

Surface Engineering for Corrosion and Wear Resistance Application.
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Lecture – 57
Laser Surface Alloying

Welcome to the 57th lecture of Surface Engineering. Today we are going to we already started discussing about a particular laser based technique called laser surface engineering and in this we have already identified as possible scopes processes like surface hardening, surface melting we have discussed those two aspects in the last couple of lectures today we are going to talk about Surface Alloying. And at the very beginning we must realize that we are talking about a process where we are in a position to not only change the microstructure, but also change the composition of the near surface regions.

So, and the near surface region depending on the application depending on the material that we are dealing with could be anything from a few as low as few micrometers few tens of a micrometers in the limit it can be even less than a micrometer. But usually with high power laser and metallic components one goes typically few tens of a micrometers or hundreds of micrometers, but less than a millimeter. So, anything from about 10 micrometer to few millimeter one can easily change the composition and obviously, microstructure as well.

So, the intention of changing microstructure and composition both is to introduce a new layer of alloy which is different than the underlying substrate and in the process improve resistance against surface degradations like corrosion, oxidation, erosion wear and so on and so forth by way of changing the composition and microstructure. So, will be first discuss will first discuss the overall scope and mechanism and then take up 3 specific examples to show you how such laser surface alloying can improve corrosion resistance, oxidation resistance and also create certain new kind of a phase aggregate on the micro on the surface which is useful for some specific applications.

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Laser Surface Alloying

LSA involves either (a) depositing alloying elements as dry powder/suspension onto the substrate surface by hand-brushing, gas jet, etc. or (b) creating a layer of alloying elements at the substrate surface and melting the added layer partly with the underlying substrate by **laser**

Intermixing of the substrate material and alloying material takes place in a thin surface layer. Thus alloyed layer forms at the substrate-surface

Advantages:

- surface geometry unimportant;
- high productivity and control
- high quality of the alloyed layer;

The diagram illustrates the Laser Surface Alloying (LSA) process. It shows a nozzle depositing powder onto a substrate surface. A laser beam is directed at the powder, creating a melt pool. The laser beam is labeled 'Laser beam (with inert gas shroud)'. The melt pool is labeled 'Melt pool'. The alloyed layer is labeled 'Alloyed Layer'. The substrate is labeled 'Substrate'. The diagram also shows a 'Pre-deposit thickness', 'Melt/Alloyed zone width', 'Heat affected zone', 'Substrate', and 'Sweeping stage'. Handwritten notes in red include 'AB', 'A', 'Feed', 'Substrate', 'AZ', '500-2000°C', 'Ar', '15-30%', and '20%'. A coordinate system with X, Y, and Z axes is shown at the bottom right.

So, the very process as I said laser surface alloying is actually mean to let us say this is a particular component we are talking about the front view and this is on the cross section this is the layer we want to create whose if this is a underlying substrate A, then this top layer could be A alloyed with B element B or it can be that B can be anything like a single element or it can be a compound. So, in the process we actually can create a microstructure which is not only going to be just a solid solution, but can be actually two phase or multi phase aggregate including dispersion of certain intermetallic phases and so on.

And the beauty or the novelty of laser surface alloying lies in the fact that we can create a microstructure which is fairly metastable in the sense the aggregate that we developed by this process is not possible to be produced by normal equilibrium processing. So, we have quite a bit of advantages here first of all the surface geometry we do not change we actually whatever is a surface geometry contour shape size we can retain that we can maintain that. So, even a complex shape can be handled, there is very high productivity and control we can achieve this surface alloying at a very fast rate. The quality of alloying layer is certainly of is very high and also fairly novel which is not possible by any normal technique.

So, the process actually can be in either of the two ways; one is if this is the substrate we are trying to develop a surface layer on top of that, then either we can create a layer

beforehand and that layer actually could be. So, this is the pre deposited layer we can create by way of let us say electro deposition or simply powder bed place pre placed powder bed or some spray units like plasma spray or any other spray technique. So, whatever is available before us.

So, we can create a certain layer on top which is compositionally different may be an element, may be a multiple element, may be a compound and an element so, whatever we choose whatever we can we deposit on the top surface and then we can use a laser beam to raster over like along x, along y and multiple directions of back and forth and in the process we can create a layer on top which is unalloyed layer.

So, this is what we call an alloyed zone. So, the substrate remains at the bottom unchanged completely unchanged. So, either with pre place powder or we can create a situation where this is the laser beam and I can also feed through a powder hopper some powder mix beforehand. It can be a powder mix, it can be a wire, it can be a tape or it can be simply a compacted feed.

So, whatever it is. So, this is how we feed the elements or compounds that we want to alloy and this is the laser beam. So, this laser beam allows. So, it creates a melt pool. So, just below the melt, just below the laser beam we. So, this is the beam fluence and in this when we feed powder so, in this region we create a melt not splat, but actually a melt and immediately due to gravity this melt will settle on top of the existing substrate and when it solidifies onto the substrate, because the substrate below will heat will act as a very important heat sink very efficient heat sink and as a result of heat extraction from the bottom. So, this layer will immediately solidify.

