**Industrial Inorganic Chemistry**
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**Lecture – 58**
**Metallic Hard Materials: Carbides, Borides, Silicides**

Hello and welcome back to the class once again. Now, we will move after activated carbon. In this class we will just consider about the different materials so, which are inorganic materials and which are hard in nature.

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So, metallic hard materials how we find and what are those the metallic hard materials how we define these as a different types of materials. So, inorganic chemistry can contribute through the development of these materials is a some aspect of the material science where we can use the metals and is corresponding oxides or nitrites or any other thing as typically very hard materials. So, these hard materials are nothing, but simply the carbides first, starting from your calcium carbide or any other, then borides and silicides.

So, these three together will now just consider for this discussion in this particular class, where we will consider that their corresponding carbides, borides and silicides the anionic part is now we fixing of the elements in subgroup of 14, 15 and 16 of the periodic table, along with that we can also consider other two based on the metal on thorium as well as urea uranium.

Because the thorium carbide and uranium carbide are also very high metallic hard materials, metallic hard materials of this, because these hardness is a skill where that particular hardness can be judged for these metallic hard materials is almost without exception between 2 quantities of thing of hardness one is the corundum another is the diamond. So, between corundum and diamond we will be able to get the corresponding hardness, we can fix the hardness on more scale we also measure the hardness for these metallic hard materials and this basically between corundum and diamond.

So, in the range of 9 to 10 you see that we have a scale of 0 to 10 basically and silicon carbide we have we know that it has also the corresponding very high hardness. So, on the Mohs scale at the upper side only at the range of 9 to 10 only will be able to consider these materials the in organic, metallic, carbides, borides and silicide's can be considered as the typical metallic hard materials of use. And they basically use also comparable electrical and thermal conductivities which are also very important characteristics of these hard materials.

Because these are not metals and also basically when we considered that is a carbide compound or a boride compound or silicide compound of the metal ion, what do you think that these are basically inorganic compounds, where the anionic part or the corresponding part of carbide boride and silicide as there, but still we have the corresponding hardness in the range of the metal, as well as the thermal as well as the electrical conductivity is in the range of the corresponding metals.

So, they have also very high melting point that is as a result because some of them are very high melting and high chemical resistance. So, these fundamental properties of metallic hard materials give us some idea that how quickly we can use them for some different useful purposes.

So, these metallic hard materials therefore, are very useful for industrial preparation their property improvement and applications.

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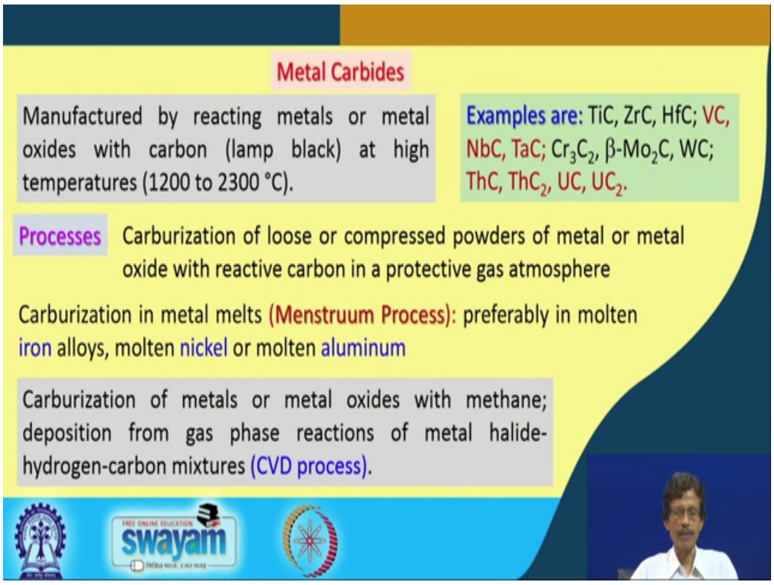


So, first we see how we get the metal iron based carbides? So, how we bring that corresponding carbon for making those carbides? So, basically if we have seen that how we make the activated carbon from the different carbon sources or the source of coal source for peach and all these things.

