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

**Lecture - 23**
**Glass-Like Carbon: Introductions and Properties**

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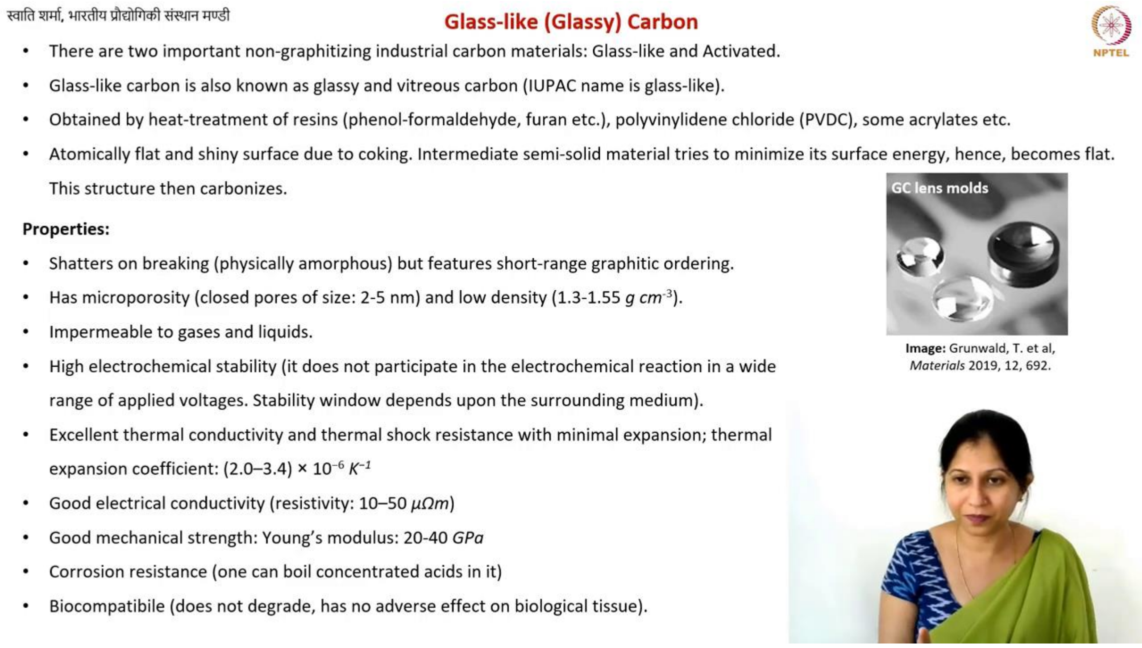


Hello everyone. In this lecture, we are going to discuss a very important non-graphitizing industrial carbon material which is known as Glass-like Carbon or Glassy Carbon. So, when we were talking about non-graphitizing carbon, you understood that there is one very important difference between graphitizing and non-graphitizing carbons is that these carbons have isotropic properties.

Isotropic means, the properties are the same in all directions; unlike in the case of graphite where you have this layered structure and if we talk about electrical conductivity, you have different electrical conductivity in perpendicular to the c axis of your crystal and parallel to the c axis of your crystal.

But that is not the case with non-graphitizing carbons; whether they are glass-like carbons, whether they are activated carbons or other cokes or other forms of non-graphitizing carbons. Because of the fact that their crystal structure does not have any preferred orientation.

You have fullerene-like structures, you have flakes that are curved which are randomly distributed in all directions and pretty much anywhere. If you find the average properties, they are always pretty much the same in all directions. This is an important property, which also makes them useful for certain applications, where we do not want to use graphite.

So, for certain applications, you do not want anisotropy. You want the properties the same in all directions. In that case, you can use non-graphitizing carbons. Now, glass-like carbon is a type of non-graphitizing carbon which is prepared by coking and that is why it settles down, its softness during its carbonization and that is why it has a very flat and shiny surface.

