Surface Engineering for Corrosion and Wear Resistance Application

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Lecture - 37
Electroconversion Coating

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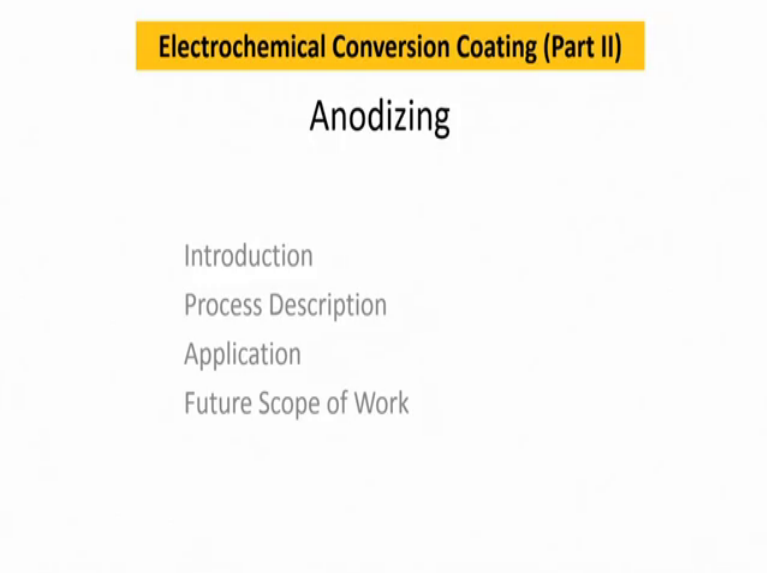

Hello in this talk we will discuss about the Electrochemical conversion Coating and particularly the electrochemical conversion coating actually deals with those techniques where you use the electrochemical means to form the compound layer on the surface of the metallic materials. So, among these all electrochemical conversion coating the anodizing is very much popular.

So, as the name implies this particular technique is called anodizing because here you are using your component as anode in the electrochemical cell and this anode when you just start electrolysis you will find that the oxygen produced at the anode basically reacts with the surface of the metal to form its oxide.

So, as it is done in the by using that component as anode you call it as anodizing. So, this process is very much applicable for again those metals which are very prone to passivate like you can apply this anodizing on aluminum you can apply it on magnesium, you can apply it on titanium and basic purpose of anodizing is again to improve the scratch resistance properties to improve the corrosion resistance property to a little extent.

And also to improve the flow coefficient of friction and to reduce the coefficient of friction as a kind of as a pretreatment for subsequent painting operation and purpose may be several folds in aerospace components in aerospace applications components in bio plant applications for several applications you can use the anodizing treatment.

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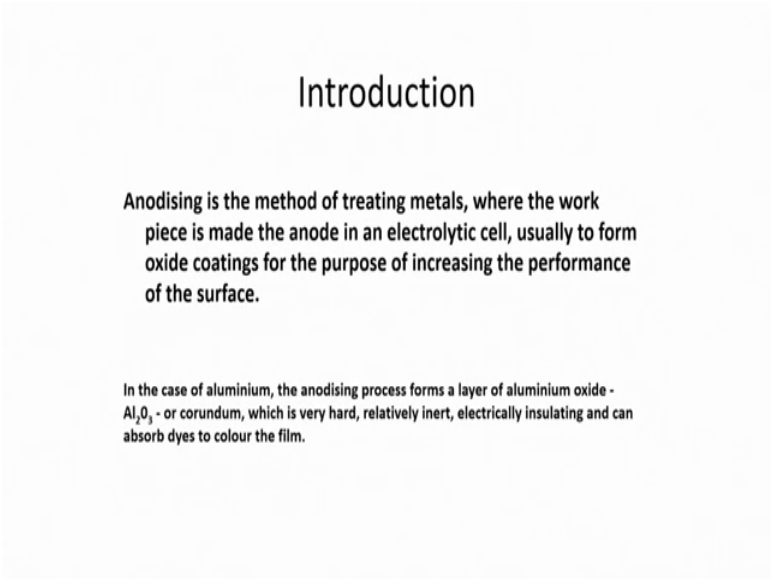

So, this particular treatment is for example, if you talk about the aluminum and anodizing of aluminum. So, in aluminum anodizing you will find that, there will be formation of very thin aluminum oxide layer or corundum layer which is very hard relatively inert electrically insulating and can absorb dyes to color the film.

So, again here again aluminium is used as anode, but whenever you use the aluminium as anode naturally on the surface of aluminium there is always a very thin oxide layer which is present. So, prior to application of the material as substrate you have to polish it properly and clean it properly. So, if you talk about the aluminium surface cleaning you will find that aluminium surface cleaning is usually carried out by using that this caustic should as a solution where you dissolve the oxides which are present in the surface rinse it with water and then dry it just prior to anodizing operation.

So, that surface is stress and there is the oxidation process on the surface.

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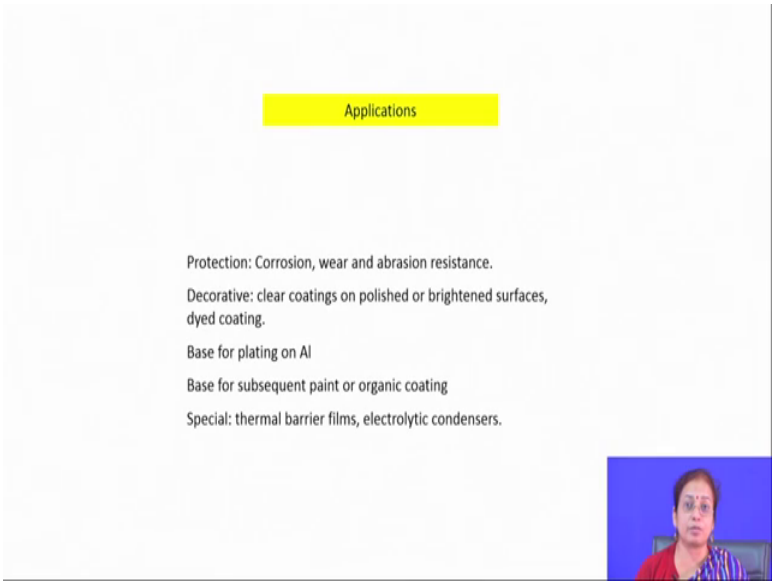

The application of this anodized aluminium is in several different sectors like protection against corrosion, scratch resistance and abrasion resistance decorative purpose base for plating of operating on aluminium, base for subsequent paint or special surface treatment like thermal barrier coating electrolytic condensers etcetera.

