Surface Engineering for Corrosion and Wear Resistance Application
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Lecture – 40
Hot Dipping – II

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So, now in continuation to the Hot Dipping operation in part II we will discuss about hot dip galvanizing process that is specifically the Hot Dipping of zinc and its alloys.

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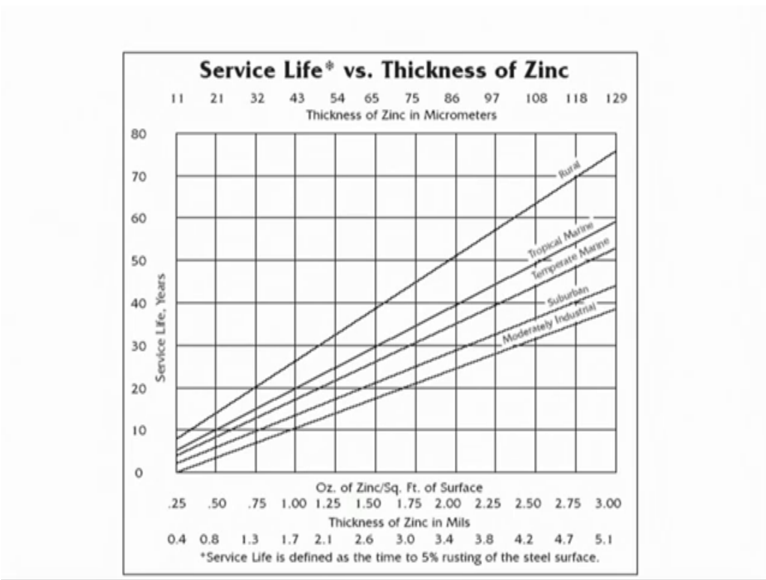

So, as I mentioned you that the hot dipping of zinc is very important and particularly for zinc deposition among most of the parallel techniques 75 percent of the industries they do look for coating by hot dipping technique. So, because of the biggest advantage of having the completely dense, pore free coating and very strong interface; now if you talk about an also very thick deposited layer. Now if you talk about the zinc coating thickness which is desired you will find that because of its application or application requirement or maybe the requirement of its surface in corrosive environment thicker the coating better is it service life.

So, service life changes from 5 years to as high as 80 years depending on the thickness. So, you will find that thickness is around 3; if you go on increasing the thickness from 0.25 mils to 3 mils the or maybe you can say that 10 micron to 120 micron 130 micron. The service life increases form 0 hour or maybe you can say that 1 year to as high as 80 years.

So, thickness of zinc is very important. So, that apart from the all the parallel techniques which are available for zinc deposition you will find that hot dip galvanizing offers the maximum thickness on the surface with strong interface. And, apart from that you will find spray deposition technique also offers very high thickness, but in spray deposition technique the interface is not really so, strong as in hot dipping and also there are few porosities or defects on the surface.

So, usually it is observed that hot dipping is preferred to spraying process for zinc deposition where you are looking for very large service life of the component. Now, if you talk about the service life of component you will find that it is certainly depends on the environment. See in the rural environment where if there is not much pollution, you will find that not much humidity, you will find that service life is higher than that of marine environment than that of high temperature marine environment than that of normal server born and then industrial environment.

In industrial environment you get minimum life time because of presence of lot of porosities in the environment better because, the presence of lot of different impurities in the environment and also different particles which are present in the environment and a lot of carbon soot sulfur dioxide these all particles are also present in the environment. So, those particles basically they get deposited on to the surface different materials and when they are deposited on the sub surface naturally the absorptivity of the surface increases.

So, we will find that surface will be more prone to absorb the moisture from the environment than that of the typical rural environment where there is not many impurities in the environment. So, as a result of which you will find that in industrial environment the service life of the component by corrosion is much lower than that of the same in rural environment.

So, you will find that the service life is basically the relative term, it depends on the environment where the component is used. But, whatever the environment may be as you go on increasing the thickness of the zinc coating you increase the service life to large extent.

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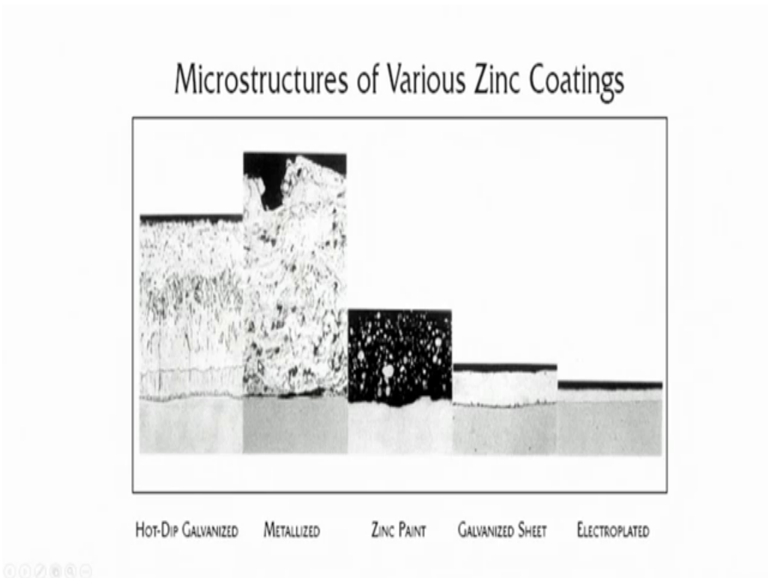

So, as I mentioned you among these all parallel techniques hot dipping offers are maximum thickness with a strong interface and apart from that the utilizing or thermal spraying load also offers a similar level of thickness, but its spraying technique the interface is not really so strong as in hot dipping. At the interface there is always mechanical interlocking or maybe the interface is basically not there is no inter diffusion layer at the interface, but mechanism of bonding is interlocking mechanical interlocking.

And lot of porosities and defects are there in the coated layer when you develop it by thermal spray deposition technique, but you get similar level of thickness, but surface is also quite rough. When you talk about up about other parallel techniques those are like painting technique, in painting you can have the zinc dispersed zinc as dispersed particle. So, there you will find that paint layer again gives the very poor interfacial bonding, but thickness is also very low not really so high as in hot dipping and also there are lot of defects in the paint layer.

Then finally, galvanized sheet if you see galvanized sheet is also galvanizing is also mechanical or maybe you can say that mechanical cladding is also another way of zinc coating. So, where you basically take zinc sheet and steal sheet together and then go on cladding it over each other by application of mechanical force. There is always a thickness limitation because if it is too thick then there will be problem of non uniformity. So, thickness is limited and interface is also very strong, but as strong as the this thermal spray deposition it is not really so strong as in hot dip galvanizing.

