Surface Engineering for Corrosion and Wear Resistance Application

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Lecture - 29
Plasma Nitriding and Ion Implantation

Hello everyone and welcome to the 29th lecture of Surface Engineering. We have been discussing various surface engineering approaches so, called conventional surface engineering approaches. So, far we have talked about introduction of carbon through various kinds of carburizing processes, introduction of nitrogen through nitriding processes, sometimes in the solid state, sometimes in the gaseous or sometimes even in aqueous or salt path. We are now going to actually combine the modern approaches with one of the conventional techniques and discuss something known as plasma nitriding.

So, the basic principle is the same that we are trying to introduce nitrogen onto the surface with an aim of producing nitrided layer interstitial compound layers between iron and nitrogen. So, the hardening processes, the improvement in properties and so on are going to be exactly the same the mechanism remains the same. Time required is less temperature also could be little lower the precision the effective the effectiveness or the overall utility of the process is much better.

In fact, we will compare with the conventional plasma nitriding with conventional nitriding processes with plasma nitriding and we able to show you as to why plasma nitriding is always considered more efficient and effective.

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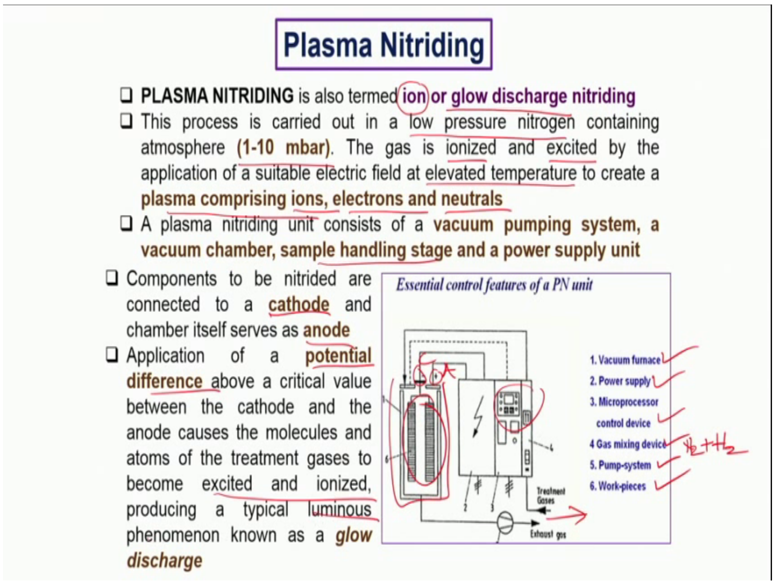

So, the process of plasma nitriding is sometimes actually also referred as the glow discharge process because you do see a blue violet glow surrounding the sample in the nitriding chamber the essentially though that glow comes from the presence of the particular ions particularly the nitrogen ions.

So, in order to get the glow discharge you required low pressure. So, we are talking about anything like a few millibars of pressure so, evacuate and then backfill and then ionize. So, the gas is ionized and remain in the excited state and the temperature would be typically anything like 450 to 525 30 or somewhere in the range of 450 to 550. So, we create the plasma, we generate the plasma which contains ions, electrons and neutrals.

The unit the plasma nitriding overall unit contains the vacuum furnace. So, so this is the vacuum furnace we need a power supply which actually supplies power to the unit for ionization we need a microprocessor control device which takes care of both the evacuation as well as the application of potential difference control of current and so on. We require a gas mixing device usually the gas that we feed in is not pure nitrogen is always a nitrogen plus hydrogen and at a definite proportion. We need a pumping device like this one. So, that we first evacuate and then open the valve and backfill and a finally, this is the work piece.

The at times the sample also needs to be rotated or moved and so, we need a sample handling stage also at a specific times. The important part is that we have two electrodes here to be able to create the plasma in the form of to DC glow discharge. So, we have the cathode and we have the anode. So, cathode of course, is connected to the work pieces. The definite electro potential difference is required to create the plasma and the gases get excited and ionized and in the process we get a luminous discharge which is also called the glow discharge.

