Course Name: Combustion of Solid Fuels and Propellants
Professor Name: Dr. Srinibas Karmakar
Department Name: Aerospace Engineering
Institute Name: Indian Institute of technology-Kharagpur
Week: 06
Lecture: 30 Metal Combustion Classification (contd..)

Hello everyone. So, we are continuing our discussion on Combustion of Metals. We had already discussed certain things related to metal combustion classification begin with like how the different metals based on their boiling point temperature of metal and the volatilization or dissociation temperature of the oxides. We have seen that metal can either burn heterogeneously means in condensed phase or it can burn homogeneously or in gas phase or vapour phase.

Now, the classification of metal combustion based on their you know thermal properties and the you know oxides melting oxides boiling point temperature metal boiling point temperatures it was nicely given by Glassman it was noted as the Glassman criterion and we have already discussed that part in detail and we have followed one table given by the researchers which shows the various you know metals and their corresponding oxides with their boiling point temperature and the volatilization temperature. Comparing that we have seen that various metals have different type of you know combustion modes certain metals for example, aluminium can burn in a vapour phase. On the other hand we have seen boron can burn in heterogeneously or the condensed phase combustion can take place. Now, we have to also recall that these conditions were given at one atmospheric pressure and oxidizer as the oxygen.

Now, if we change the reactants for example, like instead of aluminium oxygen combustion if we change the reaction to aluminium, oxygen and argon. So, I think we had begin discussing about this table sorry this plot where we have seen that if the reactants are changed to you know instead of aluminium and oxygen. Now, if the reactants are aluminium plus oxygen plus argon you can see the this is a plot basically the adiabatic flame temperature and the boiling point temperatures of aluminium. So, actually we are comparing the boiling temperatures of aluminium with that of adiabatic flame temperatures of various stoichiometric you know aluminium oxidizer inert system. Now, in the case of oxygen and argon we can say argon is the inert one whereas, oxygen is the oxidizer.

Earlier we have considered only like pure oxygen now it has been changed to like the different oxidizer like oxygen plus argon. It can be like a other oxidizer like ammonium per plate which is well known you know solid oxidizer for composite propellants we have seen it already. So, they are given in stoichiometric ratios and the adiabatic flame temperatures are calculated. Now, if you wish to do this by yourself you can definitely use the NASA CA code I think I have already mentioned earlier that NASA chemical equilibrium and application code if you use you can easily find out the adiabatic flame temperature for various you know reactant system like you can change the oxidizer, you can change the ratios if you try with the stoichiometric ratios you can find the adiabatic flame temperature, if you change the other ratios also you can find the adiabatic flame temperature. Now, in this case it is given for the stoichiometric aluminium and other oxidizer along with some inert gases as well and compare that with the boiling temperature of aluminium.

Now, what we are doing is we are trying to see that if there is a change in the oxidizer it may transit from the gaseous I mean it can transit from the homogeneous combustion to heterogeneous combustion. So, what we have just said based on the glass flame criteria it is not a fixed one because if the reactants are changing then the or enough force based on the pressure because if you recall we have said that it was one atmospheric pressure and oxygen as the pure oxygen as the oxidizer. Now, if you consider the case where aluminium is burning in the presence of oxygen and argon you see the adiabatic flame temperature has reduced to this because this is your sorry this one this is your adiabatic flame temperature. Whereas, if you burn aluminium particles in presence of ammonium perchlorate because aluminium perchlorate can donate you know oxygen upon decomposition. So, that react with aluminium and it can burn.

So, that will give temperature slightly higher than the oxygen argon combination. So, still it is much lower than the pure oxygen case this is the pure oxygen case and as you see once you increase the pressure that is also increasing. It is has a steeper rise compared to this one you see the aluminium oxygen combination it has a steeper rise in the adiabatic flame temperature whereas, the aluminium and ammonium perchlorate you remember this is the formula for ammonium perchlorate AP. So, you can see aluminium ammonium perchlorate combination versus aluminium oxygen argon combination it is kind of you know steep not that steeper, but with pressure it is increasing. Now, what interestingly we are going to see here you see earlier based on the oxygen as the oxidizer and if you compare the aluminium boiling point temperature see it is also rising with pressure you see for pure oxygen case it was much higher than the aluminium boiling point temperature.

So, we expect the gas phase or homogeneous combustion mode can take place for pure oxygen case. Now, once we change the oxidizer to different reactants like oxygen and argon you can see after a certain pressure this has you know reduced than the boiling point temperature of aluminium. This is the transition we can see you see the adiabatic flame temperature is lower than the boiling point temperature of aluminium. So, now due to this case generally it happens in a combination of you know aluminium plus oxygen plus argon case this transition generally happen the pressure beyond 200 atmosphere. So, this plot is given based on like this is a log plot.

