Advanced Materials and Processes
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Lecture - 53
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. Today we will continue our earlier discussion on Advanced Processes. So, these advanced processes are required because, there are several demands in terms of materials and properties. These properties could be the intrinsic properties or extrinsic properties.

Now, if you closely look into this nano structured materials and if we like to scale up those nano particle or nano materials then, I may start with let us say 200 nanometer finer particle or maybe let us say something like one micrometer, which have been prepared some of these sol gel processes. However, those as prepared powder need to be consolidated; consolidated means I am talking about compaction. And the theoretical density should be or the sintered density or the compacted density should be close to the theoretical density, then only we will be achieve good mechanical properties otherwise the material will be micro porous.

So, these are the challenges. Now porosity will be reduced if we anneal during centering or temperature of sintering is higher. But if we increase the temperature of sintering and time of sintering then grain growth we cannot stop, which basically means we have started with a nano crystalline powder, we end up with a micro crystalline powder. So, there is no benefit at all. And that is why this processing technique and they are very critical parameters are optimized, as well as newer processing technique has been evolved.

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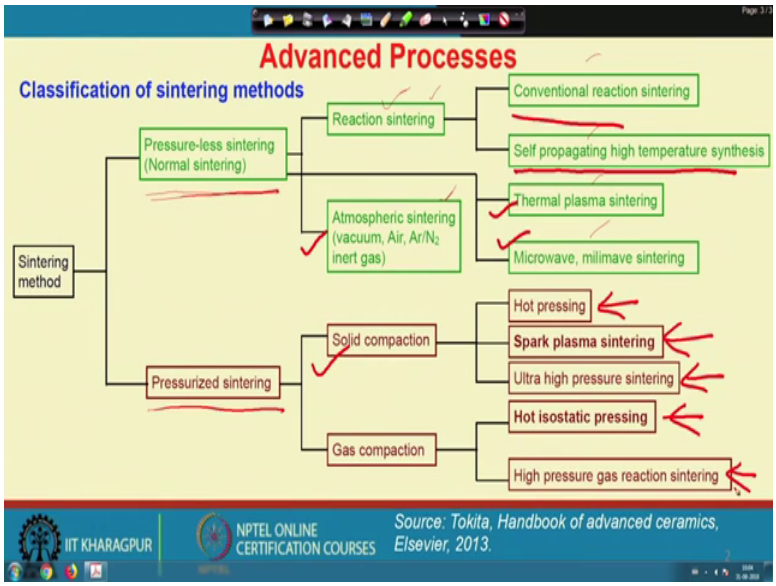

So, if we look at the scaling up process and sintering is one of such process where, we start with powder and we make bulk solid out of it. So, there are 2 major type of sintering are possible, one is pressure less sintering; that is a conventional sintering process, whereas there are pressurized sintering means, during sintering process we apply pressure.

Now let us look at the pressure less sintering process. In that case the process has many different types. So, here I show you 6 different types: one is reaction sintering means, during sintering itself the reaction goes on and we take or some heat may evolve during that reaction, so that has been utilized for sintering purpose. So, I need less energy for that particular reaction, because there is already some reaction going on in the material, which is being sintered. Such a technique is named as let us say self propagating technique or conventional reaction sintering any reaction goes on so that is a typical conventional.

But let us say if you take some iron and alumina and then, react with each other let us say then Fe 2 O 3 and aluminum they can react together and so it will basically make your self propagating type of synthesis. Once the reaction has started you do not need further activation energy, in order to propagate the reaction. So, this is one type of self propagating high temperature synthesis process. However, one should estimate how

much calorie has been involved due to the self propagating nature per unit mass and so on.

On the other hand the pressure less sintering process has a thermal plasma assisted sintering or maybe we can send a microwave so that particle can be bonded together ok. So, these are also conventional pressure less sintering. So, all these technique has been evolved for sintering without application any hydrostatic or external other kind of pressures. The last technique along this pressure less sintering is that atmosphere atmospheric sintering or maybe inert gas.

So, we can sinter under a vacuum so that the oxygen partial pressure will be very less or otherwise we can also put some air into it in the chamber, where sintering process is occurring or maybe we can put some nitrogen argon inert gas and so on. So, it completely depends on the material that you are going to synthesize, whereas any dissolved nitrogen can affect the properties of the material or not. So, depending on the inert atmosphere is chosen.

So, atmosphere should be chosen in such a way so that, it will not degrade the properties of the material after the sintering process. On the other hand, we can a conduct these sintering process under pressure, this pressure could be 2 different types. What I want to mean that, I can apply pressure by using some gas molecule or using some solid compaction means, solid means I have a die and the die we apply mechanical forces so that, powder can be compacted. So, in that way means, by application of solid compaction there are 3 other technique has been developed like hot pressing.

