Technology of Surface Coating
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Lecture 24
Coating on Ceramics by Wetting

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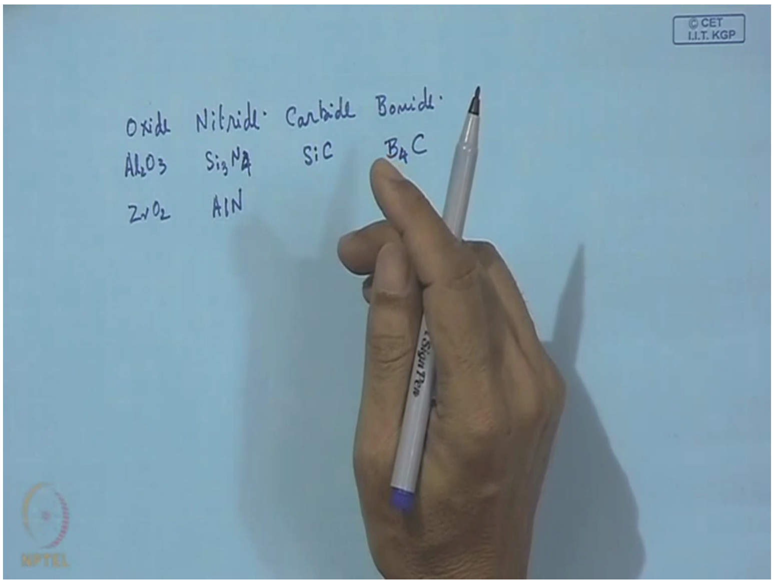

Coating on ceramics by wetting, now let us look the various Ceramics in the ceramic family mainly we have Oxide ceramic, Nitride ceramic, Carbide ceramic and Boride ceramic. So Oxide Ceramic, we can have Aluminium Oxide, Zicronium Oxide. Nitride, it can be Silicon

Nitride, Aluminium Nitride which are having engineering use than Carbide may be Silicon Carbide and Boride, Boron Carbide that is also another ceramic.

Now these ceramics have thus typical characteristics that they have a very high stability means the chemical stability and because of this they show passivity towards conventional metal and they are inert towards this metal and as such the surface of the ceramics cannot be wetted ordinarily by the commonly used metals.

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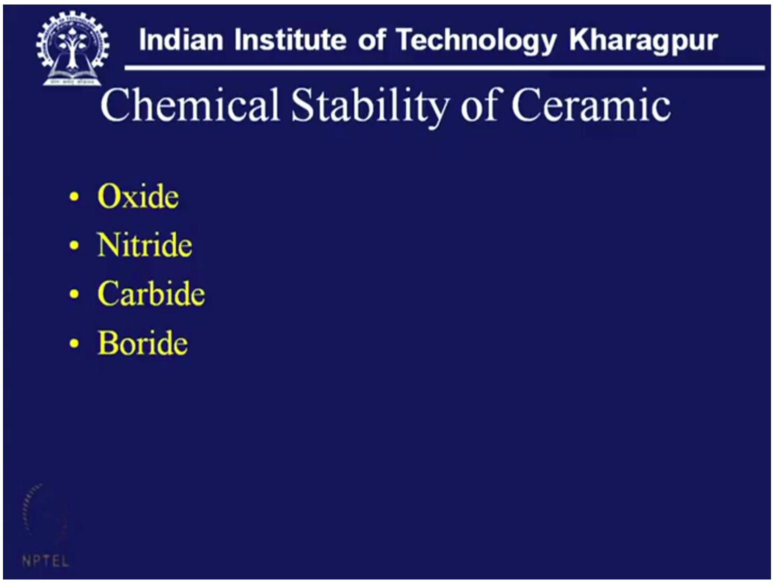

And in this scale we can also see that the Oxide ceramic is the most stable followed by the Nitride ceramic then comes Carbide ceramic and last which is least chemical stable that is the Boride. Now say if we consider Titanium as one of that material element and in that case we can see immediately that Titanium Oxide is the most stable and Titanium Boride in that scale has the least chemical stability this way we understand the inertness of the ceramic material in particular its surface towards a liquid metal and it cannot promote the wetting of this liquid metal.

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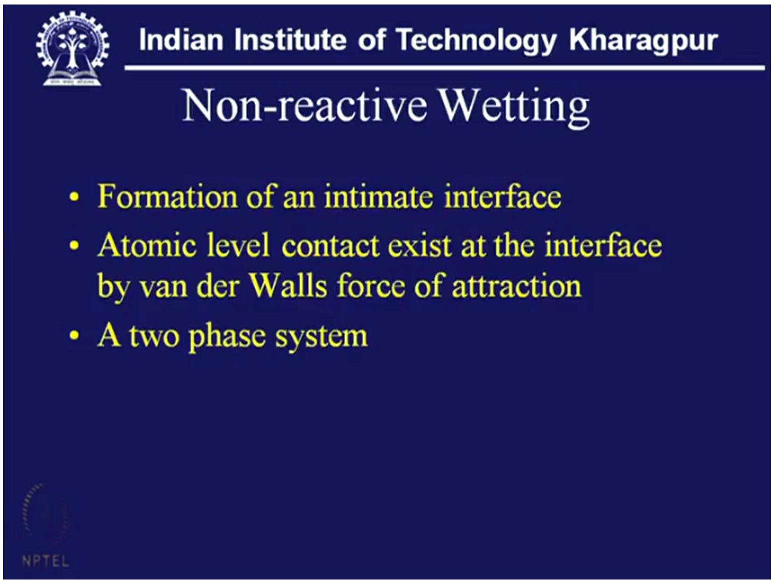

