Course Name: Combustion of Solid Fuels and Propellants
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Lecture: 28 Metal Combustion Classification-Introduction

Welcome to the NPTEL online certification course on Combustion of Solid Fuels and Propellants. So, today we are going to start a new module and the module is Combustion of Metals. Here we will talk about the various aspects of you know metal combustion. Now the question may come to your mind that why suddenly we are talking about combustion of metals, why is metal so important? Now if you recall our discussions during the you know the ingredients for solid propellants during that time I think we have spent some time on discussing the various metallic fuels. For example, like we talked about aluminum, we talked about boron, we talked about beryllium, tungsten, titanium and several other you know metal fuels. So, those metal fuels are considered to be the fuels for the propellant ingredients or the propellant formulation rather whereas, the HCPV or the polymeric fuel was considered as the binder.

So, in actual terminology of fuel binder oxidizer there the fuel is considered to be the metallic fuel only. Although the hydroxyl terminated polybutadiene acts as binder, but it is also an hydrocarbon fuel. So, there I think we have discussed about the burning mechanism of you know HCPV with ammonium percolate oxidizers in case of composite solid propellant. In case of double base propellant we have talked about the homogeneous propellant consisting of nitrocellulose nitroglycerin.

But we have also mentioned that you know aluminum particles may be present in case of composite solid propellant in order to improve the performance. Now in this module in general we will talk about different fundamental aspects of combustion of metals, but we will emphasize more on the combustion of aluminum and boron particles because they are like the prime you know attractive metal particles for propulsion applications. But you know if you look at the application point of view metal particles are also used in different other areas like of course, solid propellant is one of the areas, solid fuels like for example, we if we think of in terms of like hybrid rocket they are solid fuel and gaseous or you know liquid oxidizers may be used. And in that solid fuels the energetic metal particles may be impregnated in order to enhance the you know heat release and that way it is going to increase the combustion chamber temperature and which in turn is going to increase the you know propulsive performance. Now if we think about some lunar mission base or you know Mars mission other planetary missions their metal particles may be you know considered to be one of the potential fuels for such applications.

There are other metal other metal particle applications like you know self high temperature metal synthesis like self propagating high temperature synthesis SHS of you know metals and production of various metal oxides even nitrate nitride particles for example, like boron nitrides can be made which can be used for some you know structural applications. Metal cutting and welding can also be you know considered to be like high temperature combustion process which involve like metal with you know oxidizers may be like oxygen as oxidizers. Metal fires for example, like there are some fine dust of metal particles which is you know extremely flammable and dangerous. So, we also need to study those things because there is an explosion hazards if there is lot of you know metal dust particularly like you know metal cutting industries where there is a high chance of accumulation of you know metal dust. So, if there is any ignition source due to some stray current some you know overheating of the place or due to some you know some electrical short circuit issues which may lead to ignition and which may in turn is going to cause some explosion as well.

So, combustion of metals have various applications other than like solid propellant application, but in our you know module we want to restricts our discussions only within the you know combustion of metals with respect to the application in solid propellants or solid fuels. And then we will focus our discussion towards the combustion of aluminum particles and boron particles because they are the you know common ingredients considered for you know for propellant or solid fuel application. Now first of all why metal fuels are so attractive? So, what is the prime concern is that we first need to see that the we can compare the energetic content in terms of like gravimetric and heating gravimetric and volumetric heating value. So, you see we have plotted like gravimetric and volumetric heating value of different metal particles or metalloids also because boron is considered to be metalloid. So, various you know energetic ingredients we are comparing their gravimetric and volumetric heating values with respect to you know the common polymeric fuel or the binder which is HTPB or we can just compare with the paraffin wax also.

Sometime paraffin wax is also considered to be the binder for or the fuel for you know hybrid rocket. But if you just consider the common polymeric binder HTPB which has been discussed several time during the discussion of composite solid propellant. So, if you compare the heating value of HTPB and the various metal particles we can see the you know boron, beryllium, aluminum, then tungsten, titanium also. So, the blue color is the volumetric heating value and the red color is the gravimetric heating value means per gram basis or you can plot it as per kg basis. Here volumetric heating value is very important because you know the propulsion propulsive system systems are volume limited.

