Fundamentals of Materials Processing (Part–1)
Professor Shashank Shekhar
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur
Lecture Number 33
Powder Characterization Continued…

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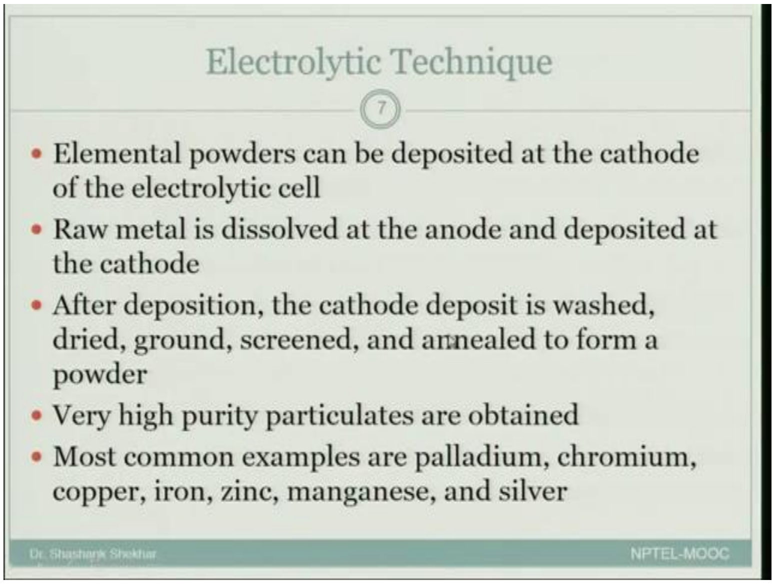

Electrolytic Technique

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- Elemental powders can be deposited at the cathode of the electrolytic cell
- Raw metal is dissolved at the anode and deposited at the cathode
- After deposition, the cathode deposit is washed, dried, ground, screened, and annealed to form a powder
- Very high purity particulates are obtained
- Most common examples are palladium, chromium, copper, iron, zinc, manganese, and silver

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So, we discussed mechanical method for fabric cutting powders, today we will look at some other method and first method today that will look at is electrolytic technique. So it is simple electrolytic cell you have a cathode and a anode and the anode the raw material is dissolved. The raw metal probably will not be very pure and it will not be in powder state. But the powder; but the material that is deposited at the cathode is very pure one and second it is usually in the powder form.

After deposition the cathode deposit is washed, dried, ground, screened and annealed to form a powder. So it is like you will see very soon it will be in a porous sponge form, it is like powdered clustered together or enumerated together. So you can first take it away dried it, ground it, screened it, and then annealed to form a powder. You are not really doing any additional step to make it powder.

It is not like that you have; what you have obtained is bulk material and then you are reducing to powder. It is actually already in very much close to powder state, like I said agglomerated powder. Very high priority particulates can be obtained, unlike I also mention that in this method you will be able to get very high purity materials.

Because the raw material that you may be using may have some contaminates, but depending on the voltage that you are using you may get only of that particular element that will be dissolved and then it will be travelled through the electrolyte to get deposited onto the cathode. Most common examples are palladium, chromium, copper, iron, zinc, manganese, and silver. So you can see this technique is much more useful for metals and particularly if you want high purity metals.

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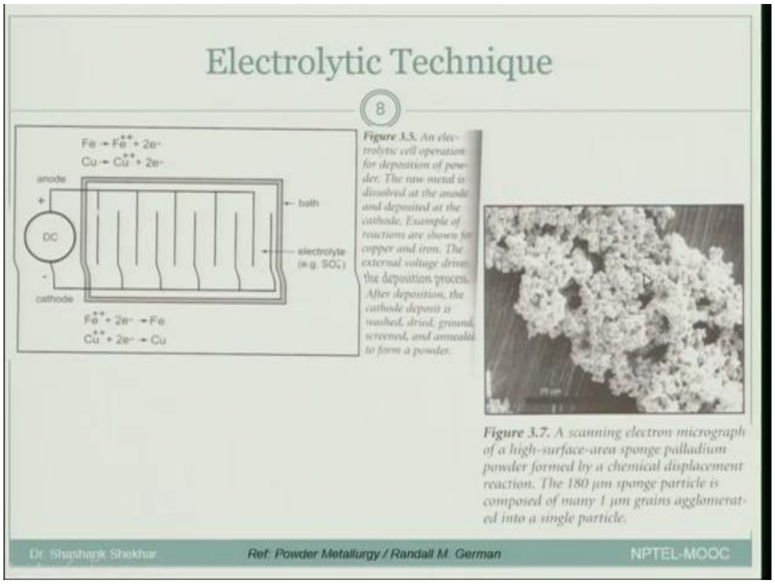

Electrolytic Technique

Figure 3.5. An electrolytic cell operation for deposition of powder. The raw metal is dissolved at the anode and deposited at the cathode. Example of reactions are shown for copper and iron. The external voltage drives the deposition process. After deposition, the cathode deposit is washed, dried, ground, screened, and annealed to form a powder.

