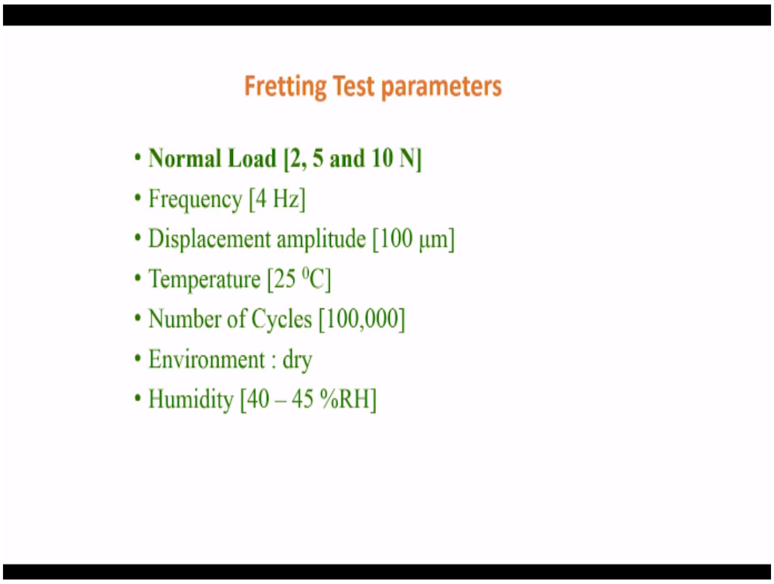

The load is varied between 2 Newton, 5 Newton and 10 Newton and frequency is 4 hertz and there is a displacement amplitude that we have also mentioned earlier.

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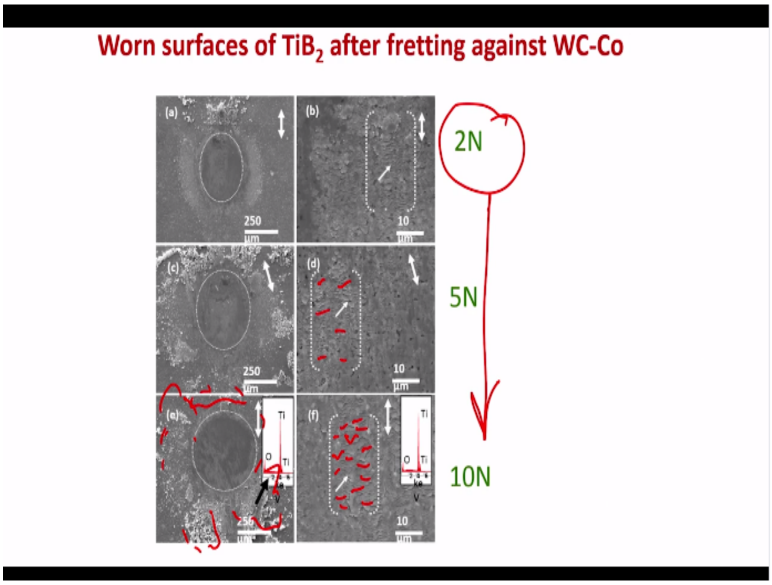

Now this is the frictional properties of the TiB2 2.5% molysilicide if you remember correctly that this particular TiB2 with 2.5% molysilicide has full density and also it has higher hardness properties. We have selected this TiB2 molysilicide for the fretting studies and what you see here that when the load is varied between 2 to 10 Newton, so the difference is the friction coefficient is somewhere around 0.05.

So it is between 0.5 to 0.55, so there is not much difference significant difference as far as the load variation is concerned alright. So this is the wear surfaces of TiB2, worn surface of TiB2 after they are fretted against tungsten carbide-cobalt that is the cermet. Interestingly, what you see here this is a 2 Newton and this is in case in the load 2 to 10 Newton, you see there is a numerous microcracking patterns.

What you have noticed sometimes in one of the earlier lecture that after cryogenic sliding conditions, the zirconia they experiences a fish-scale patterns. So it is somewhat like fish-scale patterns, very characteristic microcracking patterns and this microcracks are quite interesting enough, they have formed in a group manner and this ensemble of microcracks that are observed only at certain localized region in the worn surface.

And what you notice here that around this worn wear debris, worn surfaces these wear debris particles are also present and this wear debris particles are of different chemistry because it is certainly from the contrast that you observe certainly it cannot be pure titanium oxide so or it can be some other oxides of the TiB2 or molysilicide.