Now, another parallel road by which you can do zinc coating is by electro deposition process. So, here the thickness is a major trouble you cannot go beyond certain thickness may be 20 to 25 micron is the maximum thickness that you can achieve when you go for electro deposition and interface is also not so strong. So, if you talk about different parallel techniques you will find that so many techniques are available. So, depending on the applications you have to look for the technique which you should opt for.

So, when you are looking for the zinc coating for mild environment where the component shape is very much very much complicated in nature and you are interested to have very nice polishing fine polishing on the surface. You go for electro deposition when you talk about the galvanizing for utilities and furniture purpose there you can go for this clad modeling operation in long structures like bridges, you can go for painting operation or thermal spraying operation, in batch component where dimension is also not so weak, but medium sized dimension you can go for hot dipping operation by continuous processing.

So, depending on the applications where you are looking for the coating you can have you can choose different coating techniques, but it is important that you choose proper coating technique and proper parameters to have the desired result in the coated product or desired properties of the coated product.

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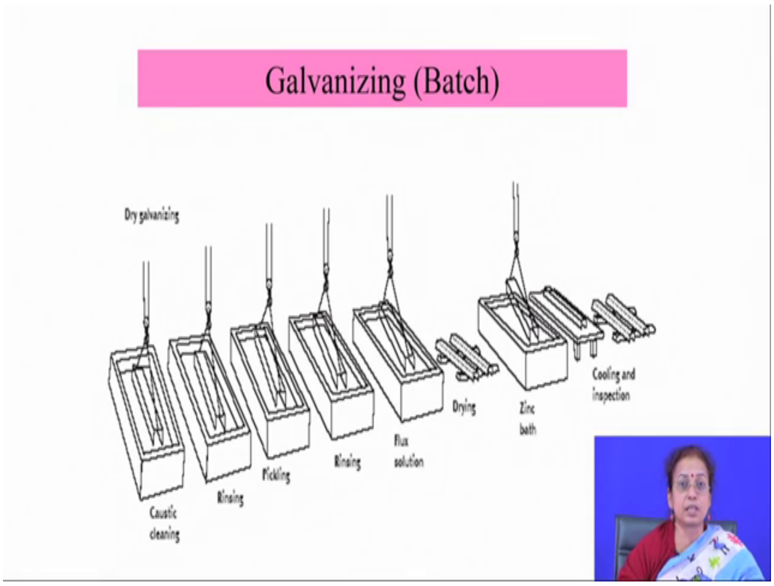

Now if you talk about hot dip galvanizing then you will find as you mentioned you in the other case here also the surface finishing is the or surface cleaning is the mandatory step which you which you should follow prior to hot dip galvanizing.

So, what you do is that, you basically go for several steps of cleaning like when there are there are dot particles or dust on the surface you go for caustic cleaning and then rinsing and if you have then lot of oxide layer on the surface you should go for pickling operation showing pickling you basically take 3 to 5 percent hydrochloric acid solution and temperature is 35 to 40 degree Celsius. So, you dip the component in the picral reagent for one we need 2 minute maximum and then you take it out and then go for rinsing operation.

And then your surface is cleaned and prior to hot dipping you can go for flux solution dipping hm. So, that your surface is no more oxidized prior to your zinc coating and go for drying operation, then go for zinc coating and then you go for cooling and inspection and dispatch the component. So, these are the steps which are followed and this is a kind of batch processing and you can also make it a continuous processing by typical having this kind of arrangement where you have the cleaning section, direct fire section and hot dipping section and withdrawer section, they are kept one after another.

So, what you do is that in cleaning section you basically clean it by different techniques like solvent cleaning or pickling or drying these all techniques and then you can go for fluxing operation and then you go for hot dipping and then finally, by jet finishing nozzle you just go on finishing and monitor the thickness and then you can go for galvannealing operation in the furnace. So, this is the hot dip galvanizing process that continuous processing.

So, now, one of the biggest advantage of the hot dipping is that that in the hot dipping you get completely dense coating its not you do not really get many defects on the surface of the coating except the spangle formations and different design designing is there and micro structural segregation. So, apart from those techniques apparently those defects apparently there is not many significant defects observed in the hot dipped coking actually.

So, it is very interesting way of depositing on the surface of metallic materials which can offer very good corrosion resistance property.

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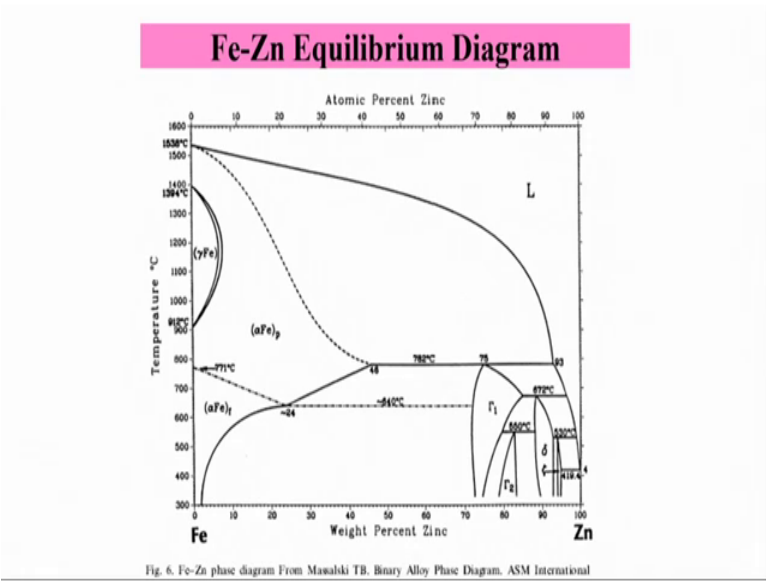

But one of the biggest disadvantage is that the interface, though interface is strong, but if you see the interface carefully you will find that at the interface there are several intermetallic clear formation. So, those intermetallics are highly brittle in nature. So, that brittleness of the intermetallic in the iron zinc system creates problem for applications or its applications, if it is pure iron zinc pure zinc coating if you talk about.

So, you find that if you just quickly go through the iron zinc interface you will find that at the interface there are this is a zinc rich corner because usually when you dip the iron reached component or iron based component in molten zinc usually there is dissolution of iron from the surface and that dissolved iron basically mixes with zinc and then forms different intermetallics.

So, you have to see the phase diagram from the zinc chris side. So, you will find that from the iron inside there are different intermetallics which might form like gamma 1, gamma 2 that then delta phase is zeta phase and then pure zinc onto the top with iron in solution. So, these are the different intermetallics which can form at the interface starting from the interface actually. So, these all intermetallics are not yet I mean they are very much a brittle in nature most of the intermetallics.

