Powder Metallurgy
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Lecture – 04
Powder Fabrication Methods: Chemical Fabrication

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So, in the previous class we were talking about the Chemical Fabrication Method of making metal powders and under these categories as I said we have different processes (refer to the slide).

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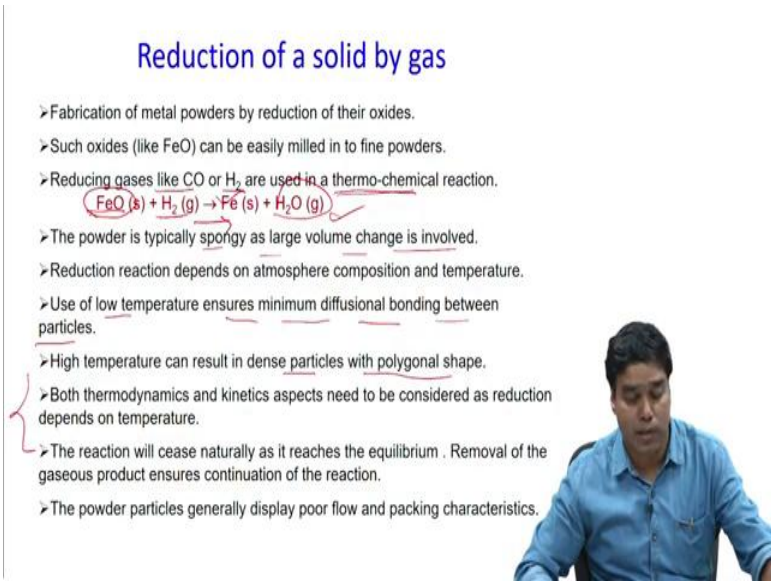

And we talked about the gas solid reduction reaction by which we can make metal powders by reducing a metal oxide in the presence of a reducing gas like carbon monoxide or hydrogen at a particular temperature.

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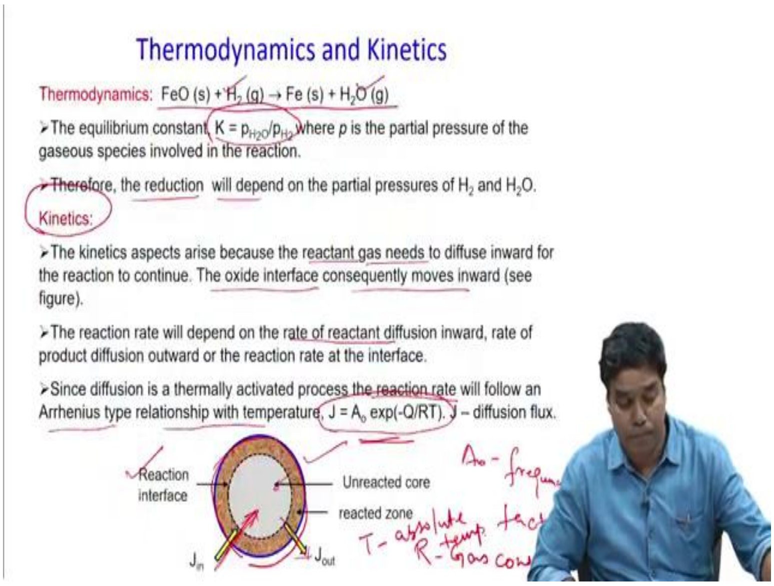

We have also seen the thermodynamics and the kinetics of this reduction reaction and how this reduction reaction depends on the temperature. Now, today let us look at the other chemical methods for making metal powders.

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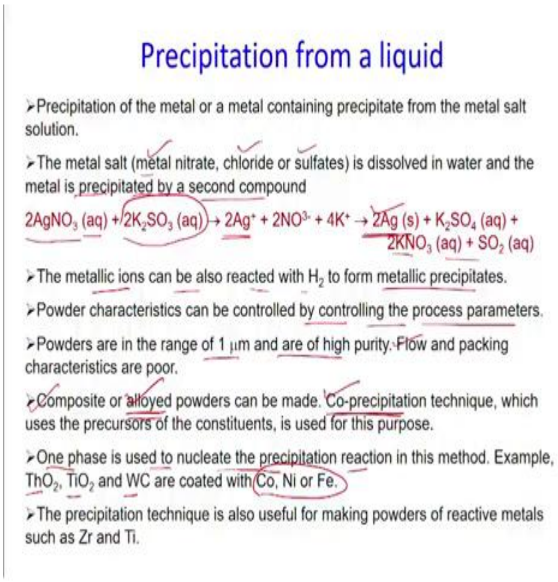

The powders can also be precipitated from a liquid. This is a wet chemical method of making powders, where you have metal ions in a solution and then you precipitate it like how you do titration. So, you have a titration kind of method which is followed here to precipitate the metal ions from a solution to obtain powders.