So, in the process we create this zone on to the surface which is called an alloy zone compositionally very different. And its not just a composition there will be also fair amount of new phase aggregate evolving. So, like as you are seeing here that here we had a pre deposited layer. So, this straight lines here this region here actually is representing a layer which is pre deposited and this is the laser beam which is moving let us say in this direction and then in the next way again in the reverse direction then again this. So, likewise there will be a movement of the laser beam.

Now, when the laser beam moves up and down and up and down like this we have to make sure that the if this is one spot the next spot cannot afford to be tangential, it has to

have certain level of overlap. And usually this overlap region is about anything between 15 to 30 percent. So, ideally I would say about 20 percent.

So, 20 percent of the width is undergoing re melting and re alloying and this is needed so, that compositionally what we create at the end will be rather uniform and will not have a situation which will be which will have a very sharp interface like this.

So, instead of making a sharp interface we create an uniform layer uniform composition throughout by way of this kind of a overlap. So, this thickness or the width of the melt alloyed zone this is very important and as I said this could be anything from a few tens of a micrometer to few millimeters, below this alloyed zone will be a heat affected zone which will only undergo a heating cycle, but no change in composition. So, micro structurally they may be a little different than the substrate sitting below, but usually this heat affected zone is very very small.

Now, in order to protect the powder feed or wire feed or whatever we are delivering we also would like to ensure that there is no undue oxidation. So, in other words the laser at the by delivery point the beam temperature could be anything 700 degrees. So, it could be anything like 500 to 2000 or even higher depending on what kind of parameters we choose. So, of course, we can control that the entire heat transfer is a purely dependent upon the parameters we choose, but the point here is that when we expose this zone which is a melt pool. So, this is the melt pool and in that melt pool we are feeding powder.

So, both the melt pool both this melt pool as well as a powder that we are feeding into it are liable to oxidation at that high temperature. In order to prevent that when we feed the laser beam, we usually cover it up or shroud it with some protective gas like argon in some cases maybe nitrogen or maybe a combination of nitrogen argon. In some cases even reactive gases a nitrogen which actually can react with this and create an alloyed layer on the surface.

So, we need a few things we first of all we need a substrate, we need either a pre deposited or a co deposited layer, we need laser beam for melting and the beam size is much smaller than the overall surface area that we want to cover. So, the beam needs to go up and down raster over the surface in x and y direction.

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And if it happens to be a curved surface then of course, we need apart from X Y we may also need certain going certain movement in the vertical direction. So, we may need movement of the stage in X Y Z direction and even some rotation in theta so, that we can take care of such curved surfaces.

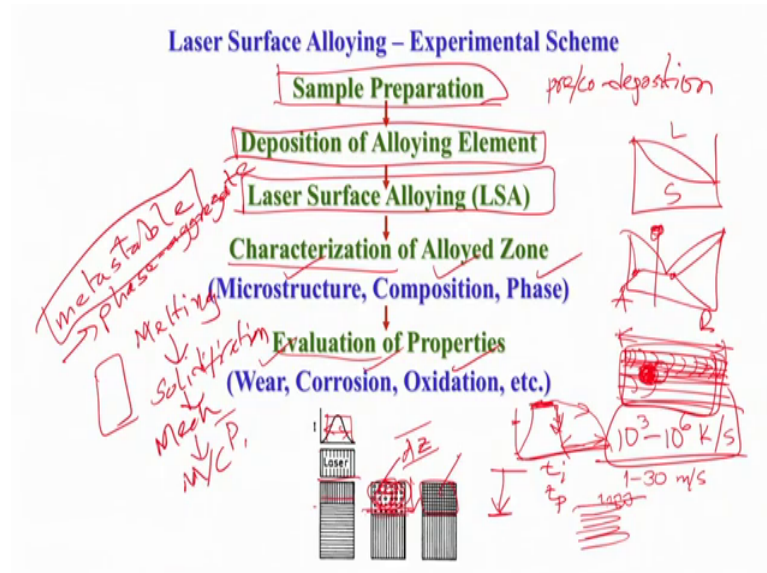
So, the stage so, after the laser beam so, the substrate the deposit the laser beam then the stage on which the component is placed the mechanism to move the stage in X Y Z or theta rotation and then we need a shroud gas and we also use certain monitoring devices for monitoring the temperature rise or certain other we need to keep track of what is happening onto the melt in around the melt pool.

The beauty is that when we are talking about laser irradiation this is the melt pool and the temperature could be anything like for 500 to 1000 2000 or whatever, but this is only let us say 1 to 2 millimeter diameter and below few millimeters temperature is room temperature around a few millimeter the temperature is also room temperature. So, 99 percent of the bulk is at room temperature only the spot which is being irradiated reaches a melting the fusion temperature or even higher and gets affected.

So, the dimensional stability or dimensional repressible accuracies extremely good in case of laser compared to this if you subject this whole component in one single isothermal chamber and then you take out then there will be lot of scope of contraction

and expansion and contraction leading to thermal stresses and distortion. So, that level of distortion is fairly its possible to be avoided to a large extent.

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One important thing let us go to the next view graph and then it becomes easier. So, process wise we are talking about a situation where first we have to prepare the sample which means either pre or co deposition. So, we first polish the surface removal oxide layers and then do certain in some cases sand grit blasting so, that we make the surface intentionally little rough so, that the melt easier and also they can wet easier with the melt pool that will be created for alloying.