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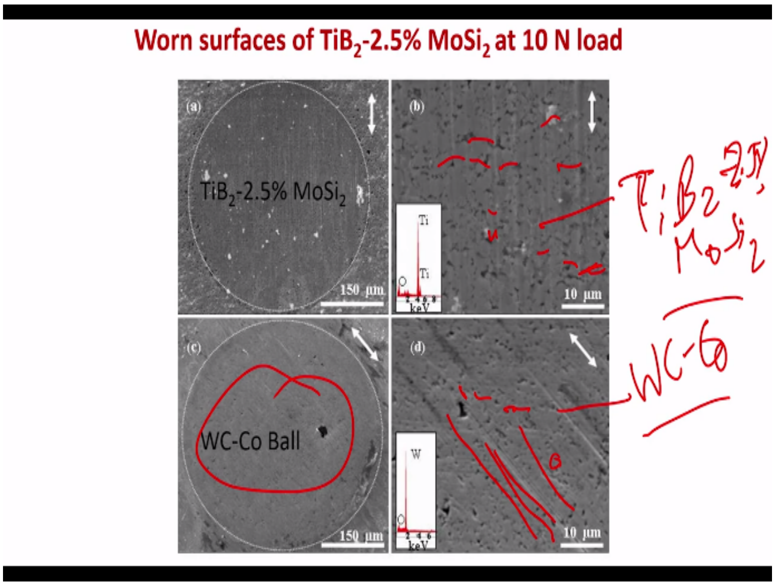

At 10 Newton load, you see that more evidences against after they have slided against the hard metal so these are the abrasive scratches here, you can see that there are abrasive scratches and then you can see there is small regions where there is cracking also observed but the severity of abrasion is certainly not much because this is what you see in the tungsten carbide-cobalt ball, so these are worn surface region tungsten carbide-cobalt.

And this is the corresponding flat that is TiB2 2.5% molysilicide okay, so this is at the high load of 10 Newton and again TiB2 2.5% molysilicide you see this cracking, this microcracking are fairly small and they do not coalesces together to lead to the major macrocracks.

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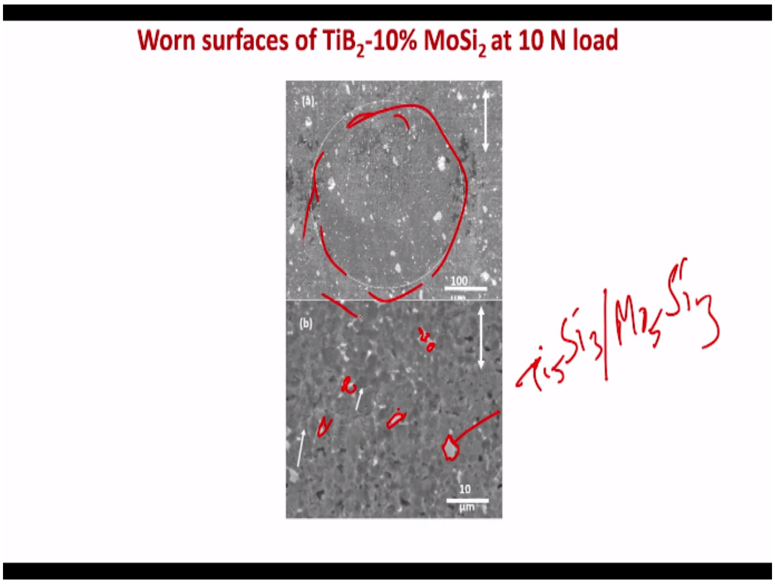

So this is how the worn surface look like after they are fretted against tungsten carbide-cobalt at 10 Newton load certainly you see this is the presence of the difference silicide phase at TiB2 10% molysilicide, this can be either Ti5Si3 or moly Si3 one of this silicide phase okay and this is the typical worn surface area wear region on this particular surface.

