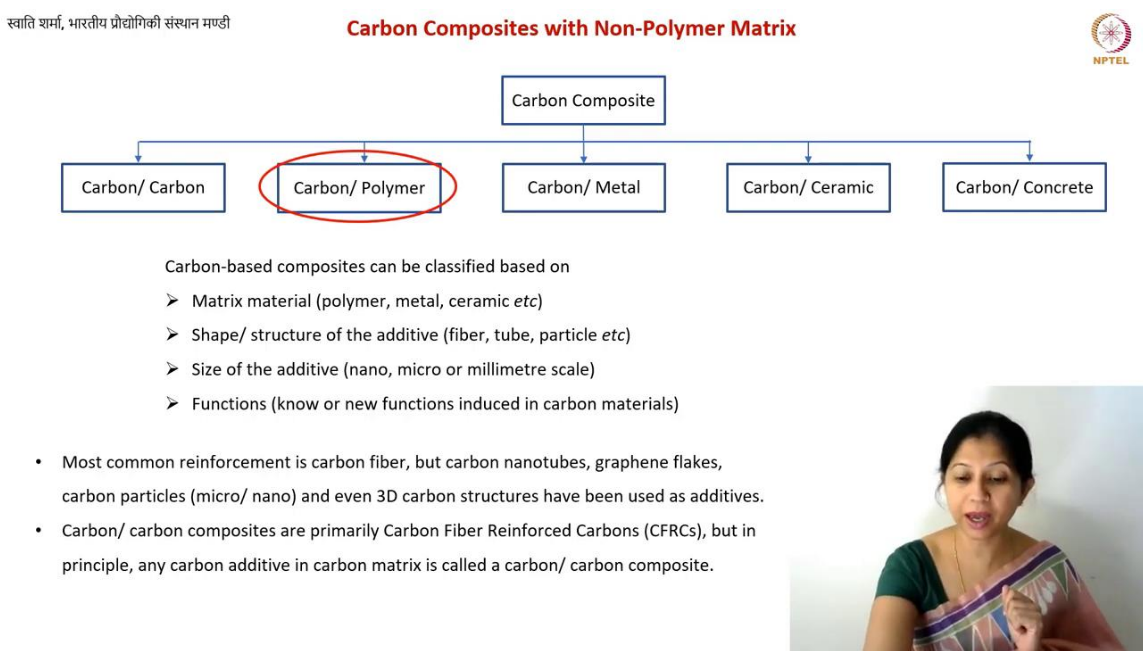
Carbon Materials and Manufacturing
Prof. Swati Sharma
Department of Metallurgy and Material Science
Indian Institute of Technology, Mandi

Lecture - 41
Carbon/ Carbon Composite

(Refer Slide Time: 00:13)



Hello everyone. In this lecture, we are going to discuss some carbon-based composites that are beyond CFRPs. So, CFRP or Carbon Fiber Reinforced Polymer are the most important or industrially relevant carbon-based composites and that is why we first learnt about them and the manufacturing techniques that are used with them and the challenges that we face when we are manufacturing.

This is just one type of carbon fiber carbon-based composite, however, that is not it. In fact, that is just one very small class. If you think about the classification of carbon composites then there are so many different types for example, instead of polymer matrix, you can also have a carbon material as the matrix. You can also have metal matrix, you can also have ceramic, you can also have concrete as matrix. In fact, carbon reinforced concrete is a very important industrial structural engineering material. So, there are all of these materials, we have learnt till now just carbon fibers inside a polymer matrix.

If we want to classify carbon-based composites then how do we do that? Composite materials have one additive in one matrix phase. So, you can do the classification based on the additive as well as based on the matrix.in fact it is done in several cases, the additive that is most commonly used is carbon fiber.

In many cases when we talk about carbon-based composites, we are often thinking in terms of carbon fibers, because well of course these carbon fiber ropes and fabrics give a lot of mechanical strength to your material and that is why you can also make laminates using them.

So, that is why they are very common; however, they are not just the only reinforcement materializers as I said. So, what you can do is number 1 - you can either classify these composites based on the matrix material or even the additive material. Now, again within the additive material, you can classify based on the shape or the structure of your additive.

I just said that carbon fibers are the most commonly used additives, but you also have tubes, you have particles and so on. You even have sometimes 3D structures made of carbon fibers and any complex structures can also be added as the additive inside your matrix.

