Carbon Materials and Manufacturing
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Lecture - 22
Microstructure Non-Graphitizing Carbon

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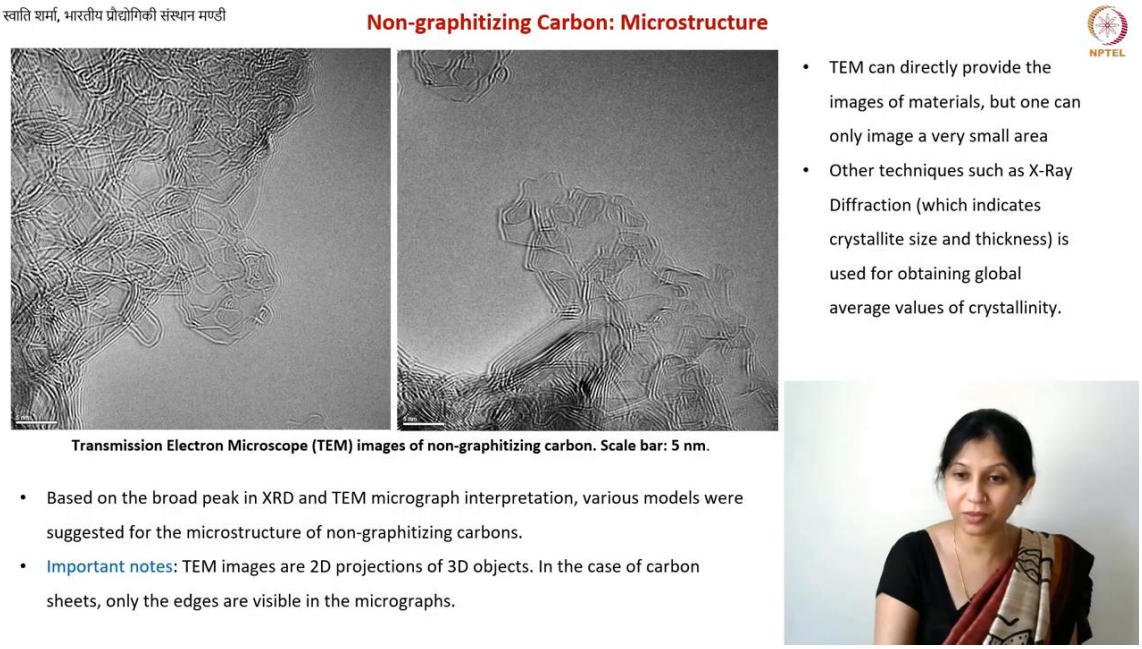

Hello everyone. In this lecture, we are going to talk about a few more things related to the microstructure to non-graphitizing carbon. You know that you have graphitizing as well as non-graphitizing carbons and these can be obtained via heat treatment of polymers. Different types of polymers will give you different types of carbon. You also know that both coking and charring mechanisms can give you both graphitizing and non-graphitizing types of carbon.

An example of a non-graphitizing carbon that is formed by the coking process is glass-like carbon and a non-graphitizing carbon formed via the charring process is activated carbon.

But we do know that there is a lot of differences in the properties of these materials, the physicochemical properties of these carbons; that is because of number 1, the chemical nature of the precursor, and number 2, the mechanism of formation. And there can be

also some other small factors like the process parameters and how did you keep them and so on ok.

We will come to the properties later on but first, let us see how these materials look like at microstructural levels. We talk about microstructure nowadays because we have these very advanced imaging techniques like transmission electron microscopy. We can actually see the nanoscale and some very advanced TEM emerging techniques can even detect down to the atomic level. Atomic-level is the solution you have in those images.

So, the point is that we talk about microstructure then this is the kind of images. So, the scale bar in both of these images is 5 nanometers, this is what you see, you see a very small section of your material, but this is how your material looks like at pretty much is a molecular level if not atomic ok. So now here I have these two images; one of them I had I think also shown you previously, but these are like much larger images.