So, certain amount of sample preparation is required and then the sample or so, called substrate preparation surface preparation of the substrate then we deposit alloying elements either prior beforehand or during the alloying process itself and then we irradiate with the laser beam and as we irradiate then at the surface alloying takes place. And after the alloyed zone is formed then we need to characterize the alloyed zone and that characterization could be in terms of micro structure composition phase aggregate and integrity or in terms of defect density and so on.

And subsequently we also would like to evaluate the properties and this properties of interest could be hardness, friction coefficient, where corrosion, oxidation or any other reflectivity or surface roughness or various kinds of properties whatever were interested in. So, the overall process if you look from the front the front view would appear as if

this is the laser beam. So, this is a laser beam and we assume that this laser beam is not top hat, but Gaussian, but in principle one can also use a top hat beam like this with a constant intensity profile as a function of width and this diameter of the beam is something that we can control and we know how much power density we are feeding in.

So, if we know exactly the beam size then we actually are talking in terms of power density not absolute power. So, in addition to this we also make sure that if this is the deposit the pre deposit and this is the substrate then as we irradiate we melt not only the deposit, but also a certain depth below the surface. So, that there is a good amount of inter mixing and this amount of inter mixing leads to formation of the alloyed zone.

So, this alloying takes place in the liquid state and advantage is that for example, if you refer to any standard phase diagram very rarely you have isomorphous system where solubility is infinite both in the liquid state and in the solid state more often than not you would come across situation say for example, eutectic or peritectic or whatever.

So, in that case there will be a solubility limit here right. So, when you want to do it in the solid state you have difficulties because diffusion has to take place which is a slow process and then you have solubility limits and so on, but in laser instantly you can take a temperature to here. And as you take the temperature here then any amount of A and B can be intermixed and instantly they can form a very homogenous alloy melt pool, because the volume that we are talking about a very small. And at that high temperature because of the laser fluence and temperature gradient, you also have good amount of convective mixing also solute or diffusion in the liquid state which is faster.

So, because of which of on this substrate if this is the melt pool we are talking about and this is probably just 1 or 2 percent of the total surface area. So, in this small area instantly we mix a and b or a b c and instantly we form an alloy of fairly homogenous composition and subsequently when we move the beam away the next. So, during if its a pulse mechanism if its a pulse irradiation process, then we make sure that the next spot is having a 20 percent overlap.

Otherwise if we are using a continuous wave radiation then this is how the beam is going to move from over the surface so, when it moves, it these are the kind of melt pool the track in the interfaces of solid liquid interfaces will move in this direction and this is how you create an alloyed zone. And obviously, when you start from this end and reach the

other end in between you have wherever is the fusion zone you have sufficient amount of churning or inter mixing.

So, throughout this length you create an alloy which is fairly homogeneous. So, now you go to the next layer and this layer will have about 20 percent overlap, then again our next layer with 20 percent overlap and likewise you are able to create cover the entire surface and create a very uniform alloyed zone.

Of course this is a rapidly stratified zone. So, there will be the microstructure is not going to be poly crystalline or annealed microstructure is going to be a typically a cast microstructure which you expect in case of very fast cooling. But this cast microstructure the advantage is that in the liquid state when a b c all of them mix together make a homogeneous melt when you cool you cool at a fairly fast rate.

So, this is a melt pool forming an alloyed zone which is fairly homogeneous. So, the solid liquid interface starts from the top and reaches until say this point. So, this is the end of the solid liquid interface because the beam is either in terms of a interaction time or pulse time this is how you have heated up.

So, in this region your formed alloy and then subsequently when the beam moves away or the pulse is off then you cool. And this cooling rate actually is extremely fast could be as high as something like 10^3 to 10^6 Kelvin per second. Now in this fast cooling rate the effective solid liquid velocity that you can achieve could be anything from say 1 to 30 meter per second. So, the solid liquid interface which starts moving from the top and goes until the bottom of the alloyed zone, moves at a very fast rate and as soon as the temperature is.

So, if you are talking about at let us say if this is the temperature maximum that you have reached and the melting temperature is somewhere here. So, by the time you actually cross the melting temperature you already have achieved a very high cooling rate and because of this very high cooling rate whatever alloy that you are formed in the liquid state will be retained will be quenched will be retained in the solid state. So, you tend to actually retain a uniform homogeneous alloyed zone alloyed layer until the room temperature and you do not allow any phase separation.

