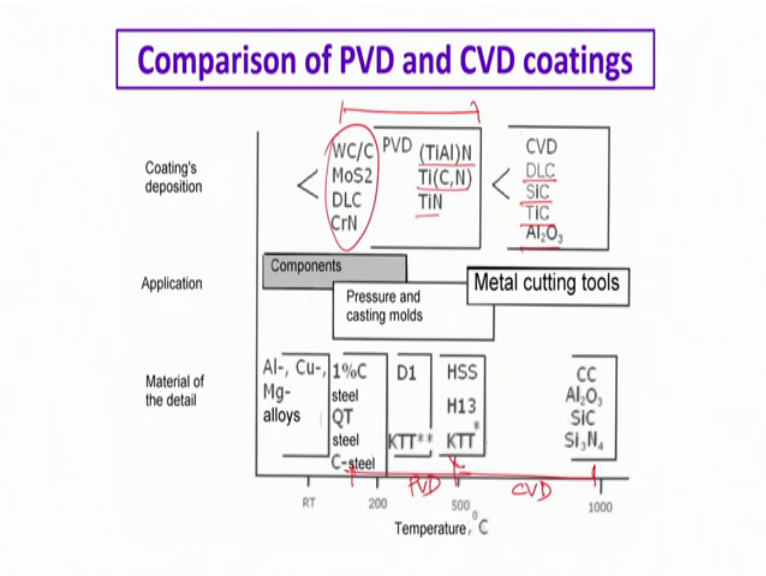
Surface Engineering for Corrosion and Wear Resistance Application

Prof. Indranil Manna
Department of Metallurgical and Materials Engineering
Indian Institute of Technology, Kharagpur

Lecture – 48
Composite Coating

Welcome to the 48th lecture of Surface Engineering. In the previous lecture previous few lectures we discussed about PVD CVD sputtering

(Refer Slide Time: 00:32)



So, when you compare these processes you realize that, first of all in case of PVD, you actually are conducting the processes at fairly low temperature.

So, in case of PVD this is the kind of temperature range we are talking about. So, up to about 400, 550 degree centigrade whereas, in case of CVD, we are talking about anything from 500 to 1000 degree or so. So this is the CVD range and this is the PVD range. So; obviously, if you are dealing with components like; aluminium, copper, magnesium, all these low melting on ferrous alloys, then the scope of application is mostly near room temperature not it is certainly not elevated temperatures.

So, all components, which are made of these alloys aluminium, copper, magnesium these are usually subjected to low temperature applications, but when you deal with steel say, quenched and tempered steel or carbon steel, they actually can be used not only as direct components, but also as pressure and casting moles or dies and so on and they, can have they can develop coatings like; the tungsten carbide or carbon composites molybdenum disulphide as lubricants or diamond like coating or carbon nitride chromium nitride coatings. These are all possible through PVD processes. You can also develop; we actually seen examples, where we can have titanium nitride, titanium carbonate nitride, aluminium nitride.

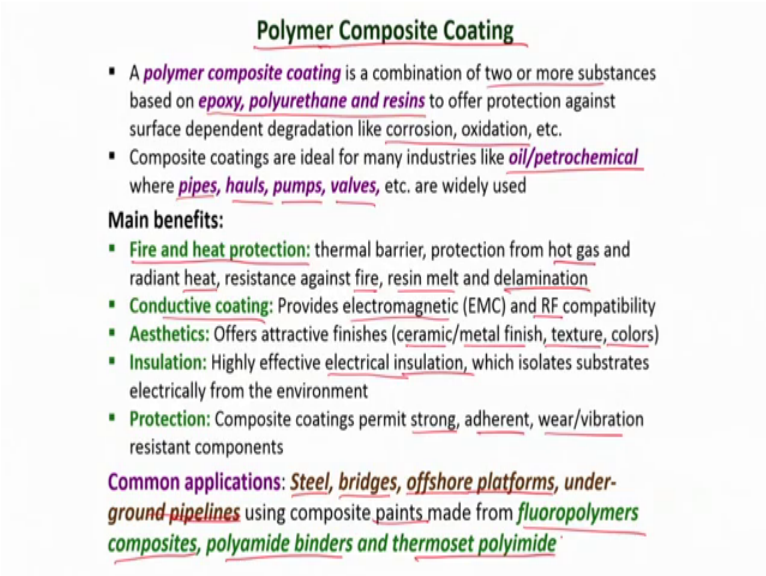
So, the cationic there could be doping in the cationic sub lattice or there could be dopant in the interstitial elements present in the compound. So, we can have interstitial compounds; we can have interstitial compound, where the cationic sites actually could also have mixtures. So; obviously, elastic modulus wise, they have different range of properties and different range of utilities. when you actually want even more adherent and more wear resistant coating higher hardness.