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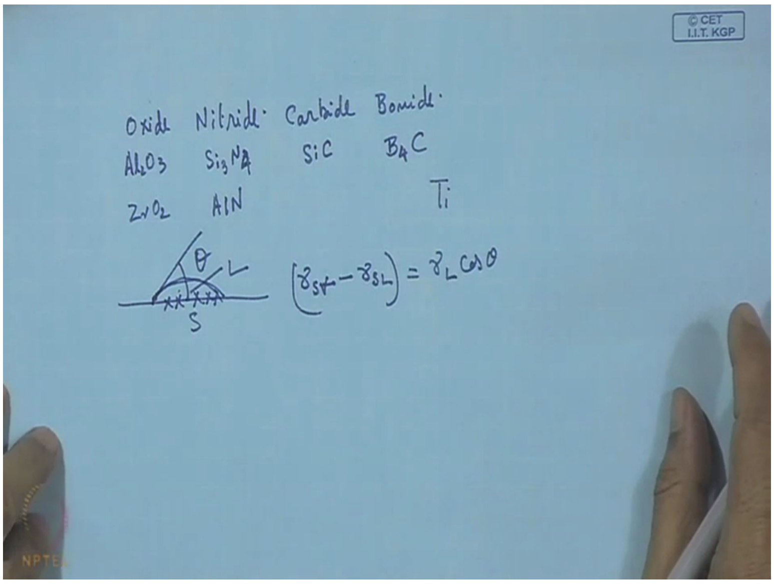

Now as we have seen or know non-reactive wetting and in non-reactive wetting quickly we can have a look, if this is the liquid and this is the solid than according to Young's equation we can immediately write this SV minus gamma SL that is equal to gamma L cos Theta where this Theta is the contact angle and there is no reactivity and this interface that is formed because of the very existence of physical force of attraction what we know as Van der waals force of attraction.

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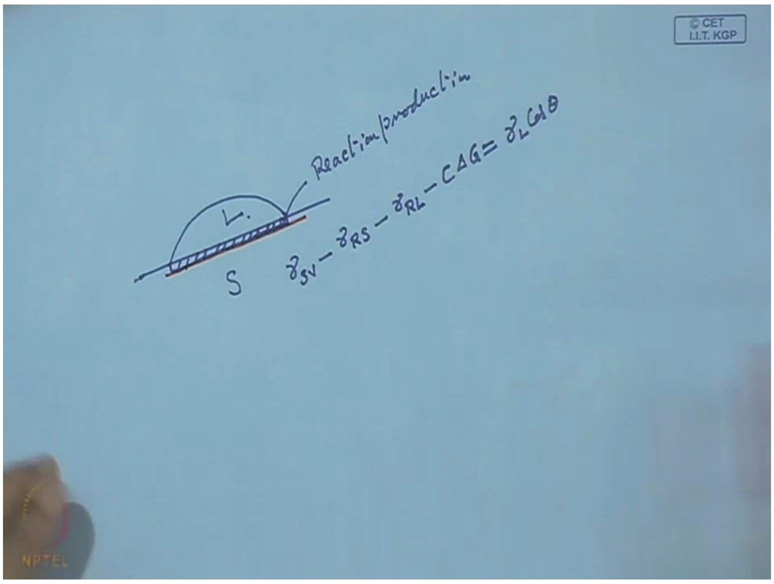

And then we have a 2 phase system liquid and solid but when we go to a reactive wetting in this case what we can see? That the liquid surface it is resting over this solid but then this wetting is promoted at least by a chemical reaction in this zone. So here we have a chemical reaction and as a result a reaction product is formed, this is the reaction product and it is now 3 body system that means this is a liquid, this is the original solid and here we have a reaction product which is also a solid.

So in that case what we have to make? It is a 3 phase system, 1, 2 and 3 and in this case we have to modify this Young's equation showing the balance of force just by writing gamma SV minus gamma RS minus gamma RL minus C into Delta G which is equal to now gamma L into cos Theta. So this is just the modification with respect to a nonwetting case. So here we have brought this is actually the interfacial energy between this reaction layer and the solid.

So R stands for the reaction layer and R is that is interfacial energy in this boundary. So this is the reaction layer this is the boundary and then we have minus gamma RL instead of SL solid liquid we have now the boundary between the reaction product and the liquid, so it is gamma RL minus C into Delta G. Now this Delta G is free energy change of this reaction that means this reaction has taken place with associated with some change in free energy which is negative in nature and that's why we bring this Delta G with a coefficient C.

And this coefficient C it depends upon the stoichiometry of this reaction product and also the number of moles of the reaction product which is formed per unit advancement of this liquid drop that means this liquid drop will keep on advancing and the value of Theta will change, so per unit advancement this mole fraction of this reaction product. So that is else actually taken care of by this coefficient C. So this is the modified version of this Young's equation.

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Now you're most important thing is that the liquid which is otherwise passive is to be activated and to make it an active alloy or a metal that must be some additive which can promote the wetting of the passive metal or alloy, it can be a pure metal or it can be one alloy.

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Now in this case what we can look into? That this way we can present that if we have a non-reactive parent material and if we can have one additive which should be a reactive element and this parent metal which is passive plus this reactive element, so they form a solution. So in this case we may consider that the passive element or the passive metal this is actually a solvent and this additive which must be a reactive element and which goes into the solution and it is the solute.

So we get a solution, now this is actually a reactive metal plus that reactive element and it becomes one alloy she supposed to react on this surface producing this reaction product and as a result of this, this equation may be followed and as a consequence of this reaction we can find that Theta value will be improved that means the Theta value will be further reduced because of this promotion of this chemical reaction.

So this will lead to spontaneous spreading on ceramic, now when we refer to this coating of ceramic by a metal and its most important application would be in metal ceramic bonding because of the simple reason that if ceramic is already metalized by this wetting action than this metalized ceramic which is basically a bonding alloy that can be held or pressed against another metal counterpart and if this temperature is rest to that point then immediately there will be a bonding between the basic metal and ceramic making a sound joint or a (()) (10:45), that's the whole idea.