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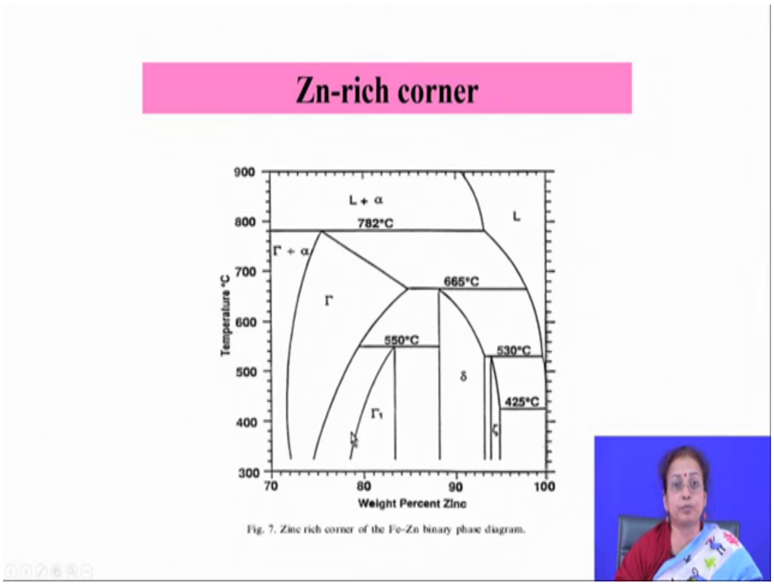

So, when you keep the iron zinc coated particularly galvanized component in the normal environment you will find that there is formation of fine cracks after a long time hm. So, these cracks are because of this all different intermetallics as I mentioned you which are found.

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Table 1
Fe–Zn phase characteristics.

Phases	Formula	Crystal structure	VHN (25 mg) [20]	VHN (25 g) [27]
αFe	Fe(Zn)	BCC	104	86
Γ	Fe_3Zn10	BCC	326	-
Γ_1	Fe_5Zn_{21}	FCC	505	-
δ	$FeZn_{10}$	Hexagonal	358	273
ζ	$FeZn_{13}$	Monoclinic	208	118
ηZn	Zn(Fe)	HCP	52	41

And, if you just quickly go through the intermetallics you will find that they are having the typical HCP structure, monoclinic structure, FCC, BCC structures, even though there are BCC structures, but they are also not really show ductile as is normal it is FCC.

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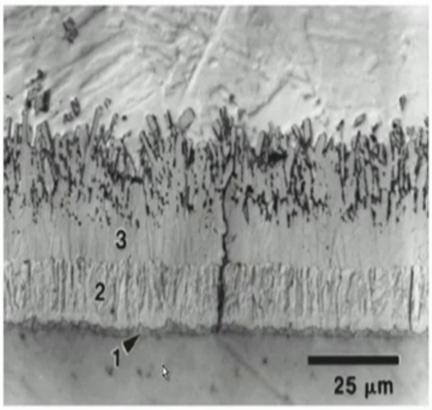

Fig. 8. Microstructure of Zn coating formed after 300 s immersion in a 450°C, 0.00 wt% Al bath on a ULC steel substrate. (1) gamma (Γ) phase, (2) delta (δ) phase (3) zeta (ζ) phase.

So, these all phases form one after another. And these all phases because of formation of these all phases you will find that when you keep the galvanized steel for a long time in normal environment there is formation of fine crack starting from the interface towards the surface. So, fine cracks are not good because it basically creates a path for the transportation of water molecules from the environment, but still it is acceptable as because of the fact that zinc also saves the surface by the process of the sacrificial action.

So, even though there are phrases there are possibilities of formation of lot of intermetallics at the interface and which are brittle in nature the presence of whom actually creates trouble because the presence of whom actually can cause crack formation at the interface, but still as it is zinc coating it can it is acceptable because zinc coating offers the sacrificial action to save the underlying substrate.

So, even though there is that this all cracks formation on the at the interface, but still you will find that as zinc is there on the surface. So, zinc basically preference any corrodes and by that process the steel is saved underlined steel is saved, but again even though that is there, but steel you will find that the overall lifetime of the component gets reduced. So, whatever the fact maybe even though the steel substrate is saved, but still you cannot really allow the this kind of degradation to occur or maybe you cannot allow these kind of defects to form at the interface because it deteriorates the overall service life of the component.

So, when you talk about reducing this particular when you talk about that saving the component by proper way what you go for is that you have to look for typical different ways to combat this kind of intermetallic formation. Usually people go for allowing with aluminium they do go for allowing with different other metals as well in order to reduce the kinetics of the iron zinc intermetallic formation, they also go for annealing operation to homogenize the microstructure.

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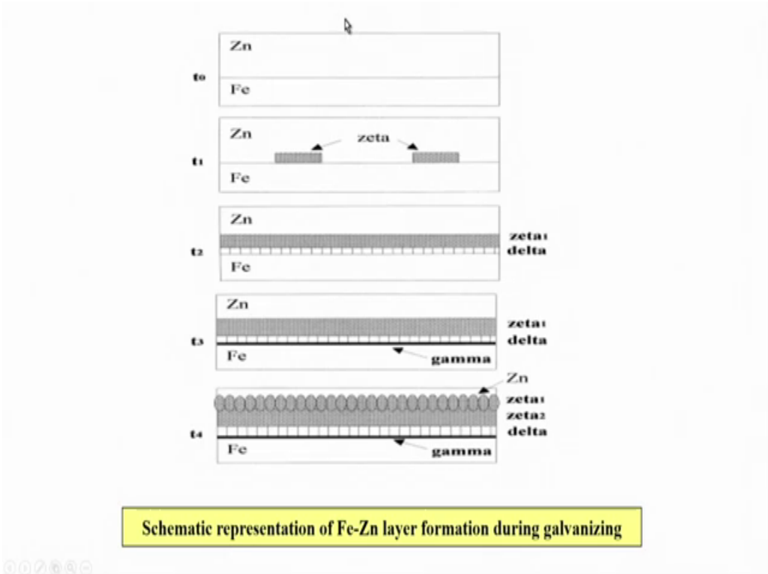

So, now, this is a slide which shows you the schematic of the intermetallic formation with time. So, when time is very short then if you just keep iron in zinc molten zinc you will find there is no intermetallic, but gradually there is formation of intermetallic. And the first intermetallic which forms is the basically eta phase and then as you go on increasing the time you will find that there is delta delta phase formation zeta transforms to zeta prime or is it a 1 phase and then gradually there is formation of zeta 1 and zeta 2 and gamma phase also at the interface.

So, finally, you will find the gamma phase at the interface followed by which there is delta phase then zeta 2 zeta 1 and then finally, zinc with Tyrone in solution and pure zinc. So, these are the different intermetallic phase formation sequence when you dip the iron based alloying into the molten zinc.