Figure 3.7. A scanning electron micrograph of a high-surface-area sponge palladium powder formed by a chemical displacement reaction. The 180 μm sponge particle is composed of many 1 μm grains agglomerated into a single particle.

Ref: Powder Metallurgy / Randall M. German

Now this figure on the right gives you a rough idea of how the particulates look like or how the deposit looks like. So this is a deposit that was obtained on the cathode and what you see this may look like a big lump, but it is nothing but cluster or agglomerate or small powders.

So you need to just clean it, dry it and break it down. So breaking down is just putting or separating the particulates together. And this is the schematic of the system that is used to produce this powders, so you have anode and you apply the voltage source. There is a cathode and in between this two there is electrolyte. So you use a system or ass; cmm; or; equipment so that you have large; large number of surface area onto which anode can be dissolved.

And similarly, large amount; large surface area for the cathode where the metal can be deposited. So here we have few more examples given FE++ going into FE, CU++ going into C. so these are the reactions taking; that are taking place at the cathode side. We need they are getting deposited as solid form. On the anode side you had the bulk metal like ion or copper so it gets dissolved, so it becomes; gets into the ion form.

This is FE++, CU gets to CU++ and once it is in this ionic form it can travel through the electrolyte which will be over between these two plates and then it will get deposited onto these cathodes. So this is the very simple to understand technique although the setup may be a little bit more involved and you will get powders like this.

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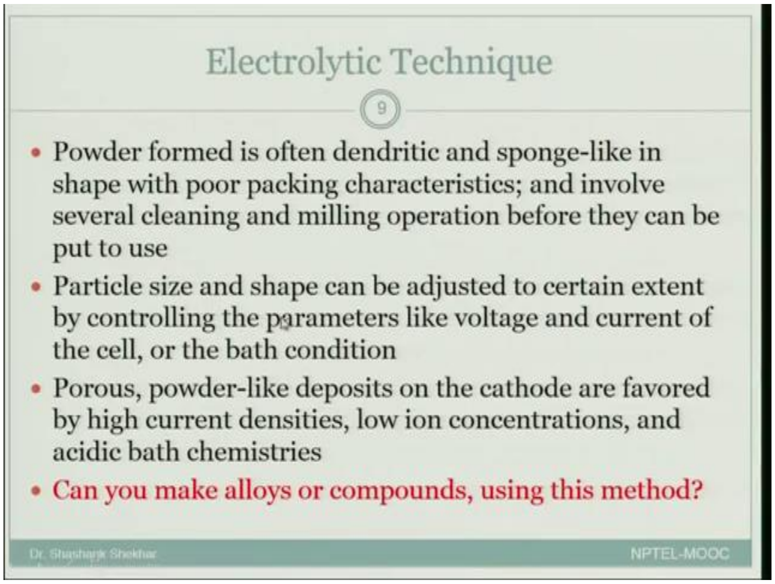

Electrolytic Technique

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- Powder formed is often dendritic and sponge-like in shape with poor packing characteristics; and involve several cleaning and milling operation before they can be put to use
- Particle size and shape can be adjusted to certain extent by controlling the parameters like voltage and current of the cell, or the bath condition
- Porous, powder-like deposits on the cathode are favored by high current densities, low ion concentrations, and acidic bath chemistries
- **Can you make alloys or compounds, using this method?**

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So powder formed is often dendritic like we saw in the earlier image and sponge like in shape with poor packing characteristics. So the powder particles that are formed or the agglomerate that you see it is not very tightly packed. It is very Porous; and with very poor packing characteristics and inv; and you need to do a lot of steps like cleaning and milling before you can make a powder which is usable for any compaction purposes. Particle size and shape can be adjusted to certain extent by controlling the parameters.

So you can change the voltage and current which are the main parameters in electrolytic cell to adjust the shape and size of the powder particulates. Porous powder like deposits on the cathode are favored by high current densities. So if you go for high current densities you may get Porous and like deposits. Lo ion; so this is not only high current densities but also low ion concentrations and acidic bath chemistries.

Having looked at this method what will your thought be on making alloy or a compound using this method. Can you make allow or method? So remember we are making from material and we egti; getting it the electrolyte in the ion form. So do you think we can make compound, no the compound cannot be made like this. Because in the compound you have bonding between the two elements that will be formed.

And you cannot ensure that bonding just by deposition. However if you are talking about alloys, in alloys there is bonding that at the chemical level. So if you are talking about alloys you can actually do get alloys, by erode or by depositing two different metals that you want to alloy. For example let us say that you are looking at NI and AL, so nickel and aluminum you can set the conditions or you can first dissolve them in the solution and then get it deposited.

And so you may have NIAL layer, but this is also not a common technique for producing alloys, because even then you may not be able to get very uniform composition. So making alloy is possible but not usually then using this method. Apart from this now we will move on to another technique; another set of technique rather I should say, chemical fabrication techniques.

