Carbon Materials and Manufacturing
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Lecture – 21
Kinetics of Graphitization

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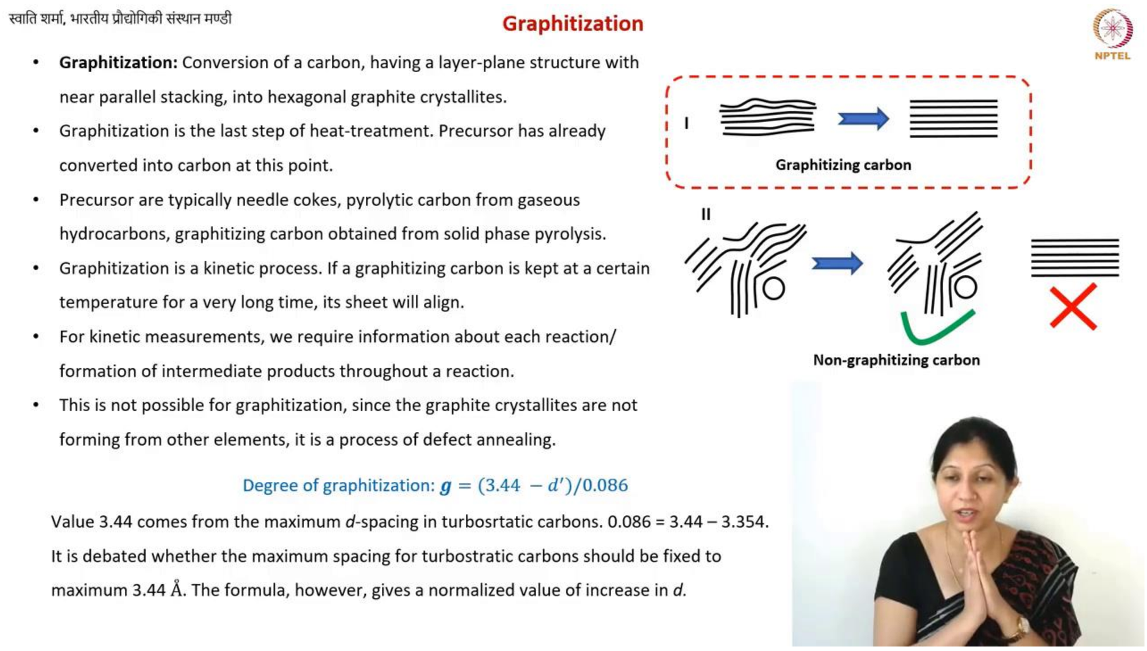

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Graphitization

- **Graphitization:** Conversion of a carbon, having a layer-plane structure with near parallel stacking, into hexagonal graphite crystallites.
- Graphitization is the last step of heat-treatment. Precursor has already converted into carbon at this point.
- Precursor are typically needle cokes, pyrolytic carbon from gaseous hydrocarbons, graphitizing carbon obtained from solid phase pyrolysis.
- Graphitization is a kinetic process. If a graphitizing carbon is kept at a certain temperature for a very long time, its sheet will align.
- For kinetic measurements, we require information about each reaction/ formation of intermediate products throughout a reaction.
- This is not possible for graphitization, since the graphite crystallites are not forming from other elements, it is a process of defect annealing.

Degree of graphitization: $\boldsymbol{g} = (3.44 - d')/0.086$

Value 3.44 comes from the maximum *d*-spacing in turbosrtatic carbons. 0.086 = 3.44 – 3.354. It is debated whether the maximum spacing for turbostratic carbons should be fixed to maximum 3.44 Å. The formula, however, gives a normalized value of increase in *d*.

Hello everyone. Mow, let us talk about what is known as graphitization. What is graphitization? We already know that this is the last step of our heat treatment process. The last step also means the highest temperature step. So, when we are going above 2200°C, then this process is known as graphitization. But, of course, depending upon the precursor, not all carbons can be converted into graphite that we know for sure.

We have graphitizing type carbons and we have non-graphitizing carbons. In this particular case when we say we are performing graphitization or at least industrially when graphitization is carried out, by definition, this is the conversion of those carbons which have a layered structure, and they have a near parallel stacking. What does this mean?

