Surface Engineering for Corrosion and Wear Resistance Application
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Lecture – 36
Chemical Conversion Coating

Hello welcome to the electrochemical or Chemical Conversion Coating for Corrosion and Wear Resistance Applications. So, this part will be covered in two parts, part I where I will discuss about the chemical conversion coating and part II where the electrochemical conversion coatings will be discussed in details.

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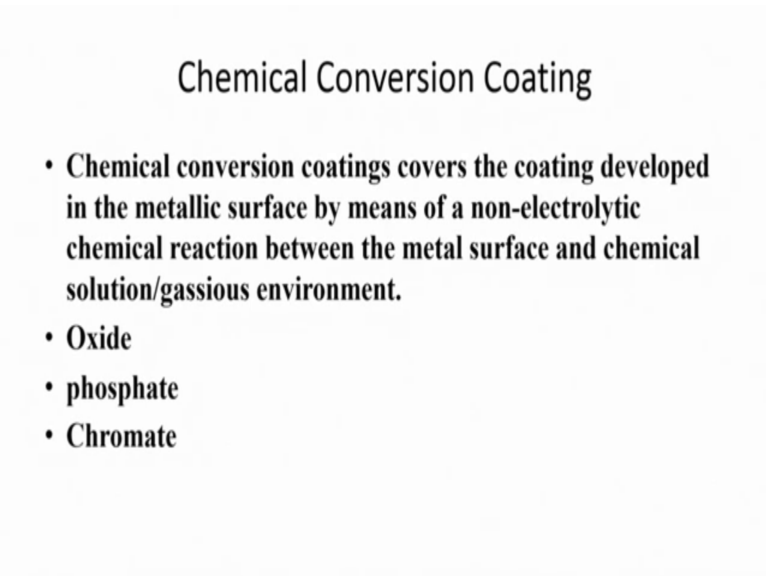

So, these conversion coating is nothing, but a kind of coating where actually the metallic material surface is converted to its compound by chemical reaction either in electrolyte where only chemical reaction occurs or maybe electrolyte where electrochemical reaction occurs and the basic objective is to develop oxide layer, phosphate layer or chromate layer on the surface.

And, the application of these chemical or electrochemical conversion coatings are to improve the corrosion resistance and scratch resistance properties as well as a pretreatment for subsequent painting operation or other surface treatment.

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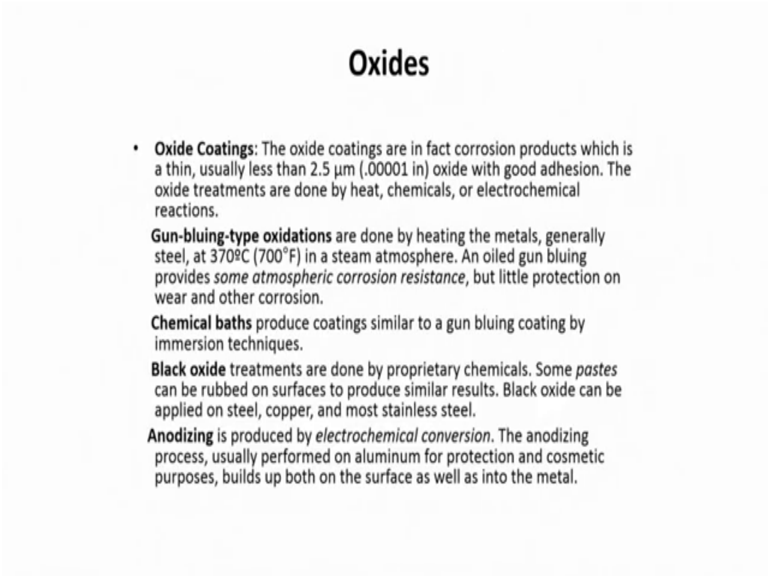

So, in the chemical conversion coating usually we have different types of coatings like oxide coatings, phosphate coatings, chromate coatings and depending on the conditions where the coating by which this particular metallic surface is converted to its compound there may be different types of solutions which are used or different conditions are applied. So, that you get the desired composition as well as desired phases on the surface to have their required properties.

So, different types of coatings which are very much popular under chemical conversion categories are oxide coatings. So, it is nothing, but a very thin corrosion oxide product which is formed under surface of metallic materials and this particular oxide coating in chemical solution is usually carried out for those materials or metallic materials which are very much prone to passivate. Then gun bluing type oxidations are done by hot heating the metals, usually by steel at three seventy degree Celsius in a steam environment this particular gun bluing type of oxidation actually gives rise to very thin oxide layer with blue in color.

Then chemical baths produces coating similar to gun bluing coating by immersion techniques. Black oxide treatments are usually done by it is proprietary chemicals, some paste are rubbed on the surface to produce the black, if black surface oxide surface on the surface of the metallic materials and particularly copper, steel and most of the stainless steel.

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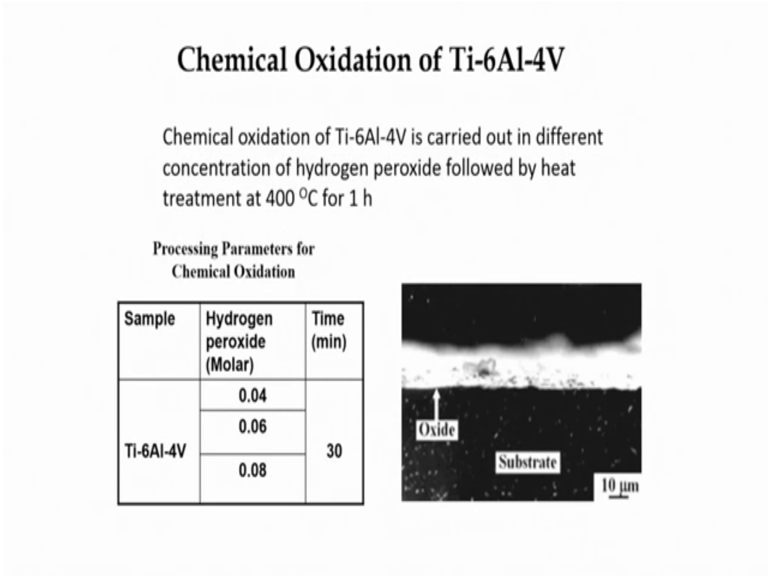

And these are a few chemical conversion coating where you get oxide layer on the surface not only on metallic materials like. Not only the ferrous based material or copper this particular chemical conversion coating can also be carried out on titanium and its alloys for the development of Ti 2 film on the surface for different applications like, oxidation registers applications or maybe corrosion resistance applications and also for by implement application.

So, typical few examples of chemical oxidation on Ti 6 4 will be shown over here in the next few slides. So, here actually chemical oxidation of Ti 6 4 substrate was carried out in different concentrations of hydrogen peroxide solution, followed by heat treatment at 400 degree Celsius for 1 hour.

So, the basic purpose of these oxidation treatment was to make the Ti 6 4 bioactive usually Ti 6 4 is a very good alloy which is having very good biocompatibility in terms of corrosion resistance, wear resistance and also because of very thin oxide layer which forms onto the surface of metal when it is inserted that particular oxide again promotes osseointegration, but that oxide is very much loose and porous in nature.

So, cell growth on field continuous and it would not be so homogeneous all throughout the surface. So, as a result of which this particular material is subjected to hydroxyapatite coating prior to implantation, but on the other hand it has been observed that if a very thin artificial oxide layer is formed on the surface by prior treatment that oxide scale promotes the cell growth very nicely and it gives the osseointegration property.

So, that was the objective of the study, so here that particular Ti 6 4 substrate was initially cleaned very nicely then polished to a level of 0.25 to 0.5 micron and then subjected to hydrogen peroxide treatment and then heat treatment.

So, after these hydrogen peroxide treatment, there was a very jelly kind of substance was found on the surface and then when it was heat treated very thin oxide layer was found on the surface.