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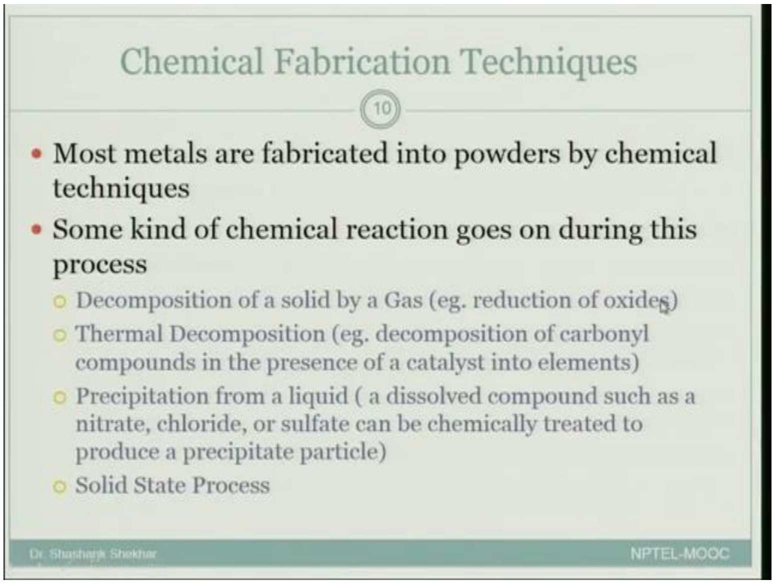

Chemical Fabrication Techniques

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- Most metals are fabricated into powders by chemical techniques
- Some kind of chemical reaction goes on during this process
  - Decomposition of a solid by a Gas (eg. reduction of oxides)
  - Thermal Decomposition (eg. decomposition of carbonyl compounds in the presence of a catalyst into elements)
  - Precipitation from a liquid (a dissolved compound such as a nitrate, chloride, or sulfate can be chemically treated to produce a precipitate particle)
  - Solid State Process

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And this itself involves a lot of other sub techniques like we will see most of the metals that we see are fabricated into powder by chemical techniques. Some of the chemical techniques methods are decomposition of a solid by gas. For example reduction of oxides and we will an see example on that, thermal decomposition of carbonyl compounds in the presence of catalyst into element. This is a very interesting method and we will see another example on this.

Precipitation from a liquid a dissolved compound such as a nitrate, chloride or sulfate can be chemically treated to produce a precipitate. So you basically first dissolve or have the material in the liquid dissolved solu; solvent state in the; into the solution and then change the condition so that a particular metal or the abb; material for example even oxide can be precipitated out.

And then you can separate out that precipitations; pracipirates and you will and those will be most likely in powder state because it will again be taking place by nucleation and growth mechanism. So the; wherever that nucleation takes place there will be those small particulates and there will be at different process and you will get small small powders at so many different places.

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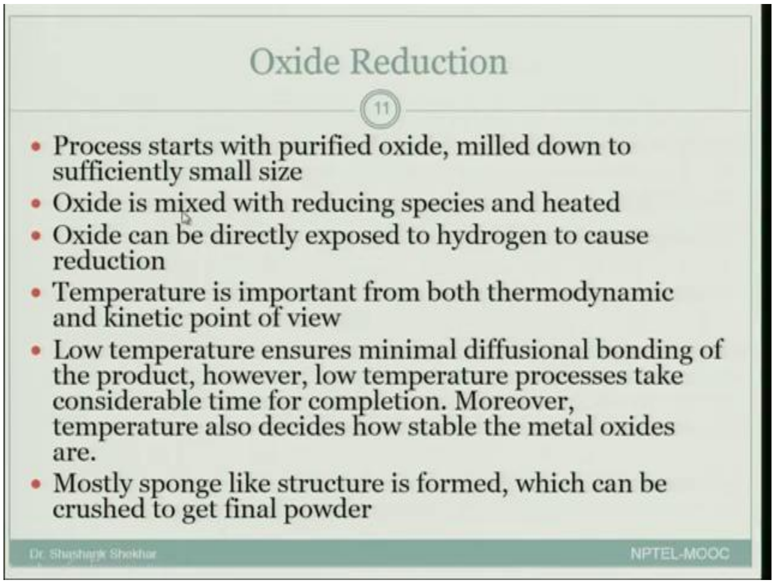

Oxide Reduction

- Process starts with purified oxide, milled down to sufficiently small size
- Oxide is mixed with reducing species and heated
- Oxide can be directly exposed to hydrogen to cause reduction
- Temperature is important from both thermodynamic and kinetic point of view
- Low temperature ensures minimal diffusional bonding of the product, however, low temperature processes take considerable time for completion. Moreover, temperature also decides how stable the metal oxides are.
- Mostly sponge like structure is formed, which can be crushed to get final powder

And you can also have solid state processes meaning all the reaction is taking place in the solid state. There is no liquid state involved as in the other cases. So let us look at the oxide reduction process, this process starts with purified oxide, milled down to sufficiently small size. Oxide is mixed with reducing species so you what; what you want is for example in this case you want to reduce the oxide.

So for example you want pure element for example iron. So you will get start with pure oxide of iron reduce it and then you will reduce it. So you will get pure iron and the method that you will use is such that you will be able to get powder size. So we will see what is that, so now this oxide can be directly exposed to hydrogen to cause reduction. So you; what we want is reduction.