Hopefully, you can see more through these images. What do you see here? What you see is this very crazy kind of structure, where you cannot say what is what. The reason for that is there is not a single plane of the material, despite the fact that this is an extremely thin film. When we talk about the characterization techniques, we will discuss more about transmission electron microscopy.

But the simplest way to explain is that there is a beam of electrons that passes through your sample or transmits through your sample and that is how you use the beam of electron for the imaging rather than a beam of light. That is what you are doing here. However, when the beam of the electron is passing through your sample, this also causes some damage to the sample especially when the sample itself is extremely thin.

Why should it be extremely thin? Because otherwise the beam may not be able to pass through it completely or the electrons will have a lot of diffractions and that is why you may end up getting very dark images.

So, you not you may not be able to see, what you want to see. In the case of materials like graphite, where you have nicely organized crystal planes what will happen? You will have one dark line and then one bright and then dark one bright because you have nicely organized crystal planes.

But in the case of non-graphitizing carbon, you see in these images that non-graphitizing carbons have a lot of curved carbon structures and some of them also are very large, some are very small, some are stacked on top of each other some are not. Sometimes you also do not understand what is what, because you see this is like a 2D projection in TEM images, what you see is a 2D projection of a 3D material.

If I have one plane like this and another plane that is very far like this, but when I see the 2D projection this is how it will look like this cross(refer to video 4:12). So, this is the problem. You will not even see any difference in the intensity of these two lines. Why? Because they are both in the focal plane. So, it is very difficult to differentiate between different structures.

But it gives you a very good idea of what kind of material it is and in fact, based on these TEM images many models have been proposed for the non-graphitizing carbon. Right now we are talking about general non-graphitizing carbon, I will come to glassy and activated separately because there we will talk more about the applications and the industrial manufacturing.

In terms of microstructures let us talk about all non-graphitizing carbons in general. You will use the TEM micrographs as I mentioned already. The interpretation of these micrographs and you will also use something called X-Ray diffraction patterning to understand what a microstructure of these materials is. Remember that there are two things; number 1, these are 2D projections of a 3D material or 3D object and number 2, because carbon is rather transparent to most of the electromagnetic radiation, at least many of them. So, you only see the edges of your carbon structures. You can call them graphene sheets or graphene-like sheets or sheets containing defects and so on.

But whatever sheets you have, whatever carbon structures you have; you only see the edges. If you see from here then you will just see the edges and the rest of it will allow the radiations to pass through in most cases, none less it is very thickened.

This is why you have this line and this is a kind of structure that you see. If you remember these two things, only then you will be able to do a good interpretation of the TEM micrograph.

When you can see the image directly using TEM, why would you need any other technique. for example, X-Ray diffraction to understand the material, understand the microstructural development of the material? You can see that the scale bar is 5 nanometers. Your entire image is that of a 50-nanometer piece of your material. What you need is global image especially when you are talking about bulk carbons. You want to know globally if whatever is valid for that very small region of few materials; is it just that local area or this is globally valid? Of course, you can take images at many different points, but to get an idea of how the crystallinity develops, or how the crystal size is developed for example, with heat treatment temperature and so on; you use other techniques such as X-Ray diffraction. There are many such techniques like X-Ray diffraction and Raman spectroscopy. Basically, the idea is that, if you want to understand the microstructure or the crystallinity of a certain material, you need to have certain supporting data, not just the TEM images because it is from a very small region and also the fact that you may have caused some damage to the microstructure, because of your electron beam itself. And there are so many challenges associated with the interpretation of such images.

Now we will see some more images anyway and we will talk about some microstructural models. People have been trying to understand the non-graphitizing carbons for a very long time and several models have been proposed and we will talk about some of those models.