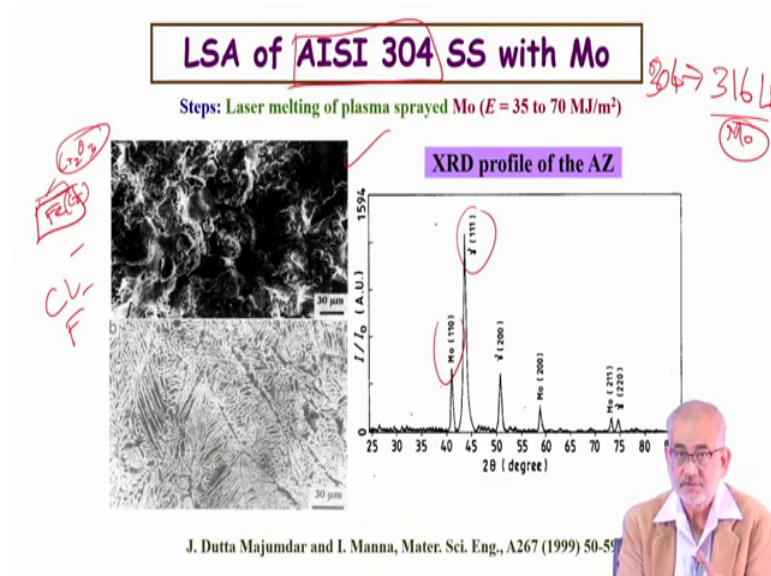
Instead of this if you could if you in a normal equilibrium process you would probably cool at a very slow rate like this and because of this slow cooling rate you actually are alloying a much longer time and because of this much longer time you actually tend to form dendrites and or even in some cases for a phase separation leading to some interdendritic precipitation interdutic interdendritic region. Whereas, in laser solidified surfaces we end up getting at the most certain directionally grown columnar grains and there may be semblance of dendritic formation, but not necessarily long primary arm, but very little short secondary arms.

So, in the process the scope of heterogeneity compositional heterogeneity it exists, but its not very large. So, that is the advantage of very fast cooling in case of laser and another very important thing we should bear in mind that when we are cooling at such very high cooling rate, the micro structure that forms is typically of highly metastable micro structure. Which means the phase aggregate that you have this phase aggregate is very different than what you normally would expect in case of equilibrium cooling. So, to my advantage I can retain certain phase or phase mixture which otherwise is not possible. So, this is the beauty or the novelty of laser surface anointing.

Now, in a if you want to create a bulk alloy then you have to go through processes like very elaborate processes like melting then solidification or casting and after that you have to go through various mechanical processes of forging rolling and so on and then you probably will have to do some machining operations various process. The whole process is very very large and also the alloy that you eventually will develop, will not be having a typical metastable microstructure in other words will not really be able to give you exactly what you want sort of different than what is normally or possible through equilibrium route.

So, you can create a new phase aggregate and a new microstructure not possible through equilibrium processing route by way of this laser surface alloying. So, this alloyed zone will create a very different phase aggregate and can give you certain advantages which are otherwise not possible.

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So, now let me take just 3 specific examples say you think of you know we all are aware of stainless steel and AISI 304 is a standard or straight exchange steel which is used bulk of the users of stainless steel is of this particular grade which has certain amount of chromium and nickel and we are all aware that stainless steel when its exposed to atmosphere, immediately form certain chromium oxide layer which is impervious to further oxidation on the surface.

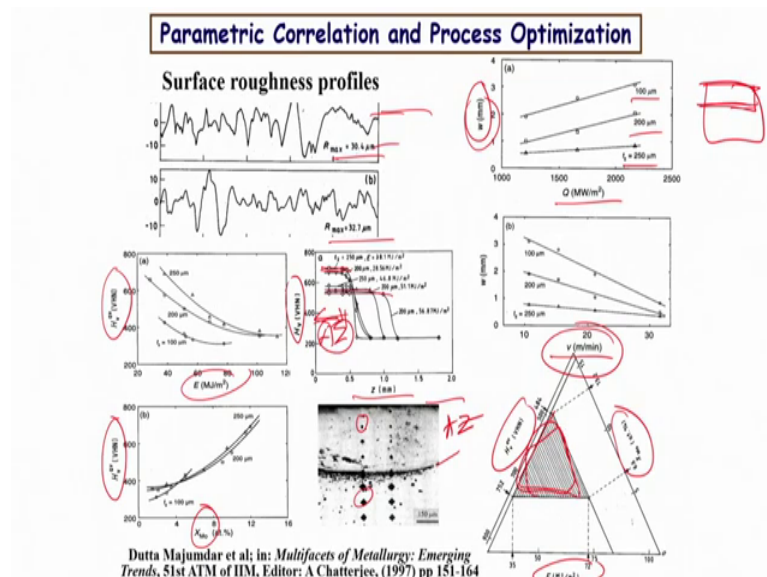
So, in order to prevent oxidation what you do is very interesting that if this is iron and if you iron if you expose to do any corrosive atmosphere will immediately form iron oxide and iron hydroxide or certain carbonates and so on and this fall off and then expose fresh layer an oxidation continues and that is how it gets corroded we see rusting. In order to prevent rusting if you allow this with chromium, this chromium actually sits on to the surface and then throughout, but then the surface the chromium atoms at the surface will immediately form a protective layer which is typically a chromium oxide layer and this fairly adherent layer.

So, it prevents any further oxidation, any further corrosion and does not allow rusting to proceed at all. So, we get a rusts less or stainless steel. Now this stainless steel is good enough until certain environmental conditions, but if you have large presence of chlorine or fluorine ions, then these ions are very aggressive ions and they can lead to pitting corrosion. So, in order to prevent pitting or make this stainless steel resistant to pitting,

you from 304 you go to another grade which is 316 even 316 L 316 L N and so on which basically has a further alloying element called molybdenum which actually protects against this pitting corrosion.