In fact, that is why you have this name — glass-like carbon. It looks like glass and it almost has this very shiny surface. To be honest, I think it even has the flatter surface compared to the general silicate glasses. This material, however, is prepared by coking that is one thing and the number 2, its electrical conductivity value is slightly lower than graphite. But it is high enough for a lot of industrial applications, which is in the case of activated carbon.

I have written here that glass-like and activated are two most important non-graphitizing industrial carbon materials. In the case of activated carbons, surface properties are utilized more. In the case of glassy-carbon, you will rather utilize the electrical and electrochemical properties.

Now, I am calling it glassy, sometimes I call it glass-like carbon. Its IUPAC name is glass-like but in the literature, you will commonly find the term glassy and also here and there you find it is also called vitro carbon. So, vitro is French for glass or glass-like. These two terms have also been used by some companies and they have been commercially used and that is why IUPAC recommends that you do not use these terms.

But unfortunately, they are very commonly used in the literature. So, do not get confused if you find any three of these terms. Now, how do we obtain it? We know that these non-graphitizing carbons are obtained by heat treatment of polymers. As such, there is no other method of making glassy carbon. One important thing is that this is predominantly a synthetic carbon material.

You do not find natural glassy carbon. You cannot mine glassy carbon. This is something that we make and in fact, we ended up accidentally making it when we were making graphite. But irrespective of that, now we want to specifically manufacture glassy carbon, what are the precursor polymers that can be used?

You must have heard of Bakelite. These are phenol-formaldehyde resins, the class of resins or polymers that are made by mixing phenol and formaldehyde with different ratios of phenol and formaldehyde. These kinds of materials give you very good glassy carbon.

There are also some other resins like a furan resin and there are some acrylic polymers, there are some PVDC, there are many other polymers which do not give you graphite but they give you glassy carbon in general. If they are natural polymers like cellulose, then you have a higher probability of charring mechanism and that is why you have a higher probability of getting activated carbon.

However, there are also certain natural hydrogels that might give you glass-like carbon but not all of them. Some gels will give you glass-like carbon, some will not. So you have to do some experiments and figure it out. These are the precursors. One thing that I told you at the time of graphite manufacturing that these polymer precursors should have a high carbon content.

That is also valid when you want to get glass-like carbon, irrespective of which type of carbon whether graphitizing or non-graphitizing, important thing is that you have a high carbon yield. Otherwise, you will get very little carbon material; otherwise, you will also lose the shape, if you already make a structure. Then you may end up losing that structure, you would lose the shape or you will get very high porosity or in any case, you will just get very little carbon, which is not worth doing all the process.

So, high carbon content also is valid in this particular case. And here if you have a higher aromatic content that helps in getting graphitic crystallites. Now, we are talking about disordered carbon materials, disordered in bulk, but they contain these graphitic carbon crystallites. So, they are graphitic carbons.

It is important that glassy carbon is made via the coking process, so that mechanism is important otherwise, you will not get the flat and shiny surface. I also actually have a glassy carbon plate with me, can you see it (refer to video at 6:41)? So, you see this is so shiny, there is light outside and you can actually see also outside of the window. This is a glassy carbon.

You see how flat and shiny it is and you can see that I am just holding it in my hands and this is not corrosive, this is not harmful. I do not need to wear glass for it. This is also a very stable material. Basically, when I touch it, nothing will happen to me, and also nothing bad will happen to the sample itself. If there is some oil from my fingers on the glassy carbon surface then I can wash it pretty much with any chemical like with acetone, methanol nothing will happen; no damage to the surface or I can also heat it. I can burn out the impurities if there is some oil from my fingers, there you can just simply burn it. Nothing will happen to the carbon itself. It will not get burnt.

This glassy carbon is a very stable material; it is stable in many ways. This is something we will talk about. Here, I have also shown a picture where you making molds for molding of glass. Now, glass is molded at reasonably high temperatures depends on the quality of the glass usually 800 degrees or more.

