Powder Metallurgy
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Lecture – 03
Powder Fabrication Methods: Mechanical and Electrolytic Fabrication

Hello everyone and welcome back. In the last class, we have started this topic Powder Fabrication.

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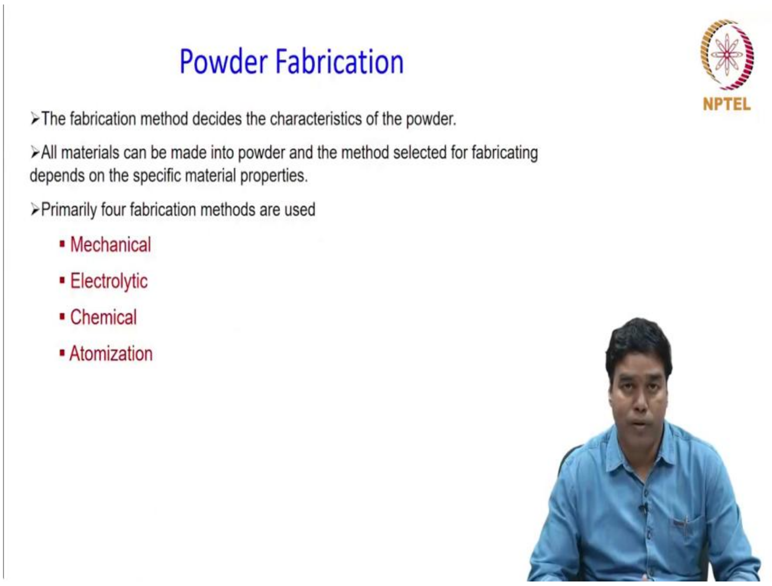

And we have seen the first method of powder fabrication which is a mechanical method of fabrication.

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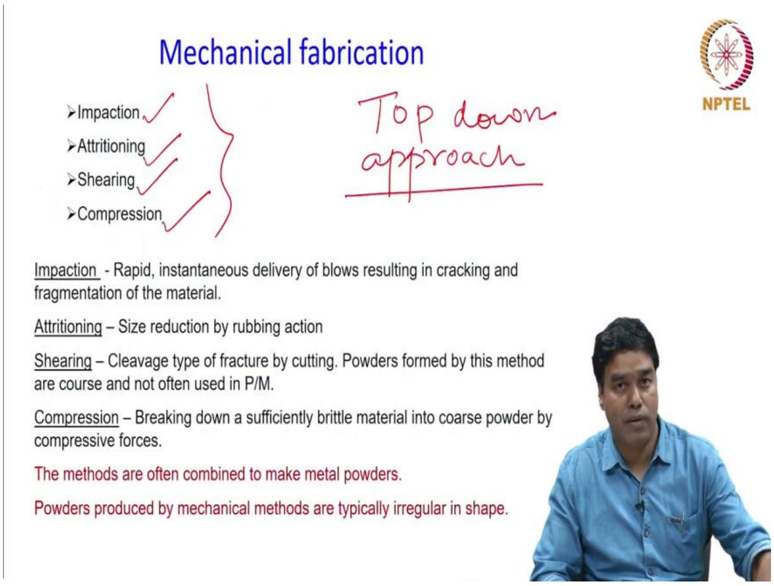

And if you remember, we have talked about these four types of mechanical fabrications which are listed over here; impaction, attritioning, shearing and compression. We have talked about them in detail.

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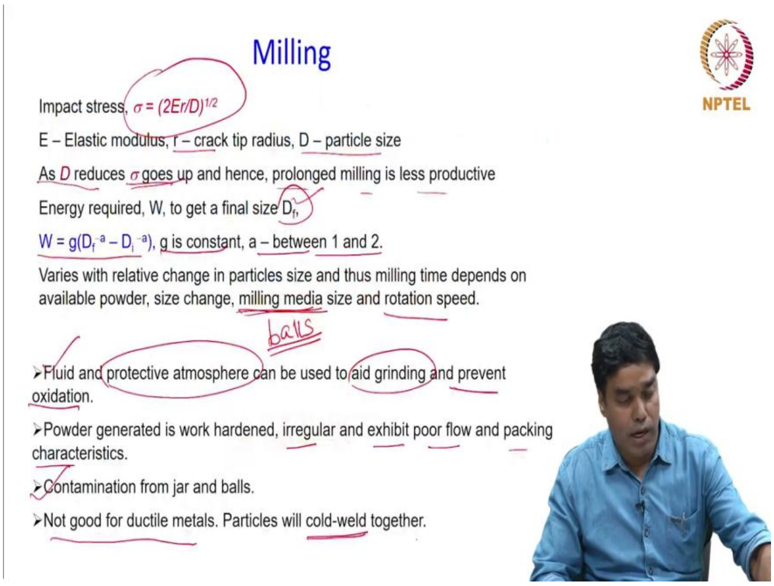

