Carbon Materials and Manufacturing
Prof. Swati Sharma
Department of Metallurgy and Material Science
Indian Institute of Technology, Mandi

Lecture – 14
Rhombohedral Graphite and Staking Faults

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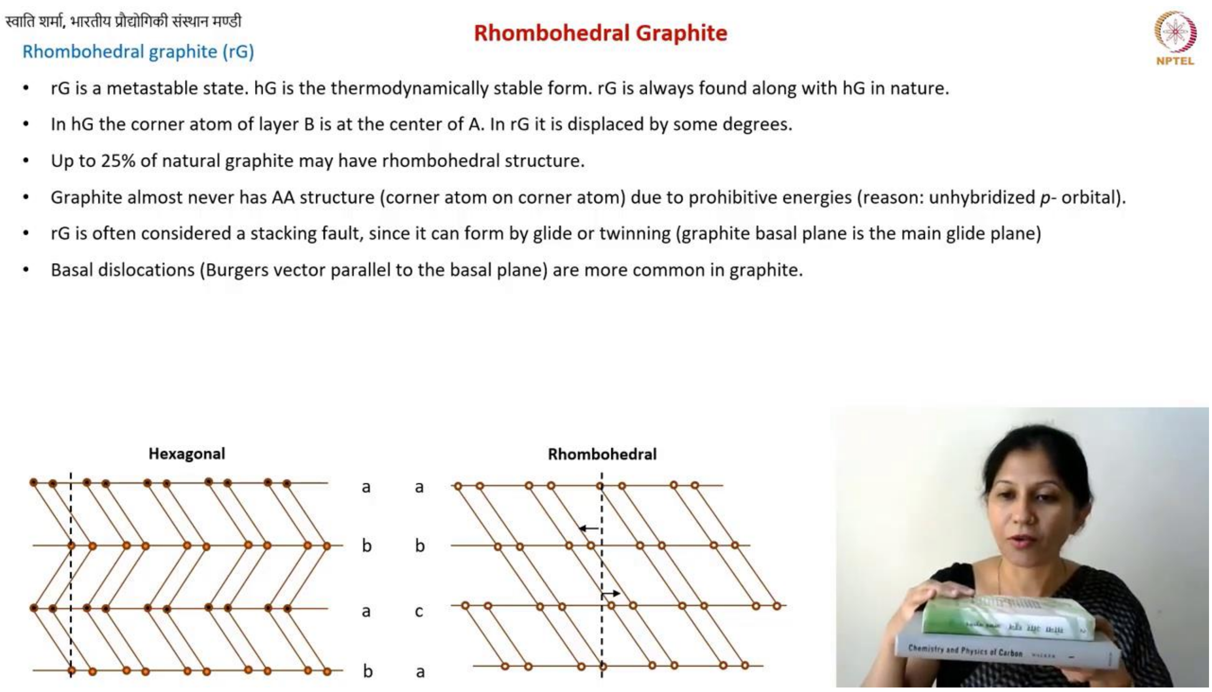

Now, coming to the rhombohedral or rhombohedral graphite. This is how it looks like. I am not going into the crystal structure of rhombohedral graphite. But rather I will show you the cross-section. So, this is the cross-section of four layers AB AB in natural graphite and in the case of rhombohedral graphite you have ABC and then ABC again.

You do not have this you know pair AB and then AB and AB. If you actually look at the crystal structure of graphite, you will see that there are other possibilities not just AB AB type.

But, if you see A B and then there is a possibility, there is a position available where you do not necessarily have to have the atom of the corner atom of the B layer in the center of the A layer. There are other possibilities that would also give you a 3D crystal.

Of course, the random rotation is another thing altogether but even when it comes to the crystal structure, there are other possibilities that can give you certain geometries, which can be detected by electron diffraction and X-ray diffraction and so on.

This is the rhombohedral graphite which is also found in nature. However, it is never found alone. It is always found along with hexagonal graphite. However, you can have up to 25 percent of the natural graphite that is rhombohedral graphite. If you want to understand the geometry, of course by looking at the picture you can see that the corner atom of one layer is not at the center of the other layer. That is very obvious.

Now, you see these two little arrows I had shown. So there is one A layer and in both B and C layer, there is a little bit offsets; one towards the left and the other one towards right and that is another possible geometry. After that, the fourth atom will then match with your first atom of the A layer and that is why you call it A layer again.

And this entire arrangement is then repeated. Up to 25 percent or in some cases you will have up to even 40 percent of rhombohedral graphite. But, what is interesting is rhombohedral graphite is considered the type of stacking fault in graphite.

