

Plasma Physics and Applications

Guest Lecture by Prof. SR Meka

Department of MMED

Indian Institute of Technology Roorkee

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Lecture 61: Surface Modification of Metallic Components by Plasma Nitriding

Greetings to everyone. I welcome you all to this series of lectures on applications of plasma in this course on plasma physics and its applications. So, I will be covering today in this lecture about a process called plasma nitriding. It is a surface modification technique that means where we try to modify the surface. So, you will see that how actually a plasma is utilized in these processes to you know create components with a better performance. So, why do we need to do surface engineering right? So, surface engineering means where we are trying to engineer the surface property of a component to give better life and serviceability to the component.

So, why is it essential? Because all the surfaces interact with the environment. So, environment can be a you know the aggressive acidic media or maybe a you know high temperature or oxidizing atmosphere or an electrochemical solution. For example, a sea water which has a lot of salt content and there you know the whatever the material we use in ship building and all that will be interacting with that atmosphere right. So, there are some aspects which actually start from the surface or basically they are only surface phenomena.

These are like suppose we look at the wear. Wear means how quickly a material removal happens in the event of a contact with an another body. It body can be even an environment, it can be a fluid also. So, we want actually the components to have a low wear rate to be able to know to sustain the components integrity for longer duration. Next comes is the corrosion or oxidation right.

So, where you know the electrochemically you know the material can leach out or something can deposit. So, there it is important that we have to engineer the surface to have a better resistance to these processes. And fatigue, fatigue is a you know the means actually a cyclic loading. For example, if we take something and then if I keep on doing

a cyclic loading that means I do I pull it and leave it, pull it, leave it then it is a cyclic loading. So, what we are doing is your surface is getting stretched you know and then compressed maybe I know stretched and compressed.

So, in this kind of processes the components also fail much or at a lower load. So, we also need to actually ensure that this fatigue resistance is higher. Of course, whenever you know any corrosion or rusting happens you know to the surfaces aesthetics will also be you know the spoiled. So, that is also you know making the components life reduced. So, second thing is why do we want to engineer is that we want to improve two things service life that means the component should be useful for longer time and functionality of components.

For example, we have a here I want to show the this is a let us say a gear and this will be under the this is where you have a continuous load being applied right that is where you are having a continuous load being applied. So, now during the process of it for example, you have a drive right for example, our bike or you know even bicycle or anywhere like you have a chain which is continuously running on it that means these teeth are under constant wear and tear right. So, now if the teeth are worn out right then automatically your you know load transfer would not be effective right maybe your chain will be slipping sometimes and then you know that there is a loss of energy in these you know additional processes. So, now if you look at it the engineering the surfaces means we are working towards the environment sustainability. For example, we make this gear ok.

So, and now this gear if we improve its lifetime ok that means we do not have to produce you know the large number of these parts in a particular year or so right that means because a one part is able to sustain longer time that means whatever the energy which we spend in making these you know the components will be saved right. So, that way actually we can actually know the contribute to the environment sustainability by doing a proper surface engineering to engineering components. So, for example, some of the you know few applications I just you know the gathered here some of the applications where one can think of you know this kind of treatments are needed. These are all the you know the here is the fuel injectors in you know the engines where the fuel is injected into the engine. So, there actually we want that the nozzle has to sustain a lot of wear, tear and also the high temperature and also any chemical attack from the fuel.

And then as I told you that the gears see the gear teeth for example, if you look at the gear teeth the gear teeth will be under constant load. So, there we want that it has to be strong. And then the cutlery suppose for example, if you see here whenever you are using any of these you know the butter knife or the you know fork or the spoons these

are continuously used with the food what we eat right. You are stirring something with a hot liquid and all that. So, we do not want any leaching out of metallic ions into the food which can go into our you know body that can create lot of you know the harmful effects.

So, we need to reduce these things and these are all you know the things where we can do the surface engineering. And in biomedical applications you know the artificial knee implants and all. So, when they are placed actually the knees and all when you see joints where actually the two surfaces are in their constant action right. So, there actually the surface needs to be strong ok that is where you know we also see it. And the watch cases or even the mobile cases right the watch which is always on you know on our hand where we are sweating and all the sweat is actually the you know the salt solution right.

So, then we do not want any corrosion to happen to the you know the back cover of your watch or the casing. So, for example, there is one you know example is given here a watch where you know this kind of you know surface treatments are done. And now heavy applications like you know the gun barrels right. Gun barrels you will have you know the lot of you know the your bullet will be fired and it will be passing through the gun barrel right in a particular path at a very high velocity. So, it will be in you know the touching the surfaces and these surfaces if they are getting worn out with the time right your gun barrel dimensions have changed I mean the internal dimensions that will not give you the same efficacy as it was designed for if it is worn out.