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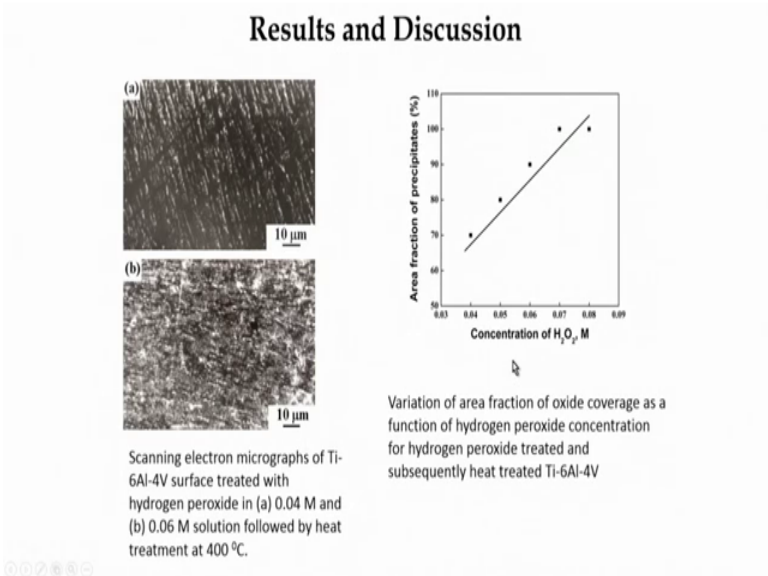

And this oxide was mainly and it is in nature and if you see the oxide scale properly you will find that the oxides are very much very fine oxides are present. And, if you see the morphology it you will find that very nano very thin fine nano cells precipitations are observed on to the surface and as you go on increasing the hydrogen peroxide concentration you will find that area fraction of the particles also increases.

So, coverage depends on the how much time you are or how much percentage of co hydrogen peroxide you are using for the oxidation purpose.

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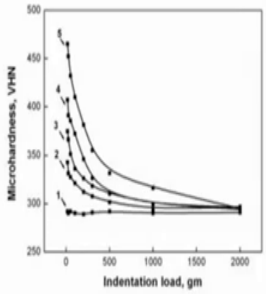
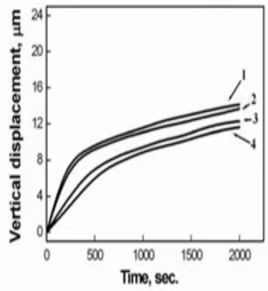


Variation of microhardness with indentation load for (1) as-received and hydrogen peroxide treated Ti-6Al-4V for concentration (2) 0.04 M, (3) 0.06 M, (4) 0.08 M and (5) hydrogen peroxide treated at 0.08 M followed by heat treatment at 400 °C for 1 h.



Cumulative loss of wear (in terms of vertical displacement) as a function of time for (1) as-received and hdrogen peroxide treated with a concentration of (2) 0.04 M, (3) 0.08 M and (4) 0.08 M followed by heat treatment at 400°C for 1 h.

So, we will find here accordingly the micro hardness also changes because of formation of anodized field, you will find that there is improvement in hardness and depth of the hardening was around 10 to 15 micron.

So, that particular amount of percentage of oxides or maybe the thickness of the oxide scale was enough to confer the good wear resistance property on the surface and as the hardness varied with the percentage of hydrogen peroxide as a result of which we see that there is also wear resistance property improvement in wear resistance property.

But which again depended on that hydrogen peroxide concentration and as we go on increasing the hydrogen peroxide concentration, we find that there is increase in wear resistance of the coated product or may be converted surface.

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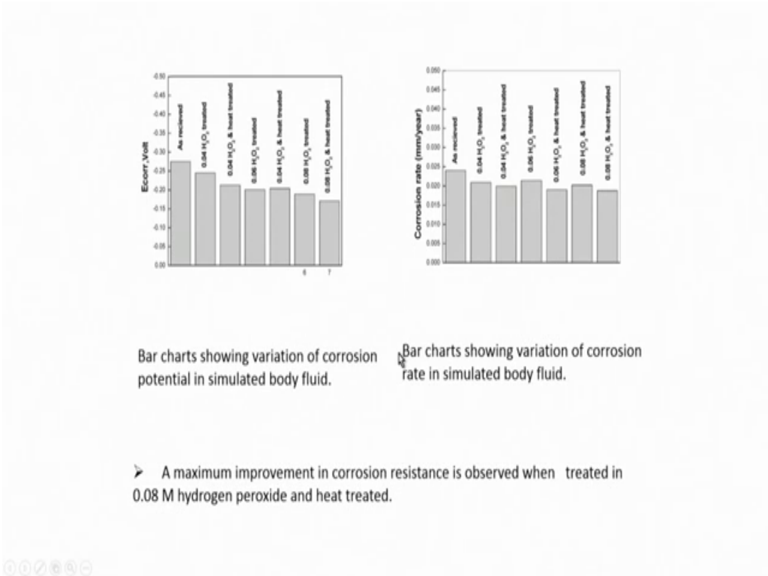

So, we also carried out the corrosion resistance property in hanks solution because this particular objective of the coating was a basically for application of this product as implant. So, the solution was simulated body fluid where, we tried to see the leaching behavior of the oxide coated product, we found that as we go on increasing the oxide percentage a percentage or maybe increasing the hydrogen peroxide concentration in the solution, there was a increase in the corrosion resistance property in terms of a ennoblement of the Ecorr value as well as the corrosion rate was also as to a little extent decreased.

But it was not really show high as was desired because this oxide layer was not really continuous, it was actually the oxide scale formed all throughout the surface in a discontinuous fashion. So, this chemical oxidation product actually offered very good wear resistance property, but for improve corrosion resistance property possibly some other treatment would be required for full coverage of the surface.

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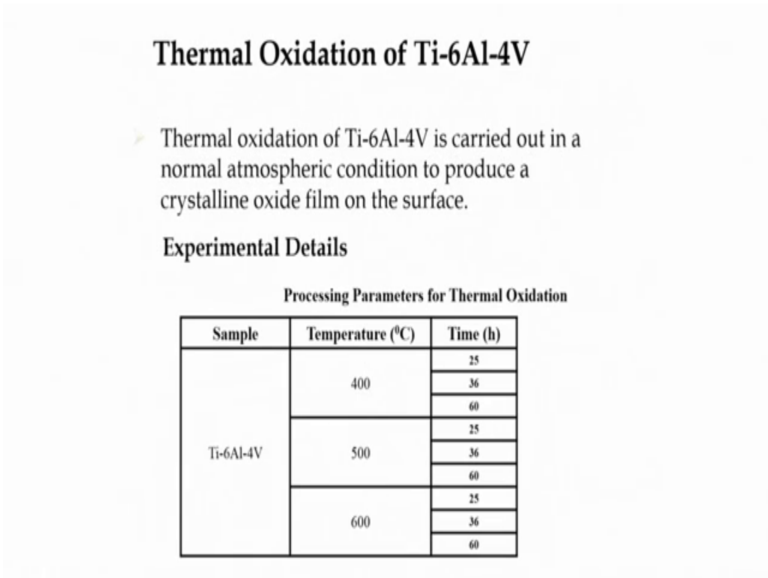

So, in order to have the full coverage of the surface we tried to go for thermal oxidation process. So, so thermal oxidation is another route for oxidation of any metallic materials me maybe I do not know its alloys steal our maybe titanium 6 aluminum four vanadium or magnesium two. So, any material metallic materials can form oxide when you heat it at a higher temperature in oxidant oxygen containing environment or maybe in air.

So, in this case the thermal oxidation treatment was carried out in air and temperature was varied from 400 to 600 degree Celsius and time was also varied and we tried to optimize their time and temperature combinations to have the desired microstructure and also properties on the surface.