So, you start with the metal salts which can be easily dissolved in water. For example, metal nitrate, chloride or sulfates can easily be dissolved in water.

And with the help of a precipitating agent, this powder is precipitated from the solution. Consider an example of making silver powder using silver nitrate in a solution in which you have a second compound. And with the help of this second compound, the silver ions, which are there in the solution, are precipitated as solid silver or silver powder. If necessary these metallic ions can be also reacted with the hydrogen to form the metallic precipitates.

So, once the precipitate is formed, it will be filtered and washed properly again with water so that all other residues are removed from it. After filtering, it will be dried so that only the powder remains.

And the powder characteristics that you have from this kind of process can be controlled by varying the process parameters like, the concentration of the solution and so on. And the powders which are generated in this method are in the range of 1 micrometer and are of high purity, but the flow and packing characteristics of such powders are poor.

This process can also be used to make composite powder; that is, you can combine two different materials into one or you can also make an alloy. That means, you can add another metal into the first metal powder that you have and make alloyed powders.

So, the process for making such composite or alloyed powders is known as co precipitation. That means, two different materials are co precipitated together to either make a composite or make an alloy. So that means, the starting powder or the starting material will have the metal salts of both the metals that are to be combined either into the composite or into an alloy.

So, you take the salts of both the metals and then make a solution of the two and with the help of a precipitating agent, get an alloy powder or a composite powder. So, when you have two different materials combined into one, one phase is used to nucleate the precipitation reaction.

The oxide or carbide materials can be coated with metal by precipitation. So, this metal coating can be precipitated over this oxide or carbide surface. The surface would actually act as the nucleation site for the metal to precipitate. So, this metal will precipitate over this surface and then we can get a coating of this metal over this kind of materials and the precipitation technique is also useful for making powders of reactive metals such as zirconium and titanium.

So, while we are talking about precipitation from a liquid, let me also give you some fundamental or some basic idea about this particular process by taking an example.

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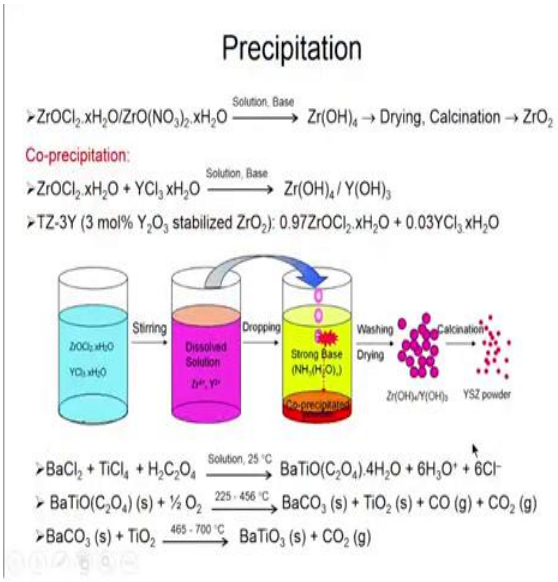

So, let us see generally how this process works. As we have seen you start with liquid which contains the metal ions and in case of a co precipitation technique, you have more than one metal because you want to combine them into single material. So, this is an example of the process of co precipitation as you can see in the figure above.

So, here I have taken an example of yttrium being added to zirconium. So, there are two precursors - one for zirconium and the other for yttrium in the form of their chlorides, which are available as metal salts. So, these are metal chlorides, zirconium oxychloride and yttrium chloride. So, then you make a solution out of this by adding these two into water and dissolve it.

And you need to make sure that the solution is basic. So, you need to adjust the pH in order to precipitate these metals from the solution. In order to adjust this solution to a basic solution, you will have to add ammonium hydroxide or sodium hydroxide, which will make sure that the zirconium and yttrium ions are hydrolyzed.

