Course Name: Combustion of Solid Fuels and Propellants
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Lecture: 29 Metal Combustion Classification (contd..)

Hello everyone. So, we are continuing our discussion on combustion of metals. So, we the previous week we have started this module. This is slightly different than what we have already learned in the previous lectures like combustion of solid propellants, let it be double base propellant or composite propellants.

Here we have paid our attention mostly on the combustion of metals which is actually you know the metallic fuel. Now, other than metallic fuel as an ingredients in solid rocket, there are various examples of combustion of metals where we can find application of such category. For example, like there are important considerations are given in self propagating high temperature synthesis or it is called SHS, where various materials are being prepared by this combustion synthesis. There are other ways to you know burning metals to produce some oxides, different size of oxides if we burn the metal particles in a control environment.

We can produce nitrides for like you know structural purpose. There are use of various nitrides to improve the structural strength. So, the synthesis of such you know nitrides are also involved combustion of metals. In other areas like the welding where you know combustion of metal or oxidation of metal is also involved. There is an chance of you know explosion hazards or even you know fire hazards if there are metal dust piled up somewhere and if there is a chance of you know heating source and abundant amount of oxygen supply if it is available, then there is a chance of metal fire.

So, that also involve combustion of metals. But we actually want to restrict our discussion only in the application of metals as fuel or ingredient for solid propellant. Now, we also discussed in the previous lecture that how we I mean choose the metal as ingredients in the solid propellant formulation. We had considered the various you know metal particles or rather we would say various metal fuels or even sometime non-metal fuels for example, boron and we have compared the gravimetric and heating and volumetric heating values of such metals with the available polymeric fuel which is like the binder such as HTPB or even with paraffin wax. And there we have found out that there are different you know metals available which has significantly high volumetric heating values compared to the hydrocarbon fuels.

So, definitely that those type of metal fuels are very much useful for you know aerospace applications where you know most of the aerospace propulsive devices are volume limited.

So, in such case the metal fuels can act as important role in augmenting the performance or enhancing performance. On the other hand we have also told ourselves that the density of metals are comparatively higher than the hydrocarbon fuels. For example, like aluminium or boron it is as high as like three times of HTPB. So, that way it can actually improve the packing inside the limited volume of the vehicle or the propulsive system.

So, that way we can see that energetic metals have potential to act as fuels in the propellant formulation. Now, comparing the various heating values we have said that beryllium is considered to be the one of the prime candidate in terms of heating values, but there are issues with you know beryllium oxides and compounds because they are very much toxic. So, beryllium is not considered rather you know second highest is the boron, although boron has the high very high volumetric heating values. So, boron is considered to be one of the important you know fuel for propellant formulation. There are several you know experiments and you know test conducted by using aluminium particles in the solid propellant, composite solid propellant.

And there are various issues of using the aluminium particles in the solid propellant because you know aluminium oxides can deposit on the nozzle surface or it can give some you know white smoke out of the tail region or out of the nozzle which is not useful for tactical application. However, you know burning metals can release high energy because of the exothermic reactions and that can eventually increase the temperature inside the combustion chamber which is eventually lead to enhancing performance. Because if you recall the I s p is proportional to the square root of combustion chamber temperature T c and inversely proportional to the molecular weight. So, if somehow you can increase the temperature of the inside the combustion chamber we can expect that this will improve the performance. So, that is the whole you know objective behind using the metal particles as fuel in the propellant formulation.

And then we had also started discussing about the classification of metal combustion by considering the you know various criterion particularly the how the metal is going to burn whether in gas phase or in condense phase. Gas phase means we can say like vapour phase reaction or gas phase reaction or we can say the heterogeneous reaction. Now the combustion of metals in oxygen is generally classified by the way the metal is oxidized to its smallest suboxide. Now this process can either happen through like the metal and oxidizer in gas phase or it can happen in heterogeneously or in condense phase. Now how do you really I mean divide the difference in the burning of metal in terms of like gas phase reactions or gas phase combustion or heterogeneous combustion.

So, the typical classification is done by considering the Glassman criterion. And I think we had wrote one equation rather we would say inequality in the previous lecture which says like the which goes like this that the limiting flame temperature of the you know metal oxide the limiting flame temperature results in generally because the boiling point of the metal oxide or the dissociative you know gasification into species other than the original metal oxide. So, that was the concept given by the Von Grosz and Conway in early 1958 or later part of 1958. I think 1958 they introduced one concept that how the flame temperature of the metal was limited to the boiling point of the oxide or the dissociative or gasification into species other than the original metal oxide. So, Glassman has proposed one criteria that the importance of the dissociation and the overall energetic of metal combustion.