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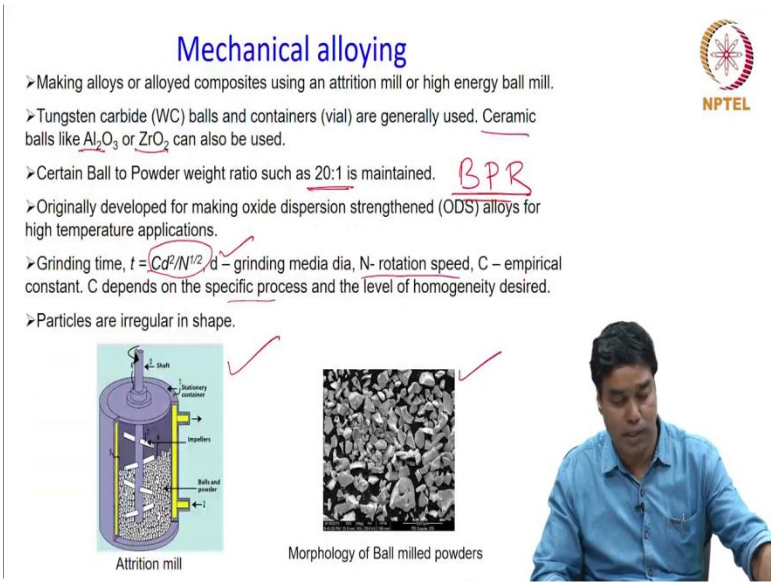

And we have also seen that the mechanical alloying or ball milling process can also be used to make alloys or composite. So, it is not only about making powders, but the mechanical fabrication method or this ball milling process can also be used to make certain types of alloys or certain other types of materials where you want to combine two or three different materials into one.

We have also talked about what is the kind of powder or the powder characteristics that you get if you use a mechanical method of powder fabrication. These powders are generally irregular in shape or in morphology as you can see from this image which is given above.

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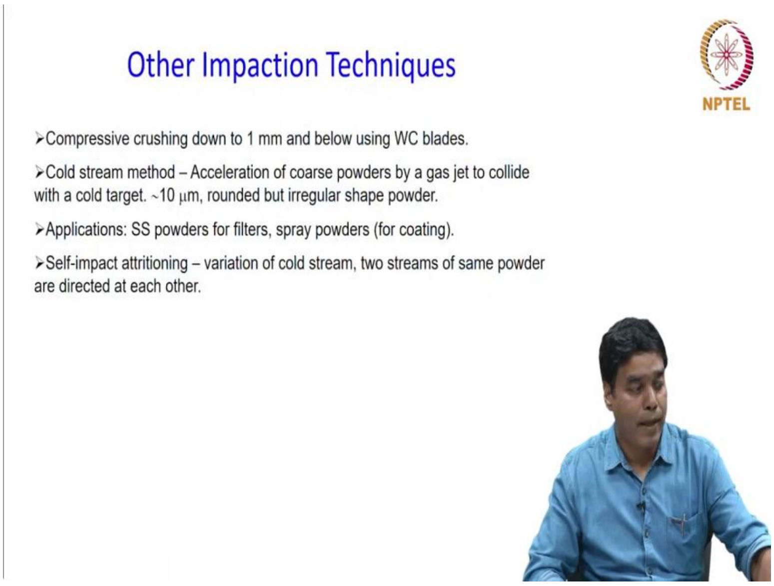

And apart from this milling and attritioning, we also talked about other impaction techniques like applying compressive forces or the cold stream method where you apply a gas jet to collide the powders against a target or you make the two powder streams collide against each other and break them down into powder.