So, one can see this is somewhere around here. So, around you know more than 200 atmosphere atmospheric pressure we can see the vaporization temperature of pure aluminium exceeding the adiabatic flame temperature for these combinations ok. So, we can expect that there is a transition can happen from the heterogeneous mode to the heterogeneous mode. So, the transition can happen from you know homogeneous mode to heterogeneous mode. This is what we are talking about yesterday I mean in the previous lecture.

Now, if you look at the other combination this figure also shows that when we change the you know oxidizer as CO2 or steam or H2O we cannot call this steam because the reactants are kept at temperature 298 Kelvin. So, which is essentially the 25 degree centigrade. So, basically we are now changing the oxidizer as water or carbon dioxide. Now, we can see here the adiabatic flame temperature is quite lower compared to the boiling point temperature of aluminium. See the boiling point temperature of aluminium is keep is increasing steeply with increasing pressure, but here for carbon dioxide and water based oxidizer it is fairly constant with pressure.

Now, we can see the transition can occur at much low much lower pressure compared to the argon oxygen combination or even ammonium per plate based oxidizer. Here we can see the transition can happen somewhere around you know 3 to 4 bar even. So, we can say that if the oxidizers are changed at a different pressure we can expect the transition from homogeneous mode to heterogeneous mode. So, based on the oxidizer, based on the chamber pressure we can expect the mode of combustion can change. So, this is certainly true for other metal particles as well we have to look through look it properly in order to understand the scenario.

So, this example gives us a typical example of aluminium combustion what we saw from the gas main criteria that it can happen only through homogeneous mode or the gas phase combustion. But if we change the oxidizer and at different pressure we can expect that the transition can homogeneous mode to heterogeneous mode can happen. So, this is one of the consideration. The other you know classifying criteria we can see based on like if you recall that we have classified the combustion based on the discriminator of the available energy. So, if the available energy exceeds the energy required to heat and volatilize the final metal oxide we can expect that the combustion can happen in a gas phase case gas phase mode or homogeneous mode.

So, that was the one only one discriminator we have used in this consideration, but there can be other discriminator as well. So, if you refer to this table this table is actually going to give us the dominant criteria in classifying the metal combustion based on the first discriminator of course, we can expect that if the energy exceeds energy required is exceeds available energy is exceeds the energy required to heat and volatilize the final metal oxide product we can expect that gas phase combustion can happen. Now, the second criteria can be whether the available energy exceeds the energy required to heat and vaporize the metal itself. So, earlier we have said the talk about the metal oxide, but what about if the energy available is sufficient to heat and vaporize the metal itself. Now, with the sufficient energy available the combination of volatile product and volatile metal indicates that metal can burn much like hydrocarbon fuel droplet.

So, if the metal is also volatile we can expect that it can burn just like a normal liquid fuel droplet. So, here it in this case that volatile product and volatile metal. So, we can expect the gas phase combustion. So, almost like a liquid fuel droplet or hydrocarbon fuel droplet. In case of a volatile product resulting from a non volatile metal during the reaction process we can compare the combustion process similar to the carbon particles.

So, we can say that it is like a you know non volatile metal, but the product is product is volatile. So, the combination of non volatile metal and volatile products. So, if you look at the carbon particle once you burn carbon particles what is going to happen there will be you know gaseous carbon dioxide is going to produce. So, we can say this is like non volatile whereas, you know this is your product is volatile. So, your product is this is volatile.

So, this is a combination of volatile product, but non volatile metal. So, if there is a combination of such you know product and metal then there is a possibility of surface combustion just like you know combustion of carbon particles. There may be the combination of you know non volatile product and volatile metal. So, if the metal is volatile, but the non volatile products the gas phase combustion can happen there is a combination of like non volatile product and non volatile metal. So, in this case we can expect the condensed phase combustion can happen or surface combustion can happen.

So, this is the you know mode based on the volatility of the metal and their corresponding oxides. So, one was the criteria based on the energy availability like if the energy available exceeds the required energy to volatilize the oxides then we can expect that the combustion can take place in homogeneous mode or gas phase mode. If that does not happen then the combustion can take place in heterogeneous mode. For example, like in case of aluminum it can happen in gas phase whereas, in case of boron it can happen in heterogeneous mode. Now, if there is a combinations where both the volatile I mean both the metal and the products both are volatile we can expect that gas phase combustion can take place.

If it is a combination of non volatile metal with a volatile product then surface combustion can take place just like you know combustion of carbon particles. If there is a non volatile product with non volatile metal of course, we can expect the surface combustion or condensed phase combustion. If there is a combination of non volatile product with volatile metal then we can expect that gas phase combustion can take place.