So, if we have the superior quality of carbon black or some inferior quality of carbon like lampblack, that can be typically used for the manufacturing of these metal carbides, because metals or the metal oxides. Because directly we can use those metal oxides from the natural sources; that means, the ores basically we know as iron, is the iron is the corresponding ore is available as the corresponding oxide ore. So, if that oxide ores directly with some preliminary purification or preliminary screening only can directly be used for reaction with the carbon, we get it at the high temperature; that means, 1200 to 2300 degree centigrade, we get the corresponding carbide.

So, what are those metal carbides we can have? So, typically the range has been told that what are those material basically the group of titanium, zirconium and hafnium, then vanadium, niobium and tantalum; so subgroup 14 subgroup 15 and subgroup 16 along with thorium and uranium. So, as per definition we have already selected the group of metal irons which can give rise to the useful metal carbide.

So, starting from titanium carbide to uranium carbide we have plenty of those and they can be used for the different purposes and different useful applications.

So, now we see how we can process for this particular manufacturing. The first thing what we can think of is the carburization? So, carburization of loose or compressed powders of metal or metal oxides. So, we will be taking that metal as powder form or the metal oxides, I whether they can be in the very loose form, that mean form what we obtained or it can be hard placed with some pressure in the compressed form with reactive carbon in a protective gas atmosphere.

So, protective gas can be there such that your carbide should not react with that particular gas. Suppose oxygen is there and the carbon is giving you the anionic form; that means, the carbide form through the reduction from the metal iron, because the metal irons will be used for your reducing counterpart which will reduce the carbon centers to their carbides. So, the gas atmosphere should be checked in such a way that your carbon should not be bond as carbon monoxide or carbon dioxide. So, this carburization process takes place with a particular process named as menstruum process.

So, menstruum process is nothing, but we have to take the corresponding molten metals. So, we have seen that the blast furnace we can use for taking out the molten iron. Similarly, those high temperature furnaces can always be useful for getting the molten metals. So, these molten metals can also be there for directly used for getting those carbides. So, if somebody is interested to get that I am not going to prepare only the iron iron rod, iron bar, or iron wires and all these things, but instead I want to make a business of making the corresponding iron or any other metal iron carbides.

So, we will go for that when the molten metal iron in this particular blast furnace or any other open up furnaces high temperature withstand furnaces can be useful for reaction with the carbon only. So, not only iron itself, but some molten iron alloy can be used also, molten nickel can also be used as well as the molten aluminum. So, the carburization of metal makes a metal oxide can also be achieved in another process where we use the carbon source as the methane. Methane can supply the corresponding carbon for giving you the carbide of that particular metal; and also the deposition of the gas phase reactions of metal halide hydrogen carbon mixtures.

So, one process is that your metal oxide or metal can be reacted at high temperature through the use of methane as gas. And the other process which is known as your CVD process; in CVD process we will be using not metal or metal oxide, but will use the metal halide because these metal halides as the metal irons which will be highly reactive, as well as hydrogen and the carbon, because hydrogen is the corresponding material for the reduction process and your carbon as the source of your carbide.

So, chemical vapor deposition technique is the technique for metal carbide preparation using metal halide hydrogen and carbon mixtures.

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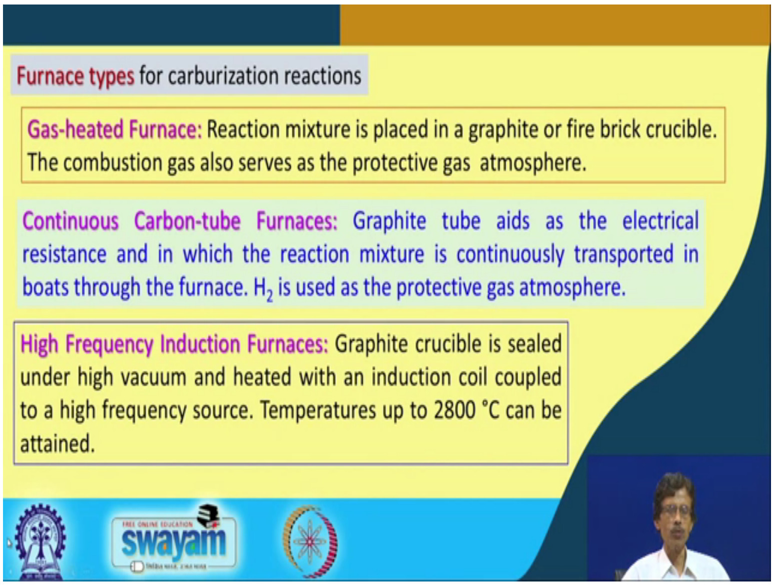