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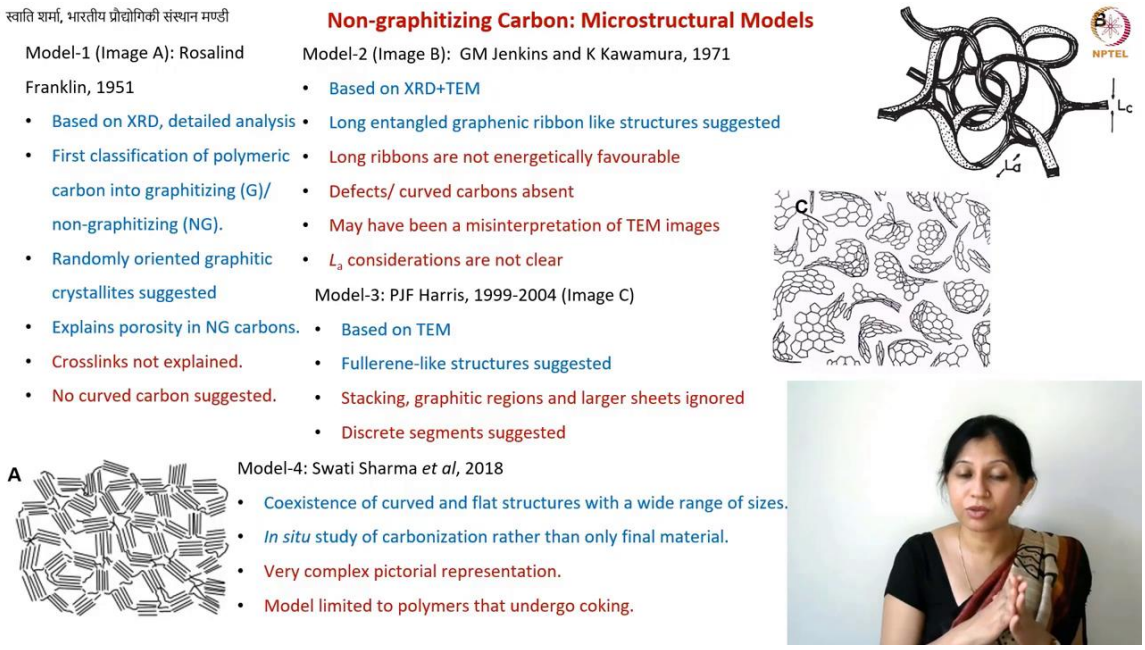

The first model of non-graphitizing carbons was suggested or was proposed by Rosalind Franklin in 1951 and it looks something like this. Rosalind Franklin was one of the first scientists to classify or to differentiate between graphitizing and non-graphitizing carbon. Here I have only shown the image that she proposed for non-graphitizing carbons, but the one for graphitizing carbons, you can see in her paper the original paper.

I have provided all the references on the last slide just because there were too many papers to read. I am going to describe four models here and then there are also several models for non-graphitizing carbons that have been proposed, but there was not so much discussion on those models.

Anyways, I am basically going to show you 3 or 4 primary models. But this is an active field of research and people are still trying to understand non-graphitizing carbons, but the very first model was proposed by Rosalind Franklin.

And this is the first time somebody said that graphitizing and non-graphitizing carbons are different. People knew that certain polymers will not give you graphite no matter how high you heat them. This is an experimental fact.

But can those carbons also be useful or should they also be studied as a different class of carbon materials? First time after this classification based on X-Ray diffraction studies,

which was done by Rosalind Franklin. Then people started sort of studying non-graphitizing carbons as a completely different class of carbon materials.

At that time, well transmission electron microcopy did exist in the 1950s also but it was not so common as we have it today. It was also the microscopy technique itself and it was in the developmental phase and X-Ray diffraction was the most common technique used for understanding the carbon material. So, this study by Franklin is based on XRD.

In fact, what is very interesting about this paper is that this is a very detailed analysis of how to perform X-Ray diffraction studies for carbon materials. So, even in that respect, this is a very interesting very useful paper. She suggested that we have randomly oriented graphitic crystallites as you can see in this picture.

These graphite-like crystallites should be in the nano scale. So they are short-range crystallites between 2 to 5 nanometers or not longer than 10 nanometers. The exact size could depend on the heat treatment temperature, but she proposed that you have these kinds of randomly oriented crystallites.