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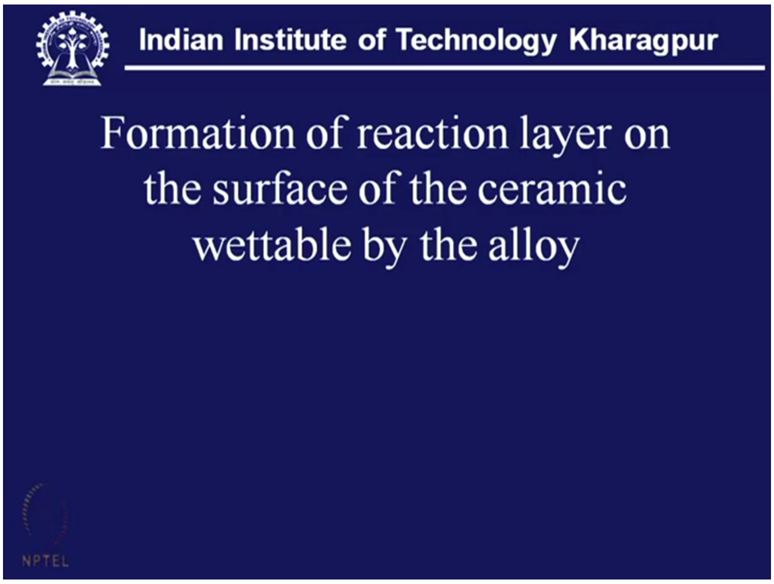

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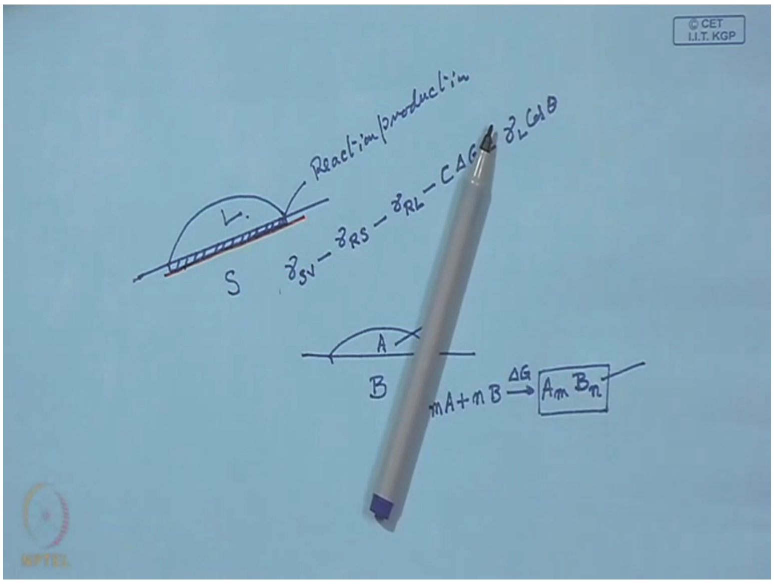

So here what we find? That formation of a reaction layer on the surface of a ceramic, so this is very important statement formation of reaction layer on the surface of ceramic that means if we consider here simply that say for example the liquid A and here we have a solid B than this liquid A having some kind of reactivity, it must react with B. So it can be put in the general form mA plus nB that will give to a compound with the suffix m for A and suffix n for B.

So if it proceeds in that direction obviously there is going to be a decrease in free energy of the reaction and this reactivity that will keep on going. However this is not the sufficient condition for wetting, what is important? That this product which is formed here that is a wettable reaction product. So it can be safely said that this reaction is not the sufficient condition, it is one of the necessary condition but the sufficient condition would be that the reaction product should be wettable by this parent metal A which is in the liquid state.

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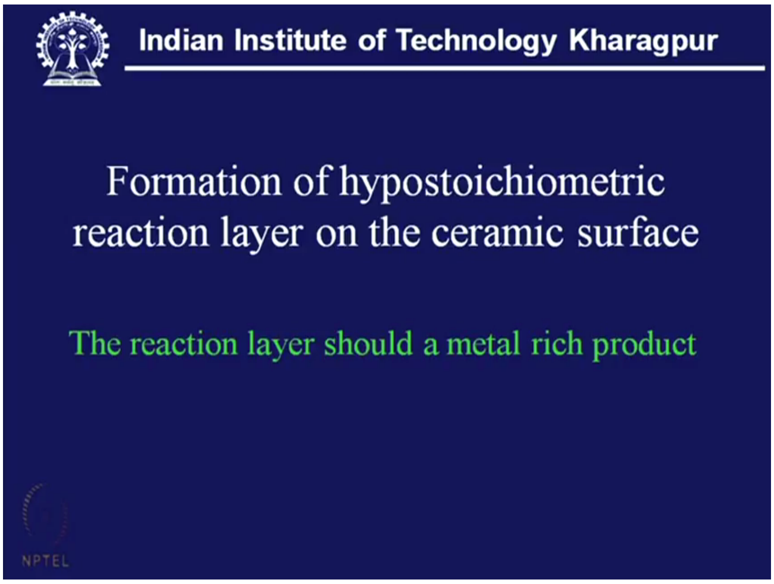

So that mean, that’s why we can emphasize give stress on this term that is the formation of a reaction layer wettable by the parent alloy. Now this call for obviously a reaction product which should be hypostoichiometry in nature that means the reaction layer should be a metal rich product.

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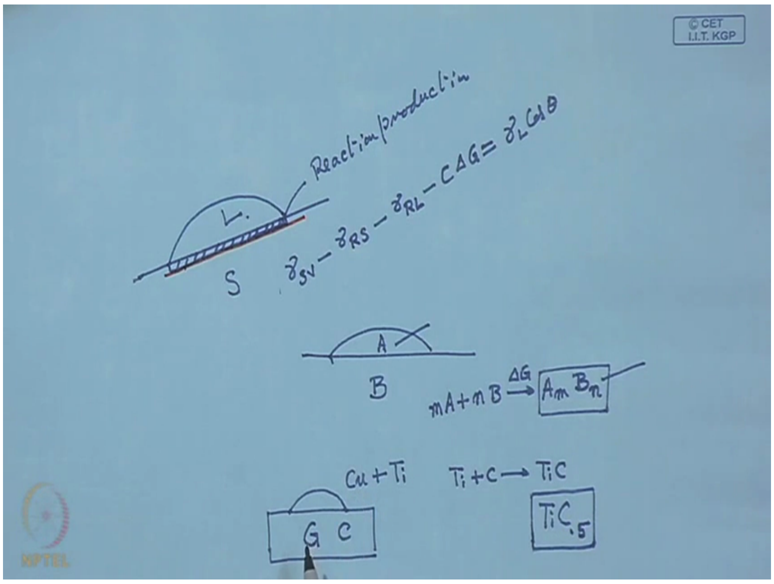

Now we can illustrate this point by this example if we have say for example Graphite or diamond and over that we have say Copper as the liquid but this Copper doesn’t have any reactivity, so it is an inert or a passive alloy. Now what can be done? As we have mentioned already here to promote the reactivity we have to have addition of one reactive element say for example Titanium is the reactive element.