Then the different types of furnaces what we can use because these are very high temperature reactions for this carbonization reaction. So, this carburization reactions what we can use for the furnaces? So, what are the furnace types you can have, what are the choices you can have for the use, the first one is your gas heated furnace. So, we will use gas for heating the furnace basically and the same gas, if we require the same gas can also be used for making the inert atmosphere while we make the corresponding carbides.

So, the reaction mixture is first placed in a graphite or firebreak crucible. So, the crucible is made up of graphite or fire brick high temperature withstanding fire brick, then the combustion gas like methane can come and solve as the protective gas atmosphere while we make the corresponding metal carbide.

Then one other furnace is the continuous carbon tube furnace. The furnace is of tube shape and is made up of carbon only, because we do not want to have take any other material for making that particular furnace, because it is useful if there is some degradation of the carbon part from the carbon furnace also, that carbon can also be utilized for the carbide preparation.

So, graphite tube basically that is also a source of carbon can be it is as the electrical resistance and in which the reaction mixture, because it is the electrical resistance can heat up that particular furnace, is continuously transported in boards basically the graphite boards through the furnace and hydrogen is used as the protective gas atmosphere. So, if we try to burn it in methane, that methane can supply the carbon then it can have the hydrogen available also. Otherwise you can just give pure hydrogen for the protective gas atmosphere such that no other type of reaction can take place in presence of that particular hydrogen gas, then we can have the high frequency induction furnaces.

So, inductively heating furnace and we use the high frequency for that particular purpose so, graphite crucible again like that of your graphite you will be using graphite crucible over there, for that particular furnace making and is sealed under high vacuum. So, high vacuum ceiling process is done. So, you do not have any protective gas atmosphere there and heated with induction coil. So, electrical induction coil is used for heating process. And coupled with a very high frequency electrical source, electrical frequency and the temperature up to 2800 degree centigrade can be achieved.

So, in this particular case; that means, in this third category of this particular furnace will be able to reach a very high temperature of 2800 degree centigrade; that means, we will be able to make some more harder carbide materials, more harder metallic carbide materials or hard materials. Because, once you make that at the high temperature the material itself should be very high and it can have very high temperature withstand capacity also when will be using as their applications.

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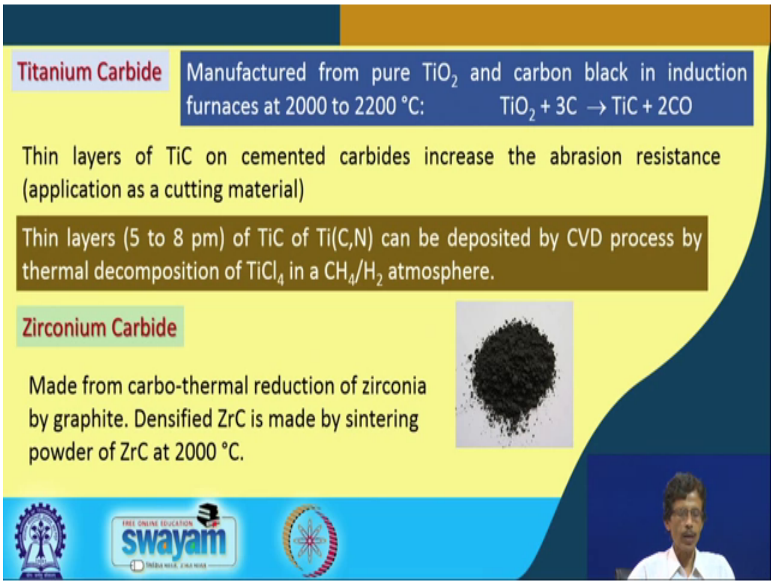


So, the metal iron best first example what we have seen that can be your titanium carbide and that titanium carbide can be manufactured basically from pure titanium dioxide.