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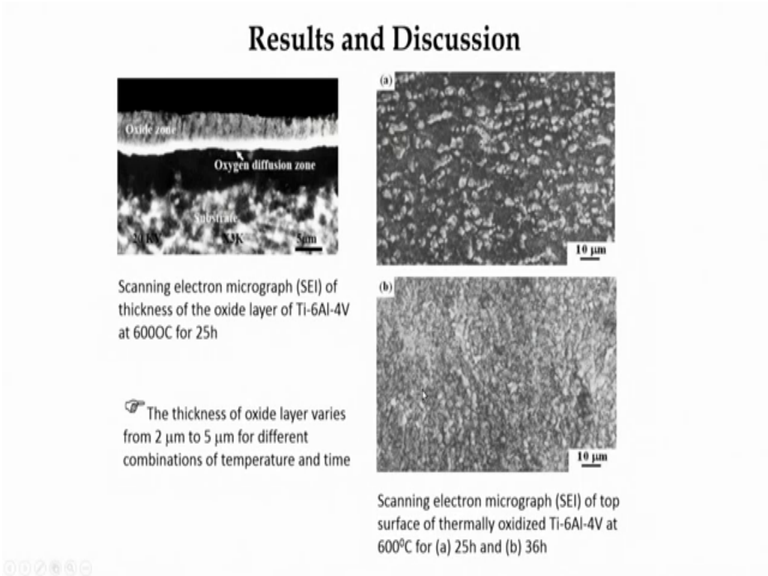

So, if you see the surface of the oxide scale when it was rooted at 600 degree Celsius for 25 volts this was the highest temperature and highest hours of study, we found that there is oxide scale and oxide within oxide layer and thickness was around 5 to 6 micron. So, that oxide layer again it is you if you see carefully you will find that oxide layer is there on top of the titanium surface and below titanium surface also there is a oxygen ingress of the oxygen and hence formation of oxygen in solution of titanium.

So, you will find that there is a counter ionic transportation of oxygen and as a result of which oxide scale forms a at the outer layer as well as inner layer there is oxidation and that oxide scale is not really a continuous and monolithic film which were present in the inner layer, it was mainly at the grain boundaries of platinum.

So, if you see the surface carefully you will find that there is full coverage of the surface with the oxide scale and you will find that these oxide was it was found that these oxides were or may be the phases in the oxide mainly was it was rutile in nature, but when you do oxidation at low temperature it was anatase.

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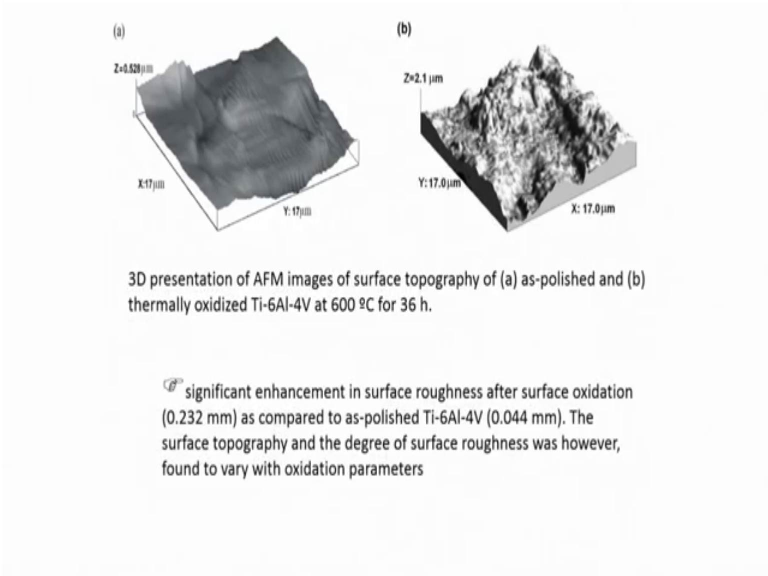

So, because of oxidation there was naturally improvement in the increase in surface roughness. So, that surface roughness enhancement was beneficial because if you have the increase surface roughness, it basically promotes a cell osseointegration and cell growth on the surface.

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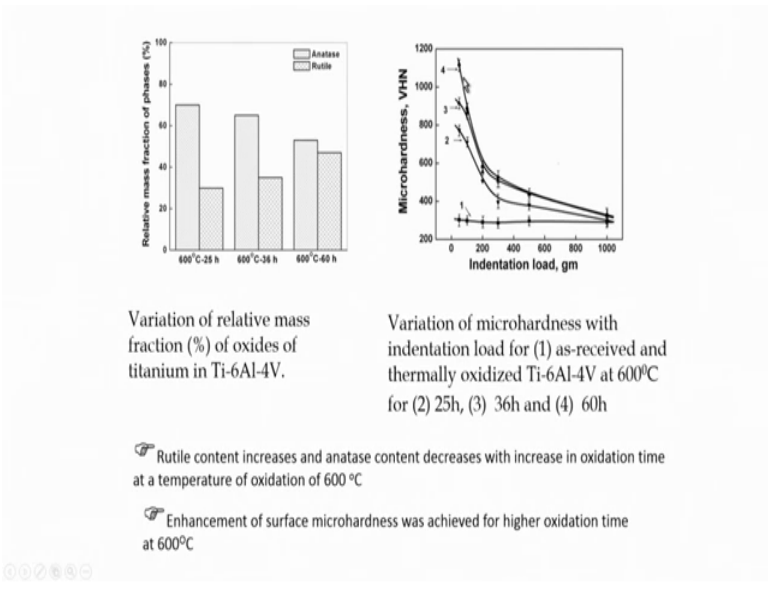

And as a result of which we found that there is improving improvement in hardness and if you just compare the hardness enhancement with respect to that of chemically oxidized layer you will find that it is 4 to 0.5 times higher than that of chemically oxidized converted titanium dioxide.

And this is again because of the fact that as you go on increasing the temperature you will find that there is a formation of both anatase and rutile phases and particularly at 600 degree Celsius if you just oxidize you will find that lot of rutile phases are present in the micro structure.

So, this rutile is very good because it offers the hardness and wear resistance property. On the other hand anatase is though not really so good for offering high wear resistance property, but anatase is quite good for promoting the sale growth.

So, our main objective was to optimize the process parameters and to optimize the phase composition in the on the surface to have the proper percentage of anatase and rutile. So, that it is raised for value type application and the work is still going on.

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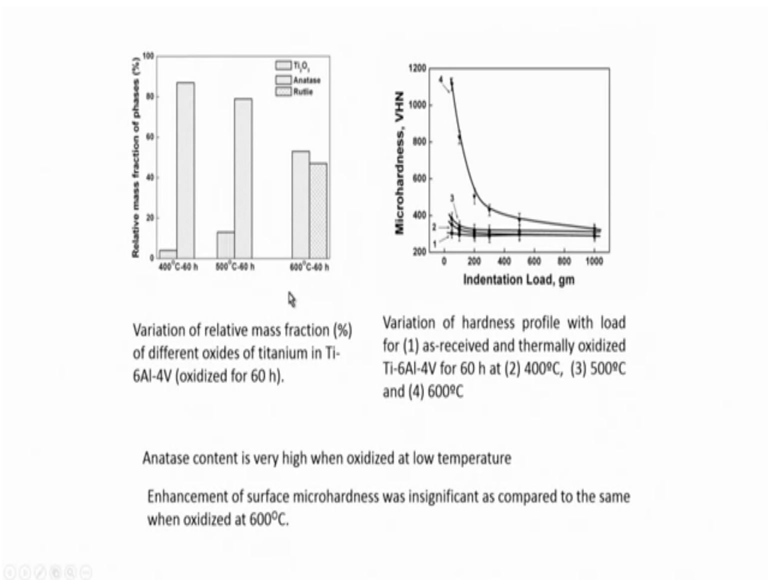

So, this is the different phases are formed at 400, 500 and 600 degree Celsius we find that as we go on increasing the temperature, we find anatase percentage actually decreases and rutile percentage increases. So, this is very important because as we go on increasing the temperature naturally you find that naturally this anatase is a product which is basically stable at low temperature.

So, when you do oxidation at 400 degree Celsius, 500 degree Celsius you get a lot of anatase in the micro structure or in the phase micro structure or maybe phase when you do exciting analysis you will get that result. On the other hand at 600 degree Celsius you find that anatase percentage decreases and rutile percentage increases. And there is enhancement in hardness also that varied with the temperature of the oxidation.