So, as per the Glassman criteria we have already seen in the previous lecture that the heat for the vaporization dissociation is greater than the available heat which is like heat of reaction of the metal minus the enthalpy required to raise the products temperature to its volatilization temperature. So, if the initial temperature is 298 Kelvin the amount of heat is required to amount of you know enthalpy required to the enhance that or increase the temperature of the products to the volatilization temperature and that too you know subtracted from the heat of reaction that will give us the available energy. So, the available energy is actually less than the required you know vaporization dissociation energy and because of that you know most of the metals whose you know the if the if the volatilization or vaporization temperature is greater than the metal oxide or the boiling point temperature of the metal there is a chance that the it will burn in a vapor phase or gas phase reaction. Now according to this criteria we can say that the metals which will burn in vapor phase in oxygen if we compare the metals boiling point temperature to the temperature at which the metal oxide product is decomposed or dissociated to gas phase species we can actually know that whether it is going to be burn in a vapor phase or in a condense phase. Now if you consider just simple you know liquid droplet we expect that if this is a liquid droplet if we expect that the liquid droplet to burn in vapor phase we must I mean consider that the temperature should exceed the boiling point of the fuel droplet.

So, if we consider that the fuel droplet should burn in vapor phase then the gas phase temperature must exceed the boiling point temperature of the you know fuel droplet. So, the fuel species will diffuse outwardly and it will going to mix with the oxidizer and is going to sustain the droplet combustion and the remaining always you know the temperature here is going to provide the heat. So, the gas phase temperature is always going to provide the heat for you know evaporation of the droplet. Now if you compare the similar analogy for metals most of metals have high boiling point temperature. So, if the metal has to burn in a vapor phase the oxide vaporization dissociation or the volatilization temperature we generally you know use the terminology like T VOL which is like the volatilization temperature this should be greater than the boiling point temperature of the metal.

If the metal has to burn in a similar manner of like liquid droplet. Now, in order to consider these Glassman criterion we had said that we need to consider the boiling point temperature of the metal and the dissociation volatilization temperature of the oxides and if we compare that we can actually find out whether the combustion will take place in vapor phase or gas phase or we can say the combustion will take place heterogeneously or condensed phase. So, in order to understand that in order to understand that we must need to consider the volatilization dissociation temperature of the oxides and the boiling point temperature of the metal. If we consider that we can find out whether the vapor phase reaction will take place combustion will take place or the condensed phase reactions or condensed phase combustion will take place means the heterogeneous combustion will take place. Now we had already shown this one in previous you know lecture as well we started our discussion there if you consider the case of aluminum what you can see here you see aluminum boiling point temperature is 2791 whereas, its oxide you know volatilization temperature is about 4000 Kelvin.

So, what it says that if we look at the Glassman criterion and we said that if the volatilization temperature is greater than the boiling point temperature of metal. So, there is a chance that this type of metal can have you know gas phase combustion or it can have vapor phase combustion. So, that is actually fitting the criteria for aluminum. So, in that case we can expect that if we consider the oxidation of aluminum we can expect that gas phase combustion can take place for aluminum because the volatilization temperature of aluminum oxides is much higher than the boiling point temperature of aluminum. Under the similar category you can see the beryllium if you look at beryllium.

So, aluminum we can say that this may happen like gas phase combustion or vapor phase combustion because T volatilize is greater than T boiling point of metal. In this category we can say beryllium is also the same you see the volatilization temperature beryllium oxide is much higher than the beryllium metal beryllium which is 2741 in comparison to 4200 Kelvin. Chromium you see the chromium is also having similar like 3280 for the oxide whereas, the boiling point temperature of chromium is 2952. What about iron? Iron is also having the similar magnesium is same, titanium is also coming in the similar category, but there is some difference I will tell you little later. But if you look at the other part of it where the oxides boiling oxides volatilization temperature is less than the boiling point temperature of the metal for example, like boron.

Boron then we have silicon you see here also silicon oxide volatilization temperature is 2860 whereas, the boiling point temperature of silicon is around 3173. In case of boron you can see the volatilization temperature of boron is 2340 whereas, the boiling point temperature of boron is 4139. What about zirconium is the same thing? You see zirconium the boiling point temperature of zirconium is 4703 whereas, the volatilization temperature of zirconium oxide is actually 4280. So, what we can expect for these that these will burn heterogeneously. So, according to Glassman criteria we can say that you know aluminum, beryllium, chromium, iron, then hafnium, then lithium, magnesium, titanium this should you know has the ability to has the ability to burn in vapor phase in vapor phase diffusion flame.

Of course, we are considering this at 1 atmosphere and oxygen as the oxidizer. You remember that if we change the pressure and the oxidizer then this scenario may change we will discuss this thing in detail little later. But if we just consider that 1 atmosphere pressure and oxygen as the oxidizer these metals because their volatilization temperature of the oxide is much higher than the boiling point temperature of the metal they have the ability to burn in vapor phase diffusion flame. So, they are having like vapor phase combustion. In contrast we have already seen that boron, silicon, then zirconium we can expect them to burn heterogeneously ok.

