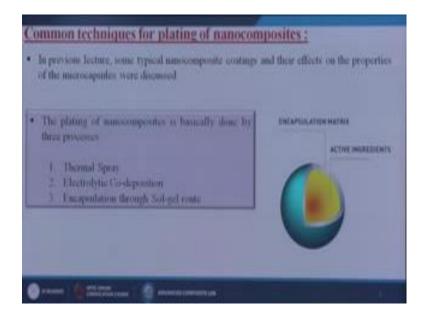
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Lecture - 34 Plating of Nanocomposite Coatings – II

Hello, today we are going to discuss our new lecture on Plating of Nanocomposite Coatings. If you remember that in the last lecture, we have also discussed about different methods that how we are going to coat our nanocomposite materials. So, this is little bit different from the previous one and also this is little bit kind of modified versions of those.

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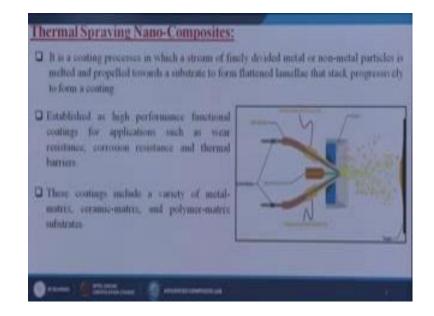


In this particular lecture, first we are going to discuss that some kind of typical nanocomposite coatings by different routes such as some thermal spraying, electrolytic coating positions and encapsulations through sol-gel route. So, in this figure, you can get that here inside is our active ingredients or maybe that base materials and the outside, you can see that there is a certain layer over there so which is denoting by the bluish color so which is giving you the coating thickness by different methods which we have already done.

First method is called the thermal spraying of the nanocomposites, from the name itself you can understand that here we are doing the spring. So, it is like a painting, but only

the difference between the painting and thermal spring is that in the painting simply we are taking the paint, then by using the brass we are coating onto our surface or wall, but in this particular case, we are taking certain kind of particles or maybe the nanofillers which we are going to coat onto the substrate or maybe the matrix, then we are heating those particles or maybe the nanoparticles, then we are spraying in a high velocity we are throwing those heated nanoparticles onto the substrate or maybe onto the base materials so that a uniform coating can be achieved. So, it is the coating process in which a stream of finely divided metal or nonmetal particles is melted and propelled towards the substrate to form flattened lamellae that stack progressively to form a coating.

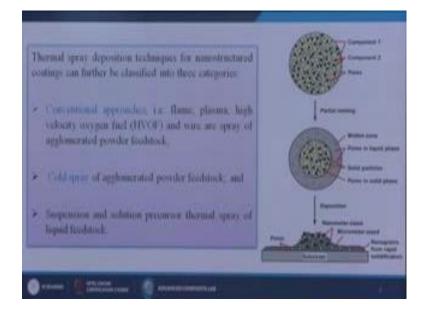
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From this particular figure, you can understand that this is our target. So, here this is our target or maybe our base materials or maybe our substrate and this is the gun actually. So, through this nozzle, high velocity abrasive heated particle is coming then we are using some kind of atomizing air. So, through air this particle is coming in a high velocity and it is depositing on to the target itself and here this is known as the nozzle, by increasing or decreasing the diameter of the nozzle you can increase or decrease the quantity of release of those nanoparticles on to the substrate not only that that nozzle can move along with your base or maybe the substrate so that a uniform coating can be achieved on to the surface.

Thermal spray deposition techniques for nanostructured coatings can further be classified into 3 categories.

