**Advanced Materials and Processes**
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**Lecture – 54**
**Advanced Processess (Contd.)**

Welcome to NPTEL. Myself Dr. Jayanta Das from Department of Metallurgical and Materials Engineering IIT, Kharagpur. I will be teaching you Advanced Materials and Processes.

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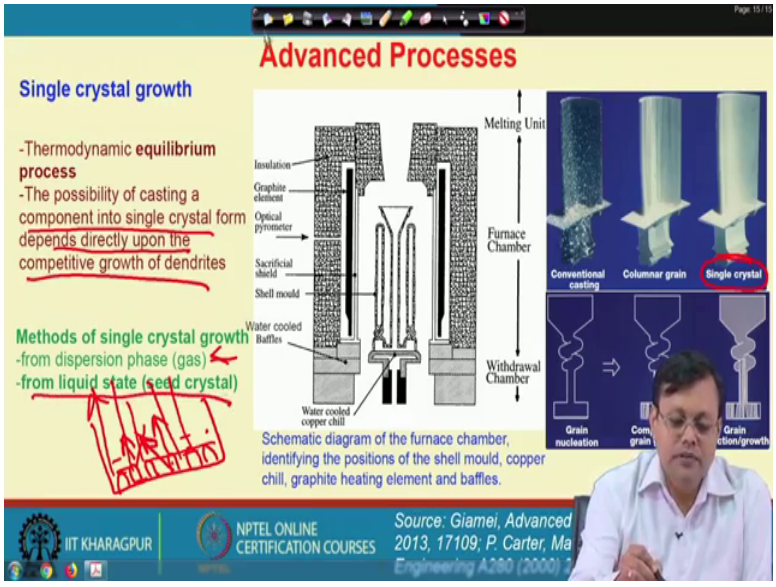


So, today we will discuss about the various technique to process advanced material from the liquid state. So, let us begin with the process that involve close to the equilibrium process. A close to equilibrium process means the temperature that drops in the liquid infinitesimally small, very very small and it is a thermodynamically close to a equilibrium process that is a crystal growth process.

In that particular process, we can get a possibility of producing a component or a single crystal form depending directly upon the competitive growth of different dendrites. What I want to mean, if I have a container that has some liquid and let us say near one of the surface the growth will begin. So, let us say these are different dendrites that would like to grow and along a direction preferentially to the easy growth direction.

Now, if any generate form along any other orientation, since they are growth velocity is less. So, the one which has a easier growth direction they will simply stop the growth. So, only few of these drain right which are aligned to a particular direction will allow to grow. Now, we have discussed about a super alloy blade, nickel based super alloys blade and we have seen that the single crystal blade is much superior in case of application at elevated temperature because the creep is also very less because there is less presence of the grain boundary.

Now, the method for producing such a single crystal growth, we can start from a gaseous phase means I have atoms or molecule that are kept in a gaseous phase and we allow in a colder region where the gas will go contact with the substrate and deposit. So, it will cause some sort of epitaxial growth. So, also we can grow some films of some magnetic materials.

Now, from the liquid state we basically need assistance of some seed crystal that we have we have already talked about during the discussion of nickel based super alloy. So, we take a seed crystal and there is a grain nucleation will occur at the surface and these grains will grow and few of the grains will basically grow through this channel and since the growth has a direction we can use a spiral feature of those where the liquid is present. So, the mechanically the growth of the different grains will be blocked. This is and then at the end we will have only one grain that is growing, ok. So, that is why we get such a single crystal.

Now, what we need to grow? So, let us say we basically need a water cooled copper chill and initially we have a shell mould that is produced this is a shell casting method and let us say like a like a zirconium oxide mixed with some silicate which produces this cell and then we can pour the liquid through here and then it basically allowed to grow and we drag these to a bottom side and we have a insulation here and these are the graphite heating element optical pyrometer just to sense how much temperature and sacrificial shield is given to the outer side.

So, this is the furnace chamber part and melting unit and withdrawal chamber let us say here. So, we simply drag these to down side and so, constant temperature is maintained here very slowly we drag it down so that the crystal can grow. So, this is a typical process of such kind of crystal growth technique.