But again if you see the application of anodizing you will find that anodizing leads to formation of very thin oxide layer because your in the anode as soon as there is a formation of oxide layer and it covers whole surface the reaction stops and then that oxide cannot grow. So, because of its nature of very thin layer it this particular oxide cannot be used for the thermal barrier application particularly for long term application, but this can be used as a pre treatment for subsequent painting or can be applied for the scratch resistance applications.

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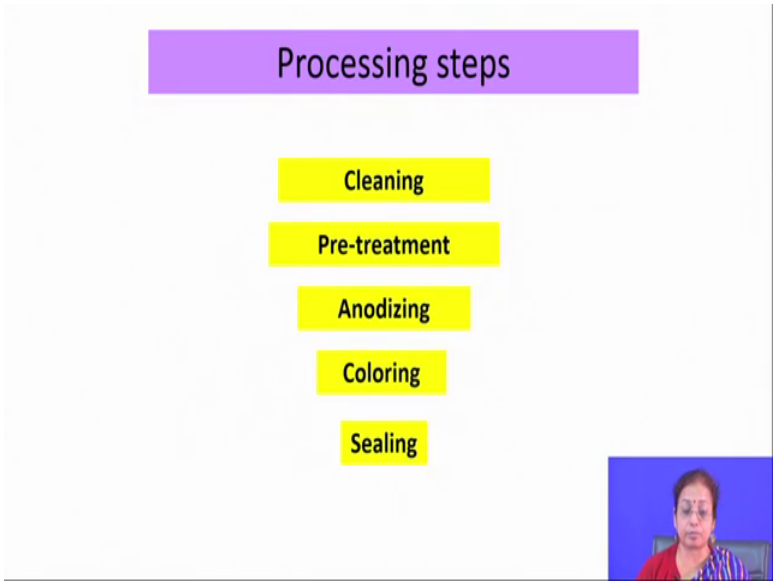

So, the processing steps for one should follow are is like that one have to someone has to clean the surface properly then pre treat then do anodizing operation coloring and then sealing. So, as I mentioned you anodizing is a kind of treatment after which you will find that lot of porosity is at there on the surface. So, usually surface porosity is they removed by coloring or sealing operation so, so that there is no more the porosities on the surface.

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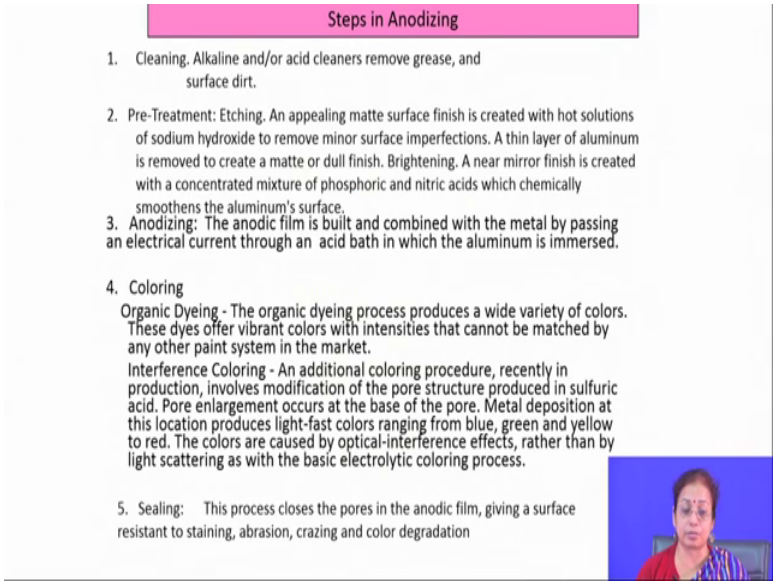

So, cleaning is usually done by alkaline solution cleaning and subsequently removal of the grease and surface dirt pretreatment etching operation can also be done. So, that it

can form it is very much clean in nature. Standardization is a process of building anodic film and combined with the metal by passing the electrical current to an acid bath and where aluminum is immersed, you have to pass electrical current and coloring may be done by organic dyeing or may be by interference coloring.

And finally, you do sealing operation because when you do sealing naturally whatever pores are there on the surface that gets sealed and usually surface becomes resistance to staining abrasion and degradation. So, usually people use the organic sealing or may be that wax sealing process to cover the surface with very thin wax evaporated wax. So, that force up field and we would not get any open porosities at the surface.

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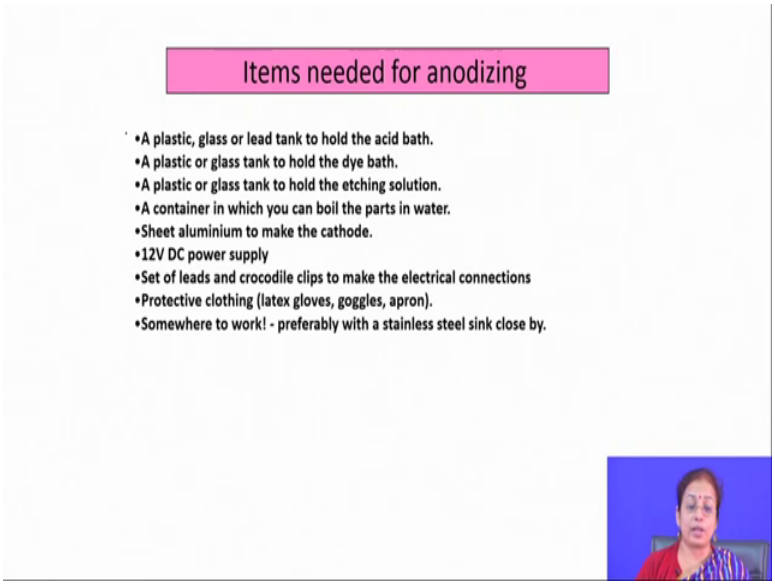

So, what you need is t that a plastic glass or lead tank to hold the acid bath and to hold the dye bath or. So, unit something a plastic or glass tank to hold the etching solution, the etching solution needs to be kept in a container and that the power supply unit is not really so, big unit it is 12 volt V DC power supply unit, the sheet of aluminium to make it cathode and set of leads and crocodile clips to make the electrical connection and protective clothing should be there and you have to have some space where you can do the anodization operation.