She also suggested that there are these closed pores between these crystallites. Whenever we are trying to figure out the model what we also need to know? We need to know the physicochemical properties of those materials, for example, if you take glass-like carbon; it is prepared by coking mechanism, so you expect that it will have a very high density because the material is shrinking during its carbonization. It is going through a liquid-like phase it has also a very flat surface.

So, you would expect it to be like really dense carbon material. It is dense compared to some other carbon formed by charring, it is dense relatively. But at some point, there are closed pores that are formed and how do we know that because the density still relatively not as high as it should be? And if there is less density that means it should have porosity. But the material is not permeable to gases or liquids which means nothing can go through it. So, how do you have pores and then still nothing can go through it? In that case, the material should have closed pores.

If you see in this image, you have certain voids empty space between these crystallites structures. So, they are responsible for the lower density of the material but at the same

time because they are closed so you do not have any permeability of the material. This is something which was explained very well by this model.

There also any limitations of the model. One limitation was that the nature of the links between these crystallites was not explained. That is what I mean by cross-links here. You have one randomly oriented crystallite and you have another one, but are they connected or not? You know that these non-graphitizing carbons are also electrically conducted but they do not have as high conductivity as graphite, but they are electrically conductive.

If they conductive what does that mean? That means, there should be a path for the electron to go or to take. But if links are missing between these crystallites then you may not have good conductivity. This is something which could not be explained by this model. Now, of course, at that time there was no discussion on curved carbon structure, even the fullerenes were discovered much later in the 80s. At that time the curved carbon structures were not explained by this model. People did not even know non-graphitizing carbons at that time. We are talking about the 1950s. So, these were some of the limitations of this model.

In the 1970s came the 2nd model which actually became very popular. Even now a lot of people often refer to this kind of model when they talk about non-graphitizing carbon.

Now we are going to learn; are there any limitations? What are the good and what are the not so good things about this model? This model was proposed by Jenkins and Kawamura and this was based on both X-ray diffraction and TEM. They also had TEM images which they interpreted and based on that and the XRD data and that is how this model came up. They suggested you have long ribbon-like structures. So, you have these long entangle as you can see in the image B.

You have very long graphene ribbons this is what was proposed by the authors. They also have a certain thickness so you can call it the Lc or the stack thickness. Now how to calculate La that was not very clear in this model? We will talk about that. Now, are there any other limitations also?

I had written limitations on this slide in red color and other things in blue color. The first limitation, do you think that it is possible to have such long ribbons of carbon? Whether or not it is graphene or not? First of all, it is not energetically favorable to have such long ribbons; however, there were some other models at that time which sort of suggested that no ribbon-like geometric is possible because the polymers have chains.

These chains ultimately lose their non-carbon atoms and then they convert into these fiber or ribbon-like structures. However, one question is still not clear that how do these ribbons also laterally grow? And if yes, how long? Because in principle your crystallite will not be symmetric. When you talk about La or the crystalline diameter what are you doing? You are imagining you are considering an equivalent sphere and then you considering the diameter.

So, diameter in all the directions should be the same, but if you have a ribbon-like structure then the length will be much more than the width, that is the definition of ribbon. So, this consideration whether we should have La or whether we should take it only along the length or take it along the width of the ribbon? These things were not very clear in this model.

And altogether it looks like not so favorable you know geometry for carbon materials to have these kinds of very long ribbons. And of course, if you have these long ribbons then you are also assuming that you have nicely stack ribbons. You have very few non 6 membered rings. You are also assuming that you have perfect arrangements. There is the possibility of getting graphite. Maybe you will not get very long crystallites because of the entanglement of the ribbons. But if you have already organized these sheets without defects or at least there was not much consideration given to the defects. In that case, it is also possible that it looks not so favorable. And defects and curved structures, none of these things were explained properly. Now, it is also possible that there was some misinterpretation of TEM images because when you see the TEM images I have showed you in the previous slide, you see only the edges and when you see the edges it will sometimes look like a ribbon. You look at the TEM image and you will say that this kind of model looks correct, but on the other hand if you think you have one carbon flake. So, this is a flake, not a ribbon. It is a flake and then I have another flake like this(refer to video at 18:00). Even in this case you will see the two lines which are my two fingers, and you will think it will look like a ribbon or two ribbons stacked on top of each other.