So, the rutile is can be your source as the corresponding ore of titanium ilmenite is also well known. So, these 2 ores can be very useful or can be used directly basically for making titanium carbide. So, the use of this particular thing for making titanium carbide is the use of that metallic oxide just now, we have seen that we can use metallic oxide for this purpose and like lamp black we can also use carbon black. So, see is there the carbon source is from the carbon black and what type of furnace the induction furnace?

So, this induction furnace and not at 2800 degree centigrade the temperature in the range of 2020 O 200 degree centigrade is sufficient for this particular reaction. So, your TiO 2 will react with 3 C, because this is the reaction stoichiometry if you try to write down the reaction, if the balanced chemical reaction will immediately tell you, that that will give you T i C the formula the solid state formula, the solid state stochiometry of the carbide is simply that T i C only.

So, this T i C will be formed along with some amount of carbon monoxide. So, two part of the carbon is utilized for formation of carbon monoxide and one part is used for converting your titanium to titanium carbide. Then we what we can have also that particular one can be very useful whereas, thin layers of titanium carbide on cemented carbides also; that means, the cementing of that particular titanium carbide material increase the abrasion resistance. So, it can be you abrasive.

So, abrasion resistance power can increase an application as the cutting material like silicon carbide we know as the hard material. So, the metallic hard material we are not talking about. So, the example of the metallic hard material is that of your useful cutting material, of different type of different property, and different temperature with stand power stability is your titanium carbide. So, thin layers is very small layer 5 to 8 pico meter of depth of titanium carbide or titanium carbide nitride the mixed when carbon is there a nitrogen is also there.

So, titanium carbide mixed can be deposited by chemical vapour deposition process by thermal decomposition of titanium chloride in a methane and hydrogen atmosphere. So, both these as well as the titanium carbide can be deposited. So, if we have the nitrogen source only, then it can be titanium carbide nitride is a mixed form of that. Otherwise, the decomposition of titanium tetrachloride basically and supply of that carbon for the carbide end from methane can be achieved with a mixture of methane and hydrogen for this particular thin layer production.

Then the analogous way of making can be used for your making the next person, the next material after titanium is the zirconium. So, zirconium carbide CPC is the powder a material is very close in look wise to that of your activated carbon. So, the black mass of this particular, because most of these carbides are in black in colour they are gray in colour most of the time. So, they can be confused with that of your activated carbon. So, this particular one through carbo thermal reduction, that carbon is the reducing agent and thermal is the temperature process of zirconia by graphite.

So, graphite will be consumed for making that carbide and is this particular densified zirconium carbide is made after that particular processing by sintering the powder of zirconium carbide. So, first you have the reduction the thermal chemically or the carbo thermal reduction at a temperature you get through that graphite and then your sintering process at a temperature of 2000 degree centigrade.

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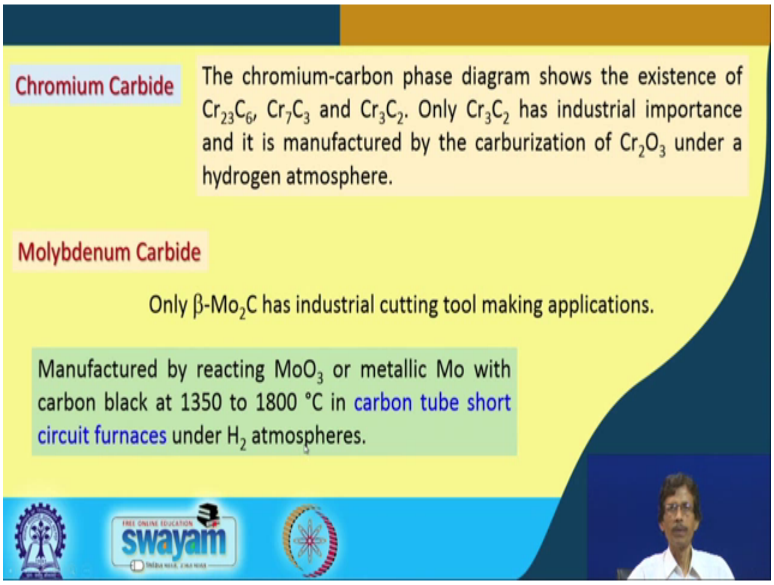


Then next one; that means, of the chromium group is the chromium carbide. So, when you get this particular chromium carbide, then you can have the corresponding chromium salt for this particular process.