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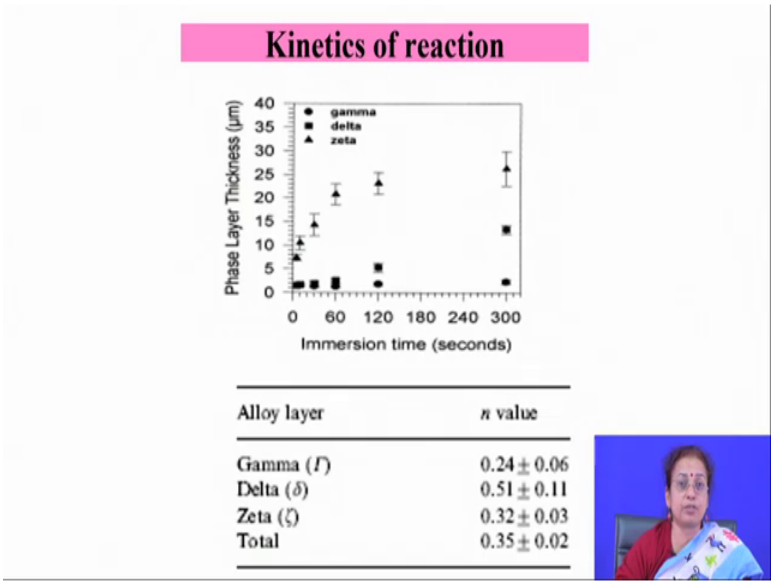

So if you see the kinetics of the different phase formation you will find that they are having different kinetics like for example, if you talk about gamma phase kinetics. So, this is actually it is slowest. So, you will find that gamma phase forms at a much slower rate than that of the delta phase and that of the zeta phase.

So, if you see the and then from the layer growth itself you can say that gamma phase kinetics is quite clear. So, it is there at the interface, but zeta and delta phase formation kinetics is quite high so, they form at a much faster rate. So, the kinetics of different phase formation is also equally important they are having different tin values.

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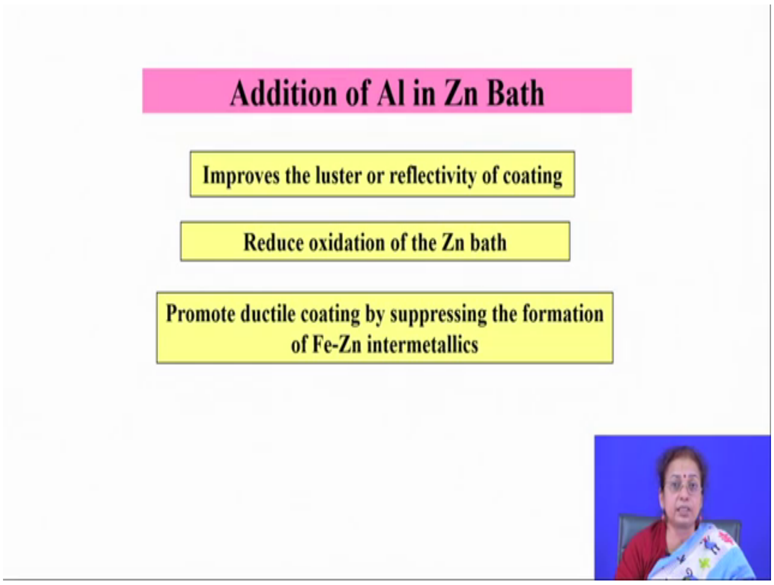

So, if you are interested to get rid of the intermetallics as I mentioned you have to add some ternary elements into the molten zinc bath. So, usually aluminium is a very popular ternary element which is added in the molten zinc in order to reduce the kinetics of this intermetallic formation.

So, if you add aluminium naturally it serves several purposes first of all aluminium includes the oxidation resistance of this bath, second purpose which is served is that there is formation of iron aluminium intermetallic at the interface as a result of which the zinc cannot form any kind of intermetallic with iron.

So, it prevents the formation of iron zinc intermetallics by forming a very thin layer of iron aluminate on the surface and third purpose which it solves is that it promotes that typical it increases the luster of the coating actually. So, because aluminium whenever you add aluminium we will find that coating is highly lusters. So, usually in code zinc bath very low percentage of aluminium up to 1 percent is added which basically serves these all purposes. So, you will find that the iron zinc intermetallic formation kinetics is reduced.

But apart from 1 percent aluminium there are also two more aluminium percentage which are added in the zinc bath by changing the composition itself one is 5 percent aluminium another one is 55 percent aluminium which are called Galfan bath and Galvalume bath.

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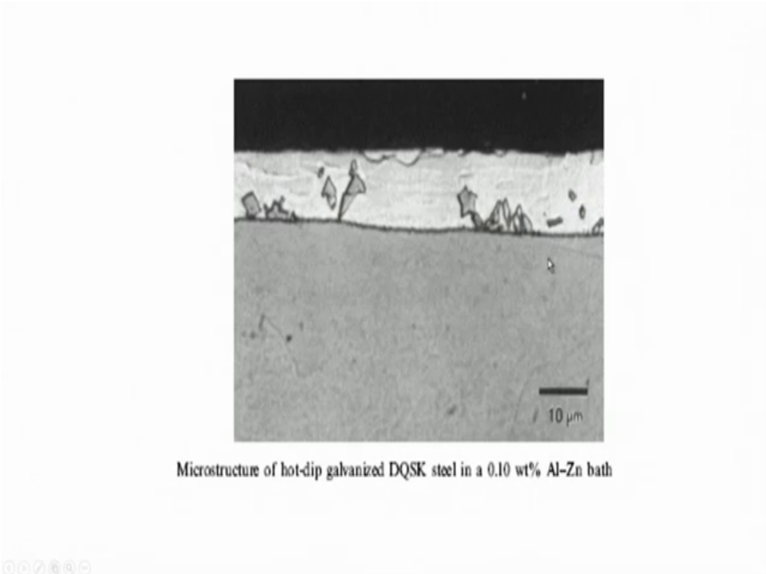

So, in case of the case in the case where you have a normal galvanizing with 0.1percent aluminium we will find that intermetallic formation is partly reduced you will find on the surface there is zinc coating and at the interface there is F e 2 AL 5 phase and the thick monolithic intermetallic formation is reduced.

