Plasma Physics and Applications

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Lecture 62: Surface Modification of Metallic Components by Plasma Nitriding - II

Greetings to everyone. So welcome back to this lectures on Surface Engineering using Plasma as one of the medium. So, it is called plasma nitriding. So, in this lecture we will be looking basically the different process parameters and how the plasma nitriding setup you know will be made. So, that you understand actually the basically about this process ok. So, in the last lecture we have covered about different fundamental aspects which are you know the essential to understand the need for engineering the surfaces.

There are several ways one can engineering the surface, but we are only talking about the surface modification as one of the you know the surface engineering process. So, where we are modifying the surface chemistry and structure of engineering components. So, now in the last lecture we have seen largely the schematic diagrams of you know the how a cross sectional microstructure looks like and here I am showing you the actual components. So, what you see here is there is a gear which is subjected to nitriding.

And now in this micrograph what is this means actually that you cut a small portion of this the teeth and then you polish it and try to see from the edge of the teeth to inside how the microstructure is ok. So, this is how it looks like that means, this is the surface what you see here it is the surface ok. And this is no no nitriding that means, it is not treated for nitriding process and you see that it is more or less the same structure here ok. And now you come here in this micrograph where this is plasma nitrided that means, this gear was kept into a plasma nitriding furnace which is at 500 degree Celsius and for a time of 15 hours using a gas composition of you know the 3 is to 1 of nitrogen and hydrogen gas ok. So, from there actually this process is done.

So, with this you understand that whenever somebody reports a plasma nitriding parameters what is expected is that one need to tell at what temperature this treatment is done and for how much time and what is the gas composition is used in that. So, these are basically the important parameters which needs to be reported. Now you I want to bring your attention to the microstructure. You see here now it is the without nitriding here and this is after nitriding. You see at the surface there is something you know appearing white right close to the surface that is the compound layer which we discussed in the last class and below that you see some region ok.

That is where nitrogen is simply dissolved and maybe some you know the nitrides like aluminum nitride or chromium nitride have developed that is called the diffusion zone. So, whenever somebody is selling a nitrided part then what he will say is that you will have a hardened layer up to this depth. That means, if somebody is doing this kind of a service of you know nitriding the parts then you need to report that up to what depth he could give the increased hardness. And now if you see here is the macroscopically you know the see that this is the teeth of a gear you see on the surface you know the about 15 micron meter thickness a layer right that is called the nitrided layer. You see here it is something is you know spallen off do not please bother about it.

And now in this region you will get higher hardness. So, if you look at what is the benefit of doing the nitriding treatment that you can see in this plot here ok. Let us focus on this area where you see that what is plotted is number of cycles for damage. That means, I am doing a some cyclic loading that means I am doing this way this way and all bending it and all. So, by the way you I want to tell you what is the you know the cyclic loading means.

Suppose if I give you a bending wire you know which we use it in regularly yeah. So, that kind of an wire you know the if I want to break this wire right by pulling it it will not be possible for me right. But if I do you know this way you know this is called cyclic loading it can break right. Very often you see that when the people are using this kind of wires they use such kind of you know the processes that is called a cyclic loading. Number of times I need to do this bending to break it that is called number of cycles for damage.

So, what you can see here is that you see here in this case when we do non nitrided that means no nitriding treatment you made just the gear then it will actually sustain only this many number of cycles. But this will be when you do nitriding you see the enhanced lifetime of the component you know drastic improvement right. So, almost about you know the 100 times improvement in the life of the component. So, now we will move to the plasma nitriding. How does actually the plasma nitriding work? Ok you are already taught in this course about you know the concepts of generation of plasma right and how to control it and what are the different ways you can generate the plasma.

So, I do not want to go into those details, but here I want to explain you the how actually a typical nitriding facility or a system will be. So, you see here there is a chamber ok this is the chamber and you need a gas right for a you know doing the nitriding you see here it is the gas inlet. Now what kind of gas you will inlet? Of course, nitrogen has to be there because you need nitriding and there is also hydrogen always some amount ok. That means, you are feeding in nitrogen and hydrogen gas into the chamber. You have a here a vacuum pump you know where you are maintaining some pressure of this gas and you know that you are continuously removing the gas here.