So, of course, weight is a concern. So, it is like a if we can make the compact propellant which can contain you know within a smaller volume if you can have more amount of propellant that is always better. So, basically the volumetric energy density which is like mega joule per meter cube or mega joule per liter or kilo joule per centimeter cube. So, which substance or ingredients gives higher volumetric heating value that is actually you know beneficial for propulsion application. So, if we compare the volumetric heating values for various you know metallic fuels with the HTPB we can see that there are many you know metal fuels which are considered to be like the prime considered with the candidates for energetic materials like aluminum, beryllium, boron.

Carbon also has like higher energy content titanium, tungsten, zirconium. Now, if we see that beryllium is actually having the highest gravimetric heating value compared to all the you know other energetic materials and second highest in the volumetric heating value. So, beryllium can be considered to be an attractive choice, but the problem with beryllium is that it is highly it is having high highly toxic beryllium oxide oxide that is the major reason that beryllium is not considered as the energetic particles or energetic ingredients for solid propellant application. So, the next available candidate is the boron which is considered to be one of the attractive you know energetic particles for solid propellants or solid fuel application. However, you know due to it is high melting temperature.

So, the melting temperature of boron is in the range of like 2350 Kelvin something around 2348 Kelvin and the boiling temperature is also kind of extremely high it is like 4273 Kelvin. So, due to it is high melting and high you know boiling point temperature it has been you know it has been observed that the complete combustion has not been possible for you know micron size particles and that that is the reason that the micron size boron particles has not been successfully incorporated in any of these existing you know solid propellant any any of the solid propellant formulation or solid fuel formulation. Because you know micron size boron means it is going to cause some it is going to cause some you know ignition delay it is going to cause ignition delay there I would rather say like longer ignition delay. So, longer ignition delay means it is going to be difficult to you know burn the boron particles within the given you know chamber residence time. Because you see the propulsive devices these are kind of high speed vehicles.

So, the amount of time present within the combustion chamber. So, if there is a flame like this. So, the particles will be impregnated in the propellant grain. So, they will come and burn in here within the flame and they will the oxide products will come out they will energy release will take place and will go out through the nozzle it will expand through the nozzle. But the given residence time may not be sufficient to burn the micron size boron particles fully.

So, the although they are the heating value is very attractive, but the micron size particles combustion within the you know within the given residence time is very difficult. That is why the micron size particles are I mean only micro size particles are not very attractive energetic ingredients for you know solid propellant applications. However, recent advancement of the nano size and nanotechnology the nano size boron particles have you know smaller or shorter ignition delay time which actually helps into burning the the boron particles within the given residence time. So, residence time does not impose much restriction on the ignition delay of the nano size boron particles. So, this makes the nano size boron nano size boron an attractive choice.

So, the nano size boron becomes an attractive choice for propulsion application. Because you know we can see that the volumetric heating value of boron particle is almost like 136 kilo joule per centimeter cube or 136 mega joule per meter cube. So, we can say it is almost like if you compare this one this is close to about 42 or 43. So, it is almost like 4 times of the common polymeric binder which is HTPB and that is why it makes is makes it highly attractive and that too the nano size boron particles. Now, if you look at titanium, titanium also poses you know high volumetric energy content, but it has not been utilized because of its high cost ah.

Of course, the nano size titanium particles are not easily available. So, that is the reason although it is having theoretically it is having the high energy content, but because of the high cost and the unavailability of nano size particles titanium is not has been used in a practical you know propulsion system. Now, major focus have been given so far on the aluminium nano particles because you know nano size aluminium particles are commercially available. And if you look at the the heating value of aluminium nano particles sorry the aluminium you can see the volumetric heating value is quite higher for aluminium nano particles compared to HTPB. So, that is also a choice and there have been a numerous studies available in literature on the you know various size of aluminium nano particles on the propulsive performance of solid propellant or solid fuels.

So, our discussions you know finally, will focus more on the combustion of the aluminium particles and combustion of boron particles. As I mentioned in the beginning of the lecture that will put more focus on these two particles. Now, another particles if you look at tungsten, tungsten is also having you know high volumetric heating value, but the problem with tungsten is it is also having like very high melting temperature which is about 3695 Kelvin and the boiling temperature is also kind of very high extremely high it is like 5828 Kelvin. So, that makes it difficult you know to use the tungsten particles in the propellant formulation. However, there is a hope that it it there is a hope that the size reductions of the tungsten particles may be useful for propellant application just because we should remember one thing although you know melting temperature and boiling temperatures are extremely higher, but igniting titanium does not require much energy compared to like boron particles and the temperature range for ignition of tungsten particles are in the order of like only you know 700 to 800 Kelvin.