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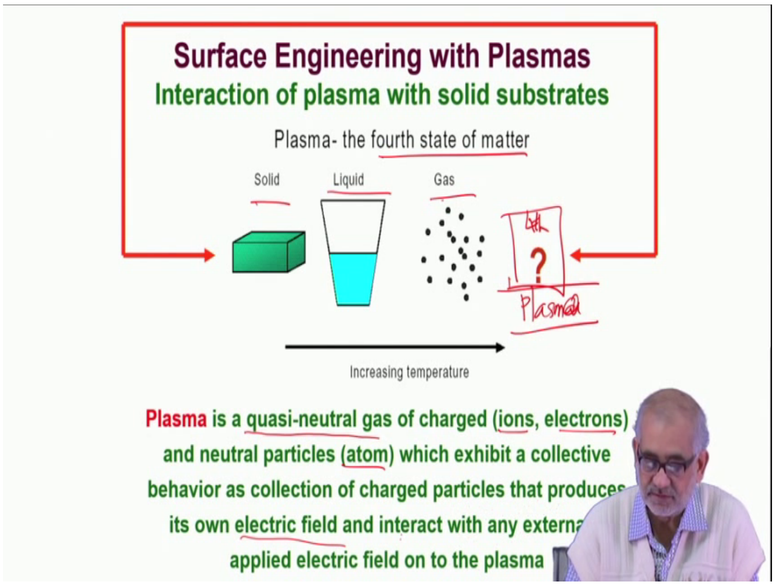

Now, from our school days we have heard that the matter whatever we can touch or perceive or see or which it actually carries a weight or volume can be can exist in either of the three possible physical states the solid, liquid and gaseous. Obviously, temperature has a role to play, but the state of the matter could be at equilibrium for various matter for example, at room temperature we do have several matter which exist as gas as liquid or also as solid which has a rigid structure.

So, essentially by sorry what we mean is that something which has a definite volume and does not change its shape unless acted upon by forces. Liquid will have a definite volume, but no specific shape and its fairly can take up any shape, but having a fixed volume and gas will be always something which does not have a neither the specific shape or the volume and certainly is not rigid.

But we also did hear a mention about the so, called fourth state and that fourth state is called the plasma state. This fourth state is not an equilibrium state it is a metastable state and this metastable state actually comprises the quasi neutral combination of the ions, the electrons, the charged species and also the neutral particles the atoms.

So, combination of the ions cations or anions and electrons and the atoms at a metastable equal in a metastable equilibrium state is called plasma. Now, we in order to create the plasma we actually excite through application of an electric field and this electric field also can interact with the species inside.

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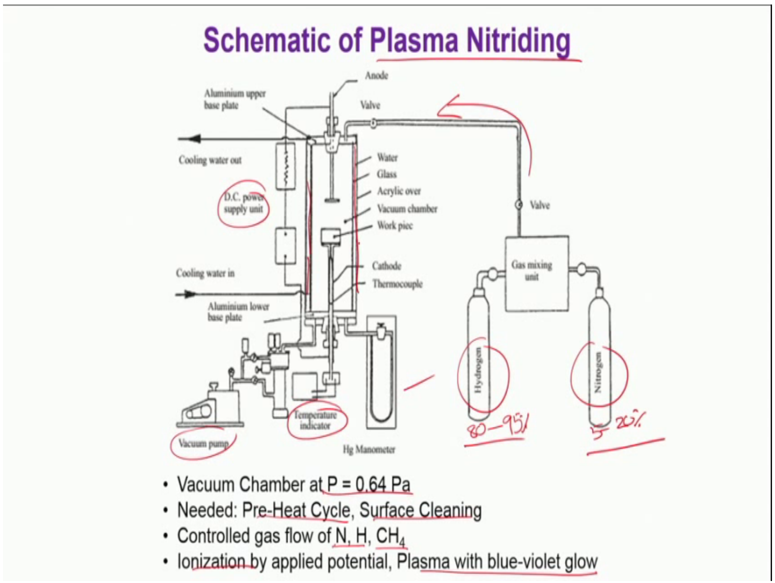

So, plasma nitriding as we have already seen is a process, where we place the sample immersed in the plasma and then we stabilize the plasma by application of a certain specific D C power that pressure inside the chamber is very low much lower than the atmospheric pressure.