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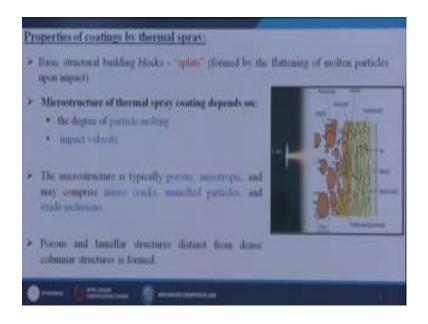


Generally we can divided these techniques by 3 different categories, one is called the conventional approach like flame plasma high velocity oxygen foil and where our spray of agglomerated powder feedstock, actually the depends upon the how much energy we are putting and what is the source of energy. So, if you are heating that material in a high temperature by different source like plasma, like arc, like some kind of flame so then, it is coming on to the conventional approaches. When you are talking about the cold spray, cold spray of the agglomerated power feedstock; that means, we are not applying any kind of heat, simply high velocity particles, we are throwing onto the substrate and we are doing the coating and the last one is called as suspensions and solution precursors thermal spray of the liquid feedstock. So, in this particular case, simple the liquid nanoparticle is directly taking and putting onto the substrate itself.

From the figure you can get that there is one component 1 and component 2, it is nothing but the different average size of these nanoparticles and in the black color we can see or maybe black color we can see that component 2, in the white color we can see the component 1 and the rest of the yellow color is known as the pores, that means, through these pores, the metal particle is going onto the substrate and it is depositing on to the substrate itself. So, here when we are throwing these solid particles so there are several pores is present in these solid particles and you can see, this is known as the molten zone because we are applying a heat onto these nanoparticles. So, when it is going onto the substrate, it is getting; it is giving a temperature onto the substrate itself through which your nanoparticles is slowly slowly going inside or maybe it is depositing on top of that by layer by layer techniques.

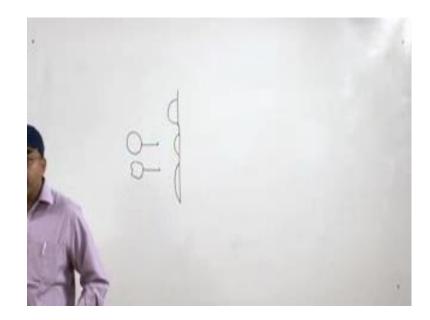
Next is called the properties of coating by the thermal press, in this particular case, what are the principles actually? Till now we are discussing that what is the technology? Now we are going to discuss, what is the principles we were behind these techniques. So, basic structural building box like splats formed by the flattening of molten particles upon impact microstructure of thermal spray coating depends on the degree of particle melting and the impact velocity.

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Yes, of course, because when we are talking about some kind of nanoparticles so nanoparticles may be into the round shapes or may be some kind of different shapes.

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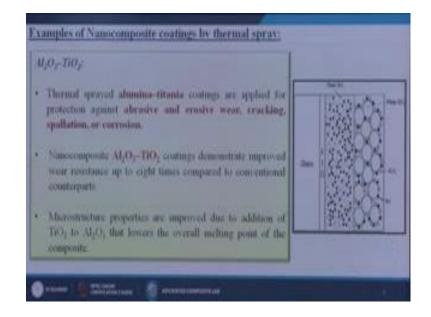
So, when high velocity, it is going onto the substrate itself, these nanoparticles depending upon how much velocity we are throwing it, it is giving a different shape onto the substrate itself.

If the impact velocity will be more, this nanoparticle will be more flattened onto the surface itself, if the impact velocity will be less then it will make a bigger droplet onto the substrate itself. So, it depends upon how much impact velocity we are using and what is the degree of the particle melting, say suppose the melting temperature of that particle may be 100 degree centigrade and if we keep the temperature up to 80 degree centigrade or may be the 90 degree centigrade, so this sample will be more tends to into the liquid formation. So, it will maybe into the viscous forms so when it will come and touch your substrate so automatically, it will try to spray it onto the substrate itself, but if it will not be properly melted so, what will happen? It will into the semi liquid formation. So, it will make bigger shapes onto the substrate itself. So, it depends upon the degree of particle melting and the impact velocity.