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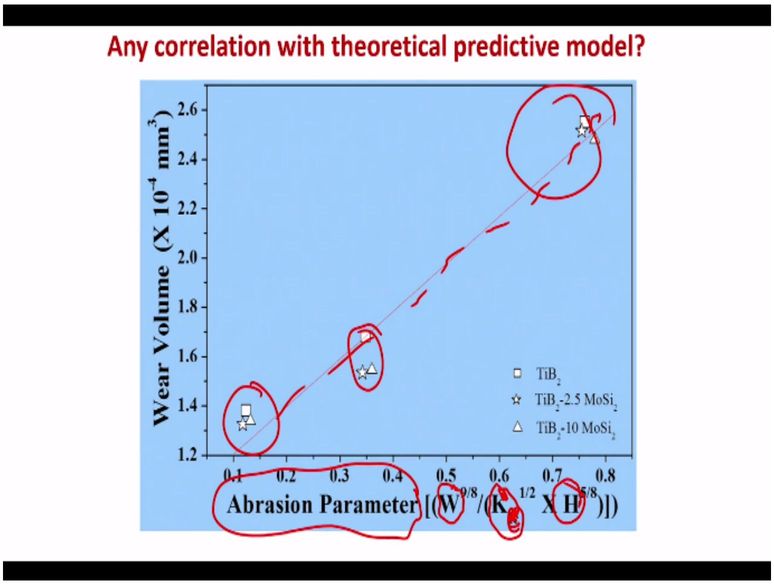

Now one of the important things in the tribology is to establish a correlation between the wear volume and dissipated energy, so this dissipated energy one can find out suppose you have a tangential frictional force and this is your displacement delta and most of your wear experiments fretting wear experiments are conducted what we call in the gross slip region. So gross slip region if you integrate this area under the curve that will give you the energy that is dissipated per cycle.

So if you calculate the energy dissipated per cycle and multiply by total number of cycles like 100,000 cycles and so on for each and every cycle if you calculate separately then it will give you the total dissipated energy and if you plot against it shows a very linear correlation, this is almost like the up square value would be 99.99 or something.

So all these materials the TiB2, 2.5% MoSi2, 10% MoSi2 they will follow a very linear variation of wear volume with dissipated energy. So the question is that whether any correlation with this predictive model, so another thing that we have noticed is this in this particular case of the TiB2 it is that abrasive wear very important and abrasive wear is the major wear mechanism.

So what we have done like energy dissipated another parameters we have used what we call abrasion parameter. Now this abrasion parameter it is not a single parameter but it is a composite of the load, fracture toughness that we have measured using indentation of cracking so instead of K1c it is better to use that is Kc because we are not using the mode 1 loading instead we use indentation cracking.

So if you plot that wear volume as a function of abrasion parameter again it shows a perfect linear correlation when we plot all the data's group of the data's of the TiB2, TiB2 2.5 molysilicide and 10% molysilicide materials. So in both the cases whether it is a dissipated energy or whether it is abrasion parameter for the titanium diboride wear volume correlates fairly well or linearly proportional to that dissipated energy or abrasion parameter.

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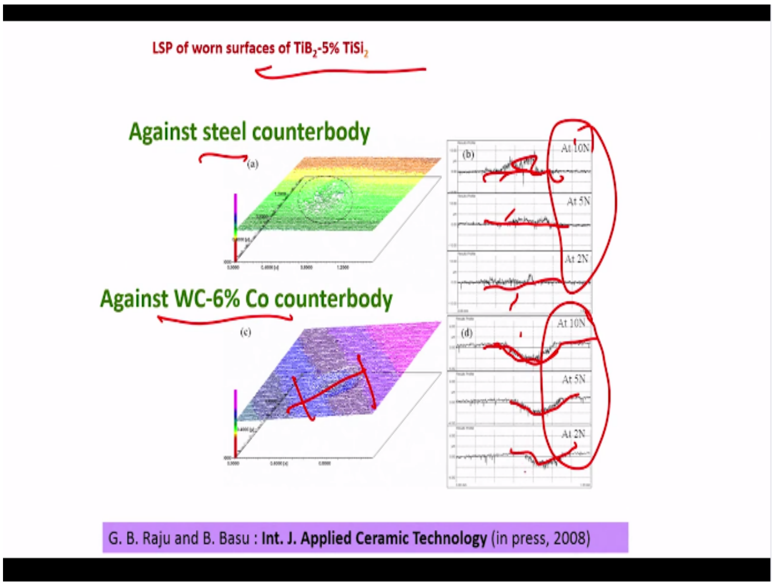

Okay so having said that next set of experiments were conducted in the titanium diboride, titanium disilicide materials. Again, we have used two counter body materials, one is steel and one is tungsten carbide 6% cobalt and what we have done in both the cases that we have finished this wear experiments at different loads like 2 Newton, 5 Newton and 10 Newton and then we have done this 2-D wear profile from several 2-D wear profile from one into another.