So, hot pressing means, at higher temperature we apply pressure, we basically sintered the compact. On the other hand we can also go for the spark plasma sintering. So, spark plasma sintering means the assistance of plasma that as that make or assist the formation of the neck between two particles, powder particle using a plasma. And then we sintered. So, the third category of this is the ultra high pressure sintering here, the pressure applied pressure is very high so you need a very good die for that.

On the other hand we can go for gas compaction means, the pressure is applied using a gas that is surrounded around a chamber and that chamber compressed the whole powder. So, this pressure goes in a isostatic manner that is called as a hot isostatic pressing or high pressure gas reaction so there is a reaction involved that is the high

pressure gas reaction sintering. However, among all these technique we are mostly concerned about the pressurized sintering, because it can yield a very high quality of the compact and by retaining its particle size the initial particle size.

So, one is the solid compaction technique like, spark plasma sintering and let us say the hot isostatic pressing. So, we will discuss these two techniques which are very important for us.

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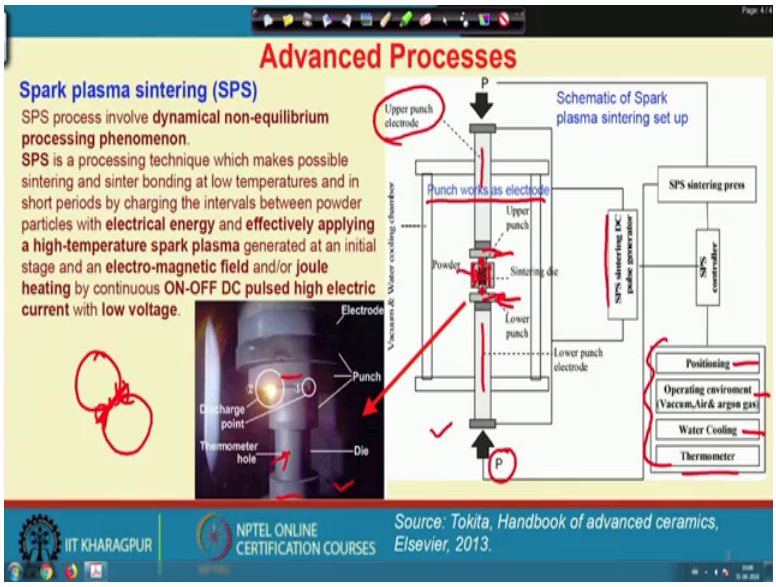

Now, for spark plasma sintering SPS process involve a dynamical non equilibrium processing phenomena; means, so the SPS processing technique which is possible sintering or sintered bonding at relatively lower temperature and in a very short period.

So, you can see the shorter the period basically, assist us that to avert the grain growth. Now, by charging interval between the powder particles, what I want to mean so, if I have 2 powder particle, if I have two different powder particles. So I can make some charge and apply some electrical energy to there. And we can create a localized plasma in that region so that, they can be they can be bonded together.

So, particles with a electrical energy and effectively applying a higher temperature spark plasma generated at a initial stage and electromagnetic field and the joule heating by continuous on off dc pulse high electric current with low voltage. So, a schematic is shown here and an image of such a spark plasma is shown here. So, let us say here there

are dies, which are lying at the top and the bottom and they actually act as a electrode; so, these are the punches.

So, you can see these are the punches, which act as a electrode. So, this one is the upper punch and this one is the lower punch. So, powder is placed in this region. So, powder is first place and this is a sintering die, which kept the powder intact and then we apply some higher pulse of DC pulse, electric field and low voltage. So, current here is very much important because, we like at a lower voltage high current to be passed so that, we can create a plasma in between two particles.

However, along this way, so these are the punch electrodes that are connected. So, these are the punch electrode that are connected and we apply some also a pressure or load. And here the hole sintering process involved is say a SPS this is a DC pulse is applied along with that the positioning is important, the environment operating environment, we need some water cooling. So that, during that plasma the die may require some cooling effect, as the same time we need some thermocouple and some hole so that, we can monitor the temperature of the process.

So, this is somewhat very much important parameters that we need to also look at. However, the mechanism of SPS or spark plasma sintering process is also very much interesting.

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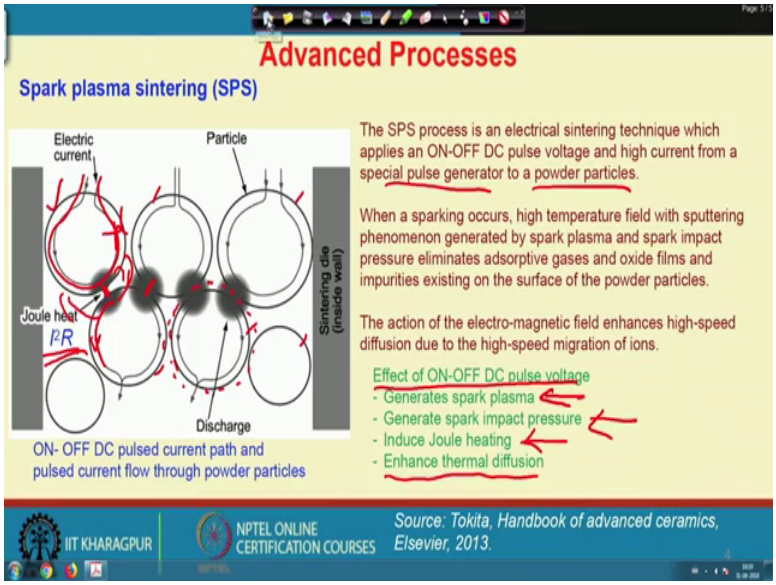