And more wear resistant coating, then you resort to this CVD processes and you can have same thing like; you can have diamond like or silicon carbide titanium carbide alumina coating and in addition, you can also have combinations of these nitrides and borides kind of coatings conducted by CVD, that slightly elevated temperature ; we also discussed, that it is not these compounds alone; you can also have a deposit of silicon or silicon dioxide or pure elements like carbon in the form of diamond or diamond like sp3 or sp2 type and so, all kinds of a possibilities exist.

The coating thickness can actually be slightly higher in case of CVD, because of the chemical reaction involved; PVD coatings are usually thinner, but what is more important is that in case of PVD the substrate deposit interface is fairly sharp? So, decohesion is a possibility one needs to worry about for the PVD coated components. In case of CVD, that is less, but then, on the other hand in case of CVD, you need a big chamber or a chemical reaction dealing with toxic gases you have to take care of the by-products that come out.

So, there are certain other disadvantages. So, depending upon the scope of application particularly the kind of materials and the end application, that we are talking about we have to choose, whether we go for PVD or CVD and accordingly the temperature of treatment also has to be decided.

(Refer Slide Time: 04:20)



Before we talk about other kinds of coatings, I think it is time, since we have discussed mostly the coatings, which are of; which are which actually within the coating or the film the composition is the same the composition may be different than the precursor, but the deposit, that we create the film that, we create will have the same composition throughout. That is what we have done.

So far in case of PVD and CVD; Of course, there was there is a possibility, that we can alternate the layers and we can make a, b or a, b, c and alternate them in a, b, a, b or a, b, c a, b, c kind of coatings, but nevertheless within the layer of a; within the layer of b, they remain the same; they maintain the same composition, but there are very many applications and in particular, the always we have discussed about either metals or semiconductors mostly are ceramic components, but we have not talked much about polymers.

So, there are there is a wide range of coatings possible, which are polymer based coatings and polymer based composite coatings. So, this is what we also would like to highlight, that this polymer based composite coatings will have a combination of two or more substances as usual typically, the that is the basis or the definition of composite, but what is important is, that this matrix the base material can be there in epoxy or a polyurethane or polyurethane or resins or various kinds of resins and with certain dispersed sides or reinforcements in that and this primary objective is to improve the self resistance against surface depending degradations like; corrosion, wear or oxidation spallation and so on.

They have defined wide range of applications in oil and petrochemical industries, where you deal with parts or components like pipes or holes or pumps valves or nozzles and so on. So, what are the main benefits? We actually can induce fire and heat protection. So, create a thermal barrier layer, which will protect these parts from hot gas or radiant heat or can also prevent fire or protect against fire melting of the resin the underlying resin and delamination.

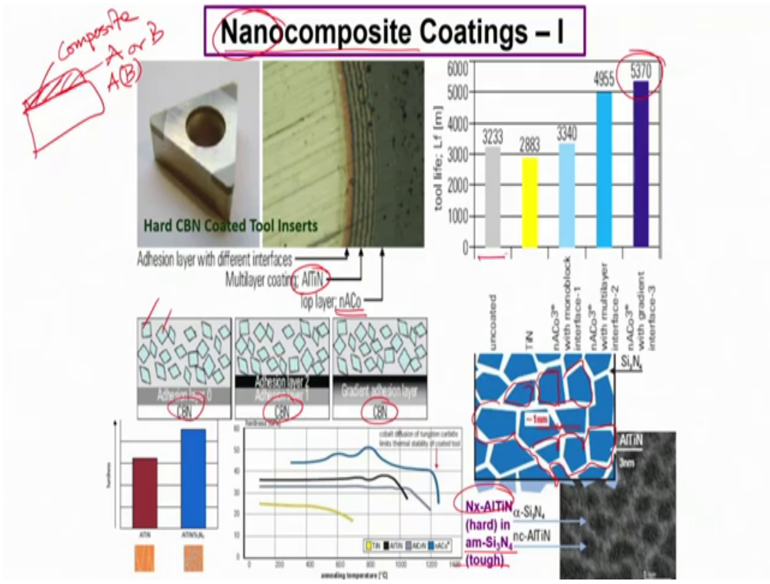
So, this is how many of these parts actually degrade. So, this kind of a composite coating can actually prevent that. The coating can actually be conducting and that is something of an advantage; normally, polymeric materials have a wide band gap. So, they are not conducting, but in order to make it conducting, you can always provide a thin layer coating and this can make it compatible to both electromagnetic and radio frequency variations.

