Carbon Materials and Manufacturing
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Lecture – 16
Synthetic Graphite Production from Needle Coke

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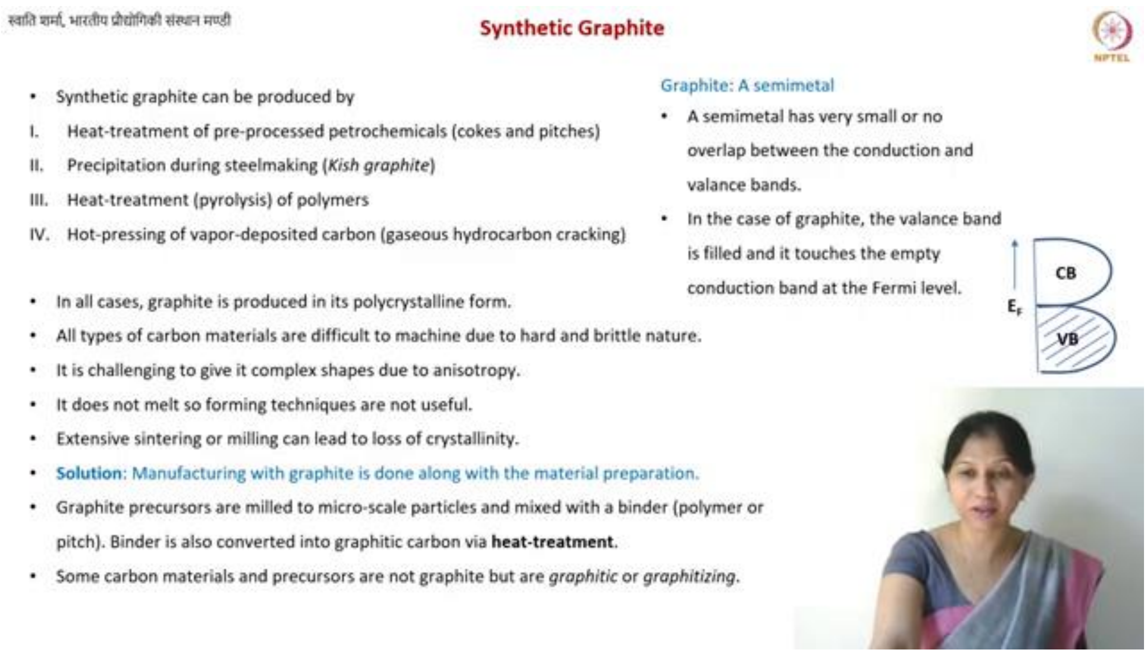

Hello everyone. From this lecture onwards we are going to talk about synthetic carbon production. Here we will talk about Synthetic Graphite. I told you in the previous lecture that we need a lot of graphite for various applications. We also need this material with high purity. Natural resources may be limited and sometimes the processing of the ore can become very expensive. So we also need to have certain methods of artificially producing graphite. Unlike other metals or elements, it is actually possible to make carbon materials artificially. You cannot really make artificial iron or artificial gold but you can make different forms of carbon because we know that the source of all the carbon even the one that we mine. The source of it is organic material. It is actually the organic material that was converted into carbon because all the non-carbon atoms left the material at some point due to extreme conditions.

Can we actually induce these extreme conditions and then can we get the carbon? If yes? if we get the carbon, then what is the type of that carbon? Can we always get graphite or can we get diamonds or can we get any other type of carbon? This is something which is very interesting and it will form a major section of this course in fact.

Before I start with the synthetic carbon production, I had in the previous lecture mentioned that graphite is a semi-metal. So, what is a semi-metal? First of all, you divide elements into four types; insulators, then semiconductors, and then within the conductors, you have metals and semi-metals. If you see the band gap of semi-metals, they have either very small or no overlap between their conduction and valance band.

For example, in the case of graphite, you can see this in this picture. You have a completely filled valance band and you have an empty conduction band but they touch at the Fermi level. So, these kinds of materials are known as semi-metals. There are other elements as well, I think antimony, there is a certain type of tin, also there can be certain compounds which are semi-metals.