You can also then classify your composites based on the size of the additive. Even within a carbon fiber we learnt that we have short fiber and long fiber-based composites. We also have fabric because when we make laminates, then we have these fabric like structures rather than just the single threads or yarns.

The size in all these cases actually vary; sometimes you have just nano scale carbon materials. For example, if you have carbon nanotubes, these are nano scale materials. These are your additives sometimes you have micro scale. So, if you have carbon fibers or the yarns of carbon fibers then you are talking in micrometer scale. Then you can also have millimeter scale when you are talking about the fabric or when you are talking about as I said more complex structures like 3D shapes.

So, based on that you can do the classification and finally, you can also classify your carbon based composites based on the functions of these carbon materials. So, you have certain carbon materials like carbon fibers, you can call them relatively traditional materials. So, they have certain functionality. They provide mechanical strength to your structures, but you can also induce new functionalities.

For example, you can use graphene flakes as additive as well and these graphene flakes. You can then have certain chemical function or you can provide it a certain structure which will provided certain other chemical functionalities you can even mix fullerenes Buckminster fullerene and others.

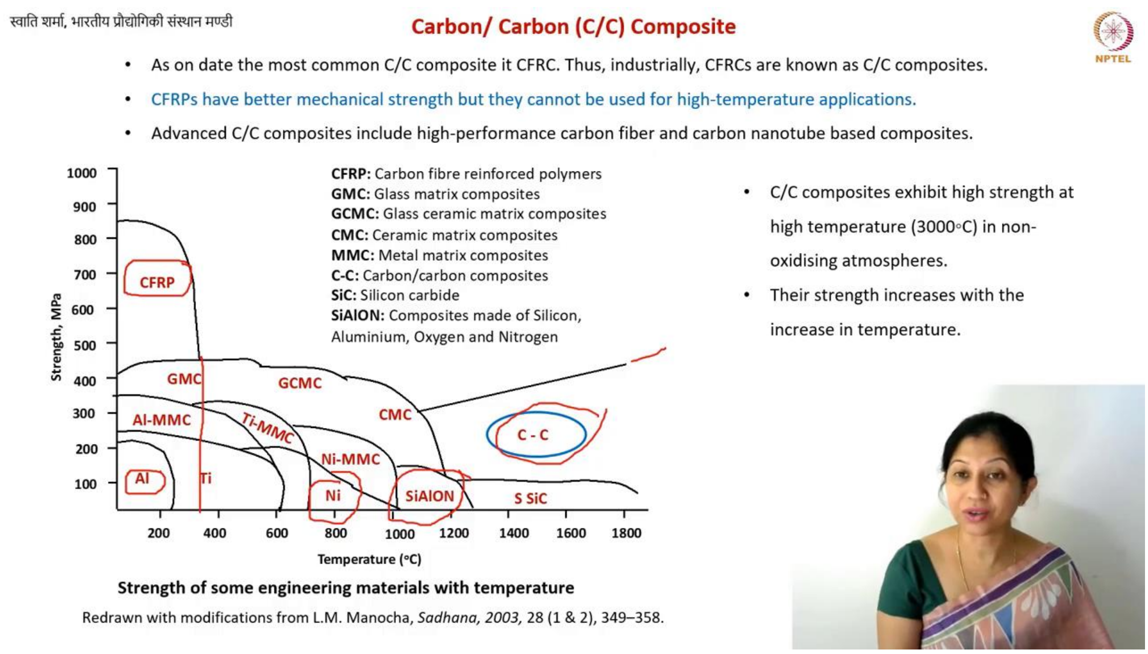
You can also mix these curved carbon structures and they have very interesting properties. They have for example, several chemical properties even photovoltaic properties, we are going to learn about them when we talk about carbon nanomaterials. So, the idea is that we can classify our carbon-based composites in various ways.

But our goal right now is to learn about other carbon-based composites since we have already learnt about carbon polymer.in this particular lecture we are going to talk about carbon-carbon composites mainly, but then we will also talk about other composites. However, it will be relatively brief compared to CFRPs and also I will go into the manufacturing aspects of carbon-carbon composites.

I am just going to cover introduction maybe some applications of rest of composites. Because anyway you can understand that you already know how to make carbon fibers and what are the properties that are important when we make composite materials. So, in that case you can even design your own composites and you can come up with some new matrix material or new functionalities in your additive.