So, if I microscopically like to show you that there are different particles. So this is a various types of I mean different powder particles that are very close to each other and the current basically passes through the powder particle. So this flows in this way and here this is another flow.

So, we will have a chance that due to this a current passing inside the particle we will have some joule heating. So, this joule heating can be estimated by i square into r; so the resistivity into the current that square term. So, if we on and off the DC pulse, current path then, in the powder particle itself the current will flow, and they will assist in the formation of such a neck due to the localized joule heating. So, SPS process is a electrical sintering technique, which applies on and off dc pulse voltage and higher current from a special pulse generator to a powder particles.

However, when this sparking basically occurs the higher temperature field with a sputtering phenomena that are generated by spark plasma and spark impact pressure eliminate the absorbed gases and oxide film and impurities that is existing on the top of the surface of these powder particles. So, what I want to mean that, there could be very small oxide or some other kind of absorb gas film. However, we can eliminate it during that pulse and application of the physical forces.

Now, the action of this electromagnetic field that enhances a high speed diffusion of the atoms due to high speed migration of the ions actually because we have already created a plasma in the localized region between the particles. So, these on off pulse that basically assists to generate the spark plasma. On the other hand, it generate the spark impact pressure and it induce a joule heating as well as it enhance the thermal diffusion. So, this is the whole process that that basically govern the whole SPS sintering technique.

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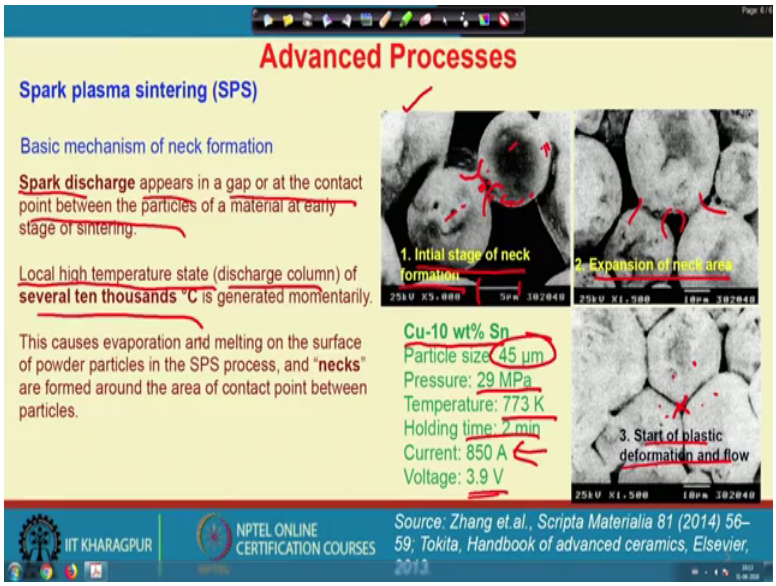

Now, we can see some microstructure or real microstructure of the initial neck formation. So, in the left hand side here a image, you can see that these are the 2 powder particle and it is a image has been taken at the very initial stage of a neck formation. So, you can see that there is a neck already formed. So, once the neck forms then definitely the atom will migrate from a higher curvature to a lower curvature region. So, that will basically assist with a convex and concave type of curvature and the migration will we will continue.

So, with that there will be a expansion of this neck area, so there will be more particle will join and at the end we can get such kind of highly compacted that is a start of the plastic deformation and flow because, we already have the powder particles that are very close. And if we apply pressure then we can eliminate these kind of internal pores and so on. So, this is a case that I have shown you in case of a copper 10 percent in particle size of 45 micrometer, this is the initial particle size average particle size the scale here is 5 micrometer so for this particle it is something like 10 micrometer diameter um.

So, the application of the pressure was 29 mega Pascal temperature was only 773k and the holding time is 2 minute only. So, so which is a very short time, the voltage is only a 3.9 volt, but the current is very high so like 850 ampere. So, this is a very high current actually. So, spark discharge appear in a gap of the contact point between the particles. So, these two particles there is a spark discharge, there is a joule heating that is a i square

r. And a local high temperature state that is a discharge column of the several 1000's that is around few centigrade 1000's of centigrade are generate a momentarily.

So, it is like a like a real spark phenomena appear in a very localized region. And this causes evaporation and melting of the surface and if there is any vaporized atom, then they will again go and sit in the neck region actually. So, if there is at all any evaporation of the atom from the surface and they will always like to go from the curvature difference. So, these are already discussed phenomena in the nanomaterial classes.