So, using laser surface alloying approach we were able to show that you not only create so, first you deposit molybdenum thin molybdenum layer by plasma spray. And then when you alloy then you create such direction solidified layers on the surface and we actually see that there is a very little amount of molybdenum precipitation, but otherwise you have a uniform austriac microstructure on the surface which is highly alloyed with molybdenum.

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And in the process we were able to first actually you know typically in a laser surface alloying process you go through certain routine approaches like you carry out and so, if this is the substrate and from the front view and this is the depth of the alloyed zone that you are formed.

So, this alloyed zone thickness as a function of power density, as a function of speed you would like to see how they vary and also your deposit thickness could be a parameter. So, you vary all these parameters and then try to find out what is the good combination of power density and speed so, that you get the right kind of a thickness. Then you characterize the alloyed zone in terms of hardness as a function of vertical depth and you

see how the profile varies and as you see this is a higher hardness zone, but this high hardness zone or is actually the typically the width of the alloyed zone.

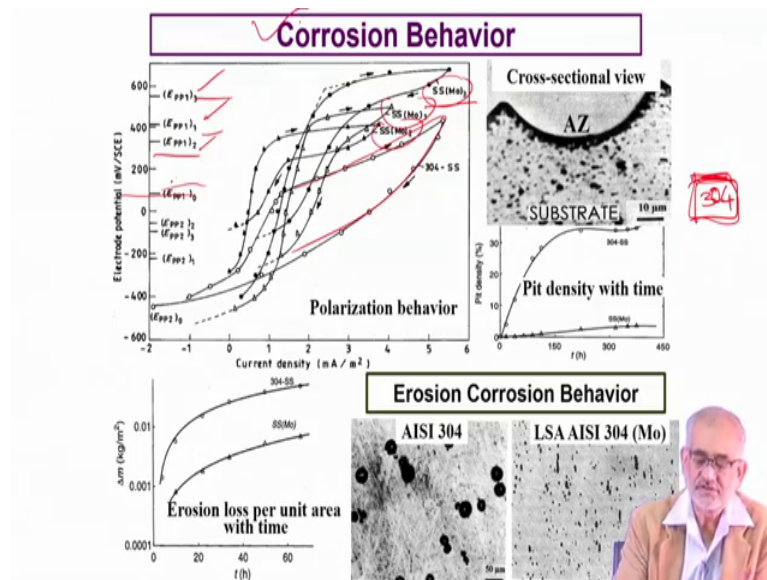
So, this is typically the alloyed zone width and this is what we have also measured here as a function of power density and speed. So, this is typically the width in which we have higher hardness because of a presence of these alloying elements in fact, if you indent on the cross section you see the indentation marks are much smaller compared to the indentation marks at the surface below substrate below.

So; obviously, this is softer and this is harder. So, this is the typical alloyed zone. Now we also carry out certain characterization in terms of the variation of hardness as a function of molybdenum in the solid solution dissolved state also we try to characterize the variation of hardness as a function of energy density, we measured the hardness surface roughness and this is.

So, typically the amplitude variation is fairly small and the average roughness is 30 micrometer for one set of parameters can be 32 for another set of parameters. So, these are the various types of characterization and testing one goes through and then eventually we are in a position to define the so, called optimum processing layer in terms of the speed, in terms of the energy density and of course, in terms of the amount of molybdenum that we have in solid solution and as thus their corresponding hardness levels that we get.

So, instead of hardness one can pick some other parameters other property and then and then this will this basically allows us to strike the optimum conditions for processing and getting the right kind of composition and microstructure.

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Without go in to details basically these kind of a polarization behavior curves or potential dynamic polarization behavior curves allows us to figure out what is a typical pitting potential where the pitting starts. And we realized that these pitting potentials can be actually fairly can we can make the alloy fairly protective in term because this stainless steel 304 which is a substrate.

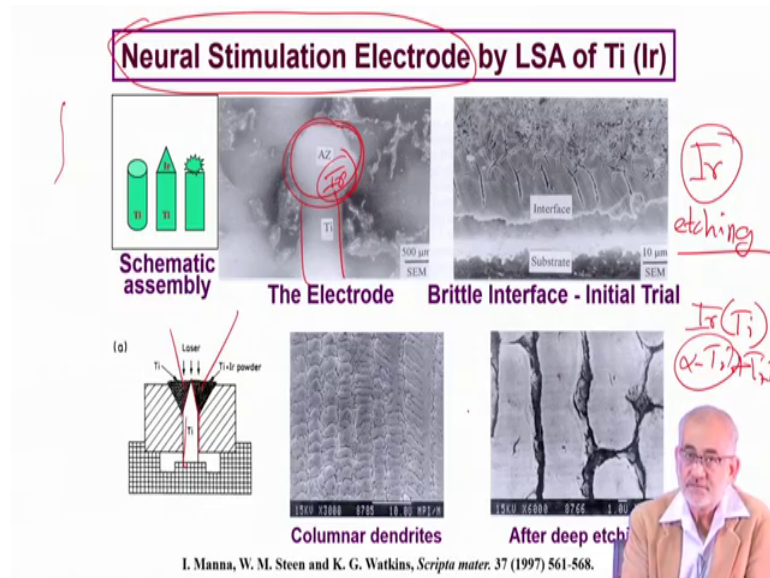
Now is alloyed with fair amount of molybdenum and as a result the stainless steel the base substrates stainless steel behavior is here and this is the typical potential pitting potential level, where as one needs actually the protective protection wise level of protection wise after the surface alloying the pitting potential pitting corrosion resistance is much higher.