So, you have something like this, which is shown here(refer to slides). You do have certain waviness in your structures, this is for example, if you do pyrolysis of a gaseous hydrocarbon and you deposit layers which you would call graphene layers, but these layers are not perfect. They do have certain waviness, they do have certain defects and they are randomly organized on top of each other, they are still turbostratic.

When I further heat treat this kind of material then I get this AB AB A crystal arrangement where you have 0.335 nanometer as the layer spacing or the d spacing between your planes. So, this is basically what we are talking about. We also have non-graphitizing carbons.

Can you perform graphitization process for non-graphitizing carbons? This is an interesting question because often when people are heating non-graphitizing carbons, let us say above 2200°C; they also call that process graphitization process.

In the case of non-graphitizing carbons you do have randomly oriented graphite-like crystallites occasionally or they are turbostratic crystallites. And when you go to very high temperatures, you will definitely get some improvement in the stacking.

You will also get some improvement, some increase in La, the crystal-like diameter and you will also get some decrease in the Lc. You can also observe in the X-ray diffraction analysis, but that does not mean they will convert into graphite.

Whether or not you should call it a graphitization process is debated. The point is that whenever we are heating any type of carbon material above 2200°C, industrially that process is known as graphitization, or if you buy a furnace then they will say this is a graphitization furnace. They do not care if you are using non-graphitizing or graphitizing carbon inside it and that is why typically this kind of heat treatment is known as graphitization.

However, fundamentally you need to understand that non-graphitizing carbons have these curved carbon structures, they also have these completely spherical, fullerene-like structures like one of them I have shown here. And that is why do not expect that you will get something like these perfect graphite crystallites or polycrystalline graphite that is not happening.

You are going to get some improvement in the graphitic content as you keep on increasing the temperature, but there is a limit after which you will not get complete graphite. So, this is the graphitization process that we are going to talk about. How do we do that? This is the process we are going to talk about; we perform the heat treatment. What happens during this heat treatment is important to us.

Now let us forget about pyrolysis, forget about the fact that you had non-carbon atoms in your material. Now, your starting material itself is basically graphitizing carbon. You know the graphitization process starts after 2000°C. We do not think about whatever happened before 2000°C. That is important because it decides the structure of our raw material, but our raw material does not contain any non-carbon atoms, this is what we need to assume.

Now, what is going to happen to this raw material? You are going to get graphite which means that these turbostratic sheets have more than 0.335 nanometer spacing between them, they need to somehow come closer, and then we need to get to the level which is graphite crystallite. For example, if we start with coke; again there are two types of things here – one is the solid or liquid hydrocarbon. So, heavy hydrocarbon or gaseous hydrocarbon, you know from which hydrocarbon we get pyrolytic carbon, which is graphene-like carbon.

Let us first talk about coke like carbons or coke like raw materials – solid raw materials. We do this solid-phase pyrolysis and we get our graphitizing carbon. What is important is now the process becomes more kinetic rather than thermodynamic.

What does this actually mean? That does not mean that you can perform the process at room temperature. This is still a thermally activated process with very high activation energy and that is why you need to provide the very high temperatures because that is the activation energy of your process.

However, how much graphitization you will get depends on the time for which you are carbonizing or graphitizing your material. You can keep your material at 2500°C for 5 minutes, 15 minutes or 5 hours; that will also make a lot of difference. Graphitization is a thermally activated kinetic process. So, this is important.

When we want to understand any kinetic process then what do we need? Also, again I will say that you go back to this graphite-diamond conversion class. Whenever we are doing kinetic measurement then we need to basically know everything about that reaction, what happens at different time points? What are the byproducts that are forming at different time points?

But, there is a fundamentally slightly different way of calculating these things for graphitization because we are not thinking in terms of reactions, we are not thinking in terms of byproducts anymore. We do not have any byproducts so to say. In fact, we have our carbon material with a lot of turbostratic sheets, at this point, we are doing basically a defect annealing process.

So, do not think in terms of traditional reactions where you have reactants and byproducts, and we know everything about the rate of the reaction according to this. Now, what are the important parameters that we are going to measure? Well, La and Lc. How much your La increased and how much your Lc decreased, this is what will decide your kinetics of this reaction.