So this is now Copper solvent Titanium solute, so that is a combination which can now act to promote wetting and that can go in a very favourable way. However, since it is a source of Carbon, so obviously we expect Titanium and Carbon to form TiC. So that is the reaction and at a favourable temperature it is expected that this Titanium can react with Carbon making Titanium carbide.

However this Titanium Carbide cannot provide any wettability towards Copper. So this is stoichiometry Titanium carbide, so this stoichiometry will not help. However if we can have a hypostoichiometric reaction product that means there we have say for example C.5 that means here atomic ratio is 2 is to 1 in that case Titanium it is this Carbide it is rich in Titanium and it can show some metallic character and this can be wettable by this Copper.

So this is exactly what we mean by hypostoichiometric reaction layer formation at the surface and this is the sufficient condition to promote wetting. So this is exactly what we mean by hypostoichiometric reaction layer formation at the surface and this is the sufficient condition to promote wetting.

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Now the question is how do we select this reactive element? Which are the best element and in respect of what? What are the criteria for choosing the best reactive element for a particular wetting activity? Now here one can look into these transitional elements of group 4B, 5B and 6B.

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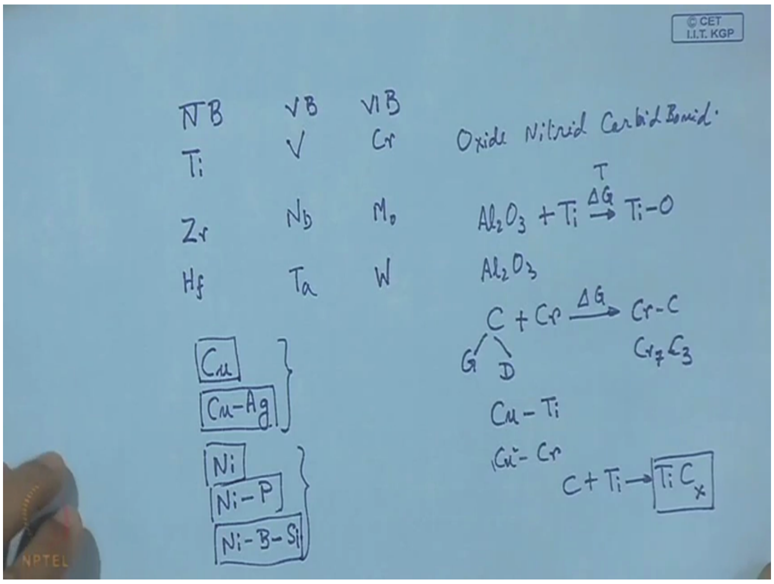

Now if we look group 4B, 5B and 6B we have here Titanium, Zirconium and Hafnium. Here we have Vanadium, Niobium, Tantalum and in the group 6 Chromium, Molybdenum and Tungsten. Now these transition elements are known as very good Oxide former, Carbide former, Boride former and Nitride former. So these are the strategic elements which can be used as a solute to make the parent element, parent metal or parent alloy which is otherwise passive towards the ceramic surface and that can be activated.

Now here one should look into this point that whether this particular element, whether it is Titanium or Tungsten or anything which can react with the surface of ceramic which can be Oxide, Nitride or Carbide or even Boride. So there one has to look into whether this element at a particular temperature of can react with this Oxide, Nitride or Carbide or Boride which is a basic ceramic forming Titanium Oxide, Titanium Nitride or Titanium Carbide or Titanium Boride.

For example if this happens then this could be a good candidate is one of the solute or reactive element for promoting the wettability of this is so-called passive alloy. If this is not the case then we have to choose the right element which can promote wettability for example if it is Aluminium Oxide then one has to look whether by having Titanium in the alloy whether we can have a reaction by this Aluminium Oxide and Titanium leading to some Oxide of Titanium this is one important issue to be addressed.

Or whether with Aluminium Oxide this transitional this 3 into 3 metrics, one has to look into the suitability of 1 element in order or say its capability to react at a particular temperature and then this Delta G should be negative. Say for example, say it is Carbon, it can be graphite or it can be diamond. So in this case whether we can use Chromium, so whether we can use Chromium for this that answer will be given by this value of Delta G whether this can lead to some Chromium, Carbide say Cr7, C3 for example and which will be wetted by the liquid metal and in that case perhaps Chromium can be used.

So if the basic material is Copper say for example and we add Titanium or we add Chromium with Copper and to see whether this Chromium Carbide is formed, so that this Copper can wet the surface or it can be also if it is Titanium with Copper to look whether we get this Carbon plus Titanium, Titanium Carbide but it should be hypostoichiometric rich in Titanium, in order that Copper can also wet this surface.

So this way one has to look for the right element, reactive element which goes in solution with the parent material. Now parent material normally what we see for in common use, common engineering use? Copper may be one of the strategic material used for this wetting purpose, it can be Copper Silver also. In nickel family it can be nickel, it can also be nickel phosphorous system, it can be nickel boron and silicon. Now these are the metals or alloys which can be used for common brazing or joining purpose and this alloy this Copper or Silver Copper or nickel-based family they readily wet the metal surface.

But when it is the question of wetting the ceramic surface then this formulation has to be changed and this formulation has to be changed by bringing one of those strategic elements from group 4, 5 or 6. So that they can go into solution either in this Copper base system or Copper Silver based system or in the nickel-based system, so that that becomes useful active alloy which can lead to spontaneous wetting and spreading over the ceramic surface.

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Now one important issue, also one has to consider the parent passive material. Now what we have seen here that these are the strategic reactive material and here what we see? That this is just a pure metal this is one binary alloy, this is pure metal this is binary alloy and this is even with 3 ternary. Now here the basic objective is to promote wetting that means there will be spontaneous spreading of the liquid once it is brought in contact with the solid surface particular temperature maintaining certain environment and maybe reducing atmosphere it can be in atmosphere flushed with argon reducing means with, enriched with hydrogen or it can be high vacuum.

