Inorganic Chemical Technology
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Lecture - 33
Refractories, Specialized Ceramic Products and Vitreous Enamel

Welcome to the MOOCs course inorganic Chemical Technology, the title of today's lecture is Refractories, Specialized Ceramic Products and Vitreous Enamel.

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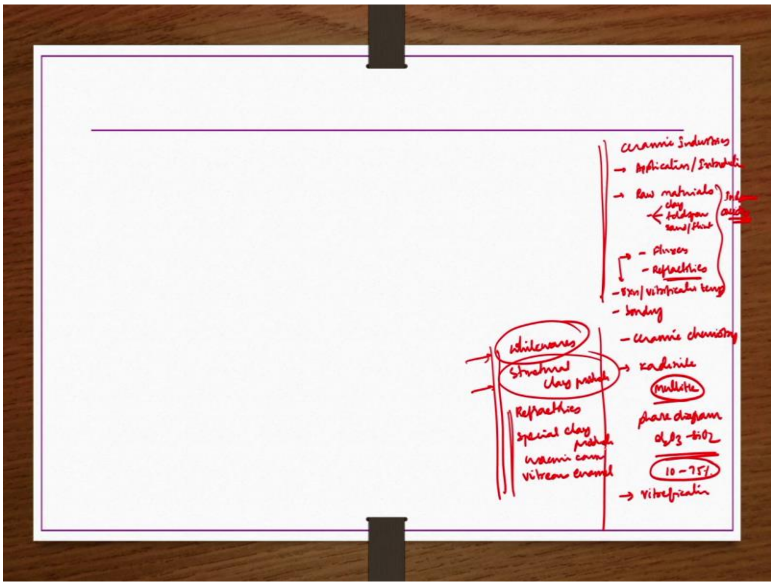

In last two classes we had discussed several aspects about ceramic industries right. So, in this ceramic industries you know applications after some introduction etcetera. Then what are the raw materials? In general, we have for ceramic industries. We have seen several raw materials common out of which three are very common in almost every ceramic product making that is you know clay, feldspar and then sand or flint.

In addition to this we know that several types of fluxes and then refractories are also used. So, and in what we understand that you know most of these raw materials that we use for ceramic products making all of them are oxides you know inorganic oxides in general most of them, in fact, almost all of them ok. So, the fluxes are used for you know reducing the reaction temperature or vitrification temperature if you wanted to reduce for that purpose it is required.

It is also used for you know bonding in order to make the materials or particles of the mixture to be binded together. So, you need some kind of fluxes so, these fluxes are used for that purpose also where are the refractories are used for the thermostability etcetera. Then we have also seen the ceramic chemistry, basic ceramic chemistry here.

So, especially you know how this kaolinite etcetera or you know being reacted to produce mullite etcetera these kind of things you know we have seen so, the mullite is one of the important refractory. So, we have also seen the phase diagram of Al 2 O 3 Si O 2 mixture. And then from here we found that you know mullite is forming even at moderately lower temperature as well likes 800, 900 degree centigrade by varying the composition between 10 to 75 percent something like that those things we have seen.

And then this has led to the development of you know mullite which is you know has taken refractory industry to the different level higher level ok. Then after that we discussed different types of ceramic products depending on the degree of vitrification and another property.

So, then where we have seen different types of products possible like you know white-ware, then structural clay products, then refractories, then special clay products. And then vitreous enamel etcetera these kind of different types of a ceramic products are possible.

These are the classification of products etcetera those things we have seen, out of which we have seen the manufacturing process of this white-wares as well as the structural clay products through proper flow chart etcetera in the previous lecture. In this lecture we are going to discuss about the remaining types of ceramic products. Like we also had something like you know ceramic composites etcetera those things also we are going to see now.