These are the things that I have already told you. Now carbon-carbon composites that we are going to discuss in this particular class typically, carbon-carbon composites are carbon fiber-based again. If there is some carbon nanotubes in a carbon matrix that is also carbon-carbon composite. However, most commonly used or industrially used carbon-carbon composite is carbon fiber in a carbon matrix

(Refer Slide Time: 06:02)



So, how do we make them? Before we go into how to manufacture our carbon-carbon composites. Let us first think about this, why do we need carbon-carbon composites at all? Why not CFRPs? Actually, CFRP offer much higher mechanical strength compared to your carbon-based or carbon matrix composite. You can also get a lot of flexibility which you may not be able to get because you can already imagine that if you have carbon matrix, that matrix is not going to be as flexible as your resin matrix. So, why do we actually need these materials? Well, think about resin and what temperature can it withstand. Most of the polymers resins would degrade at 300-400 °C even if you make certain advanced polymers or you come up with new types of resins. Even then 400 is sort of the limiting factor. After that, your entire material would degrade, even before that temperature. As soon as your polymer goes above its glass transition temperature, you will start to lose sort of the integrity of your overall composite material. So, you cannot use them for high temperature applications. And high strength is often required for high-temperature applications.

For example, if you want to use for aircraft applications for a number of engine parts and so on. You need the materials to be able to withstand higher temperatures and not just provide mechanical strength at room temperature. That is where we can use our carbon-carbon composites or even other types of carbon-carbon-based composites.

As I already mentioned, there are not just carbon fiber-based but other carbon material-based composites as well, but industrially carbon fiber mixed inside a carbon matrix is known as carbon-carbon composite. This is the most commonly used material. Now, I will show you this diagram which is very interesting. Here you see the comparison of strengths of a lot of engineering materials.

Not just carbon-based or carbon fiber-based composites or just composite materials, but also a lot of engineering materials. So, often it happens that if you want to propose that. I can make this structure using carbon fiber or carbon fiber-based composites. You often are asked how does it compare with other engineering materials? Why should not we use nickel or titanium or a certain super alloy?

Because for metal-based materials, the manufacturing processes are rather well established. That is not the case with composites. We learnt in the previous lecture that we do not have all the standards although composites have been used for almost 3 to 4 decades.

But still compared to the manufacturing with metals, these are very new materials. First of all let us compare our CFRPs, CFRPs are here. You see that you can get very good strength compared to other materials. This is this offers some of the highest strengths.

However, the application is limited to as I said 400, even 400 is too high. Between 300 and 400 typically most of your polymers would degrade or their properties will change. So, this is number 1. Now you see other materials here. You see other metals. So, aluminium, nickel, titanium and there are also certain special types of alloy materials which are based on composite materials that are based on silicon, aluminum, oxygen and nitrogen.

So, these alloys are also high-performing alloys, they can withstand higher temperatures 1000 to 1200, but then their mechanical strength is limited. So, there are pros and cons of using all of these materials. Our carbon-carbon composites fall here. And this includes all kinds of carbon-carbon composites, here I have not shown just carbon fiber based.

But even whatever advanced carbon composites, we are designing nowadays, even within carbon fibers you can have high-performance carbon fibers or general-purpose carbon fibers, we are going to discuss in a while. So, this is where our carbon-carbon composites fall and you can see the temperatures they can withstand are very high from 1200 up to 1800.

And when we talk about withstanding the temperature that basically means without any deformation without any structural changes. So basically at these high temperatures, your material does not lose its integrity, it is stable at these high temperatures. However, as I mentioned compared to CFRPs, the mechanical strength is relatively lower but since the research is going on. So, you see that this line is going up. Hopefully we will come up with some carbon-carbon composites in a few years that have better performance. This is a very active area of research because this is also very important for manufacturing applications.