So, that you are maintaining some pressure in the chamber and now you know that the nitriding is a thermochemical treatment. That means, we need to provide heat to my components to be so that nitrogen can diffuse in right. If I bring in nitrogen something which is at room temperature nitrogen may not diffuse inside you can bring in nitrogen, but we have to make sure that we bring in nitrogen atoms as well as we give enough energy that it can also diffuse into the material. So, what you see here is these are all called the heaters wall heaters ok you have here the heating ok. It is a cylindrical furnace you are looking at a cross section you can imagine that the heaters are placed like that ok.

And with this you will heat your material and now here you have your specimen stage where you place the your samples your gears or anything you know you place it here. And now comes is the you need to make plasma right. So, usually there are different ways people do it either you can use a DC you know the pulsed DC you know power source to generate the plasma ok or you know the also you know RF related technologies are also available, but I will not go into details. What will happen is that the biasing how you do it is that your specimens will be you know the cathodic ok they are made cathode. So, that the positively charged nitrogen ions are attracted to the your samples ok.

And then actually they will be diffusing into the samples ok. This is the basically the you know the complete you know the my setup. So, now before you do nitriding right for example, now I talk about typically of stainless steel. We all see the stainless steels right when you have a stainless steel railings or you know you have a you know stainless steel cutlery or stainless steel vessels they always shine right. Why is it so? If I have let us say something which is not stainless steel a grill made up of a mild steel it can start to rust ok.

For example, I can show here the two things one is stainless steel another one is a mild steel. You will be able to understand the difference. You see this two this is the you know the stainless steel this is the mild steel. You see how you know the shininess is gone here there is something reddish you know the iron oxide here we call it rusting which you do not see here. That this special character for stainless steel comes from the presence of chromium in the stainless steel.

What this chromium does is that chromium has a large affinity to nitrogen sorry oxygen. It forms a very thin layer of oxide film on the stainless steel surface very thin layer that protects it from further oxidation. It does not allow it to oxidize ok. It is like a cell filling. Suppose if somebody scratches this film then again a new film forms because oxygen is always available in the atmosphere and chromium is present in the entire material.

So, it can always oxidize and form a thin layer and protect it. So, now, when you want to introduce nitrogen into a stainless steel component then this nitrogen has to go through this thin oxide layer right. So, for example, if I have a stainless steel surface and then you have a very thin layer which is only 2 to 3 nanometers thick oxide layer and now I bring in nitrogen atoms here and now this nitrogen atom is now sitting on top of this oxide film. Now it has to cross this oxide film to be able to go into the steel. Unfortunately this oxide film does not allow the nitrogen to diffuse through.

It acts like a diffusion barrier that means things cannot the nitrogen cannot diffuse through it. That means to do nitriding of stainless steel first I need to remove this oxide film. How can we remove the film you know existing film? If I just you know the grind off I can remove the oxide film, but the moment I leave it again it forms oxide film because oxygen is available in the atmosphere. So, what you have to do is that first you take them into the chamber of plasma nitriding. You first evacuate the chamber, you create a vacuum and then introduce gas like argon or hydrogen and then you ionize this gas that means you create a you know hydrogen or argon plasma and let this ions bombard the surface of your component.

It is called sputter cleaning ok. You are bombarding to clean the surface. What are you using for bombardment? Again the ions of argon ok and then you can clean it. Once you clean it now it cannot form again oxide layer. Why because there is no oxygen in your plasma nitriding chamber because you have already evacuated it before.

Now you can introduce the nitrogen and now you can create a nitrogen plasma so that now nitrogen can diffuse into the steel. I hope I made it clear to you the challenges involved in nitriding stainless steel and that can be dealt very well in plasma nitriding because plasma nitriding always involves a vacuum system where you remove the oxygen in the system and you have a provision to sputter clean because you are creating a plasma these are actually the you know ionic state and then you can bombard these ions on the surface to clean it ok. So a typical process cycle for plasma nitriding is shown here. You see here this is the how you increase the temperature as a function of time. Initially you apply the vacuum ok that is where you create a vacuum and then you do some preheating that means small extent of heating.