In terms of physical sense, you have basically some properties which are like metal. Graphite for example it’s a conductor, it also has a shiny surface but on the other hand, there are also some properties that are not like metal. You cannot you know melt and mold or form your graphite.

This is important also for manufacturing applications because we cannot use what we use for metals. You cannot have the same elasticity; you cannot do manufacturing and pull fibers out of graphite. So, this is important for us. This is just for your information.

Now, coming to the synthetic graphite. There are four major techniques, and sometimes you use a mixture of these techniques.

First of all, you can do heat treatment of pre-processed petrochemicals. Petrochemicals is a completely different subject area. You have so many different organic materials, not just petroleum, not just diesel and petrol, you also have so many gases, you also have certain other high carbon residues.

High carbon residues will contain what is known as coke and pitch. These are some of the materials which are also used in different applications, but they can also be used or at least some of them can also be used to give you carbon. When you heat organic material and remove all the non-carbon atoms and you can get carbon at some point at a certain high temperature.

Which organic material should you choose? You should choose something which already has a high carbon content. If you want to get graphite then you should also have the certain possibility of having a crystalline structure, similar to an anisotropic crystal structure. So, we can take these petrochemical precursors and we can heat them and then we can get graphite out, that is number one.

When we make steel, iron and carbon are mixed. Now, often happens that if there is some additional carbon or there are certain reactions that lose carbon when you are forming steel, then that carbon precipitates out. Precipitates mean either it will deposit onto the surface or it will just basically come out of your steel. So, that is also interestingly often in a very crystalline form. Why so? Because there are a lot of small carbon units which are getting together and the most stable form is anyway graphite. So, they end up forming graphite. This type of graphite industrially is called Kish graphite. We are going to discuss that most likely in the next lecture.

I said heat treatment of petrochemicals and then heat treatment of polymers also. There are minor differences because, in terms of the process, you have pretty much the same processes, but different in terms of the chemical structure of your precursor. In the case of polymers, you need to learn a few different things like not all polymers will give you graphite. So, this is the third method that we will talk about.

And the fourth one is making carbon from hydrocarbon precursors or gaseous precursors. So, you can actually deposit carbon also by cracking the hydrocarbons that are in gaseous forms like methane or acetylene. And then you get these layers of carbon and then we are going to learn how do you get graphite from that.

In all of these cases, the graphite that you get will be in its polycrystalline form but on the other hand, you also know that graphite crystals are not too large, unlike other materials, you have relatively smaller crystals. Anyway, for most of the manufacturing applications, the graphite that you are going to have will be in its polycrystalline form and not a single crystal form.

We had discussed previously for manufacturing applications, it is difficult to machine any carbon material, not because of its hard and brittle nature but because you do not want to compromise on the crystal structure of the graphite. And today we are going to see what is the solution to this? We find it difficult to machine carbon. And also because you have this anisotropic structure, then you cannot give complex shapes to graphite, because you have this layered structure, you cannot really bend it or you cannot without compromising the crystal structure you cannot really give it you know any if you cannot give it random shapes ok.

And other things, it does not melt, it sublimates you know that. So, you cannot use a lot of manufacturing techniques also, sintering or any kind of you know crushing techniques also, cause the loss of crystallinity and also induce defects, so that is undesirable.

What is the solution? The solution is that we make the graphite and other carbon materials from the organic precursor. So, is it possible? Now, these precursors are polymers or petrochemicals and they may be in semi-solid or solid state.

Can we actually shape them and then do the heat treatment? What do we get in the final material? We already know the shape we want and then we pattern our polymer in that shape and then we convert it into graphite. So, that is actually what is most often done. And how do we do that?

Another option is that you can take graphite precursors, you can mix them into a certain binder. So, either you can take the graphite precursor directly if that is difficult because it has not the best viscoelasticity or viscosity, not the optimum one. So in that case we can also mix it into a certain organic polymer, for example, a resin and then we can convert it again into carbon. Basically, you are mixing the different four techniques that I have discussed. We will talk about that when we come to it.