Because you see volatile metal means it can evaporate easily and it can try out to pass through the non volatile oxides and it can actually penetrate through it and react with the oxygen or oxygen can diffuse through it. So, it can eventually you know lead to like gas phase combustion.

There is a third criterion you know of course, other combinations we can compare the clean surface combustion of boron particles can also an example of the you know surface combustion. Because if you see we have already told that most of the boron particles are covered with a native oxide layer. So, this is the native oxide layer B2O3 and the core boron stays inside. So, since B2O3 has a melting temperature of 722 Kelvin and the boiling point temperature is about 2340 or sometime 2316 Kelvin. So, we can expect that you know these oxides are kind of volatile whereas, the metal boiling point temperature is quite high it is about like 4000 Kelvin we have seen in the previous table.

So, we can expect here that once the boron oxide becomes you know evaporated once the clean surface combustion of boron happens. So, once all the oxide layers evaporate the bare boron can react with oxygen. So, this is the oxygen. So, we can expect that surface combustion can take place. So, this is another example what we compare earlier that you know volatile product with non volatile metal this is a combination of clean surface combustion of boron.

So, we can expect this one. Now a non volatile oxide products and volatile metal you can expect for magnesium, aluminum because there actually we can expect that non volatile metal oxide and volatile metal. So, if you look at in case of aluminum I think we can this part we can bring it later on once we talk about the combustion mechanism of aluminum. So, what happens for aluminum? Aluminum oxide is kind of non volatile whereas, the aluminum can keep on you know temperature can increase and it becomes volatile. So, this may lead to some crack in the oxide layer and aluminum can actually react with oxygen this is going to react with the outer oxidizer. So, this is another example of the case where non volatile metal oxide product and volatile metal.

So, this is the combination of non volatile metal sorry volatile metal and non sorry this is not this one non volatile oxides. So, this is the combination that it is a non volatile product whereas, the metal is volatile. So, in this case we can expect aluminum, magnesium this can happen in this mode. We can expect for hafnium, zirconium that can have like a non volatile metal oxide with a non volatile metal which can happen if we burn the hafnium and zirconium in air at one atmosphere. Now, so far you have considered mostly based on you know energy consideration or the volatility of metal and metal oxide, but there is a third discriminator which is like inter solubility between the metal and its product that is also relevant to the combustion behavior.

So, you can look at the first one was the energy based, second one is based on the volatility of metal and metal oxide, the third one third discriminator is based on the inter solubility of you know metal and metal oxide. So, for case of you know volatile metals certain solubility combinations can lead to disruptions and breakup of the original particles. There are certain you know volatile metals which can you know have some solubility within the oxide and that can lead to like you know disruption and breakup. For non volatile metals purely let us say condensed phase reactions it can result in the one process is called like there are you know some combustion synthesis process for synthesizing materials. So, this is it is not only important for you know propellant application, but there are other applications for making materials using combustion synthesis.

And there actually this you know combustion process of various metal combinations are very important. You know combustion synthesis of materials are actually going to have classified on many ways based on the physical nature of the initial reactions. So, one such important reactions are called SHS. It is like self-propagating high temperature synthesis which is one of the important combustion synthesis combustion based methods for synthesizing materials. Self-propagating high temperature synthesis.

This is very very important in preparing different materials where the inter solubility of metals and their oxides are important. And this is actually going to play a role in case of various combination of metals. So, you know there are many examples of preparing different type of particles like iron, sometime titanium. There are many ways you know combustion synthesis can be used to prepare material. So, one is SHS, but there are other combustion synthesis for example, like solution combustion synthesis SCS.

This is like you know initial reactions are in aqueous solution. So, this is another way of synthesizing materials using combustion synthesis combustion based method. This is known as the solution combustion synthesis. There are other method is called flame synthesis FS. This is for solution combustion synthesis you know initial reaction initial reactants are aqueous solution.

So, the reactants are kept in water aqueous solution whereas, in case of SHS they are in solid state initial reactants are in solid state. In case of flame synthesis this is again gas phase combustion. The other pyrolysis process is also there which is called spray flame pyrolysis. This is another combustion based method for making materials which is known as spray flame pyrolysis. In that case also precursors can be both liquid and gas phase.

But coming to in our case you know this metal combustion case what is very important for you know volatile metals certain solubility can you know lead to disruption and breakup of original particles. For non volatile metals you see for non volatile metals purely condensed phase reaction can take place and that can result in you know different materials. That is one of the example for you know self propagating high temperature synthesis for making materials. Sometime you know in addition to that products coating can also may build up on the surface of the metal or within the metal.