We may need certain pre cleaning cycle to remove the thin oxide layer or other contaminants from the surface and then we actually allow a flow of gases usually nitrogen and hydrogen at times also with methane. And application of electric potential difference between the electrodes at very low pressure causes ionization and then we create the plasma, which has a typical blue violet glow.

This mixture nitrogen hydrogen actually could be anything from hydrogen amount could be anything from 80 to 95 percent and nitrogen is typically about say 5 to 20 percent. This is premixed and through this gate valve, we allow the gas to flow in after we have evacuated and we maintain the monitor the pressure the temperature is controlled, the vacuum pumps evacuate and then allow. We also have a cooling jacket outside the chamber so, that the chamber is the outside the chamber or the shell is maintained at room temperature.

Now the sample is usually placed on this stage and if needed this stage can be moved or rotated, but usually this is a static state and then this is the anode and this is the cathode. So, the cations that we create here namely nitrogen plus ions they will gradually come and then sit on top of this work piece get absorbed and then subsequently will create a division profile inside the material.

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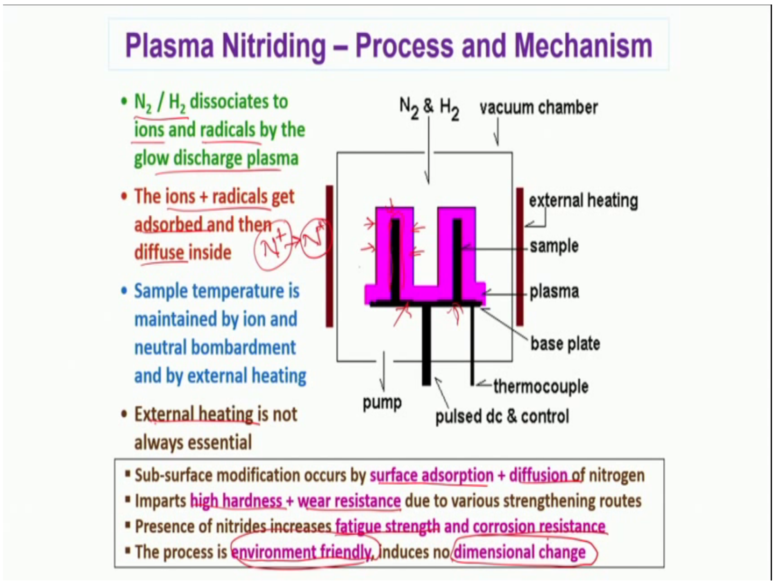

So, this is sort of a schematic cartoon to show that you actually have a violet or blue violet sheath around the samples and the sheath essentially is a certain concentration of ions. So, what we do is, when we actually feed in the nitrogen hydrogen mixture they dissociate in inside the chamber and create the ions and radicals along with some density of neutrals and that creates the glow discharge. So, the ions and radicals they come onto the surface and get adsorbed.

So, once they get adsorbed then thin surface layer through this chemi absorbed layer we will now allow diffusion of the species, in this particular case we are talking about nitrogen. But this the nitrogen in an activated state or the Nascent state actually when they come in contact with the surface the free electron cloud from the surface allows them to convert into nitrogen nascent nitrogen atoms.

So, this nitrogen ions coming from the environment from the plasma comes in contact with the surface of the work piece acquires electrons and then reaches a neutral state, but this is in an activated state and now its ready to diffuse inside. So, nitrogen now comes from all sides and then that is how it actually gets adsorbed and then diffuses inside.