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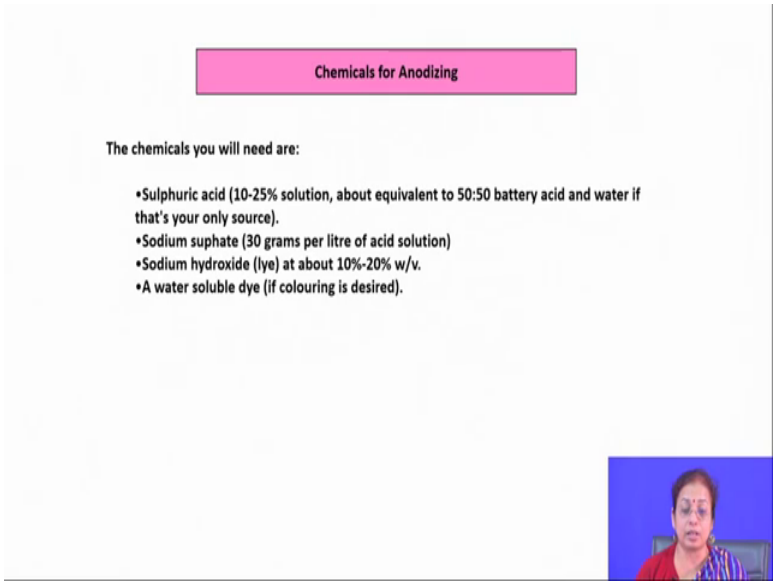

And chemical solution may be sulfuric acid 10 to 25 percent solution about 50 to 50 to 50 battery acids and water if the I mean that is only source or sodium phosphate, sodium hydroxide and water soluble dyes are required.

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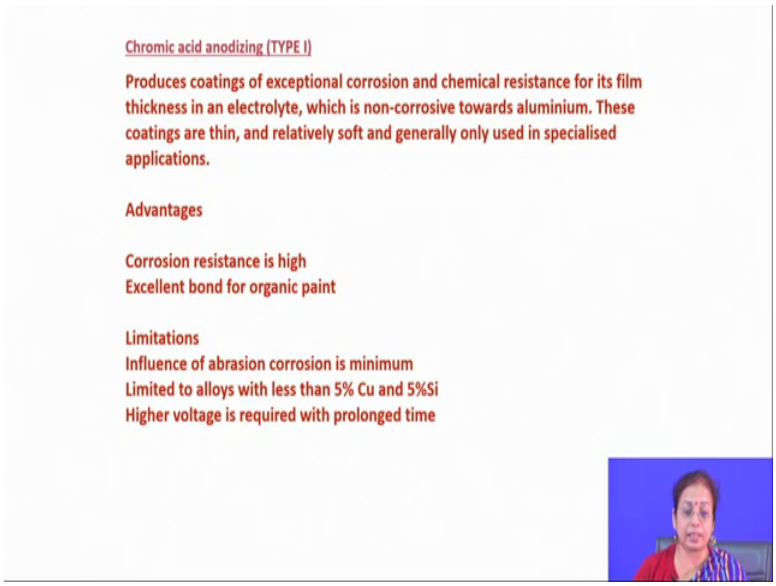

So, you will find that you can do anodizing in two different solutions; one is chromic acid solution another one is a sulfuric acid solution. So, chromic acid solution when you use then in that case there produces coatings of exceptional corrosion resistance and chemical resistance to extreme. So, whenever you are using chromic oxide naturally

chromic acid, so, whatever oxide is formed that is having very good corrosion resistance property, but influence of abrasive resistance is minimum.

So, this cannot be used for wear resistance purpose and where aluminuim is having one of the important limitation of anodizing is that, if it is aluminuim based alloy or magnesium based alloy then the kinetics of analyzing is very poor actually.

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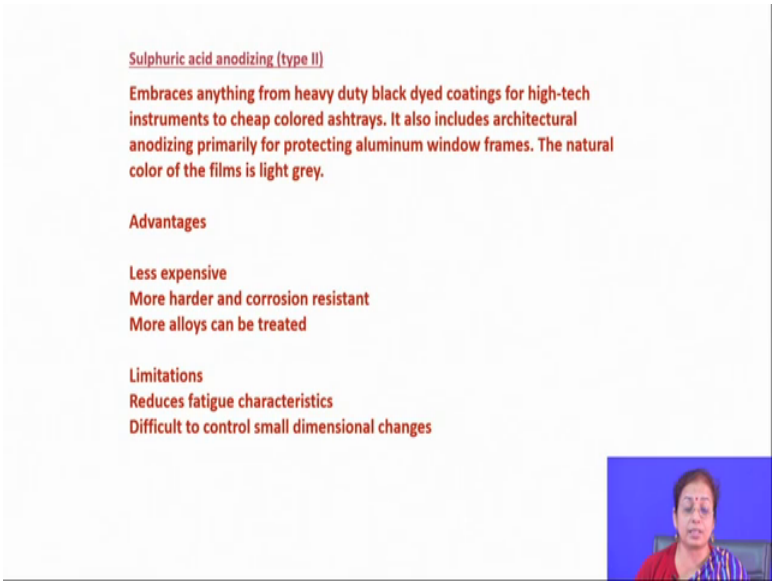

So, usually anodizing is applied on pure metallic materials, but whenever it is alloy system it is very difficult to have the anodizing process. Then sulfuric acid anodizing it reduces anything from the heavy duty black, black dyed coatings for high tech instruments to cheap colored ashtrays. It is also it is it also includes the architectural anodizing primarily for protecting the aluminum window frames from natural color of the field as the natural color of the. I mean this can be used for protection against the corrosion can also be used for scratch resistance application and this is also having the improve fatigue property and it is having sometimes it is harder and more corrosion resistance.

So, some cases sulfuric acid as a solution is preferred to chromic acid because of its peculiar nature of high hardness and as a result of which it is having good corrosion resistance as well. This is mainly because of the fact that when you do sulfuric acid anodization the density of the oxide scale is much higher here than that of density of the oxides values formed chromic acid anodizing operation. So, oh sorry.

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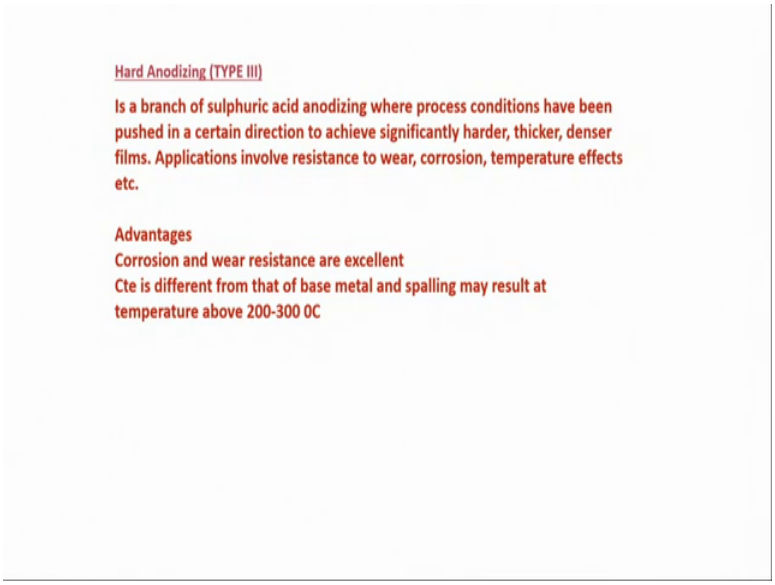

So, another type of anodizing is there where sulfuric acid anodizing is done, but process conditions are boost in such a condition that such a level that there is significantly harder thicker and denser films is obtained films is obtained and it is for corrosion and wear resistance applications coefficient of friction is different from that of base metal. So, spallation may be done may be I mean, there may be the chance of spallation particularly when temperature is a little higher. So, this is about anodizing.