It is not considered as an independent material for two reasons; one because you do not find it by itself, it is always mixed into your hexagonal graphite. And the second reason is also that, you can actually obtain the rhombohedral geometry by gliding the planes of hexagonal graphite.

So, that basically kind of makes it like a staking fault. In fact, rhombohedral graphite is not studied so much. One interesting thing is that graphite does not have AA AA structure. It is possible right.

If you just think of it, there is a separation between layers, why cannot we have AA AA structure? Because of our unhybridized p-orbital, because that creates some prohibitive energies. So, this would be a very high energy structure if you had AA AA A. Even in the case of multi-layer graphene, you will never have AA staking. You will always have some sort of rotation. The atoms would try to gain a minimum energy state.

But AA is almost never found, corner atom on corner atom does not happen in the case of graphite. As I already mentioned that the rhombohedral graphite, which is mentioned as rG by the way, can be obtained by glide or twinning. Within the next slide, I will tell you briefly about some stacking faults of graphite then you will probably understand this better.

Now, I told you what are basal planes. What are basal dislocations? So, think of it as if you want to have any faults or any dislocations in the case of graphite which plane is the is more prone to you know gliding? You are not going to break the c-c bonds. If you have your graphite like this, you cannot break it like (refer to the video at 4:59).

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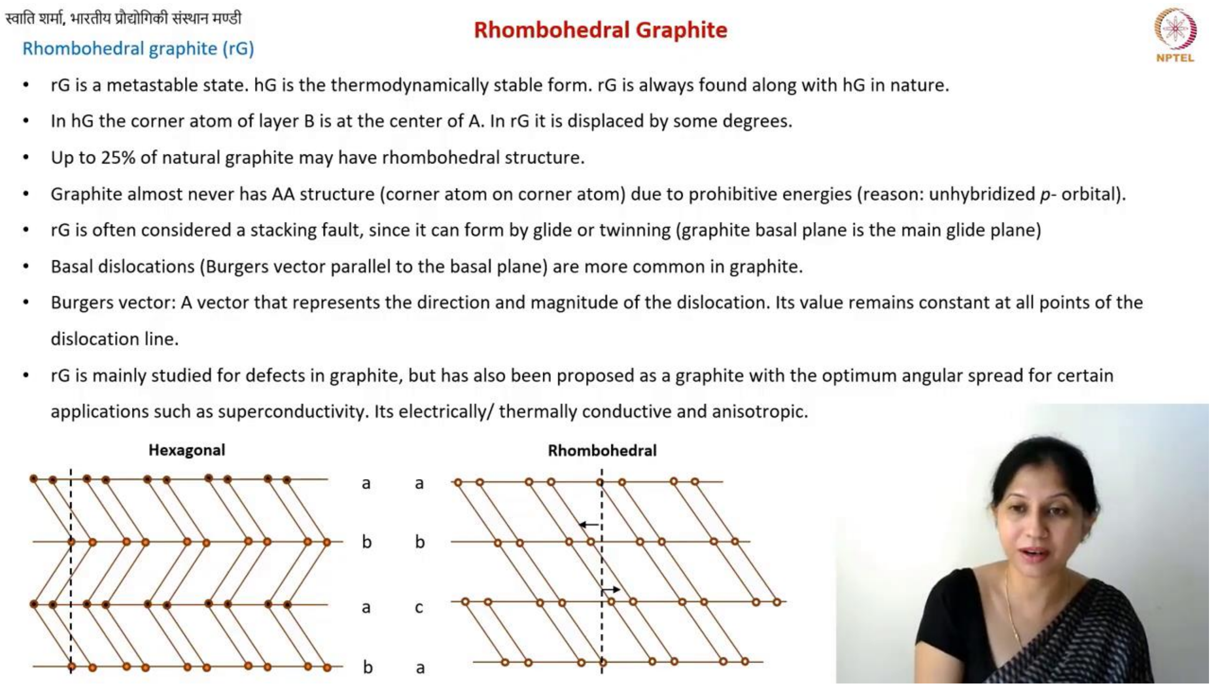

But if you have two planes of graphite then the sliding is easy. So, these are your glide planes, these kinds of stacking faults would be more common and we study the stacking faults with the help of Burgers vector. If you do not know what is burgers vector? This is the vector that represents both direction and the magnitudes. It is a vector quantity.

So, it shows the direction and also, the magnitude of your dislocation. You can figure out different types of dislocations and how to draw the burgers vector. But if you have dislocation, in that direction you will have your burgers vector. It will also show the magnitude. So, based on that we will then learn more about the dislocations.

