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Lecture 35 : Ignition and Combustion of Boron Particle (contd..)

Hello everyone. So, we are continuing our discussion on the combustion of metals. So, metals part two and we had started discussing the ignition and combustion of boron particle. As you can recall that why boron is so important fuel for you know propulsion application just because the energy content in terms of like gravimetric and volumetric heating values boron has you know very high volumetric heating value which is very very important for you know volume limited propulsion system.

And there it has been you know significant interest to see how boron can be utilized in practical propulsion application. But as I mentioned earlier that due to the presence of the native oxide layer on the core boron surface the ignition process is inhibited or ignition is delayed. And because of that you know boron particles although it has significant energy potential, but the practical propulsion systems have not utilized boron boron's full energetic potential. So, in this lecture we will try to understand the ignition of boron particles and combustion of bare boron.

Because you know ignition and combustion of boron particles very much dependent on the presence of the oxide layer there are contradictory mechanisms also exist on the ignition of boron particles. So, we will try to bring out the mechanisms and we will try to understand what is the important you know dominant reactions, what are the influencing factors in boron ignition and also we will try to see what are the ways to enhance boron ignition. So, if you recall what we discussed in the previous lecture like the major problem with boron is it has the pre-existing oxide layer which plays a important role on the ignition process sorry it is this one. So, basically the core boron is covered with some oxide layer if you look at here this is the oxide layer. So, if the particle radius is let us say r p and if you say that thickness of the oxide layer is x p.

So, this is like boron particle radius which is x which is r p and oxide layer thickness is x p. So, in that case the total particle radius will be r p plus x p. Now, one thing we have to understand that this is not like a constant parameter like depending on the you know oxidations of at the surface like this negative oxide layer thickness may change for a micron size particles this oxide layer thickness may be couple of you know micron couple of nanometer depending on the you know amount of you know oxidation happened already based on that the oxide layer thickness can vary, but it plays a very important role in the ignition process of boron particles. Now different approaches have been applied by the researchers to understand the problem of boron ignition and they have you know considered various assumptions, boundary conditions to their you know different set of experiments. In general it has been you know mentioned that the due to the presence of the oxide layer on the boron surface the ignition process becomes complex because if you recall the melting point of boron oxide is 722 Kelvin whereas, the which is much higher than the core boron.

So, in a combustion scenario it is so happened that the oxide layer will melt and it will create some molten oxide layer which is going to cover the core boron this is the core boron this is the oxide layer. Now this molten oxide layer may stay there for the temperature range between the you know melting temperature of B2O3 and the boiling point temperature of B2O3. So, it will still stay as a molten state which is actually going to cover this you know particle surface or the core boron surface. Now this actually involves many things in a general descriptions we can say that it involves the radiative and convective heat transfer. So, there will be convective heat flask radiative heat flask there will be reaction at the.

So, if there is a water vapour present in the surrounding. So, that may actually going to react with the B2O3 layer and it actually helps in removing the oxide layer. So, typically the at the surface if the water vapour present this may actually going to create some reaction with liquid oxide layer and it is going to form H B O 2 metabolic acid which is eventually going to improve the gasification of boron oxide or we can say it can help in removal of boron oxide because it is reacting with the water vapour and some of the liquid oxides are actually going to react with water and form this one and that way it somehow it is So, this is one such reactions when there is a you know presence of oxide presence of water vapour in the surrounding. Now at the bare boron if you look at the bare boron can react with the oxygen. So, the oxygen presence here.

So, oxygen can penetrate through the molten layer and they can react with the core boron this is the core boron and typical reaction may involve like this may be like solid or liquid depending on the temperature of the bare boron that will react with oxygen and there is there will it is going to form like B2O3 liquid. So, this is kind of a typical representation of you know generalized description of the boron ignition process while the particle is covered with some oxide layer. Now you know the particles may be amorphous particles may be crystalline. So, many researchers studies the ignition of amorphous particles crystalline particles in different you know oxygenity environment different temperature conditions. So, how the diffusion process takes place in the B 2 B2O3 interface the reaction of B2O3 liquid with the water vapour.

So, many things are involved there, but however, this is kind of a general description of how the boron ignition takes place, but we will talk about the mechanisms proposed by various researchers and how they contradicted to each other and there is some you know kind of agreement has been followed as well. So, in a summary we can say that the boron oxide layer presence on the core boron surface is actually acts as an inhibitor for the ignition of the boron particles. Also been observed by numerous you know researchers that the crystalline particles actually difficult to ignite. So, crystalline boron is difficult to ignite then amorphous boron particles. So, it has been already shown in different studies by burning you know particles in a post flame region of any burner and it has been seen that crystalline particles are actually taking longer time to ignite.