So, this is how you actually can make the polymer component conducting. The aesthetics are certainly one of the biggest advantages. You can create a ceramic or metal metallic finish with certain very exotic texture and color or combinations of this. You actually, also can create a completely insulating layer heat protection I mentioned, you actually you can also make it insulating against electrical conduction so, can make it completely insulating; electrically insulating.

And so, that is how you can prevent electrical shocks or any other possibilities of arcing and so on. The protections actually can give you a very strong adherent and wear or vibration resistant these kind of protections, you can induce onto the components. So, applications typically, I have picked up a few examples here like; steel components, bridges, offshore platforms, underground pipelines and or all components, that are used for joining them and.

So, you use an application is very easy. You can apply them in the form of paints based on fluoropolymers; fluoropolymer composites, polyamide binders, thermoset polyimide. So, basically if you are dealing with large and complex shapes and you need to apply coating periodically; for example, on the big steel bridge structures. So, with the brush, you can create a paint and that, paint actually can contain these bases like polyurethane or resin base or maybe epoxy base and have certain dispersoids or reinforcements in that and in the process that is how, you can make it highly protective against atmospheric corrosion or heat protection or fire resistant and so on.

(Refer Slide Time: 09:34)



But, talking about composite coating for more sophisticated applications, what actually has really emerged as a very exciting field is the possibility of applying nano composite coating.

Now, the application of these coatings can actually need not be through one single methodology, they can be applied through a vapor based technique like; PVD or CVD or even alternate sputtering or reactive sputtering or they can be done using a laser based deposition like; pulse laser deposition can be done even using a laser surface alloying or deposition can be done with the other directed beams like; electron beam, even through aqueous based coating techniques like; electro deposition or core position, even spray techniques like; plasma.

What is important is now? So, we are talking about a small possibility that, this is the component and this is the coating that, we want to develop. This coating is not a alone or b this coating is going to be a in b as reinforcement. So, it is not just alloy it is not a single layer; it actually is a single layer, but having not a single phase; it actually is a multi phase.

So, this is the composite coating. Now the question is, why are we bringing in the objective nano? So; obviously, we are aware of the utilities of nanometric structures nanometric solids in bulk form or in thin films or in other possible architectures and combinations, but in case of coating having the second phase in nanometric dimension is very useful, because in that case, you gain in terms of uniformity and also the amount that, you require will be reduced. So, you actually need lower amount of reinforcement if the size is ultra fine typically, submicron and few tens of nanometers and to have them uniformly distributed and dispersed, you actually need a binder you need a matrix.

And that matrix can be a polymer, can be a metal or can be for that matter any other solid. Essentially, which should be compatible with the reinforcement? So, here is an example it is a proprietary item. So, if you have a cubic boron nitride coating already developed in order to make this substrate or surface even more wear resistant and reduce; for example, the friction coefficient and make it more compatible, you actually can have for example, these are the harder particles which are dispersed in a softer binder. Surprisingly, in this case the softer binder is actually an amorphous material silicon nitride not in crystalline form, but in amorphous form.