So, these are all descriptions about those things let us not worry about those things. So, what I am trying to say is that if you take a 304 stainless steel you do not necessarily alloy molybdenum into the bulk. So, you consume more expensive alloying element more amount of expensable alloying element like molybdenum, but instead if you can just alloy the surface with adequate amount of molybdenum and retain more molybdenum than what is allowed by equilibrium processing.

So, you make the surface fairly resistant to pitting corrosion and this is possible on the finish component fairly fast maintaining all dimensional accuracy and most importantly creating a microstructure which is not possible by equilibrium processing.

So, this is how we can improve resistance to corrosion of stainless steel pitting corrosion resistance of stainless steel by way of laser surface alloying with molybdenum.

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Take we were talking about corrosion in so, most of the cases corrosion is not desirable rather you would like to prevent corrosion. And here is an example where we wanted to bring in corrosion in something which otherwise would not corrode. So, we are talking about iridium which is a noble metal and if you alloy if you actually try to etch iridium, it does not etch simply because it is so resistant its one of the noble metals.

But then for a specific application called neural stimulation electrode which is used as a substitute for defective neurons and for whatever reason if certain bundles of neurons stop functioning or start malfunctioning, then it leads to very severe neurological disorders in human beings and in order to rectify that you need artificial neurons.

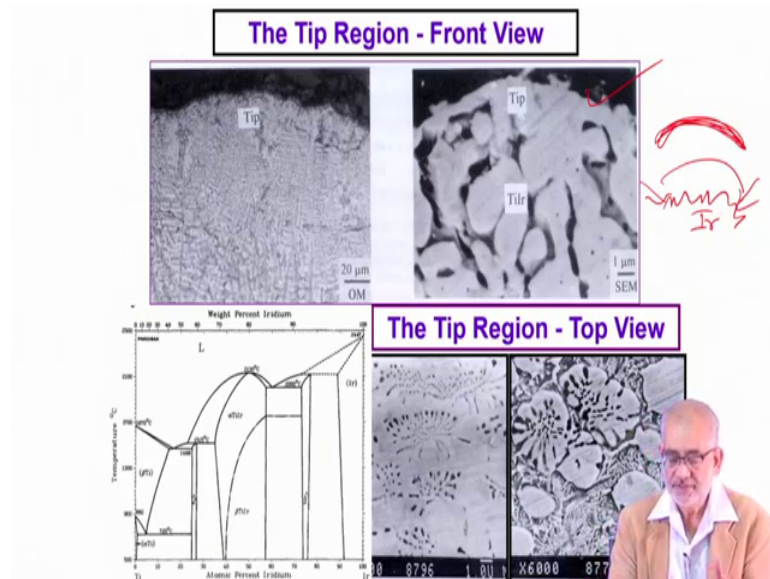
So, essentially you are looking at some wire which can mimic a actual neuron. So, typically few micrometer diameter and few tens of micrometer long artificial ones, but should have the characteristics of a neuron should be able to mimic a neuron which means all the neurological activities in human system is done through electrochemical process ionic exchange process.

So, this tip of this neuron should be able to discharge very high density of ions and receive also signals through ionic discharge and you know. So, essentially we need something which will be corrosion resistant, which will be compatible to body fluid, which can be drawn into a very thin wire of the order of a few micrometer like a neuron and most importantly can mimic the spatiotemporal activation of normal neuron in a human body.

So, there is a long story as to why we chose this, but the process the demanded that we take titanium as the thin wire and then create an alloyed zone on top which is having a very high concentration of iridium. Because iridium has the unique property of having the highest rate of ionic transfer in biological fluid condition. So, we went through. So, this is the titanium pin that we covered with iridium rod and then exposed it by pulse lasers we immediately created an alloyed zone like this and the whole process was basically the challenge was to create an iridium rich layer which also will be amenable to etching.

Now, how do you do that? Pure iridium will not etch, but when you create an iridium layer alloyed with titanium and make a two phase aggregate where you will have alpha titanium plus TiIr or TiIr₃ or one of these intermetallics then this fellow can be amenable to etching. So, the whole exercise was to create a two phase aggregate with certain distribution certain volume fraction of titanium rich phase so, that we can allow etching electrochemical etching and expose much larger surface area.