An interesting part is that when you learn about graphite or graphite-related materials then there are certain definitions that you need to know. That is where all the confusion comes from in the field of carbon because people do not know these definitions like what is graphitic? What is graphitizing material? What is non-graphitizing material? And what is graphite and what is graphene?

So, these are the definitions that you need to know because only then you will be able to differentiate between the materials that you have. Otherwise, you may end up calling something graphite which is not really graphite. And then you will be contributing to the confusion. So, in the next slide, so we are going to learn about some of these definitions.

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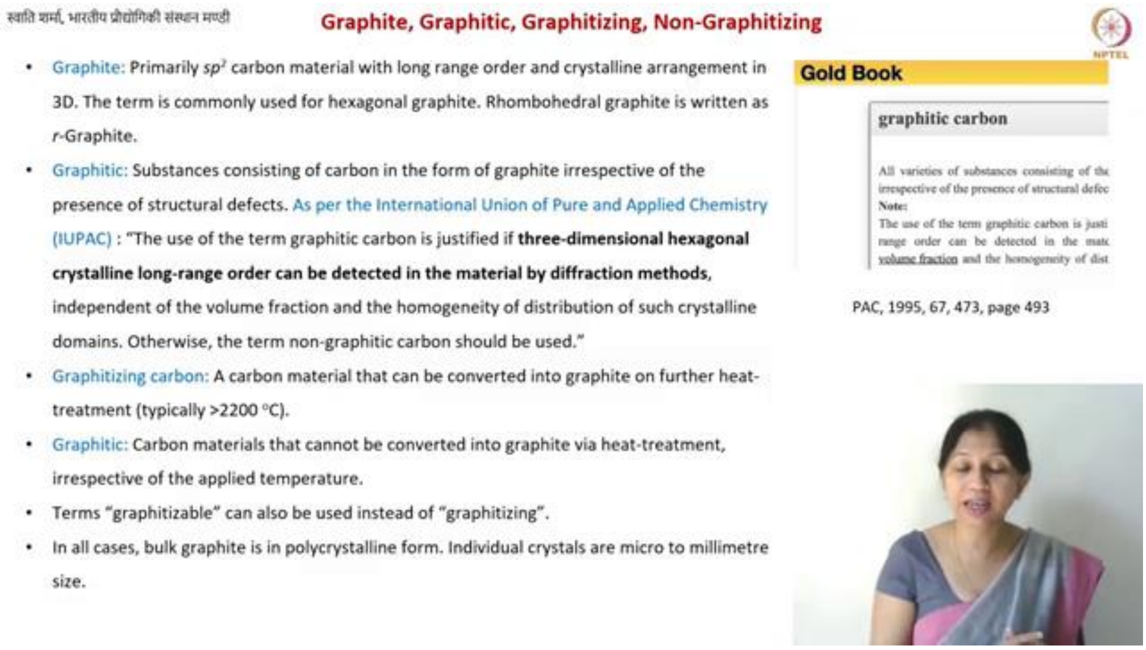

I have listed the definitions of graphite, graphitic, graphitizing and non-graphitizing on this slide. I am not going to discuss each one of them individually because you can just read through what I had written here. One thing I must definitely tell you is that most of these definitions I have taken from what is known as the IUPAC Gold book. You know what IUPAC is.

IUPAC decides all the names for organic materials and carbon-related materials. Now, what is this IUPAC gold book? This is where you find all the definitions and you can easily do an internet search and you can find the definitions.

If you are reading a research article and somebody says I have made graphene, but you look at the spectrum or you look at the data and you be like no this is not really graphene or this is not really graphite I would not call it graphite, I probably would call it graphitic or graphitizing. So, if there is any confusion just have a look at the IUPAC gold books.

IUPAC is International Union for Pure and Applied Chemistry. And this is the sort of agency that determines that establishes a name. Now, you might also say that what is in the name? It is just about terminology. I have heard it from many people like I made what I made and what is in the name.