So, here are some more examples like a crankshaft you know in automobile industries right. So, in automobile so, these crankshafts are also you know the surface engineer. And for example, here you see you know the a turbine ok. So, the turbine means like for example, I will give you like we are talking about a hydro turbine where you know the water with a high pressure or a high you know potential is falling onto the blades of these turbines. And this water is not a filtered water right.

So, you are having all the hydro turbine plants where the water is coming from you know the rivers and from the reservoir and it is falling on it, it can have a slit ok some stone some sand. So, with all those things will be falling on these blades right. So, then these blade surfaces have to sustain wearing out of that ok that is the case with a hydro turbine. But if you look at a steam turbine right where you are operating at a high temperature with a high pressure steam right. Now at this high temperature the the the blades have to sustain that high temperature they should not sag down and at the same time the oxidation because you have a oxygen presence and it should not actually oxidize severely and spell off right.

So, those are the conditions which we can see. Then screws and nut sleeves ok. So, the especially when you look at the screws and nut sleeves right. So, when you have these threads on these nuts and all that right and you want to use it you know frequently right you you tighten it and then sometimes you open it again for some repair and then you want to tighten it. So, if these threads are not strong enough ok if you do it 2-3 times then you know that it is gone ok all will become flat.

So, some you know biomedical applications here what is shown is one you know dental implants for you know enhanced biocompatibility which are also usually titanium alloys or stainless steels ok which also gets you know the surface engineered and lot of surgical instruments right. So, the surgical instruments also need to have a you know surface which is very smooth and you know though no roughness. The reason being surfaces being rough means it can capture lot of microbes and all that right. So, the bacteria or you know viral things can sit on those devices so that the cleaning would not happen perfectly right. So, that is where actually these kind of treatments are done to the surgical instruments too.

So, now how this surface engineering is done right. So, there are different ways one can do it as you can see either you can change the chemistry of the surface chemistry means you have made let us say that something with a titanium and now you component you have made, but the surface chemistry you want to change it, it would not be titanium, but it can be maybe titanium plus something ok. So, that kind of a surface engineering can be done. So, there actually you can do the change in the chemistry, chemistry means the composition of the surface will be changed or you can change the structure. Here the structure means the crystal structure let us say that you know that there can be material can exist or elements or alloys can exist in different phases.

Phases means usually they are distinguished based on a difference in the composition or the crystal structure. For example, if I have a iron FCC then it will be relatively you know that easy to deform right. If I have a iron BCC it will be difficult to deform. So, I do not want to go into the details of it, but I would like to you know make you understand that the crystal structure gives also the specific property to the material. So, how can we change the chemistry of a surface? You have to diffuse in something right.

So, that is the one way you have to you know provide some element which diffuses into this surface regions that means only up to some depth this element will diffuse and changes the property there ok. That is the one way the chemistry of a surface region can be changed and you can also do that you know the plastic deformation of the surface that means you have a sample surface you just hammer it or you know you take a sand and then blast it with a sand. So, that you create a lot of deformation on the surface because

of the deformation it becomes harder ok. It is called hardening by straining ok. It is called strain hardening ok.

So now, to change the properties of the surfaces of components you can do simply the thermal treatments that means where the skin of the material can be heated up to some temperature and cooled at a certain rate to change the surface characteristics or you can do also the thermo mechanical that means you heat up and also deform the surface ok and then cool it in a particular way it is called thermo mechanical. The other variant is the thermo chemical that means you heat up the substance and bring it in contact with an atmosphere which is able to supply a element which you want to diffuse into the surfaces of the components. So, one thing you must realize that surface engineering comes as a last step usually in any component manufacturing. Suppose if somebody is making this gear right. So, the surface engineering comes once he machines it and makes all the teeth you know the everything by you know machining of the material and then you do the surface engineering at the last right.

Why it is important why it is you know that that means whatever the method you choose to make these gear teeth harder and can sustain for longer time you have to do it in such a way that its dimensions are not changed by your finishing treatment. Suppose if I heat it up some temperature and cool it down and all there will be thermal stresses right. When we take anything you heat up and suddenly put it in water sometimes you see that part is cracking or it can bend also because of thermal stresses. Thermal stresses come because of differential cooling and heating of the you know material at different locations of the sample right. So, that is why we need to make the component when it is soft we like it right.

If I am given a material in a soft condition I can easily cut it and make it into a shape ok. And after that I want to make it harder I want to make it harder only the surface not everything ok. Why we need to only harden the surface not everything is there are two properties I want to you know bring it here. One is called the toughness, toughness means for example, if I have a gear sometimes you know the it will it will receive shock loads. Shock loads means suddenly some accident has happened ok it will receive some impact.