Now, the necks are formed around the area and contact point between the particles.

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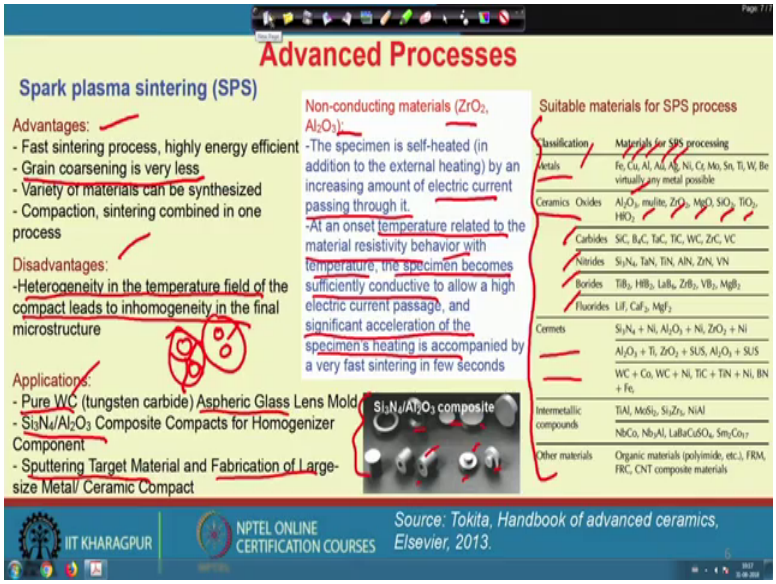

Now, there are also other techniques that are very much important, but before going to that, we must think that whatever I have discussed so far, that is with the conductive type of particles. Now if I like to sinter a ceramic material, means I have particle they are ceramic. So, ceramic are very bad for conduction, electrical conduction, can we simply compact using that spark plasma sintering that is the question. So, yes it is possible.

So, usually, all different kinds of material can be possible. So, starting from different metals like, iron, copper, aluminum, gold, silver they are automatically the electrically conductive material. However, the ceramic oxide like alumina, a mulite and a zirconia mulite it is basically a compound of alumina and silica. So, magnesia, silica, titania they

on carbides nitrite boride we can almost sinter any of these high temperature materials by using this spark plasma sintering and the effective product is also very high.

However, in case of a non conducting sample, the specimen is self heated in addition to the external heating, by an increased amount of electrical current that passes through it. So, to sinter a ceramic material, we have to pass a much higher current. And at the onset of the temperature. that is related to the material resistivity behavior with temperature the specimen becomes sufficiently conductive to allow a high electrical current passage and significant acceleration of the specimen heating is accompanied by a very fast sintering in a few seconds.

So, with that actually, we can sinter a non conducting means, I am talking about electrically non conducting material. There are very good advantages of this particular SPS technique like, it is a very fast sintering technique, the grain coarsening which is very important aspect is very less and variety of materials that I have already different classes of material can be synthesized.

Compaction sintering combined process, so it is not a one way process we also use some physical forces. The disadvantage is that, heterogeneity in the temperature field of the compacts and lead to in homogeneity in the microstructure. It basically says that, in some region the particles there are plasma. And there may be the temperature field that is localized is different in this region than this region. So, I may have a larger grain size in a localized region, I may have a finer grain size in other region.

So, this is like a microstructure in homogeneity that is a small disadvantage we have to accept. Now the application that I have told that pure, let us say metal tungsten carbide and aspheric glasses lens mold. And let us say a different nitride and oxide composite can be done or let us say a different sputtering target material fabrication of a large size metal compact can also be done. So, in such a case let us say the silicon nitride aluminum composite that is shown here, you can see the outer loop of those product with the top lead and hollow a hollow cylinders that has been produced by spark plasma sintering.

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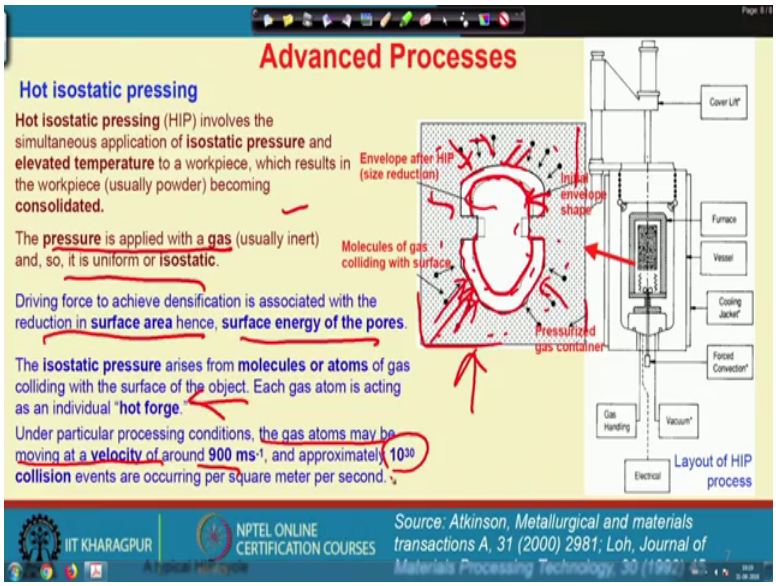