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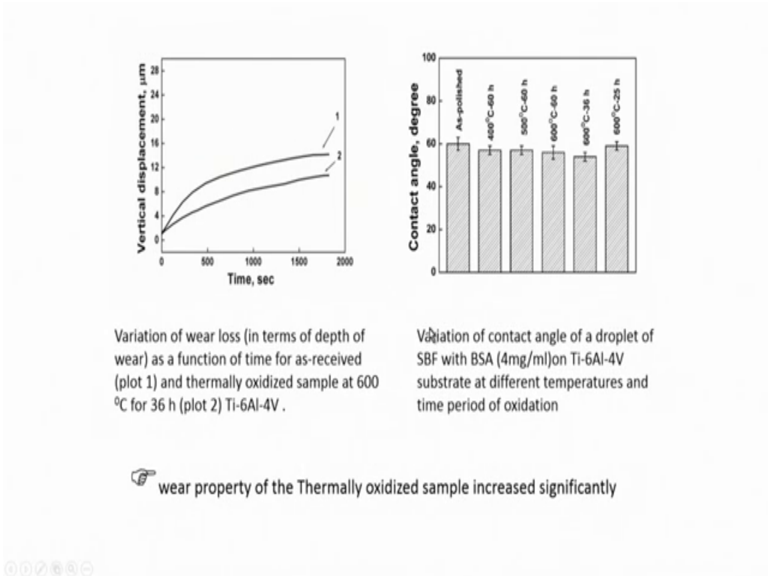

So, finally, we try to see the weight ability of the surface we found that weight ability there was not much change in weight ability weight ability was more or less same as that of a smallish surface, but we find that there is enhancement of the wear resistance property for both the oxidation at 500 degree Celsius as well as 600 degree Celsius.

So, you can say that thermal oxidation is again another way of a converting the surface of metallic materials to its oxide and that oxidation helps in improving the wear resistance property, improving the particularly scratch resistance properties, abrasive wear resistance properties as well as the corrosion resistance property.

Because it acts as a passive layer and when there is coverage of the full surface. So, it is very important that you optimize the process parameter, so that the full coverage is there and also you get the desired result.

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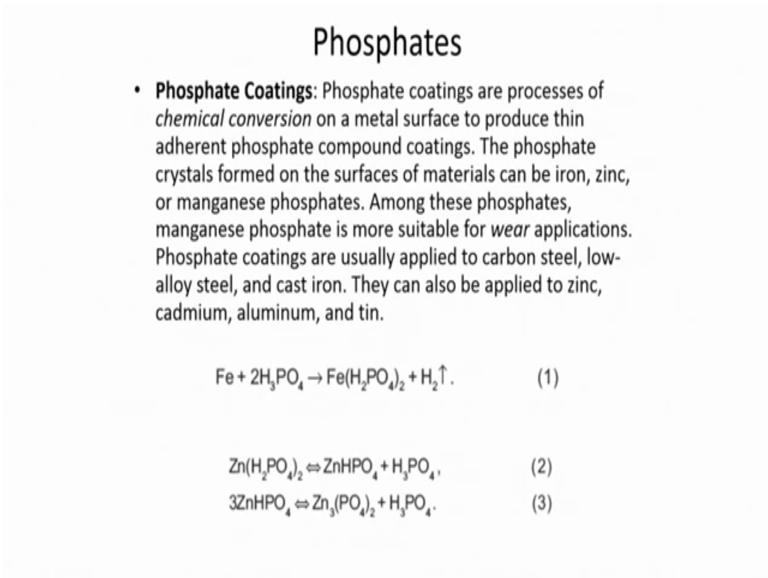

So, this is this was about oxidation now you can also develop the phosphate layer on the surface of metal. So, in for that is called phosphatization, so in phosphate coating we basically try to convert the surface of the metric materials to its phosphate and it may be any phosphate like iron phosphate, zinc phosphate or manganese phosphate each phosphate is having its own color.

So, basic purpose was phosphatization is that phosphatization process or phosphate coating is not really so hard as oxide coating and lot of porosities are also there. So, mostly the phosphatization process is applied as a pretreatment for subsequent painting operation. So, this is very important treatment and it also is use sometimes to colorize the surface, if you are interested to have different color on the surface you do simple phosphate coating.

So, that phosphate coating actually it can be used for a marker actually of different materials when you keep it in environment, particularly when it is metallic, so it offers the environmental corrosion resistance property as well as it colorizes the surface and on top of the phosphate coating you can also develop painting. So, that it offers the further corrosion resistance property of the surface.

So, if you talk about the different reactions that occurred that is nothing, but if you just think of the reaction of iron with the phosphoric acid it forms that iron phosphate similarly zinc phosphate may be formed magnet manganese phosphate may be formed.

So, these phosphates are very much stable in nature and it remain on the surface very nicely.

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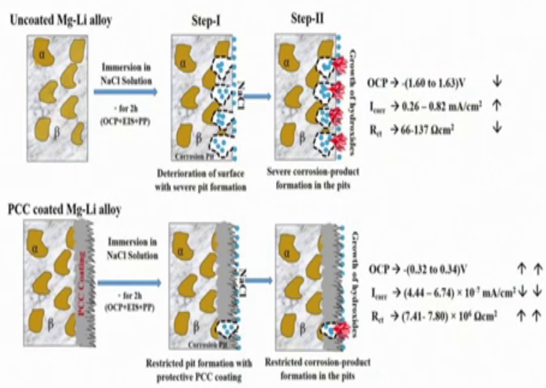

And if you think of the particular corrosion resistance property, so this is one such research result where that magnesium surface was converted it to its phosphate and it was found that it offered very good corrosion resistance property in terms of the you can say that in ennoblement of the Ecorr value sifting of Ecorr to the noble direction, decrease in the Icorr value; that means, corrosion rate decrease and increase in the corrosion resistance in 3.56 percent sodium chloride solution.

So, this particular phosphatization operation when is carried out on to the metallic surface, it also offers the corrosion resistance property significantly.

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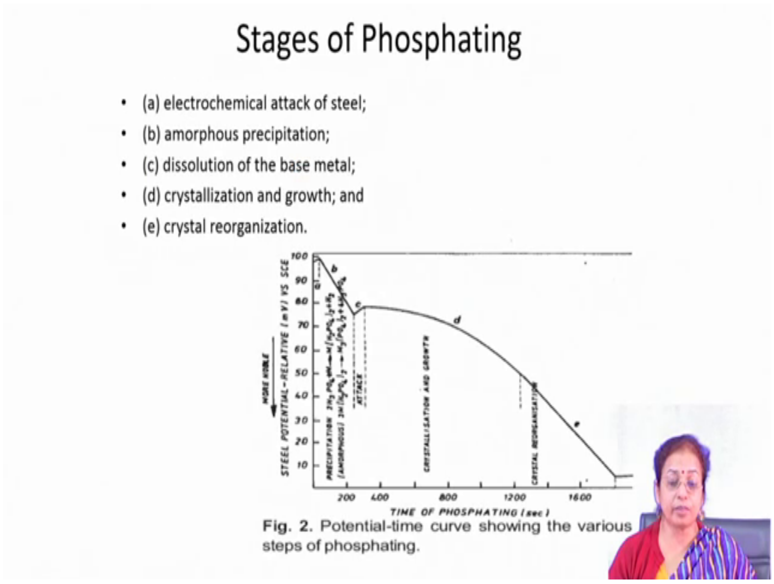

If you see the stages of phosphatization stages are like this electrochemical attack is there on the steel, then there is a when there is electrochemical attack on the steel naturally there is a increase in that potential with that of time of phosphating.

And then as you go on you as you go on apply some more time you will find that there will be that amorphous coating which does not have any crystallized structure; crystallize structure. And then there is dissolution of the base metal and then again there is crystallization and growth of the phosphate layer and finally, there is crystal reorganization.

So, whenever it is there then you will initially you will find that it is having very high the OCP value, but as we go on increasing that time you will find that it convert it seeps towards the noble direction. So, because of the full coverage of the surface and you will find very nice crystals of the phosphate on the surface of iron.

So, if you see the surface carefully you will find that; you will find that the phosphates are in fact, flakey in nature and in between two three flakes there are a lot of porosities and that porosities are usually very good in terms of the fact that when you do painting operation on the surface of the phosphate layer.

Because when you do painting naturally there is a intact there is a seepage of the paint layer in the poorest regions or inter flake region and which improves the adherence of the surface.