Let me give you an example, right now we have this coronavirus pandemic going on. Now if there is some company that comes up with a drug that really has nothing to do with coronavirus, maybe it is some just immunity booster or something like lemon juice. Now, if that company gives it a name like *kill corona*, although it does not have anything to do with the coronavirus that can create a lot of confusion. Many people may end up buying it just because it is called kill corona. Now, the company might say that no I have nothing to do, I am not claiming that I am curing a coronavirus, I am just this is the name, what is in the name?

No, it does not work that way. There is something in the name because if you give confusing names then that is something that you are intentionally doing and then you are this is not a good thing to do right. I will not go so far that it is ethical or unethical. But if you are knowingly creating confusion for any, for example, a lot of companies are doing that with graphite-related materials, because they call something graphite which is not graphite at all now which may just be a graphitic material. And graphitic material you know if you read this definition of graphitic materials that as long as you can detect the peak for graphitic regions you can call it graphitic.

But that does not mean it is graphite, it may actually be a disordered carbon material. So, there is a lot of confusion because of the commercial reasons, and it may also be for certain scientific reasons because certain materials become what should I say too popular, and then everybody wants to say that this is what I am working on. So, be careful you need to go through these definitions.

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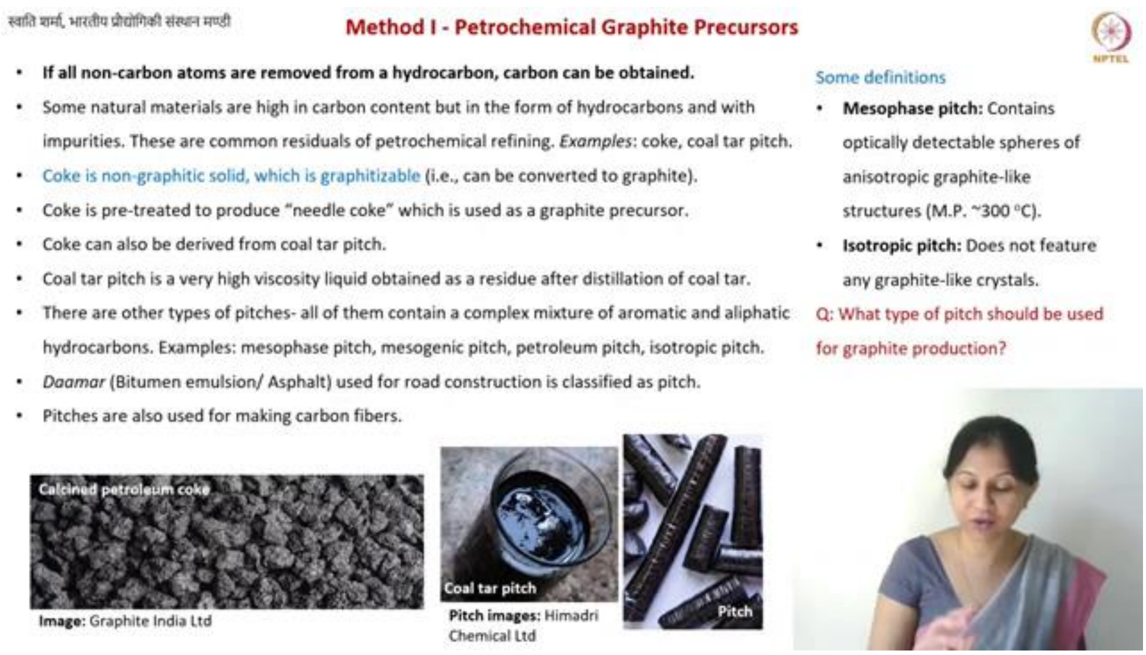

Now I come to the first method that we discussed about making the graphite from petrochemical precursors. What is a precursor? A precursor is anything that is your initial material, that is what you are going to heat and then you are going to get your final material. This will remove your non-carbon atoms and you can get carbons not necessarily graphite, but some sort of carbon. Now, certain materials for example, petroleum products such as coke, tar and pitch. You know what coal tar and pitch are. I will show you some pictures maybe that will make it clear.