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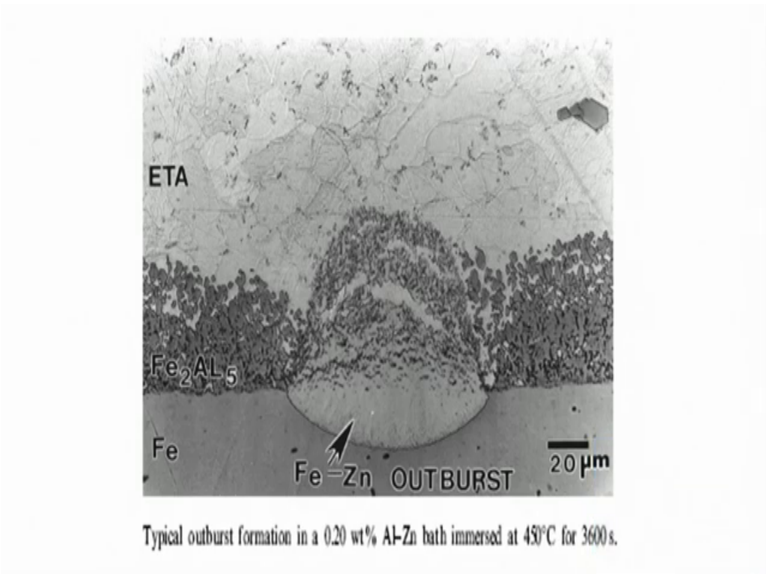

So, for example, this is the case of 0.2 percent aluminium percentage galvanized coated microstructure here you will find that at the interface there is F e 2 AL 5 phase formation. So, these phase actually as I mentioned you it reduces the kinetics of F e zinc intermetallic formation, but as the aluminium content is quite less you will find that if you do not really control the time carefully you would see that there is the failure of the coating in a very large extent basically; so, it is called outburst formation.

So, outburst formation is one of the biggest trouble associated with iron zinc associated with the galvanizing where you have very low percentage of aluminium. So, aluminium percent is quite low so, 0.2 percent. So, if time is very less there is no problem, there is F e 2 AL 5 first formation on top of that there is molten zinc actually with Tyrone solution.

But if your time is quite high what happens is that because of large time which is available there is that molten metal diffusion through the inter columnar porosities of the F e 2 AL 5 layer and that molten zinc actually can go inside the iron through grain boundaries and then for creates form presence of or be may be it forms different types of intermetallics at the grain boundary regions.

So, you will find that there is local change in the concentration of the zinc as a result of which local formation of iron zinc intermetallics that iron zinc intermetallics creates trouble because it applies pressure and as a result of which after a while there is over breakage of the F e 2 AL 5 layer which is called outburst formation hm. So, outburst formation is never desired because not only it basically breaks the F e 2 AL 5 layer, but it can also apply such a high pressure that your coating can also spore out.

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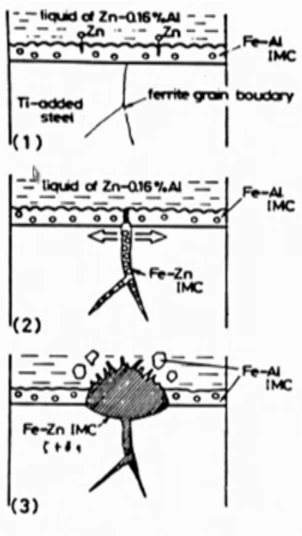

Schematic diagram showing the Fe-Zn outburst growth behavior.

So, this is the typical mechanism of outburst formation which is shown here. So, usually if aluminium percentage is quite low like 0.5 percent if you dip it for 0.5 minutes; for example, when there is no chance of diffusion of the zinc there is no trouble. But if you allow more time what would happen is that zinc will go on diffusing through the grain boundaries of the iron aluminate interface and which grain boundaries actually match with the grain boundaries in alpha or maybe alpha phase. So, what happens is that this particular zinc gets diffuse tin.

And when it diffuse tin through the grain boundaries naturally there is always chemical potential difference along the grain boundaries and the between the gain boundaries and inside grain as a result of which zinc again goes on diffusing from grain boundary to the grains and there is intermetallic. Wherever there is diffusion of zinc it reacts with iron and there is iron zinc intermetallic formation.

So, intermetallic formations are there at the interface over there as well as intermatellic formations are there along the grain boundaries. So, gradually there will be highly applied pressure on the grain boundary regions and this particular intermetallic grows on the surface. So, after a while you will find that it applies lot of pressure. So, when you just go on taking it out you will find that the iron zinc coating basically spores out.

So, you have to be very much careful and control the time carefully. So, that there is no chance of outburst formation.

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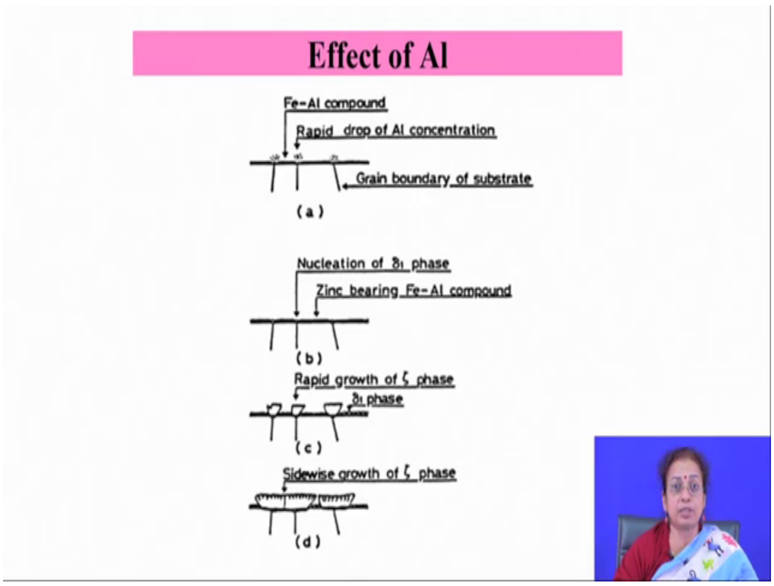

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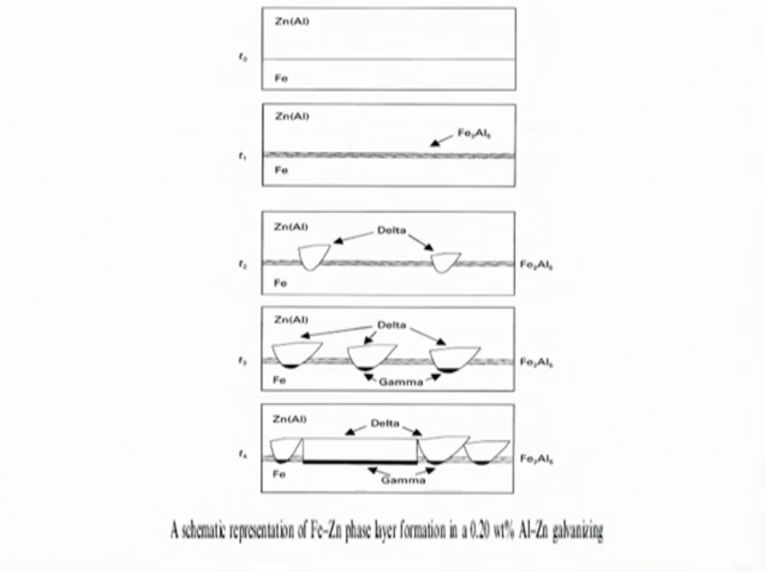

Otherwise you apply some more aluminium in the coated layer so, that there is no possibility of the outburst formation at the surface.

