

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

Lecture – 12
Introduction to Engineering Carbons

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Engineering Carbons: (i) Natural Graphite

- **Engineering (bulk industrial) carbons:** carbon materials used in large-scale manufacturing. This excludes micro/ nano carbon structures/ materials.
- **Carbon manufacturing** has two aspects: (i) processing or making the material itself, and (ii) making structural components/ devices using the carbon material.
- **Examples of engineering carbons:** graphite (natural and synthetic), granular porous carbon, activated carbon, carbon black, glass-like (or glassy) carbon, carbon fibers, carbon/resin composites, carbon/carbon composites etc.
- **Natural graphite mineral** is found in metamorphic sedimentary rocks (e.g. embedded in mica/ marble/ quartzite) in elemental form with impurities.
- **Metamorphic rock:** A rock that has transformed into another from due to high P, T.
- It is also formed by thermal metamorphism in coal seams (smaller crystals).
- **It is formed by the removal of non-carbon atoms from the organic material under extreme conditions.**
- Graphite ores are classified based on impurities and crystallite size.
- India produces 15-20% of world's graphite. Himalayan graphite is known for its large crystals. This is of high interest to geologists.

Further reading (Himalayan graphite): Rakhi Rawat, Rajesh Sharma, Journal of Asian Earth Sciences 42(1):51-64.



(Photo: R. Weller/ Cochise College)



Hello everyone. We are going to move to engineering carbon materials. In the previous lectures what we have learned? We have learned so many things about the hybridization of carbon, the atomic structure of carbon, the classification of carbon, the phase diagram of carbon and many other basic things.

This was all about fundamental things about the carbon atoms. Now, we talk about specific materials and I will start with engineering carbon materials. So, what are engineering carbon materials? They are also known as industrial carbon materials because they used in bulk, they are also known as bulk industrial carbon materials.

So, what are these? Basically any type of carbon material which is used for bulk or large-scale applications. You may make some structure out of them, sometimes you can just process the initial raw material, for example certain petroleum byproducts may give you certain type of carbon material. The fact that you obtain the carbon material and the

processing that is done, so these are part of carbon industry or industrial carbon processing.

You can use some of these carbon materials for making structures and devices. What are the structures? And what is the difference between structure and device? Structure is just any shape that you give to any material for example any specific shapes of specific dimensions. And device is something where you use multiple structures and now that particular set of structures has a function and it is functional then it is known as device. For example, if you have a copper wire, copper wire is just a structure, but when you use that wire to complete circuitry and then you make a device out of it which can perform a certain function. Then you now have this set of structures and your copper wire now becomes a component of that device. Similarly with carbon, you can make carbon structures, and then those structures can be used for making devices. Now, when we talk about these large-scale bulk carbons, we are excluding the micro-nano carbon materials as well as carbon devices. We will come to them and that will form a separate session. Typically micro and nano scale carbons are not called bulk industrial carbons. Even though some of them may be produced in very large quantities, but they are not used for making large-scale structures and that is why they are not called industrial carbon materials.

So, my first industrial carbon material is graphite. It is actually obvious to start with graphite because the graphite crystal structure and the properties of graphite are fundamental to understanding all other carbon materials. So, it is the best idea to start with graphite and also it is one of the better-known materials as compared to the newer carbon material. Now we will talk about carbon-based manufacturing and it has two aspects, making the material itself and then making something out of that material.

You can take bulk material and then mix it into something, for example you can take a lot of carbon black and you can mix it into certain rubbers and then you manufacture tires out of it. Similarly with carbon fibers, you can make composites and then you can make orthopedic influence out of it.

So this carbon-based processing happens in multiple steps. Sometimes you will start with raw materials and from the raw materials you will first do the fundamental processing and then you will get the purified carbon material itself. And then this carbon material is

further processed and you make structures and then you make devices if you need to. So, these are all these different aspects of carbon-based manufacturing. Now, there are many examples of engineering carbons. All of these names we will talk about all of these things in our lectures in this course.

For example today I will be talking about natural graphite. In fact, I will be talking a little bit about the crystal structure of graphite, but you can also have synthetic graphite. In fact, it is an interesting story about synthetic graphite. In the process of making synthetic graphite, scientist actually ended up making some other interesting carbon materials. These are activated carbons, glassy carbons and many other types of carbons that were obtained if people would try to make graphite and it turns out that this material cannot be converted into graphite. However, the carbon material we get out of it is very interesting and has its own interesting properties.

So, you know that is why it's important to start from graphite. We will also talk about carbon fibers of course, we will also talk about carbon-carbon composites and carbon resin composites. I have written these as two different types of carbon. You have carbon fibers and you have a polymer. Resins are specific type of polymers that are very thick viscous type of polymers. So, you have carbon mixed into resin or you have carbon mixed into another carbon material, carbon is the filler and carbon is also the matrix. So, we will talk about all of these materials but let us start with graphite.

We will talk about natural graphite. It is found in nature as a form of a mineral, where do you find it? You find it in metamorphic sedimentary rocks. What are they? So, it looks something like this. Metamorphic rock is basically a type of rock which initially has some other structure, but over long periods of time or under very high pressure and temperature condition its form changed. Now, it is a different type of rock. So, I will give you an example of limestone, if limestone is at under very high pressure and temperature conditions, it converts into marble.