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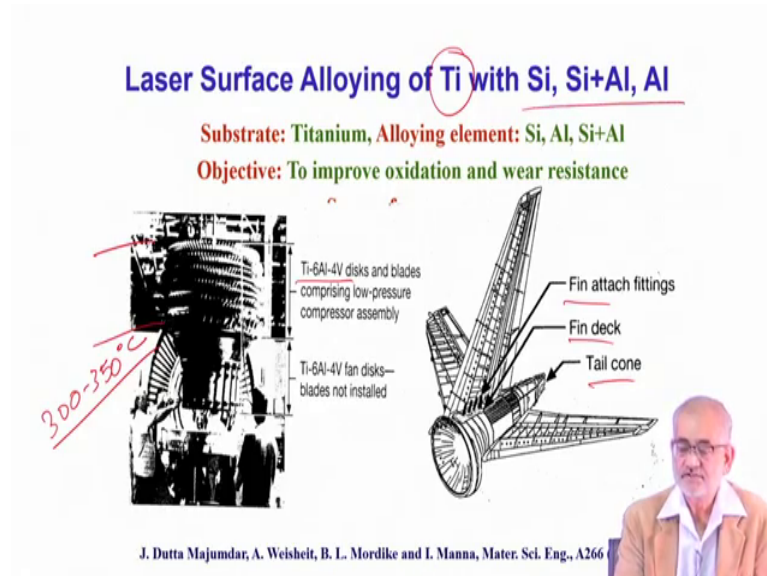
So, compared to a smooth surface like this, if you create a surface like this you can immediately make out that these deep fissures and intentionally added all these roughnesses actually make this surface or the specific surface area of this tip will be much larger than a component which has a smooth surface like this. So, instead of having a smooth surface we want the surface to be as rough as possible.

So, that the specific surface area increases and this we are trying to do on iridium which is not possible directly, so we use laser surface alloying as a strategy to create that titanium iridium rich layer and then use certain specific etching process to create such two phase aggregate which is amenable to etching.

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Laser Surface Alloying of Ti with Si, Si+Al, Al

Substrate: Titanium, Alloying element: Si, Al, Si+Al
Objective: To improve oxidation and wear resistance



Ti-6Al-4V disks and blades
- comprising low-pressure
compressor assembly

Ti-6Al-4V fan disks—
blades not installed

Fin attach fittings
Fin deck
Tail cone

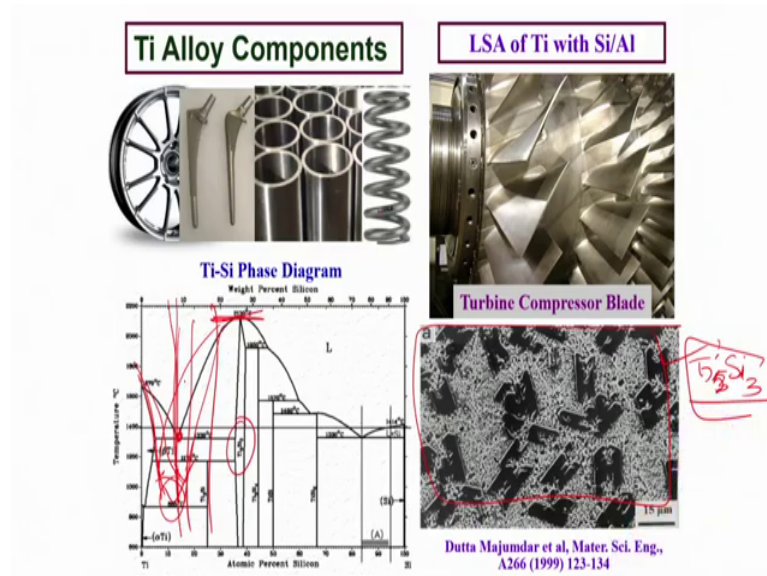
J. Dutta Majumdar, A. Weisheit, B. L. Mordike and I. Manna, Mater. Sci. Eng., A266

The last example I want to take is concerning titanium again, but for a different cause altogether. So, this is typically the compressor part of the turbine blade titanium is a workhorse material titanium alloy alpha beta alloy the only for compressor part say Ti 6 Al 4V, but also into the fins or certain tail cones and so on some other parts of the aircraft.

So, standard temperature that it is exposed to or it can easily withstand would be as high as 300 350 degree centigrade. The question was if you can actually pump in more air compress more air through the compressor and feed more air to the nozzle where the combustion is taking place, then the thrust you develop will be higher with higher thrust you actually can fly longer consuming the same volume of fuel.

So, in order to make the jet engine more efficient you would like to have a possibility where titanium compressor blades can withstand higher temperature, because during high ratio of compression the frictional temperature rise at the surface would be higher. So, we wanted not to change the titanium bulk, but alloy the surface with silicon, aluminum or silicon and aluminum.

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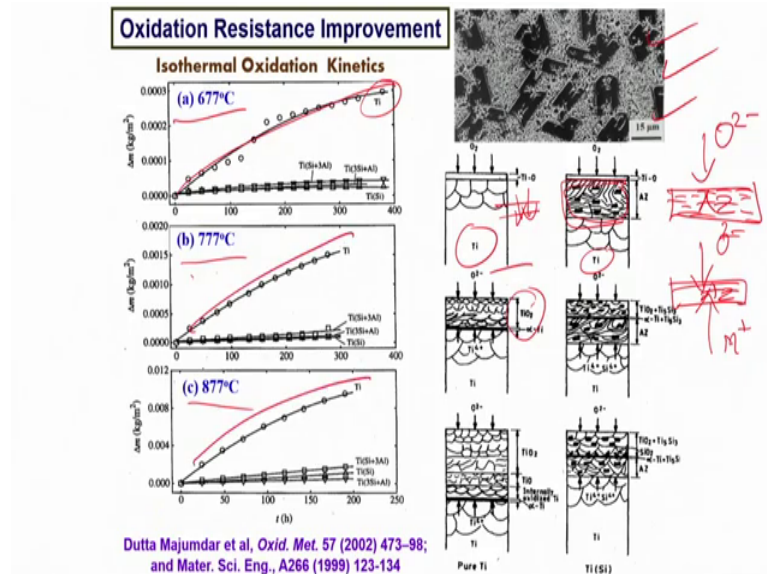
So, to cut the long story short, we were able to create such a hyper eutectic microstructure. So, typically you require so, much of alloying elements to create a hyper eutectic microstructure with Ti_5Si_3 as the primary phase. So, these are the faceted Ti_5Si_3 phases and this kind of an intermetallic phase has a very high congruent melting temperature and is fairly resistant to oxidation.