Now, the second process is the hot isostatic pressing. So, the hot isostatic pressing involved a simultaneous application of the isostatic pressure, and elevated temperature to a workpiece which result in the workpiece that is usually powder becoming consolidated. So, in that case, the pressure is applied as a gas. So, let me explain you the process which is schematic. So, please have a look at the first schematic that is shown here, the schematic is shown here. So, this is let us say the initial shape of the powder that is going to be conducted ok; means I have powders inside this chamber and this is a envelope. So, this is a initial envelope that contained all the powders and I have actually the gas which is outside ok.

So, though the pressurized container is here ok, gas container is here. Now, I apply pressure, so that the gas molecule will heat the surface of this envelope and it will be compacted at a final shape of such ok. So, initially it was like this and after that it was like that. So, from all the sides the gas molecule hit the envelope and assist the compaction of the powder that is basically the process called as hot isostatic pressing. So, the applied pressure goes to the material through a gas usually, it is a inert gas and since it is a uniform pressure that goes from all the sides to the envelope it is called as a isostatic pressure.

Now, driving force for the adhesive let us say or to achieve densification is associated with the reduction of the surface area and surface energy of the pore. The isostatic

pressure arises from the molecule or atom and gas colliding with the surface of the object. Each gas atom is acting as a individual hot stretch and they are hot forge between the particles. So, under particular processing condition, the gas atom may moving at a velocity of around 900 meter per second.

So, this is a very high speed the gas molecule goes and hit the surface. And let us say something like 10 to the power 30 collision event that goes on per second which is per square meter. So, this is a very high value of collision event. So, in that that basically, assists to get a very high compact density. And a schematic of such hot isostatic pressing chamber is shown here, like a furnace here this is a furnace that provide us the heat, we may need assist of a force convection or not that completely depends on the user choice.

However, for this gas handling we may need some vacuum. So, initially we put some vacuum and then we put some inert gas may inside and some electrical circuits are there. So, this is just a layout of the cover lift and so on. So, this is a total schematic of such a hot isostatic press.

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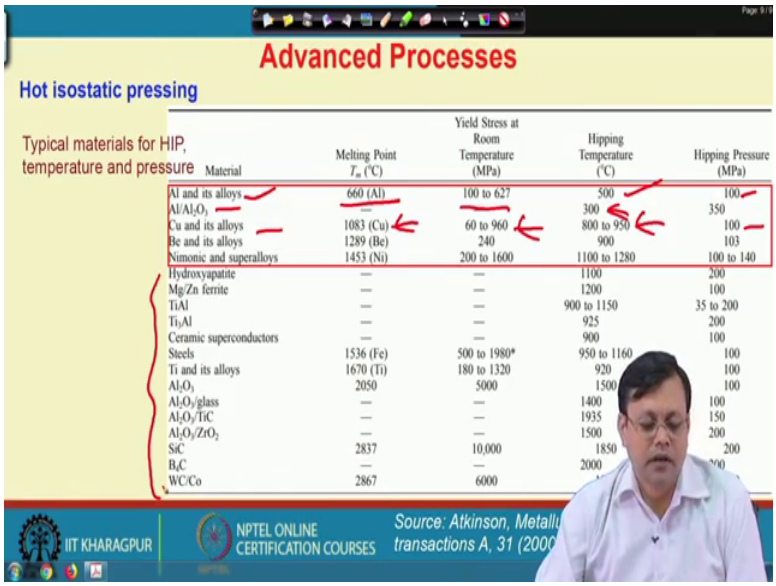

Material	Melting Point T_m (°C)	Yield Stress at Room Temperature (MPa)	Hipping Temperature (°C)	Hipping Pressure (MPa)
Al and its alloys	660 (Al)	100 to 627	500	100
Al/Al_2O_3	—		300	350
Cu and its alloys	1083 (Cu)	60 to 960	800 to 950	100
Be and its alloys	1289 (Be)	240	900	103
Nimonic and superalloys	1453 (Ni)	200 to 1600	1100 to 1280	100 to 140
Hydroxyapatite	—	—	1100	200
Mg/Zn ferrite	—	—	1200	100
TiAl	—	—	900 to 1150	35 to 200
Ti_3Al	—	—	925	200
Ceramic superconductors	—	—	900	100
Steels	1536 (Fe)	500 to 1980*	950 to 1160	100
Ti and its alloys	1670 (Ti)	180 to 1320	920	100
Al_2O_3	2050	5000	1500	100
Al_2O_3/glass	—	—	1400	100
Al_2O_3/TiC	—	—	1935	150
Al_2O_3/ZrO_2	—	—	1500	200
SiC	2837	10,000	1850	200
B_4C	—	—	2000	200
WC/Co	2867	6000		

Now, the typical hot isostatic pressing here, the temperature almost reaches in case of aluminum and its alloy. Since, aluminum has a melting temperature of six hundred 60 degree, the yield stress at room temperature maybe something like 100 mega Pascal.