Coke, coal tar and pitch, are some petroleum products that already have pretty high carbon content. They have often very complex molecular structure because they are a mixture of a lot of hydrocarbons. A lot of things are almost carbon, but not completely carbon.

You know hydrocarbons degrade over time and they get fragmented. They make smaller hydrocarbons and then some of them are so small and volatile that they come out as in gaseous form. And then we still have these solid residues with very high carbon content. Some of them are in solid form, some of them are in liquid or semi-solid form. These can be used for making graphite. So, we just need to give them a little bit of push and they will convert into pure carbon forms.

Here is a picture of coke. This is how coke or processed coke looks like. We do a certain process known as calcination. Calcination is also a heat treatment, but you may have some air in the case of calcination. Air means you can have some oxygen. So, there may be certain burning that is taking place. Now, you may want you basically trying to burn out the organic impurities. So, after the calcination, you get this kind of raw material which is known as petroleum coke.

Now, coke in itself is a non-graphitic solid. So, if you have read the definitions that I gave you before, what is non-graphitic? That means when you do its characterization let’s say you do x-ray diffraction studies or something characterization techniques that we are going to learn separately. So, when you do the characterization, you will not see the peak for graphite that is what is meant by non-graphitic solid. In the beginning, it is non-graphitic and we heat treat it to convert it into graphite. So, it can be converted into graphite, which means it is graphitizable.

So it is non-graphitic to start with, but we can potentially convert it into graphite by heat treatment, that is why we call it a graphitizable solid. Now, when we do this pre-treatment of coke, as I mentioned already that we do certain calcination processes for a little bit of refining. This is the first raw material is that you get from your petrochemical refineries, but after that, you also need to do certain preprocessing to get the actual raw material that you are going to use which is known as the needle coke.

When we separately discuss raw materials maybe we will go into more details. Today our goal is to learn how to get graphite out of these precursors. Other than that, you have something known as pitches. You have seen the roads, you know when you see road construction, you have this what is known as damar, also known as asphalt. So, this bitumen is basically your coal tar pitch.

Sometimes on a very hot summer day, you can also see on the road a little bit of this pitch comes out. You know that this is a very viscous black nasty-smelling liquid. That is what actually can be used for making graphite after processing, but not all kinds of pitches.

You have something called isotropic pitch. You have something called mesogenic pitch. Many of them are classified as just petroleum pitches. And then you also have something known as mesophase pitch, and this mesophase pitch is what is primarily used for making graphite. Isotropic pitch is also used for making carbon, but that carbon may not be graphite. So in the case of graphite, our 3D crystal arrangement is very important to us.

There is another picture of pitch that I have shown, this is almost solid, for example, the mesophase pitch. Its melting point is I think around 300 C, which means it is a very high melting point, almost solid like material.

Pitches come in various viscosities and these are our raw materials for getting graphite. Also, pitches are used for making carbon fiber. You see they are very highly viscous liquids. You can already see when you see the road making when they pour this on the road, you see that there are long fibers like things coming. It is like honey, it has high viscoelasticity.

This can be used for making carbon fibers and in fact, it is used for making carbon fibers. Isotropic pitch is used for making just carbon fibers not graphite. So, this is what we do with the different pitches.

Here is the definition of mesophase pitch, the one that we use for making graphite. Why? Because it has already certain graphite crystallites, kind of floating in it. These are already anisotropic; that means they have this graphite-like structure. They have the layered structure.

Isotropic means it will be same in all directions, but this already has a preferred direction let us say, and these are even optically detectable. This material is more like a liquid crystal. So you have crystals, but all together they can have a certain flow, so you will not call it crystalline solid.

So, that is your mesophase pitch. Isotropic pitch on the other hand does not have these kinds of graphite-like crystals. Now, yeah I already told you the answer to this question. I thought I will ask you which one should be used for graphite production. Now you know, it is mesophase pitch.