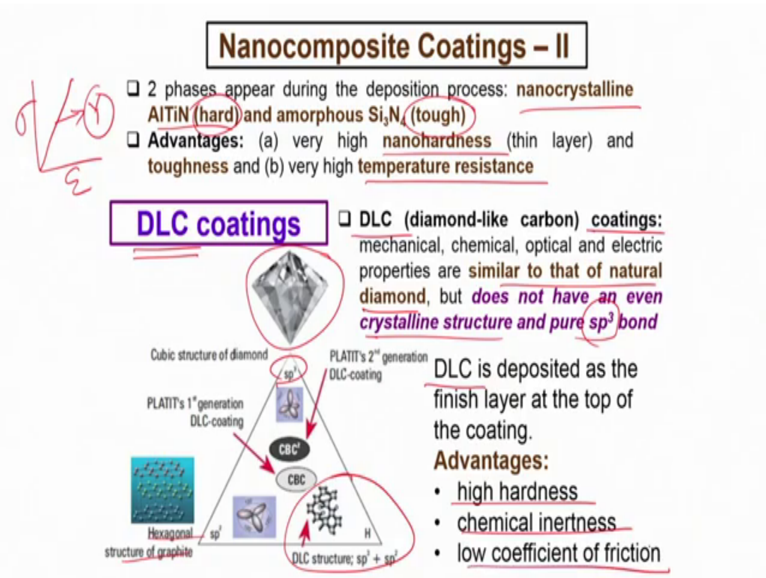
So, the harder phases are actually a mixed nitride; aluminium titanium nitride in nanometric form. So, this nanometric nitrides of aluminium titanium nitride is dispersed in this amorphous layer, which is which is a silicon nitride. Now, stichiometrically this may not be exactly Si 3 N 4, but somewhat similar.

So, this coating actually from the top; so, this is on the cross section from the front view from the top it would appear something like this. So, you will see such faceted phases, which are these aluminium titanium complex nitrides; mix nitrides and the matrix, which is the sort of binder, which is the continuous phase that you are seen. So, this continuous bright or white phase is basically, this silicon nitride which is in the amorphous form and this is how you actually can get very high to life very high to life compared to a situation, where you have no coating or only titanium nitride coating or some other combinations.

So, in order to increase the life of such tool insert, which is a very exotic tool; exotic in the sense, this can be used at a speed; at a cutting speed for, which is not possible with the pure metallic inserts like; high straight steel or even coatings with certain tools with certain coatings like alumina or silicon nitride and so on. So, this tool insert the tips are coated finely with this kind of a composite nano composite coating and these are typically, the dimensions of these reinforcements reinforcing phases of this complex, complex nitrites could be in few nanometers.

So, they are ultrafine tiny little particles dispersed in an amorphous silicon nitride matrix.

(Refer Slide Time: 14:53)



So, these two phases, it can be actually multiple phases to have them in the nano crystalline form is useful, because one is very hard and the other one the amorphous base is relatively softer or tougher. So, the advantage is that, we have we get very high hardness. In fact, the thick layer of the thickness of the layer is so thin; that you will actually, use a nano indenter with milli Newton level of load application. So, the range of load that, you apply is very small you indent very small depth and when you make such very thin indentation, you actually can produce a typical stress strain curve for a very limited region.

So, you have a proportionality limit and from this proportionality limit, you actually can also calculate the Young's modulus. So, using this nano annotation technique, one can not only measure the hardness; but, also the elastic modulus of the material. These materials also very they produce very high temperature resistance, because of the chemical nature of the deposit, that you develop its not pure metal its actually compound and these compounds have very high melting temperatures. So, they are and also are very strongly bonded compounds. So, they are resistant to heating and this is not isothermal heating; this is basically, contact heating, adiabatic heating during the high speed cutting operations.

And so, the dimension of the tool is better retained by application of such nano composite coatings. A similar kind of a exotic coating or a very sophisticated coating could be either diamond or diamond like coating; now we all are aware that, in the pure form when carbon actually creates carbon is present or manifests itself; we are aware that carbon has a number of allotrophies, number of allotropic forms.

So, in a completely crystalline form; So, this is the typically a naturally occurring diamond, but artificially also one can create this diamond by converting graphite into graphite to force them into a situation, where they assume a typical diamond cubic crystal in structure, which is derived from an FCC structure, but with a larger number of atoms per unit cell, but without going in to those structural details what is very important is that, this diamond will; you will call carbon a diamond only when it has pure sp three hybridized bonding state.