So, for molding glass, you need what you need? Number one, you need something material that can withstand high temperatures without any distortion in the material itself or its surface and number 2, you also want a very flat surface. So, glass molding has actually been one of the very important industrial applications of glassy carbon. And I have taken this one example from a paper. So, now, let us talk about the properties. One thing you already know, it has a flat and shiny surface.

Now, it is physically amorphous and that is why sometimes people end up calling it amorphous, which is wrong and this is something very important for you to know this material is electrically conductive. Although, its electrical conductivity is not as high as that of graphite but it is electrically conductive. It is very different from silicate glasses. When you think about glasses, you think of silicate glasses, the common glasses. This material is very different in terms of its physicochemical properties and that is why despite the fact that its name is glass-like, it is not really glass. It is just glass-like in the sense, that it is flat and also the fact that it shatters on breaking. This is one of its physical properties which kind of led to the nomenclature glassy but at the same time, it has short-range graphite crystallite. It is a disordered carbon material.

It is a non-graphitizing carbon material and the exact fraction of graphitic content will depend upon the heat treatment temperature. But it is definitely not an insulator. It is definitely very different compared to the physical glasses, despite the fact that it is hard and brittle.

Now, I had mentioned before that it has microporosity. So, micropores are basically pores that are in the nanoscale; 2 to 5 nanometre size, when the pores have this size and they are called micropores, they are not called nanopores. So, if you look at its micro-structure, then it contains these micro porosities. And when we talked about the microstructure of non-graphitizing carbons, we have learned that this is because of the presence of fullerene and fullerene-like structures. So, either they are completely closed or not completely closed, but they are highly curved carbon structures. Because of these structures, the material has a relatively lower density. So, relatively means it is lower than what we would expect from something that is prepared by coking. Also, compared to graphite, it is slightly lower. You have 1.3 to 1.55 g/cc3. That is again a range because the exact density will depend upon the heat treatment temperature which will depend on what kind of precursor you used and these are the things that we will learn later on.

There are many factors that influence the exact microstructure of any non-graphitizing carbon. The point is that the material has a lower density because of the microporosity and despite that, it is impermeable to both gases and liquids. And this is what actually led to a lot of intriguing questions about glass-like carbons. Why do we have less density which means we should expect some porosity; but at the same time, it is impermeable, because the only possibility is that it has closed pores and what people are still studying and trying to figure out what kind of structures they are.

But these pores, again they are micropores, they are very small pores. Then you will not find any visible physical pores as in the case of charring or activated carbon where the pores are much larger, but here they are very very small. Now, one more interesting property of glass-like carbon and it is used a lot in battery applications also. In many cases, you will use glass-like carbon rather than graphite. Why? Because it has a very high electrochemical stability.

Now, what is electrochemical stability? If I have an electrode of glassy carbon or any other material and now, I want to perform a certain reaction in a cell. We can have electrodes for batteries, we can have electrodes for capacitors, supercapacitors and so on.

So certain electrochemical reactions are taking place in batteries. Now, what you want is that your electrode itself should not participate in that reaction, or sometimes you want to have an electrode just for reference. So, that electrode itself should not participate in the reaction that should be stable and there is something called an electrochemical stability window.

This window is basically -x to +x volt. In that range, your battery can operate safely without the electrode participating in the reaction. That is the electrochemical stability of the electrode material that, let us say -2V to +2V, my electrode is safe to use. Glassy carbon has one of the widest electrochemical stability windows, so the material is very stable under electrochemical environments and that is why this is used for a lot of reference electrode fabrication.

It has very good thermal conductivity. So, I can make a crucible out of my glass-like carbon and I can first of all place this glassy carbon thing outside, nothing will happen to it. I can leave it for 10 days, nothing will happen to it; several years, nothing will happen to it. I can burry inside the ground for several years, nothing will happen to it. I can put this inside some concentrated acid, nothing will happen to it. If I make a crucible out of this and I boil concentrated acids in it, still nothing will happen to it. That is the inertness of this material.