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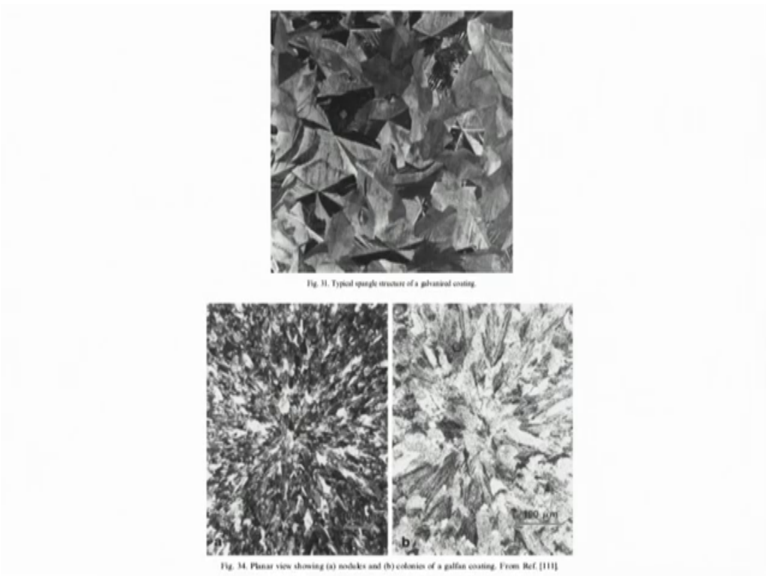

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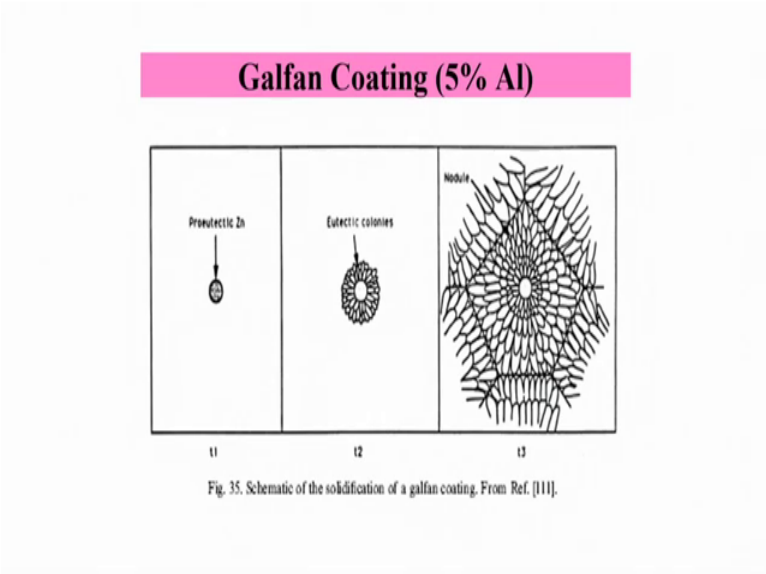

So, in order to prevent that outburst for adverse formation or maybe in order to improve the quality of the zinc coating further galvanized coating further you can have two more solution; one is Galfan coating where you add 5 percent aluminium in the coated layer.

So, when you use 5 percent aluminium in zinc that is typical eutectic composition. So, what happens is that there is typical eutectic columns of iron and aluminium and zinc formation. So, you will find that as aluminium percentage is quite high the outburst formation the time can be increased or maybe threshold time for outburst formation start can be enhanced.

So, you have enough time for the galvanizing to do and on the other hand another advantage of this the Galfan coating is that in the microstructure you will get typical eutectic microstructure which offers higher strength. So, in this kind of coating you get bit superior strength, you get good corrosion resistance property, in addition to that you avoid the formation of the outburst because here aluminium percentage is very high. So, at this aluminium percentage if you are interested to form that outburst naturally you have to wait for some more time.

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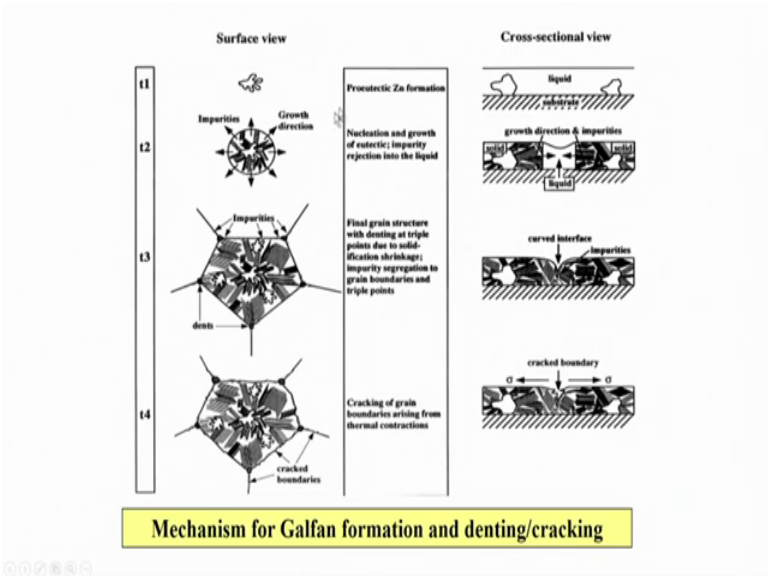

, but one of the biggest advantage of these hot dip Galfaning is that or maybe where you use Galfan as a bath or 5 percent aluminium as the bath there is dent formation at the interface basically. So, this is because of the fact that when you go on solidifying it that at the middle layer there is still liquid because it is the eutectic composition, so, temperature is quite low.

So, if you think of solidification process you will find that all other layers solidifies, but last layer where it is still in liquid state it gets contracted because of solidification shrinkage and they will be formation of the difficult dent mark on the in the middle of the Galfan coated components hm. So, there you have to put some extra liquid. So, that this problem is this problem is probability of this tin information can be minimized.