One can integrate to get the wear volume particularly for tungsten carbide-cobalt we see that is more or less smooth 2-D wear surfaces but in case of steel there is negligible wear in fact this steel tribolayer is formed on the material surface and it does not show any positive wear as far as the steel is concerned.

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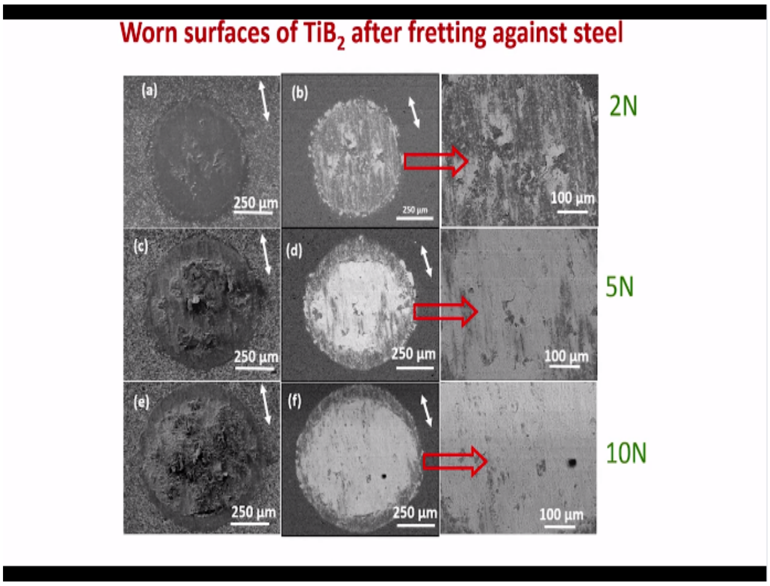

So if you see that from the top to bottom the top analysis for 2 Newton load, middle one for 5 Newton load and bottom one for 10 Newton load. So the left most surfaces are mostly these surfaces on the flat that is titanium diboride, middle column is for the steel ball and you can see steel ball is completely covered with the tribolayer and this is iron oxide rich layer.

And if you look at the little bit closer view of this material of these worn surfaces, you will see that steel layer is not only there on the material on the ball material but also on the flat material essentially it gives rise to three-body wear situations okay.

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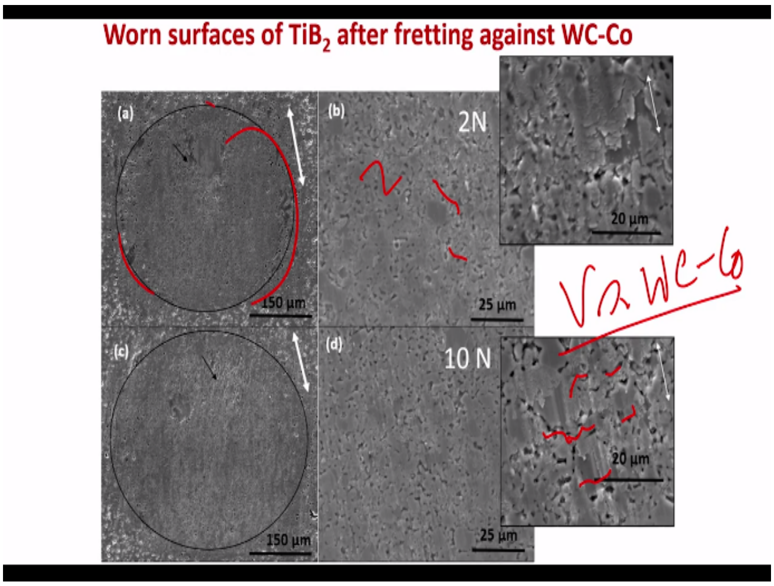

So after tungsten carbide-cobalt so this is after against versus tungsten carbide-cobalt so you have this 2 Newton load and 10 Newton load and you will see in the 2 Newton load there is some occasional presence of the cracking but mostly this is the very evidence of mild wear. At 10 Newton load, the observation of cracking is much more and you can see that there are some places these cracks are generated not only perpendicular but also at other different angles to the fretting directions.