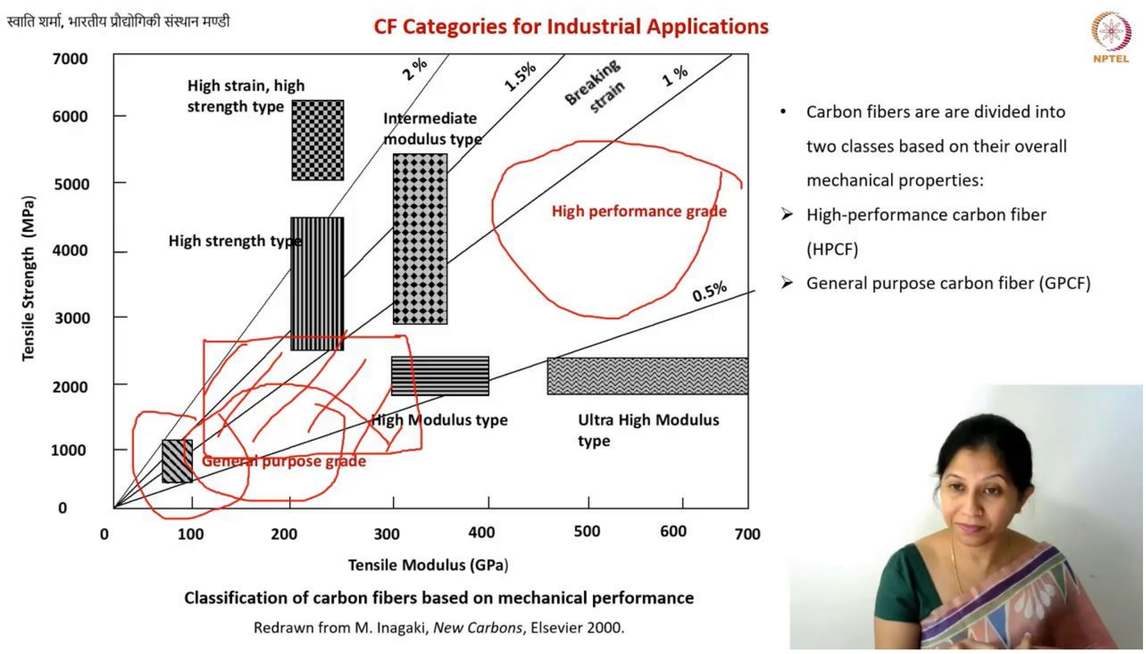
Just write it down for yourself, which applications would require very high mechanical strength at the same time high temperature applications? Let me give you one hint, gas turbine blades. So, these are the kind of structures that require that operate at very high temperatures.

And they operate continuously for several months together and they have very harsh environment, corrosion, and all kinds of stresses. People are often using silicon carbide and superalloys for manufacturing these kinds of blades.

But carbon-carbon composites can be potentially used there because they will also offer a lighter weight. So, that is one advantage anyway with all the carbon materials. So, I already mentioned that you can actually have good strength up to 3000 °C centigrade, but in non-oxidizing atmospheres and that is something. That is a challenge; the surface oxidation of carbon based.

We are going to discuss some of this as well and there some potential solutions to it. One important aspect is that in many cases the mechanical strength of your carbon-carbon composites actually increases with temperature. So, that is one very interesting property. So, you can already imagine these are very useful materials.

(Refer Slide Time: 12:54)



As I mentioned, you can have high performance carbon fiber and also general purpose carbon fiber. So, you call them HPCF and GPCF. These are the terms you will hear commonly. This has nothing to do with composites.it is about the carbon fiber itself, but this term terminology is more used in the composite manufacturing industry.

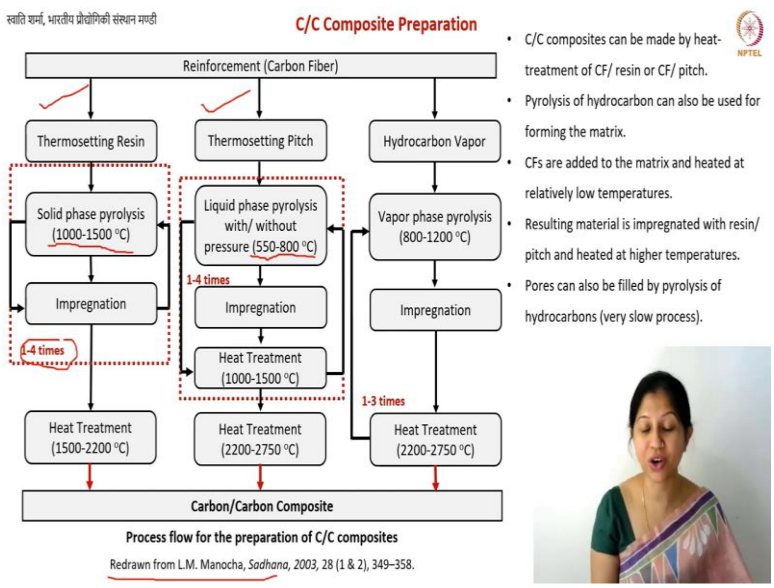
Here I have shown this big chart where you can see there are different types of carbon fibers, we already discussed that we have 2 important properties: one is the tensile modulus or the Young's modulus and the other one is your ultimate tensile strength. So, both properties are important. Some for some fibers for example, the PAN derived carbon have a higher ultimate tensile strength, but relatively lower Young's modulus.