One more property that you want in the crucible is when you are heating it, the heat should be transferred and reach your chemical inside. So, it has also a very good very high thermal conductivity and a very low thermal expansion coefficient.

That means, your crucible will not get damaged and that is why you are using this for making glass molding lenses, many types of glass molds, where you can pour melted glass or melted metal. So, you are using this material a lot for mold fabrication. So, it has also very good thermal properties, also very good thermal shock resistance. Now, electrical conductivity as I said, I will not call it excellent electrical conductivity but you have it in the range that can be that is usable for most of the applications.

So, graphite definitely has a higher electrical conductivity than glassy carbon but it is usable for a lot of applications. For any electrochemical application, electrochemical stability becomes very important that is why you can kind of compromise a little bit on the electrical conductivity.

If you compare the mechanical strength of glassy carbon with carbon fibers or other carbon materials, maybe it is slightly lower but compared to many other carbon materials, it is much higher. It is again between 20 to 40 Giga Pascal that is Young's modulus value.

Now, again, it will depend on what is the heat treatment temperature and what are the exact conditions, depending upon that, it maybe you know 20, it may be in 35 or something like that. But it has a reasonably high Young's modulus as well, ok.

It is corrosion resistant as I said one can boil concentrated acids in it and if you leave it outside, tr does not get affected by humidity and many other environmental factors, this is a highly stable material in general.

Now, one more interesting property is that it is biocompatible. Now, what you call biocompatible? This is interesting. If something does not badly affect the tissues or cells of the body, then it is biocompatible. But, at the same time, you need to know it is not biodegradable. Biocompatible is different, biodegradable is different.

By biocompatible, what we mean is if we make any implant using glassy carbon, that will not really have any adverse effect because it is a very stable material in itself.

So, it does not you know erode or anything and number 2, also it is compatible with biological tissue. So, your tissues, your cells, do not mind having a glassy carbon implant. So, in that sense, it is biocompatible; but it is not bio-degradable.

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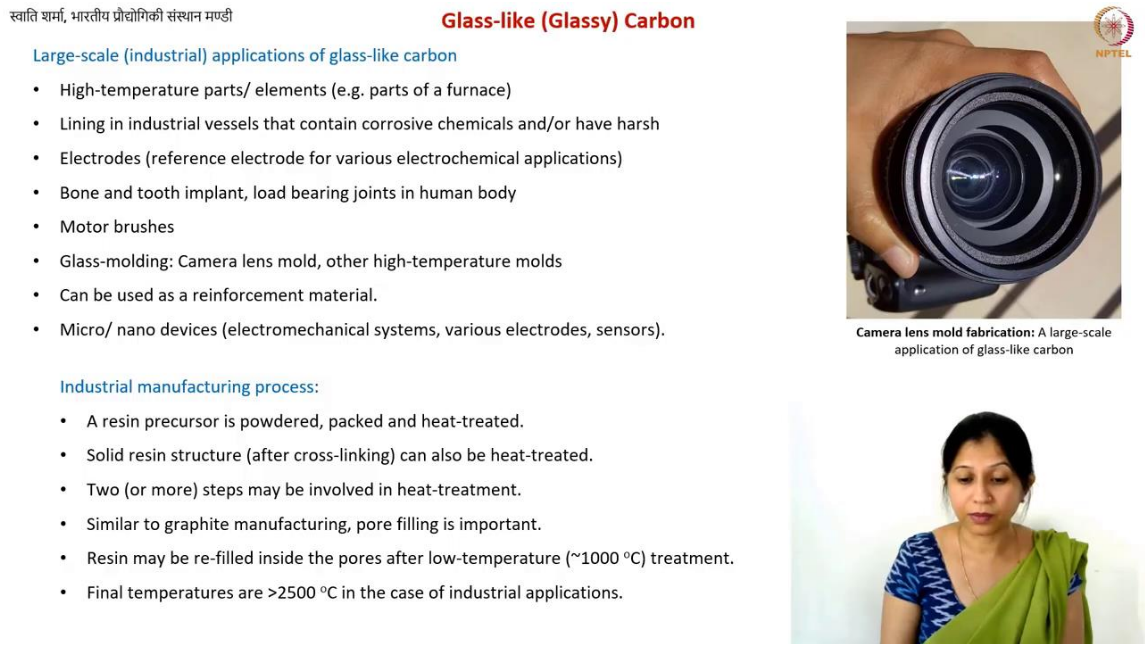