Generally external heating is not required, but at times in order because we maintain this at a particular isothermal condition, but then at times we actually may require external heating attached to the stage here to make sure that, we actually are able to maintain a specific temperature very precise temperature of the sample. So, the subsurface modification occurs by adsorption followed by diffusion, this ingress of nitrogen from the atmosphere leads to formation of nitrides and causes increasing hardness and wear resistance.

The nitrides increase also the fatigue strength and corrosion resistance we have discussed at length in the previous lectures and the process is extremely environment friendly. Now this is very important part as to why this will clarify as to why plasma nitriding is always given a choice favored over the other processes of liquid or gaseous and nitriding. Because the temperature exposure is limited time is smaller and environment is plasma.

The dimensional change that may happen is minimal in this case and there is no quenching there is no drastic dropping temperature required. So, the dimensional change is minimal. Even if it undergoes some amount of expansion due to exposure to 550 or so, when we bring it to room temperature without any quenching, it does not really suffer any major dimensional change. So, there is no question of any distortion or warping or cracking.

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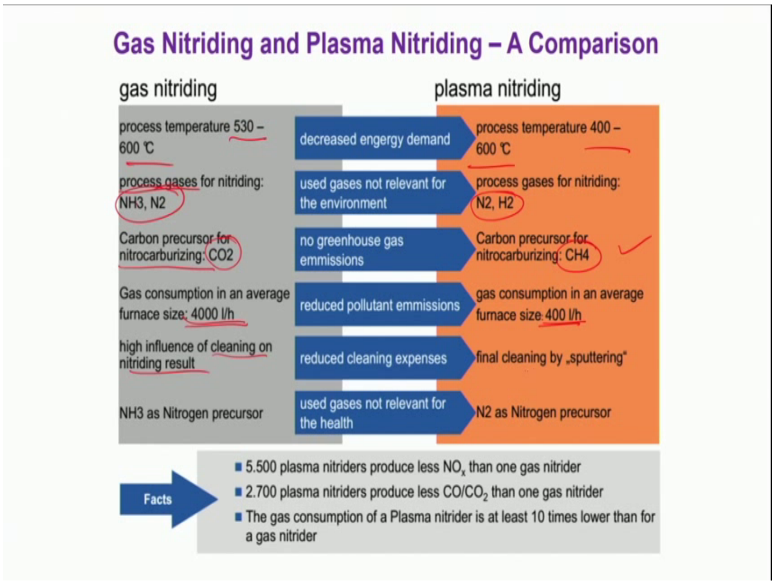

So, we would like to now compare the gas nitriding and plasma nitriding these two are let us say these two are competing processes. So, process temperature wise about the same in fact, it could be a little lower. A process gas or the precursor mixture is ammonia and nitrogen in case of nitriding a gas nitriding and its pure nitrogen and hydrogen in case of plasma nitriding. So, this ammonia actually is supposed to crack may crack actually during the processing, but in this case we use two pure gases. So, we actually can maintain the very precise ratio of these two gases.

When we compare this with nitro carburizing which is a gas based process wherein we actually have combination of both carbon and nitrogen introduced to the surface there is possibility of emission of carbon dioxide and this carbon dioxide is one of the greenhouse gases. Now, instead of that if we want in plasma processing, if we want carbon to actually be used then we do not use any of these CO2 or pure carbon, but we use hydro carbon and this is and this is not a hydrocarbon gas its not an harmful gas it does not affect those on layers.

So, even if we emit some of these gases its not going to affect. So, it is much more environment friendly. The gas consumption this is a very major advantage of plasma nitriding is almost an order of magnitude lower because, we are feeding exactly the precise ratio of the gas composition that we need and consumption or utilization is much better with a higher efficiency.

So, the consumption is almost an order of magnitude lower. Cleaning prior cleaning to the treatment is very important because in any of these high temperature processes of iron based components why only iron? Let us say titanium or chromium or all these metals are very prone to formation of very thin oxide layer onto the surface in case of iron this is actually a very major tendency.