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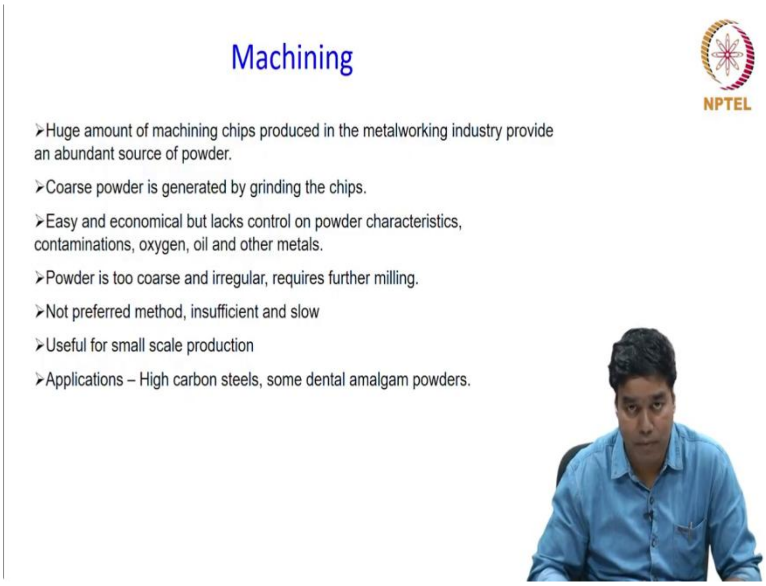

So, next we are going to talk about some other mechanical process like machining. As you all know a huge amount of machining chips are produced in the metalworking industry, where they machine different types of materials and these machining chips are produced as waste. So, these waste chips can also be used if we can fragment them into smaller pieces. We can make metal powder out of it by fragmenting or grinding these metal chips.

So, this is an easy and economical process because as I said these machining chips are available as waste from the metalworking industry. These are easily and readily available. So, the process, in terms of the economy, is quite attractive. But the main difficulty with this process is the lack of control on the powder characteristics.

Because you already have the starting material in form of those chips, you cannot do much about that. The properties inherent to the metal chips are carried over to the final powder. So, that is why you do not have much control over the characteristics of the powder which has generated from the chips.

And the other difficulties are contaminations. For example, you can have the oxygen, oil or other metals being mixed or contaminated with the metal chips and the powder that you make as a result also gets contaminated. And the powder which is generated by this machining process or by these machining chips is too large or too coarse and irregular in shape and therefore, it requires further milling.

Because of this kind of difficulties, although very economical, such methods are not preferred because they are insufficient and also slow. But it may be useful for small scale production when you do not really need high productivity rate. This method is used for making high carbon steel powders and some dental amalgam powders. So, this will bring us to the end of the mechanical method of fabrication of metal powders.

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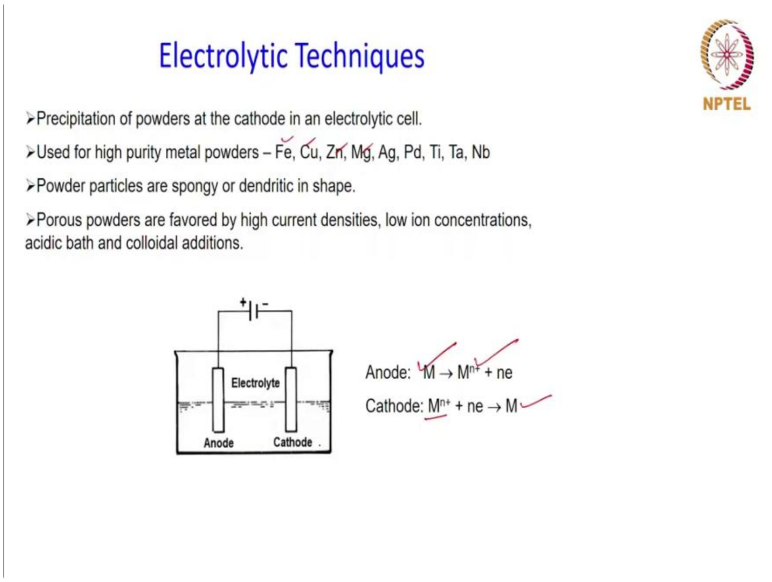

So, now let us go to the other process that we had listed before. Today we are going to talk about the electrolytic technique. So, this is nothing but the precipitation of powders using an electrolytic cell where you have an anode and a cathode. So, anode is the material that you want to make as a powder and cathode is something on which this material can be deposited with the help of this electrolytic cell. This method can be used for making all types of metal powders of high purity.