Because there is no concept of reactants and products at this point. You can measure the increase in La and decrease in Lc, how do you do that? Well, the most common technique is X-ray diffraction.

You can measure the properties of the material that you have at that point, you can also do some in-situ measurements and so on. Most common still remains X-ray diffraction techniques. Now, when you perform X-ray diffraction, then there is a certain parameter that you calculate, this is known as the degree of graphitization.

What does the term degree of graphitization mean? There is this expression that I have written here:

$$g=(3.44-d')/0.086$$

d is the spacing between the two layers. This is the layer spacing and this layer spacing is half of the c value of your unit cell because in your unit cell the c parameter basically equals 2×d. So, d is equal to c/2 because you have one layer in between also A B and A.

Where does this expression come from? Where do these values 3.44 and 0.086 come from? 3.44 is assumed to be the maximum separation possible for a turbostratic carbon, although as I have written here that has also been debated.

Rosalind Franklin first did these kinds of calculations a long time ago and he also gave some of these papers. I will provide you with reading material at some point.

The point is that we take these values. We assume that 3.44 is the highest separation, the largest separation value and the largest d value for any carbon. Although that is not true you will have sheets also that are far apart, which typically would not happen for a graphitizing carbon.

That is why if you take 3.44 as the largest value of d and the smallest value of d what is that? That is 0.335, here I have written it in un-struck. So, this is the value that you get in your graphite crystals. So, it cannot be smaller than that.

So, you know the largest and the smallest values and then you practically need to find a normalized value of your experimentally calculated d which is written as d dash here. So, the 0.086 this factor comes from just simply subtracting 3.44 minus 3.354. So, maximum minus minimum, this number is your 0.086. Basically you normalize the value and find the experimental d. You keep on finding the experimental value of d and that is how you determine the degree of your graphitization at any given point.

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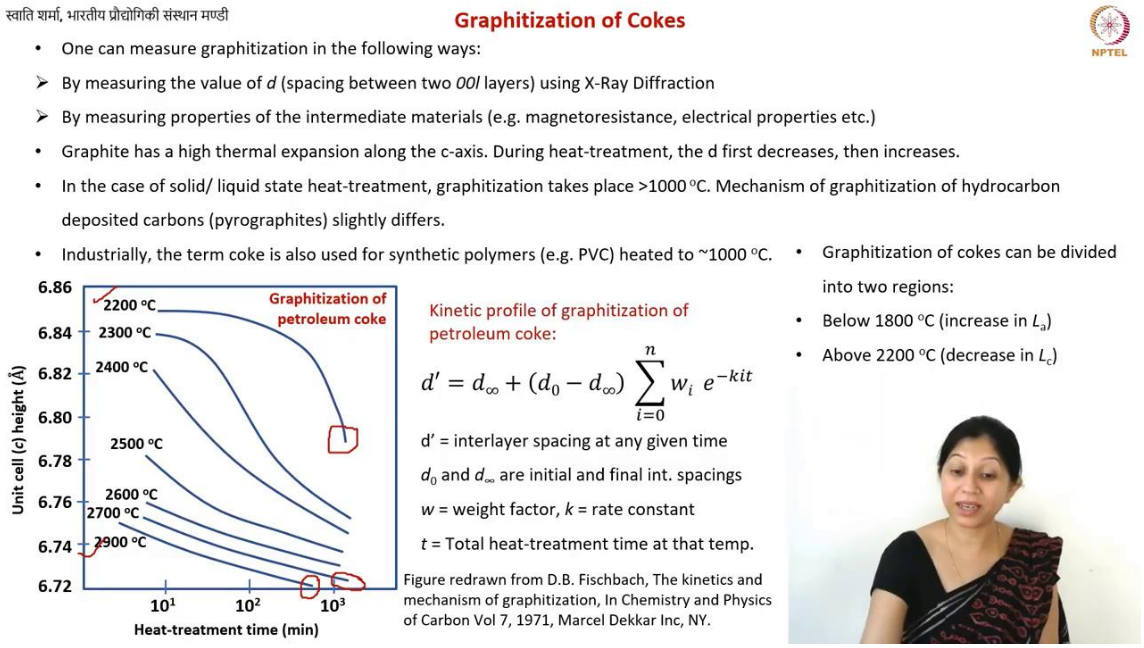