Now, let us talk about the applications of glass-like carbon. You can already guess from the properties, what are going to be the applications. With biocompatible means, you can immediately make some implants. Now, what kind of implants? You can make tooth implants and you can make bone implants.

There are issues with it. If you want to make bone implants, then you need to give the shape of the bone. How are you going to manufacture it, that is what we are going to see. But on the other hand, you can already imagine the electrochemical applications, you can make electrodes or some of these things you already saw. You can make glass molding; you can make molds for glass molding, other molding things.

High-temperature parts elements: we also said that graphite is used for making high-temperature for example furnace elements. Sometimes the replacement of graphite is glassy carbon because well what you need in a high-temperature material? High temperature withstanding material. You do not really care too much about its electrical properties or other properties. As long as you have good thermal conductivity or thermal shock resistance especially thermal shock resistance and also reasonable mechanical strength, then you can make furnace elements or any high-temperature elements. So, this is also used sometimes instead of graphite.

Now, one important thing because I mentioned that you can boil acid in it. At high temperature also, it shows very good chemical resistance, or corrosion resistance. So, in that case, if there are certain chemical processes where you need to perform certain reactions which are highly corrosive or there is a certain by-product that is forming that can actually damage your reaction vessel itself, then you can make these vessels of glass-like carbon or if not the entire vessel, at least a lining you can put. Basically to protect your vessel, you can have a layer of glassy carbon in between your vessel. If you ever think, there are so many chemicals that you buy and some of them are very highly corrosive and if you touch them something bad will happen.

How do these chemicals are prepared? When you are performing the large scale chemical reactions when you have the plants where you manufacture chemicals, there you also need to have the pots and vessels, where performing these high temperatures and highly corrosive reactions and those vessel materials should also be very stable.

And they should also have good durability, you cannot use one vessel just for one reaction. Chemical plants are running for you know 24-7 for several years. So, in such cases, you need really stable materials and glass-like carbon is a material that is used for making such vessels or the lining source of these reaction vessels.

Electrodes: you already know it is used as reference electrodes for a large number of electrochemical applications. If you are research scholars and you have worked on any electrochemical application, then you must have at some point, used a glassy carbon reference electrode.

Now, I was talking about implants, let us not think about how we will make it; but if you make a bone implant, then because the material is so inert and its biocompatible and the cells in the human body, they do not really mind having this material around and that is why it is you can make bone implants.

Nowadays a lot of composite materials are being used for making bone implants. That we are going to learn about them in the carbon fiber section. But for tooth implants, glassy carbon is very good material. Of course, your tooth will look black but people put gold in their tooth, I mean gold is no better. So, either you make the tooth which is of the color of the tooth itself otherwise it can be any color right. Anyway if not for humans, there have been studies where people use glassy carbon for animal tooth replacements or implants. So, this is a material also which has certain biological applications.

Motor brushes: so you see that most of the motors have these carbon brushes and those carbon brushes are not necessarily graphite. In fact, they are rather not graphite because graphite has this layered structure, it is soft material. So, here the electrical conductivity does not have to be very very high in the case of a motor brush. You can use glassy carbon for this purpose. In fact, if you see a carbon brush in your motor, then it is going to be one of the non-graphitizing carbons.