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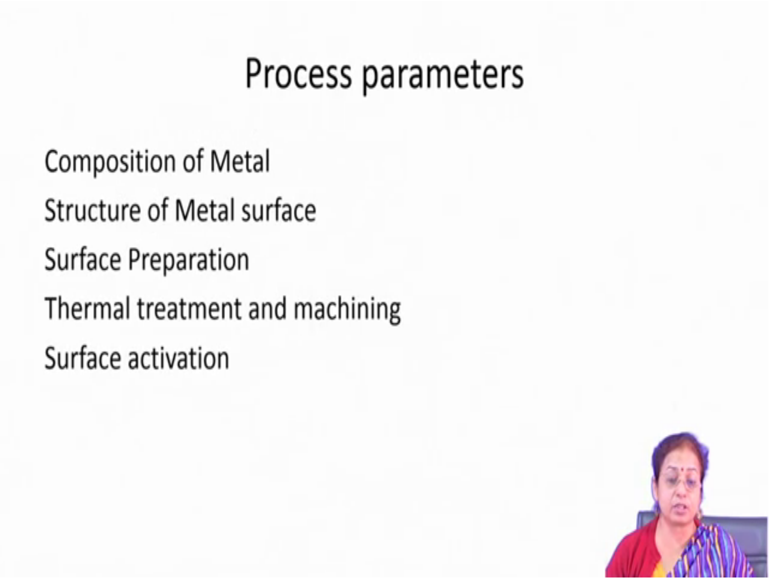

Typical parameters are composition of metal, structure of metal surface, steel preparation, thermal treatment and machining whatever you have carried out and surface activation.

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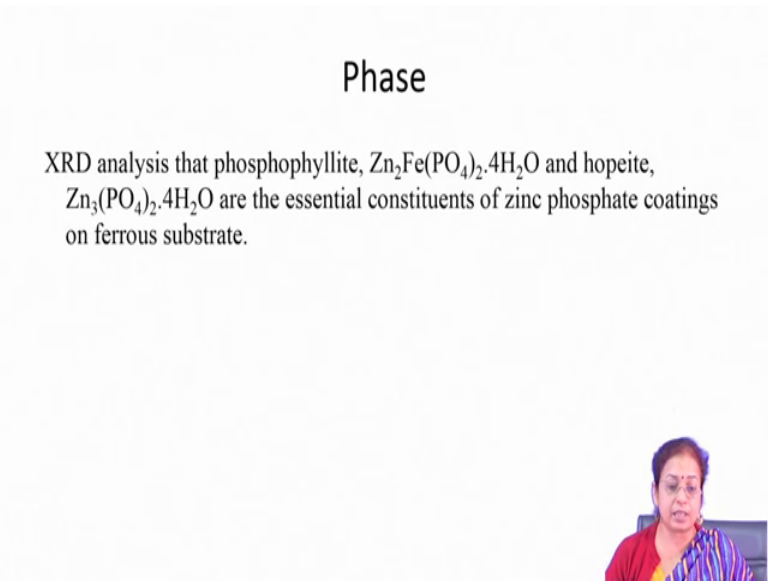

Usually depending on the kind of phosphate you are using, solution you are using they are may be zinc phosphate or manganese phosphate or this iron phosphate that forms or zinc iron phosphate forms.

So, the kind of phases which are forming on the surface depends on the kind of solution you are using for phosphating and this particular phosphating operation is not only good for improving the paint adherence or colorizing the surface this is also good to reduce the coefficient of friction to a large extent.

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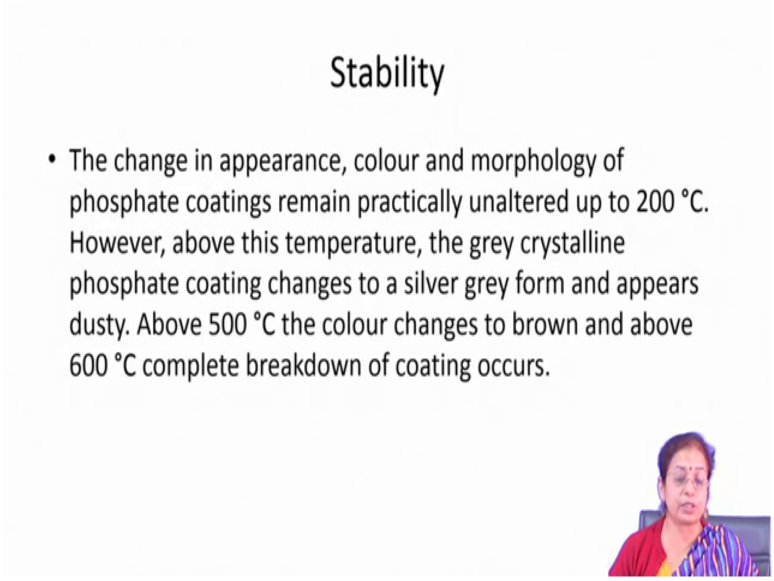

Usually it is observed that when you do coefficient of friction measurement, it is much lower in phosphated surface as compared to that of un phosphated surface. So, usually this phosphate coating is not really so stable at high temperature up to 200 degree Celsius there is no problem, but above this temperature there is a grey crystalline phosphate coating changes to a silver grey colour and becomes dusty.

And above 500 degree Celsius the colour changes to brown and above 600 degree Celsius there is complete breakdown of the coating. So, whenever you talk about phosphated coating you have to be careful about the application particularly the surface temperature.

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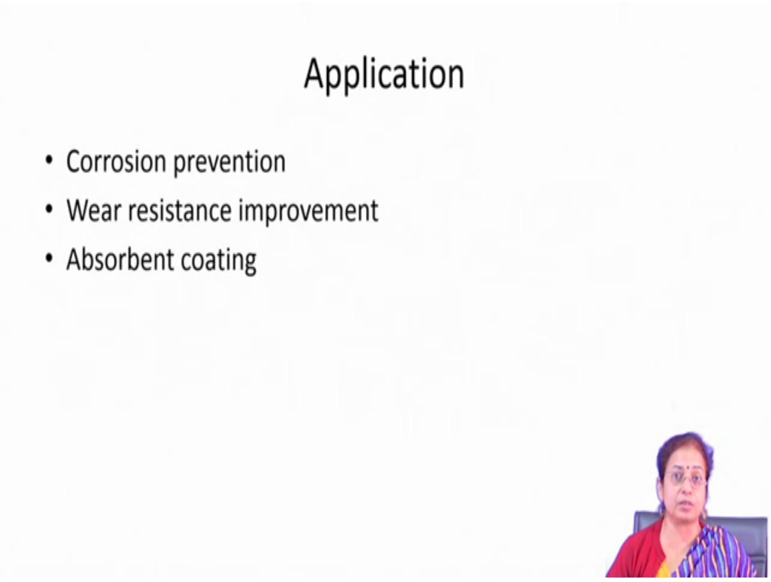

So, this phosphate can be applied for corrosion prevention wear resistance improvement or absorbent coating.

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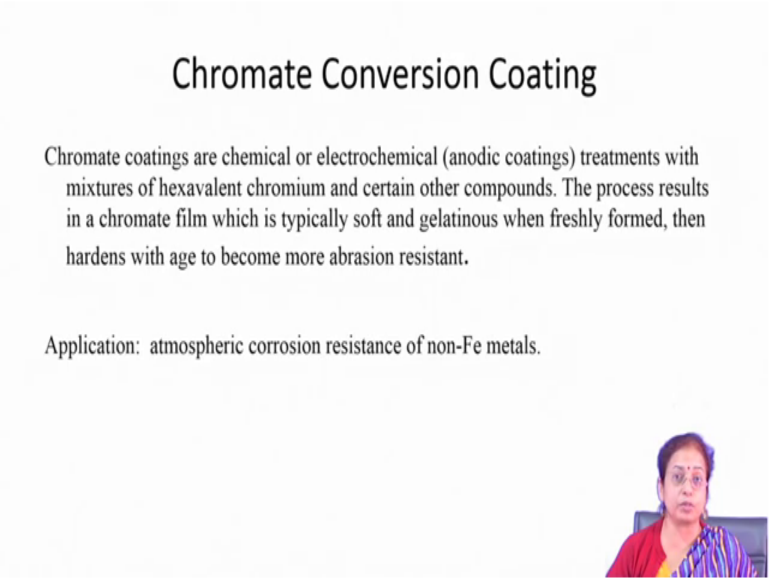

So, another type of a conversion coating which is again very popular, but these days because of the environmental regulation, these coating is actually is not applied too much that is chromate conversion coating.