So, if we consider the corresponding chromium carbon phase diagram, because the phase diagram can only tell you that what are the different stochiometric or the different composition of these carbides can have the stability and can be separated from that particular reaction of a chromium melt with that of your carbon. So, basically the corresponding stability of those components can be known from the phase diagram only and that typically tells us a very complex one.

The first one is typically a complex one which is the chromium 23 carbon 6. So, C r 23 and C 6 material is it typically a different type of material unlike other one which is C r 7 C 3 C r 2 C 2 2. So, the most simplest one is therefore, your C r 3 C 2 that can have typically the industrial importance. Otherwise, what we can see that, what are the other high variety of that chromium content material is available, and is formed basically when you have the component heating component of chromium and carbon?

So, the last one; that means, the C r C 3 can be manufactured by carburization of again the metal oxide, the chromium oxide, that chromium trivalent oxides C r 2 o 3 under a hydrogen atmosphere now. So, if you have the carbon source as the graphite. So, again you can use the hydrogen atmosphere for this particular p, then we can have the molybdenum carbide. So, the molybdenum carbides are very useful we know and one particular form basically the formula is a more to see now.

So, the formula of that carbide is different because the solid state formulas are all the time is different and that depends on how you consider carbon. So, if their carbon is 4 minus. So, molybdenum can be considered as the bivalent 1. So, the different varieties what we know that we can level it as the alpha form, beta form, and the gamma form, the delta form, but the molybdenum based industrial cutting tool basically industrially they are also very much useful to make them as the cutting tools.

So, we will use molybdenum to get the corresponding molybdenum carbide. So, it has typical applications as the cutting tool and like other we can also take that corresponding oxide. So, molybdenum trackside which is hexavalent or metallic molybdenum itself, because in one case you have to consume you have to reduce that particular oxidation state of the molybdenum from molybdenum 6, or you can use the molybdenum in the metallic state which is molybdenum 0 with simply the carbon black. In a temperature range depending upon your source whether you are using oxide or the metallic molybdenum a temperature in the range of 1350 or 1800 can be useful.

And which can be achieved in carbon tubes short circuit furnaces. So, a type of furnace made up of carbon and the electrical heating is that of particular temperature rise also can be achieved through short circuit of the electrical connections, under hydrogen atmosphere once again.

So, hydrogen is basically giving you the reducing atmosphere, because your carbon what is the available from there as the carbon black should be reduced. So, this reduction of this carbon basically if you have not sufficient molybdenum is available for the reduction of this carbon hydrogen is being consumed for that particular reduction process.

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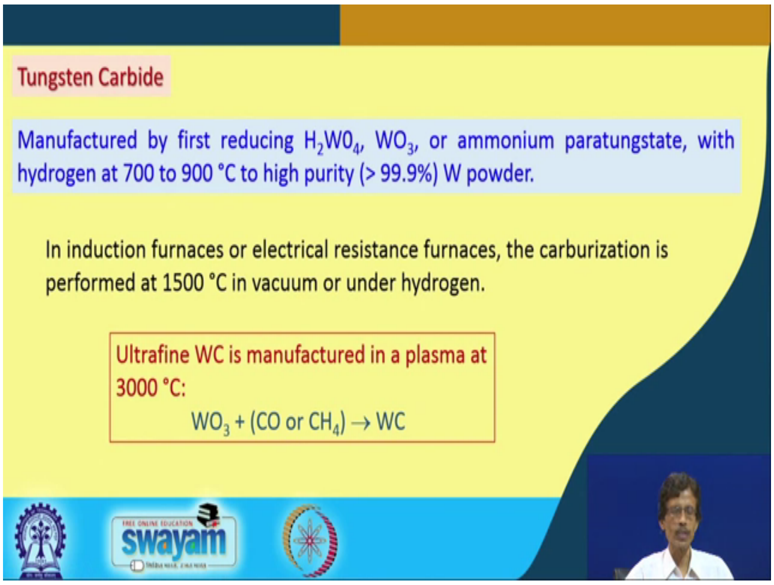


Then Tungsten Carbide WC, the tungsten carbide can be also available to us while you react it or use it for the reaction with the Tung state a C H 2 WO 4 or WO 3 the tungsten oxide, hexavalent tungsten oxide, or ammonium paratungstate the polyoxide metalex we know the ammonium poly paratungstate.