So, when this oxides form they act as barrier for any amount of ingress of gaseous atoms from the atmosphere. So, we do not want that impediment. So, we want to clean and in case of plasma nitriding this is much easier because we actually can reverse the polarity of the electrodes and then allow sputtering of ions or atoms from the surface and that is how we can clean a few atomic layers from the surface. So, there is no separate cleaning required, it can be done in situ in the chamber itself. So, here we are using ammonia as a precursor and in plasma nitriding we are using only nitrogenous precursor.

So, there is no health hazard involved at all. So, in general what one can see by comparison is that plasma nitriding a general gas nitriding produces a lot of NOx gasses produces a greenhouse gases and also gas consumption in general is higher.

So, in comparison plasma nitriding is free from this emission of NOx or greenhouse gasses and also consumes much lower amount of gas mixture. So, more time wise and material wise more economical and more energy friendly.

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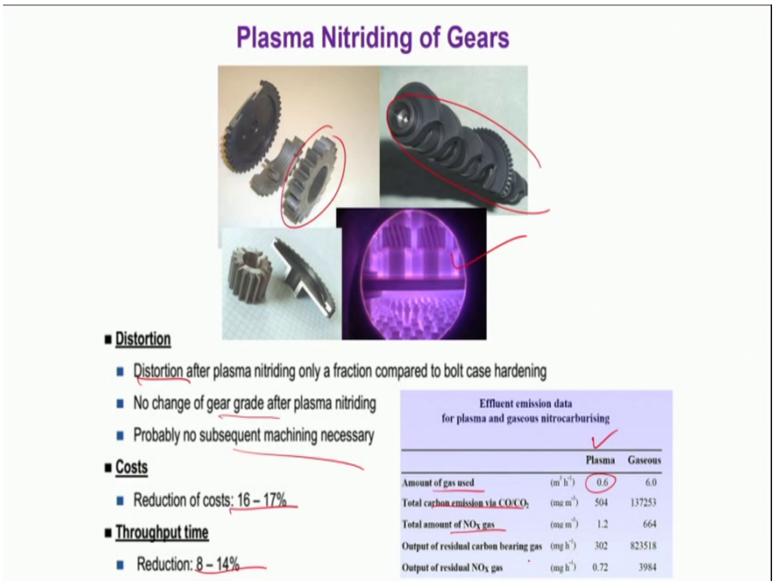

I already mentioned that distortion is minimum because there is no direct quenching there is no drastic change in temperature even temperature exposure is lower. So, all these components possible components like gears or shafts or cams or let us say valve sheaths or nuts and bolts and so on whatever is plasma nitrided they actually will are prone to less amount of distortion or warping.

So, this is the typical blue violet glow discharge which actually proves the presents the physical appearance proves the presence of nitrogen plasma. Usually, plasma nitriding is done on finished components so like this. So, there is no further machining required generally and because there is no distortion. So, the finished component can be just subjected to plasma nitriding as the final heat treatment, final treatment surface engineering treatment. So, that we actually create a few 10s of our micrometer maybe a close to a millimeter thick of nitrided layer.

The cost is lower, so the process is more economical and also the time wise you require less time maybe 10 15 percent less amount of time. So, this is what we have already discussed that then the gas used is much lower about an order of magnitude lower. The carbon emission the NOx emission they are much lower in case of plasma, also the carbon bearing gases are emitted from the chamber is much lower in case of plasma.

So, economical both time and material wise more efficient temperature lower, gas consumption lower and certainly more economic environment friendly.