So, here actually you are trying to develop the chromate layer on the surface of the freshly prepared metallic sample and here again whenever there is chromate layer then naturally that there is formation of the thin chromium oxide film naturally, that film offers resistance to corrosion particularly atmospheric corrosion may be they are ferrous or non ferrous materials.

Then that particular application of this particular format coating is mainly for atmospheric corrosion resistance purpose as well as this can be applied for scratch resistance purpose, as well as a primer for subsequent painting operation.

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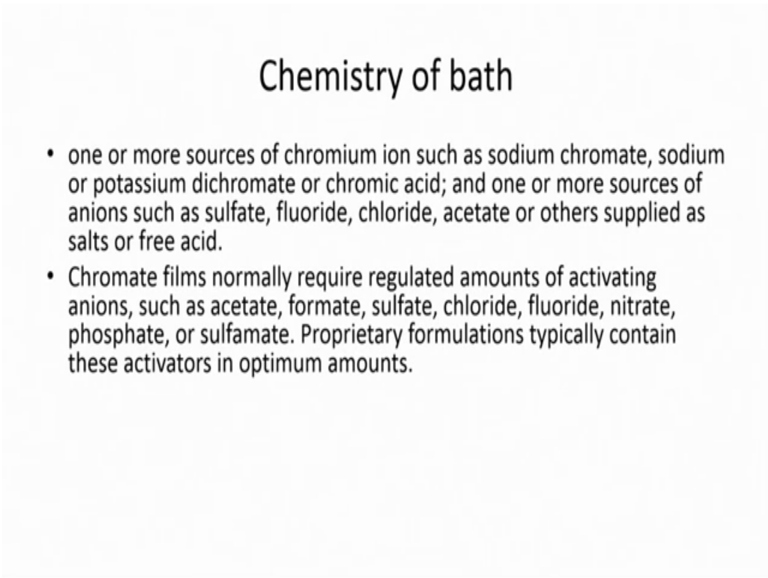

So, usually that one or more sources of chromium are such as sodium chromate sodium or potassium dichromate to one or more sources of anions such as sulfate fluoride these are used as a ingredients for the solution where you are doing chromate conversion coating. And, it normally required regulated amount of activating anion such as acetate formate, sulfate and proprietary formulations typically contain these activators in optimum amount.

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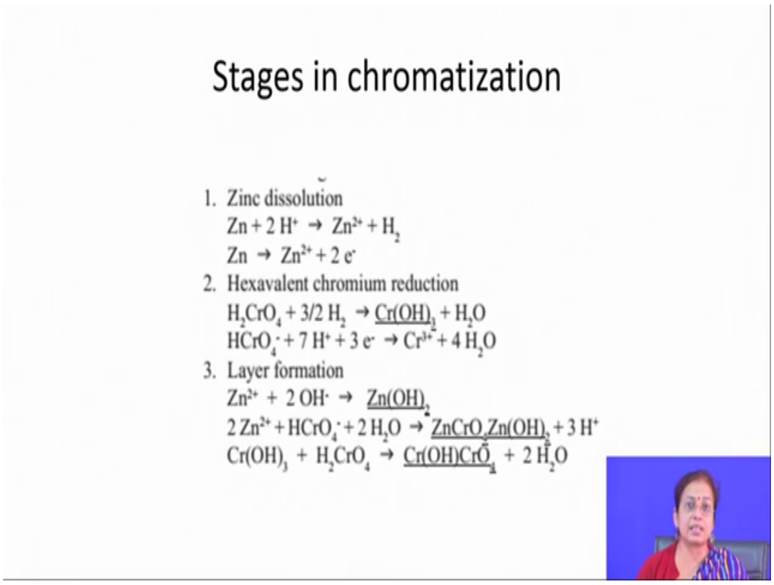

Now, if you see the stages or chemical reaction this is nothing, but that accelerant first there is dissolution of the zinc if you do chromate coating on zinc surface and then exvalent chromium reduction is there and then there is layer formation, but when you use tetravalent chromium, then that second stage is no more there, then you directly neglect chromate on the surface of the zinc.

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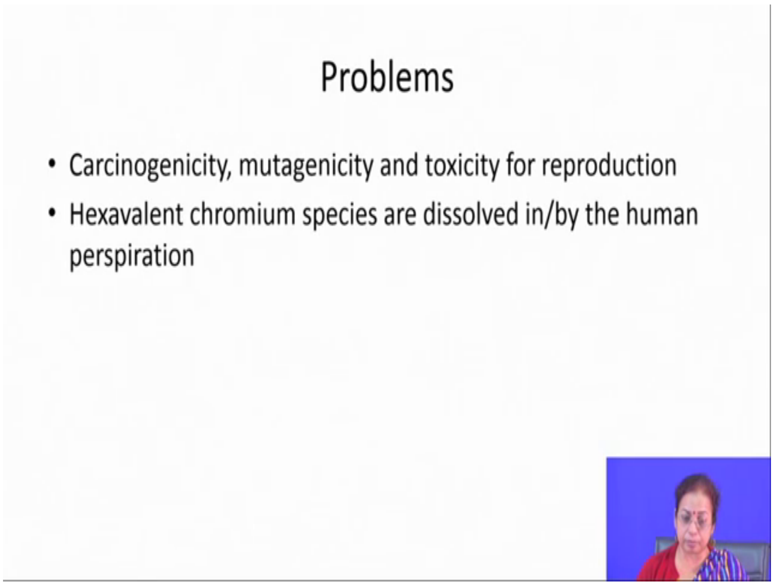

But as I mentioned you that, this zinc chromate solution is not environment friendly; so, there is problem of carcinogenicity or mutagenicity or toxicity and they are at sometimes dissolved in human perspiration, so this chromate coating is basically these days are replaced by phosphate coating to a large extent.

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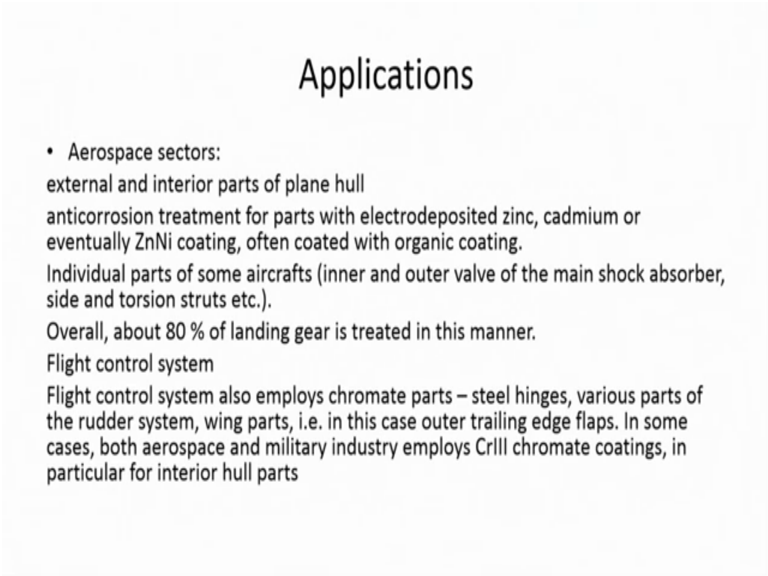

But some of the sectors it is having application like aerospace sectors where prior to application of painting this particular coating is applied to a large extent. And like anti corrosion treatment for parts with electrodeposited zinc, cadmium or eventually zinc nickel coating after coated with the organic coating. So, individual parts of some aircrafts they entered, 80 percent of the landing gear is treated by chromate conversion coating. In flight control system it also employs chromate part.

So, chromate conversion coating was having several applications in the past and even now also where it has to be coated with the other paint and also where the applications is that application area is not really in the environment particularly in the somewhere else where that the drainage of the solution is not a problem, there you can always apply the chromate conversion coating.