When such a thing happen we do not want this to break into pieces right rather we like that it can deform a bit, but still remain as a part ok. So, that is why we use always the metallic materials which have a toughness. For example, if somebody is constructing a building in the pillars you use a steel reinforcement because why the steel reinforcement because the steel will not allow that building simply collapse it will show that at least it is sagging down you know you it will give you a signal that you know yes it needs to be

repaired or something. So, that the safety is you know the highest when you have a metallic structure, but now in this case if I make the entire material of this gear very hard yes the surface property will be good, but when it receives any impact load it will break into pieces ok. That means, it cannot absorb the energy because energy absorption can happen if the energy can be utilized in changing the shape internally right.

So, that is why these treatments are given at the last and that means when I do the treatment there should not be too much change in the dimensions otherwise this would not fit into the application for which I have made it. Once I do surface engineering I want to avoid doing any machining because you only change the surface and if you want to machine it off then you will lose whatever the you know the property change you introduce it there. So, this is about you know the modifying the existing chemistry another way is coating the surface with another material ok. We also hear about coatings right that means you simply deposit something else on it which can protect it from environment. The best example is you know the all the mild steel grills and you know railings which we see they are all painted.

So, that atmosphere interaction is minimized by having a another material and there are also you know the one can do the electroplating right in lot of you know places where the people use electroplating or you can do also PVD or CVD kind of processes where you can deposit something else on to the existing you know the component. So, we will be you know the in this lecture I will be focusing on surface modification ok. Surface modification is like you know the you want to modify the existing surface chemistry I do not want to deposit something as a separate layer on top of this material ok. So, how we can do this? You know whenever you want to change the surface you bring something else which you want to enter into this material and give the temperature right you make a junction let us say I have a steel I bring in let us say aluminum I attach it and keep it at some temperature. Then aluminum diffuses into my other material ok and then it leads to the property chain.

So, now which elements to diffuse in? We have agreed that we should not alter its dimensions right that means I should not heat it up to very high temperatures ok. So, the low temperatures are preferred and now when I want to diffuse something into the material at low temperatures then obvious choice would be small elements ok not the large element. I cannot diffuse in tungsten into steel at low temperature right I need a very high temperature to make tungsten to diffuse into steel. But I can choose the elements like nitrogen, carbon, boron these are all actually the small elements that means their atomic radius is smaller in comparison to let us say the sizes of iron or nickel atoms right and they are so small they can easily fit into the interstitial sites in the metallic lattices. For example, here you can see that these are all the elements let us say a crystal

structure which is made up of these elements for example, let us assume that these are iron atoms and in between you have these regions right these are all called interstitial you know sites.

That means, these vacancies are already there it is a vacant space. So, if I have a small elements like nitrogen or carbon and if I bring them they can easily diffuse through these spaces available ok. That means, in a at a low temperature in a reasonable time you will be able to diffuse in to a larger depth a element like nitrogen or carbon ok. So, and next thing is what are the different processes available right. So, we we have we when we want to diffuse in the nitrogen into the component there is a treatment called nitriding.

Nitriding means you are diffusing into the metallic lattice and nitrogen atoms ok. And when you diffuse in the carbon atoms it is called carburizing ok. There is a process called nitrocarburizing where you can diffuse in both carbon and nitrogen ok, that simultaneously both can diffuse. So, it is called nitrocarburizing. Well now let us say that when we take example of nitriding then you need nitrogen right which needs to diffuse into the material.

So, what would be the obvious choice for nitriding? Nitrogen source in nature is highly sustainable source is only the molecular  $N_2$  gas which is available plenty in our atmosphere right. We all know that 70 percent of our atmosphere contains nitrogen. So, that nitrogen is present as a  $N_2$  molecules and these are very strongly bound ok. The binding energy between the nitrogen and nitrogen atom which is a covalently bonded in a  $N_2$  molecule. And unfortunately  $N_2$  molecule cannot fit into these interstitial voids available ok.

It cannot fit in as a  $N_2$  molecule is much bigger than the void size. A single nitrogen atom can fit in. So, that implies that first I need to dissociate  $N_2$  molecule into nitrogen atoms then I can diffuse in the you know the nitrogen into the substrate. Unfortunately, the considering that it is a strong binding energy between nitrogen atoms in  $N_2$  molecule. So, we need to apply very high pressures and high temperatures which are not practicable in reasonable sense.

So, then other way is that look for nitrogen source in which nitrogen is not very strongly bound. For example, ammonia  $NH_3$  molecule right in which nitrogen is not very strongly bound because  $NH_3$  is a very metastable you know compound ok. So, it can easily dissociate into nitrogen and hydrogen. So, that implies it can always release one nitrogen atom whenever  $NH_3$  dissociates and that means, if you use ammonia as a nitrogen source we can pump in nitrogen. In the current context of this course because we are talking about plasma applications see we can easily break the bonds of the

compounds by using by creating a plasma right at a relatively low temperature.