For example, all different kinds of metals like iron, copper, zinc, magnesium and so on can be converted into powders by this process. And, as far as the powder characteristics are concerned, the powder particles are spongy or dendritic in shape in this particular process. And, porous powders will be generated by high current densities, low ion concentrations, acidic bath and colloidal additions.

The material as the anode is ionized in the electrolyte. Then these ions travel through the electrolyte gets deposited on the cathode as the metal. And then, it can be easily scrapped from the cathode as metal powders.

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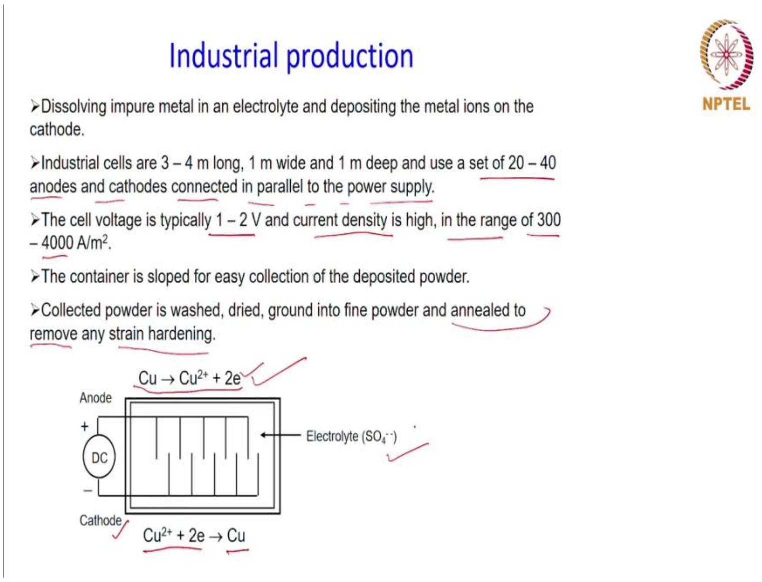

So, if you see the details of this process, it starts by dissolving an impure metal in an electrolyte and as I said it can be then deposited on the cathode. So, on an industrial scale, these electrolytic cells are 3 to 4 meter long, 1 meter wide and the 1 meter in depth. They use a set of 20 to 40 anodes and cathodes connected in parallel to the power supply, in order to scale up the whole process and generate high quantity of metal powders in one single batch.

And in terms of the process parameters if you see, it is a low voltage high current process. The voltage is in the range of only 1 to 2 volts and current density is high and is in the range of 300 to 4000 ampere per meter square. It varies depending on what quantity powders you are processing and what material you are processing and so on.

And this whole container is sloped so that, the powder is collected at one end and you can easily collected the deposited powder from that particular end. And, once the powder is collected, it is washed, then dried and ground into fine powders and finally, heated to certain higher temperatures or annealed so that the strain hardening that might have been caused in the process can be removed.

This is an example of making copper powder wherein the electrolyte is a sulfate containing solution in which the copper ions can easily travel or can easily dissolve. And once the copper ions go into the electrolyte through this anodic reaction, they travel to the cathode once you apply this current and at the cathode, it is reduced by accepting these electrons and it gets deposited as copper metal which can be easily collected from the cathode.