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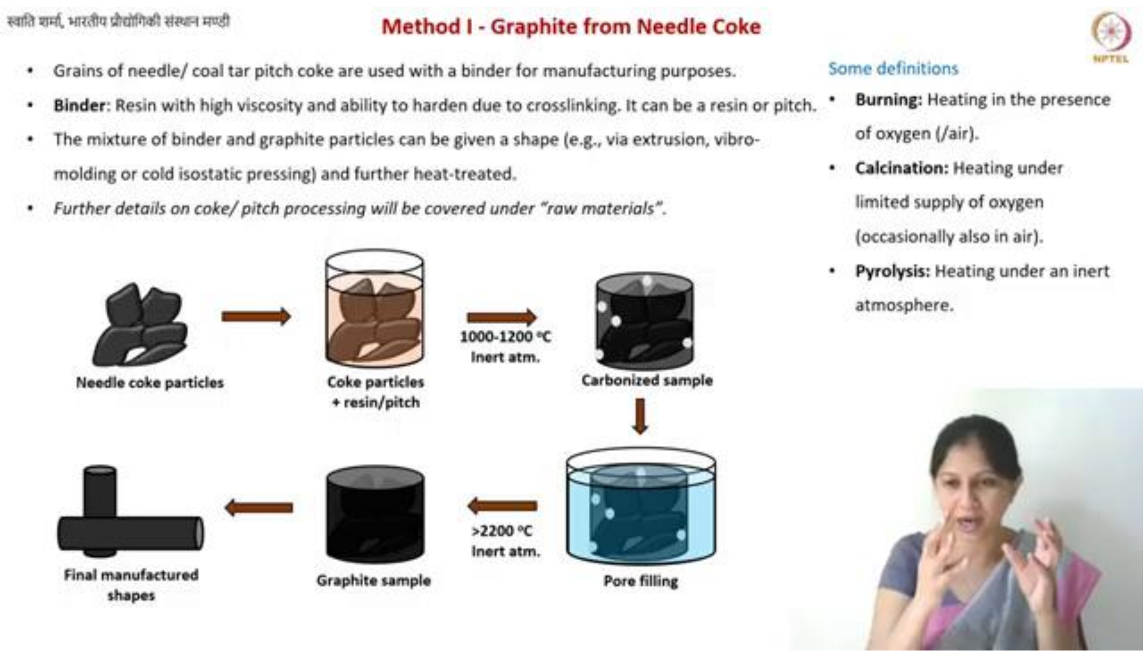

What do we do with, let us say coke or pitch, but pitch because it is a little bit viscous, so we are rather going to use it for making fibers. So I will cover the fiber fabrication in the carbon fiber section. Then we will talk about the mesophase pitch and so on.

Now, let us talk about needle coke particles and how do we make something out of them. I mentioned to you that you can already give a shape to your precursor when you want to make something out of it. So this is what we are going to do.

But the needle coke is in the form of granules or in the form of big lumps or not powder, but you have particles grains. So now what do you do with these grains? So you want to heat treat this grain and then you will get graphite out of it. But you need to bind these grains and give them a certain shape. What do you do? You take a certain type of high carbon-containing resin.

As I mentioned before that resins are very viscous polymers. You may have also heard of epoxy glue you get. So, especially for a lot of research purposes, you will get something called epoxy glue which is nothing but a very viscous polymer. And sometimes you also have two components of this glue; one is a polymer, one is the crosslinker. When you mix these two things then this polymer gets cross-linked and that becomes hard then serves as your glue. That is also a type of epoxy resin. Now you take your needle coke particles which may be of random shapes like these grains and now you want to make a cylinder out of it, you want to make a graphite rod. Graphite rods are used as electrodes.

What do you do? You now give it a shape of a rod. Let us say I take a cylindrical some pot and then I put my resin and as well as the coke particles and now this resin is cross-linked. Cross-linked means you want to harden it. Cross-linking basically means different polymer molecules are attaching to each other and the overall material becomes hard. That can be done by adding another chemical which is your cross-linker.

It can also be done by just heating. Certain polymers have a chemical property that by heating they will convert into certain radicals and then they will attach with each other. So that can lead to hardening. Some we will also learn about some polymers that can be cross-linked by exposure to UV light. These are known as photo resistant; this is what we use in photolithography.