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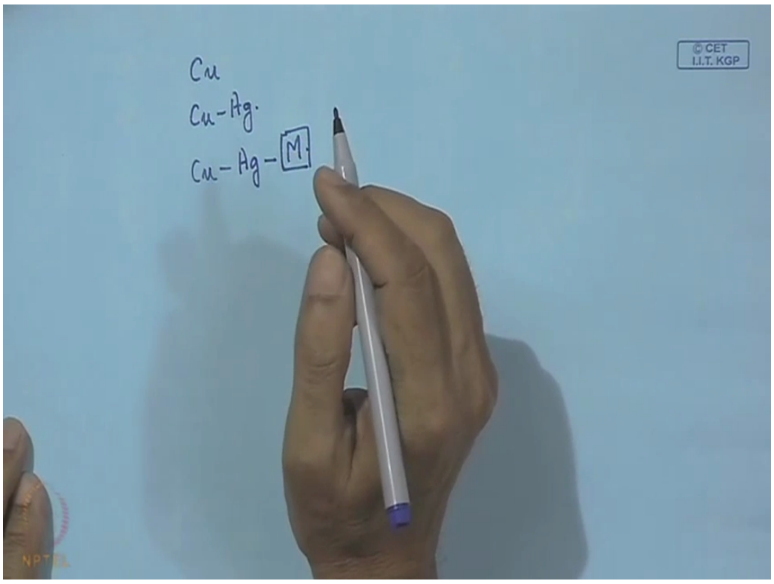

So at that under that environment this is supposed to have spontaneous spreading but here comes the question whether we use this pure metal or a binary alloy or even a ternary alloy that means it is Silver Copper and M, now what is the role of this M?

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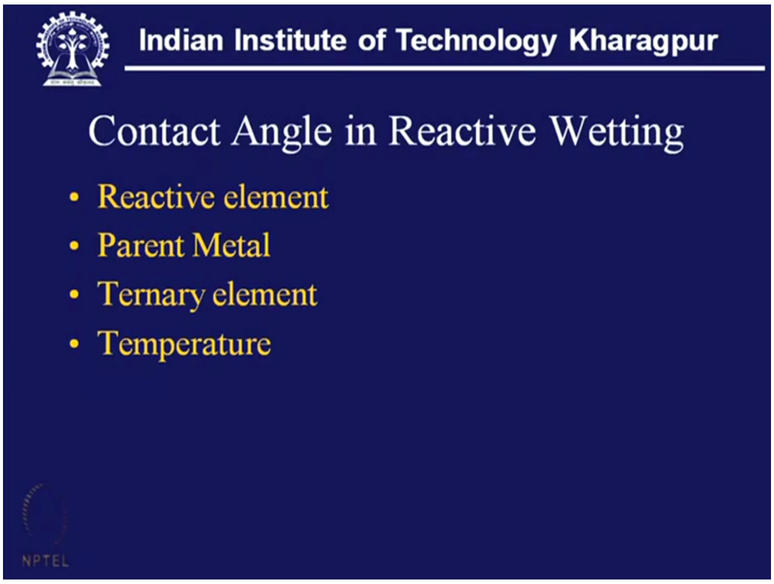

Now to consider this particular issue we have to look in this question is that what is the Contact angle? Contact angle means this wetting angle, contact angle is the index of wetting whether it is good wetting our poor wetting that is straightforward given by this contact angle and it can be experimentally measured it can be observed, so one can immediately get a first-hand information on the effectiveness of the alloy.

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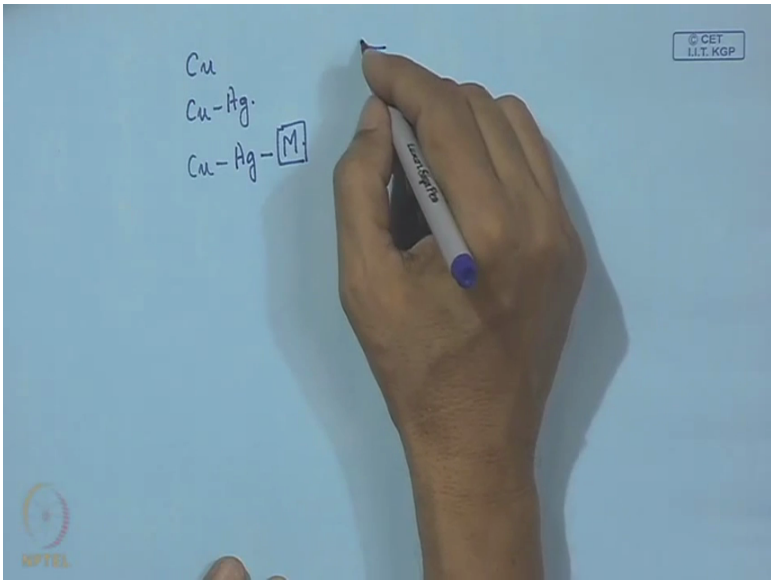

Now here comes the question, if it is a reactive element says for example Titanium, what should be the concentration level of Titanium to promote wetting? Whether it is the same amount of Titanium required with Copper whether it is the same amount required with this Copper Silver or when we have a ternary passive alloy whether we have to increase the concentration and we can decrease the concentration. Now question is if this higher level of Titanium that is detrimental to the quality of adhesion or it favours or promotes adhesion larger quantity of Titanium.

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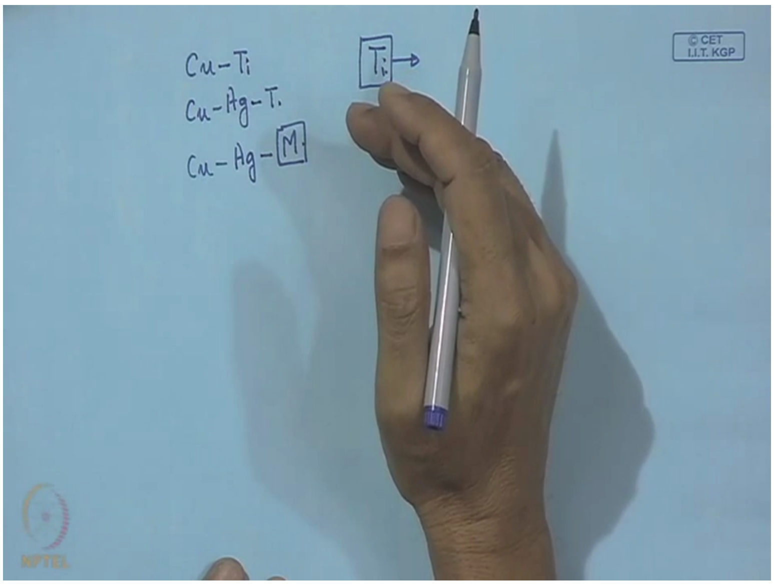

So here one can look into this particular issue that Titanium which goes in solution with the basic metal, so how much is the heat of solution? That means what will be the level of solubility in that parent metal or parent alloy and what will be the activity level of Titanium?