So, basic problem of the anodizing is that the film thickness is not really as high as is desired because anodizing the steps in anodizing is that initially there is formation of oxide scale and then because of nucleation and growth of the oxides as soon as the whole coverage of the surface is there, the kinetics of the oxidation stopped it is very slow it becomes very sluggish.

So, usually it is from 1 to 4 micron thickness is their maximum thickness which can be achieved by anodizing operation. So, because of this very low thickness this cannot be applied for wear resistance application where gauging wear or may be very hard thicker layer is desired, it cannot be applied for high temperature oxidation resistance purpose like for thermal barrier coating application.

And so, these are two important limitations of the anodizing. So, in order to and also third limitation is that this anodizing treatment can be carried out only on pure aluminium it cannot be carried out on the aluminum based alloy. So, in order to

circumvent these 3 limitations people have these days come up with another solution that is plasma electrolytic oxidation process so, our micro arc oxidation process.

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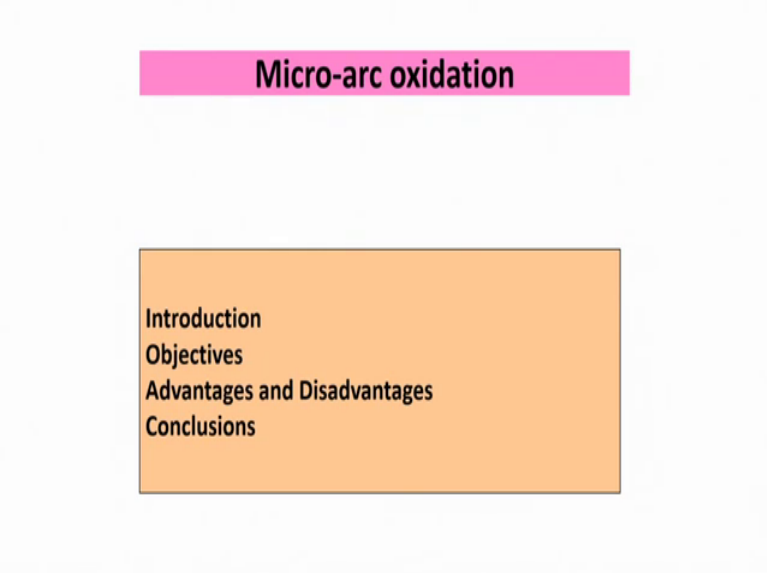

So, this is a little bit the Taylor Ment of the anodization process, but here because of that Taylor Ment you get significantly increased hardness value that is one of the best require this requirement of this particular one of the basic deliverables of the micro arc oxidation. And another advantage of this micro arc oxidation is that because of a very thick oxide layer this oxide can also be used for thermal barrier application and wear resistance application to a large exchange.

So, these freaks behind the formation of plasma electrolytic oxidation or micro arc oxidation is that here basically you use a very high voltage AC current for formation of oxide layer on the surface of the metal which is again used as anode. And but as soon as there is formation of very thin oxide layer on the surface of anode because of the application of very high voltage the oxide layer breaks down and because of the breakdown of the oxide layer there is formation of very narrow channel.

And in that channel there is plasma generation because it acts as a kind of high resistance region and because of the generation of arc you will find that the underlying substrate. Sometimes gets melted because of high temperature of the micro arc oxides product and it comes out and then through the channel on the surface of the metal and then there is formation of the oxide scale further.

So, like that you there are step wise in each phase of this current in there is formation of the oxide layer and then like that this particular because of the step by step oxide layer formation there is growth of oxide to a large extent and this grown oxide does not have much residual stress or interfacial stress as would be there if the oxide layer would be monolithic.

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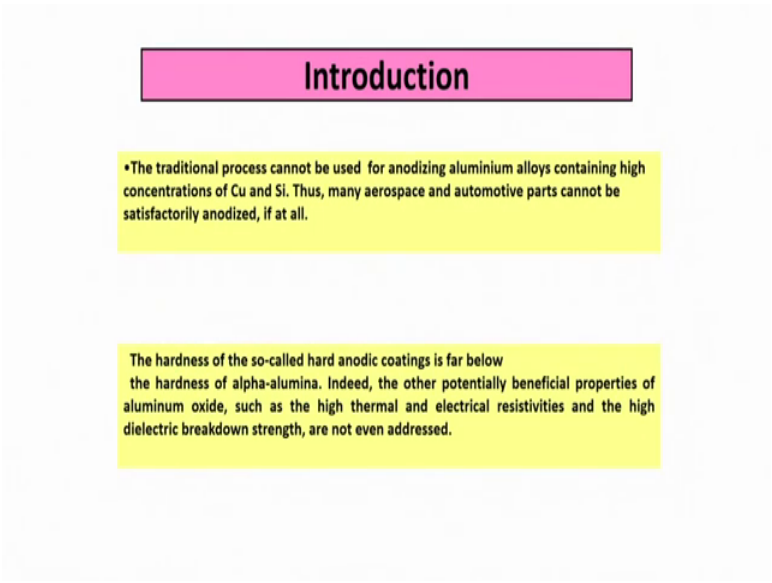

So, these are the advantages associated with this micro arc oxidation process. So, it can be again applied on the surface of the metals like magnesium, titanium and also the aluminium which are very prone to oxidation. So, this particular case micro arc oxidation is very important in recent technique.