But they might actually be two discs, they may also be two ribbons. If you see a structure like this and if you see it like this then you may have different angles to see this kind of structure, but you will always see these two lines only the edges.

It may not really necessarily be ribbons. So, there may have been some misinterpretation of the TEM images. And as I told you before that whether we should consider La along the length of the ribbon or width of the ribbon, is not very clear.

Now, then came the 3rd model in the late 90s. PJF Harris suggested a third model of non-graphitizing carbons. Here he considered a sort of both previous modules and also some of the physical properties of the carbon materials, and he did extensive TEM studies to come to this conclusion. And this was also the time in 80s when fullerenes were discovered and now people knew that curved carbon structures can exist and in fact, they can also be very stable.

The discovery of fullerenes did not just tell you that these kinds of structure can exist, they also told you that these kinds of structures can be can actually be very very stable. So, based on all of these aspects, then came the 3rd model which is here shown in picture C where Harris suggested that you have these curved carbon structures, a lot of them.

If you see very carefully, you will see non 6 membered rings in these curved carbon structures. So, these are some simulated geometries. There can be a lot of these curved carbon structures and we are seeing only a 2D projection of 3D materials here.

If you have multiple layers of such structures, then you will see this completely crazy structure that you see in your TEM images. This is a third model that was suggested, and this is pretty much extensive entirely based on TEM studies and it suggests that you have fullerene-like structures, not necessarily fullerenes, but curved carbon structures that is what is proposed in this model.

Now, what are the limitations of this model? Well, you can see one thing that it looks like the ribbons. These curved carbon structures are discrete, they are not connected to each other. In that case, you cannot really explain the electrical conductivity of the material very well. Now, another thing is that the model does not really show any stacking. It says that these are all discrete flakes.

So, is there any stacking between the flakes or between the sheets, is not very clear from this model? And because of these things, you cannot explain all the properties of these kinds of carbons. However, the fact that it is a fullerene-like structure; the fact that you can have curved carbon structures is very useful. It is very useful for us not just to understand the non-graphitizing carbon, but also other curved carbon materials.

How are these curved carbons formed from a polymer precursor? All these things we can understand very well based on this model. So, this is also a very useful model. Now you see there are 3 models and none of them can explain everything about glass-like carbons or non-graphitizing carbons. But each one of them has a lot of advantages and it tells you certain things or you can see how things developed over time. And transmission electron microscopy became more and more common. People started using it more and more for micro structural investigations, you can see from these models. Now, I am also going to explain another model which I and my research group previously had proposed. Now, this was also based on TEM studies, but it was in in-situ TEM.

In ins-situ TEM means when a polymer is carbonizing, so you keep on heating it and keep on taking pictures. How it converts from polymer to carbon? So, we did in-situ investigation of this entire process before and based on that we proposed this one model. There is no image of that model. So, this is in fact one of the limitations of our model. The fact that it is so complex that it is very difficult to explain if I make the kind of model I am proposing, then if the image will again become so complex then it looks like the TEM image all over again.

I am going to also show you some more images from this study in the next slide, what we saw was very interesting that we have not just fullerene-like structures, but we also have complete fullerenes in these kinds of carbons. We saw some very interesting completely spherical-looking molecules. This also sort of substantiates the previous models that, yes, we have curved carbon structures, but this is the first time we saw also not just curved carbons, but we also have fullerenes.

And the interesting part is that these flakes, the ones shown in the previous model, there are all these curved carbon flakes and sheets, but they y can be very different from each other in terms of sizes. So, some of them can be just a few Angstrom in their sizes and some of them can be several nanometers.