But in the case of mesophase pitch derived carbon, basically the graphitic carbon fibers you have a higher Young's modulus or often it is just called higher modulus, but lower tensile strength. So, now you can already see that we can distribute these fibers and we can say which ones are relatively low quality and also quality would then determine the value.

So, low value and high value carbon fibers fall in this region. They are your high-performance carbon fibers and those that fall somewhere here, they are here and so on. They are general purpose carbon fibers. This diagram can also be further modified. you can add more things to this for example, you can also see where your vapor growing fibers fall.

In this diagram you mainly we are talking about commercial fibers that are melt spun or electro spun. But you can also have for example, your vapor grown fibers that will mostly fall somewhere here in this region. So, these are regions not exact numbers and then also of course, based on the heat treatment temperature, based on few parameters you can also have few changes to the. But these are the more or less the regions where does your carbon fiber fall. Now, both low and general purpose and high performance both of them are used for making composites CFRPs as well as CFRCs.by the way these carbon-carbon composites you can call them CFRCs because as I mentioned they are mainly made of carbon fiber. So, carbon fiber reinforced carbon.

(Refer Slide Time: 15:39)



Now, coming to the most important aspect of our of today’s lecture, how do we make carbon-carbon composites. So, you already know how do we make carbon that is something we have already learned. That there are many precursors; you can use resins, phenol formaldehyde resins, you can also use polymers like PVC which will rather give you graphite-like carbon, you can also use different pitches isotropic pitch and mesophase pitch.

These are the precursors for carbon. What you need to do is now also add carbon fiber to it. So, that is pretty much it, but there are certain things that you need to ensure like at what time do you add your carbon fiber? How many times you need to reheat it? because you will have porosity and now here you do not have just general porosity that you had in the case of graphite or in the case of glass-like carbon.

What you are also going to have is voids between the fibers. Remember that your fibers are already in the form of carbon in the beginning. So, you are starting with the carbon fiber. However, after you mix it inside your polymer or pitch matrix. When you reheat it, the fibers are also going to be reheated.

They are also going through some micro structural change. Maybe some graphitization and that is why now there is a higher probability of getting voids or getting all sorts of defects. So, this is what we need to take care of and that is how we will do the manufacturing.

However, now see this diagram I have taken from this review article. This is a very interesting article I think you should read, you will gain a lot of information about carbon-carbon composites. You see in this chart, this is the process flow that you first take your reinforcement material. That is your carbon fiber.

What do you do? Now you can either mix it with a resin which is typically a thermosetting resin not thermoplastic. You can also use a pitch as your matrix. Typically that would be isotropic pitch, but you can also use mesophase pitch depending upon your application; what crystallinity what stiffness do you want in your material?

The third pathway here is something we have not discussed for manufacturing large-scale carbon materials yet. The pyrolysis of hydrocarbons you know already what it is. But we are going to discuss this more when we talk about the chemical vapor deposition of graphene e or when we make carbon nanotubes.

So, that is why we are going to go into more detail. But you can already see that industrially, pyrolysis of hydrocarbons is also used at a larger scale to make this matrix material around your carbon fibers. So, 3 pathways; you can either take a resin or pitch and then you perform the heat treatment or you can take your bundles of carbon fibers or whatever structure you want. And then grow pyrolytic carbon using hydrocarbon precursors on top of it.

And you can grow several layers and you can also perform further annealing or hot pressing depending upon what kind of structure you want. You can also place the entire thing inside an autoclave and then you can get a certain type of sheets. So, these are the 3 pathways that are used. All of them are industrially used for making carbon-carbon composites. So, let us talk first about the pathway number 1.

So, you have thermosetting resin. You mixed carbon fiber into it. Now, you will pyrolyze it, this is called solid phase pyrolysis because we are using for polymers. For pitch we call it liquid phase because it is a liquid material, often they are cured they are cross linked.