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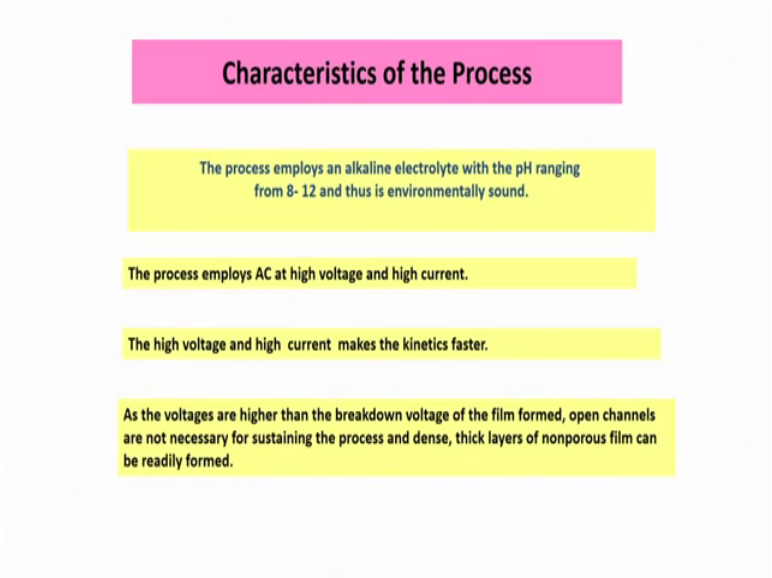

So, that as I mentioned you the characteristics are that this process another advantage of this process is that in this micro arc oxidation process usually people do we use basic bath show as they use basic bath there is no problem in the environment. So, drainage of the solution is not a problem. So, the process employees alkaline bath with the p H range between 8 to 12 and is the environmental is sound and the process employs AC current at high voltage and high current and high voltage and high current makes the kinetics faster.

And as the voltages higher than that of breakdown voltage of the film then naturally there is formation of open channel and which are naturally which acts as a kind of path for transportation of the molten metal from the below oxide level to the surface of the oxide scale.

Usually, if you see the surface carefully or cross section carefully there would not be the monolithic oxide scale, but rather composite oxide scale or rather solid scale formation where as aluminium pure aluminium channel is there in between two oxide channel aluminium or titanium or magnesium channel.

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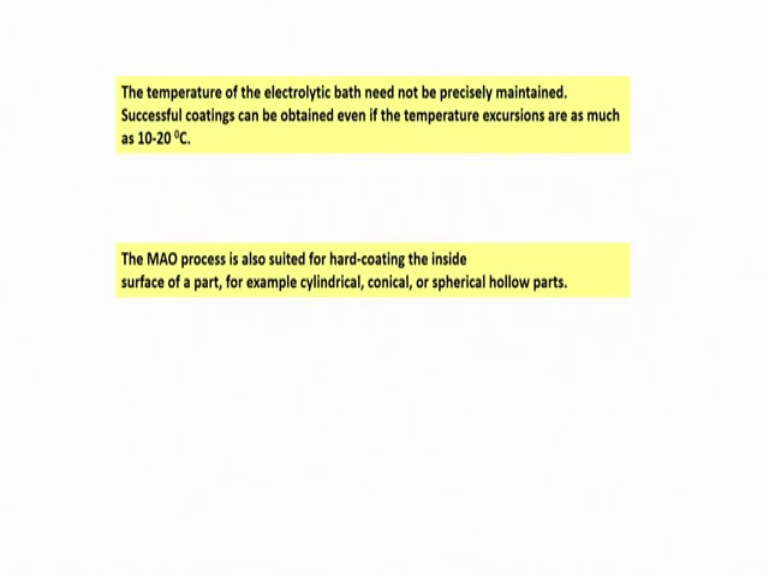

So, temperature of the electrolytic bath is not really so high. So, micro oxidation is also suited for hard coating inside the surface of the part. So, it is very important technique.

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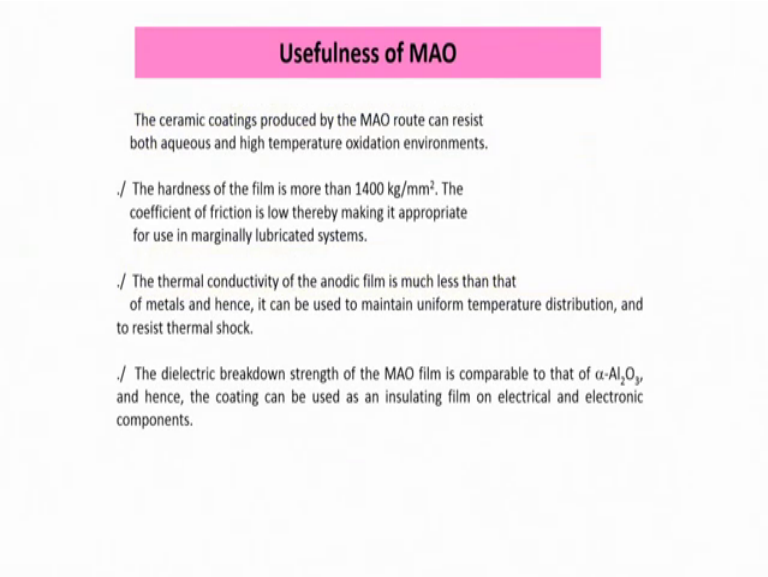

And can be applied for wear resistance as well as thermal barrier coating application and in particularly this micro arc oxidation coating can very much be applied on the alloy which is otherwise not possible to do oxidized oxidation by typical the technique of anodization.

So, this is what that that these are if you usefulness of this micro arc oxidized product the hardness of the film is more than 1400 kilo Joule per millimeter square. The thermal conductivity is much lower than that of metal and hence can be applied for thermal barrier coating application. Dielectric breakdown strength of the MAO film is comparable to that of alpha aluminium and hence the coating can be used as an insulating for the electrical and dielectric generator application.

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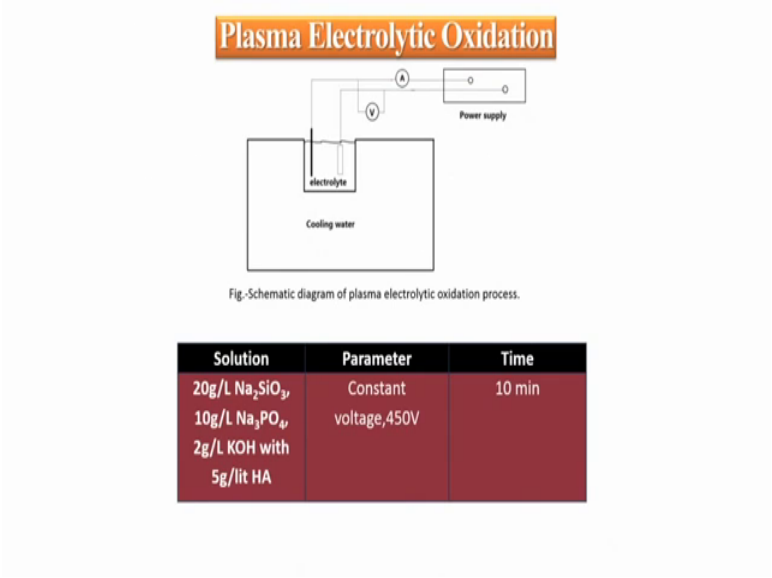

Fig.-Schematic diagram of plasma electrolytic oxidation process.