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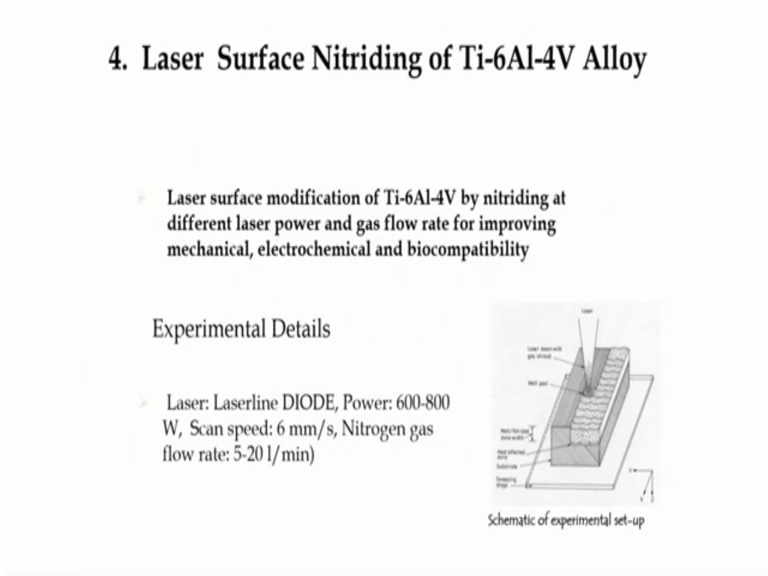

Now, another way by which you can also convert the surface of metallic materials to its nitride or oxide is by melting and subsequent just subsequent application of that reactive stout. For example: the surface nitriding is one such example where it has have it is a lot of examples on the titanium as well as a steel substrate where you can melt the surface using the high power laser beam and then use nitrogen stout, so that there is formation of nitride layer on the surface.

This particular treatment is very much applied for it is it may be termed under surface alloying, but may be under chemical conversion coating also because instead of heating you are using the melting phenomena and nitrogen stout to form nitride layer on the surface.

So, this is such example where high power laser beam was used to melt the surface of titanium and we wear nitrogen shrouding environment was applied. So, you see that on the surface of titanium there was formation of very thin not monolithic, but dispersed nitride layer.

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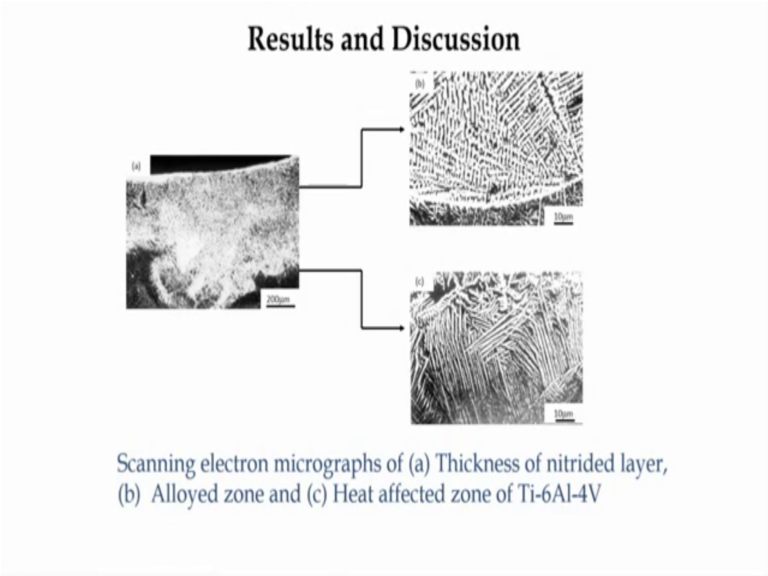

If you see the surface carefully you will find that there is lot of dendrites containing the nitrides titanium nitrides and also the continuous and monolithic continuous and defect free solid liquid the interface where nothing was present, as it was melted with laser beam the heat affected zone was also negligible in nature

So, you get very thin not thin rather, but rather it is it can be treated as bulk deposition or bulk of nitride formation layer. For example, the here layer thickness varied from hundred micron to as high as one millimeter. So, you get a very thin convert with not only thin letter rather thin to thick depending on the process parameters you are applying. The disperse nitride layer on the surface of titanium, so titanium surface is chemically converted to its nitride these nitride see if it would be by physical vapor deposition or chemical vapor deposition in that case there would be a very soft interface and that layer would be very brittle.

But as it is carried out by melting and subsequent alloying process; so, in that case your converted part is not purely converting into its nitride, but rather it is dispersed nitride it is in the form of disperse sides. So, these dispersed nitride layer helps in improving the hardness without sacrificing the toughness property.

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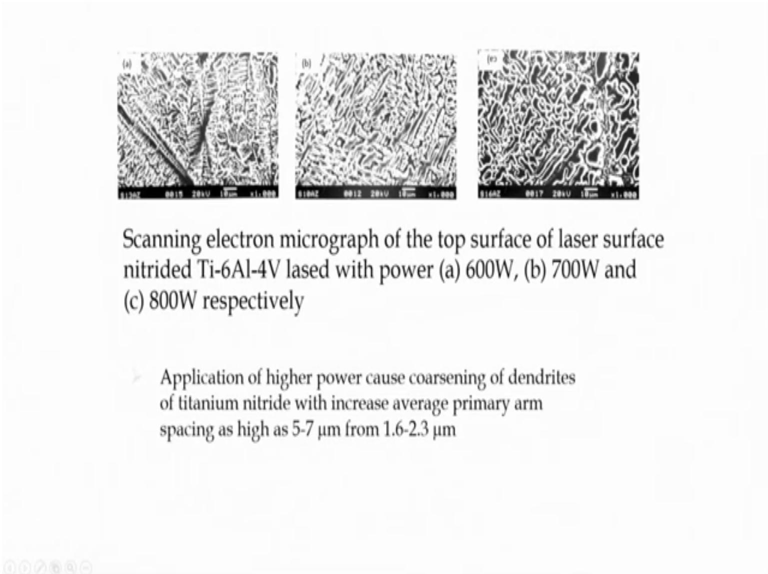

So, it was observed that as you go on increasing their power this particular thickness of the that area fraction of the dendrites increases as well as you can say that here dendrites are basically mostly very long dendrites in nature particularly when your temperature or that power of laser is very high. On the other hand whenever it is very low you will find that dendrite count spacing is quite low because of very high cooling rate.

So, you can play with the process parameters to just have different kinds of micro structures and these micro structures are very good in improving the hardness of the surface to a large extent.

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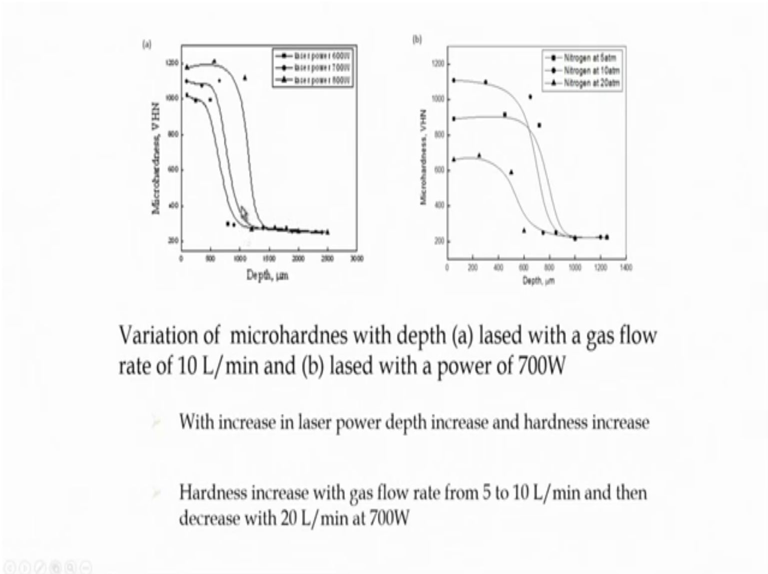

So, you find that as we go on increasing the power you will find that there is decrease in hardness because of the increase inter dendritic spacing. On the other hand if you just go on here, in this case we also had the shrouding environment pressure as another variable.

So, we found that as we go on increasing the pressure of nitrogen stout we had very fine dendrites broken dendrites that that was have failed to improving the toughness further.