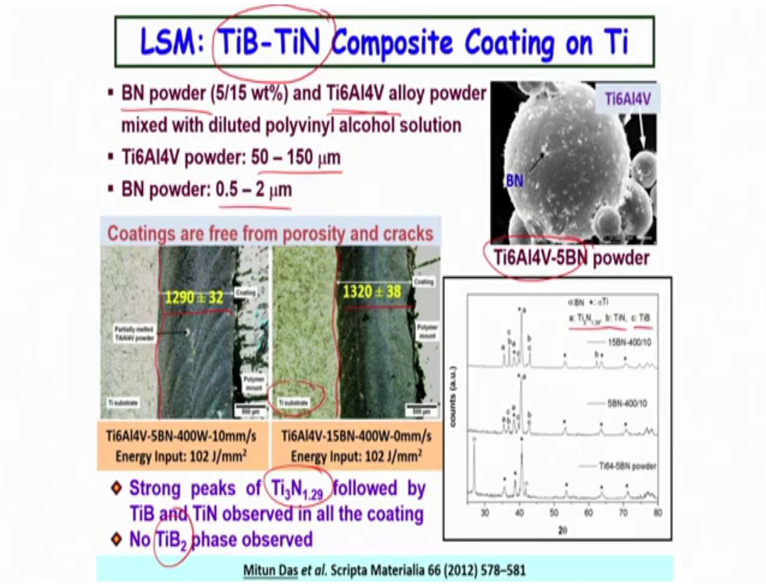
So, in such a situation, if it is completely crystalline having a diamond cubic structure and having pure sp3 bond then, you have these diamond structures. This is the hardest possible; naturally occurring material. Synthetically of course, you can produce slightly harder or much harder materials like boron cubic boron nitride and so on, but this diamond coating is very important, but there is no necessity all the time to aim coating, which is pure diamond.

One can also produce a diamond like coating and this diamond like coating can have a mixture of sp 3 and sp 2 bonding. Otherwise typically, carbon is very widely available in the form of hexagonal layered structures; graphitic layer structures, but of course, the in plane bonding is covalent, but out of plane bonding is not so pure covalent and as a result these layers or sheets are known to provide very good lubricating effect.

So, graphite is never considered a very hard material. Graphite is rather a lubricant material, but the same composition the same chemistry; it can be converted into ultra hard diamond or diamond like structures, but diamond likes instead of diamond like structures, what is important is to create diamond like coatings? The diamond like coatings, they are very similar to natural diamond; but, they do not have a pure crystalline structure and also they do not carry the typical sp 3 bond. So, you if you have diamond like coating on top of component or a tool, you have high hardness, you have chemical inertness and low coefficient of friction so; obviously, these are the advantages.

So, if you do not need very high hardness or very high extraordinarily high strength at the surface; you can go for this diamond light coating and this will still provide you so many advantages.

(Refer Slide Time: 19:43)



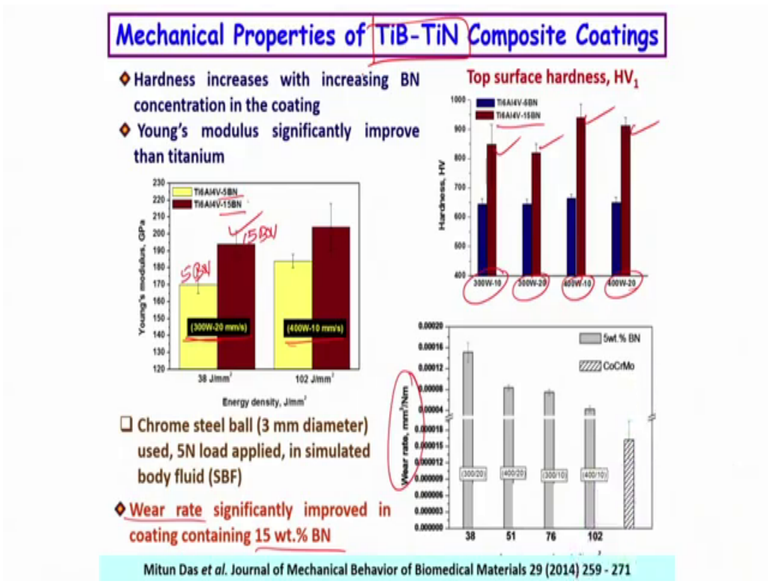
I want to just show you, an example from a certain research output from our own group. This is picked from the PhD thesis of Mithun das, he is a scientist in CSL laboratory. see for example, if you want a composite coating of boride and nitride together; now, there is no single synthesis process; a pure synthesis process, which will give you a such a composit or a complex combination of a boride and a nitride both on top of a surface.