And in fact, the reaction can be faster if we if the temperature of the ambient goes beyond like 800 Kelvin. So, you know there is a hope that tungsten powder can also be you know useful if we somehow can manage the you know high you know cost and the size range if we can maintain. So, that way the tungsten can be another potential choice. Of course, it is it is gravimetric heating value is compared to be very low compared to HTPB. Now, another important consideration is the you know density of the solid fuels.

If you look at the density of the different solid fuel different you know metal particles compared to HTPB except lithium I think. If you look at except lithium we can see almost all are having like very high energy sorry very high mass density you see there may be mistake in this data probably and to refer to literature this is some type of mistake. So, if you look at the density of aluminum, beryllium, boron, carbon for all the you know metal particles we can see except lithium is having like high density. So, why high density is important because you know in case of the performance of propulsive system higher volumetric is one important the other important parameter is the density because it is not only ISP, but it is row ISP is important for you know volume limited propulsive or volumetric propulsion systems. So, higher the density will there is a chance that is going to give.

So, it is a combination of like density and the volumetric heating value if you have high heating high volumetric heating value and high density that is definitely going to give us like row ISP higher and that is going to be beneficial for volume limited propulsion systems. So, now after this basics you know understanding of why energetic particles are important for solid propellant application we will now focus on to understand the metal combustion classification because you know the metal particles are not exactly the similar like the hydrocarbon fuels there are different metal particles are available and the burning characteristics of metal particles are also not be the same because you know some metal particles are having very high melting temperature or boiling temperature their oxide counterpart is also having like higher melting temperature or oxide temperature.

So, if we look at the various metal particles corresponding they are you know oxide volatilization this is in temperature we can try to understand that whether the metal particles burn in vapor phase means everything will be in gaseous state and they will burn or the metal will burn in a heterogeneous combustion mode or like in a surface reaction is going to take place not in not in vapor phase. So, we have to understand this metal combustion classification and it has been nicely given by one criterion is called you know Glassman criterion. Now before going into that I think we should first try to understand one important consideration is that if you try to burn the metal particles the flame temperature of metal it has been reported by Van Gross and Conway during like early I think late 1950s it has been reported that the flame temperature they have introduced a concept that the flame temperature of a metal was limited to the boiling point of the oxide or we can say like the or the or dissociative gasification into species other than you know metal oxide.

So, what does that mean that flame temperature is not going to go beyond the dissociative dissociation volatilization temperature of the you know oxide and that will is going to give the limit of the flame temperature. Now you know most of the metals have high boiling point temperature. So, the metal to burn in the vapor phase the oxide vaporization or dissociation temperature must be greater than the you know boiling point temperature of the metal. Now if the that vaporization dissociation temperature is less than the boiling point temperature of the metal then of course, they will burn in a heterogeneous combustion mode. So, this concept is given by you know Glassman and it is known as the Glassman criteria for vapor phase combustion of metal.

So, we will try to understand this by comparing the boiling point temperature of metal and we can consider the vaporization dissociation temperature of the oxides and by comparing that we can come to an understanding that how this you know heterogeneous combustion and vapor phase combustion take place. So, the condition says that the Glassman criteria if you look at the Glassman criterion it says that the why it is happen in the limiting flame temperature results from the fact that the heat of vaporization. So, this concept is actually given in early 1958 by two scientist called Von Grosz and Conway. They are they are research reported this concept that flame temperature of metal oxide was limited by the you know boiling point of the oxides or the dissociation gasification into species other than the metal oxide. So, you know the flame the the limiting flame temperature results from the fact that the vaporization dissociation of the metal oxide formed is greater than the available energy to raise the temperature of the you know condensed phase oxide above its boiling point and that is actually the limiting condition which imposes the whether is going to be vapor phase or the heterogeneous combustion.