There is a coexistence of larger graphene-like sheets and very small graphene-like discs and structures. Some of them are also completely closed circular spherical structures. Some of them can also be circular because we only see the 2D image so we cannot differentiate between circle and sphere. So, there we need to see is how stable is that structure.

If there is a circle or a disc, typically it could continue to float or it will try to bond with something or merged with the structure next to it. But if it is a fullerene then it is highly stable. So, these are the kind of things that in addition to what you see in the images, then you use the other data in order to interpret what you have in these materials.

In our model, we suggested that there is a coexistence of curved and also some flat structures and you can also have some curved structures with very high curvature. And of course, all of these have they are in a range of sizes. And the one important thing of our model was that we did not only just consider the final material, we also saw how it is formed and there are certain things, like how do you differentiate between the sphere and the disc in TEM.

Well, that depends on the stability with temperature. When we are looking at the process, you know while increasing the temperature, then we can see what is the effect of temperature increment That is how you can see the entire process rather than just believing in the final material. And sometimes when you are preparing the sample because you need these extremely thin samples during the sample preparation itself, you generate some stresses which will not happen if you are doing the in-situ studies.

The one major limitation as I said that this has a very complex pictorial representation that is why I have not shown a picture here. The point is that just imagine very long sheets which are flat or curved or parts of it are flat and parts of it are curved and you also have certain spherical, completely closed structures, which definitely explains the density and porosity of the material. You definitely have closed pores and voice.

It explains that you clearly see fullerene-like structures or closed structures, but at the same time you also have these very long sheets which are responsible for the electrical conductivity. You do see a lot of different structures, pretty much everything related to

carbon. All kinds of carbon structures are in one place and that materials called the non-graphitizing carbon.

However, the pictorial representation of this model as on data, I would say it is complicated. And we have done this study in in-situ, we have done it on one type of polymer which goes through coking mechanism. Coking means then the polymer flakes are floating, they are allowed to because they go through a semi-solid type of phase. They are allowed to join or merge into another sheets, or some sheets are also allowed to separate out because they have a certain flow, a certain movement during their carbonization. Now, we do not know if the same thing will happen during charring, maybe it does, maybe it does not. This model is currently limited to those non-graphitizing carbons which are obtained by coking.

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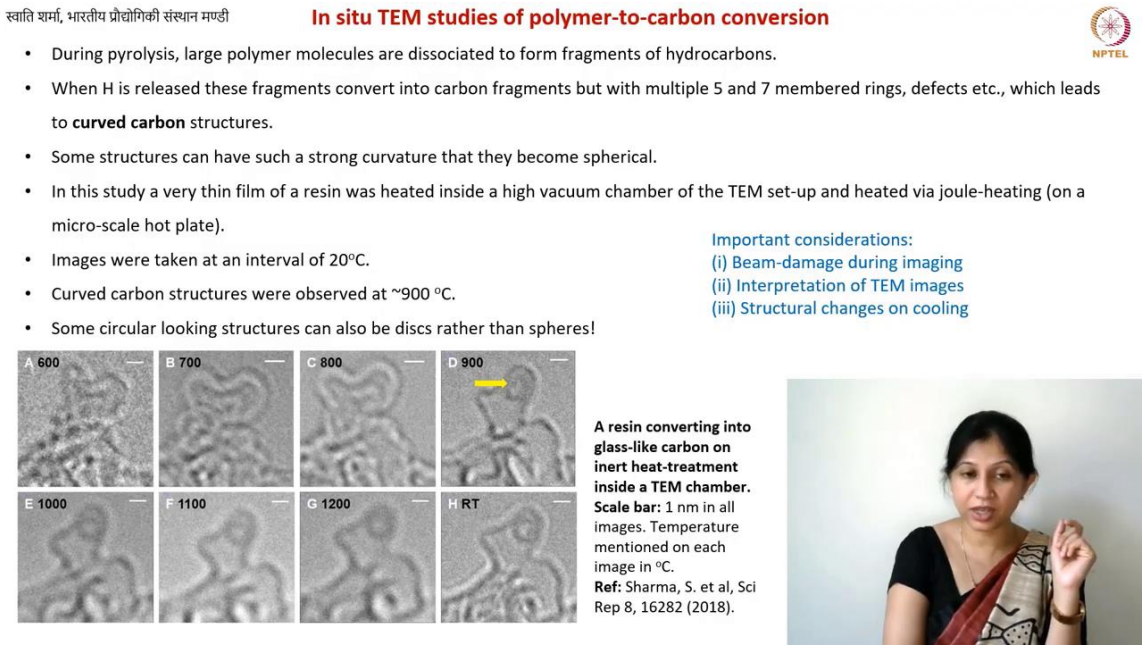