So, using a laser based technique, you actually can create. So, what you start with boron nitride powder and titanium alloy powder, mix them in. So, you pick them powders in different sizes mix them well and then spread it onto the surface, carry out a laser surface melting and then in the process you can produce layered structures with very high hardness extremely high hardness, but what is even more important is that, the substrate is for example, a pure titanium or the titanium alloy on top, which whose hardness would be in Vickers scale much lower than these numbers, maybe one third of these numbers or even less, but on top of that, you can produce a coating, which is fairly adherent, because this is growing on the titanium substrate and then, is providing you fairly thick.

Now, compared to the PVD, CVD kind of vapor based processes; these kind of laser based process can give you easily half a millimeter or close to a millimeter thick layer. So, fairly thick layer and this is reasonably defect free and most importantly very well adherent into the substrate.

So, I mean, but what is also important for us to note is that, we intend to produce boride and nitride, but the nitride that we develop; actually, it is not stoichiometric nitride and that is possible, because there are defects in the crystal itself. So, crystalline defects make these kind of coating slightly more slightly deviate from the usual stoichiometry. In this approach TiB2 was never formed, but we did form various other forms of a borides say, for example, so, the precursor is for the powder mixture and then, what we develop will be various kinds of complex nitrides and boride, but not necessarily diborides.

(Refer Slide Time: 22:28)



So, as a result of such composite coating, you realize immediately the advantages the Young's modulus is much higher easily 50 percent higher then, when you. So, if you use two different levels of mixtures; if you load higher amount of boron nitride instead of 5. So, this is 5 BN and this is 15 BN. So, with a higher amount of loading, you get almost 50 percent in higher Young's modulus and at two different levels. So, these are different laser parameters, under which you produce these kind of things.

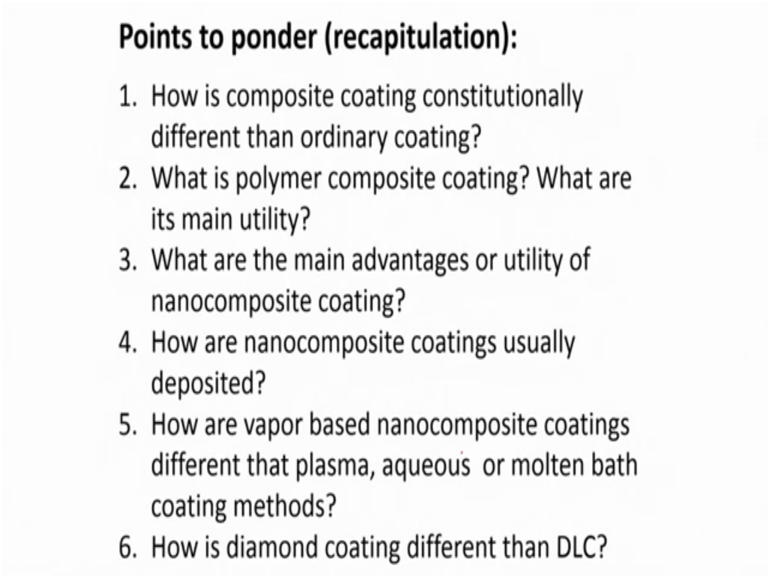
So, so, this kind of coating would be very useful on not only titanium based components, but also on steel to develop wear resistant coatings. In fact, wear resistance does improve significantly, when you apply such coating. So, the wear rate, what we realize is very significantly decreased, because of this coating and most importantly the hardness is exceedingly high. These are for different combinations of laser power and speed combination. So, leaving aside those experimental details; what is important is that, we are able to produce such exotic combination of a boride and a nitride using such composite coating and in this particular case laser is the agency with, which we are able to create such composite coating.