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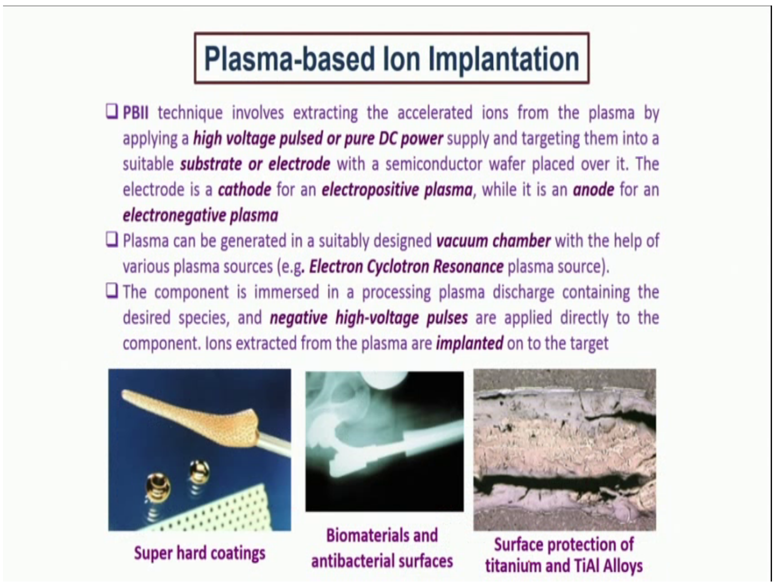

So, the other processes I have already mentioned about plasma nitriding is exactly the same as gas nitriding or even liquid nitriding; that means, you create nitride layer onto the surface and like we discuss in the previous lecture at details the first layer could be the zita nitride and then we can have epsilon nitride or gamma prime nitride and so on.

So, anything from Fe 4 N to F e 2 N mixture of that gradient from the surface to the core and that is the reason why we get all these high hardness, high wear resistance, even fatigue resistance corrosion resistance and so on and so forth; so, exactly the same. Now even in plasma nitriding now we are going to discuss a little variation and offshoot of the normal plasma nitriding which actually can give us better functionality and this is by either of the two approaches; one is called plasma based ion implantation. So, essentially you create a plasma environment you insert your specimen inside the chamber and then you actually apply negatively biased pulses.

So, when you apply negatively bias electrical pulses, you actually make the nitrogen ions cations to move faster accelerate them and move make them move faster and get implanted with a certain velocity onto the surface of the specimen which is on the cathode. So, the positively charged ions are accelerated towards a negative electrode and they get implanted and then apart. So, earlier on all the processes of nitriding discuss so, far we expect the nitrogen either atom or ion to come onto the surface become in the Nascent state, they are supposed to get adsorbed and then they diffuse in.

But here is a process where we actually implant the ions directly as a projectile onto the surface and they are diffusing. So, there is a very exciting possibilities of using such approaches for particularly for biomedical processes prosthetics like this femoral joint know that knee joint or hip joints and so on. And this is applicable not just to steel or stainless steel, but to titanium and several other metals even nonmetals when they are actually coated with certain metals.

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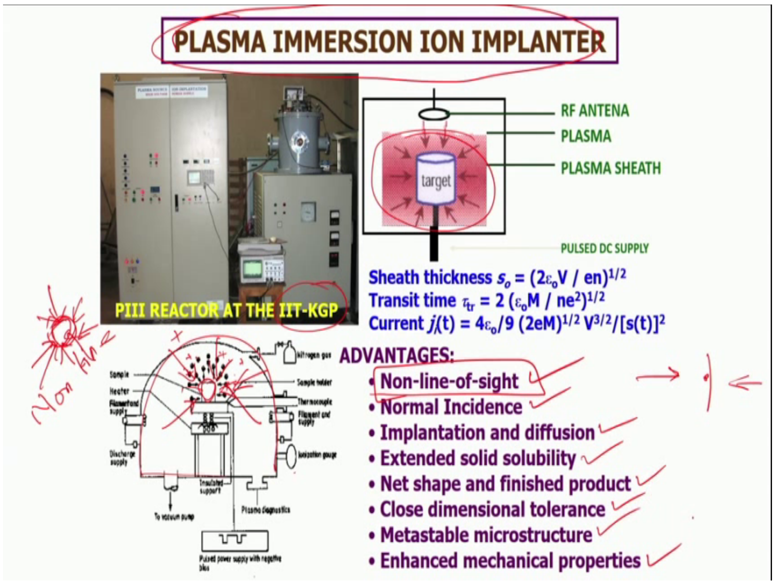

So, a variant of that plasma based ion implantation another variant of that is called plasma immersion ion implantation and this is an approach. Basically, these two approaches came one from plasma based ion implantation came from USA patented technology and plasma immersion ion and implantation was patented in Australia from another organization.