The microstructure is typically porous and isotropic and may comprise micro cracks and melted particles and oxide inclusions because we are applying a huge quantity of the nanoparticles, maybe sample nanoparticles get good enough temperature, maybe are not. So, some nanoparticles those who are getting the enough temperature maybe they are melting properly, some of them are not. So, it depends upon it is a mixture, some particle maybe into the solid form, some maybe into the liquid form, some maybe into the semi viscous form. So, it depends upon the temperature and the impact velocity, you will get a structure may be uniform coating or maybe non uniform coating onto your substrate itself.

And then porous and lamellar structure distinct from dense columnar structure is formed, it depends upon the how much velocity we are applying and what is the degree of particle melting. So, here we are just for better understanding here we are giving a better examples, it is a mixture of alumina and titanium dioxide so we are having that substrate materials.

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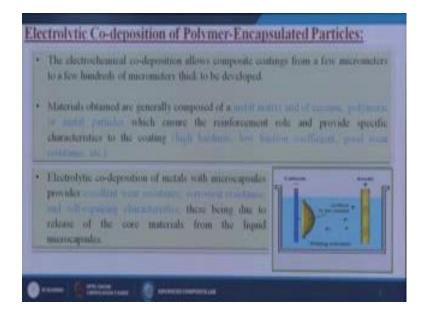
This is the substrate materials generally we are putting, first we are putting onto the glass, maybe it is the FTO glass generally we are using, So, first we are giving a mixture of titanium dioxide layer onto the glass substrate, then again we are giving a alumina coating onto that top of that titanium dioxide. So, here the thermal spread alumina titanium coatings are applied for protection against abrasives and erosive wear, cracking, spallation, and the corrosions. So, these all are the advantages when we are doing the alumina titanium oxide on to the substrate itself.

Next, nanocomposite alumina titanium dioxide coatings demonstrate improved wear resistance up to 8 times compared to the conventional counterparts so that is the added advantage for this type of thermal spring. Next microstructure properties are improved

due to addition of titanium dioxide to alumina that lowers the overall melting point of the composites so; that means, the melting point of the composites is lowering that is also another advantage for these particular conditions.

Next technique is known as the electrolytic co-depositions of the polymer encapsulated particles, from the name itself you can understand that there is one term is added that is called the electrolytic; electrolytic that means, here we are going to apply certain kind of current or maybe certain kind of voltage, we have to do the potential difference in between that by which we can do the modifications or maybe the coatings.

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The electrochemical correlation allows composite coating from a few micrometers to a few 100s of micrometer thick to be developed. So, here we can understand that the coating thickness; it is easily controllable by us, whatever the coating thickness we need based on that we can change the coating thickness that how much time we are keeping our substrate materials into the electrolyte, if the coating thickness will be achieved just simply we have to take it out, we have to clean it and then we have to dry it and if you need for the more coating thickness, you have to keep your substrate for a longer time into the electrolyte, then when it will reach then automatically you have to take it out.

Then materials obtained are generally composed of a metal matrix and of ceramic polymeric of metal particles which ensure the reinforcement role and provide specific characteristics to the coating like high hardness, low friction coefficient, good wear resistance, actually these all properties is depends upon the nanoparticles characteristics. So, whatever the properties you need, same type nanoparticles you have to apply on to your substrate, if you made for the higher corrosion resistance you have to take some kind of nanoparticles which is having the higher corrosion properties. If you need the higher wear resistance or maybe some anti corrosive or maybe some kind of anti abrasion material then you have to use those kinds of nanoparticles and you have to do the coating onto your substrate.

So, electrolytic co-depositions of metals with microcapsules provide excellent wear resistance, corrosion resistance and self repairing characteristics, these being due to release of the core materials from the liquid microcapsules. So, here it is one kind of example. So, we are having that materials, it is dipping into some electrolyte solutions, then we are having 2 electrode, one is known as the cathode which is negatively charged, we are having the anode which is positively charged then we are keeping our substrate materials onto the cathode side, then simply we are doing some chemical reactions is going on, due to that the anode material suppose I am going to coat up copper materials or maybe the zinc materials. So, the copper ion and the zinc ion, it will release from the anode side and simply it will deposit on to your cathode side or maybe the substrate.