Now, we should say few things about boron. In the case of boron although there is a sufficient energy to vaporize the oxide because you see if you look at the volatilization temperature of the oxide is actually much lower than compared to like melting point boiling point temperature of the metal. And it is considered to be lower in case of others actually they are in the higher side like silicon you see silicon is 2860, zirconium is also 4280. So, compared to that B 2 O 3 in the lower side. So, although we can say there is a sufficient energy to vaporize the oxide, but there is insufficient amount of energy available to you know to raise the temperature of the metal of the to vaporize the metal.

Because you see the boiling point temperature of boron metal or like the boron particles is much higher. So, although this energy may be sufficient to vaporize the oxide, but it is not sufficient to you know raise the temperature of the of the metal to its boiling point temperature. So, there is a difference it is going to change its phase you know it is it is very difficult to its you know make it vapor. So, there is a difference between like boron, silicon and zirconium. Although they are coming under the category of heterogeneous combustion because the volatilization temperature of the oxide is lower than the boiling point temperature of the metal.

Now, what do we expect according to this category that the aluminum particles the large aluminum particles can burn in a vapor phase diffusion flame. So, although it is not exactly you know in a oxygenated environment combustion, but just to give you an idea that if aluminum particles are impregnated in a strand type of you know prop in a in a strand of solid propellant. So, it consists of like you know oxidizer as the solid oxidizer for example, like ammonium percolate and binder as the HTPB binder. And if we add aluminum particles in that composite propellant we can see that aluminum particles are actually coming out from the strand and they are burning as the separate you know particles and you can see the aluminum flame which is like kind of see here separately. So, if you look at this one they will look like you know particle streak if you just simply look at the color flame video or color film pictures they are kind of just like a particle streak.

But if someone can experiment this using some high speed you know imaging technique and taking the video at a larger you know frame per second rate one can actually look at the each particles burning separately and they can see the flame zone and the particulate trail here and you can see that the aluminum particles are burning. So, if you look at the burning surface also you can see the particles there is a like a it is difficult to tell here directly, but we can expect as per the glass main category and that we can expect the vapor phase combustion to take place. On the other hand if you see the table you see the aluminum oxide volatilizing temperature is about 4000 Kelvin compared to the metal you know boiling point temperature. So, if the temperature is very high enough there is a high chance that the aluminum metal will melt is going to vaporize and we can expect there will be crack formation at the oxide layers and the particles the metal the core metal will keep on you know reacting with oxygen and they will oxidize and eventually it may so happen that it may lead to some void inside the particle core because of the you know outside the oxide layers will you know lead to penetration I mean lead to you know metal aluminum metals to melt and boil and react with oxygen. So, there are some literatures available on this on the aluminum particle combustion.

So, I think we can bring those literature in the later part of this lectures or later part of the of this module just to see how aluminum particles burn and how boron particles burn separately because we can see aluminum particles burning is a representative of you know vapor phase diffusion flame or vapor phase combustion whereas, boron is considered to be like heterogeneous combustion. So, I think we can talk these two modes of combustion in detail considering aluminum in one case and boron in other case in the later part of this module. Now, having said that if we just want to look little further we if we remember that Glassman criteria what it is telling that it was given the criteria based on the one atmosphere pressure and oxygen as the oxidizer if you compare these properties of metals and metal oxides we can actually get to know that how the metal is going to burn whether heterogeneously or you know vapor phase combustion. Now, in case if we change the oxidizer there is a chance of transition of these the heterogeneous and heterogeneous and vapor phase combustion. One more thing we should remember if you look at carefully for chromium, for hafnium and iron you see the difference between their metal boiling point temperature and the metal oxide volatilization temperature is within the range of only 400 Kelvin.

So, if you just look at the difference between T volatilization temperature minus T boiling point temperature of their metal is you see look at hafnium is within the range of like you see it is about like 5050 minus 4876. If you look at for this is for you know hafnium what about what about for iron? For iron you can say here it is iron it is like 3400 minus 3133. What about chromium? So, this is for iron. What about chromium? Chromium we can see it is 3280 minus 2952 for chromium. So, what it is telling that these three metals the difference between the volatilization oxide volatilization temperature and the boiling point temperature of the metal they are in the range of around you know 400.

So, difference between the volatilization temperature and the boiling point temperature is in the range of you know 400 Kelvin. So, what does that mean? We can say that if there is a heat loss from the reaction zone that can change the mode of combustion. So, what we just straight away was telling that you know this type of metal can have vapor phase combustion mode, but see if there is a heat loss from the flame zone or the reaction zone this mode may actually change. So, that means, the depending on of course, the flame temperatures may drop for example, like in case of hafnium the flame if the flame temperature drops below the boiling point temperature of the metal. So, if you consider the case of hafnium if the flame temperature drops below the boiling point temperature of the metal then both the metal and metal oxide would non-volatile.