So, this is the plasma environment that we create inside the chamber incidentally I must mention here that this kind of a facility exists at IIT Kharagpur this was an special facility created through a special grant from the Department of Science and Technology and we actually made very substantial use of this. So, this is what I was trying to say that, you create these nitrogen ions cations and when you apply electric field. Then the advantage here is that this whole chamber this whole chamber is your anode and this sample whatever is that shape dimension or contour is your cathode.

So, all these positive ions or cations when you apply the negatively biased electric electric pulses they all will get energized and accelerated to go on implant from all sides. So, if this is your specimen it will have implantation from all sides and normally in a gas nitriding or plasma nitriding, you actually do have the sample exposed to the atmosphere. And then a particular environment and the atoms or the ions actually flow in and sit onto the surface and here you actually are projecting them propelling them onto the surface.

So, the implantation is very uniform and its, that is why its called a typical non line I think I better be writing here oh. So, it is written here its a non line of sight process which means in normal beam line implantation if this is the beam then you implant only here not on the other side. But since you are implanting from all sides in V i cube you actually a can brand it as a non line of sight process. So, all the normal incidents you have both the effect of implantation and diffusion.

In the process you can create extended solid solubility a divider solubility limit, the all the products can actually be in the final shape net shape there is a very close dimensional tolerance possible you can create metastable micro structures and also can enhance their mechanical properties significantly.

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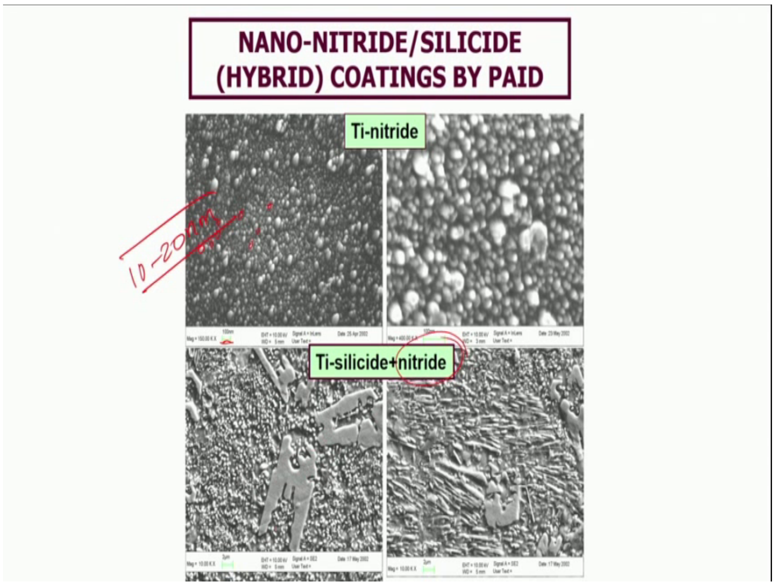

In fact, one very bright example I would like to show to you is that this is the kind of ultrafine this length scale is 100 nanometer. So, each of these nitride that you are seeing are implanted on and grown onto the surface would be about at 10th of that. So, typically we are talking about something like about 10 to 20 nanometer nitrides created on you can do it on steel on titanium on any other nitride forming substrates.

In fact, this also gives you a very exciting possibility of having a pre alert surfaces which contain certain silicides and in addition to silicide you can also create nitrides through this plasma immersion ion implantation. All these results are published and I am sure you can refer to the literature and CDs for yourself.