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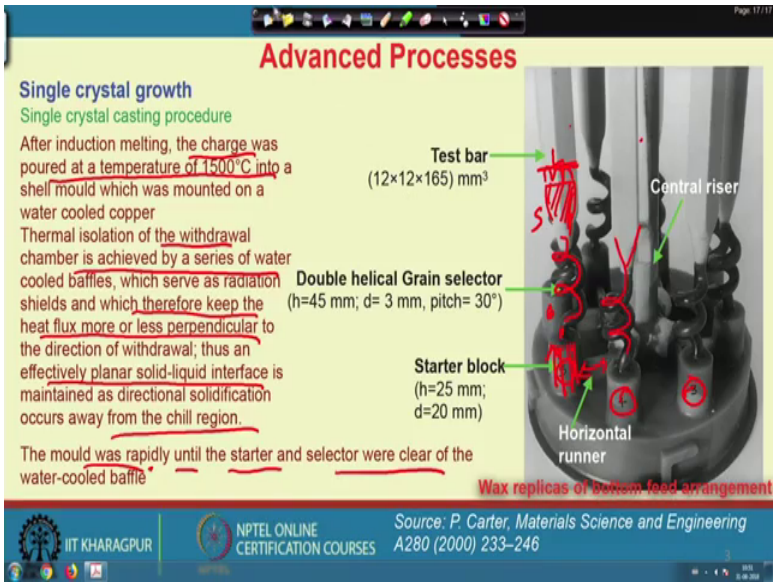


However, for a single crystal casting procedure, I show you once again the process. So, here these are the horizontal runners that are linked with the bottom side of this individual seed crystal and then mechanically the grains are blocked here and then ultimately we get only one grain that will grow.

So, after basically induction melting in this process, the charge was poured at a temperature to a very high temperature like 1500 degree centigrade and we are mostly talking about let us say in case of some super alloys and shell mould was mounted on a water cooled copper and thermal isolation of the withdrawal chamber that is achieved by a series of water cooled baffles and which serve as a radiation shield and therefore, keep the heat flux more or less perpendicular to the direction of the withdrawal thus a effectively planar solid liquid interface is maintained.

And, planar solid liquid interface means that the liquid is present here and let us say the solid is present here. So, this is like a single grain that is growing. So, if you have multiple dendrite then you do not have a planar solid liquid interface. So, only if one grain grows then only you will get a get a planar solid liquid interface and maintain at a directional solidification from the chili region.

The mould is rap the mould was rapidly until the starter and selector to clear the water cool baffle. So, we have the starter block. So, there are multiple starter block we can start with and multiple casting we can make using the same and these are just like a helical

grain selector because multiple grain will grow from the bottom side and they will be mechanically block through this spiral, that is basically the intention and this is just a wax replica of the bottom feed arrangement that is shown here.

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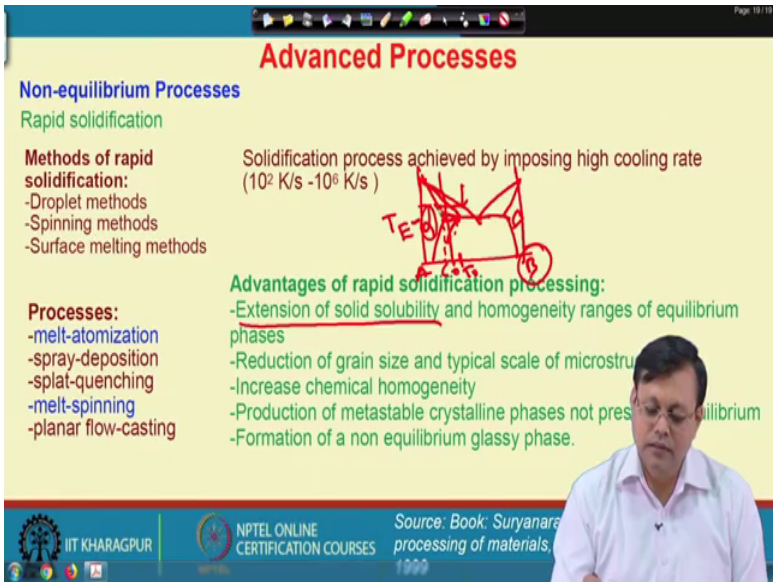


Now, in case of a rapid solidification process, the name itself says that the it is a non-equilibrium process and the cooling rate is an obtained for a specific material to be produced is very high. So, these high means the cooling rate varies between 10 to the power 2 means a 100 Kelvin per second to 10 to the power 6 Kelvin per second.