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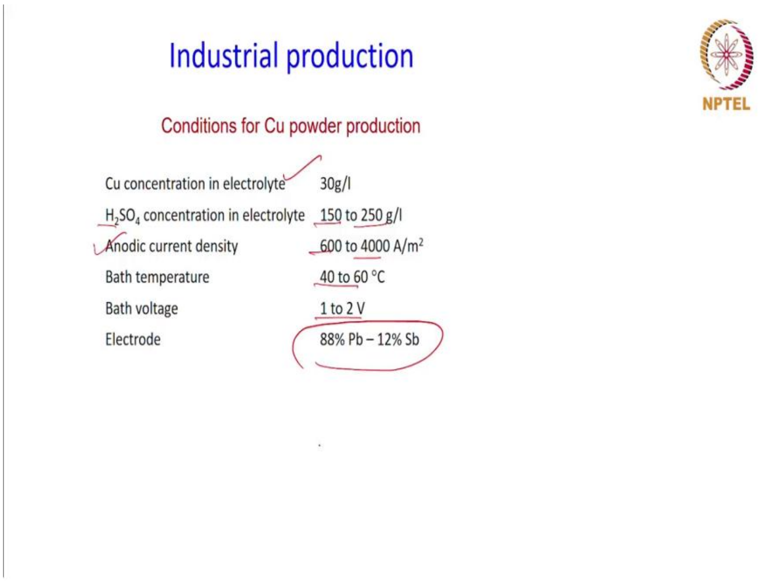

And, these are the process parameters for making this copper powder by this electrolytic method. The copper concentration in the electrolyte is 30 grams per litre and the sulfuric acid concentration in the electrolyte is in the range of 150 to 250 grams per litre.

The current density is in the range of 600 to 4000 amperes per meter square. Bath temperature is maintained at 40 to 60 °C and the applied voltage is in the range of 1 to 2 volt. The electrode used here is a lead antimony alloy. So, this is about the electrolytic method of making metal powders.

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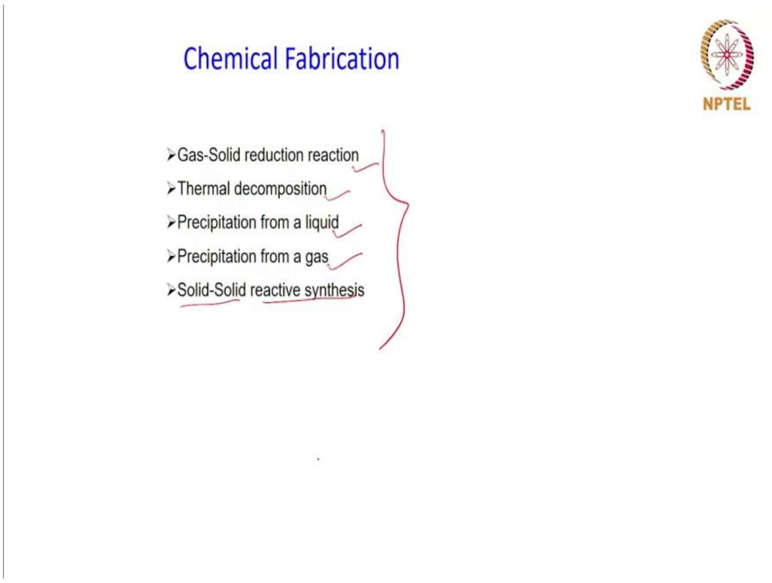

The next method is chemical process or chemical fabrication technique. Under this, there are several methods which can be used to make metal powders:

i. gas solid reduction reaction,

ii. thermal decomposition,

iii. precipitation from a liquid,

iv. precipitation from a gas and

v. solid-solid reactive synthesis

So, let us take this one by one and see how this process is done to get metal powders.

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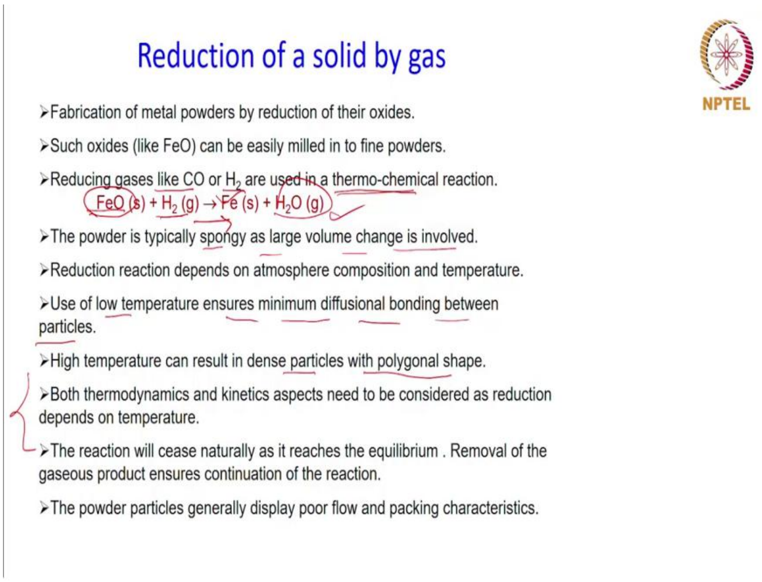