In fact, it is very difficult to ignite the crystalline boron particles. So, for propulsion applications where we are thinking of involving boron particles as fuels of course, we are going to intend to use the amorphous boron particle instead of crystalline boron particles. Now, the experimental studies conducted you know during 1960s one of the pioneering studies by Messek and sample in the era of like or studies by Messek and sample in the year 1969. I think if you search it on the ignition and combustion of boron particles this article may be you know available. You can see that they have mentioned that boron particles combustion of boron particles always occurs in two stages.

The first stage combustion is believed to be associated with the removal of the oxide layer the oxide layer presents here. So, the first stage involves the removal of the oxide layer whereas, the you know the ignition will you know burning will continue, but still the particle will be covered with the pre pre existing oxide layer. Whereas, the second stage combustion is you know fully full phase combustion of bare boron particles. So, once all the particle all the oxide layers are removed from the core boron. So, then the second stage combustion will happen which is the burning of bare boron.

And this has been you know initially observed by Messek and simple from their experimental study. Later on it was confirmed by other researchers such as you know professor K K Kuo's group they have also observed the same thing. The one thing it is mentioned in most of the researchers studies that the removal of liquid oxide layers plays a most important role in the ignition and combustion of boron. Now, the difficulties of boron ignition combustion has been remain a problem or you can say it is it is an hindrance it is a hindrance to extensive utilizations of boron although boron has high energetic potential. Now, this is you know partly due to the presence of the oxide layer.

What has been observed in the experimental studies that the typical you know flame boron flame plumes are like three different colors. A bright yellow zone which is interpreted as the boron ignition. Now, here I tried to show you one you know droplet combustion of boron particles. So, I had actually loaded boron particles in just liquid ethanol and I do not remember exactly what percentage it was there it was done by me during my you know p s g studies. So, this is one study just like ethanol containing boron nano particles and what we observed there.

So, we intentionally chose ethanol there. So, that we can see the clean burning of ethanol which will not interfere much with the boron particles burning events. So, if you see what researchers have mentioned that the bright yellow zone which corresponds to the boron ignition. White glow zone corresponds to boron combustion whereas, the bright green zone corresponds to BO 2 emission. So, BO 2 is one of the important intermediate species formed during the ignition combustion in boron.

So, this species emits the green light. So, this is the emission from the BO 2 is actually going to give you this you know green light from the particle burning. So, if you look at these flames also it is showing something around like boron is burning, yellow then white and then some green hue.

Of course, we are not able to see each of the particles clearly, but at least the combined effect can be visible from this droplet combustion figure, but one can refer to literature some of the old studies one can see and they can actually observe this thing that if the single particles are burned in a post flame region we can see that it is actually associated with like bright yellow zone, white glow zone and one bright green zone. And they are actually corresponding to bright yellow zone is boron ignition, white glow zone is boron combustion whereas, the bright green zone is the BO 2 ignition.

So, you can actually see the green zone in all these you know droplet combustion figures where particles are actually coming out and they are burning. So, particles are coming out from this ethanol droplet and they are burning and they are producing this you know nice green flame there. So, it is important to note here that the ignition of boron depends on the on a balance between the rate of B2O3 production and vaporization you know. So, after a critical temperature the vaporization of B2O3 will exceed the production of B2O3 and it will remove the oxide from the particle surface and that will eventually you know lead to combustion of bare boron. Now, the proposed mechanism on boron ignitions are like proposed by King and then later on Glassman and Lee Williams also proposed.

So, there is a contradictory theory between these two group of researchers like King proposed that oxygen can diffuse through molten oxide layer. So, what we just said that oxygen can penetrate through the molten oxide layer whereas, Lee Williams and Glassman they proposed that the boron dissolves and diffuses through the oxide layer. So, according to their proposition that boron oxide sorry boron can actually dissolve through the oxide layer and they can react with oxygen. So, this is the two opposing theory one is saying that oxygen diffuses through molten oxide layer other is saying the boron dissolves and diffuses through the oxide layer. Nevertheless like it is very important that ultimately boron has to react with the oxygen to have the combustion to begin.

So, once we have that you know sufficient energy transfer to the boron oxide layer there may be some phase you know transformation can happen from solid to liquid. Of course, the fraction of liquid layer can also evaporate from the surface and you know during that time the ambient gas temperature may be sufficiently high because you know oxides vaporization temperature is around like 2316 or 2340 Kelvin as you reported in the table while we comparing the volatilization temperature of oxides versus the metal. Now, in order to react the boron to oxygen it has to have like you know pass through this molten layer. So, as I said this contradictory theory is proposed by them eventually talks about that that either oxygen diffuses through the molten oxide layer or boron dissolves and diffuses through the oxide layer. Now, the heterogeneous reaction between the boron and oxygen is going to provide the you know energy input for the temperature to particle temperature to rise.