So, that can you know lead to ignition difficult. If the product coating is actually going to cover the pure metal that can lead to like inhibition of the ignition. For example, like in case of boron where boron oxide is covering the core boron surface which is basically an inhibitor for ignition process. So, that actually leads to delay in ignition. So, although there are certain categories of you know metals which may be beneficial for making the oxides, but there are certain issues that can that product can actually coat it which can if you consider in case of like a propellant application of course, the coating can actually delay the ignition. But in case of like some you know other applications other than combustion other than propellant application if you are looking at making the coating of some certain metal oxide on the metal surface.

So, this process may be beneficial by making use of this you know self propagating high temperature synthesis which can actually make materials. So, of course, we can see that other than propellant applications the combustion based method of synthesis can be useful where the knowledge of you know combustion of metals are very very important. So, I think with that we understood the concept of I mean the classification of the various combustion modes, but that is not actually all because in order to understand the different modes of combustions we of course, want to understand the thermodynamic properties of the metal and metal oxide which affect the combustion mode, but they can also affect the ignition behavior of the metals. But what about the melting temperature of the metal the melting temperature of the oxides so, I mean there will be some relationship which with respect to the you know melting temperatures to each other to the volatilization temperature we must need to consider this in order to understand the combustion mode of the particular metal. For example, like aluminum combustion particle ignition typically is associated with the melting of the initial oxide layer you know that protects the metal because we have already said that you see the aluminum oxide is actually covering the core aluminum.

So, the ignition of aluminum you know typically associated with the melting of the initial oxide layer which is actually protecting the aluminum. In case of you know flame spread across the aluminum surface the melting of aluminum is going to you know once the temperature goes higher the melting of aluminum is going to evaporate and you see it is going to create the vapor pressure higher which will lead to some crack of these oxide layer. And typically the ignition temperature which is the typically the associated with the ignition temperature at the flame front. Now due to the change in temperature there is a possibility that it may change the phase the crystal phases may also will change. And in certain metals they may change their phase from let us say alpha-romohedral to beta-romohedral there are examples of that.

Now, we in order to understand this combustion mode we have to keep all these consideration in mind before we considering the various modes of combustion. So, I think with that understanding we go ahead and we try to you know look at the combustion regimes of metal particles. So, that will be our next task in order to you know understand. Now, in order to under the metal particle combustion regimes what we have seen earlier that the metal combustion can happen either you know heterogeneously on the particle surface that we already discussed that based on the Glassman criteria if you just look at the combination of metal and oxide I mean the oxygen is the only oxidizers there we have seen that based on the Glassman criteria it can have like heterogeneous combustion or homogeneous combustion. Now, the formation of the final product can also be you know I mean can also be heterogeneous or homogeneous process like how the final product is forming this can happen in a homogeneous mode or through heterogeneous mode.

Now, this actually the combustion of metal particles is actually introducing a new length scale into the problem. So, this is actually making the problem even difficult. So, we must need to consider the time scale for mass and energy transport in order to understand the you know mode of I mean in order to understand the combustion regimes we need to understand the time scale for mass and energy transport and we should compare this we must need to compare this with the chemical time scale. What does this mean that if the transport time scale can be compared to the chemical time scale we can actually know that how it is going to control the macroscopic features of the combustion such as like the burning rate, the ignition delay. So, we need to understand the time scale we compare with the chemical time scale and we can try to see the macroscopic features of the combustions like burning rates, ignition delays of various metals.

Now if the reaction time scale is larger than the transport time scale we can say that the reaction rate is slow compared to the rate of mass and energy transport and we can expect that the there is no special you know non uniformity exist or basically the special non uniformities can be ignored and in that case we can say that this mode of combustion is basically this regime of combustion is kinetic control. So, what basically saying that if the reactance time scale is or reaction is kind of a slower compared to the transport process or transport time scale is actually shorter than the reaction time scale then there is you know no special non uniformity of the species and we can expect that the combustion is controlled by the you know kinetic regimes or kinetically controlled combustion. Whereas, in other case when the reaction is faster the special non uniformity such as like the temperature, the composition which is now cannot be ignored because the transport process is kind of slower compared to the reaction rate. So, the reaction time scale is now smaller than the transport time scale. So, in that case we can expect that special non uniformity cannot be ignored now and this type of you know regime we can say it is like a diffusion controlled because the diffusion of the species is now very important and that is going to control the combustion.

So, that combustion regime we call the diffusion control combustion. I think we will bring this one again the importance of this regime we will talk further and we will try to understand that through the combustion of single metal particles and we compare the analogy with the droplet combustion in the following lecture. Thank you.