In the first method, that is, reduction of a solid by a gas, you start with the oxide of the material that you want to process as powder and then, reduce that oxide by using a reducing gas like hydrogen. For example, if you want to make iron powder, you can start with iron oxide and react it with reducing gas like carbon monoxide or hydrogen at a higher temperature. So, it is a thermo chemical reaction, because it happens at higher temperature.

When you pass this reducing gas at a particular temperature, iron oxide is reduced to iron and then water vapor is produced. The powder which is made by this process is typically spongy as large volume change is involved (you are reducing the oxide to the metal). The density of the oxide and the metal is very different from each other; that means, there is a significant change in the volume and as a result, the powder becomes spongy.

And the reduction reaction depends on the atmosphere, composition and the temperature at which the reaction takes place. The temperature is chosen considering the properties expected in the final powder. If you have a high temperature, it is likely that these particles will bond together. So, you might end up with coarse powder.

And therefore, if you use low temperature, it will ensure that there is minimum diffusional bonding between the particles. And, high temperature on the other hand can result in dense particle with a polygonal shape. As far as the understanding of the process is concerned, you will have to see both the thermodynamics and the kinetics of the process to actually understand it; the process - how it goes, what is the temperature - time cycle and so on.

The reaction will cease naturally as it ultimately reaches the equilibrium and removal of the gaseous product (that is, water vapor) will ensure the continuation of the reaction. So, if you want to ensure that the reaction goes to complete and this entire solid that we have used in the beginning is actually reduced into metal powder, then it is better to vent out the gaseous product from this reaction so that, the reduction reaction can move in the forward direction.

The powder particles which are produced by this method generally display poor flow and packing characteristics.

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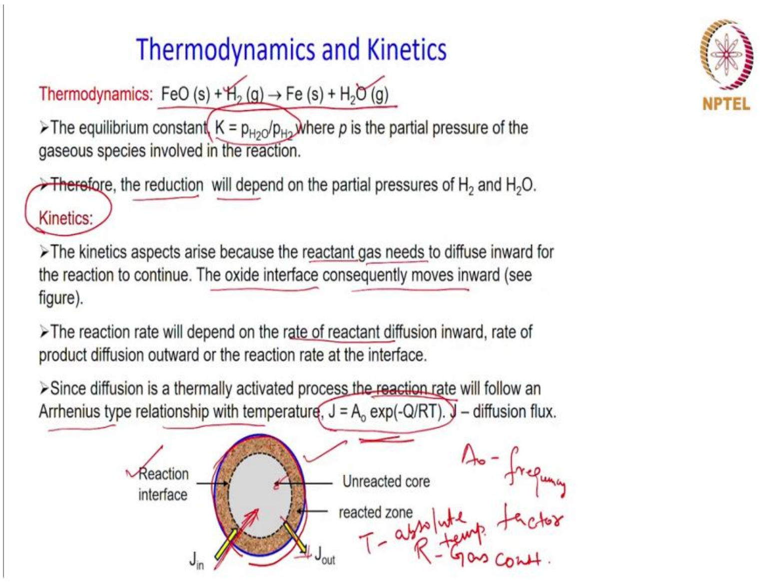

Now, as I said if you want to understand the process, you will have to see the thermodynamics as to how the reduction reaction proceeds and what kind of conditions you need to make this reaction proceed in the forward direction and get the powders out of the oxide (starting material). So, this is for example, again taking the same reaction that we considered before (reducing iron oxide into metallic iron).

The equilibrium constant for this reaction is given by,

$$K = \frac{p_{H_2O}}{p_{H_2}}$$

Where, p stands for the partial pressure of the gases (H_2O and H_2) which are the product and the reactant. So, the reaction would depend on the partial pressure of the reactant gas as well as the product gas. So, you can either supply more of the reactant gas or remove the product gas continuously for the reaction to move in the forward direction.