So, these are the two extreme end which is almost defined as a for a rapid solidification. So, let us say if I take a copper mould and if I inject a liquid in a copper mold of let us say 2 millimeter or 3 millimeter diameter then it is expected that the cooling rate should reach up to 100 Kelvin per second, but if we simply inject the same liquid on a rotating copper wheel and produce 60 to 100 micrometer thin ribbon then expected that the cooling rate will be 10 to the power 6 Kelvin per second. There is always some methodology how to estimate those cooling rate and so on. We will discuss slowly with those processes.

However, if we think about the method of rapid solidification process we can start with a liquid and we can end up with very fine powders, and this is like a droplet method. Means a liquid droplet will fall and then they will solidify during the process this is a very old turbine Turnbull's process Turnbull's experiment in US and the spinning method

that I have said that a liquid is injected on a rotating wheel and the very thin ribbon will be will be will be produced.

So, this is like a spinning, on the other hand I can have a bulk solid and I can make a localized melting by some electron beam and the rest of the material will act as a sink. So, it will also chill the melted pool inside that material. So, this is like a surface melting method. So, that can also be a rapid solidification process.

Now, the typical process involved like a melt-atomization which is one of the droplet method like spray-deposition on a surface or splat-quenching and melt-spinning is a technique that is called as a spinning method or let us say the planar flow-casting is also a spinning method. However, there are several benefit of these rapid solidification processes.

The first important of importance of the rapid solidification processing is that we can get a extension of the solid solubility what does it mean? I have probably explained you earlier, if I think about a eutectic phase diagram a simple eutectic phase diagram containing alpha and beta here at this T eutectic temperature the maximum solid solubility is let us C 0 containing A and B constituent elements.

Now, component and here if we rapidly cool a liquid very close to it or little bit higher B reach then also will be able to produce this alpha. So, there are thermodynamic explanation which will be covered in the next class, but we can extend this solid solubility from C 0 to a T naught curve actually. So, we call it as T naught curve.

So, at the same time we can avoid segregation because segregation required diffusion of atoms and if we slowly cool it then inside a grain and grain boundary there could be segregation of the atom. Because the residual melt which at the last liquid they will have a different composition then the initial.

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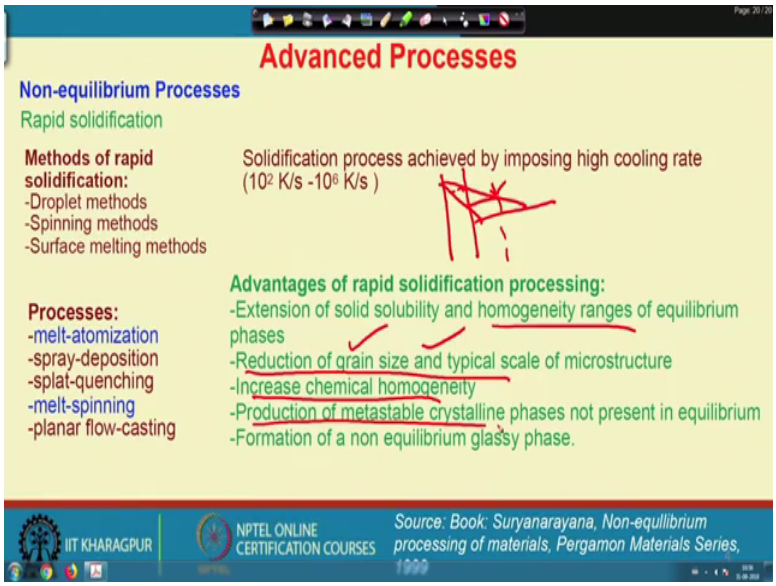


So, what I want to mean that, if I am solidifying a composition which has such a composition so, so here this is the last liquid which has a composition of this right and here this is the initial composition of the solid. So, we will automatically produce some compositional difference during solidification even inside a dendrite. And, therefore, we can avoid such kind of heterogeneity in case of composition and we can we can increase the homogeneity range of the non-equilibrium or equilibrium phrases.

Now, it is for sure that, higher cooling rate promote a higher nucleation site. If we increase more nucleation site means I am refining the microstructure. So, we can get a reduction in the grain size and if the cooling rate is very fast then diffusion will be slower, so grain growth will be slower. In that case we can reduce a gain size than the typical conventional equilibrium microstructure.