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Graphitization of Cokes

- One can measure graphitization in the following ways:
- ➢ By measuring the value of *d* (spacing between two *00l* layers) using X-Ray Diffraction
- ➢ By measuring properties of the intermediate materials (e.g. magnetoresistance, electrical properties etc.)
- Graphite has a high thermal expansion along the c-axis. During heat-treatment, the d first decreases, then increases.
- In the case of solid/ liquid state heat-treatment, graphitization takes place >1000 °C. Mechanism of graphitization of hydrocarbon deposited carbons (pyrographites) slightly differs.
- Industrially, the term coke is also used for synthetic polymers (e.g. PVC) heated to ~1000 °C.

Kinetic profile of graphitization of petroleum coke:

$$d' = d_\infty + (d_0 - d_\infty) \sum_{i=0}^{n} w_i \, e^{-kit}$$

d′ = interlayer spacing at any given time

d_0 and d_∞ are initial and final int. spacings

w = weight factor, *k* = rate constant

t = Total heat-treatment time at that temp.

Figure redrawn from D.B. Fischbach, The kinetics and mechanism of graphitization, In Chemistry and Physics of Carbon Vol 7, 1971, Marcel Dekkar Inc, NY.

- Graphitization of cokes can be divided into two regions:
- Below 1800 °C (increase in L_a)
- Above 2200 °C (decrease in L_c)

As I already mentioned that there are various methods of measuring the d value during the graphitization process, but X-ray diffraction remains the most common technique and the most extensively used technique. You can also measure the properties that will give you some idea of its extent of graphitization or degree of graphitization like we just discussed.

What properties should you measure? You measure the properties in situ. In situ means, at the time of the heat treatment and also then you can cool down your material and then measure it afterward. Of course, you will get more accurate values if you are measuring something in situ.

But remember that these kinds of measurements at the temperatures that we are using are extremely difficult. The techniques do exist, even you can do high-temperature XRD(X-ray diffraction), but it is very difficult to conduct any experiment at such high temperatures. Also, there are some other challenges related to the thermal expansion of your graphite.

So, what you can do is you can measure the magnetic properties of your graphite. So, we will at some point discuss the magnetic properties of graphite typically you will measure the magnetoresistance or also the diamagnetic susceptibility of your graphite and that is how you will understand what the change in the d value is.

You can also measure other properties like; electrical conductivity, but these properties will typically not give you a very accurate value because with that very minor change in your d spacing will not actually be so different from one another.

So, the best option still remains the X-ray diffraction technique as I mentioned that one challenge in the measurement of d spacing which we had in this particular case for all kinds of graphitization is that your graphite has a very high thermal expansion coefficient along the c axis of your crystal. What does that mean? That the layers of graphite separate.

So, the value of d that you are getting at those temperatures, you know how accurate that is. You need to factor the thermal expansion in, but often it is not possible with high accuracy because you do not know the exact size e or the exact properties because it is a graphitizing material.

What will you often see? You will see a pattern. What will you see is initially when you have your turbostratic carbon and then you increase the temperature? You will get some decrease in d and then at some point the thermal expansion becomes more effective and then you will see an increase in d.

You will plot it and you will find the minimum value. This is the pattern of the change in d and this is also the pattern of graphitization. The value of d decreasing and then further increasing at some point.

What is the temperature at which graphitization takes place? We know that graphitization takes place at very high temperatures. However, sometimes also at slightly lower temperatures like anything above 1000°C. If it is a graphitizing carbon and if you are getting the increase in La and decrease in Lc in that case you can call it, at least industrially, you can call it a graphitization process.

However, remember that the idea here is not to get rid of non-carbon entities, the idea here is to decrease the d spacing and converting graphitizing carbon into graphite.

Also in industrial terms some materials such as pyrolyzed PVC up to 1000°C can also be called the coke or coke derived from PVC and these kind of cokes then above 1000°C you can say that at least industrially that the graphitization process started, but you will not call it graphitized unless you go to at least 2200°C temperatures.

So, the process can start at a slightly lower, but the final graphitization only takes place at a higher temperatures. Now probably it will be more clear from this diagram here. What do you see here? I mentioned that your 2d equals c. This is the unit cell height this is what I have taken here, this is in angstrom and 6.72 is the minimum value of c and then there is heat treatment time.