(Refer Slide Time: 24:04)

We can also create similar coating of silicon carbide and titanium using a similar laser based techniques and so, this is where you see that; So, this is the substrate and this is the coating layer, that we have developed and; So, you can have multiple coating layers and this is of course, the molding material. So, this is a surface that you create. So, this is the coating layer that you create on top of this substrate and if you look into the microstructure of this coating by playing with the laser parameters; you actually can make relatively a coarser or much finer coatings.

Now, you see this is a semi side, which is extremely hard and wear resistant also has very high congress melting maximum. So, now, you are seeing a microstructure, which comprises carbides and silicides both, but you applied only silicon carbide. So, the silicon carbide during the laser resisted surface annealing process intermixes and then, creates these kind of combinations of carbides and silicide. So, in a laser assisted process, you are able to develop a composite layer onto the surface, which otherwise is not possible by a simple deposition techniques and the findings of the aggregate the microstructure makes this whole coating much more tougher and much more adiabatic.

(Refer Slide Time: 25:44)



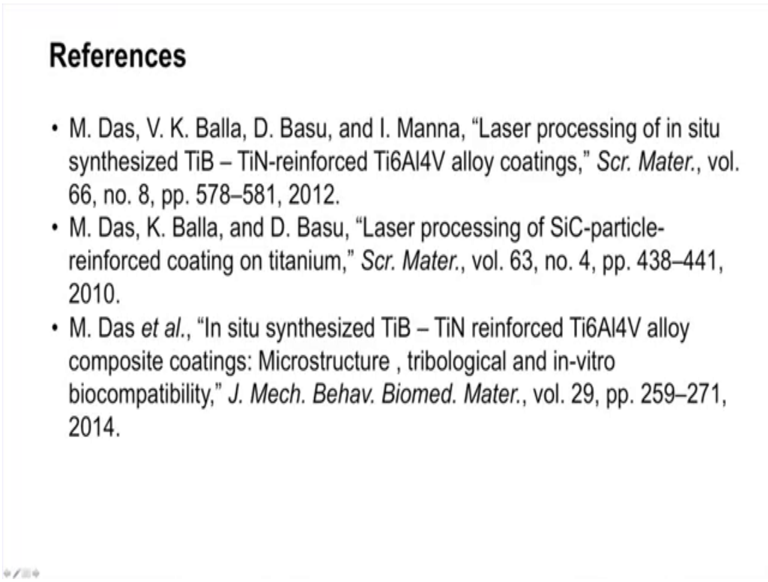
So, what all, we discussed in this composite coating approach? So, constitutionally this is different. This is not pure a or pure b this is not an alloy this is not a compound, but this is a combination of two or more number of phases. We found that, we can have one reinforcement or we can have multiple reinforcement like a nitride and a boride or a silicide and a carbide and so on.

To have these components in ultrafine sizes has its utility in the in the in the form, that we actually can have very uniform distribution and hence, we do not we actually can afford to have lower volume fraction of these reinforcements and yet, get a higher level of properties. The polygon composite coatings are a very very useful material, which can be an epoxy based or a polyurethane based coating or resin based coating, which can be applied simply with the with a brush or with the much easier approaches of or a roller and so on.

And it can be applied on steel structures, on metallic structures, on the ceramic structures and so on and can offer very good resistance again atmospheric corrosion or high temperature oxidation ; not very high, but high temperature oxidation. On the other hand, nano composite coating, I just mentioned is very useful because the uniformity and the exotic nature of the microstructure, that you can develop. So, nano composite coatings can be deposited from the vapor state, but more importantly, it is possible with laser based approaches.

In fact, we will discuss more of these when we go into laser assisted surface engineering. Nano composite coatings can also be done using plasma aqueous based on molten bath cladding methods and so on and in these processes of course, the thickness can be much thicker than the vapor based techniques. Diamond coating is extremely one of the highest possible hardness coating, that one can develop, but this is not always desirable in that case diamond like coating would be very very useful.

(Refer Slide Time: 28:05)



So, with this, we stop here for all these thin film based coatings and we ended with the discussion of a composite and nano composite coatings. After this, we will take up coatings or surface engineering based on direct energy beams like; iron beams, laser beams or electron beam and so on so.

Thank you very much.