Chemical homogeneity can be increased and production of metastable crystalline phases that are not present in the equilibrium and formation of a non-equilibrium glassy phase that can be also produced that we have already discussed in the classes where we have discussed bulk metallic glasses.

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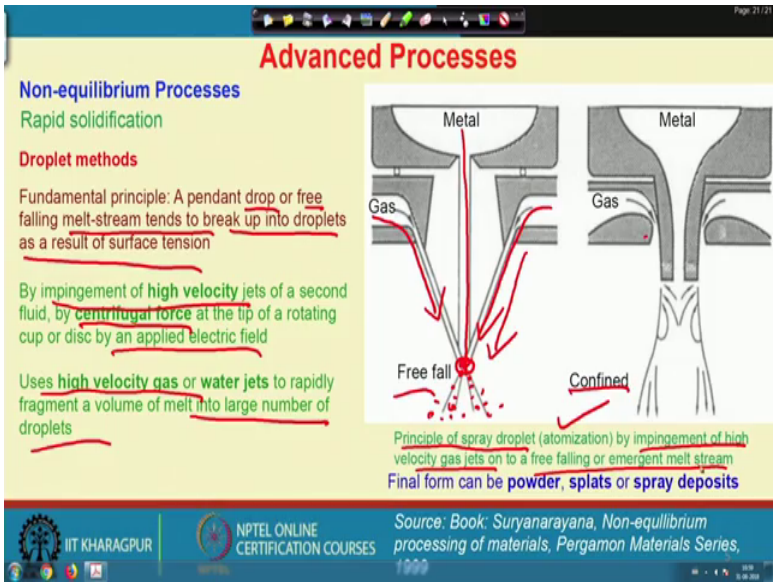


Now, in case of this rapid solidification we will start with a typical droplet method. So, droplet method means like a spray forming or where we can produce powder directly solid powder directly from a liquid metal. In that particular droplet method the fundamental principle is that a drop or a free falling melt stream tend to break up into a droplet as a result of a surface tension, and if we assist with a gas which will which will interact with a free falling metal then we can easily produce such kind of very fine powder.

So, by impingement of a very high velocity jet of a second liquid or by some sort of centrifugal force at the tip of this rotating cup or disc we can apply also a electric field. So, it uses very high velocity gas or water jet to rapidly fragment this liquid droplet and large number of droplet can be produced.

So, from a stream of liquid we are produce in multiple droplet of liquid droplet which finally, solidify into a solid solid powder particles. And, here these are the two cases that are shown in one case it is free falling and another case these are the geometry of a confinement. So, this is a principle of a spread droplet or otherwise it called as a atomization process.

By impingement of a high velocity gas jet that is interacting with a free falling or emergent melt stream. So, final form can be powder, splat or spray deposit. So, this is a

typical technique that is shown here in case of a rapid solidification process in case of a droplet method.

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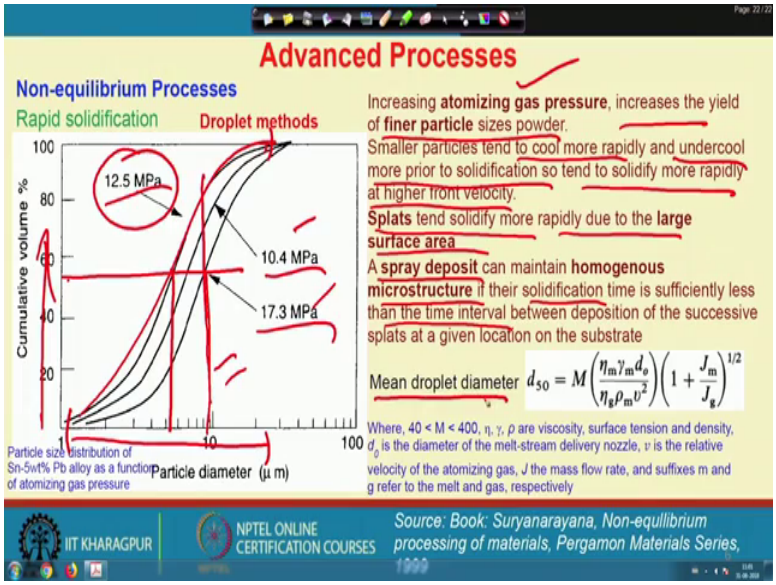


And, if you like to see the application of various parameter like different pressure, ok. So, here this is a pressure that is applied like 12.5 mega Pascal or 10 mega Pascal or 17 mega Pascal with a cumulative volume percentage that can be produced with a particle diameter. So, we can produce different particle diameter with their mean size actually.