Again, let me remind you this is a kinetic process. So, we are not talking about heat treatment temperature here. We are talking about it, but that is just for the activation. Here we are talking about for how long we kept the material at that temperature. So, this is the heat treatment time in minutes.

Now you see here this is an example of petroleum coke, the graphitization of petroleum coke and these are the different temperature values. So, starting from 2200°C all the way to 2900°C and you see these different curves, what do you see here? This is the change in your spacing between the layers.

So, you can see that only in some cases when the temperature is 2900°C, that is when you will be able to get perfect graphite-like crystals. Or you can go close to it, but then the time increases a lot then you have to place them.

So, even if you are performing graphitization at 2700°C, then you may have to keep your material at 2700 for a very long time and then when you are performing this kind of heat treatment for a very long time. Definitely, it is a very energy-consuming process and definitely, it is a very expensive process, but if you need to get perfect graphite crystals then this is the price you pay.

However, you can perform your graphitization in large scale manufacturing, for example, when you want to make electrodes for arc furnaces, massive electrodes, several centimeters in diameter. Those kinds of structures you call them graphite, but they may not have perfect graphite like crystallites. They may actually be carbonized at something like 2200°C and you see that at 2200°C, you can actually get a value of d spacing definitely higher than that of graphite, but you have at least a better arrangement and very few defects.

So, at least this is not a turbostratic carbon, you can still call it graphite. So, accordingly you will choose your process based on what is your precursor and based on what is your requirement from your final material.

Now if I want to see what the kinetic profile of this overall reaction is, again this differs for solid polymers or solid precursors or the graphitizing carbon derived from solid precursors or which is derived from gaseous precursors. The kinetic profile slightly differs because the physical arrangement of the material is slightly different.

In the case of the gaseous pyrolysis, you have layered structures. you have a thin film like structure, but for graphite production you will typically have relatively thick film. So, you have film-like structures and in this particular case, you have a bulk material. Sometimes as I said that for manufacturing applications you have very complex shapes.

You may have cylinders, you may have any geometries, you may even have very thick structures. In that case, the kinetic profile slightly differ and also the parameters that influence your process slightly differ. In this particular case here is the expression.

These are the terms of this expression if you take any particular value then you will see that this is kind of a discrete distribution of rate constants. For a certain duration the reaction will take place very fast. So, by reaction I mean the decrease in d.

For certain durations this reaction will be very fast. So, there will be a rapid change in the d. So, rapid decrease in your d, but the complete decrease or the decrease down to graphite value then though for that parts, the reaction becomes very slow.

The summary of this entire graphitization of this slide and the one before is that you must have already understood that there are two regions in graphitization. One is where you have increase in the crystallite diameter La and the second one where you have the decrease in Lc, reduction of the d spacing.

And these regions can also then be divided according to the temperature, below 1800°C basically, La increase and above 2000°C, is when we get decrease in Lc and that is the reason graphitization is performed above 2200°C. What is it between in during 800°C, 1800°C and 2200°C what happens in this region? Nothing much happens, there is not much change. So, this is a transition period.

What is also interesting and probably in one of the lectures, may be the coke derived carbon lecture I showed that graphitization is a stepwise process, it is not a continuous process. You will actually never hear that in a certain company or somebody is making graphite or any type of carbon at 1900°C or at 1300°C even for that matter.

You either have carbonization temperature 900 – 1000°C or you go to something like 1500 – 1600°C or you then generally would go to very high temperatures then you will go to 2200°C because that is when you graphite. You will pretty much have the same properties in 1500-1800°C and between 1800 and 2200 between pretty much the same properties.

Then why would you spend energy if the properties are not going to change very much? So, graphitization, in fact, the entire carbonization or heat treatment that we perform these are stepwise processes and rather than you know being continuous.