So, that is possible you know the by having a glow discharge that means, you feed in nitrogen gas and strike the plasma right. That means, you are actually dissociating the nitrogen molecules and then making them into neutrals or some ionic states right. A mixture of that can be developed. So, accordingly we have you know different methods one can say the gas nitriding when you use an ammonia kind of a gas as a nitrogen source or plasma nitriding when you use actually the nitrogen plasma or salt bath nitriding that means, there are some salts like mostly cyanide or cyanate salts where also nitrogen can be easily you know the released for you know feeding into the materials.

So, what happens when you do nitriding of a steel ok. Now onwards let us say that we will stick to the steel because steels are you know largely used metallic materials ok. So, where we make lot of components out of steels. So, what exactly happens when we do the plasma nitriding of a steel? A schematic is shown here. This schematic is the cross section after treatment. For example, I do the nitriding for this you know material that means, I soak this material in a nitrogen containing atmosphere it can be nitrogen plasma then nitrogen diffuses in.

Now, I want to understand what has happened when the nitrogen diffuses. So, what you will do? You cut this and then you look at this way you are looking at this cross section. So, that this is the surface and as I go down you can see what changes have happened. Such a schematic is shown here ok. So, what happens when nitro initially when you start the nitriding? Nitrogen simply dissolves through the octahedral voids in BCC iron ok.

I am considering a ferritic steel for example. So, that means, crystal structure is now BCC of the matrix phase. And then this nitrogen can go in and it gives you the hardening and when it is only dissolved ok the nitrogen is only dissolved that means, the iron atoms and chromium atoms and other atoms of the steel they do not move they remain as they are. Only nitrogen is going and sitting randomly in the available voids ok the interstitial sites. Then it is called diffusion zone that means, things have simply diffused ok.

And now now you are diffusing in nitrogen right. Let us say that you have some element in your steel which has a strong affinity to nitrogen for example, aluminum ok or titanium. Then the titanium and you know the nitrogen can come together and develop the titanium nitride particles ok. So, you can have actually the you know the particles of titanium nitrides ok can develop in the diffusion zone. Now these are very hard particles they are very strong these are nitrides compounds right that give rise to increased hardness and also it give rise to the improved fatigue endurance ok. Fatigue endurance means let us say that I take something I am applying a cyclic load right.



I pull it by certain magnitude and leave it pull it leave it. Now up to some load it survives large number of cycles it will not fail up to some load ok. So, up to that load it is called you know that is the fatigue endurance limit ok. Up to that load in a cyclic condition it can survive. So, now once the nitrogen is you know coming in more and more right then you will develop a so called compound layer ok. You can see here on the surface you know that this is called a compound layer that means, here now nitrogen and the iron together they form a different structure that means, different crystal structure.

It is no longer steel it is a nitride ok. So, there are you know different nitrides gamma prime and epsilon ok. These nitrides are very hard ok and then they give rise to the lot of wear and corrosion resistance ok. In summary compound layer offers wear and corrosion resistance and the diffusion zone offers fatigue resistance ok. So, just to give an example here what is shown here on this right side you know bar chart is that this is a particular stainless steel ok. 316L means it is a grade name you do not worry about it, it is a stainless steel and people have studied what is the wear rate.

Whenever we want to study the wear rate for example, I am rubbing two means two pieces then how do you quantify the wear rate is actually the amount of material removed per unit time right. So, that is the kind of a wear rate you can offer. So, that is plotted here on this y axis wear rate and this is actually without any nitriding ok. This 800 is the wear rate that is millimeter cube in the unit you can see here. For a un nitrided, un nitrided means as stainless steel I made a gear and then how it is eroding.

Then you see here there are different treatments are given. You see the drastically reduced wear rate here ok. These are all the nitrided conditions ok. So, that is just to give you an example that one can drastically you know improve the wear resistance. So, now I would like to summarize this lecture. So, in this lecture what we have discussed is that what are what is the importance of modifying the surface properties of engineering components like gears, crankshafts or some biomedical implants or you know steam turbine you know materials there are many actually ok wherever there is a wear and tear.

And now we discussed about actually the you know different ways one can modify the surfaces you know what is the choice of elements one can choose like elements like small elements like nitrogen or carbon you know are the best choice because we want to diffuse in at low temperatures. And then when these elements diffuse in they will you know give rise to hardening of the surfaces and even also forming a new compounds on the surfaces. So, like for example, it can form a compound layer or a diffusion zone when we do the nitriding and then accordingly we can expect certain improvements in

the properties. So, with this now I would stop with this lecture and in the next lecture we will basically look at more on the plasma nitriding aspects. Thank you. Thank you.