So this point has to be looked into with utmost care and only under that condition we can really find out the best quantity or the best concentration of Titanium which will promote wetting of a particular base metal that means in this case for example here this M we can replace this M by either Indium or by Tin. Now what is the role played by this Indium or tin that's why what we have mentioned here?

If we go here we have the reactive element, contact angle depends upon the concentration of the reactive element than the basic parent metal that also influence the quantity of, minimum quantity of this reactive element that is necessary to promote wetting and here wetting means we understand that it should be less than Theta should be less than 10 degree and that we consider as spontaneous spreading.

So to satisfy this condition of contact angle what are those which are really dictating this particular contact angle? One is the reactive element that means the choice of the reactive element whether it is from group 4, 5 or 6 then it's concentration then what is the parent metal whether it is the parent metal or one binary alloy or whether it is a ternary alloy and what is the role of this ternary element?

And last but not least it is the temperature, prevalent temperature at which this wetting process is initiated it is conducted. Now one major issue to be considered here is the solubility of Titanium in the alloy because it is a solution or activity of Titanium. If solubility is higher than activity of this reactive element that will decrease, exactly what does it mean? That when we add Indium in this system what happens?

The solubility of Titanium in this alloy that decreases and thereby the activity of Titanium increases. So we have activity on one side and we have solubility on the other hand other side. So if this refers to Titanium that means if solubility increases then the activity falls but we don't want such situation, what we want? That we must take the minimum quantity of Titanium or the reactive element which is sufficient enough to promote wetting that means this metal should be highly active and for that the condition should be maintained is to reduce the solubility of this reactive element, which one?

Here Titanium for example and its solubility in this basic alloy or in the solution that should be brought down and this reduction of solubility of this Titanium is possible by one strategic material and which has been found to be Indium or Tin. So their basic role is to, not only to reduce the melting point or the solidas and liquidas point that is one advantage but more importantly is to increase the activity of Titanium and to reduce its solubility in the parent alloy.

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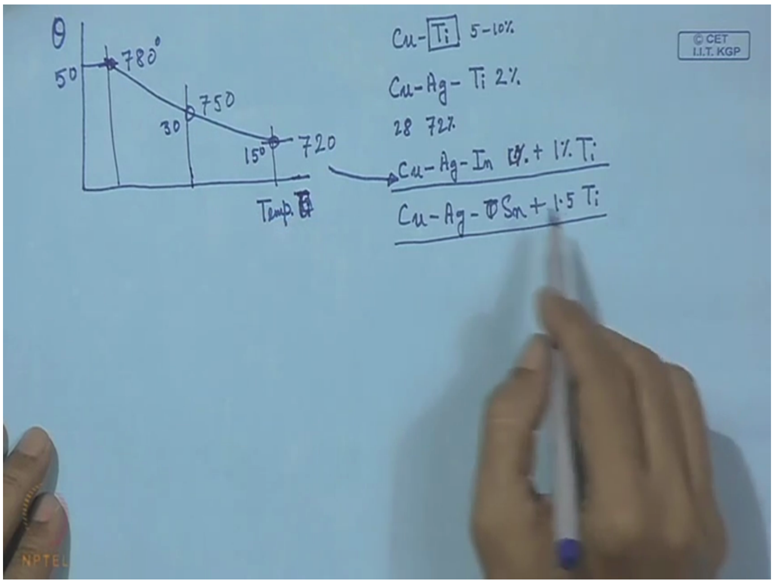

So here we see the wetting process parameters. So it is actually concentration of the reactive element in the parent material, processing temperature, time and temperature and environment. Obviously when it is an alloy say containing Chromium we can use either vacuum environment or reducing atmosphere if it is permitted by the base material metal to be jointed.

So if it is the Chromium as a reactive element than either this reducing atmosphere or a vacuum environment can be used. Now inert atmosphere, to use this one high-grade argon or similar gas is to be injected are admitted in the reactor to reduce the level of oxygen but when it is the activator is Titanium or similar materials from group 4, in that case we know that this reducing atmosphere by passing a stream of hydrogen that is not desirable because of this hydride of Titanium will form readily.

So in that case a vacuum environment is most desirable to promote this wetting and for this kind of material, so vacuum environment is always desirable and vacuum desirable is not a rough vacuum, it is a high vacuum and in that case the Titanium is prevented from getting oxidised and it can be 100 percent utilized in promoting wettability by this reaction over this ceramic surface.

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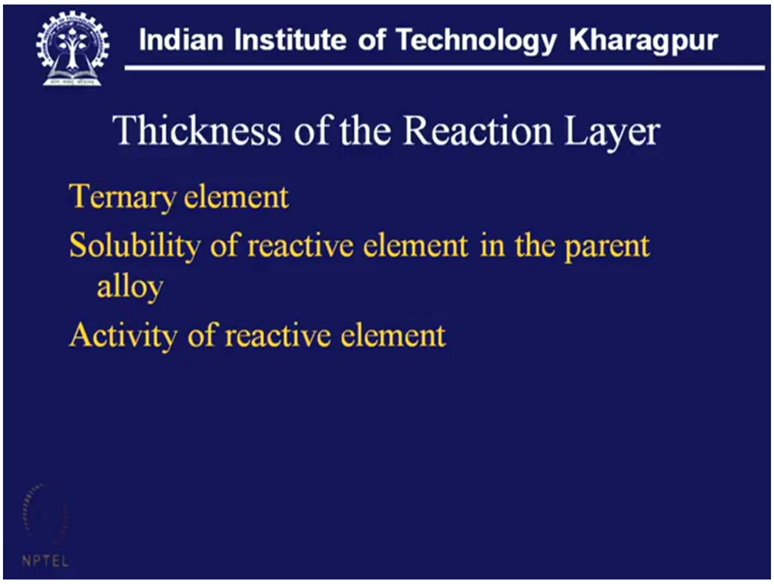

Now here one thing is extremely important thickness of the reaction layer. Now what is the importance of ternary alloy, ternary element that can be realized here.