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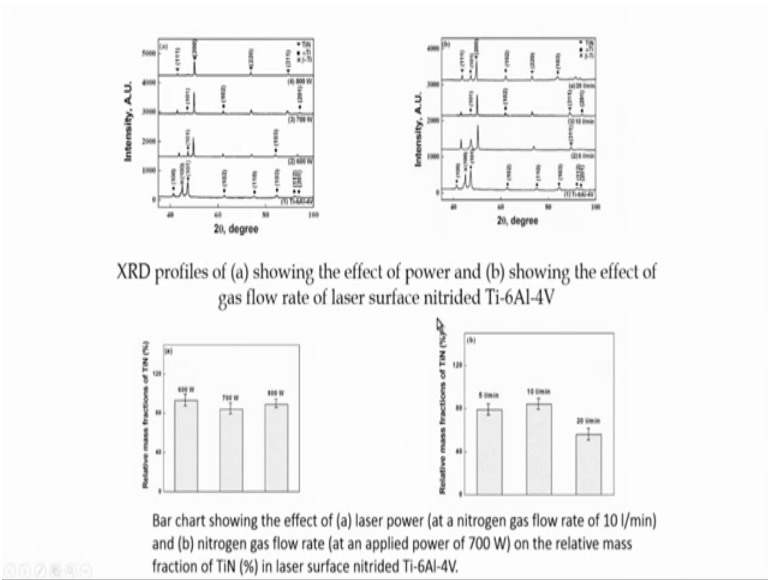

So, in the microstructure we had a lot of nitrite phase as this is a the evidence of that is shown in the extra diffraction file and in a fraction of nitrate changes with the process parameters.

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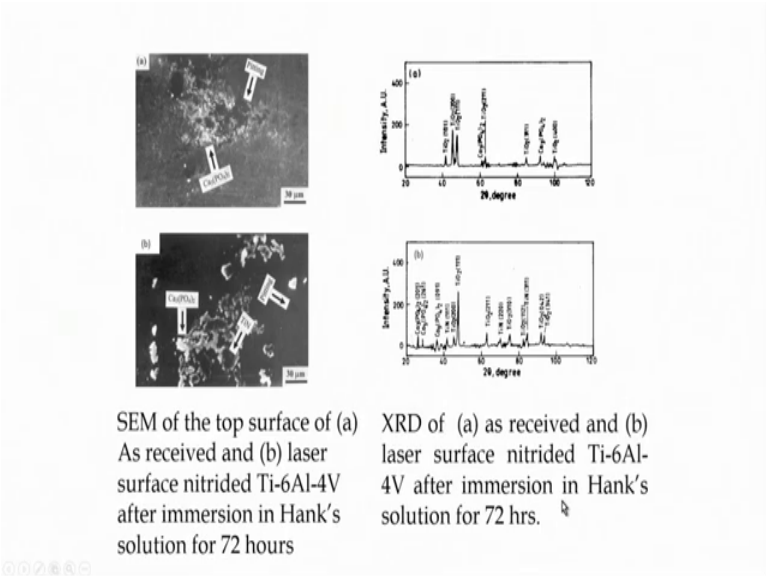

And interestingly again this particular nitriding operation was also aimed at improving the bio activity of titanium surface. So, we try to see the bio activity behavior by immersing it in Hank's solution and subsequently measuring the calcium phosphate deposition rate regular interval.

So, we find that as we go on doing nitriding, so by nitrided surface the deposition rate was much higher than that of as sits surface because of its roughness as well as because nitride also promotes the bone growth actually.

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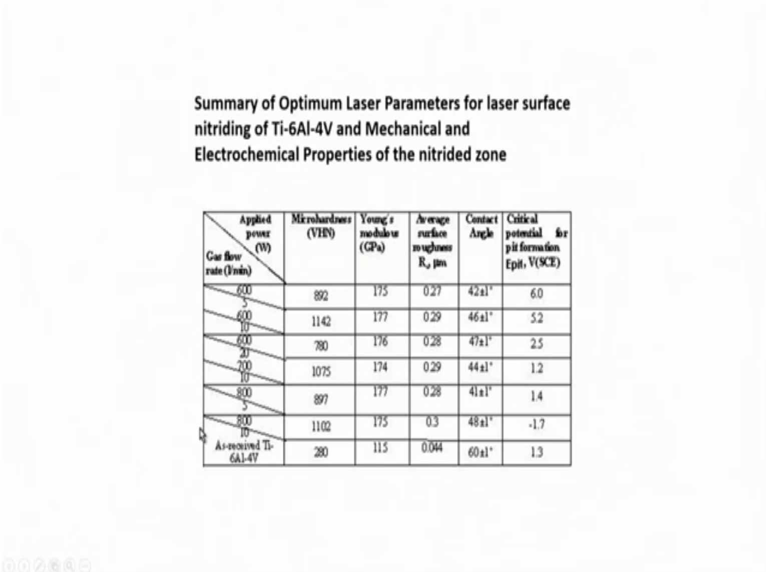

Summary of Optimum Laser Parameters for laser surface nitriding of Ti-6Al-4V and Mechanical and Electrochemical Properties of the nitrided zone

Applied power (W) / Gas flow rate (l/min)	Microhardness (VHN)	Young's modulus (GPa)	Average surface roughness R_a, µm	Contact Angle	Critical potential for pit formation Epit, V(SCE)
600 / 5	892	175	0.27	42±1°	6.0
600 / 10	1142	177	0.29	46±1°	5.2
600 / 20	780	176	0.28	47±1°	2.5
700 / 10	1075	174	0.29	44±1°	1.2
800 / 5	897	177	0.28	41±1°	1.4
800 / 10	1102	175	0.3	48±1°	-1.7
As-received Ti-6Al-4V	280	115	0.044	60±1°	1.3

So, finally, we ended up with optimization of the process parameters to have the desired results in terms of contact angle, in terms of the corrosion resistance property, in terms of the Young's modulus. So, one interesting problem related to this particular nitriding operation is that because of nitriding there is increase in the Young's modulus of the surface.

But again that is on the surface only show it's not so important, might not be so important for proper application, in that particular specific application, but contact angle was reduced to a large extent critical potential for pit formation again was if was found to vary with the process parameters and it was increased. So, you can say that pitting corrosion resistance also increases because of nitriding operation.

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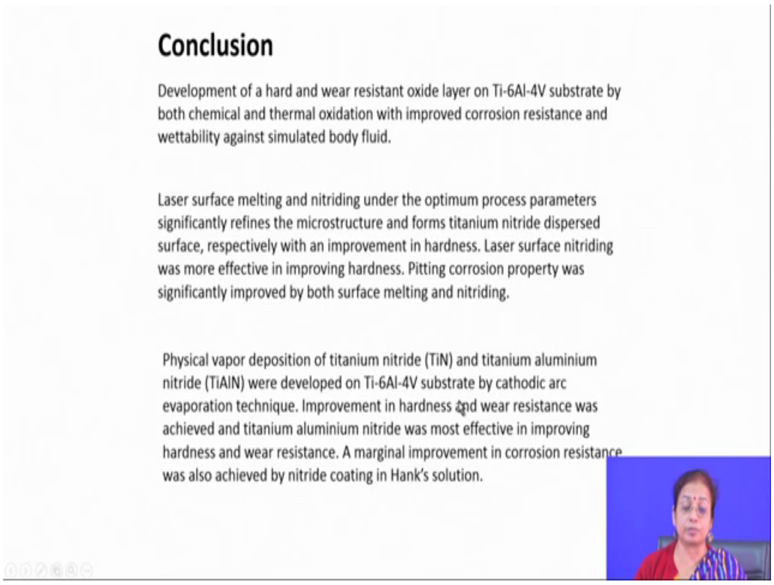

So, it can be concluded that the oxide layer, nitride layer may be I mean oxide layers on the surface of metallic materials may be developed by chemical oxidation route, may be developed by thermal oxidation routes, may be developed by typical laser processing route and is very much applicable treatment for improving the corrosion resistance as well as wear resistance of the surface.

Laser surface nitriding is another way of converting the surface of titanium as well as steel to its nitrides and as it is carried out in molten state you will find that the there is a quite homogeneous surface and also interface is quite stout there is no problem at the interface.

So, in both the cases we improve the hardness and wear resistance to a large extent and also biocompatibility enhancement is there. So, these are few important notable results out of these particular things and also this particular chemical conversion coating is very much important route for improving the hardness and wear resistance and different other properties like corrosion properties, bio activity of the surface of the metric materials.

But you can choose any route as I mentioned that thermal route, you can choose the chemical simple chemical low temperature route, you can also choose laser processing route to have that layer on the surface, but you have to be careful in optimization of process parameter. So, that whatever results you are looking for same results is obtained on the surface for the desired applications.

Thank you very much.