So, marble is a metamorphic rock. Similarly, you have a lot of sedimentary rocks especially in the Himalayan region. Now you know what sedimentary rocks are. They are formed by the sediments, at some point because two pieces of land collided.

So, they are formed by the sediments, but overtime or over several thousands of years, their form changes as they experience a lot of pressure and temperature conditions or

sometimes because of tectonic movements they also experience sudden pressure and temperature and because of that some organic material in these rocks may convert into graphite.

So, typically the natural graphite is found in metamorphic rocks. Now, this can also be formed by what is known as thermal metamorphism. Thermal metamorphism is again transformation because of heat but in the coal seams.

You will often find different types of solid carbons also when you have petrochemical refinery and when you are mining coal. You will often find some fraction of that coal, which has converted into graphite because it experienced a very high temperature at some point.

It is also not clear if it is it was coal and then it converted into graphite or from the beginning itself the crystal arrangement of the carbon was slightly different. However, in coal seams you will find some fraction of graphite.

Basically if you remember I have also mentioned previously that how are these carbon minerals formed. In most of cases you had certain organic material which was buried done under the ground and then over very long periods of time and several different types of conditions. And it also depends on what kind of organic precursor it was, what kind of crystal structure that organic precursor had and what kind of chemical structure it had whether it was aromatic or whether it was aliphatic. All of these things will make a difference, we will learn about all of these things in future lectures. We will talk about which polymer will give you which type of carbon.

But in all of these conditions ultimately the non-carbon atoms from your organic material need to cleave and leave and after that whatever is left is your carbon. And now these carbon materials can be in different forms, graphite being one of them.

You know what is an ore. When you just mine something, the first material that you get is known as the ore. Now, graphite ores are classified based on two things. One that is more important is the crystallite size, so larger crystals of graphite in a certain ore obviously has more value because the larger the crystal dimension better you will have the properties of the single crystals. So, basically based on defects and the size of crystallite that is number one how you will classify it.

The second thing is also based on impurities. why do we classify some mineral-based on impurities? Because those impurities will then determine what processing conditions we need to use, for example, if something has a sulfur-based impurity then we will need to clean it in a different way or if you have silicon-based impurity then we need to clean it in a different way.

So, these are the two things, based on which the graphite ore is classified. Now, interestingly India produces a lot of graphite. About 50 to 20 percent of world's graphite actually is produced in India and refined in India especially in the Himalayan region. We also have in Aravalli Mountains and other places also have graphite mines.

But Himalayan graphite has some special properties. The specialty of Himalayan graphite is the crystallite size. So, as I said this is something that increases the value of your ore and because of the formation of Himalayas because I mentioned it before in one of the first lectures that you had two large tectonic plates colliding, rubbing against each other which led to extreme pressure and temperature conditions. And those plates probably contained also a lot of organic materials because after all one island collided into a bigger chunk of land. So, there was also a lot of organic material. And at that time because of these extreme conditions, you had large crystals of graphite forming. So, Himalayan graphite actually is known for that.

So not only just for technological application, but also this helps you understand the formation of the Himalayan Mountains. So, it is also very important for the geologist and there are many publications on it. So, one reference I have given, but you can probably find some more.

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Large-scale applications of Graphite

Moderator in nuclear reactors

- Moderator is the material that reduces the speed of neutrons during a nuclear reaction.
- Ideally, it should be a small atom, which does not capture neutrons.
- Nowadays water is more commonly used for this purpose.

Solid state battery/ other energy storage devices

- Graphite and other carbon materials are common anodes Li-ion batteries.
- In older solid state batteries graphite rod was used as cathode.

High-temperature elements

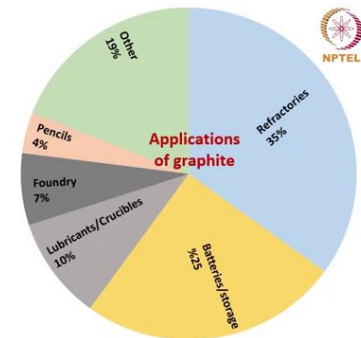
Graphite sublimates at temperatures $>3500\text{ }^{\circ}\text{C}$ at 1 atm pressure.

- Foundry and refractory

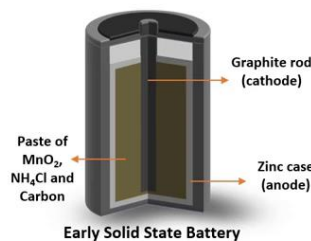
(refractory materials is a materials that retains its strength and high temperatures/ under thermal shocks)

Others

- Steel manufacturing
- Lubricants
- Pencils



REF: Chelgani et al., Mineral Processing and Extractive Metallurgy Review, 2016, 58-68



So, coming to the large-scale applications of graphite. This picture here, I had also shown you before. You can see the some of the well-known applications of graphite are listed here. You will use it especially in batteries, storage devices and energy storage devices, you must have heard that we used graphite. You know you have graphite in your pencils and you also use graphite in the foundry. It is also solid lubricant. So, these are some of the very basic and very well-known applications so graphite. So, one application that I have not mentioned here because lately, this application is not so common anymore, but rather in the early nuclear reactors in 50s and 60s. At that time graphite was used as a moderator material in nuclear reactors. What is the moderator material? When you have the nuclear chain reaction inside the nuclear reactor, then you need to slow down these neutrons. Actually, there is a certain speed of neutrons that is optimum for the nuclear reaction.