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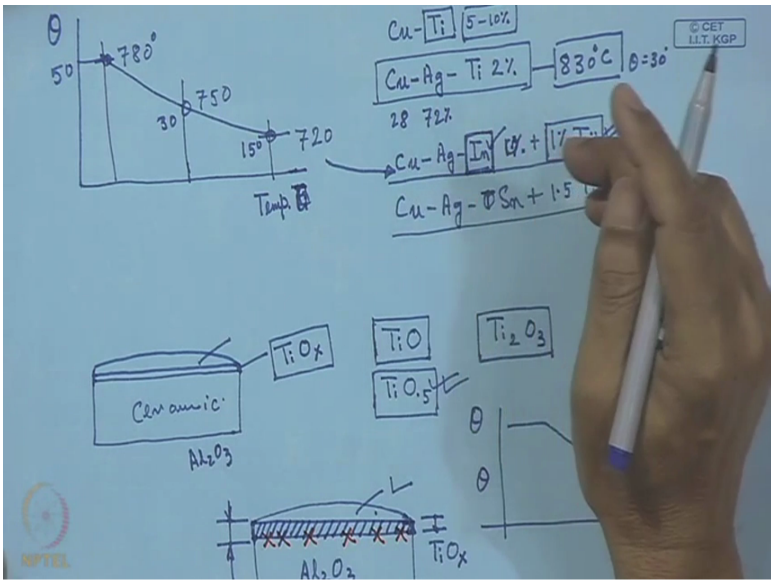

Now if we consider wetting angle and amount of Titanium which can promote wetting in the same level, what we can see? That when it is just Copper and Titanium we need a percentage of Titanium to promote wetting but when it is Copper and Silver which is an eutectic composition 72 and 28, here it is about 5 to 10 percent and when it is Silver-Copper it can be just 2 percent but when we use Copper -Silver- Indium this can be reduced to around just one percent.

Similarly just plus one person Titanium, similarly we can achieve such a good result with Tin with just 1.5 percent of Titanium. So not only this is not only one issue but at the same time the temperature, required temperature to promote wetting that can be also reduced say when we use Copper-Silver-Indium with one person Titanium we can have a curve. So here it is actually temperature.

So with this temperature what we can see? It is a falling curve and this may be for example 720, 750 and 780 degrees and here the wetting angle, say for example 50 then this is around 30 and it is around 15 degrees this is just an illustration and this can go pretty well with this alloy. Now to have a good wettability even with this to get a value of 30 degree with such an alloy one has to go even as high as 830 degree to get a value around wetting angle of 30 degree, so what we see from this finding?

That this activity of Titanium which is not actually bonded by this alloy, here this is free. Here this is free and solubility of Titanium in the Silver-Copper system that is reduced and activity of Titanium is increased but here though it is 2 percent activity of Titanium is not that high and that's why we need higher temperature to promote wetting and since this is high percentage of Titanium which is still higher just with Copper and Titanium it is around between 5 to 10 percent at least necessary to promote this wetting and in this case what happens?

The reaction layer what forms on this surface? This is ceramic and on that we have this reaction layer and on that we have this brazing material, so this is the ceramic that means say AL2o3 and here we have the Oxide layer which will be in form of TiOx and over that we can have this parent alloy. So this reaction layer of TiOx that formation is very important here and this x should be at least one or favourably desirably less than 1 this is our experience that if it is around TiO than good wetting, the sign of good wetting that is visible.

But if we have still lower than that around 0.5 immediately this attains a metallic nature and it becomes a metallic Oxide and this is readily wettable by the Silver-Copper, mostly it is Copper but if it is not the case then what happens that before TiO is formed the reaction layer could be also Ti2O3 and over this surface wetting is all extremely difficult and this is not a favourable case.

So what we understand? That this presence of Indium or Tin that increases the activity of Titanium and with the small amount of Titanium a thin reaction layer is formed readily and which is promoting the wetting but when we have higher percentage of Titanium this is not just our desire but this is our necessity without which this wetting is not possible. So if we just put here Theta against Titanium with this Copper.

Now here it is a Copper-Titanium system, so we can find this is something like this so this good wetting it comes around 5 percent of Titanium and in this case what we see? Because of this high amount of Titanium we get a thick reaction layer over the surface. So this is AL2o3 and over this surface and over this surface we get a thick reaction layer and this thick reaction layer definitely promotes wetting there is no doubt about it.

So this is now a thick reaction layer and outer surface is also OX and where X is around 0.5 but this is thin and this is thick over which we have also good wetting but the main problem is that the problem of adhesion of this wetted surface wetted film it is simply because of the reason that this reaction layer is thick it has different mechanical properties in comparison to basically liquid and that of the ceramic.

It cannot adjust itself to the changing volume because of this changing temperature that means coefficient of thermal expansion of this reaction layer that is quite different from that of liquid and that of Aluminium Oxide and as a result of that what is going to happen this may lead to crack formation and the joint may break and this can happen with any of the ceramic, it is not only the question of Aluminium Oxide it can happen with Silicon Valley, silicon Nitride and other material boron Nitride, boron carbide.

So the main objective in wetting in deposition of a coating by spontaneous spreading or wetting it is just not getting a good value of this theta but also to have good adhesion at this point and this calls for fine reaction layer or a very thin reaction layer which will not affect this stressed differential or changing volume at the interface because of this large size and to achieve that, one has to formulate this alloy in such a manner that the role of the ternary element that is well realized, well understood and it plays one of the important role to promote always activity of this reactive element, that means its role is basically to reduce the solubility of this reactive material in the basic parent material.

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So here we look into this adhesion and wettability. Now adhesion and wettability one would like to achieve both of them that mean good wettability is important to have a uniform coating. So it should not come in the form of a lump, it should have spontaneous spreading over the surface and at the same time the surface which is liquid material by virtue of its spontaneous spreading must also build a very strong interface with the best material.