Now, if the heterogeneous reaction between the oxygen and boron is sufficiently high then of course, the remaining oxide layer is going to actually melt and evaporate away. So, the oxidated layer will then be completely removed from the boron surface and we can achieve the second stage combustion which is like a full fledge combustion of you know bare boron particles. So, that depends on the if the sufficiently temperature is rising sufficiently and at a point at which the remaining boron oxide layer is you know completely evaporated. So, the bare boron can react with oxygen and the second stage or the full fledge combustion of you know boron will proceed. Now, this is you know confirmed by some experiments as well this contractive theory.

So, I have presented this one by taken from one you know book. So, sorry from one literature you see it has been presented by Ye and Kuo in this journal. So, they have reviewed the mechanisms for first stage reaction. Now, as proposed by King the set of reactions mentioned here that boron you know diffuse is going to oxygen is going to diffuse through the molten layer and is going to react with oxygen. So, boron is going to react with oxygen is going to form B2O3 whereas, the vaporization process will continue which is happening at the surface.

If water vapor present in the surrounding the reaction with water vapor is going to continue heterogeneous reactions as I mentioned earlier that liquid boron oxide is going to react with the water vapor and is going to form the H B O 2. If we look at further that boron can actually react with water and the molten oxide and is going to form this compound which is like H3BO3. So, basically what is happening here that the boron oxide layer exothermally is going to react with both boron and B2O3. So, water vapor is going to react with that diffuses through boron oxide layer and is going to react with boron and boron oxide and is going to form this H3B3O3. On the other hand if you look at the mechanism proposed by Glassman and later it was supported by the study of Lee and Williams.

So, what they proposed that it is actually that it is not there oxygen is actually diffusing through the molten layer rather the boron actually dissolve and diffuses through the molten oxide layer and ultimately they are going to react with this boron and B2O3 oxide and they will create this boron oxide polymer which is like a vitreous type of substance is going to form and the other process will involve like the vaporization of B2O3 which is you know from B2O3 liquid to B2O3 gas that will continue. So, if you look at the two global heterogeneous reactions on the particle surface this is going to react with oxygen is going to react with boron and they will form B O 2 which is important intermediate species during boron ignition and combustion as I said the other reaction is going to happen like boron will react with boron plus B2O3 plus water and oxygen is going to react and is going to create like or produce metabolic acid. Now, this is the model developed by Lee and Williams with the studies presented by Glassman earlier. So, basically what it says that during the ignition stage boron will dissolves at the boron and B2O3 interface. So, this is the interface and diffuses across the liquid layer at the same time it is going to form a vitreous complex such as like you know B O 3 vitreous complex and this vaporization of B2O3 liquid is going to continue.

So, that is going to happen and one exothermic surface reaction is going to happen between like boron and oxygen and water vapor and is going to form like B O 2 and H B O 2. And once the heat is sufficient enough and if it removes the oxide layer from the particle surface it is eventually is going to remove the oxide layer and the bare boron is going to react with oxygen and that is going to happen like boron and oxygen reaction is going to happen and that is we can say the full fledge full fledge boron combustion. So, I think we can show one summary of you know boron combustion chemistry here. So, what we said that surface oxide layer inhibits the combustion process of boron which actually reduces the availability of energy from a given particle. So, you can understand that if there was a pure boron even though let us say its particle size is one micron or maybe some let us say 2 micron.

Now, if the particle is covered with the oxide layer you can understand that some amount of energy is actually taken up some portion of the energy is actually taken up by the oxide layer. So, it is not pure boron anymore it has some oxide layer and because of that its full energy is not now is not available now because of this thing. On the other hand since this is this B2O3 layer is acting as a protecting surface or protecting layer on the core boron it is actually inhibit the ignition process. So, one hand it is actually reducing the energy available from the given particle on the other hand boron oxide layer is actually protecting it and it inhibits the ignition process. And, that is why the researchers have already performed several experiments in various environment and one thing they have come to a consensus that the boron combustion can happen in two stage.

The first stage involve the removal of oxide layer whereas, the second stage involve burning of bare boron. So, in the ignition stage it can also happen that boron particle is still covered with oxide layer, but ignition can continue one once the temperature is sufficient the boron oxide molten boron oxide can be evaporated and bare boron can now react with oxygen and full phase combustion can happen. So, typical reaction mechanism which involves in like a boron, hydrocarbon and air environment and that is quite obvious like if you use boron mixed with some hydrocarbon and if we burn that in a air we can expect that this will follow the sequence that boron will form this vitreous boron monoxide which will react with oxygen and form the boron dioxide. Now, depending on the you know the water vapor or hydrogenated compound present in the mixture the reactions can have different pathway it can form HBO2 which actually going to you know involve less energy release. The other option is like B2O3 liquid which is the preferred end product you know this is supposed to be the preferred end product for you know better utilization of energy from boron combustion.