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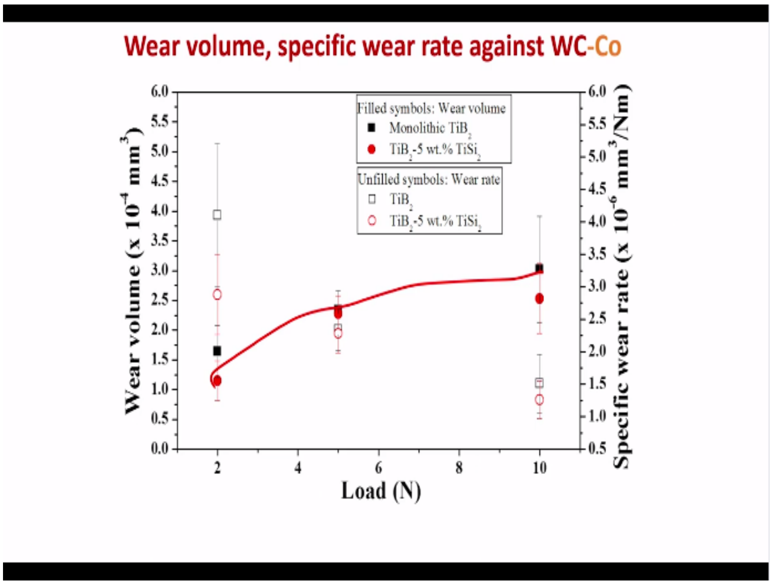

So now this particular slide essentially shows the wear volumes is plotted against the load and you will see how these wear volumes their this filled symbols are essentially wear volumes so if you plot against the load so TiB2 TiSi2 case the wear volume increases and wear rate actually decreases because wear rate when you do wear rate, it is essentially normalized with respect to load and sliding distance and it is 10 to the power -6 millimeter cube per Newton meter.

Against tungsten carbide-cobalt again the filled circles for the wear volume it shows some increase with load but this increases certainly not significant and here the wear rate is of the order of 10 to the -6 millimeter cube per Newton meter.

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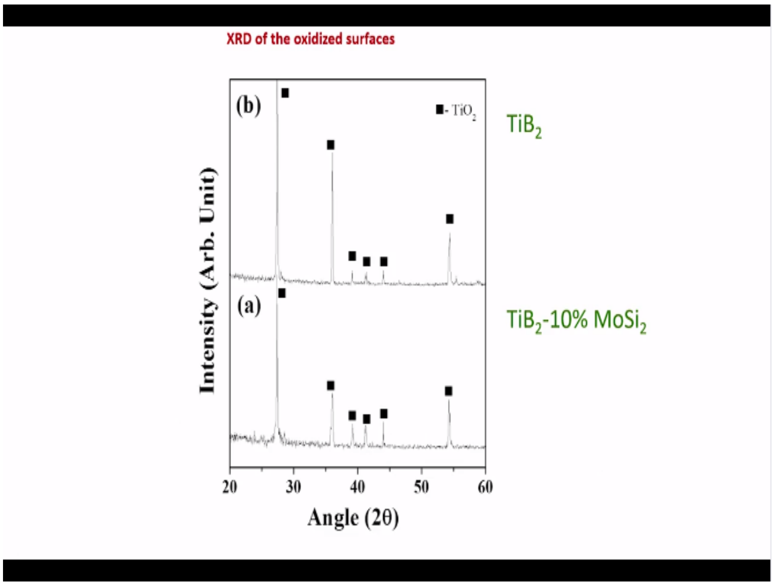

Now when you do this tribological properties so essentially what you see here that although these materials they experience abrasive wear so their wear rate is not very high or in other words it follows or it is fairly similar to the earlier model ceramic materials like alumina and so on so there also that wear rate vary somewhere 10 to the -6 millimeter cube per Newton meter.

So in the next lecture, I will describe the friction and wear properties of niobium boride but in those cases I will be showing you the erosion wear results but not the fretting wear results but at high temperature. So high temperature wear properties is somehow remains a challenge as far as the highest temperature capability of the wear tribometer but here in this next lecture I will show you that how the high temperature wear properties I mean how the erosion wear varies with respect to temperature up to 800 degree Celsius. Thank you.