Here is one more image from this experiment that we performed and here is also the reference to this publication if you are interested you can read more about it. You see 600, 700, 800 these are the temperature points and by the way the scale bar here is 1 nanometer. You can see this image is zoomed in and what is the magnification.

Around 900°C, you see something that looks like circle, it can also be disc by the way. But as I said that based on other parameters, we thought it might be a completely closed

structure. It may be the case or may not be the case. These kinds of structures start to form during around 900 degrees and many other curved structures. You can see in this material 600 that the material was like almost completely amorphous.

This material still has a lot of hydrogen which is almost a polymer, you cannot call it carbon because the impurities are high enough. You have a lot of impurities at 700-800°C. I mentioned that 900°C is the point where you get reasonable carbon. There is a lot of data to support this, also the electrical conductivity and a lot of mechanical property suddenly changes at 900°C.

All properties of non-graphitizing carbons typically will have a jump around 900°C. Between 800°C and 900°C you will see a sudden change in the properties, which is also clear, you can see from this image. And now you also see that these curved carbon structures are formed around 900°C or you can clearly see them at that temperature point.

They are stable and the last image number where I have written RT that is room temperature, that is after cooling. At 12,000°C and you cool it down, you will see that there are micro structural changes during the cool down because the material now becomes more stable.

There are so many other aspects of this carbonization process. You can also see that the hydrogen is released, then there are certain 5 and 7 membered rings formed and then there are certain defects and that is why you do not see corners or perfectly angular graphite like structures. You rather see more curved structures in non-graphitizing carbons.

Why are these curved carbons form? They have multiple reasons; you have completely floating structures which is releasing non-carbon atoms at all points. Now, every molecule of this graphene like sheet, that is forming will also have so many other molecules near it. It cannot completely spread and become flat sheet.

There are many restrictions when these molecules are being formed because polymers themselves contain 5 and 7 membered rings and they are not all just 6 membered carbon

materials. They have also non carbon atoms, so from the beginning itself you will have these defects; defects are non 6 membered rings, which will give sheet certain curvature.

And when the sheets from the beginning have certain curvature and then somebody is pushing it from all sides and it depends on the how much space does that material have for spreading itself. Based on all of these factors whatever is the most stable geometry at that given point which can be 700, 800, 900 or you know 1500°C. Whatever is the temperature at that point whatever is the most energetically favorable suitable geometry for the carbon sheet, it will take that geometry at that point. And there are also physical constraints, there are chemical constraints and there are energy constraints because of all of these things you will get the curved carbons from the beginning itself.

And some of them as I mentioned can also become completely spherical, If you go to this publication, you will also see some other images where you have completely spherical structures, maybe at some point of time I might also show it of much better spherical structures, which are 0.7 nanometer in diameter, which is also the diameter of C60 the buckminsterfullerene.

We took an extremely thin film; one thing that was very important was to ensure that there is no beam damage, which means when you take the image because your electron beam is passing through the material all the time. So, that can damage the material itself and if you want to take the image at the same point, then it is very important that we just click the image and then turn of the beam. During heating when the pyrolysis is taking place, the beam is turned off and this was done on a joule heated plate.