So, they will be forming their hydroxides as you can see in the solution. So, after you add the base and make it basic you have the metal ions in the form of their hydroxides in the solution. And then once you hydrolyze it, you can get the precipitate wherein both zirconium and yttrium ions will co precipitate together.

So, this is why the process itself is known as co precipitation because there are two or more metal ions which are precipitating together. So, once this is precipitated, the precipitate is collected and then it is washed and dried. For many materials like oxides, you will have to heat it to some higher temperature so that you can convert these hydroxides into oxides. So, that is the process which is actually adapted for making ceramic powders like the oxides. In this case, for example, you have this yttrium zirconium oxide, which is obtained from the hydroxide precipitated from the solution by heating it, which is known as calcinations.

Calcination is heating this precipitate at some higher temperature and once you do that these hydroxides will be converted into oxides. So, this is how the whole process goes. Starting from a solution you obtain the precipitate and then you can wash it and dry it to get the powder.

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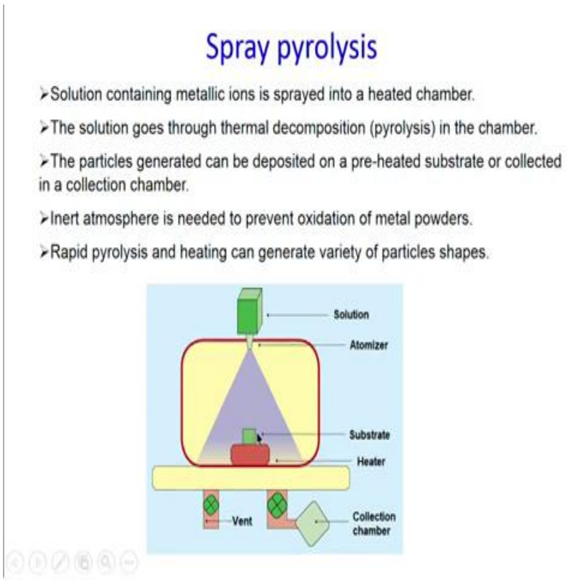

And precipitation can also be obtained from a solution by actually atomizing it into smaller droplets inside a chamber and then you heat it inside the chamber to get the precipitate in the form of a powder,. So, this process is known as spray pyrolysis because as I said you start with spray.

And then you pyrolyse or heat it inside a chamber, where it goes through the thermal decomposition process. And then finally, you get the metal ions, which are present in the solution, precipitated at the end of the chamber, which can be collected in a collection chamber.

So, you have the solution which contains the metal ions and the solution is first sprayed. Then, it is sent through a heated chamber. So, this spray can be created by an atomizer as you can see over here.

So, as you send it to this chamber where you have a nozzle and you atomize it, which can be done, for example, by high velocity gas jets. Sometime, the aerosols are first made in a separate unit and the spray of that aerosol is then sent to this chamber where this solution or this spray is heated up and the powder is collected at the end in this collection chamber. The powder which is precipitated after going through the thermal decomposition process can also be collected on a pre heated substrate.

So, once the pyrolysis happens inside the chamber as it is heated up, the particles are generated and this can be either collected in the collection chambers or deposited on a pre-heated substrate and then it can be coated on the substrate. And in that case, this particular process of spray pyrolysis can also be used as a coating technique, wherein you keep your substrate in proper position and coat it with the powder which is generated by this process.

So, this is not only useful process for making powder, but this can also be used for getting coating on a particular surface. And in case of metal powders, an inert atmosphere is needed inside this chamber so that the metal can be prevented from oxidation.

Otherwise there are chances that the powder will be oxidized because this whole chamber is heated up and if there is oxygen present inside the chamber, if it is not evacuated, or if it is not flushed with an inert gas, then there are chances that the metal powder will be oxidized.

In fact, in many cases, after collecting the metal powders, they are actually subjected to a reduction process in the presence of hydrogen or other reducing gases so that, if there are any oxides which might have formed inside the chamber during the process, those oxides can be reduced and we can obtain pure metal powders.

And often, the heating is done in stages; meaning, the chamber has different stages of heating, starting from top and going to the actual thermal decomposition or the pyrolysis zone where the temperature is higher compared to the temperature when the solution actually enters the chamber.

So, it is gradually heated up first to a lower degree, where it is actually a kind of drying process and then the temperature is gradually increased. So, you can have two or three stage heating inside this chamber, so that the solution goes through a gradual heating instead of a single step heating. So, that is also done, in order to make sure that the thermal decomposition is gradual and you allow enough time for this solution to get converted into powder particles.