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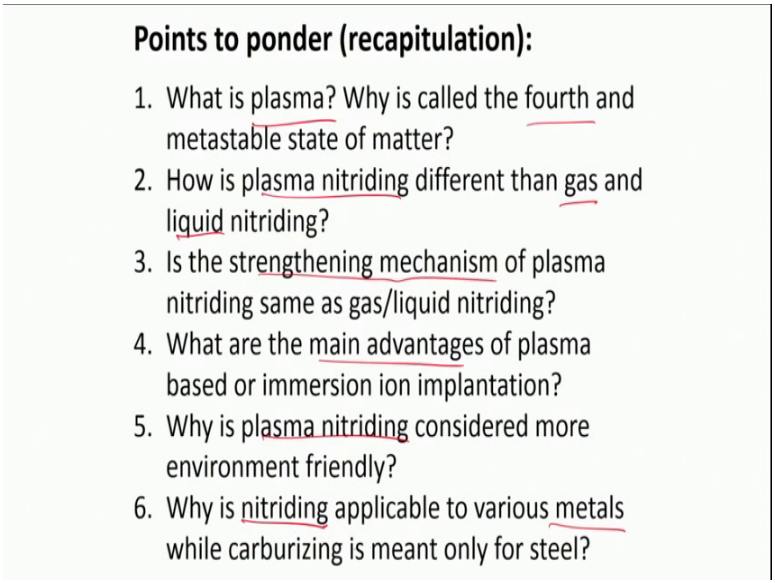

So, we should now try and recapitulate the whole exercise we learned what is plasma? We understood why is it called the fourth and the metastable state we understood what is plasma nitriding and how do does it differ from the so, called gas or liquid nitriding? We realized that the strengthening mechanism is identical that we have in case of other forms of nitriding.

The main advantages we had a very nice comparison with between gas nitriding and plasma nitriding and we also realized that plasma based or immersion ion implantation offer us a non line of sight process of implantation. And hence it actually is a very huge advantage. This is environment friendly plasma nitriding because of the lack of emission of these kind of NOx or a greenhouse gases. And what we also should appreciate is that nitriding as a whole is a process which is applicable not only to steel, but all other various other ferrous or non ferrous metals whereas, carburizing is primarily meant for steel.

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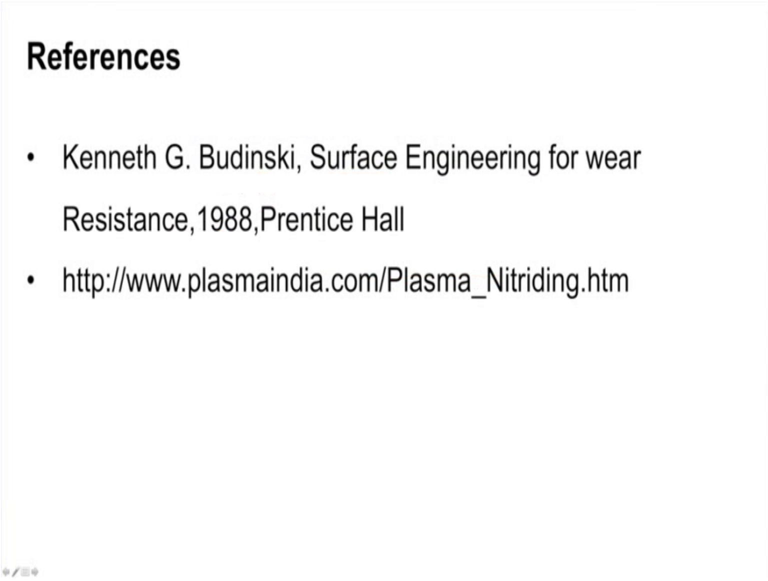

So, with this we come to the close of the process description of carburizing and nitriding treatments and now what remains is to take a quick look at the overall scope of heat treatment why these are necessary after this kind of either carburizing primarily carburizing treatment and sometimes also nitriding treatments.

So, thank you very much.