There can be many ways of cross-linking the resin, but the idea is to harden it. So, you will give it a certain shape, you mix your coke particles with your resin or sometimes instead of resin you can also use pitch depends on which type of pitch and also the viscosity of the pitch if it is optimum. Then you need to give it a shape.

Now, you first heat treat it to up to let us say 1200 °C or between 1000-1200 °C. Typically most of the non-carbon atoms will leave by 700 °C in principle. I am saying most of them not all of them. So, at 700 °C most of the non-carbon atoms go away and then you have carbon-carbon bond formation, and that around 900 °C you will get let us say 98% purity in your material. That will also depend on the size and shape like if you have a very thick sample. Then you can imagine that it is very difficult for the impurities sitting at the center will find it very difficult to go out, to anneal out. So, you need also the surface area. In the case of carbon fibers, things work differently because you have much higher surface area. It is easy for the non-carbon atoms to anneal out in the form of certain volatile small hydrocarbons or gaseous forms.

The first step is to heat it up to let us say 1200°C but in the presence of an inert atmosphere. We are going to do most of the things in the inert. In the beginning, we did to preprocess our coke with the calcination process. But now on, we are going to mostly work under the inert atmosphere and that is why it is not a burning process at all.

Whenever you are confused about whether you should call it burning or calcination or whatnot, just call it heat treatment because that is never wrong. Now, you will get some sort of your carbon material; however, this carbon material will still have impurities. And it will also have pores. Why will you have pores? Because all the non-carbon atoms are gone and there is some net mass loss from your material. So how will that mass be lost? Either the entire thing will shrink or you will get some porosity.

In this particular process, you will typically get pores because also you have sort of non-uniform things like you have coke and you also have a resin or pitch that it is already a mixture of the two materials. So, you will typically get pores. Now, what do you do? How do you fill these pores? Now think about it if you have a carbon structure with pores and now you want to fill those pores, but with carbon itself.

What are you going to do? You are going to again take another resin, maybe this time with a lower viscosity so that it can get filled inside the pores. And now you will carbonize it again, but this time you will carbonize it now above 2200 °C, in most industrial processes up to 3000 °C, again in the inert atmosphere, and this time what you are going to get? You are going to get graphite.

At 1200 °C you would not get graphite, you will get certain form of carbon which may be graphitizing carbon, but it will not graphite. And graphite you will only typically get about 2200 degrees. Now you will heat treat it again in the inert atmosphere in order to ensure that there is no burning. Now, this resin filling you can do actually multiple times depending upon how many pores do you have and how complex is your shape and how big is your shape.

So, you may have to do it more than once and that will determine the quality of your graphite. You want your graphite with no porosity or is it acceptable for a certain application to have some porosity depending on that, you will do the pore filling one or multiple times.

And then finally, you get your final manufactured shapes. So, you understand how you can get graphite from the raw material by already start giving the shape that finally needed. This is kind of the fundamental principle of carbon-based manufacturing. You cannot machine carbon and you do not even try to do that, because that might actually create so many defects in your material that is not worth it. You rather just start giving shapes to the precursors and then make your carbon out of it.

Whatever process I have shown in the figure, I think written it here. So, you can go through it. Now, there are some more details about these raw materials you still might be wondering about how do we differentiate between different pitches and our cokes? What exactly is a coke? We will cover it in more detail in further detail during our raw materials section. Right now, I just wanted to give you an idea of the manufacturing part of it.

We have used terms like calcination and burning in these lectures. So, here are some definitions; burning always takes place in the presence of oxygen. Burning in fact is a name for oxidation. So, you will always do it in the presence of oxygen or air in general because air contains oxygen.

You should do calcination when you have limited to no supply of air. You can also use calcination in the presence of air but in a controlled atmosphere and controlled air. In burning, you just leave it outside, leave it in the open and let it get as much oxygen as it wants. But calcination has a controlled quantity of air/oxygen.

Now, there is a third process which we will discuss extensively that is known as pyrolysis. Pyrolysis is actually the process of breaking of organic molecules, but necessarily in the absence of oxygen. With that, I am going to conclude today's lecture.