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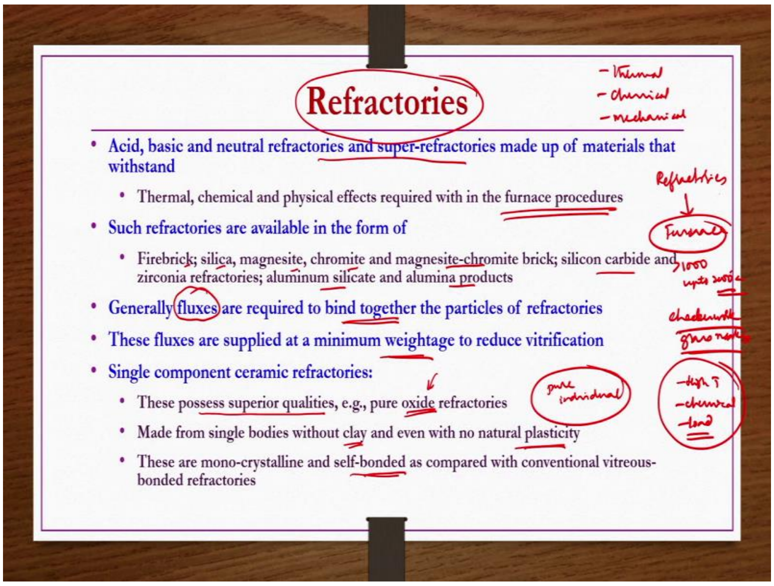

So, in this lecture let us start with discussions on refractories. Refractories by chemical nature they can be acid, they can be basic or they can be neutral refractories as well. So, these refractories and super refractories are made up of materials that withstand obviously, what you understand like you know thermal stability and then chemical stability. And then mechanical stability are important in any of the refractories that we have already seen.

So, they should have or they should withstand thermal, chemical and physical effects required within the furnace procedures. Because what we have seen this refractories primarily you know used in making of these furnaces right. These furnaces are usually you know operated at very high temperature about 1000 degree centigrades and sometime up to 2000 degree centigrades also.

One example we have seen you know checker work refractories etcetera in glass making industries or glass making when we are discussing we have seen such kind of you know furnaces where these refractories were used. So, in these furnaces different types of raw materials are taken and they are you know melted by applying the heat.

And then that heat is often started supplying by you know fuel gases. When these fuel gases burn within the presence of oxygen so, then what happen different types of fuel gases may also possible to be produced right. So, along with that one some slags may also be produced and then products may be in the you know molten conditions, because of that one you know what you have you have the high temperature. And then different types of chemical natures etcetera are there and then you know load is also one essential thing because this glass making mostly it is done in batches right.

So, load how much load are you giving so, you know mechanical strength is also required o, all these things are in general required to be maintained in furnace. So, what you expect these refractories or super refractories made up of material so, that materials you know they should have a you know thermal chemical and mechanical stability.

Such refractories are available in the form of firebrick silica, magnesite, chromite or combined magnesite chromite bricks, silicon carbide and zirconia refractories, aluminum silicate and alumina products etcetera. Generally, fluxes are required to bind together the particles of refractories, the purpose of the fluxes we have already seen.

So, this fluxes also inorganic oxides, but they reduce the vitrification temperature as well as the reaction temperature plus they get fused even at 900 or 1000 degree centigrades itself. So, that is just moderately high temperature only not high temperature with respect to the ceramic industries right. So, at such moderate temperatures itself, they are fusing.

So, when they fuse so, then what they do they try to keep the materials compacted together, packed together ok. For that purpose, you know this fluxes are used, but you know in refractories you do not want any kind of vitrification right. So, but binding is required for that definitely you need to use the fluxes, but if you use abundant amount of fluxes and then you operate at very high temperature like you know more than 15 or 1600 degree centigrade then complete vitrification takes place right.

But these refractories are used in making or furnace construction purpose. So, in such cases vitrification is not required indeed that is not going to be useful also that is going to be detrimental effect. So, vitrification has to be reduced, how you reduce them? You cannot have a refractories without fluxes, why? Because, fluxes you know they keep particles binding together right.