And if they are nano powders or nano crystalline then, it may reach up to 600 and let us say if aluminum alloys contain some nano intermetallics of very fine size intermetallics then it also can increase the strength. So, the typical heaping temperature is like a like a 500 degree centigrade and pressure of a hundred mega Pascal, so that is good enough for aluminum alumina composite. So, we can apply a much lower heaping temperature because, we have pure aluminum and so heaping pressure you need a little bit high in order to move those alumina

Let us say for copper the melting temperature is 1080 degree centigrade and let us say the yield stress varies between 60 to 960. So we apply some temperature around a 800 to 950 degree centigrade with a pressure of 100 mega Pascal. So, there are also many hydroxyapatite, titanium aluminides and ceramic superconductor steels all of them can be heaped and the process parameters are also listed here.

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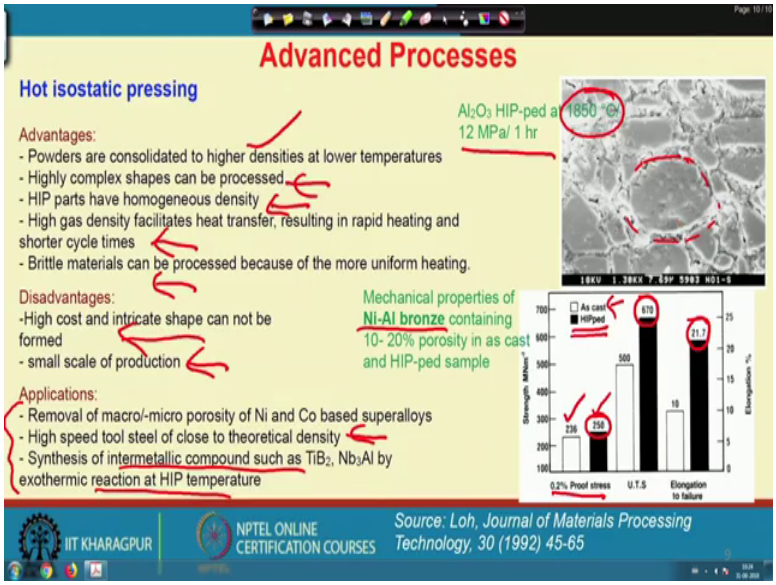

Now, the advantage and disadvantage of this hot isostatic pressing is like here the powders are consolidated at a much higher density and much lower temperature that I have already shown you in my earlier slide.

And a highly complex shape can be processed because we apply gases which apply the pressure. So, we first put the pressure into gases and that gas causes the isostatic pressing. So, if I have a envelope that can goes into a very complicated geometry, the gas can go everywhere and can apply the pressure. So, that is why a very complex shape can

be generated. And hip parts have a homogeneous density whereas, high gas facilitate high gas density facilitate a heat transfer and brittle material can be processed.

Now, the disadvantages are the high cost of the intricate shape that cannot be formed and small scale production of this heap, so we have some disadvantage because of the cost and the small scale production. However, the removal of micro and macro porosity in case of nickel or cobalt based super alloy we can apply these hot isostatic pressing, and high speed tool steel that is close to theoretical density can be acid and synthesis of inter metallic compound like titanium boride or exothermic reaction can also be done.

And the benefit you can see very clearly that, this is the yield stress of a as cast material and another was the heaped material ok. So, this is a nickel aluminum bronze we are talking about. So, the heap product has a higher yield strength. Now, if we go for ultimate tensile strength that is also higher that is 670 mega Pascal. The elongation to failure is also high because we have very less porosity and material is almost defect free. So, all these process the heap process shows a much beneficial effect than the as cast material of a nickel bronze and this is another example of a alumina heaped powder at kept at something like a 850 degree centigrade for 12 mega Pascal at one hour.

So, you can see that that almost there is no porosity involved and the microstructure is fully densed.