However, the amount of HBO2 versus B2O3 in the products is determined by this. So, this may be have some reversible reactions, but of course, this is influenced by the presence of water vapor in the mixture and that will tell us whether it is going to form HBO2 or it is going to form B2O3 liquid. Now, the B2O3 liquid means if the temperature at the engine exhaust is very high we can expect that some energy is going to be taken away by the B2O3 liquid. So, if the B2O3 liquids are coming as a liquid sorry B2O3 are coming as a gas initially. So, if we somehow condense this to B2O3 liquid some of the energy involved due to the evaporation of this B2O3 which I am talking about the product B2O3.

So, let us say boron has already combusted and it is formed B2O3. Now, since the temperature is very high there is a high chance that B2O3 is in B2O3 gaseous state. Now, we can actually recover some of the energy from the B2O3 gas by some condensation process. If we somehow you inject some additional air in the secondary chamber and somehow if we make them to liquid B2O3 some energy may be recovered. So, this is another approach researchers have mentioned that instead of having a single combustor if you use a two stage combustion and I am not talking about the boron two stage combustion rather I am talking about like if we have a two stage combustor where some of the energy which was actually lost due to the evaporation of the B2O3 product B2O3 that can be recovered if we just cool down the B2O3 gas into liquid.

So, that is energy can be utilized. So, in a nutshell what we can say that because of the native oxide layer presence in the presence on the particle surface it not only inhibits the ignition process, but also it actually reduces the energy available from the boron particle as I have mentioned here. So, there should be something required in order to have like a faster gasification or evaporation of boron oxide. So, that core boron can actually have access to oxygen and react with oxygen and go the go with the exothermic reactions and produce energy. So, in order to improve the boron combustion we must need to play with boron oxide layer and how to you know remove the boron oxide layer faster so that ignition delay can be you know removed. So, there are various processes involved in I mean enhancing the boron ignition.

For example, like the halogen containing environment it has been observed that if the environment is containing halogen for example, like fluorine. If the fluorine containing environment is present and this actually helps in you know removing the boron oxide layer faster such as like it can react with the molten liquid. So, fluorine can actually become like boron fluoride plus it is going to give some oxygen also. Later it may also react like B2O3 liquid plus we can use like hydrofluoric acid as well that can also form like BOF plus HBO2. So, fluorine containing environment or halogen containing environment can actually improve the ignition process.

The other option is like if we coat by coating boron particles with some with relatively easily ignitable metal relatively easily ignited metal for example, we can have like magnesium or zirconium or titanium. So, that will actually going to boost it is going to give some energy boost which will enhance boron ignition. So, somehow you know if we can improve the if we just enhance boron ignition there is a better chance of borons to be utilized. So, I think numerous work is still going on one can refer to the boron combustion literature and one can find out that what are the you know various ways researchers are trying to find out to improve the ignition and combustion of boron particles and to use them in a actual propulsion application maybe in a propellant system or in ramjet mode, but it is better I mean suitable for ramjet application just because you know it requires some additional oxidizers particularly like for full combustion or complete combustion of boron therefore, the ramjet would be the more suitable engine for boron loaded fuel or propellant. So, I suggest that interested you know participants they can look the literature further for this you know boron combustions applications how boron ignition combustion can improved by adding you know different other metals or even different oxidizers such as like fluorine or even some other catalyst which can actually improve the ignition of boron particles ok.

So, I think with that we stop this discussion on boron ignition combustion part I think we can look at little bit about the oh I think we can talk about the combustion time also for boron particles combustion because if you recall we can actually easily you apply the diffusion control mechanism kinetic control mechanism and the total burning time will be you know given as the T b diffusion and T b kinetic and the equations what we already got because this is proportional to d square whereas, this was proportional to d. So, we can actually use this total time for the burning and we can actually get an idea about the what about the burning time.

So, you know in way to understand the details of the burning time how the other parameters are being taken I mean this is not the you know direct you know part of this course, but one can actually refer to the literatures just to understand how the you know burning time has been you know derived for different boron particles depending on the particle size depending on the pressure depending on the heat transfer depending on the other parameters depending on this you know surrounding oxidizing environment. So, but at least if someone is interested they can refer to it and you can look for more information. So, with that I think we close this lecture we will continue the ignition of ignition combustion of aluminum particles in a brief and then we will talk about the application potential of energetic metals for you know propulsion application. Thank you.