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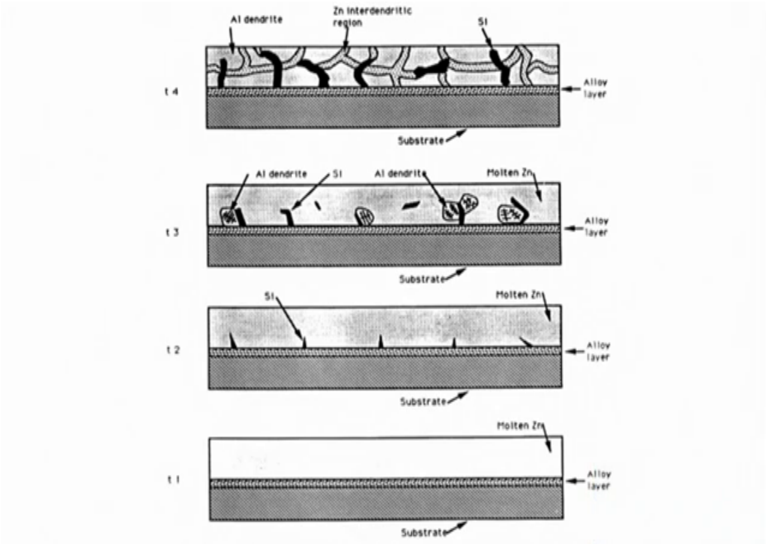

Fig. 40. Schematic of the solidification of galvalume, $t_1 < t_2 < t_3 < t_4$. From Ref. [111].

So, another coating composition in Galfan where you use 55 percent aluminium; so, as you are using 55 percent of aluminium it is always better this is typical hyper eutectic composition. So, you will find typical primary dendrites of the primary dendrites of typical aluminium in aluminium zinc intermetallics, but here you have to add a little bit of silicon because if you do not add silicon then naturally the fluidity of the bath will be quite low.

So, usually 1 to 2 percent silicon is added. So, if you add this silicon naturally fluidity increases, but on the other hand there is also the silicon whisker formation at the interface. So, this problem is always there, but it is to some extent beneficial because, when you have these whiskers of tin naturally so, whiskers of silicon naturally. It can also improve the strength of the bond strength of the coating to a large extent and from that whisker itself there is a microstructure development when you do solidification processing when it is solidified actually.

And at the interface there is F e 2 AL 5 layer formation which is actually quite thick and the possibility of outbursting is also minimized.

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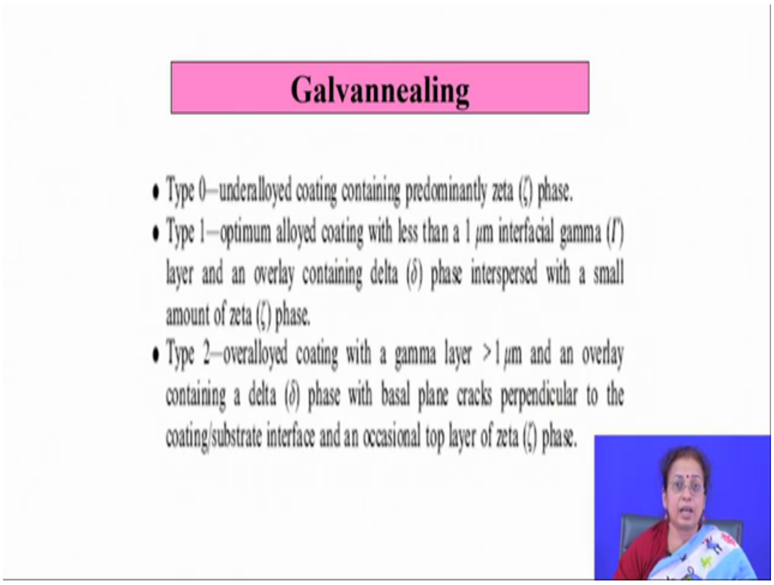

So, as I mentioned you that these are the three important ways by which you do galvanizing process and each and every step is having each and every each and every process or bath is having its own advantages and disadvantages and also there is lot of cost associated with aluminium addition.

So, if you add aluminium to a large extent the temperature of operation goes high and that is also the bath also maintenance of the fluidity of the bath can have the you have to take proper precaution to do that these all problems are always there. But again some of the advantages you get which is not possible to achieve by the single step normal single galvanizing process.

So, another way of typical reducing the possibility of the stress which are a possibility of the relieving the stress or maybe minimizing the possibility of this (Refer Time: 29:39) formation is by galvannealing operation. So, galvannealing operation is nothing, but after galvanizing you go for typical annealing operation. So, there are three types of galvannealing process one is type 0 which is applied for underalloyed coating containing predominantly zeta phase where time is quite less.

So, where you do not get any other phase, but only zeta phase and type 1 galvannealing which you apply for those case where optimum alloy coating is there less than 1 micron interfacial gamma layer. And an overlaid coating of delta phase interdispersed intersperesed with small amount of zeta phase and overalloyed coating which you have very thick gamma layer and an overalloyed coating containing delta phase and basal plane cracks perpendicular to the coating substrate interface.

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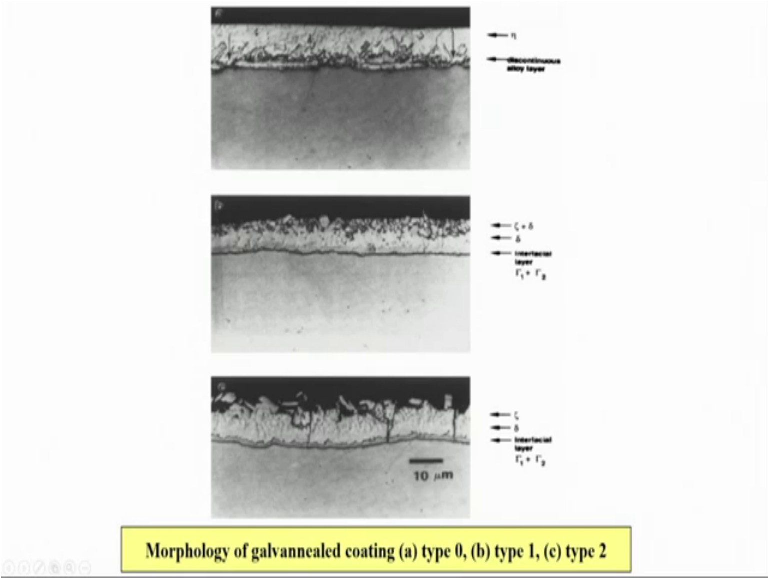

So, in all coating in all galvannealing you will find that this is type 0 galvanizing, type 1 galvanizing and type 2 galvanizing. So, here you will find that in all cases what you do is that you basically change the time of the annealing operation. So, time of galvannealing is temperature of galvannealing usually from 600 to 650 degree Celsius and depending on the alloy which you are using your time also changes.