So, this is how the whole process of the spray pyrolysis is done to obtain powders.

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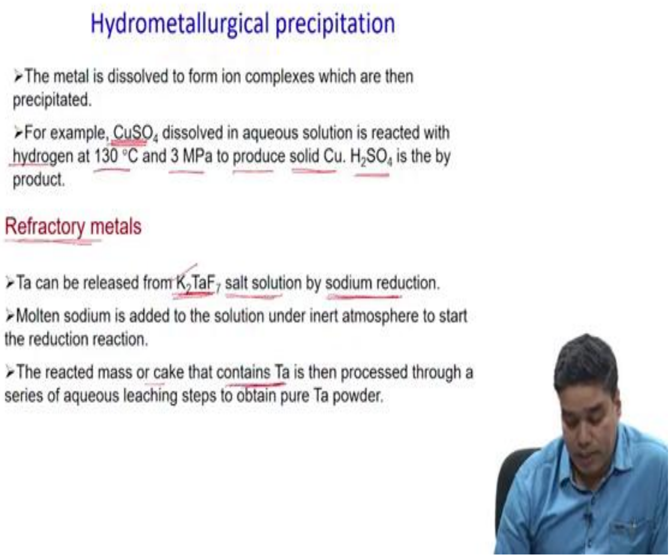

There are other precipitation routes like the hydrometallurgical precipitation process which involves a metal dissolved in a solution to form the ion complexes which are then precipitated. In that case, an easily soluble compound of the metal is dissolved in a solution to have the metal ions which will then be precipitated from the solution.

For example, copper sulfate can be used to make copper powders. In this process, copper sulfate is first dissolved in a solution and then it is reacted with hydrogen at 130 °C and 3 MPa pressure to produce solid copper as powder or as the precipitate which comes out from the solution and then it is reacted with hydrogen. And in this case, sulfuric acid is generated as the byproduct.

Then the hydrometallurgical route can also be used to make refractory metal powders. For example, tungsten, tantalum. Here is an example of making tantalum powder by the hydrometallurgical route.

So, in this case, a halide salt that contains the metal is used to make a solution first and then it is reduced by sodium. So, in this example, the salt K_2TaF_7 contains tantalum and it is reduced by sodium to release the tantalum from this particular compound.

So, once the solution is formed, molten sodium is added into the solution under some inert gas atmosphere to start the reduction reaction. And once the reaction is completed the reacted mass, which comes out as a cake, will contain tantalum and in order to release this tantalum from the cake it is processed through a series of leaching steps and series of washing steps to obtain pure tantalum powder. So that is the final product once it is reduced and then washed out thoroughly, tantalum is obtained as the powder. So, this is a process which can also be used to make powders of refractory metals.

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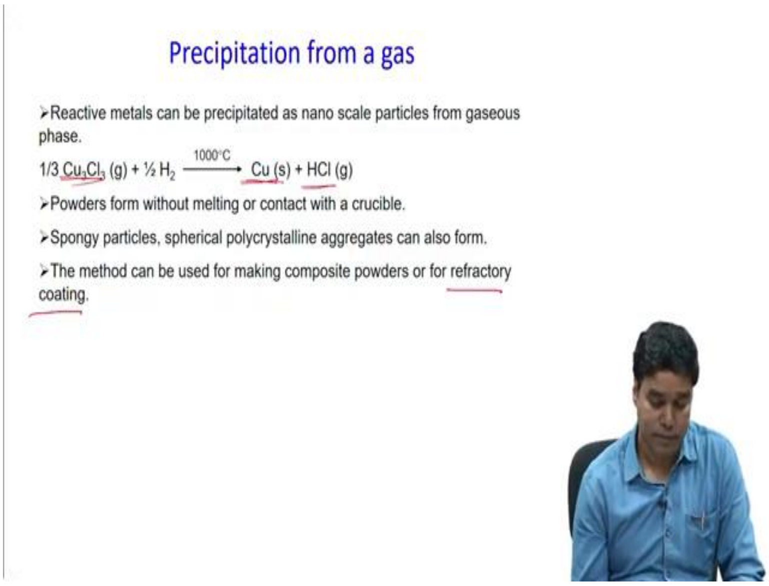

This precipitation can also be obtained from a gas, like what we had from a liquid. So, in this case, like how the liquid contained the metal which is to be obtained as powder, the gas will contain the metal. For example, copper chloride is a gaseous compound of copper. So, if this can be reduced by reducing gas like hydrogen, then copper can be released, but again this has to be done at a high temperature like 1000°C.