Then you do the sputter cleaning ok. In this window you use hydrogen, argon, plasma to clean the surfaces. Now oxide layer is gone on your components and now you create a nitrogen-hydrogen plasma in this window to have the nitriding happen and then you cool the samples to room temperature before you take them out. So that is how actually one can understand this plasma nitriding process. So now the what is the role of the amount composition of the gas? You see we said like we should have some hydrogen in the plasma.

Why? You see here in this plot here what is shown is what is the hardness of the surface after treating in certain plasma. It can be plasma can be hydrogen nitrogen, argon and nitrogen. We know that what we need is only the nitrogen plasma. Common sense tells that if I have a nitrogen plasma nitrogen in you know the ionic state it should be able to do the nitriding. That means if I have a nitrogen-argon mixture I should get nitriding right.

So what the people have seen is that when I have only nitrogen and argon you know this triangle symbols they saw that no nitriding is happening because hardness is not changing it remains as it is in before. But when you look at the H2N2 mixture that means you have now nitrogen and hydrogen mixture you see that after some percentage of nitrogen you start to see that hardness is increasing ok. What we understand from this is hydrogen is must in addition to nitrogen to be able to have the nitriding effect ok. That this can be understood as hydrogen allows the formation of intermediate species maybe NH, NH2 or you know the NH plus some species with together with the hydrogen and those species will be able to transfer the nitrogen to the surface of the steel. In the absence of hydrogen I think whatever the nitrogen ions you create they recombine and then form into gas ok rather than diffusing into the solid ok.

That is the understanding we can have. That means hydrogen is must in the nitrogen you know plasma nitriding in addition to molecular N2 gas. Now you see here the layer thickness, layer thickness means after doing this plasma nitriding there is some thickness of the layer which is you know the nitrided layer. That means up to what depth below the surface I made the material harder. That thickness is plotted as a function of nitriding time ok.

What is done here is that somebody do the plasma nitriding at 420 degree Celsius and he used the different gas compositions. As you see plasma nitriding setup as a you can control the gas chemistry. That means I have a nitrogen and hydrogen I can control separately their flow rates ok. That means if I you know more nitrogen to flow and less hydrogen to flow then I am changing the nitrogen to hydrogen ratio. What they have seen is that here they have taken only 5 percent nitrogen 90 percent is hydrogen and they see that there is a very small increase, but with the time the rate at which the layer is increasing is slow ok the thickness of the layer.

When somebody increase to 20 percent hydrogen there is an improvement. But when you made somebody only 5 percent hydrogen that means 90 percent is nitrogen gas then you see that there is a drastically improved thickness of the nitrided layer. So this is how one optimizes the gas chemistry to be able to do the treatment in a reasonable time. You see more the amount of time more cost you are paying for it because you are heating at that temperature you have to hold it. So you are burning electricity that means you have to pay for it.

And now what you see here is on this right side you have nitrogen concentration ok as a function of depth sputtering time means you think this is the depth into the sample right. So you see that at the surface obviously because nitrogen is supplied at the surface you will have more amount of nitrogen at the surface because of consequence of diffusion process you see that nitrogen concentration is dropping like this as I go into the material. And now if you see that how this is changing with gas composition ok when I see here when I took 70 percent nitrogen or 10 percent nitrogen see the treatment is done for the same amount of time. You see that I get the large amount of nitrogen at the surface as well as up to the larger depths in case of higher nitrogen ok. So that implies that it is important to know the optimal gas composition that allows the efficient nitriding ok.

So you see here these are all listed here you know important parameters are temperature and nitriding time ok and the gas flow rates composition and pressure ok. The voltage means the plasma characteristics you see you are feeding in the gas but now out of this gas molecules what fraction is ionized what fraction is neutral right that depends on your plasma you know generating parameters where you are having a certain you know the voltage and you know or maybe a pulse or a duty cycle. So those are controlling actually the amount of gas is ionized ok those things are also important and the current density tells in principle actually about the the extent of ionization. So when we want to do the nitriding of a stainless steel so what we see is that we should do the nitriding but not allow the chromium nitride to develop. As I explained to you chromium has to be present in the stainless steel everywhere so that it can everywhere form a protective oxide.