Now, what are the applications of rhombohedral graphite? We studied for understanding the defects or just for understanding the stacking behavior of graphite, the answer is mostly yes.

Most of the studies on rhombohedral graphite have actually happened because you want to understand the layer arrangement of graphite and how much can it slide, and what are the possible low energy orientations and which ones are very high energy. So, mostly rhombohedral graphite is studied for this purpose.

Also, the properties of rhombohedral graphite are rather similar to hexagonal graphite. The electrical conductivity is not so much different. This material also features thermal conductivity. And in fact, if you have a little bit of rhombohedral graphite mixed into your hexagonal that will not make too much difference to the properties.

So, you do not need to always purify it or separate it out. That is why, in terms of applications, people have not really taken too much interest in studying rhombohedral graphite alone. However, there are some reports where they say that the angle that the layers make could be an interesting angle. Because it is a low-energy configuration. In some papers here and there, I read they call it the magic angle. And with this magic angle, you can have some very interesting properties which provide a twist to your hexagonal graphite, and then you can have even properties like superconductivities.

However, very similar to hexagonal graphite, this is also anisotropic material. Anisotropic means you have the properties different in the basal plane compared to what you have in you have perpendicular to the plane.

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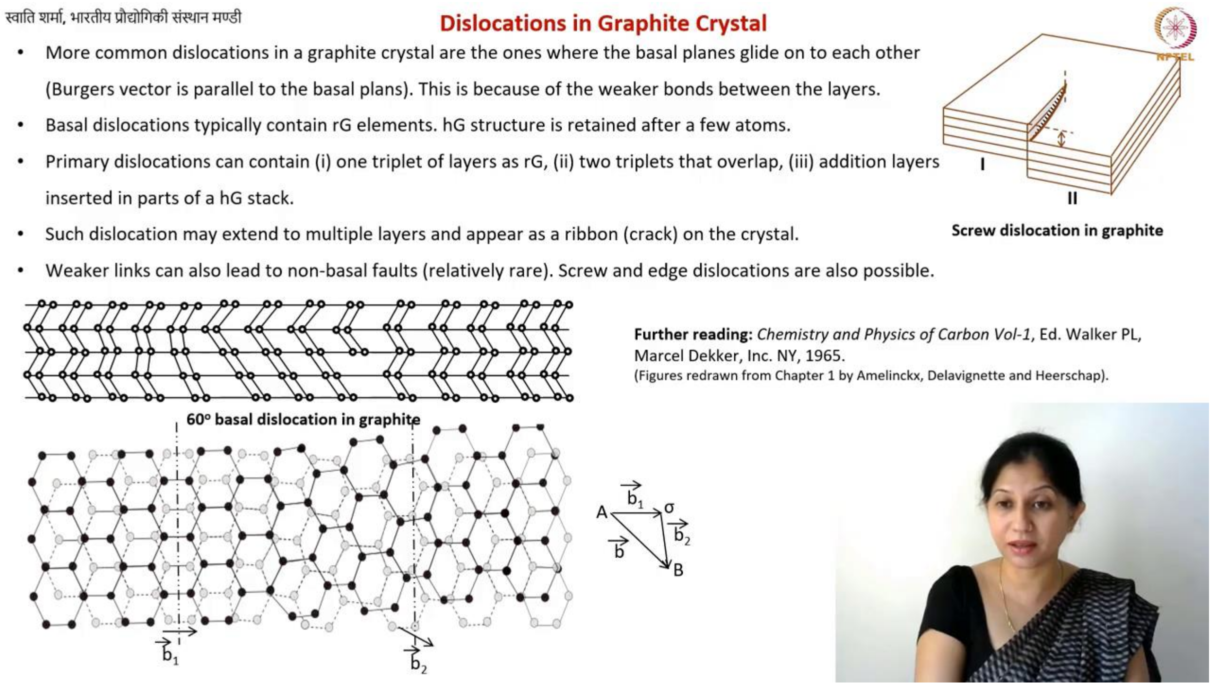

As I mentioned, the more common dislocations in graphite would be when you have the planes gliding on top of each other, where the basal planes are gliding on top of each other. In this case, your burgers vector will be parallel to the basal plane. So, it can it is parallel, it can take any orientation depending upon your glide or dislocation. But it will be parallel to your basal planes.

Now, of course, because you have the weaker Van der Waals forces between the two layers compared to the carbon-carbon bonds that are very strong and very short.