And for this reduction temperature is important from both thermodynamic and kinetic point of view. At above a certain temperature oxides will be stable, at a lower the pure element will be stable. However on the kinetics it is different; for the kinetics higher temperature will imply higher kinetics, lower temperature will imply lower kinetics. So you have to find optimum condition of temperature where you are able to get reduced species or the uhh; reduced material which is stable. And at the same time the kinetics is high enough.

Low temperature is ensures minimal diffusional bonding of the product,however, low temperature processes take considerable time for completion. Another; so low temperature; is also desirable from the kinetics point of view because it ensures minimal diffusional bonding of the product. However, again the kinetics become slow. And then thermodynamics again the temperature has to play a role bhh; above a certain temperature oxide will be stable and below a temperature the reduced species will be stable.

Mostly sponge like structure is formed, which can be crushed to get final powder. So here is a diagram which explains the role of temperature and another pressure; and also the pressure. So for example what we are talking about here is reduction of iron. So let us look at what is the usual equation for iron reduction.

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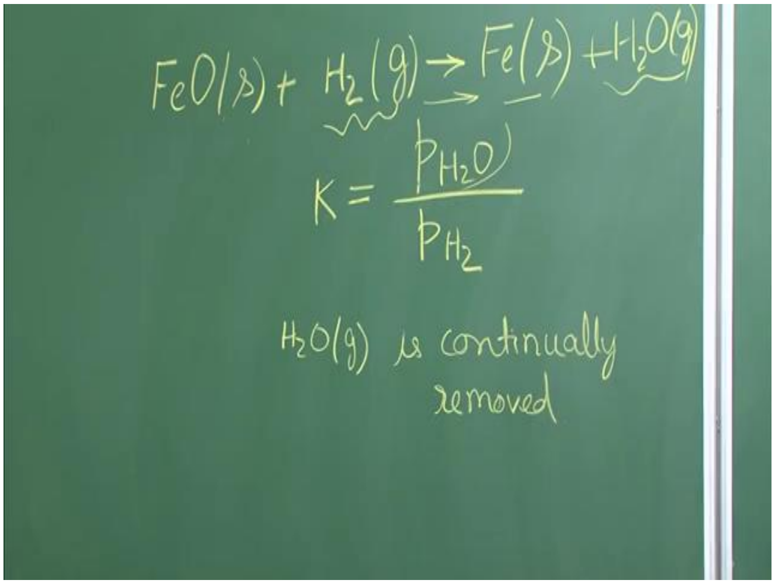

$$FeO(s) + \underset{\sim\sim}{H_2(g)} \rightarrow Fe(s) + \underset{\sim\sim}{H_2O(g)}$$

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

$H_2O(g)$ is continually removed

So it will be of this form, you will start ff; FeU which will be in solid state and you will react or reduce with hydrogen, which will be in gaseous state. And from here you should get ion; pure iron which is in solid state and moisture. This reaction will be equilibrium and you need to find aequilibriumconstant and that equilibriumconstant can be given by because the other two elements other two compo; components which is the FeU and Fe they are in a solid state therefore there activity will be equal to 1. And therefore the overall reaction equilibrium will be controlled by the partial pressure of hydrog; partial pressure of hydrogen and partial pressure of water or the moisture.

Now in order to take the reaction to completion if you want that this reaction goes keep going on, what we want, you want that H2O which is in gaseous state is continually removed. What will happen when H2O is continually removed, it will mean that this amount; this ventricular factor is reduced and therefore to balance or to bring the equilibrium the reaction will go into the forward state. And therefore more and more FeO will get reduced into iron state.

So this is an one way of making sure that the reaction keeps on going in the forward direction. You take away H2O so H2O has to also reduced by the same amount. And therefore at that will be possible only if it reacts with FeO/S. and therefore your reaction will keep going forward.

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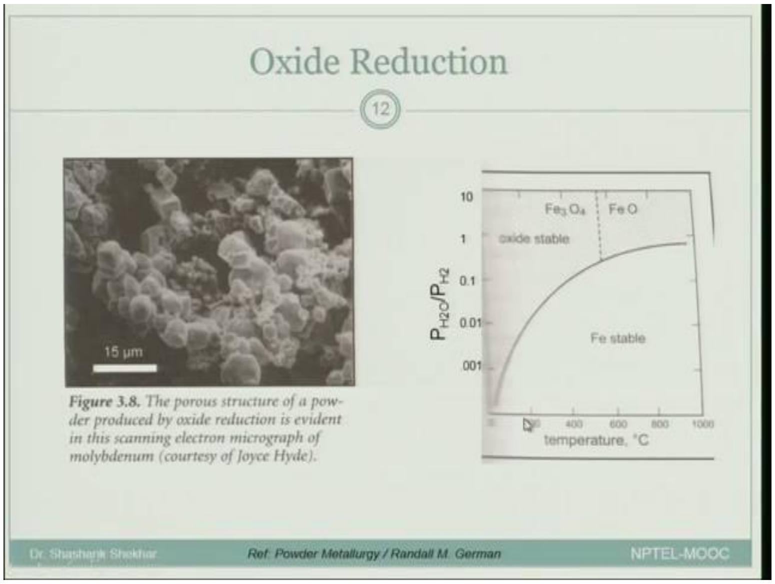

Oxide Reduction

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Figure 3.8. *The porous structure of a powder produced by oxide reduction is evident in this scanning electron micrograph of molybdenum (courtesy of Joyce Hyde).*

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Ref: Powder Metallurgy / Randall M. German

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So that is one aspect of it, another aspect is explain by this diagram, here you have on the Y axis, you have the PH2O by PH2. And on the X axis you have the temperature.