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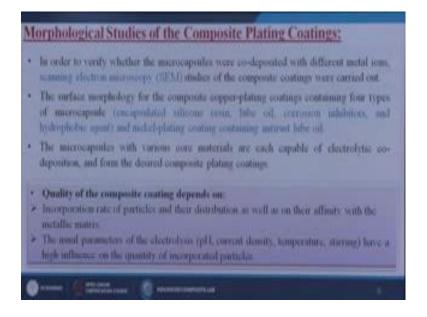
Details of the bath composition nickel-plating containing liquid				cobbei- un
Prepared interocapoiles with an appropriate some were added to the plating both and co-deposited electrolytically onto metal surfaces with different metal ions such as Ni ²⁰ . Co ²⁰ and Su ²⁰ , this resulted in the corresponding composite copper-, mailed-, and timplating contings	Copper plating	Completions	Toubel photong	Conditions
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So, by these techniques, we can do the coating of these particular nanocomposites or maybe that material. So description and different parameters for the electrolyte for depositions, so simple, it is some kind of gathered information from the literature review and just as a example we are trying to show that if we are going to do some kind of coatings, what will be the conditions and what will be the input parameters for these particular techniques? So, here the copper plating, suppose we have to take the copper sulfate and water solutions over there, conditions is that 150 gL to the power minus 1, then we can do some kind of sulfuric acid solutions, emulsion containing microcapsules, temperature is generally 25 to 35 degree centigrade, electric current should be 30 milliampere per centimeter square. So, these are the input parameters for the copper plating.

But when we are talking about the nickel plating, we have to take the salt or nickel then we are going to use some kind of boric acid, then emulsion containing microcapsules, temperature is little bit more than the previous one, it is around 55 to 60 degree centigrade, electrical current is also a little bit more it is around 150 milliampere per centimeter square. So, here the prepared microcapsules with an appropriate core were added to the plating bath and co-deposited electrically onto metal surface with different metal ions such as nickel copper tin etc. So, as I told already whatever the material you are going to coat, you have to take that material into the anode side, then it will release the ion and that ion is simply depositing onto your cathode side and by these techniques you can do the coating of maybe copper nickel and the tin plating on your substrate.

So, what is the morphological study of the composite plating coatings?

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First is that in order to verify where the micro capsules were co-deposited with different metal ions, scanning electron microscopy study of the composite coatings were carried out. So, these all are like the different types of characterizations by which we can verify that our coating thickness is uniform or not, our coating is properly or not and how to check that how the coating is good or not, adhesion properties is good or not in between your substrate and in between your coating materials.

First the empirical one or maybe that mostly used in the world method is known as the scanning electron microscopy method by which either we can break the samples, we can cut the samples and simply we can put the samples into some microscope and we can take the picture or may be simple, we can put the material into the equipment itself and passing through the electron through these materials, we can check whether the coating thickness will be proper or may be homogeneous or may be the heterogeneous one. The surface morphology of the composite copper plating coatings containing 4 types of microcapsules, first one is called the encapsulated silicon resins, lube oil, corrosion inhibitors and the hydrophobic agent and nickel plating coating containing anti rust lube oil.

The microcapsules with various core materials are each capable of electrolytic co depositions and from the desired composite plating coatings. So, depends upon which properties we are going to do, then by layer by layer method you can do the plating onto your substrate so that you can get a mixture of properties mixture of rather we can say that a mixture of enhanced properties of these microcapsules by these techniques.

Quality of the composite coatings depends on incorporation rate of particles and their distributions as well as on their affinity with the metal matrix. Yes, of course, so, when I am really doing some kind of nanoparticle, simply it is going and it is depositing on to your substrate, if the adhesion properties of your substrate or maybe that of your metal matrix composite is good, then the nanoparticles will simply attach onto a substrate and it will not come out, but if the surface roughness or maybe the addition properties of your metal matrix composite is very very poor, then at that time, this nanoparticle simply it will go, but after certain time it will come out.