These materials are known as the moderator materials; the materials which would absorb the neutrons but not completely absorb. They will slow it down. So, graphite is used because it is a small atom. Graphite actually serves as a good moderator material and that was one of the first very large-scale applications of graphite. A very large quantity where you need 100 kilograms of graphite and that graphite could not be reused because so many neutrons were hitting it afterward, it was not useable anymore. So, this was an application that required, demanded very large quantities of graphite. Not just very large

quantities, it also demanded very clean and high purity graphite because you cannot take too many risks with the nuclear reactor. So, this is one of the major applications of graphite that actually led to synthetic graphite production which we will talk about later.

Now, again I have written the properties of an ideal moderator. It should be in a small atom that does not completely capture the neutrons. So, at least it has the very high efficiency of providing the neutrons with the right speed that are optimum for your reaction.

Nowadays, however you a lot of nuclear reactors are using water and there is a reason for it. If you read about the Chernobyl accidents which took place in Russia, I will not discuss that because that is not a part of this course, but if you read about that there graphite was used as a moderator and the nuclear reactor caught fire. And unfortunately, graphite also participated in that fire. So, since then graphite or carbons are typically not used for nuclear reactors. However, you'll find in some reactors more common material for this purpose nowadays is water because water is so much cheaper. In fact, the efficiency of water is not that great, but since it is really cheap practically for free. You can use water that is why nowadays water is used very much.

But this is one of the early applications of graphite and of course solid-state battery. This image here shows one very early solid-state battery. Actually, not much has changed in the case of solid-state battery. The materials have been modified a little bit the efficiencies have gone high.

But in terms of design not too much has changed in the case of solid-state batteries. You will see that there is a zinc casing that forms the anode, and the graphite rod makes the cathode. Now, you will see that what is filled inside the paste of MnO_2 and ammonium chloride that paste also contains some carbon materials.

So, you can see the carbon was very much important in the case of solid-state batteries from the very beginning. Even today a lot of batteries now with the advent of lithium-ion batteries, they also utilize carbon very extensively. There also we use graphite-like materials or materials with some modified properties, but typically carbon materials are also used.

Why do you think for solid-state battery carbon is a good material? Because it is mechanically strong and also thermally strong. Batteries heat up and you do not want something that cannot withstand heat. Carbon can withstand heat and carbon is mechanically strong and carbon is also very light. So, if you make a very large battery for example, if you use a metal that has a lot of weight then your battery will become too heavy but carbon is also light. And of course, it is electrically conductive and it is electrochemically very stable. These are the fundamental properties. So, because of all these properties, we do use graphite in the case of solid-state batteries.

So I just mentioned that graphite can withstand high temperatures very well. In fact, if you remember from the phase diagram what are the properties of graphite? It sublimates and it does not convert into a liquid form. So, at one-atmosphere pressure, it will directly convert into a gaseous form, but that will happen only around 4000 Kelvin.

Most of our common applications do not go to that high temperature. So, for all practical purposes, all manufacturing applications graphite can withstand a lot of temperature as compared to other materials for the cost that it has. It can actually be used for a lot of high-temperature elements manufacturing, what are high-temperature elements by the way? If I have a furnace, what do I do in the furnace? I heat something. Now, I want to use that furnace for heating something up to 3000 degrees. Now, what is interesting is that how will I make my sample holder? The sample holder should also withstand that temperature not just once, but it has to withstand that temperature every day multiple times. So, it will also have thermal fatigue over time. It will definitely have thermal shocks. So, in all kinds of high-temperature conditions, the sample holder or all the other parts of that furnace need to withstand. Graphite is used for making these kinds of parts.

So, these are called the high-temperature elements not just you know the laboratory furnace, but also other types of furnaces where you process for example, other minerals. Sometimes lab crucibles are made of not graphite, but graphite-like materials that we will talk about later.

We also use this material in the foundry as a refractory material, what is the refractory material? Something that can withstand and can retain its strength at high temperatures. So, again the fact that graphite can withstand high temperature and it is also used in the case of this foundry industry. For example, if you are doing casting of aluminum gear,

you use a sand cast. So, sand in that case is a refractory material, but if you want to go to much higher temperatures. And you want to ensure that the thermal expansion is negligible. In that case, for more sophisticated casting applications you will use graphite.

Actually, I have listed a few applications here and maybe you can find some more. Steel manufacturing also being one very important industrial application where you use different types of carbon and where you not only use graphite, sometimes you also end up getting some graphite precipitates during the steel manufacturing.

So, steel manufacturing is an industry very closely related to carbon because we have carbon and iron, and graphite is very much useful for those applications as well.