In the case of some natural events or any particular extreme conditions, you can also have non-basal defects in graphite. But more common one are the basal plane. So, here is an extensive image and this image actually shows you how the two planes can glide on top of each other. If I again take my books and then what do you what is happening? Actually, this is happening but not to the entire structure to a part of the structure (refer to video at 9:01).

Think of it like long extensive layers of graphite, some part of it has this kind of defect or this kind of dislocation. This is an image that shows the 60-degree basal dislocation. You can see the directions of the burgers vector. As I said, these are going to be parallel, but the angle can be 60 degrees. So, that is how you calculate the angle of your dislocation.

Here what is very interesting is that it is a dislocation, the structure has not completely changed. Dislocation or defects basically mean that only a certain part of your crystal structure is distorted and not the entire crystal. If the entire crystal is distorted, maybe you will have rhombohedral graphite then you will not have hexagonal graphite at all.

Here you see, you will always have certain rhombohedral type elements because the glide kind of takes it in that direction. So, if you see it in the side view image, you have these AB AB A arrangement and then at some point you something that looks more like the rhombohedral graphite something that looks more like ABC ABC. Typically when you have dislocations in graphite in bulk, graphite minerals and ores then you have these kinds of rG elements or the rhombohedral elements inside your hexagonal graphite crystal.

So, if you read a little more then you will have mainly three types of dislocations. One way you have a triplet of these rhombohedral graphite-like geometries, then you can also have two triplets of this kind. Triplets mean three layers ABC.

But of course, when you have this ABC kind of arrangement, then you are slightly distorting the top and bottom layers. Now, you can also have two triplets that could overlap on top of each other and then you can also sometimes have additional layers which may be of ABC.

Sometimes if there is one little additional layer inserted inside your hexagonal graphite, then that layer would also do something to the crystal structure. It will typically make it more like a rhombohedral structure. These are the different types of stacking faults that you have in graphite. These are called stacking faults because we are always talking about the staking of the layer and how that stake is organized in terms of the crystal structure.

So, these are the primary staking faults in graphite and now, of course, from here you can also conclude that these staking faults take your hexagonal graphite more towards rhombohedral. These were just staking faults but then they continued and they propagated to the extent that large portions of your hexagonal graphite crystals, large portions, large chunks actually converted into R graphite if such dislocations extend to multiple layers.

If you look at your graphite crystal not in the electron microscope, but standard microscope then you will see lines like they are curved. So, they look like what you call graphite ribbons, and these graphite ribbons result from these kinds of stacking faults.

So, what you see here is the cross-section. Now, if you see in the top view in the second image, you have the slightly tilted and curved sheet on top. What is very interesting here that you see there are no carbon-carbon bonds that are broken. You also see that there are no point defects. So, there are no seven-membered rings and there are no five-membered rings because those are the things that will take you more towards the fullerenes or curved carbon structures. But here, the curvature is not caused by five and seven-membered rings and that is why your structure will not fold up.

These are just in-plane distortions. So, you do have a slightly curved structure on top and if this curvature continues then you can also have more like a ribbon-like structure.

Here, all your 6-membered rings are stretched a little bit. Their position is changed a little bit so they are under a certain strain. The five, seven, or any non-6-membered rings do not exist in most of these cases. However, if you have a point defect for a certain reason which does not typically happen in natural graphite, but if you do have point defects if you do have non-6-membered rings that can lead to a staking fault of this kind.

Now, are only these kinds of dislocations possible? As I said that, this is the most common one but it is not impossible to also have the crystal braking like of biscuit. So, that is also possible, one such example is here. This is the screw dislocation in graphite.

You can have screw dislocations; you can also have certain edge dislocations. For example, when we were talking about inserting an additional layer, that can lead to edge dislocations. So, there is this one layer between the two layers. So, edge dislocations are also possible, and this example is that of a screw dislocation in graphite. This is basically all about the dislocations in graphite and I just wanted to introduce you to the rhombohedral form of graphite.

As I mentioned that its properties are rather similar to the standard hexagonal graphite and in the case of industrial manufacturing applications when you have graphite ore and you have processed graphite, it does not really matter if you have a little bit of rhombohedral graphite mixed in. People do not even bother about that. So, we will only learn about the applications of the manufacturing processes and cleaning processes etc. for graphite, which we will do in the next class.

Now, if you further interested in reading about graphite, there is this series of books called Chemistry and Physics of Carbon. I have cited volume 1 here but you have several volumes. It is a very old book so this one is from 1965. Several old volumes are out of print nowadays.

So, it is difficult to find these books. I found it in some old libraries here and there. In the libraries, you can potentially find it or if you are lucky, you can get a used copy. But these are very fundamental books related to carbon materials.