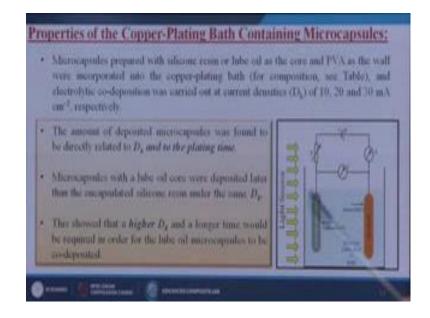
The usual parameters of the electrolyte is like pH content, current density temperature stirring to have a high influence on the quantity of incorporated nanoparticles, this pH current density temperature and steering, these all are the input parameters for these particular conditions, how much potential difference you are giving, how much pH whether it is acidic or basic conditions and how much current you are going to put, whether you are doing the stirring and stirring also the different types, whether you are going to do the mechanical stirring, whether you are going to do some kind of magnetic stirring. So, depending up on that you can get different types of coating thickness and different types of coatings properties.

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Here, it is also one kind of FESEM image that has been observed or maybe that has been obtained from different literature review. So, here you can see that there is a substrate then on the top of the substrate you can see there is a form line onto the different coatings, this is nothing but the layer thickness of this type of coatings. So, when you are talking about that layer by layer techniques, simply we are having the substrate, on top of that by layer by layer method, we have done the different types of coating materials on to the substrate itself, here also we are having that base materials, then we are having some kind of coating materials in which we are putting some kind of micro capsules. So, by these methods we can do the coatings of different materials onto the surface itself.

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Next properties of the copper plating bath containing micro capsules. So, microcapsules prepared with silicon resins or lube oil as the core and PVA as the wall were incorporated into the copper-plating bath for composition and electrolytic co-depositions was carried out at current densities for ranging from 10, 20, 30 milliampere per centimeter square respectively.

Here we are having that different materials that technology is the same, but here we are having the different base materials and which we are going to coat some kind of other materials. The amount of deposited microcapsules who are found to be directly related to the Dk; that means, the input current density and the plating time that how much time you are dipping your substrate inside the electrolytic solutions. then microcapsules with a

lube oil core where deposited later than the encapsulated silicon resins under the same current, this showed that the higher input current and a longer time would be required in order to lube oil microcapsules to be co-deposited because it depends upon that which type of materials we are going to coat, what is the activated temperature or may be the activated current for this particular nanoparticles so that it can be activated and then simply it can deposit onto your substrate itself.

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Core Da	Silicon resin	Lube oil
10 mA cm ²	A Tew microcaptules found after 24 min	A fire microcaptules found after 30 min
20 mArm ²	Microcapsules start to deposit on the auting after 18 min, amenatic increase with time	Microscopeniiss start to depend on the coating after 70 min, answers increase with time.
30 mA 2m ⁻¹	Microsciptules start to depend on the uniting after 14 min, 10 min later microsciptules of variant starts dispersed homogeneously in the costing	

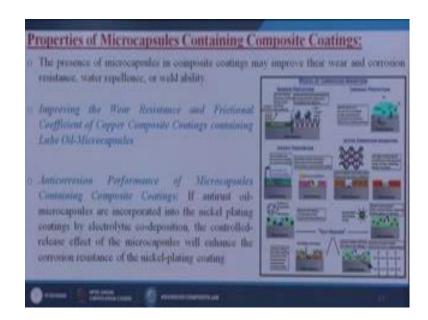
Here also we are giving certain kind of examples. So, compositions of copper plating, but with silicon resins and lube oil so when you are applying the 10 milliampere per centimeter square current densities, silicon resins a few micro capsules found after 24 minute, lube oil a few micro capsules found after 30 minutes. So, you can see that it needs different time zone to activate kind of materials, for silicon reasons it needs 24 minutes to activate and then for lube oil it needs the 30 minutes for activate.