So it shows for different temperature range what is the equilibrium constant or PH2 by PH; bhh; PH2O by PH2, where sta; iron is stable and where the oxide is stable. So this line over here represents that ratio of the pressure, equilibrium pressure. And for different temperature this amount is different and not only that for a particular condition you have FeO more stable. So this is the FeO stable, so at this particular if you are mois; PH2O by PH2 is and the temperature range is like this over here FeO will be preferred over Fe3O4.

And this gives you condition or this gives you the parameters that must be maintained for iron to be formed. So if you want the iron to be formed the temperature, the pressure must be below this. For example let us say we are doing it at 600 degree Celsius, then PH2O by PH2 must be less than this pressure. And only then iron will be stable and then you can apply it along with our second para; second thing that we discussed, that is to keep taking away PH2O that way you will have, this will ensure that the reaction keeps moving in the forward direction.

So this is the technique of getting oxide reduction particularly in FeO. And here is a micrograph which shows the powder particles obtained using this method. And this is again as you can see a very poorest structure of powder which has been produced by this oxide reduction method. So this is the oxide reduction method. Another aspect that you need to be aware when we are talking about oxide reduction is that there is a reaction front.

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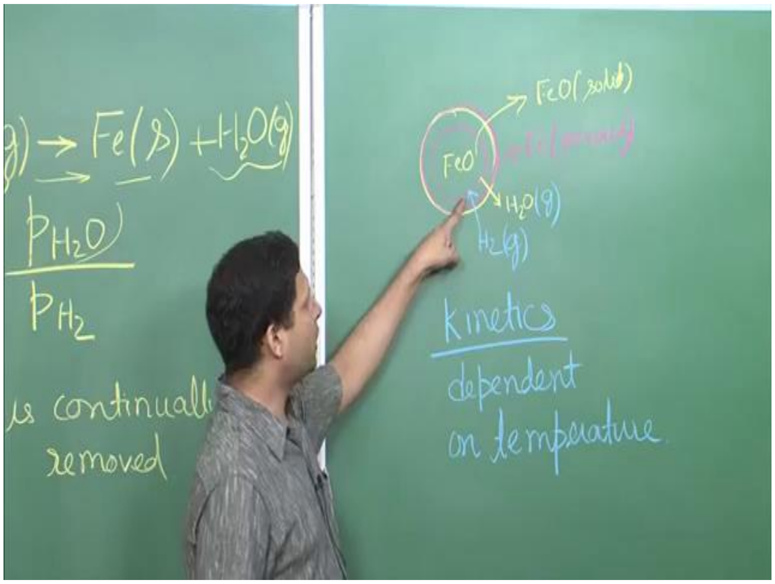

Let us say this is our initial FeO powder, now when och; H2; is it is exposed to H2, there will be a reaction front onto the surface and Fe will start to form. So let us say I use this; this is the reaction front after sometime this part has become Fe, poorest Fe remember this will be still. But this is inside it is still solid cor; solid FeO. At this stage if the reaction has to proceed then H2O must come out and H2 must diffuse. So these two gases species must diffuse at this boundary layer to ensure that the reaction keeps on proceeding.

And again this is why there will be a dependence on temperature that is the; it is this; that; this kinetics that is dependent on temperature. If the temperature is higher the diffusion of H2O coming out will be larger, H2 going in will be larger and therefore the reaction will take at place at a faster rate. If the temperature is lower than the diffusion will be lower and therefore the reaction would not take place at a faster rate. So it will take much longer time and this is explain in our next figure which is over here.

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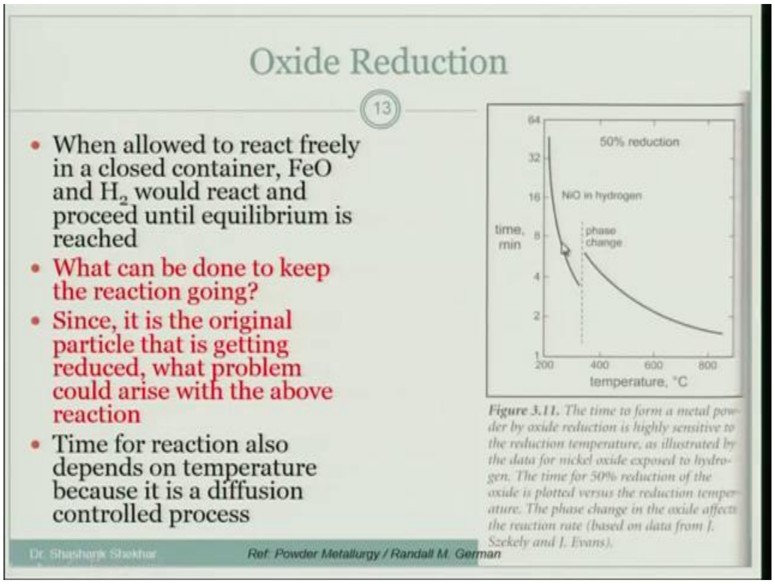