So, they are below their glass transition temperature when we are starting and that is why we would call it solid-phase pyrolysis. Of course, you take liquid phases pitch and gas phases. So, you perform solid-phase pyrolysis between 1000 and 1500. Now as I mentioned, you will get some porosity and some voids will be generated.

So, what you need to now do is you need to impregnate it with more resin. This is something similar to what we did when we were making graphite structures using needle coke. So, you make these needle coke structures you perform relatively low temperature carbonization and then you get certain pores because your non-carbon atoms are leaving at this point. So, you will get some porosity. Now you refill your structure may be with low viscosity resin into it and heat it.

Still that resin will also lose some non-carbon content. So, you will again get some porosity then do it again and do it. So, this process can be done 1 to 4 times depending upon how much porosity did you have to start with. So, you may have to do this multiple times. You need to impregnate your structure or your overall material with more and more resin.

And then keep heating it again. So, you can already imagine from here. The materials are very expensive because you are performing very high-temperature operations and not just once, but multiple times. So, once you get rid of most of your porosity, you may still have some microporosity, but you got rid of most of it then you perform your high temperature treatment. So, then you go up to 2200, you can even go slightly higher.

So, now you perform this kind of heat treatment and you get your composite material. Pathway number 1 same thing, but with pitch, the parameters slightly vary because first pyrolysis that you perform. That is only up to 800 °C and then because resins are polymers, they have a lot of non-carbon entities, but your pitch may have up to 95 percent carbon content.so the porosity may be less. In fact, the porosity that you get maybe more like mesoporous or macroporous. Even in the case of resin you will get more microporosity. So, you perform the first pyrolysis or heat treatment, and then you again impregnate it with more pitch.

You can also use resin, but if you starting with pitch then you will do also further impregnation with pitch. And then again you may have to do it multiple times till you get rid of all your pores or most of them and then you perform a heat treatment again at 1000 and 1500. This was not the case with polymers, but typically this is done in the case of pitch.

And then you will perform your high-temperature heat treatment. Also depending upon the pitch if you use mesophase pitch, they going to be graphitic and they will also have relatively less porosity.

So, here we are doing this heat treatment twice because we get these larger pores, larger voids. And then we are filling it again and again and that is why we are doing the 3 step heat treatment in this particular case. Now the 3rd one which is the important one, I mean all of them are important but important in the sense that we have not talked very much about it.

You perform the pyrolysis of hydrocarbon vapors. Your methane or acetyl, you crack these hydrocarbons. Till now we have only learnt that or whatever we have talked about CVD, we only talked about metal catalyst on which you can pyrolyze or crack these hydrocarbons. But these hydrocarbons can also be cracked at carbon surface itself if your carbon surface is heated.

So, if you have carbon fibers and a mixture of your carbon surface. First let us start just with carbon fibers; if you have your fibers then you heat them, your hydrocarbons can actually crack on the surface of fibers themselves and they can deposit. Then you will perform as I said some annealing or depending on the structure you can perform hot pressing and then layer by layer you will make your pyrolytic carbon on top of this.