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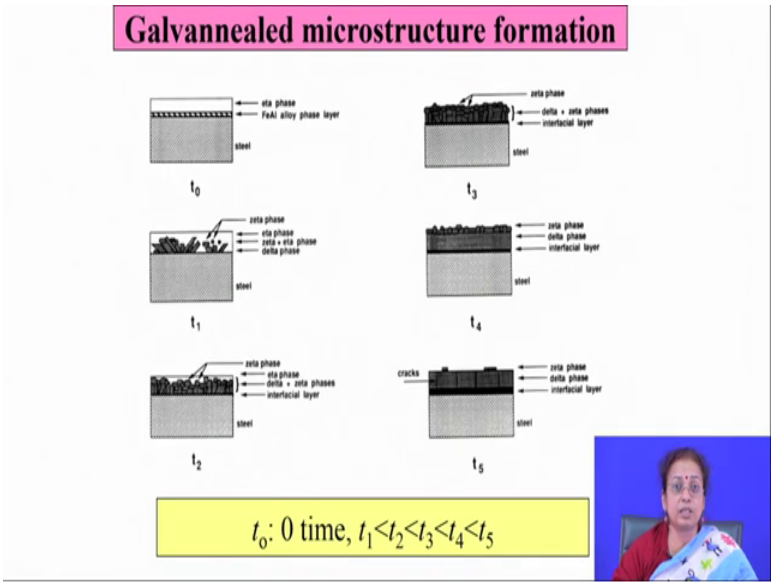

So, with optimum timing you can have the typical based microstructure which is consisting of for example, at the end of the galvannealing you can have the microstructure containing zeta phase on the top, then delta phase in the middle and the interfacial layer very thin interfacial layer hm.

So, this is nothing, but typical annealing operation to homogenize the microstructure and also to release the stress which is developed in the galvannealing process which is developed by galvanizing process.

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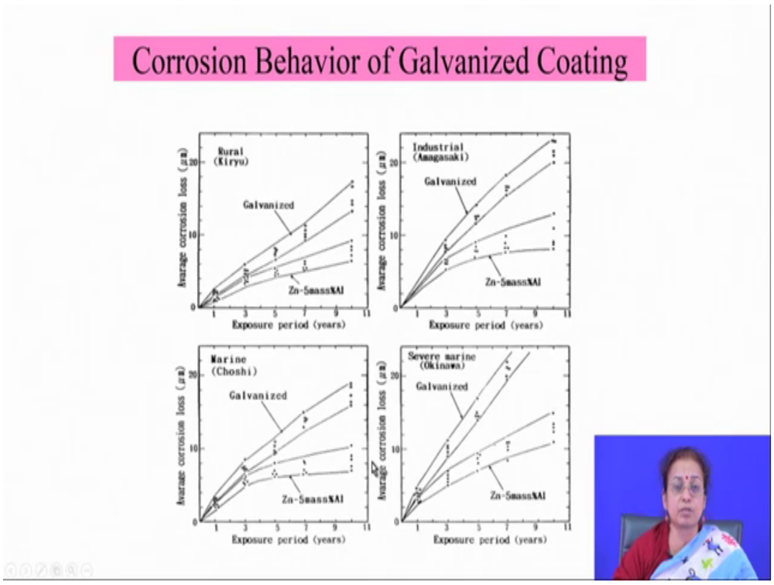

Now, if you talk about the difficult corrosion rate or maybe lifetime of different coated product, you will find that by addition of the aluminium your corrosion loss average corrosion loss is reduced to a large extent. So, aluminium addition is very good because its not only reduces the possibility of the intermetallic formation at the interface, but it also reduces the possibility of typical it also reduces the possibility of reduces the corrosion loss to a large extent hm.

So, its very important that you do add aluminium and you apply Galfan bath where your service environment is quite hectic in terms of the environmental species like severe marine environment or in marine environment.

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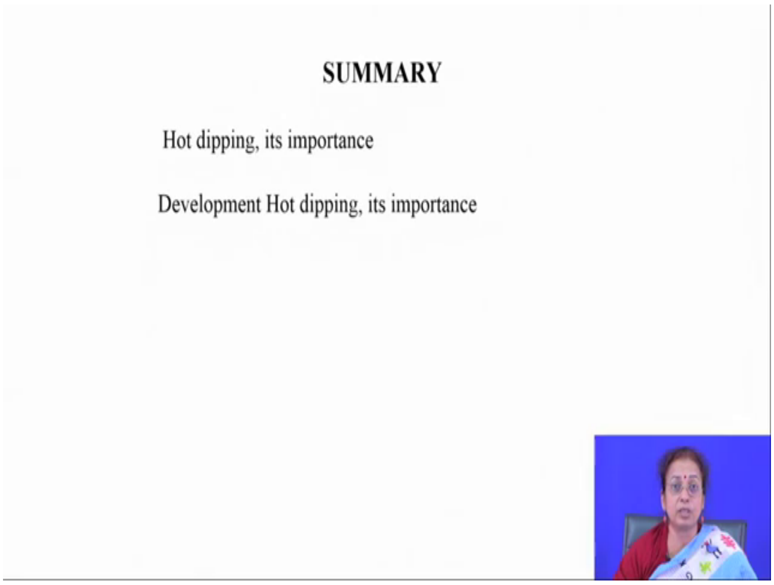

So, in brief we can say that in this particular talk we discussed about the hot dip galvanizing process and its the importance particularly the importance of using different baths in hot dipping operation like Galfan and Galvalume bath.

And also the galvannealing operation which is very important and steel one research work is going on to minimize the typical intermetallic formation by addition of different ternary element like aluminium silicon copper titanium. So, effect of those elements are also being studied to a large extent.

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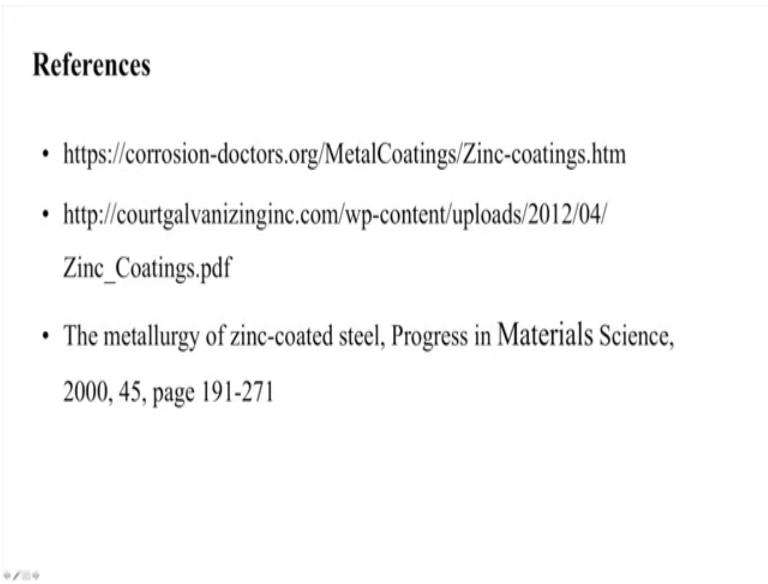

And finally, you do optimize the process parameters for galvannealing operation. So, that you get the desired result you get the desired homogeneous microstructure with minimum stress level in the coated product.

Thank you very much.