So, but if you use too much of fluxes then vitrification is taking place. So, that is the reason this fluxes are taken at minimum amount, minimum weightage they are supplied ok. They are supplied only in at minimum weightage to reduce the vitrification. There are also cases of single component ceramic refractories something like pure oxide refractories they possess superior qualities. Obviously, pure individual components you know they will have a superior properties of their own right.

So, you know whatever the pure oxides are in a inorganic oxides if you take you know they have a better properties if you mix with them with some other property of lower quality. So, then you may get a product of a intermediate quality, but if you take a pure oxide of a better quality as a single component to make the single component refractories. So, then obviously, the refractories going to have such superior qualities as individual inorganic oxides that they posses.

These are made from single bodies without any clay without any natural plasticity as well right. And then good thing that you know these they bind together they bind together amongst themselves without any need of fluxes. Because, fluxes are also inorganic oxides and then these single component ceramic refractories are also mostly inorganic oxide components.

So, such components are only used as a kind of making for single component refractories. So, then separately you do not need fluxing agents to keep particles together. These are mono crystalline and self-bonded as compared with conventional vitreous bonded or the chemical reacted bonded refractories.

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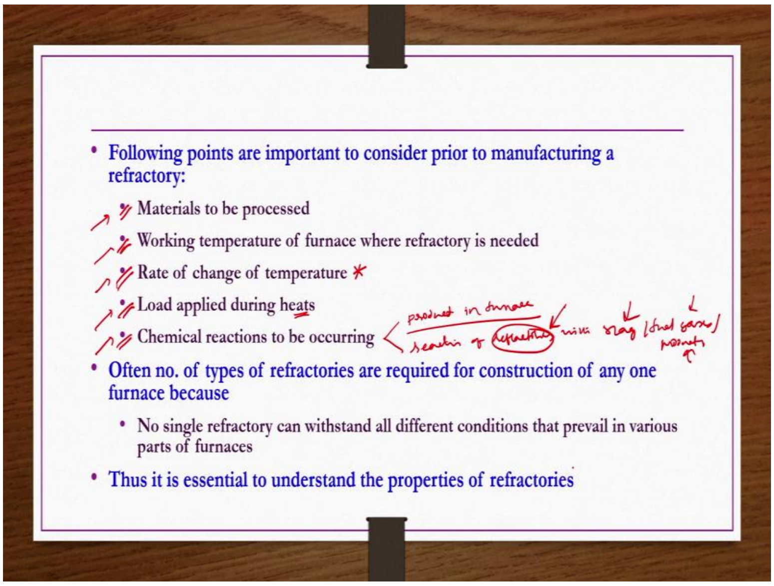

Now, what do you see kind of important thing any refractory that you are going to be produced? So, following points are important to consider prayer manufacturing of a refractory. What are they? Materials to be processed. Let us say if you are making a furnace using a refractory and then you are using acidic refractories for construction of furnace. And then in that furnace if you are using alkaline materials to be handled so, that is not advisable.

So, what kind of materials to be processed in the furnace for which you are making a refractory or manufacturing refractory is very essential ok. Then working temperature of furnace where refractory is needed, let us say you are constructing a furnace and then you are aim to operate at 1800 degree centigrade something like that. But you are constructing refractory which fuses at 1200 or 1300 degree centigrades itself so, that is not going to work.

So, working temperature of furnace where refractory is needed that is also very essential point ok. Then rate of change of temperature, this is very much essential because some materials you know thermal expansion coefficients are such a way that. If you do rapid heating or rapid cooling then some kind of fracturing within the refractories may takes place.

So, such kind of fracturing or flaking of refractory should not take place. So, for that you know you need to consider rate of change of temperature for making refractories. How you decide it? Let us say you are making a glass in a furnace that we have already seen. So, at what heating rate are you melting the raw materials, at what temperature are you melting the raw materials and then at what temperature are you cooling them down all these things are important.