So, what essentially the condition is that vaporization dissociation the heat of vaporization and dissociation of the metal oxide is greater than the available heat in the reaction. So, that is basically that is the available where Q r is known as the heat of heat of reaction of the metal at the reference temperature. So, reference temperature here is given as 298 Kelvin. The H0 T volatilizing is given as the or you can write the difference actually that H0 T volatilization minus H0 T H0 298. So, this is basically H0 T volatilization minus H0 298 is the you know enthalpy required to raise the temperature to its volatilization temperature.

Basically, to raise the temperature of the product sorry temperature of the product to its volatilization temperature at you know reference pressure that at the pressure of concern at concern pressure ok. And we have in many occasions we have seen that for that for a condensed phase fuel droplet to burn in the vapor phase you know the gas phase temperature must exceed. So, in order to have like vapor phase combustion the gas phase temperature must exceed the boiling point temperature of the metal. So, if we take some example we can understand that if the metal has to burn in vapor phase in let us say in oxygen oxidizer, oxidizer oxidizer this will be decided by the metals boiling point temperature compared with the temperature at which metal product oxide is decomposed or dissociated to gas phase molecules. So, that is actually this you know this heat for heat of we have not defined this one that what is the heat of this one is defined as the heat of vaporization dissociation of the metal oxide of the metal oxide ok.

So, what essentially we are understanding here is that so, if the metal has to burn in vapor phase the gas phase temperature must need to exceed the boiling point temperature of the fuel droplet. So, if we need to burn the fuel droplet say metal droplet we want to burn in vapor phase. So, the gas phase temperature must have to be higher than the boiling point temperature of the fuel droplet. Now, you know most metals are having like high boiling point temperature. So, it is very likely that metal to burn in the vapor phase you know the oxide vaporization dissociation or volatilization temperature must be greater than the boiling point temperature of the metal.

So, we need to have like the volatilization temperature of the oxides must need to be greater than the boiling point temperature of the metal boiling point temperature of metal. So, if this condition is met then you know metals can burn in the in the vapor phase. Now, if the oxides vaporization dissociation temperature is less than the boiling point of the fuel combustion will you know proceed in the heterogeneous mode and the flame will you know the burning will take place on the particle surface. And this concept of heterogeneous combustion or gas phase combustion is given by this Glassman criteria ok. It has been given by this Glassman criterion.

Now, if we compare the table here see this table is listed the boiling point temperature of various you know metals and their corresponding oxides the volatilization temperature of those oxide are given here the value of delta H F value of delta H you know volatilization is given this value is also given. So, if we simply compare the boiling point temperature of the metal compared to its volatilization temperature of the oxide we can get an idea about whether it is going to happen in a gas phase or the vapor phase combustion or it is going to happen in you know heterogeneous combustion. So, according to the Glassman criteria what you can say you see beryllium which is having like the boiling point temperature 2741 Kelvin and the beryllium oxide is having the volatilization temperature of 4200. Similarly, in this category we have chromium which is 2952 and its oxide volatilization temperature is 3280, iron 3133, 3400, hafnium 4876 5050, magnesium 1366, magnesium oxide 3430. So, what about titanium? Titanium is also 3631, titanium oxide is 4000, aluminum 2791 boiling point temperature of the metal aluminum oxide is 4000.

So, they are having the capability to burn as vapor phase diffusion flame at 1 atmosphere because this reference is given as 1 atmosphere pressure and oxidizer is pure oxygen. So, they can have the vapor phase diffusion flame at 1 atmosphere pressure and in the presence of oxygen as the oxidizer. In contrast to that if you compare the the boiling point temperature of metal and corresponding volatilization temperature of oxide we can see boron is having like 4139 versus 2340. So, actually the oxide volatilization temperature is less than the you know metal boiling point. If you look at the silicon is having this 3173 versus 2860, zirconium 4703 versus 4280.

So, you know it is less than the boiling point temperature of metal. So, we are expect that the there is a chance of having like heterogeneous combustion for these type of metals. However, you know in case of boron that the these there is a sufficient energy to vaporize the oxide, but still you know the the the energy available to raise the temperature of metal is to boiling point ah it is insufficient to you know burn in vapor phase. So, these are the different example of vapor phase combustion versus the heterogeneous combustion and we can actually consult this table and we can get an idea about how they are taking place ah consulting the glass main criterion as we discussed over here ok.

So, I think we can continue this thing again in the following lecture ok. Thank you.