So, in case of the higher pressure that is applied in that case the powder particle size is somewhat in the range of let us say of a cumulative volume that has a smaller a smaller particle diameter, when we apply a lower pressure or optimized pressure and this is the whole distribution that the which range of particle size can be evolved for a given parameters.

So, one has to optimize these particular particulars powder particle size which is linked with the applied jet pressure. So, increasing the atomization gas pressure it basically increases the yield of the finer particle size of the powder. So, that we have learnt from this plot.

Now, smaller particle size tend to cool more rapidly because it has a larger volume to surface area. So, it has a much higher surface area we compared to the volume because it has a finer size. So, that will always try to cool much faster and the microstructure will

be much more finer and sometimes we can also reach to a glassy state when we can apply such kind of very fine powder particle produced from a from a atomization process. Or under cool more prior to the solidification tend to solidify more rapidly at higher front velocity.

So, the splat tend to solidify more rapidly due to large surface area. A spray deposit can maintain homogeneous microstructure and their solidification time is sufficiently less than the time interval between deposition of the successive splat at the given location of the substrate.

Now, mean droplet diameter that is let us say the d 50 so, so for a particular given we can mean droplet diameter means, this is a mean size we will get a particle diameter for each case. So, you can see this is a d mean and which is linked to it let us say where M a is a constant which vary between 40 to 400 where eta gamma and rho they are the viscosity and the surface tension and the density.

So, d 0 is the diameter of the mailed stream that is delivery to the nozzle and v is the relative velocity of the atomization gas. So, here we again know the viscosity of the gas and the density of the mass and the velocity. So, that will tell us about the whole process of the mean particle droplet diameter that is linked with. So, J is the mass flow rate of the miss a mass basically means I am talking about the liquid and solid mass and the gas is for the gas.

So, this basically optimizes the mean droplet diameter. So, a spray deposit can maintain a homogeneous microstructure if their solidification time is sufficiently less than the time interval between the deposition and successive splat at the given location of the substrate.

Now, a splat always tend to solidify a more rapidly due to the larger surface area. So, we can produce powder as well as we can make it on a surface as a plate type of morphology.

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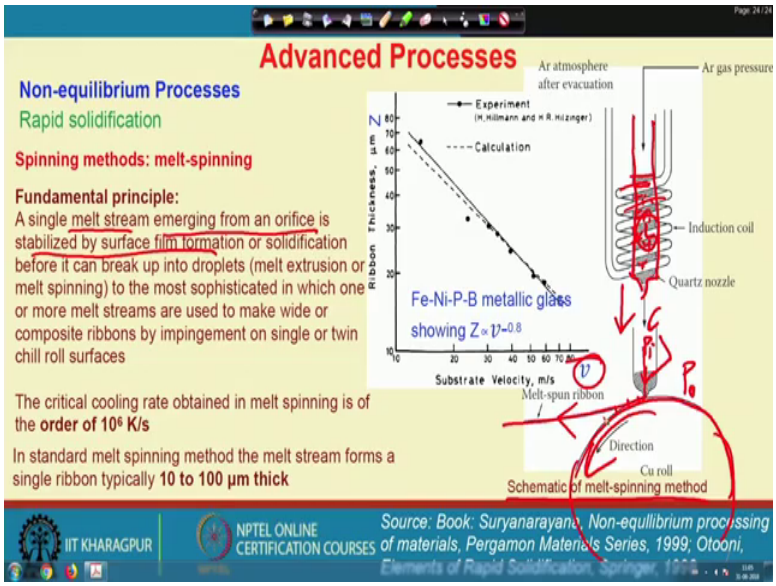


Now, in case of the second processing method that we have that we will discuss that is the spinning method. The spinning method here we are talking about the melt-spinning. In that particular case we simply take a crucible that crucible could be made of let us say boron nitrite crucible, maybe graphite crucible or maybe quartz tube, which can withstand higher temperature we put some solid, solid mass of inside and using a induction coil we make a liquid inside, ok. So, this is a liquid.

Now, after that the crucible bring down close to the rotating wheel. So, this is the wheel and wheel is rotating along a particular direction and after bringing close to the wheel we put a higher pressure inside the crucible than the pressure outside. So, this is the pressure outside and this is the pressure inside. So, pre inside is greater than the p outside.