Solution	Parameter	Time
20g/L Na_2SiO_3, 10g/L Na_3PO_4, 2g/L KOH with 5g/lit HA	Constant voltage,450V	10 min

So, this is the process which is shown here. So, you have the you take your component as anode and you can use stainless steel as cathode or any other non consumable like graphite can also be used as cathode. So, you have very high voltage power supply unit which is attached to this is a cathode and anode and whenever the, this is the AC basically.

So, whenever the other there is the current is on you will find that there will be formation of oxide scale and then its breakdown and high resistance region generation and subsequent melting of the underlying metal and its transportation on the surface. During off cycle you will find that the transported state metal get melted and then again in the one time it gets oxidized.

So, each a each on and in each on time there is oxidation process and you know off time there is basically the transportation of molten metal from the below oxide surface on the surface. So, like that this per process actually proceeds in a layer by layer fashion.

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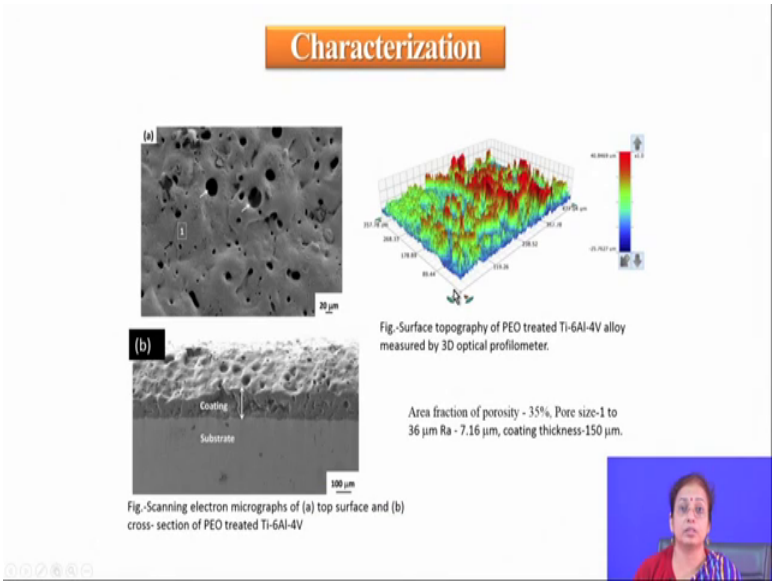

This is the case for micro arc oxidation of titanium on Ti 6 for substrate. So, you will find that on the surface there is a lot of porosities and if you see the cross section there also porosities are the one interesting thing is that this is the research investigation. So, you will find that these porosities are not really interconnected. So, even though there are porosities on the surface, but these are not interconnected mainly because of the reason that whenever there is channel formation because of the channel formation there is porosity, but.

So, the channel is again closed because of the molten metal flow from the below oxide region on the surface. So, intermittent portion if you see you will find that is full of the molten metal, but outer part there are a lot of oxides which is actually closed in nature because of this fact there is a lot of roughening of the surface.

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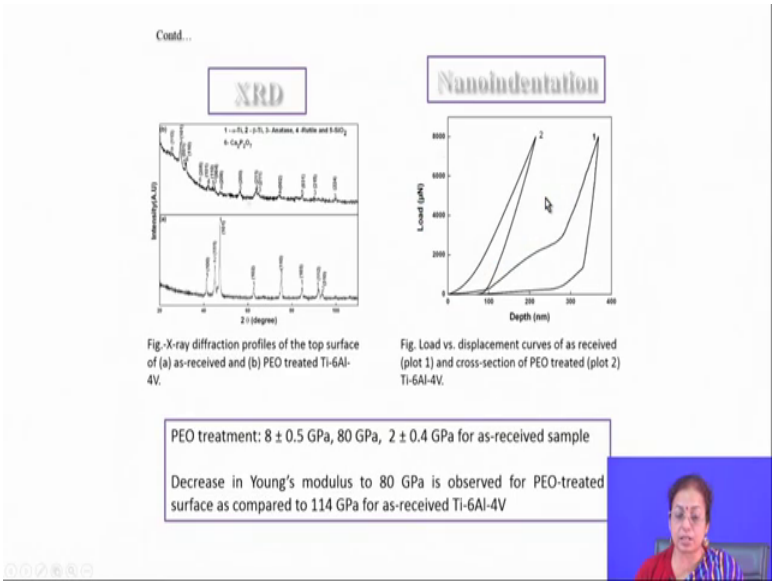

And that rough surface is beneficial to promote the cell growth. If you see the extra diffraction analysis there is presence of rutile as well as anytus in the surface. In addition to that there is also a few calcium phosphate phase formation.

And if you see that in nano indentation properly you will find that nano indentation decreases the because of nano indentation if you see the Young's modulus (Refer Time: 18:56) distribution you will find that hardness increases and Young's modulus decreases in the (Refer Time: 19:01) film and this decrease is beneficial where decrease was mainly because of presence of porosities on the surface.

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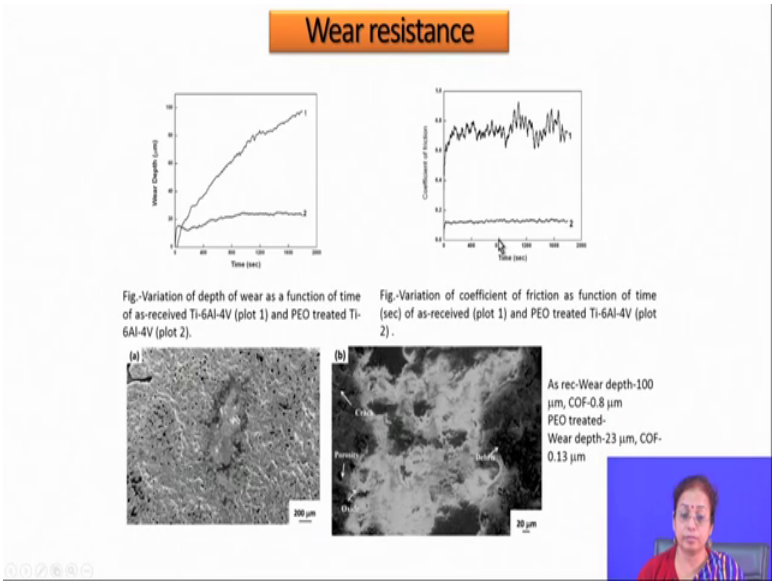

There is significant improvement in the wear resistance that is also typically for that oxide layer because of the presence of the oxide layer the corrosion wear resistance property increases and another interesting feature is that there is decrease in the coefficient of friction. So, decrease in coefficient of friction was mainly because of formation of the oxide sieve on the surface and if you just use sinusoidal fluid while doing corrosion test you will find that its coefficient of friction further decreases.