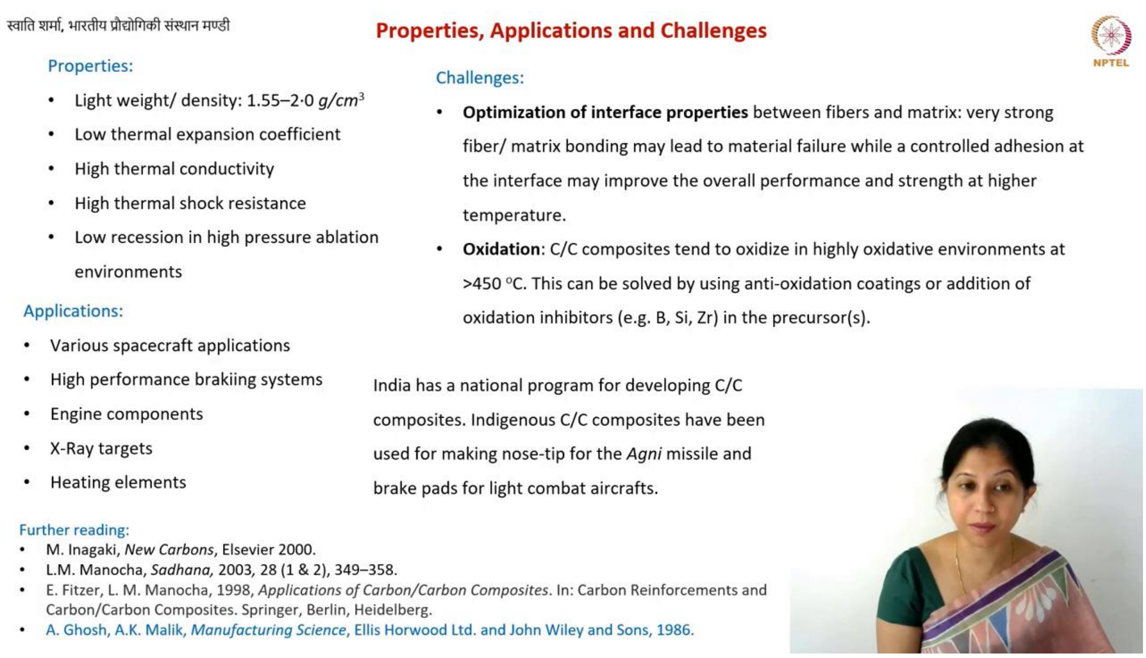
Because you do not have non-carbon atoms. So, you are able to control the porosity at every stage. However, you can imagine that this is a relatively much slower process. the issue is that typically what you want from your hydrocarbon gas is that it will go inside all the pores and voids between your carbon fibers because it is a gas.

In principle, it should go inside the voids and then crack and then it can fill all the pores, even including micropores, but often it happens that the top surface gets saturated with the pyrolytic carbon first, and then there may still be some voids inside. So, this process needs a lot of optimization and this process can actually go on for 4 weeks together.

So, this is slow and it is also an expensive process, but the quality of carbon that you will get in your matrix material is going to be much superior. So, these are all the processes that you will use.

Now I have one question for you and you can think about it yourself if you want to provide a certain shape to your structure, let us say you want to make a cylinder using this carbon-carbon composite, at which stage are you going to give it a shape of the cylinder? I think the answer is easy, but still think about it.

(Refer Slide Time: 26:26)



Now coming to the applications of carbon-carbon composites I have mentioned a few here, but you will see that there are many other applications. In fact, while we are speaking, there may be some other applications that people have found. And we have a number of high-temperature applications for sure, which also require high strength of the material.

Before that let us just talk about the properties. When we know the properties of the material, we can find new applications for it. These are lightweight materials and the density is in the range of 1.55 and 2 g/cc does that sound familiar.

That sounds like other carbon materials. Now this is our comfort zone carbon material. This is a purely carbon material unlike CFRPs. I mean CFRPs are great, but they are only 60 percent carbon right. What is the density of glass-like carbon, it is often above 1.55 and the density of graphite 2.26 so, it is below this range.

So, now you see that your carbon-carbon composites fall between glass-like carbon and graphite which is also obvious right, because glass-like carbons have these fullerene-like structures and therefore, they have closed porosity and very low density. On the other hand graphite has AB AB A type crystal arrangement and that is why it has very good density.

What you would expect from something that contains carbon fibers and a relatively disordered carbon matrix? Because it is disordered that means, it may have some curved structures. So, it will not have the density of graphite for sure.it is not polycrystalline material. You may even have turbostratic carbon fibers.

So, your density has to be lower than that of graphite, but it is more than that of glass like carbon because you may not have as much closed porosity as in the case of glass-like carbon. Because here you also have you have different structural components and you have carbon fibers, they did not have so much microporosity as compared to glass-like carbon. Also, you performed several times densification.

So, that is why you will get your density and other properties in this range. Now we are thinking of properties similar to other carbon materials. The thermal properties for carbon-carbon composites are the most important ones. So, you have a low thermal expansion coefficient. And you have good thermal conductivity. You also have good thermal shock resistance and in fact these materials are used for a lot of high-temperature applications.

You can also perform a range of manufacturing techniques with these kinds of materials which you could not do with carbon fiber reinforced plastics because there again thermal properties become very important. You had very different thermal conductivity of the carbon fiber and the polymer matrix. So, there it becomes difficult whenever you are performing any manufacturing operation.