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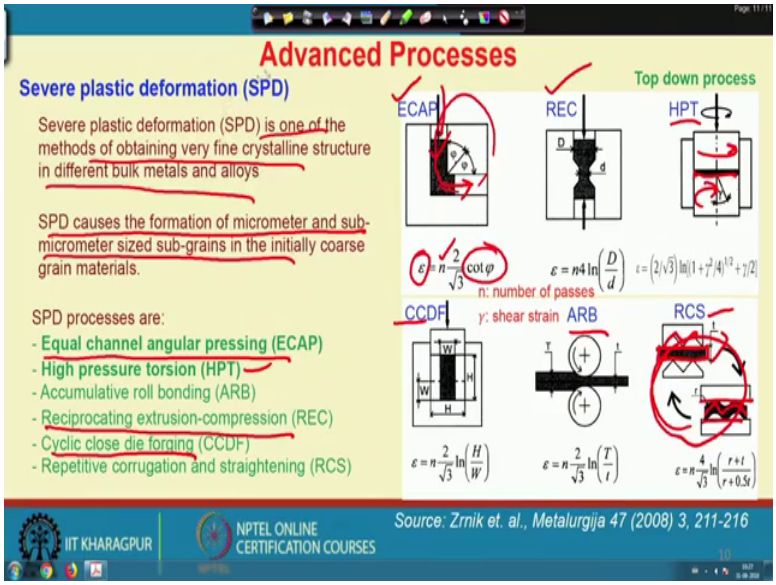

Now, there is other technique that is the so far technique I have discussed from the powder we consolidate to make a bulk scale. However, if we have to produce bulk structure then, we can also go from or start from a bulk solid and keep on modifying the microstructure and go up to the nano scale. So, that is like a top down process and that another technique is the severe plastic deformation. We introduce plastic deformation into a bulk solid which basically, means we introduce dislocation and defect inside it.

So, there will be several micro structural mechanism that will operate and assist the formation of the very small scale grain into the microstructure. Now, severe plastic deformation is one of the methods for obtaining very fine crystalline structure of a different bulk metals and alloys. So, there are typical technique like e cap, e cap basically means equi channel angular pressing.

So, I pass a bulk solid through a channel and I the specimen move at a particular angle and because of that the plastic deformation is introduced. So, there is a estimation, how much strain is involved that is epsilon which is linked with that angle of the bending. And the number of turn means, how many times we pass the material through the channel that will also increase the amount of the strain. Now the second process is the REC, REC basically means reciprocating extrusion and compression.

Now, the third technique is the HPT, that is high pressure torsion and here also we have a flat a disc we will go into detail and then we make a torsional strain and definitely we can produce bulk nanostructure using this. The fourth technique is the CCDF that is cyclic close die forging and accumulative role bonding or the repetitive corrugation and straightening. So, in this case, we take a bulk solid and simply we use such a die and so we make a corrugated structure. After making the corrugated structure, we take a flat die and again we repeat this process by making it flat.

So, the more the process this cycle goes on, we can introduce more and more strength. So, this SPD causes the formation of micrometer and sub micrometer size sub grain that are initially coarse grain material.

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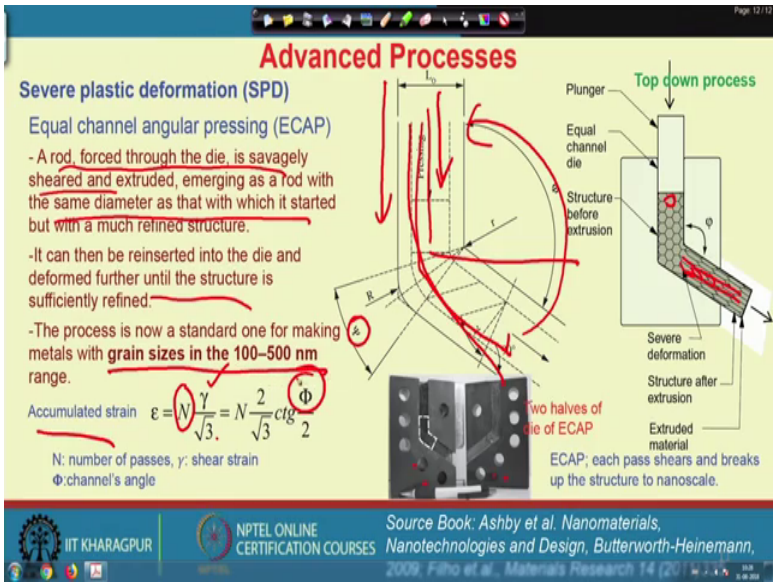

So, I can show you some of the schematic of such a SPD process and you can see that by simply pressing through a SPD process like a ECAP, the material is pressed through that. And we have a angle that is let us say psi and so the accumulated strain that is the number of the passes and the strain shear strain that we introduce divided by root over of the 3 and that is also linked with how much angle we provide.

So, we can make a direct 90 degree angle or maybe we can reduce the angle. So, there are dies so which are shown here and if we start with such a coarse grain microstructure, yes, the due to the elongation of the microstructure then we can produce very very finer structure. So, a rod is basically forced through the die and it basically shared and extruded emerge rod that same diameter with what is started with and it can be reinserted several times; and so that the die deform, but reinserted so that we can introduce the more number of terms.

So, here we can achieve a grain size in the range of a 100 to 500 nanometer.