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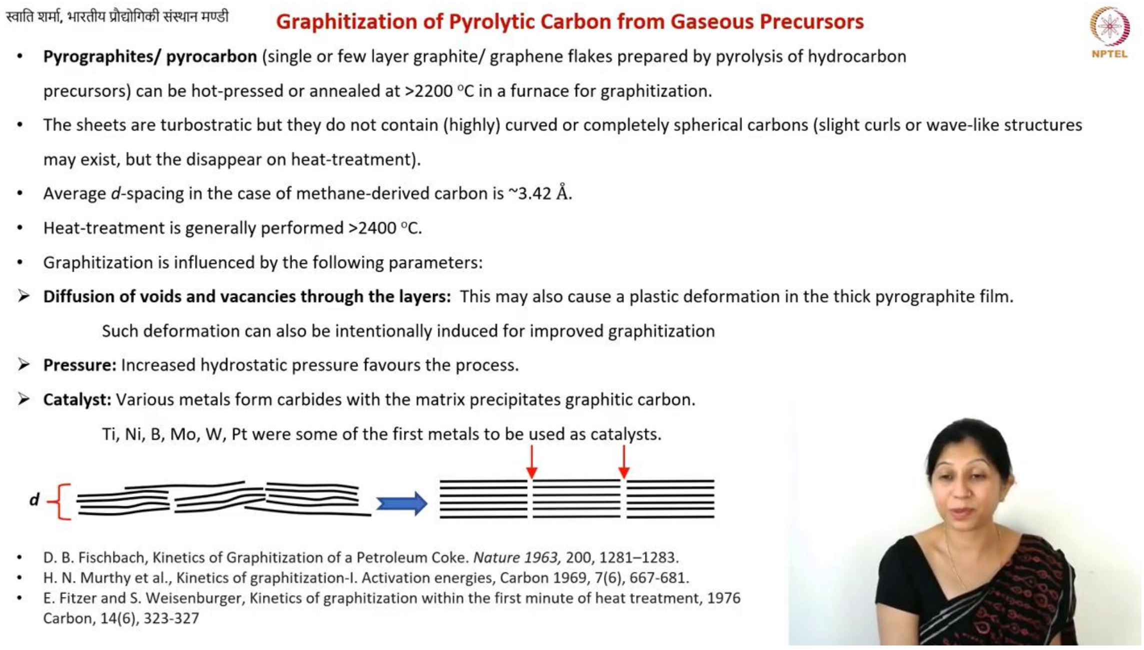

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Graphitization of Pyrolytic Carbon from Gaseous Precursors

- **Pyrographites/ pyrocarbon** (single or few layer graphite/ graphene flakes prepared by pyrolysis of hydrocarbon precursors) can be hot-pressed or annealed at >2200 °C in a furnace for graphitization.
- The sheets are turbostratic but they do not contain (highly) curved or completely spherical carbons (slight curls or wave-like structures may exist, but the disappear on heat-treatment).
- Average *d*-spacing in the case of methane-derived carbon is ~3.42 Å.
- Heat-treatment is generally performed >2400 °C.
- Graphitization is influenced by the following parameters:

➢ **Diffusion of voids and vacancies through the layers:** This may also cause a plastic deformation in the thick pyrographite film. Such deformation can also be intentionally induced for improved graphitization

➢ **Pressure:** Increased hydrostatic pressure favours the process.

➢ **Catalyst:** Various metals form carbides with the matrix precipitates graphitic carbon. Ti, Ni, B, Mo, W, Pt were some of the first metals to be used as catalysts.

- D. B. Fischbach, Kinetics of Graphitization of a Petroleum Coke. *Nature 1963,* 200, 1281–1283.
- H. N. Murthy et al., Kinetics of graphitization-I. Activation energies, Carbon 1969, 7(6), 667-681.
- E. Fitzer and S. Weisenburger, Kinetics of graphitization within the first minute of heat treatment, 1976 Carbon, 14(6), 323-327

If we again take the example of the pyrolytic carbon from gaseous precursors. So, why we are taking this example because this process is relatively simple to explain also in terms of the carbon, the orientation of carbon and how these carbons spread in the form of a thick film.

They also have a better orientation that typically they are all on top. These are graphene like carbons. They are stacked on top of each other. They are layered structures. They do have waviness; they do have defects but at the same time they are relatively all of the same size not exactly the same size but the size distribution of these flakes is also within a measurable range and that is why these are easier materials to talk about.

In the case of needle coke or a PVC derived graphite you will have all these randomly oriented your needle coke particles and that is why even though you do get graphitization, but it is more complex. It the mechanism is or at least the explanation is a little more complex.