Oxide Reduction

- When allowed to react freely in a closed container, FeO and H_2 would react and proceed until equilibrium is reached
- What can be done to keep the reaction going?
- Since, it is the original particle that is getting reduced, what problem could arise with the above reaction
- Time for reaction also depends on temperature because it is a diffusion controlled process

Figure 3.11. *The time to form a metal powder by oxide reduction is highly sensitive to the reduction temperature, as illustrated by the data for nickel oxide exposed to hydrogen. The time for 50% reduction of the oxide is plotted versus the reduction temperature. The phase change in the oxide affects the reaction rate (based on data from J. Szekely and J. Evans).*

Ref: Powder Metallurgy / Randall M. German

So over here on the right you see that the time that it will take as a function of temperature. So what it says that as you keep increasing the temperature let us say 800 degree Celsius it is taking for this particular condition. It is taking only less than 2 minutes to complete. Now when you reduce the temperature to somewhere like 300 or 400, you see that the time has increased.

So let us say this is somewhere around 250 so time has increased to 8 minutes. And below a certain temperature, let us say for example in this particular case it is 200 no amount of time is sufficient to get the reaction to completion. That is because diffusion becomes so slow that it is virtually; it has virtually come to a stop. So when allowed to react freely in a closed container, FeO and H2 would react and proceed until equilibrium is reached.

Provided; we are providing it the vv; sufficient condition. For example taking away H2O and also that the pressures; pressure ratio is maintained. We have answered this part of the question which is what can be done to keep the reaction going. That is to take keep removing the moisture, if you keep removing the moisture then the reaction will proceed in the forward direction because H2 has to be removed by similar amount.

And that; that will ensure that Fe is formed. Since it is the original particle that is getting reduced what problem could arise with our reaction. We have seen this since it is the original particle which is shown over here, which is reacting. So this is FeO and slowly it becomes Fe. It is not that ll; for example in electrolysis we had a new particle forming at a different place.

But here it is the same particle, we started with where reaction is taking place and moving into the front and finally the whole thing has; is supposed to become reduced. And therefore kinetics has a role to play or diffusion has a role to play and therefore it changes with temperature. And it also depends on face change, for example in this particular case there is a different phase beyond this temperature and there is a different phase below this temperature.

And therefore the total time taken, there is a step in this plot of the total time taken as a function of temperature. So you can say that at this particular temperature and this particu; this particular temperature is very suitable because here you are able to reduced the time as well as keep the temperature low enough. So this may be a desirable set of parameter for this particular condition.

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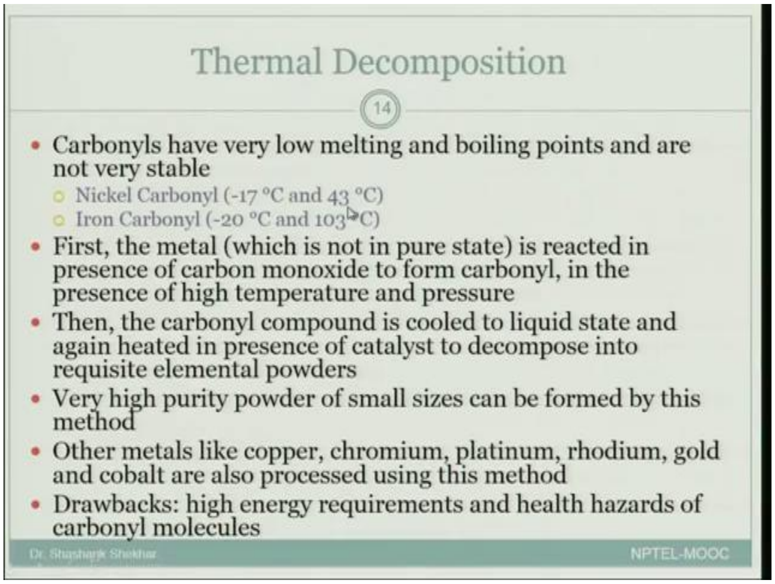

Thermal Decomposition

- Carbonyls have very low melting and boiling points and are not very stable
  - Nickel Carbonyl (-17 °C and 43 °C)
  - Iron Carbonyl (-20 °C and 103 °C)
- First, the metal (which is not in pure state) is reacted in presence of carbon monoxide to form carbonyl, in the presence of high temperature and pressure
- Then, the carbonyl compound is cooled to liquid state and again heated in presence of catalyst to decompose into requisite elemental powders
- Very high purity powder of small sizes can be formed by this method
- Other metals like copper, chromium, platinum, rhodium, gold and cobalt are also processed using this method
- Drawbacks: high energy requirements and health hazards of carbonyl molecules

So this is the method of oxide reduction, let us move on to still another method and we said we talk about briefly thermal decomposition. Now this thermal decomposition is a very very interesting technique as you will see. Carbonyls are compounds that have very low melting and boiling points and are not very stable. For example nickel carbonyl has a melting point of -17 degree Celsius and boiling point of 43 degree Celsius. Compare it with the melting point of nickel which is in access of 1000 degree Celsius.