Glass-molding: in the previous slide, I showed you a picture that was in millimetre scale. It is a small lens, micro-scale millimeter scale. You can also use glassy carbon for that purpose. We will talk about how to do micro-fabrication with glassy carbon which is another field altogether. This is a picture of my own camera. These kinds of lenses, how do you make them and how do you get such a beautiful precision in the camera lens? In all the optical elements, you need very high precision and you cannot have any joints. So, how do you make glass lenses? Glassy carbon actually was responsible for the revolution in the camera industry. Especially in Japan, people started using it.

A lot of glassy carbon companies are established in Japan. So, Japan and Russia have been the countries that have utilized glassy carbon for a lot of industrial applications, at least in the past. So, when glassy carbon, people started using it for making the molds for camera lenses that really changed a lot in the camera industry.

So, what do you do? You can make a glassy carbon structure which can be made from a master mold and that master mold can be made of any other more expensive like tungsten or high temperature withstanding metal and then you make glassy carbon structures. We will see how you make it and once you have this glassy carbon mold, you pour glass and then, you get the mold out of it. This is very important and even today, a lot of optical elements and lenses use glassy carbon molds.

What else? It can also be used as a reinforcement material. And then, micro, nanodevices, we will talk about that. We will talk about that in detail.

Let us now talk about the large-scale industrial manufacturing process. So, you know that you can use a glassy carbon mold to make other things, but how do you make the glassy carbon mold itself? How do you pattern itself? You remember from our graphite lectures, what do we do?

In the case of graphite, it is not possible to, or it is at least not convenient to do machining. It is a hard and brittle material; all of those things are also valid in the case of glassy carbon. So, what can we do?

Again, we can take a precursor, already give it a shape and then carbonize it. So, a very similar process is also used for glassy carbon. However, the precursors are not needle coke or not petrochemical materials, except for isotropic pitch, which is used also not for making a glassy, carbonized isotropic pitch is used more for making carbon fibers.

In the case of glassy carbon, we have mostly synthetic polymers and, in most cases, phenol-formaldehyde resins. You take this resin precursor, now you have two options; you somehow need to make a shape which you need to carbonize, and you need to take care of the shrinkage that will take place. Because you know that when you have coking, you have dimensional shrinkage. So, that is something you need to optimize which you can do with the help of also software and any CAD program.

You can also make a fine powder of your resin rather than making one large structure, you can use the techniques that you use in powder metallurgies. You can make a powder and you can pack it and then crosslink it. Sometimes you can even crosslink it using laser and altogether, you can even do 3-D printing with this powder, depending upon the properties of the resin. If you can cross-link it with the help of laser or heat, then you might do that.

So, you can use all of these techniques. Basically, you want to make a shape using your resin. So, either you can have a fine powder or you can have liquid resin, which can be cross-linked and then finally, you take this solid resin structure which then is heat treated.

Similar to graphite, you can do these two or more steps of heat treatment. First you will heat it up to let us say 1000°C and then, you will have some porosity or some shrinkage. In this case, maybe shrinkage is more probable. You can have both porosity and shrinkage. Then, you can refill the resin and you heat it up to 3000 degrees. This is the industrial process.

Now, if you have the powder, you may not have porosity. That will depend on how you are using your raw material and then the second step is the high-temperature heat treatment, which is in the case of the industrial process, you will use 3000°C, generally about 2500°C. But here we are only talking about large-scale structures, I mean the structures that are thicker than a few millimeters.

If the structures are very small or if they are in the micro or nanoscale or if they have a very high surface-to-volume ratio, in that case, lower pyrolysis or lower carbonization temperatures can be used for getting glassy carbon of reasonable quality. Again, you may have to compromise on certain properties. For example, you may have slightly lower electrical conductivity, if you have lower temperature.