Let us take an example of again methane derived carbon. You get something like this(refer to slides). You have a certain d spacing and what do you want? You want something like this which also something similar we also learned during HOPG formation. You know that what do we want you ultimately for making HOPG highly oriented? You need less than one degree of mosaic angle between these different sorts of tiles of graphite.

What is the value of the average value of d spacing in this methane derived carbon? It is typically approximately 3.42 angstrom. If you remember when we were calculating the degree of graphitization, we said that 3.44 is the maximum value that we have in these kinds of carbons. That was typically based on these gaseous pyrolytic hydrocarbons. In these particular cases the 3.44 is generally the maximum value of the spacing.

In the case of methane-derived carbon 3.42 is what we get, and now we need to further anneal it. I showed you during HOPG formation, we can also perform hot pressing because there is also certain pressure on your material. But depending upon the quantity of the material, depending upon how large and how extensive your sheet is, you can also just simply perform thermal annealing then you can also of course perform it under higher pressure hydrostatic pressure in that case.

You take this kind of pyrolytic carbon and then you anneal it out or you perform the graphitization at the temperatures higher than 2400°C. From the previous also, this the curve that I showed to you or you know the plot with a lot of curves. The point is that you can perform the graphitization at 2200°C, 2400°C, 2600°C, or2900°C that depends on exactly what is the final value of the d spacing that you are looking for.

Fine we perform this heat treatment and now what happens during this heat treatment? Yes, we graphitize it for a long time and then we get graphite crystals, but there are also certain process parameters that will influence this graphitization reaction.

Number 1: what is happening at this time? Well the diffusion of voids. This graphitization process is primarily a defect annealing process, because whenever you have a non-six membered ring that is going to destroy your crystal structure; that is going to make it turbostratic. So, you need to basically anneal those things out.

However, there may also be some other larger voids because these are deposited carbon. Maybe there are between two graphene like sheets. You have certain other types of defects and you want to get rid of these defects. Of course, this is the diffusion of these voids through your material and their annealing is very important parameter to you.

What is interesting when these defects anneal out? Let us say you have just a graphite film without any weight on top of it or any pressure. You just have this pyrolytic graphite film and then you are annealing it. Sometimes the release of these voids will also cause the sort of cracking of the film. You can call it the plastic deformation.

There are so many studies about the film cracking. Whenever the defects are annealed out, at some point there can be cracks developed in the film. Similar thing happens also in the case of graphite film formation. We are not surprised. What we can also do is we can pre-crack the films. In that way you can have the defects annealing out rather easily because we also provide more surface area for the defects to anneal out. So, you can pre-crack the films at the right places. So, you can induce plastic deformation in your graphite graphitizing carbon.

And that is how you can actually also increase the rate of graphitization because you are allowing the defects to anneal out. You see here with the red arrows; I have shown that you can actually kind of cut your films into pieces.

Now, what else will influence the process, pressure for sure. So, and that is why we do hot pressing., You can also use hydrostatic pressure as I mentioned this will favor the process because obviously you are trying to get less d spacing. If you press the material and if you increase the pressure that is going to increase the or accelerate your graphitization process.

You know about CVD or when you learn about CVD you will know that catalysts make a lot of difference. It is not that only at the time of CVD we thought of a catalyst. This is something that has already been investigated for also bulk graphite production.

Not just catalytic substrates, but also the addition of catalytic particles which nowadays are nano particles, but also they could be micro scale particles; powder of your metal, which is typically a transitional metal, could be used as a catalyst for improving the graphitization process.

And the mechanism of this kind of graphitization or why does it increase the graphitization process? The fact that there is certain carbide formation and when these metal carbides move through the metal, this carbide actually precipitates graphite or it increases the formation of graphite.

At the end you will have to get rid of your metal particles, but catalysts also make a lot of difference and then this is why these are the parameters that can be used for improving the rate of graphitization. For further reading, refer to these papers. I think I had a couple of books that I had mentioned previously in the pyrolysis mechanism class, those books are also useful for understanding graphitization.

Other than that, there are few publications that I have mentioned here. All of these are very useful. Actually, Kinetics of Graphitization is a very interesting topic and that has been not only studied in the past, but also it remains very industrially relevant even today. So, you can find more literature as you like.