Then this is where depth actually you get. So, it is oxidized layer there is formation of something which was oxide layer which is present and that oxide if you see carefully after the where you will find that. If you do wearing what happens is that there is the removal of the material from the surface and that remove material actually if you check carefully, it will consist of oxides actually because this is oxide layer only that. So, you will find lot of that charging effect from the surface actually.

And because there is formation of oxide layer again now when you do wearing further you will find that that oxide reacts as a inter layer and as a result of which coefficient of friction decreases because the 2 body wear changes from 2 body to 3 body wear.

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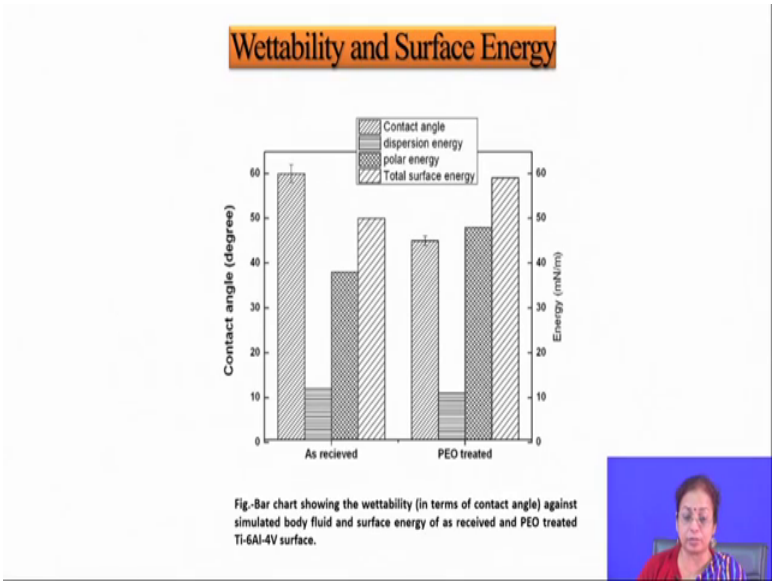

It is very interesting to note that when you do the contact angle measurement of the PEO sample you will find that there is significant decrease in the contact angle value of the PEO treated sample as compared to that as received sample. So, this is contact angle of as received example this is for PEO treated sample.

So, contact angle decreases when if you sell because you can conclude that there is increase in weight ability of the surface by the PEO treatment.

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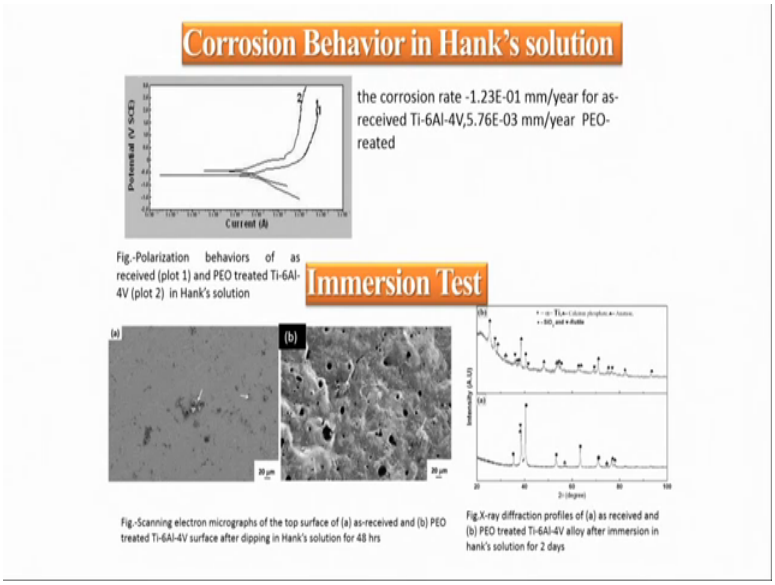

If you check the corrosion behaviour you will find that corrosion behaviour also is improved because you see that because of free treatment there is shifting of the equal value towards normal direction.

And when you dipping in hanks solution and see the calcium phosphate deposition rate you will find that there is not much significant difference in the deposition rate, but if we keep for a longer time possibly we would get some results. So, this is again this again needs further investigation to conclude on the bond formation behaviour of this PEO treated surface layer as compared to that of as received substrate.

But as weight ability is increased naturally you can say that sale probe sale adherence will be more on the oxide layer. So, for you can understand that not only that oxide scale which is for example, if you talk about that plasma electrolytic oxidation, this plasma electrolytic oxidation can be applied for formation of the oxide layer, this can be applied for formation of phosphate layer if you use NH PH 4 as a solution it can be applied for the formation of silicate layer if you use sodium silicate as the solution.

So, depending on the solution choice you can have different types of product on the surface different types of compound on the surface not only oxide formation. So, you depending on your requirement you can basically vary the process parameters and get their desired thickness get the desired (Refer Time: 23:17) and also desired properties on the surface of the metallic materials particularly titanium magnesium and also the aluminium and purpose may be anything for example, titanium and magnesium the purpose may be corrosion resistance application, purpose may be wear resistance applications. So, both purposes it can be applied.

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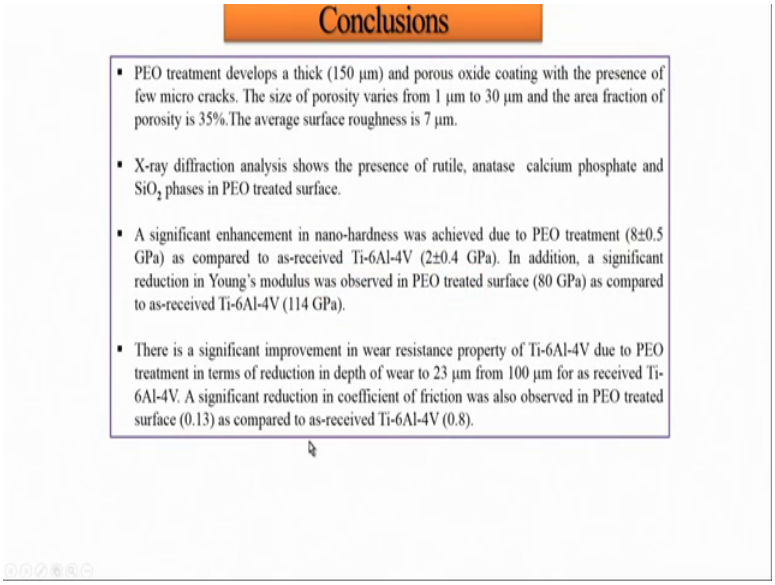

So, you can conclude that this per plasma electrolytic treatment is even very nice and interesting treatment and a kind of modification of the anodizing operation where you get very thick coating of oxide or modification of any chemical converts in electrochemical conversion coating you can say. Wear thickness can be as high as 150 to 200 micron and as compared to that of 2 to 5 micron of anodized surface and in fact, for any other chemical conversion coating.