So, anything we can start from tungsten state acid, tungsten trioxide or ammonium para tungsten, again with that of your carbon source at with hydrogen at 700 to 900 degrees indicate to high purity tungsten powder. So, first we get the tungsten powder through hydrogen reduction at 700 to 900 degree centigrade then that powder will be consumed for making carbide.

So, we are not directly using the oxide or the other variety for making your tungsten carbide. Then an induction furnace can be bought or electrical resistant furnace can also be used for the carburization process. So, the carburization process in all other cases we see that whenever we make the carbide, it is the process is your carburization process and is performed at 1500 degree centigrade in vacuum or under hydrogen, no atmosphere or hydrogen atmosphere.

Then, we get through this particular reaction the ultrafine tungsten carbide which is being manufactured in a plasma at 3000 degrees centigrade. So, if we go for very other quality; that means, the fine quality the ultrafine quality of your tungsten carbide. So, that ultrafine quality of tungsten carbide can be obtained by simply going for a high temperature reaction. So, if the plasma temperature is fine. So, the you use the plasma. So, definitely it is a costly affair, but the ultrafine tungsten carbide have some special use, special purpose material. So, we can consider that we can go up to a temperature of 3000 degree centigrade.

So, at this particular temperature what you see now that WO 3 will be reacting with carbon monoxide, if you can get carbon monoxide through graphite or oxidation of some other carbon matter or again the thing what we are using, what we are seeing is your methane. So, these two basically giving you your tungsten carbide or the other part what can be obtained, when you use methane you get water molecules or otherwise, it is typically the carbide and your hydrogen atmosphere can take that oxygen for your hydrogen as water.

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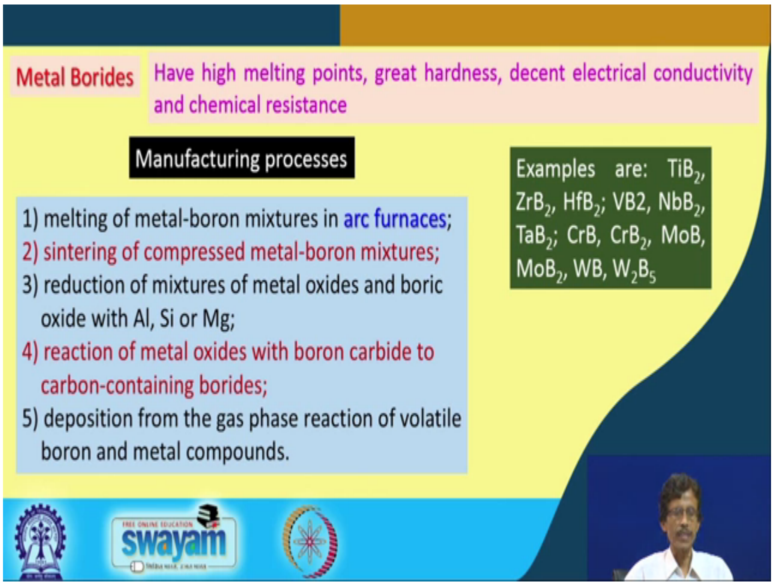


Then, we will see that how we get the metal borides. So, carbides, borides and silicides, these were our hard material that we are trying to cover in this particular class. So, this has also very high melting points, great hardness and decent electrical conductivity, because the electrical conductivity is not very high like that of your carbides and chemical resistance also of moderate character.

So, these are slightly softer material compared to your carbides. And, like those like that of your carbide here also a big list of those, starting from titanium boride to tungsten boride, only thing you should always be careful when we talk when we give the corresponding informations in a large number of compounds, basically these are prepared in the industry, that can be very useful also in the industry that the formula of those compounds. So, whether it is the titanium b 2 t i b 2 or it is w 2 b 5.