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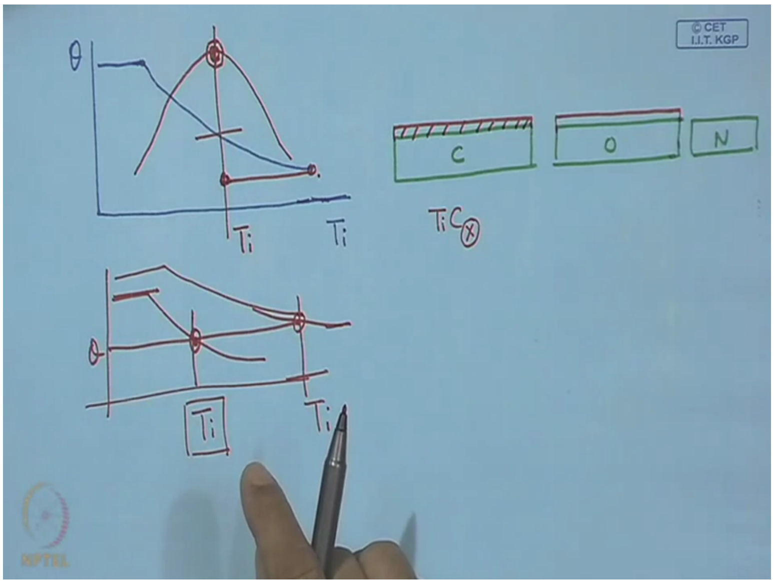

And in normal case what we see? If this is the wetting angle and this is the percentage of Titanium then with ordinary alloy what we see? That it goes unless we have certain percentage of Titanium it doesn't show any sign of falling theta, it will be more or less marginally I mean for all practical purpose it is same and then it shows the sign of falling. So it is falling like this and here one should aim at getting the value of this theta which is around 10 degree and that we accept as the very good wetting or spreading.

But at the same time if we consider the bond strength, the bond strength comes like something like this, it comes like this that means this is actually where we get the highest bond strength and on the 2 sides we have low bond strength. Now this can be explained by this simple fact that when it is small amount of Titanium we don't have enough Titanium to have this reaction forming a continuous layer.

It is a continuity of the layer and Titanium should be continuously uniformly distributed over the entire wetted surface, so we have Carbide formation in case if it is a source of Carbon, if it is an Oxide ceramic then it should be a Titanium Oxide. If it is a Nitride ceramic, most likely it should be Titanium Nitride, okay it should be Titanium Nitride but in all cases that we need a certain amount of Titanium to promote this reaction throughout the entire contact zone.

So this can be oxygen and this can be nitrogen that means it is a source of Carbon, source of oxygen or nitrogen. So unless we have certain quantity of Titanium this is not going to happen and with certain percentage one attains the very peak of adhesion strength and this we can call work of adhesion that means energy required per unit area to separate this interface into 2 surfaces.

However after certain point what we see? That this bond strength is falling, now this bond strength is falling because of the vigorous reaction. Now vigorous reaction means here instead of a fine layer it is the thickening of the reaction layer and this thickening of the reaction layer that goes along with Titanium, amount of Titanium and this amount of increased amount of Titanium actually thickens the layer and at the same time making the outer surface richer in Titanium.

So the outer surface which is richer in Titanium that means here a very low value of X and with that we have a still further improved wetting but that is at the cost of bonding. So this thick reaction layer no longer supports any externally applied force and the breakage occurs at this interface. So what should be the aim of this investigation? Should be to have proper formulation of this material which is a reactive metal or a reactive alloy which can have spontaneous wetting and in this case it should be the sole objective to have the highest possible reactivity of this reactive element.

For example in this case of Titanium with lowest possible concentration that means it is the highest level of activity with its lowest possible concentration and in that case we can achieve the outermost layer which should be rich in Titanium that means the sole objective would be to have in the quickest possible time, a outermost layer of this reaction layer, outermost surface of this reaction layer which is thin and outermost surface is rich in Titanium.

So in that case we can achieve this wettability even with less percentage. So that means if we draw this graph, it is something like this one should try to have something like this that means the percentage of Titanium what is necessary to have wetting good wetting with certain formulation? That can be still modified with a better value of Titanium that means with a still lower value of Titanium to have the same level of wetting and in that case we can also have good bonding.

So in this graph we can see, if this is our satisfactory wetting so say this point must be shifted here and we must be able to find out a proper formulation of the alloy. So that is small amount of Titanium we can get the same level of wetting but without sacrificing the bond's strength.

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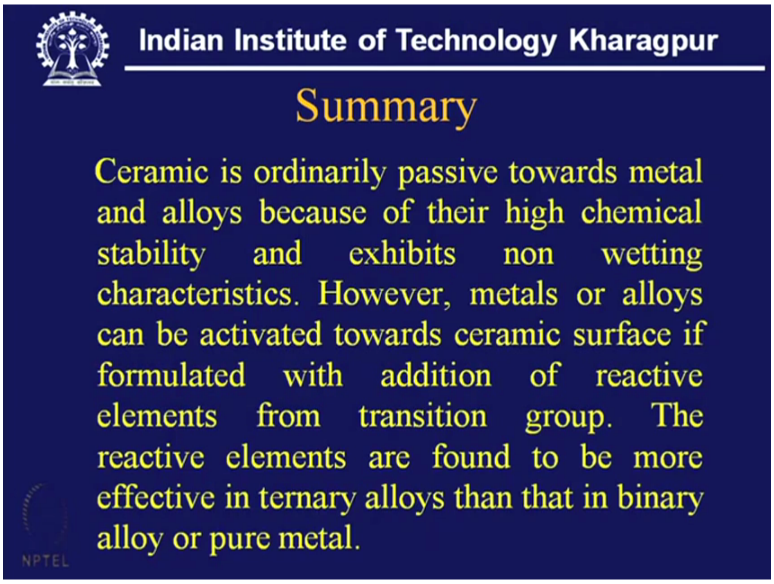

So with that we can summarize this subject as, ceramic is ordinarily passive towards metal and alloys because of their high chemical stability and exhibits nonwetting characteristics.

However metals or alloys can be activated towards ceramic surface is formulated with addition of reactive elements from transition group. The reactive elements are found to be more effective in ternary alloys than that in binary alloy or pure metal.