Also there is only very thin oxide very thin oxide or very thin phosphate layer which is which are formed because as soon as the surface is covered the reaction stops. So, that is the limiting point. So, as soon as the whether you use dipping in solution there is formation of nucleation of that product and then its growth and it continues till the full surface is covered. So, as soon as this full surface is covered everything stops.

But in plasma electrolytic oxidation or parse electrolytic oxidation that thing is not stopped, but that a rather beginning. So, as soon as the surface is covered with oxide scale then there is breakdown of the oxide scale because of a high voltage application and because of the breakdown of the oxide scale there is channel formation. And in the channel there is the plasma generation because of the fact that the inner channel region acts as the high register region and very high amount of heat is generated in that region.

And because of that high resistance region generated and high heat generation the underlying substrate gets melted and that voltages material they pass through the channel

towards the surface. And then again there is formation of oxide scale on the surface like that the cycle continues. So, the thin monolithic layer oxide is acts as a kind of base for the subsequent oxidation on the other hand in case of anodizing or any other chemical conversion coating when there is very thin oxide layer it acts as a kind of it is the last point clean when the process will continue.

So, after that process stops actually, but here the process starts beginning when the surface is covered with the oxide layer. So, though there is there are porosities which are not there in anodizing if you think of anodizing again in anodizing operation if you see carefully your chemical conversion coating see carefully there is formation of your micro porosities where the porosity diamond cells are quite less not really even micro level, but nano level porosities are there.

But here porosities are porosity diamonds inside and for varies from 1 micron to 30 micron, but those porosities over here is a little different from the porosities in the process of anodizing or chemical conversion coating in their porosity is there all throughout the coating, but here porosity remains on the surface. And below surface region porosities are not there because that is covered with the molten metal.

So, the roughness is because of porosity there is roughness generation roughness is beneficial for some of the properties like biocompatibility, weight ability these all properties. So, this is another uniqueness of this particular process. So, third uniqueness may be in the other case whenever you talk about anodizing the surface is full of oxide layer and that is monolithic, but here thick oxide layer even there, but still it is not really so, brittle because it is composite in nature.

There is a presence of aluminum, molten aluminum or solidified alumina in the channel which actually offers the toughness on of the surface or oxide layer. It is basically a kind of solvent layer which forms on the surface of metal then because of the X-ray diffraction you see that there is oxide layer which is present very nicely.

So, this particular technique can be applied for alloy of for oxidation of alloy of aluminium alloy of magnesium or alloy of titanium which otherwise is difficult to do in case of anodization. So, anodization can only be applied for pure metal, but can very well be applied on the alloys actually alloy system.

And you will find that due to PEO operation there is decrease in the Young's modulus value which is beneficial for improving the I mean for application as bio gland particularly when it is titanium based substrate hm. Because of the PEO operation there is significant enhancement in wear resistance thickness is quite high.

So, you can use the coating for not only scratch resistance application as is there in anodizing, but can also be applied for high stress were resistance application then gauging your resistance application for different applications it can be applied and can also be applied for thermal barrier coating. So, because thickness of the scale is quite high, so, you can always use it for thermal barrier coating application.

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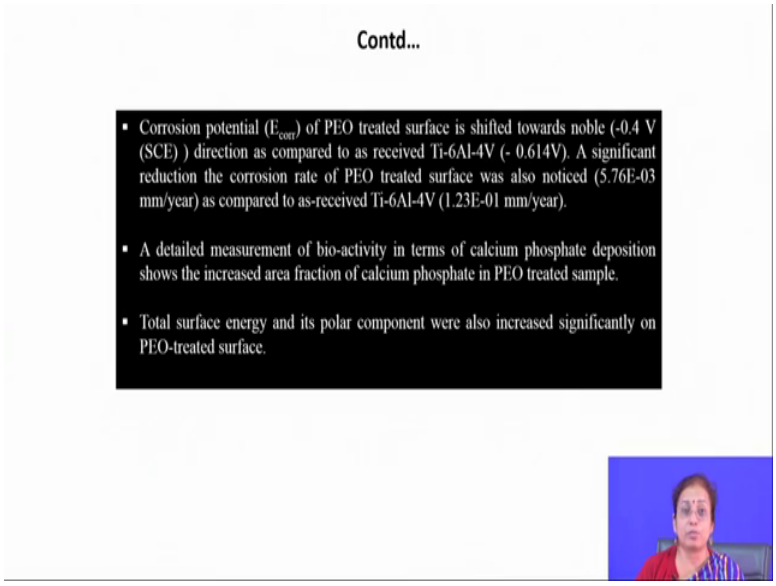

So, but people have not started doing these all things because this process is patented and again in research stage where most of the studies concerned microstructure investigation and understanding the effect of process variables on the properties of the coating.

They are there is enhancement in corrosion resistance even though porosities are there because they are not interconnected and naturally these oxide layer can also be applied for improving the biocompatibility particularly bioactivity of different alloys and metals which are used for bio implant application.

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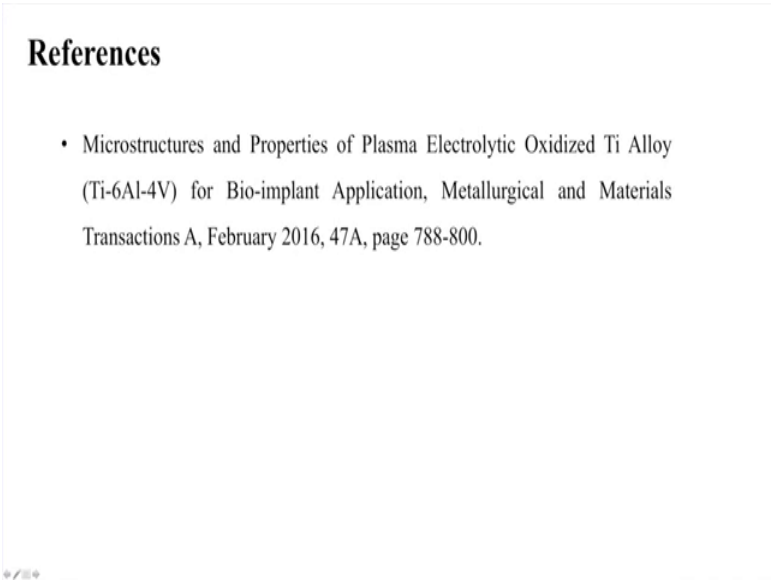

Thank you so much.