Whenever your polymer goes above the glass transition temperature, it is difficult to machine, but that is not the problem with carbon composites because we have very good thermal properties of these materials. When you are doing manufacturing, you do not need worry of heat that you generate by drilling or milling, it is not going to do anything to your carbon material.

Applications; so various aircraft spacecraft applications require high-temperature materials which also have high strength, so there are many examples. You can also use these materials in high performance braking systems, engine components, a lot of turbo engine or other types of engines or components of turbine blades and so on.

There is a problem with oxidation that we are going to talk about in a while. We will talk about it. multiple biomedical applications; carbons is transparent to or mostly transparent to X-rays and therefore, for a number of purposes we use X-ray targets. Actually they are mostly made of carbon. They can be used of highly oriented pyrolytic graphite. They can also be made of carbon fiber-based carbon-carbon composites.

Heating elements; as I already mentioned for a number of high-temperature furnaces and many other applications. The heating elements can be made of carbon fiber composites. Because now their mechanical strength is good and they can withstand thermal fatigue even better than before.

If you are interested especially for the Indian students, India has a national program.it has been in place for a long time. For developing our own carbon-carbon composites and this program has also been quite successful. The nose-tip of Agni missile was made of carbon-carbon composites also. Several brake pads for light combat aircrafts are often made of carbon-carbon composites.

So, if you are interested, there are various opportunities. Now coming to the challenges. So, one thing I already told you is oxidation. Other than that there is one more important parameter and this is not just for carbon-carbon composites, but also for CFRPs is the interface properties. So, how well is your fiber or the additive mixed into the matrix?

What is very interesting in the case of carbon-carbon composites? I told you that their strength actually increases with the increase in temperature. However, this does not happen for all carbon fibers or all carbon fiber-based composites. If you have very good adhesion between your additive in matrix, even in that case your material can be failed.

there is a certain range in which you need to have a your interface properties and the adhesion between the additive and matrix only then you get good mechanical properties. So, it is not really a challenge, but it is something that you definitely need to optimize. So, this is 1 and number 2 is oxidation.

All carbon materials tend to oxidize at very high temperatures, do not think that you will be able to immediately burn these materials. No, that does not happen, you try to even take your pencil lead and put it on top of a burner.it will not it will become red hot, but it will not burn. So, it does not oxidize, it does not immediately burn the carbon materials. But what happens is this surface goes through certain oxidation at higher temperatures above 450 °C. And also you need excess oxygen. So, that is also the case with glassy carbon above 500, 600 °C. If you provide excess oxygen to them then their surface starts to oxidize a little bit. This is a big challenge because we are developing these materials for high-temperature applications. So, the temperature is always going to be higher than 450 °C. And in the case of engines and in many applications, you are often going to have oxidative environment.

So, this is a challenge what can we do? The solutions; well number 1 is you can make what is known as a thermal barrier coating. So, thermal barrier coatings are often used, for example, if you make a superalloy blades for your gas turbine engines. But you also on top of them you have what is known as a thermal barrier coating which is often made of silicon carbide or other ceramic materials. These are thin coatings that prevent your material from suddenly being exposed to very oxidative and hot environments.

So, this is something that can be done also for carbon-carbon composites. What you can also do? One flexibility that we have with carbon materials and not with super alloys or other materials is that you can add things inside your precursor before the carbonization.

So, adding things and especially when you are making CF based composites then it's always easy to add things into your matrix.

There are certain metal particles that are oxidation inhibitors. So, you can add these kinds of particles into your precursor and that is how that also would prevent oxidation of your structures. Now for further reading well, there are a lot of books on the mechanics of composites. I have not gone too much into the details of the mechanics because that would make an entirely new course in itself.

We have learned till now some fundamental things about carbon-carbon composites and also some of the things regarding CFRPs. There are several books. You can already see here, a couple of articles and books that I have also used and I have also taken certain pictures from there. The 1st one the book New Carbons that is not just for carbon-carbon composites, but also other carbon materials. For example, porous and activated carbons and for also just carbon fibers this is a useful book. The 2nd article by L M Manocha and the 3rd one by Fitzer and Manocha; these are the articles that are very specific to carbon-carbon composites, its applications, many structural properties and the microstructure property relationship of carbon-carbon composites.

The last one the textbook is Manufacturing Science by Ghosh and Malik. This is a very useful textbook for all manufacturing-related processes and especially numerical problems.it is a good gold standard kind of book and I have also used it myself. So these are some for your further reading.