Similarly, iron carbonyl has melting point of -20 degree Celsius and a boiling point of 103 degree Celsius. In this process first the metal which is usually not in pure state is reacted in presence of carbon monoxide to form carbonyl. So you take the metal whatever it is, for example nickel or iron which is not yet in pure state. And then you form aarr; expose to carbon monoxide, so that you get this carbonyl.

Now you know that the carbonyl will be very very low melting point material and therefore it will be in vapor state. So once you home appliances ve formed that carbonyl which will usually be in the vapor state, then this you cool down this carbonyl to liquid state. So you will have to bring it down to for example, if you have nick; nickel carbonyl you will have to reduce it to 43 degree Celsius, less than 43 degree Celsius, so that it comes in liquid state and then at this stage again heat it presence of catalyst.

So you will have to use some catalyst and then heat it again and what happens is that in this particular condition the carbon and oxygen or the carbon monoxide gets released and you are left with only the nickel compound; nickel element. And therefore you will be able to not only get pure material but you are able to get powder size of that material. So you the steps are first you make the carbonyl compound at by applying very high temperature and pressure.

Then you reduce it to below the melting point, and then you again heat it in the presence of a catalyst. So that it decomposes and forms that elemental powders. So again like electrolysis we are also be; we are also able to do some purification here. So very high purity powder of small sizes can be formed using this method. Other metals like copper, chromium, platinum, rhodium, gold and cobalt are also processed using this method.

However there is some drawback, that this method is very energy intensive. You need to first put high temperature and high pressure so that you can convert it to carbonyl and that requires a lot of energy. And then again heat it first bring it down to below the melting point, then again heat it in the presence of catalyst. So it is not a very easy to access method, however, it has several advantages you get purity; high purity and second you get very small size powder.

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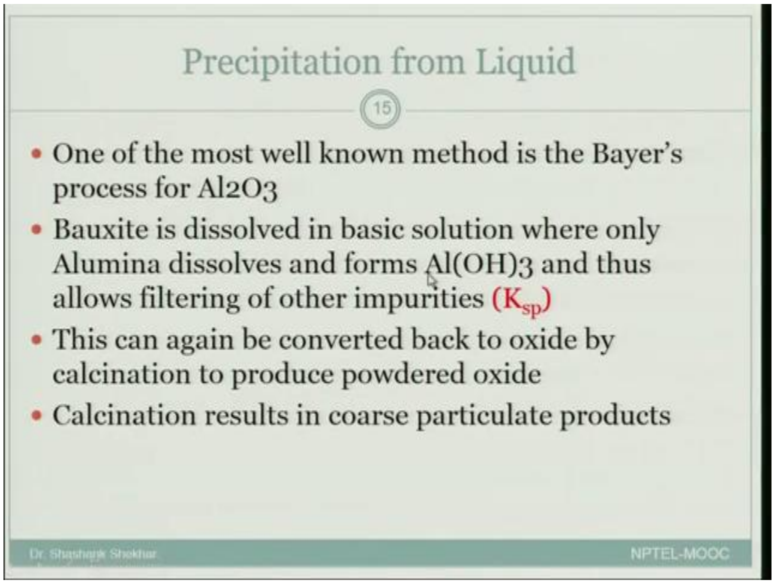

Precipitation from Liquid

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- One of the most well known method is the Bayer's process for Al2O3
- Bauxite is dissolved in basic solution where only Alumina dissolves and forms Al(OH)3 and thus allows filtering of other impurities (K_{sp})
- This can again be converted back to oxide by calcination to produce powdered oxide
- Calcination results in coarse particulate products

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Let us move on to still another chemical process and this is precipitation from liquid. And one of the most well known methods that you can say come; that comes in this category is bayers method for producing AL2O3. Now, ii; in the bauxite which is the over for aluminum. There are AL2O3 and also some several other compounds. So bauxite is dissolved in some basic solution where only alumina dissolves.

So you you; when you dissolve it in base only alumina of that whole bauxite gets dissolved. And it forms ALO whole; OH whole 3. So now this will be in first in a liquid state and in liq; when you have it in the liquid state you will get rid of other compounds. So you will filter out other and you will have AL(OH)3 in a liquid state. And then from this liquid state you set the condition such that AL(OH)3 forms precipitates out.