So, the manufacturing process what you can have in our hand are the 5 types is the melting of the metal boron mixtures in arc furnaces can give you that, or sintering of compressed metal boron mixture directly we can take the metal and the boron mixtures and we go for the sintering process, or the reduction of the mixtures of metal oxide and boric oxide or B 2 0 3. So, this boron oxide does a boric oxide sometimes people also tells as their boron oxide basically B 2 or 3 with aluminum silicon or magnesium.

Then, reaction of metal oxides with boron carbide; so carbide to carbon containing boron oxide so, these metal oxides with some boron carbide basically we can have we know that the B C A we can add. Then we can go for the corresponding carbon containing boride making also is a particular process or deposition from gas phase reaction of volatile boron and the metal compound.

So, like that of your carbon as graphite as lampblack or any other carbon supply, we get the corresponding carbide. Similarly, the boron can also be supplied the boron we all know the elemental boron. Even the boron acid or the borax or the boron carbide can also be supplied for the preparation of these borides.

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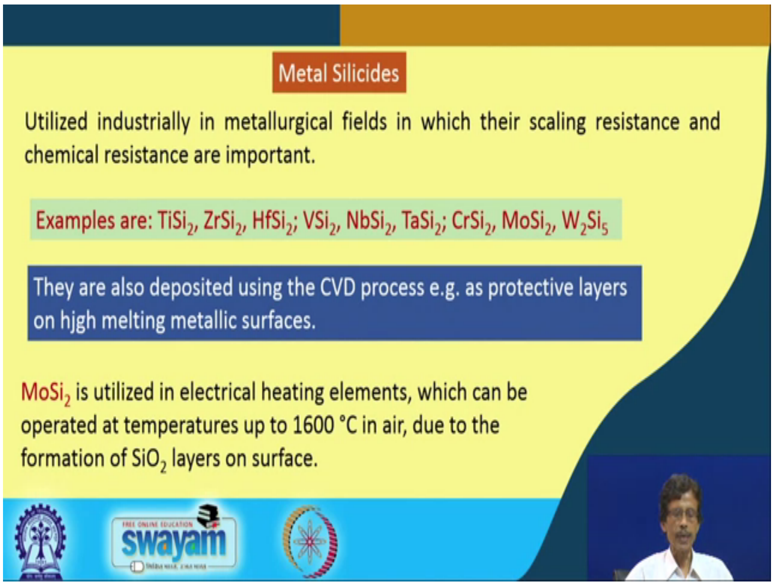

Then we will see lastly that of your metal silicides these are not well known and well conversant to us also, particularly we try to see how we can write the formula of those silicides and what are those important silicides from the entire periodic table?

So, like that of your carbide like that of your borides silicides can also be of preparation processes, then utilized industrially in the different metallurgical fields in which they are scaling corresponding resistance and chemical resistance are important. So, their scaling resistance, than the chemical resistance or of different type compared to your carbide or boride.

So, that is why they are the special purpose hard material, metallic type, and they are basically these from $TiSi_2$ to $W_2Si_5$. So, you see like your carbide boride and all these things the number of Si unit as silicide unit as the negative part of the silicon to the metal is that different. So, you should be able to try to write these because most of them are $MSi_2$ type mostly all of them are $MSi_2$ type only exception is that of your tungsten one. So, it is $W_2Si_5$.

So, they say typically more number of silicones are there and the tungsten number is not 1 it is 2. And, they are basically deposited using CVD processes as for example, as protective layers on high melting metallic surfaces. So, through chemical vapor deposition metal silicides can be obtained on different high melting metallic surfaces. So, is basically a protective layer, because the metallic surface from his degradation from his environmental degradation also or assist resistance or reactivity with gas it can be protected through a coating of these metallic silicides. And, this molybdenum silicide $MoSi_2$ is utilized for electrical heating elements.

So, high temperature electrical heating material can also be obtained only with $MoSi_2$ which can be operated at temperatures up to 1600 degree centigrade in air, because it can have the typical coating of your quartz type $Sio_2$, because we know that the quartz can have high temperature withstand, but the metallic hot material what we are using having a $Sio_2$ coating also can also be useful in that particular purpose of electrical heating elements. So, all these carbides borides and this silicides are very useful high temperature withstanding and chemically resistive material of industrial applications ok.

Thank you very much.