Then if we apply that 20 milliampere per centimeter square current densities, the microcapsules will start to deposit on the coating after 18 minutes. So, from this particular figure, you can understand that when you are using the current density is more so automatically our activation time is decreasing, initially it was 24 minutes, after that it became 18 minutes and then after that it became the 14 minutes. So, if the current density will increasing then automatically your activation time will be decreasing.

The same thing is happening in this particular case also, initially it was 30 minutes, then it is 20 minutes and if we go for that type 30 milliampere per centimeter square, the time is start to deposit on the coating after 16 minutes, 30 minute later microcapsules of various eyes dispersed homogeneously in the coating itself. So, depending upon the current, depending upon the current densities and depending upon the time that we are dipping our substrate materials into the electrolytic solutions, we are getting different kind of properties.

Next, we are going to discuss about the properties of micro capsules containing composite coatings. So, this is the important parameters or maybe the important studies for our lecture itself, the presence of micro capsules in composite coatings may improve their wear and corrosion resistant, wear repellents and the weld ability.

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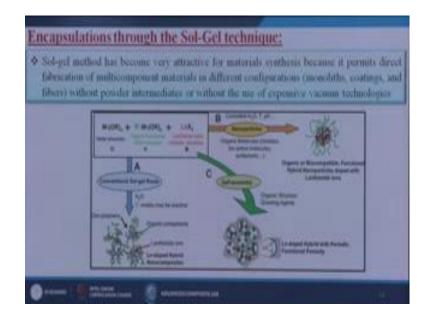
From my first lecture, I am telling you that rather to make the newer composites, rather to change the whole composite properties, it is better to change the outer surface of these material properties so that it can give you the better properties and you can use that material for different applications.

Here the improving the wear resistance and frictional coefficient of copper composite coatings containing the lube oil microcapsules, anti corrosion performance of micro capsules containing composite coatings, if anti rust oil microcapsules are incorporated into the nickel plating coating by electrolytic co-depositions, the controlled release effect of the microcapsules will enhance the corrosion resistance of the nickel-plating coating.

The thing is that what type of properties you are going to use based on that you have to choose the perfect microcapsules, then that microcapsules you have to mix with some kind of metal ions and the whole thing in a composite form, you have to deposit onto your substrate itself so that you can get the better properties. So, here the example is that for barrier protections, we can do these kind of modifications where we can take certain kind of materials which will give you the good barrier properties onto your substrate, for cathodic protection like I am using some kind of materials which I have to either deep into some chemical solutions or maybe some kind of basic solutions, but there should not be any chemical reaction.

By changing the outer surface, we can change the metal properties so that it will not be active in that particular acidic or may be the basic solutions, some active corrosion innovations, some kind of materials which will reduce the corrosion properties of that particular materials, some kind of cell filling, this is the very good new technology that these kind of materials we can use for the biomedical applications. So, automatically if there will be any cracks or maybe some kind of pores will be observed onto the surface of your materials so automatically the coating material will change its properties and it can cover those cracks or maybe those kind of pores so that then the outer surface of your substrate will not come out and directly come contact into the environment itself. So, automatically the coating material itself. So, that is why it is called the self healing materials.

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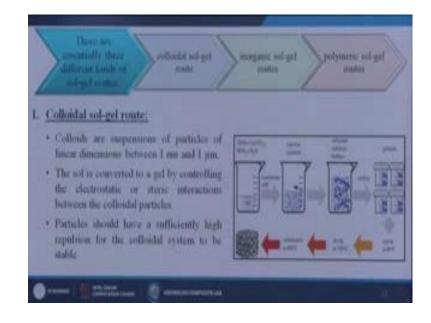


Next is called the encapsulation through the sol-gel technique, this is the last one of this particular lecture. So, from the name itself we can understand that there are 2 terms is added together, one is called the sol and another one is called the gel sol is nothing, but the short form of the solutions and gel is nothing the short form of the gelatin.