Now, to know how much time it will take for the reaction to complete at a particular temperature, you need to consider the kinetics; that means, you need to understand how the reaction proceeds after it has started.

So, the kinetic aspects actually come into being because you know the reactant needs to diffuse inward for this oxide to get reduced. Because, the reduction process starts at the surface and then, this reducing gas has to move inward for more reduction to happen and ultimately reduce the whole oxide into metallic powder.

So, as you can see from this particular drawing, here this first (outer) circle that you have is the interface between the reducing gas and the oxide which is being reduced. So, this is the reaction interface. So, now as I said for the reaction to proceed, this reducing gas has to diffuse inward.

So, you need to have an inward flux of this reducing agent or the reducing gas and the reaction rate will depend on the rate of reactant diffusing inward and the rate of product diffusing outward. So, as the reaction proceed or as the reactant goes in, the product diffuses out. The reactants will diffuse in and the product will diffuse out and the reaction rate or the kinetics of this reaction will depend on this rate of diffusion.

So, when this gas, this reactant gas or the reducing gas diffuses inward, the oxide interface has to move inward for the reaction to proceed. Because as more and more of the oxide is reduced, the reaction product (the metal) will grow and as a result, this reaction interface will move inward. And, as it moves or proceeds inward, more and more of this metal oxide will be reduced into metallic powder. Therefore, the oxide interface that you had in the beginning has to move inward for the reaction to proceed.

And since it is a diffusion control process, it is a thermally activated process and as a result of that, the reaction rate will follow an Arrhenius type of relationship with the processing temperature which is given like this,

$$J = A_O \exp^{\left(-\frac{Q}{RT}\right)}$$

where J is the flux of the reactant, A_O is a constant which is known as the frequency factor or the pre-exponential factor, R is the gas constant and T is absolute temperature.

So, this is how the whole reaction depends on the processing temperature.

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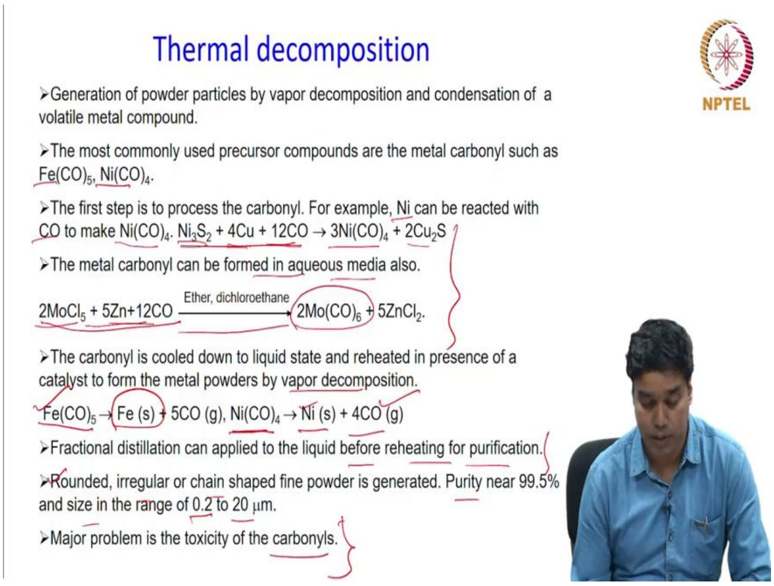

The next in this category is thermal decomposition. So, this process is to generate powder particles by vapor decomposition and condensation of a volatile metal compound. You take a compound of the metal that you want to make and vaporize it. So, this compound should be volatile enough so that, it can be easily vaporized and then, you condense that vapor to get the metal powder.

So, the most commonly used compounds are the metal carbonyls because this type of compounds can be easily vaporized. For example, iron carbonyl and nickel carbonyl. This kind of compounds can be used to make iron and nickel, for example. So, the first step in this process is to make the carbonyl and that can be done by treating the metal with carbon monoxide.

For example, you can react nickel (which can be in bulk form) with carbon monoxide to process this nickel carbonyl. Similarly, it can be also processed using some other compound of nickel. For example, nickel sulfide can be used in the presence of another metal (eg. Copper) that has higher affinity for sulfur. From nickel sulfide, nickel can be derived and sulfur can combined with copper in this case.