In a way it is a micro fabricated hot plate that is very nicely controllable. You can control the heating rate and how long you want to keep it at a certain temperature. It is done in very highly controlled environment with a very low voltage of the beam; the lowest possible voltage that would give you know a reasonable image.

Considering all of these fact factors; however, you can still not say that this is perfect because some damage is always possible. When it comes to the interpretation of TEM images, which again we are going to learn more about in TEM and related lectures, there are many factors that you need to understand and you need to you know consider when you are doing interpretation of TEM images.

They may have been minor issues also with this model based on all of these things. But now you understand one thing definitely that non-graphitizing carbon is still an ongoing research field. Despite the fact that we have such advanced and a sophisticated instrumentation, we are trying to understand the non-graphitizing carbons since 1951. Every other day there are new additions to the existing knowledge in this field and therefore these materials are very interesting for us.

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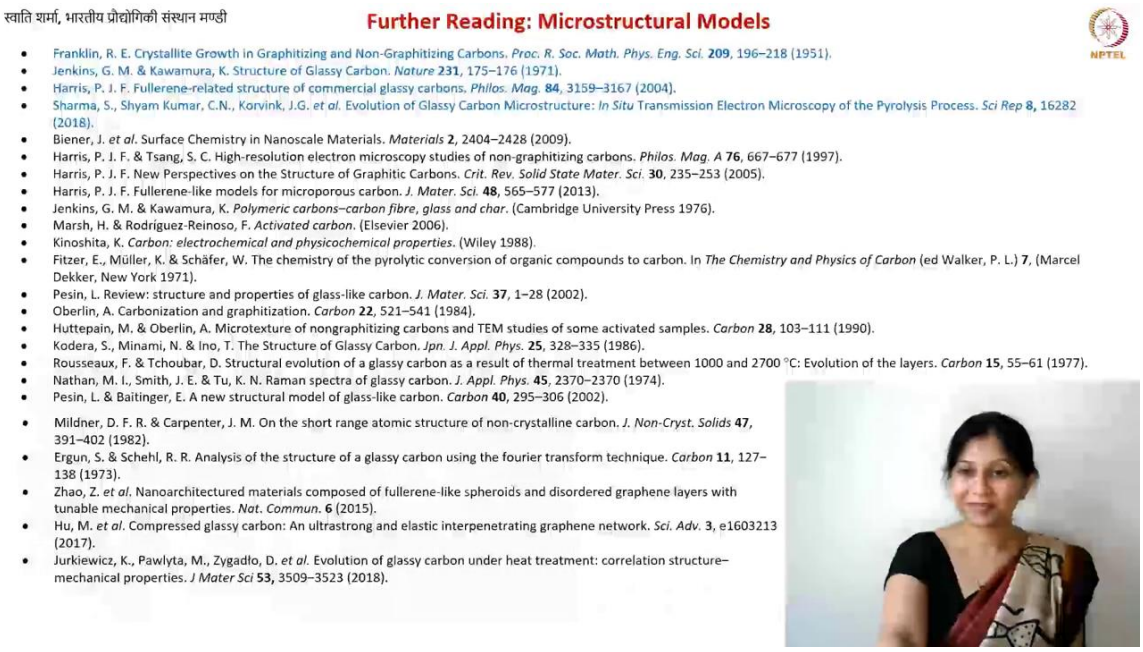

Now, on this slide I have listed all the references as I told you, this is also not an extensive list. I had rather mentioned like review articles so if you go to those reviewed articles then you will have many more articles that review article will tell you what to read.

The first 4 blue colored references are the ones from where I took the images of 4 different models and then the other papers are also definitely very interesting. And there are some also describe different characterization techniques for example, neutron diffraction analysis and different model. Some of them also suggest simulated models and so all of these papers are very interesting and that explain the structure of non-graphitizing carbon.

In some cases, you will see it is just glassy carbon or just activated carbon, but that is also a type of non-graphitizing carbon. So, these are the references related to the micro structural models of non-graphitizing carbons.