For example, I formed a chromium nitride that means I removed the chromium in the surroundings I formed a chromium nitride. Now in the immediate surroundings of chromium nitride chromium is gone that means there it cannot act as a stainless steel so then you will have a problem. That is why when we introduce nitrogen into the stainless steels we should ensure that nitrogen is only dissolved so that chromium is present as it is before ok. So that is only possible when you play with the temperature and time of nitriding. So when I take a low temperatures see the nitrogen is very small it can diffuse chromium is bigger it cannot diffuse so that means nitrogen can go inside and dissolve but chromium nitride cannot form because chromium nitride formation requires chromium and nitrogen to come together.

So this plot shows here suppose if somebody chooses 450 degree Celsius as a nitriding temperature then you should do 20 hours of nitriding time only. If increases the time beyond that time you will form chromium nitride it is bad for the corrosion resistance because chromium is essential in the dissolved state to improve the corrosion resistance ok. So these are all called low temperature nitriding of stainless steel. Suppose if I reduce the temperature if I go to 400 degree Celsius you see that there is no problem you can nitride for very long time and still you will not get any chromium nitride ok. So that is why usually the stainless steels are subjected to nitriding below like you know the 400 to 450 degree Celsius.

So what is shown here is that you know the this is the cross section of a nitrided stainless steel you see this is the layer where you have a nitrided region where lot of nitrogen is dissolved here. About you know the 20 to 30 atomic percent nitrogen is dissolved in this layer this layer is extremely hard ok as compared to the substrate. So this is the substrate original material and this is the modified material ok. So this is the kind of layer which develops and you can see that you know effect of gas composition on the surface nitrogen content which is already discussed in the last slide. This is also the surface nitrogen content how it is changing with time ok.

So a typical hardness depth profile that means how the hardness is varying as I move into the material is shown here. So this is like when I introduce the carbon the hardness at the surface is you know the about this value and it is dropping down as I go inside because it is a diffusional treatment. You are introducing nitrogen from surface highest will be at the surface it will be dropping down as I go inside. You can see here carburized and nitrided and then nitrided case how the you know the different aspects can be realized. So with this I want to come to the you know the one important slide here why plasma nitriding because I we discussed about you can do gas nitriding also you can do salt bath nitriding also.

So the advantages of plasma nitriding are listed here. First of all it is environment friendly you are not using any you know gases which are harmful to environment here you are using nitrogen and hydrogen ok and making a plasma to generate the things as compared to ammonia and it consumes very less amount of gas as compared to gas nitriding ok. And it is a low operating cost and you know operator involvement is less very versatile of course these are all you know the advantages of nitriding in any nitriding you will have a good dimensional stability that means before and after nitriding the change in the dimensions of your components are very small. That is why you do not need any post treatment that means after doing the nitriding you do not have to do anything you can use the part ok. In this table you see the you know quantitatively how the you know the gases are you know emission data for nitrocarburizing that means plasma nitrocarburizing it is compared here when you do the plasma when you do the gaseous process ok. You see the drastically reduced you know the emission percentages right these are all you know you see that it is that is why known as a you know the environmentally you know the very good to adopt plasma nitriding for you know the applications involving hardening the metallic engineering components.

So with this I thank you all for your kind attention just to summarize quickly in case of a plasma nitriding the feed is nitrogen and hydrogen gas mixture this will be made into a plasma it will create some nitrogen ions some nitrogen neutral some hydrogen ions and then these things will you know allow the these positive charge ions are attracted towards the your samples which are cathode. And then you provide the thermal energy by having a separate heating there are two heatings can happen plasma itself can also provide certain heat to raise the temperature you additionally also have the temperature from the heaters. So with this you can modify the surface and plasma nitriding is environmentally friendly process because you have very less emissions and doing a less damage to the environment. So with this I end my lecture. Thank you. Thank you.