Here first we are trying to do is that suppose we are having 2 solid particles or maybe one solid particle and the one liquid particle, so, first we are trying to deep into that solutions then we are trying to make mixture of these solutions, then we are trying to mix those solutions and then the mixing solutions, we are putting onto the substrate itself. So, first we are making the solutions, then after mixing we are making into the gelatin forms then that gelatin we are applying onto the substrate itself.

Sol-gel method was very very attractive for material synthesis because it permits direct fabrication of multi component materials in different configurations like monoliths coatings and the fibers without powder intermediates or without the use of expensive vacuum technologies. So, here these are the materials, suppose I am taking some kind of metal oxides, I am taking the organ of functional metal alkoxides and I am taking the lanthanide salts some kind of (Refer Time: 24:58) or may be the anti oxide. So, we are mixing those materials then we are putting onto the substrate itself so that it can do a coating of different materials. So, a same material can give you the better properties in

terms of maybe the corrosions, maybe the frictions, maybe some kind of electrical properties. So, variety of applications, we can use these kind of materials together.



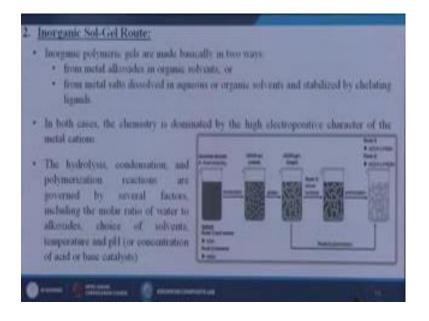
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So, here these methods are divided into 3 distinct parts. First one is called the colloidal sol-gel routes, next one is called the inorganic sol-gel routes and the last one is called the polymeric sol-gel routes.

What does it means by the colloidal sol-gel root? Colloids are suspensions of particles of linear dimensions between 1 nanometer to 1 micrometer, the sol is converted to a gel by controlling the electrostatic or steric interactions between the colloidal particles; particles should have a sufficiently high repulsion for the colloidal system to be stable. So, from this particular figure you can understand that we are taking a mixture of TUS, then calcium nitrate plus sulfuric acid plus water, then we are making solutions, we are doing the vigorous agitations means by the mechanical stirring or maybe the magnetic steering, we are doing the steering. So, after that surfactant stabilizer a bubble is applied. So, some kind of gelatin is forming in to that we are casting these then we are edging this materials then we are drying into some 130 degree centigrade stabilization and we are getting a structure like this. So, that is why it is a mixture of different properties.

Next is called the inorganic sol-gel route. So, in this particular case, inorganic polymer gels are made basically into 2 ways.

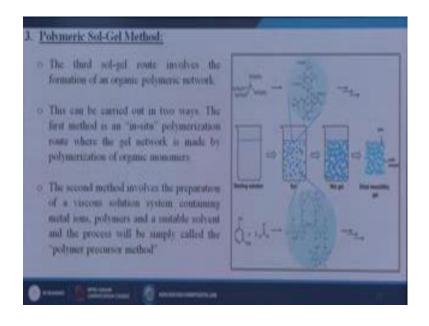
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First one is called up from metal oxides and inorganic solvents or from metal salts dissolved in aqueous or organic solvents and stabilized by chelating ligands. In both cases the chemistry is dominated by the high electro positive character of the metal ions. So, here first we are dissolving these alkoxide into some solutions, we are doing by condensation methods, we are making into the colloid forms then, we are forming the gelations, then we are doing the solvent exchange by route 1 then we are doing the polymerization process. So, first, route 1 is nothing but the inert solvent that is ETOH and route 2 is the monomer that is the HEMA. So, that is why here that 2 different routes we are applying and then we are using the hydrolysis, conventions and polymerization reactions are governed by several factors including the molar ratio of water to alkoxides, choice of solvents, temperature pH etcetera.