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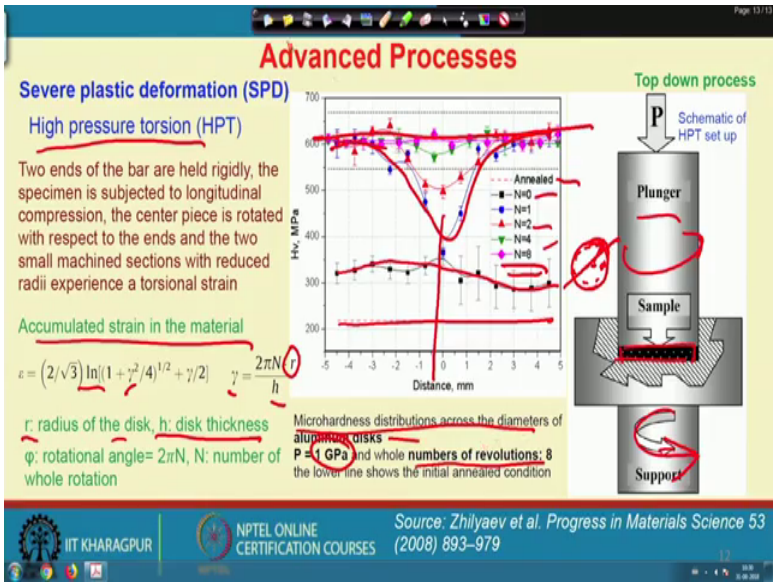

Now, the second severe plastic deformation process is the high pressure torsion, in that particular technique the two ends of a bar, so here there are 2 plunger and we have the sample here and we rotate this plunger in the opposite direction ok. So, if I have a disc then at the circumferential region I will introduce maximum amount of strain because, the more strain is achieved at the r theta.

So, the accumulated strain here in the material can be estimated by the logarithmic of the shear strain that is evolved, and the shear strain is linked with the radius divided by the h. So, h is the thickness of the disc and r is the radius of the disc. So, if you place this the shear strain in the surface, near to the surface is very high than the center, so we expect a microstructure inhomogeneity or gradient of microstructure along the along the radial direction. So, that is also represented here. So, this is like the hardness of a as started material which was a an yield and then, we applied a 0 a 0 turn so the an yield sample has a lower.

However the hardness will keep on increases and then if we go to a much higher number of turns then you see that the hardness will be fluctuated at the same that the hardness will be less. And if we increase more number of turn, then almost hardness is getting saturated. So, this is a micro hardness distribution across the diameter of a aluminum disk at a pressure of 1 Giga Pascal. So, the total number of revolution was 8. So, this is also a very very novel technique of producing such kind of nano structured material.

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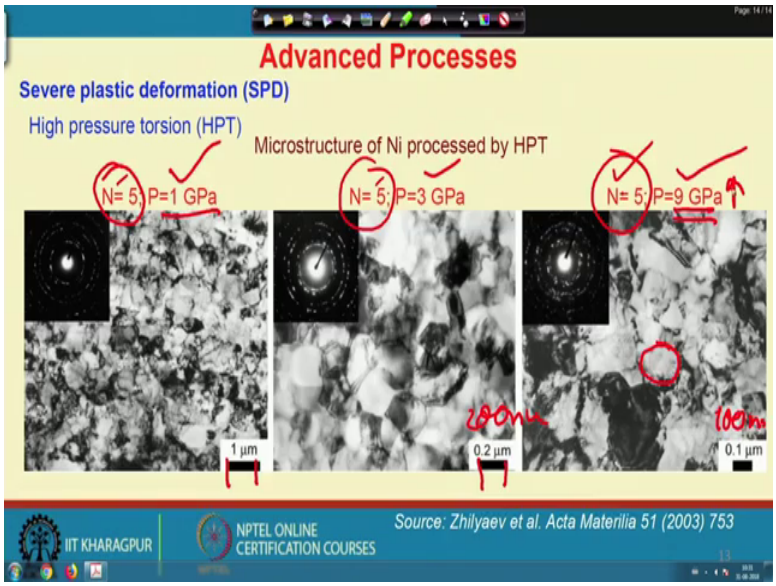

I show you a just 3 example of such microstructure. Here this is number of turn is 5, here also number of turn is 5, here also number of turn is 5, but the effect of pressure it is 1 Giga Pascal, 3 Giga Pascal and 9 Giga Pascal during high pressure torsion. So, the scale bar here is 1 micrometer, 0.2 micrometer means, 200 nanometer and here this is 100 nanometer. You can see that by application of a higher pressure, we can easily reach to a nano scale grain by the same number of turn by increasing the applied pressure.

So, this is such a novel technique that, we have many different process parameter to control the resulting microstructure in a very very bulk scale. So, this is another top down process of synthesizing nanostructure materials, without compromising with the any kind of grain growth while, there is no question of such a grain growth and we can process such a material a novel material much easily.

With this we stop our discussion today. We will continue the discussion in the next class.

Thank you very much.