So, the liquid will automatically come down and it will be injected on the wheel and a given velocity is given so, where the substrate will form that is the ribbon that will form at a given velocity. So, in that process we spin a wheel and this is a schematic of that such kind of spinning method. So, a single melt stream that emerging on a orifice is stabilized by a surface film formation.

Because if the flow rate is very flow very small then we will get a discontinuous film that is not expected what we want a continuous film to be maintained then only we will be able to make a very long ribbon or with a very high length and the width that depends on

the orifice size and the pressure that is applied. So, there are so many different parameters.

The interesting point here that if we look at one of the very critical example of such a iron based magnetic glasses iron nickel phosphorous boron which was a very initial made glass and derivative of them. So, the ribbon thickness which is Z here is shown in a micrometer. So, with increase of the substrate velocity then we can decrease the thickness of the ribbon without forming any discontinuity in the in the ribbon.

So, this is somewhat very very interesting feature as well as the not only the thickness of the ribbon can be can be optimized, but the width so, also other processing parameter can control. So, so, here the a single melt stream is emerging on an orifice and by surface film formation before it can break where up to into droplet and this is one of the very sophisticated technique or more melt stream are used to make wider composite ribbon by impingement on a single or twin chill roll surface. What I want to mean that I can give a two roll where the melt is falling.

So, instead of single wheel I can also give two wheel to in roll and the liquid will go inside the roll. So, in that particular case the advantage is that the liquid will fall and we apply pressure. So, during solidification we are straining the liquid and that may assist evolution of different metastable phases. So, this is like a twin roll chills surfaces.

Now, the critical cooling rate in case of such melt spinning process can reach up to 10 to the power 6 Kelvin per second in a standard melt spinning method the melt stream form on a single rebound typically 10 to 100 micrometer thick. So, these are some very interesting action optimization parameter that we can play with. So, from a 80 micrometer we can reach to let us say 15 micrometer just varying the velocity of the wheel.

So, these are just a very small parameter that can be optimized of the product.

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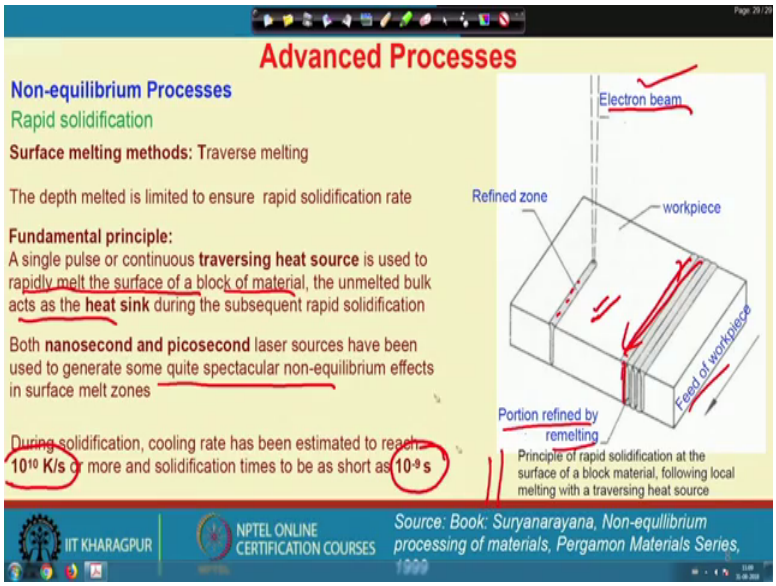


Now, another rapid solidification technique is the surface melting method. We also call it as a traverse melting, means a electron beam traverse across a sample. So, this is like a electron beam that traverse across a sample and this is a feed work piece and the portion which is a refined by the remelting process by assistance of a very narrow beam like a electron beam.

So, here the fundamental principle lies that a single pulse or continuous at traversing heat source is used rapidly to melt the surface of a block of a material and unmelted bulk that act as a heat sink during the subsequent rapid solidification both nanosecond and picosecond laser sources have been used to generate some quite spectacular non-equilibrium effect in surface melt zone.

During solidification, cooling rate has been estimated to reach to up to 10 to the power 10 Kelvin per second. So, this is much higher than the melt spinning method, because here the work piece act as a sink itself and we melt it localize and this time of melting is 10 to the power minus 9 seconds such a very very small teeny second time that is allowed.