So, if the gas mixture of copper chloride and hydrogen is heated at such temperature, then hydrogen will reduce this and copper will be released as solid copper or copper powder and HCl is the byproduct. So, this kind of powders can be formed without melting or contact with any crucible. Such powders are generally spongy and they are spherical and polycrystalline in nature.

And this particular method can be used for making composite powder as well or can also be used for refractory coatings, if it can be precipitated over another surface like what we have seen in case of the precipitation from liquid. Here also this can be precipitated over a surface and the precipitate can get coated over that surface. So, you can get coatings for example, refractory coating on another surface.

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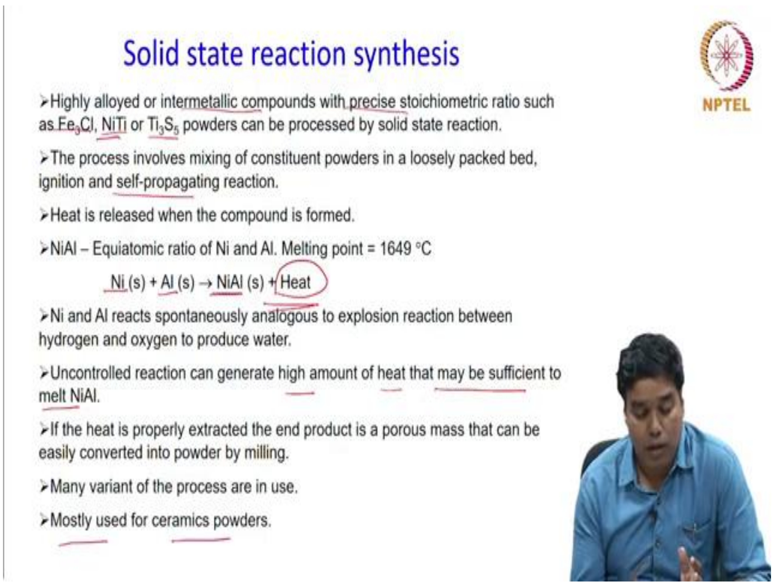

And finally, there is another chemical method of powder fabrication. This is using a solid state reaction in which a solid material is the starting material which is reacted with another solid to make the final powder. And this is particularly useful for highly alloyed or intermetallic compounds with precise stoichiometric ratio such as iron chloride or NiTi or titanium sulfide.

The intermetallic compounds have a particular ratio between the two atoms. For example, in this case iron chloride (Fe_3Cl); this is 3:1, in the case of NiTi, it is 1:1 and in for Ti_3S_5, the ratio is 3:5. So, they have very precise stoichiometric ratios and the solid state reactions are useful for making powders of such materials.

And the process involves mixing of these constituent powders in that particular ratio in a loosely packed bed which is then ignited and the reaction proceeds in a self propagating manner. So that means, once you ignite and the reaction is started, the reaction will propagate by itself because, it is an exothermic process. So, the heat, which is generated from the process, will actually help the reaction to proceed further.

This is an example (figure above) where nickel and aluminum is reacted in solid form and in the reaction, nickel aluminide (NiAl) is generated and heat is produced, which is helpful in making this reaction self sustaining or self propagating.

So, once the nickel and aluminum reaction starts, the reaction goes spontaneously and this is very similar to an explosion reaction that happens between hydrogen and oxygen which produces water.

But if the reaction is not controlled, then it can generate high amount of heat, which may be sufficient to even melt the reaction product, the powder which is obtained. So, therefore, if the melting has to be prevented, it is necessary to control the reaction so that the temperature does not rise to a very high extent.

Therefore, it is necessary to extract the heat. If you want to prevent the melting and over-heating, then the heat which is generated has to be continuously extracted from this reaction. And there are many variants of this process and this kind of method is mostly used for ceramic powders rather than metal powders because as you can see from the reaction (NiAl reaction) that the two metal powders are actually reacting with each other to make a ceramic or a intermetallic compound.

Thus, solid state reaction method is more suitable for making ceramic powders. So, with this we come to the end of this particular class.

Thank you for your attention.