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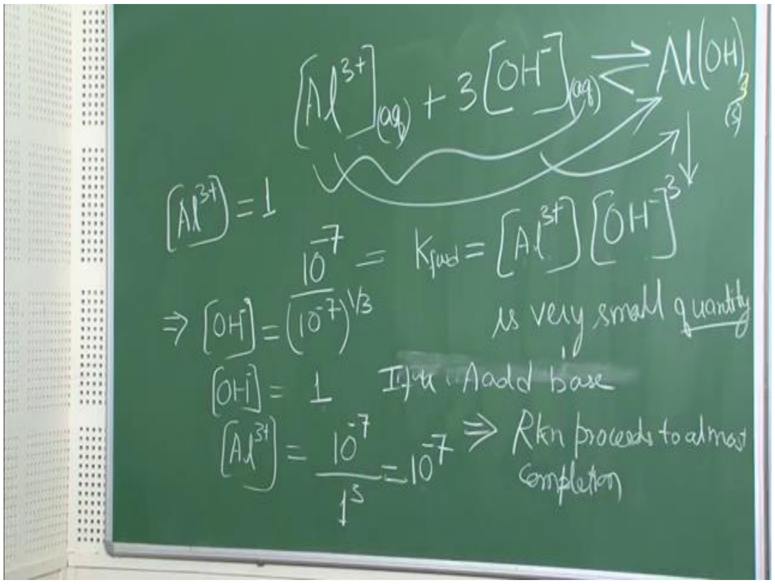

$$[Al^{3+}]_{(aq)} + 3[OH^-]_{(aq)} \rightleftharpoons Al(OH)_{3(s)}$$

$[Al^{3+}] = 1$

$10^{-7} = K_{fwd} = [Al^{3+}][OH^-]^3$

is very small quantity

$\Rightarrow [OH^-] = (10^{-7})^{1/3}$

$[OH^-] = 1$ If you add base

$[Al^{3+}] = \frac{10^{-7}}{1^3} = 10^{-7} \Rightarrow$ Rxn proceeds to almost completion

And once it precipitates out then you can again reduce it to form aluminum. So let us; let me write down a little bit of equation over here. So we are looking at bauxite where and we have put it in a mm; basic medium so only AL O AL2O3 dissolves. So let us say this has divose; this has dissolved and you have formed. So initially what you will want is that when you put in the bauxite, the basic medium it is in this particular state. That is it is in the aqua state.

And rest of the compound will be in the solid state, you will filter them out and you are remained with only AL(OH)3 in the aqua solution. And that; after that once you have filter it out you will want the reaction to go forward. Here you will be able to precipitate out AL(OH)3 and then you can convert it to AL2O3 and then A2, aluminum; pure aluminum.

Now what is the method to control this reaction, this reaction if you write. So this is in solid state and therefore list is not then so this activity will be equal to 1. Now if you want to write the forward rate constant for the forward reaction, we can write it like this. So this is the rate constant for forward reaction and this is a very small quantity, is a very small number.

Now if it is a very small quantity and you put and you put this in base or you add base basically what I am trying to say, if you add base it will imply that the reaction will proceed in the forward direction. Because if you add base then it would be this has become large and therefore this much is reduced to a much smaller quantity. And the only way for it to reduce to a smaller quantity is to form this.

And we will just take a quick look at the numbers to understand this. So if you add base reaction to almost completion. For example let us say that K forward is equ; K forward is equal to 10 to the power -7, ok. So this is the quantity K; 10 to the power -7 and now let us say that AL3+ to begin with is equal to 1. This will imply that OH minus concentration would be equal to 10 to the power -7 to the power 1 by 3.

However, now let us say we add some base, so that OH minus becomes 1. Now if OH minus becomes 1, so the product of this; but the product of these two should still be equal to 10 to the power -7 and therefore it will mean that AL3+ should now equal to this 10 to the power -7 and this is OH minus cube equal to. So the AL3+, just because you have added some amount of OH minus whose concentration initially was cube root of 10 to the power -7 and we have increased it to 1. So the aluminum concentration reduces from 1 to 10 to the power -7.

And how is that possible, the only way it is possible is by AL3+ getting converted of; getting precipitated out as ALOH3. So this is a very powerful method to not only get rid of other compounds that where there. But to also precipitate out and get powder size particulates. So you will get AL(OH)3 in particle size and then you can do some secondary operations to convert it to alumina.

So this can again be converted back to oxide by calcination to produce powdered oxide. So you can get powdered oxide out of it, calcination results in coarse particulate products. Precipitation from the liquid is also used in many other methods. A dissolved compound such as nitrate, chloride or sulfate can also be chemically treated to produce precipitate. The idea is same you always want to precipitate out compound or the element that you want in the powder form and since it is precipitating out, it will always be in very very fine powder size.

Similarly, silver can be precipitated out of silver nitrate method and so we cannot only use nitrate we can also cal; chloride, sulfate and some other solutions. There are several methods that are used to get particulates out of solution also. So the precipitation is one thing but you can also use other methods to get the particulates out of the solution and two of those are called spray pyrolysis and freeze drawing.

So will start from this; amm; these two prom; methods in the next lecture. So we have looked at some of the precipitation from liquid method, next time we will look at how to get from gets precipitates or particulates out from the solu; solution and the two method that we will discuss are spray pyrolysis and freeze drawing. So will continue our discussion on powder fabrication in the next lecture, thank you.