So, we create a surface which is about 30-40 percent covered with these faceted intermetallic phases and another 60 percent or so, also is coming because of the eutectic here. But the advantage is that we are able to create just with a few percent of silicon because if you refer to the corresponding T₀ concept and if you quench very fast.

Then and if you can go below the T₀ intersection point then you can retain an extended solid solution and so, in this case we did not retain an extended solid solution, we allowed phase separation in the form of eutectic, but then this eutectic point actually got shifted because of fast cooling.

So, instead of eutectic point at 11-12 percent the eutectic probably got shifted to hardly 3-4 percent. So, as a result with 5 or 6-7 percent titanium we silicon in titanium we were able to create a Ti_5Si_3 or hyper eutectic phase aggregate.

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And when we create such hyper eutectic phase agreement on the surface so, if this is pure titanium and this is titanium silicon alloyed zone what we see is that in case of pure titanium when you expose to temperatures like 677 say 400 or 500 or 600 degree centigrade, they merrily react with oxygen from that phosphorite high temperature and create titanium oxide layer which is fairly porous and non adherent and its falls off and exposes few titanium.

So, in the process this titanium substrate is lost increasingly because of this oxidation attack from the atmosphere at high temperature. Now instead of that if you create an alert zone like this kind of a micro structure. So, this micro structure has nearly 70- 80 percent of silicides and the remaining part is titanium. So, titanium does not see the atmospheric oxygen very easily the this surface because of this kind of an annoyed zone actually has 80 percent covered by this silicides which are very resistant to oxidation and this silicides actually cover up the rest of the titanium matrix to a large extent.

So, diffusion becomes diffusion of oxygen becomes very difficult for oxidation to proceed we know for oxidation or corrosion anything like this we know that this oxide layer needs to grow and this is possible by inward ingression of the cation from the atmosphere and outward diffusion of the cation from the substrate. So, if we prevent this cationic diffusion and anionic infusion ingression from the top by creating this kind of an alloyed zone, then the oxidation or corrosion is prevented here its high temperature

oxidation and that is exactly what happened. As a result of which what we see is that titanium, pure titanium will oxidize so, fast and too that such a large extent whereas, that alloyed zone will undergo practically negligible amount of oxidation.

So, you create a huge difference of oxidation resistance, you make the substrate highly oxidation resistant because of this kind of surface alloying.

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Points to ponder (recapitulation):

1. How does laser surface alloying (LSA) differ from bulk alloying or laser surface cladding (LSC)?
2. What are the main approaches of LSA?
3. Why is LSA mostly applicable to metallic alloys?
4. What are the main process parameters and advantages of LSA?
5. What are the characteristics of alloyed zone in terms of microstructure and composition?
6. Why can the phase aggregates be different in LSA than that in usual cast or wrought products?
7. How is AZ effective in improving resistance to wear, corrosion and oxidation?

So, let me try and conclude now. So, surface alloying actually is a very different strategy than bulk alloying or even cladding. Cladding you create a completely clad layer we will discuss that in future which is compositionally very different, but in case of alloying the composition if you are if this is an a large zone of B in A, then if you plot the percentage of B you will see a profile like this.

So, this is a very diffused interface. So, this is a alloyed zone and this is interfacial zone and this is the substrate. So, from alloyed zone to substrate the composition is not sharp like this which is the case in case of cladding in case of alloying you actually have a diffuse interface. So, the adherence and the bonding is much better. The main approaches could be based on co deposition or prior deposition, pre deposition.

It is mostly applicable to metallic alloys because they are they undergo complete melting and inter mixing in the liquid state whereas, oxides do not have easy liquefaction facility. The main process parameters just like any other laser processing will be the power

density and interaction time and of course, the location of the focus and the composition of the layer that you create and so on the alloying elements that you feed in.

We actually need a very thorough characterization of the microstructure and composition and the main advantage of laser surface alloying lies in the fact that we create a microstructure which is metastable which is different than equilibrium process microstructures, which actually gives us very many advantages like we saw in the few examples before. And this phase aggregate that we form will be different than a typical cast or wrought product because of this metastability of the microstructure deviation from the equilibrium processing.

So, the highly non equilibrium processing very fast cooling rate very high re solidification velocity thermal gradient and most importantly all very good convection driven intermixing in the alloyed zone within a very short period of time, induces all these advantages that we talked about and in the process we get huge advantages in terms of resistance to corrosion oxidation wear hardness and so on and so forth.

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So, we will stop here now and in the next lecture we will discuss the advantages of laser surface planning.

Thank you very much.