Next is called a polymeric sol-gel method.

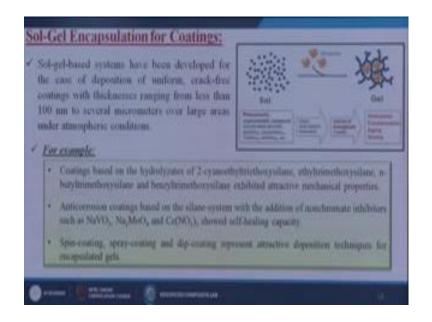
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This one is the last methods; here the third sol-gel route involves the formation of an organic polymeric network. So, simple here we are doing a one kind of polymeric coating on to the substrate itself. So, here this can be carried out in 2 ways, the first method is an in-situ polymerization route where the gel network is made by polymerization of organic monomers, another one is called the second method involves the preparation of a viscous solution systems containing the metal ions polymers and suitable solvent and the process will be simply called a polymer precursor method.

Here we can do the coating of a single virgin polymer or maybe a mixture of some kind of polymeric materials, metal ions and some kind of solution. So, here we are doing some kind of polymers, we are putting into the solution then we are making the gel, then we are using the dried monolithic gel, then we are getting at this kind of structure onto the substrate itself. So, by applying these 3 different methods, we can do the coating of different substrate by the sol-gel methods. So, another example is that sol-gel encapsulations for the coatings.

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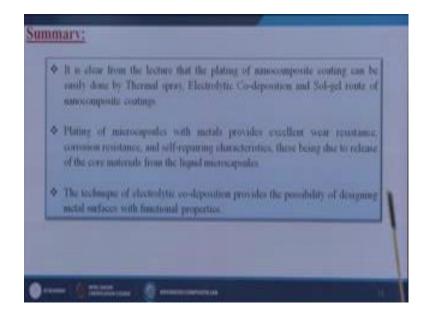


So, sol gel based systems have been developed for the easy of the position of uniform crack free coatings with thickness ranging from less than 100 nanometers to several micrometers over large areas under the atmospheric conditions.

Here also we can see that we can change the thickness of that particular coating onto the substrate itself, not only that we can change the properties of that particular substrate. So, here we are having that sol, then we are forming the gel, then this gel is making some kind of composite structure or maybe this gel can be applied onto the substrate itself. So, for example, coating based on hydrolyzates of 2 cyanoethyltriethoxysilane, ethyltrimethoxysilane, n-butyltrimethoxysilane and benzyltrimethoxysilane exhibited attractive mechanical properties if you are going to use this kind of materials.

Anti corrosion coating is based on the silent systems with the addition of monochromatic inhibitors such as NaVO 3, Na 2 MoO 4 and the CeNO 3 showed self-healing capacity. So, depending upon which type of property we are going to get or may be which type of property we want, depending upon that we have to choose that different types of coating materials or maybe that sol-gel method on our substrate itself. Spin coating, spray coating and deep coating represent attractive deposition techniques, for the encapsulated gels these also are the different types of coating materials by which we can do the modification of our substrate itself.

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And then the last is just a summary of this particular lecture which will give you that it is the clear from the lecture that the plating of nanocomposite coatings can be easily done by the thermal spray, electrolytic code deposition methods and the sol-gel root which we have already discussed in our lecture. Plating of micro capsules with metal provides excellent wear resistance, corrosion resistance, self repairing characteristics, these being due to the release of core materials from the liquid microcapsules; the technique of electrolytic co deposition provides the possibility of designing the metal surface with the functional properties.

Depending upon the different properties whether I need that metallic properties onto the substrate itself or maybe I need some non conductive properties of the substrate itself, some kind of anti corrosion properties, some kind of anti wear properties, I have to adopt different types of coating technology by which I can change the outer surface of our material so that it can exhibit the exact or maybe the desired property.

Thank you.