So, this is just like a principle of a rapid solidification technique of a block material followed by localized melting by traversing a heat source.

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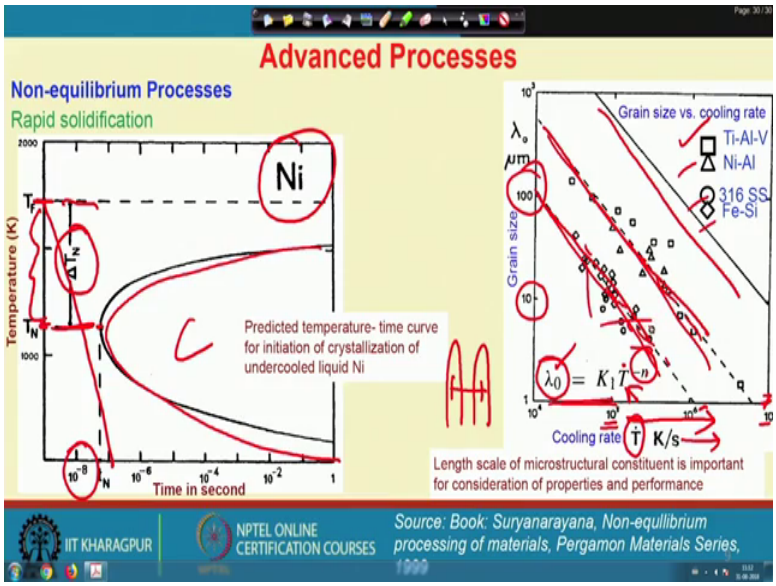


Now, all these different rapid solidification process that require for formation of any equilibrium or non-equilibrium phases so, micro structural constituent depends on the cooling rate that has been evolved.

So, to understand this fundamental we can think about a simple TTT diagram. So, if we consider a typical nickel and I would definitely have a TTT diagram for the crystals. So, this is a typical predicted temperature time curve for initial crystallization of a under cooling liquid. Now, under cooling to cause and bypass the nose of the TT curve we need a minimum under cooling so that we can bypass the nose with delta t N.

So, the temperature at the nose and the temperature here of the liquid the difference is the under cooling that is required to bypass this nose, so that we can avoid any crystallization at all. The time scale is very very small you can see, this is 10 to the power minus 8 second whereas, if we think about these grain size, how it scales with the under cooling. So, this under cooling is represented here with the t dot and that scales with the grain size or lamellar spacing like in a in case of a eutectic we call it as level a spacing or let us say in case of any dendritic growth the dendritic arm spacing is also can be called as lambda 0.

So, this lambda 0 scales with the under cooling that is given to the power minus n; n is a exponent which differ with different materials. Now, if we increase the cooling rate or let

us say the cooling rate can be applied. So, then we can produce different grain sizes and the grain size will decrease from hundred or micrometer to 10 micrometer and so on.

So, all these different material you can see they almost appear as a linear. So, there is a relationship with let us say this is in a log scale actually. So, that is why the power comes. So, the cooling rate is represented with the T naught where 10 to the power 5, 10 to the power 6 Kelvin per second or 10 to the power 7 Kelvin per seconds are given. So, we can get a linear relationship and exponent can be calculated from the slope of the curve.

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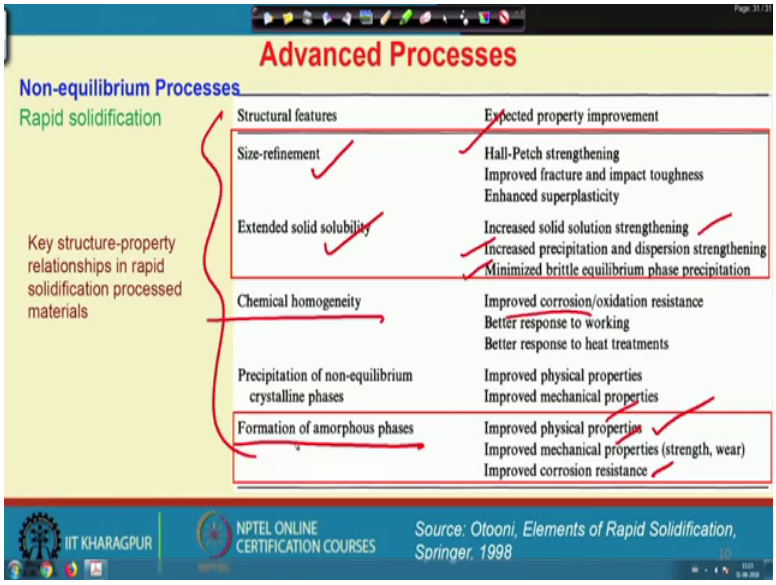