And we can say the oxidation would occur on or within the particle particle itself because you see the temperature of hafnium is around 50 50 the volatilization temperature. On the other hand the boiling point temperature of hafnium is also very high. So, if the temperature drops below the boiling point then we can expect that both metal and metal oxide will become non-volatil and in that case the oxidation of hafnium is going to occur on or within the particles. So, you know depending upon the reaction mechanism a gas phase intermediate need not exceed need not exist. So, what we said that whether it can have like gas phase intermediate, but that that is not guaranteed.

So, we have to remember that if the volatilization temperature and boiling point temperature differences within the you know reasonable limit the particular mode of combustion it is not necessary that they will hold all the time because if there is a heat loss from the reaction zone it can change the mode of combustion. Although this table and the criterion was set for comparing the volatilization temperature and boiling point temperature of metal at one atmospheric pressure and the oxidizer was considered as the pure oxygen. Now, if you consider the case if you consider the case where you see that how much you know what will be the adiabatic flame temperature of the reactant combinations. For example, like if we have aluminum and oxygen the temperature the adiabatic flame temperature can keep on increasing after you increasing the pressure. You see this side it is like a temperature versus pressure kind of plot.

So, this is showing the comparison of boiling temperature of aluminum with adiabatic flame temperatures of various stoichiometric aluminum oxidizer in our system at different pressure. So, if you look at the boiling point temperature is mentioned here how the aluminum vaporization is taking place at different pressure. So, it is like increasing like this. Now, considering the case for pure oxygen as we said earlier using the Glassman criteria what we said that the aluminum oxygen reactants it is always having the adiabatic flame temperature much higher than the vaporization temperature of aluminum. So, we can expect that the vapor phase reactions will take place.

Now, if we consider a different oxidizers like let us say we can actually change the oxidizer here. So, the available energy sorry the available enthalpy will change as a result of change in the heat of reaction. So, the mode of combustion may actually going to change. Now, if we just compare the effect of pressure on the flame temperature and it is effect of pressure on the volatilization temperature or the vaporization temperature of metal reactants, we can see in case of pure oxygen combustion of all practical conditions occur in vapor phase. Now, if you just mix it with argon let us say we now having the reactants you know oxygen plus argon where it is mentioned here you see.

Instead of pure oxygen if we have the reactants as aluminum and oxidizer as oxygen plus argon. Now, we can expect the transition is going to occur you see where the temperature how the temperature is increasing you see now the temperature is falling below the vaporization temperature of aluminum if you look at this part. So, generally it is said that the transition occurs beyond pressure occurs at pressure beyond 200 atmosphere. So, basically the mode of combustion is changing instead of vapor phase combustion now they are going to burn in heterogeneous phase. Because you see the aluminum vaporization temperature is not now higher compared to the available adiabatic flame temperature.

Because now we have changed the reactants change the reactants means aluminum now is burning with oxygen and argon earlier it was like pure oxygen. So, you can say that at different pressure at different you know reactants the mode of combustion is actually changing. Similarly if we just compare the other cases like how the you know reactants are actually going to change the adiabatic flame temperature you see for aluminum plus carbon dioxide aluminum plus water. If the initial temperature of the reactants at 298 Kelvin you see the their temperature of I mean adiabatic flame temperature is somewhere over here which is much lower than the aluminum vaporization temperature you see it is already lower starting from here. So, the mode of combustion is going to change even at a much lower pressure you see the pressure is somewhere around 5 bar or so.

So, we can say that if we change the reactants either aluminum is burning with carbon dioxide or with water. So, if we consider reactants at initially 298 Kelvin the combustion process occurs in a heterogeneous. So, this part is going to happen in heterogeneous combustion you see because after that it is actually mode has already changed because the aluminum vaporization temperature is now increased compared to the adiabatic flame temperature here for different reactant cases where the oxidizer is carbon dioxide and here it is water. So, the heterogeneous combustion is going to or heterogeneous reactions going to take place going to happen. So, what does it mean that mode of combustion is actually changing increasing from vapor phase to you know heterogeneous mode.

So, what we just compare earlier that was considered to be like oxygen as the oxidizer and at a one atmospheric pressure, but once the pressure is increasing and the reactants are changing or the oxidizer is changing the mode of combustion is also changing. So, this I think it is very important you know consideration we should keep in mind that it is not always you know fixed whether it is going to burn in vapor phase or in heterogeneous phase based on the reactants, based on the pressure this mode can also change.

So, I think let us stop here today we will continue the discussions in the following lecture. Thank you.