In the presence of carbon monoxide, if you do this reaction, then this nickel sulfide will be converted into nickel carbonyl. Sulfur will go to copper and copper sulfide will form.

Now, once the metal carbonyl is formed, it can be vaporized and condensed into metal powder. This metal carbonyl can also be processed in aqueous medium. For example: this molybdenum pentachloride can be treated with carbon monoxide in the presence of zinc, in a medium like ether or dichloroethane. Once this reaction happens, you can obtain this molybdenum carbonyl. So, once this carbonyl is obtained, it is cooled down to liquid state and then again reheated in the presence of a catalyst to form the metal powder by vapor decomposition.

Consider an example of iron and nickel. First the metal carbonyl is processed through this kind of processing route, and then, it is cooled down to liquid state. Further, it is vaporized in the presence of a catalyst to deposit iron in the form of powder, when condensed on a surface.

Similarly, nickel can also be processed and the carbon monoxide which is generated can be recycled again to make the metal carbonyls. And, fractional distillation can also be applied to the liquid before reheating for the purpose of purifying the carbonyl.

So, if that is done, the metal powder which is finally obtained will be more pure. And as far as the powder characteristics are concerned, this process will generate rounded, irregular or chain shaped fine powder. And, purity of such powders is nearly 99.5 percent and the size of the powder particles is in the range of 0.2 to 20 microns. One of the major problems in this process is the toxicity of these carbonyls and therefore, it is difficult to handle this kind of chemicals, as they are hazardous. So, that is one of the main limitations of this process.

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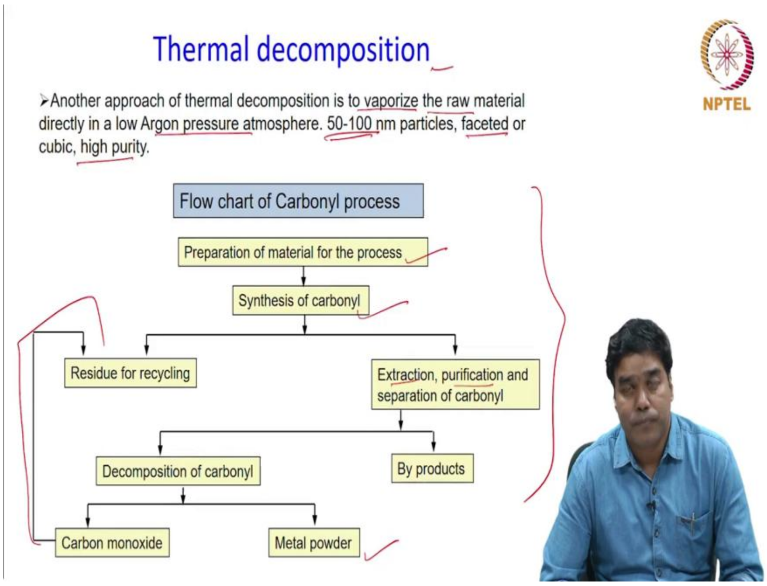

So, if you see the flow chart of this process, it goes like this. First as I said, you prepare the material, like the metal and the other reactants to make the carbonyl either through this (residue) process or through the aqueous process and then, synthesize the carbonyl first. And once the carbonyl is synthesized, it is extracted, purified and separated and once the carbonyl is separated, it is decomposed by heating it.

So, it is a thermal decomposition process as the name says. So, once you heat it, it vaporizes and when once you condense this vapor, you get the metal powder and carbon monoxide which is generated as a reaction product in this decomposition process can be recycled.

If someone does not want to use the thermal decomposition of the carbonyl, then the material itself can be vaporized. The raw material itself can be directly vaporized in a low argon atmosphere. So, you need a certain chamber or certain atmosphere in which the material that you want as powder can be directly vaporized. And then, you can condense that vapor inside the chamber on a substrate or on a surface and collect it in the form of powder.

So, the powder that is generated through such process is very fine in size, in the range of 50 to 100 nanometers in size and these powders are faceted or cubic and they also have high purity. So, with this, we have come to the end of this class. I will see you again in the next class.

Thank you for your attention.