So, the key structure property relationship in case of a rapid solidification process material is definitely the size reduction; size means the grain size can reduced we can get a extended solid solubility increased solid solution strengthening, increased precipitation and dispersion strengthening minimize brittle equilibrium phase precipitation and hall pitch strengthening, improve fracture and impact toughness enhance super plasticity and we can also improve the homogeneity range. So, there will be less heterogeneity in the microstructure.

So, chemical homogeneity can be improved and if we can improve chemical homogeneity in a material then we can improve corrosion resistance then galvanic corrosion. So, because the potential difference will be created due to the composition difference and also we can form amorphous phase, which will improve the physical

properties of the material higher hardness and higher corrosion resistance because there is an absence of grain boundary grain and grain boundary they have potential difference and grain boundary will preferentially attack by any kind of chemical agent.

So, we can improve many of the corrosion resistance mechanical properties and physical properties by adopting these kind of rapid solidification processing. So, it depends on the users choice which material can be used and what processing technique can be adopted.

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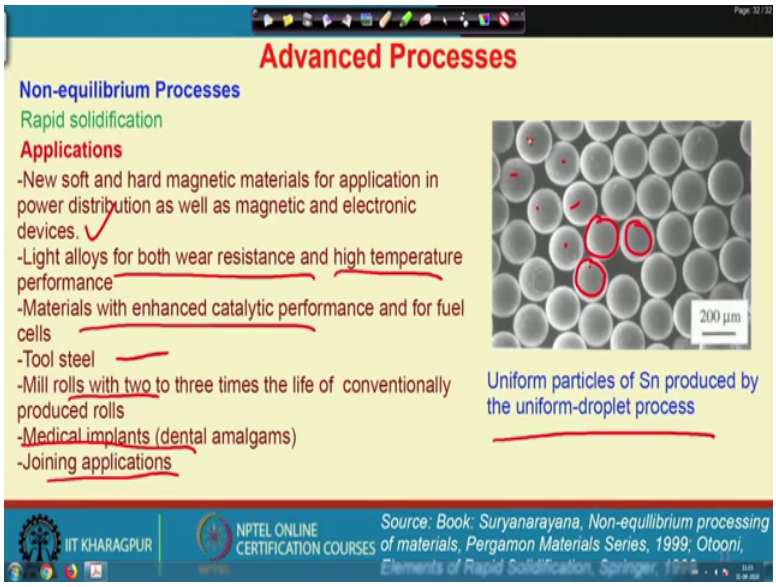


So, if you look at the typical application now we have discussed about soft magnetic material with a very nano scale structures and rapid solidification is one of the mandatory technique to produce such a magnet of very soft magnet or any kind of composites. So, we need amorphous precursors for that we can go for let us say making ribbon and then those ribbon can be annealed in order to form alpha around precipitates.

So, there will be a coupling of the amorphous matrix and a alpha iron phase, alpha iron nano crystals, embedded in a amorphous matrix, which has been discussed in the magnetic material classes. So, new hard and soft magnet that can be produced for application, for power distribution as well as magnetic core and electronic devices.

Light alloys which improve wear resistance capacity can be produced also with a higher temperature performance material with enhanced catalytic performance with a very

finest size or let us say for fuel cell we can use, maybe tool steel can be used and mill role of two or different three times of life conventionally produced roles.

So, using those technique we can we can make such kind of medical implants we can add up are with a amalgam we can produce by higher cooling rate 10 to the power 2 or 10 to the power 3 also for other kind of joining application we can also use such kind of localized melting and solidification.

I just like to show you some of the uniform droplet how uniform processing condition can be can be achieved so that individual spheres of those your particles steam produced by some droplet process can we assume off of 200 micrometer. So, they are just like very unique shape.

So, with this actually we finish our discussion today on the rapid solidification process. We will continue this rapid solidification processing and some of the very important fundamentals to discuss in the next class.

Thank you very much.