So, the rate of change of temperature is also essential otherwise fracturing or flaking of refractories may takes place ok. Then load applied during the heats for examples, most of the furnaces that are used for the chemical plants are batch wise right. So, how much load are you giving? Accordingly, the strength of the refractory should be decided.

So, for that you know this load applied is also very essential characteristic. And then load not in the cooling condition not in the normal condition, but the during the operating conditions or whatever the 1500 or 1600 or 2000 degree centigrades are you supplying the energy to the furnace for your process to occur.

So, at those conditions what should be the load applied, because at such conditions these raw materials may be in a melted conditions. And then their densities viscosities of those materials after melting may be very different compared to their densities and viscosities when they were taken as a raw materials at atmospheric conditions so, load applied during the heats is very essential.

Then chemical reactions to be occurring what kind of chemical reactions are occurring? So, this is both towards the product that you are going to make in furnace obviously, that is one and another one is that a reaction of a refractory with slag's or fuel gases or you know products etcetera such kind of reactions may also be occurring sometimes so, that is again very essential.

So, actually you should select a refractory such that it should not undergo any kind of reaction either with the slag's or fuel gases or the products that are formed in the furnace ok. If at all they are not avoidable and then what are those reactions, how to handle them, those kind of things you have to worry about.

Then obviously, now you see so many types of characteristics are there. All you expect to have all these characteristics in one type of refractory is not going to be possible. Even if it is going to possible technically, but economically it may not be possible. That is the reason any furnace you take it is not one single type of refractory that is used for the construction of a furnaces. But rather you know different types of refractories are used for construction of any furnace that you are operating right.

Now, that is the reason you know so many properties are essential to note while manufacturing of a refractories. It is very essential to understand the properties of a refractories those things we are going to see. Properties in the sense physical properties as well as the chemical properties right or you know during the chemical reaction what is happening all those things we have to see now.

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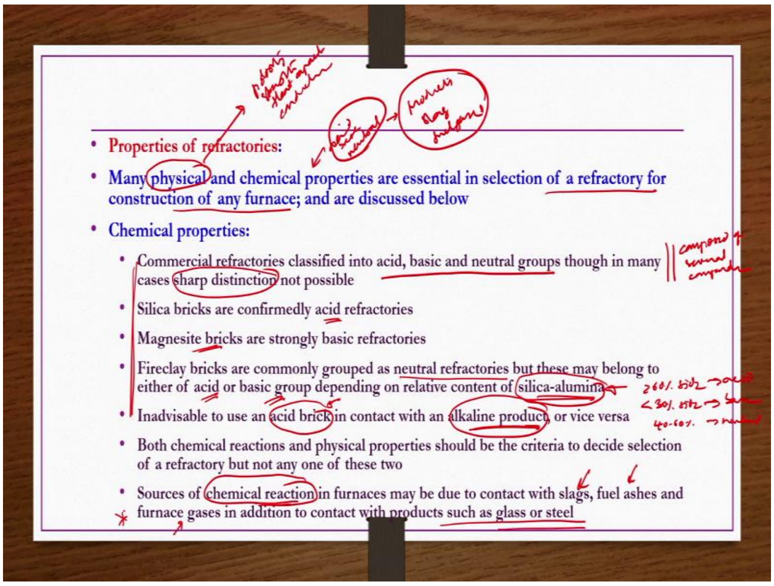

So, properties of refractories, many physical and chemical properties are essential in selection of a refractory for construction of any furnace and are discussed below. What do you mean by physical and chemical properties? Let us say you have a something like acid or base or neutral kind of refractory which one should you use. How is it going to interact with the products slag's or fuel gases etcetera within the furnace. So, those thing should also be considered so, that is what you mean by chemical properties.

Then what do you mean by physical properties? Physical properties in the sense what is the porosity, what is the strength, what is the heat capacity, what is the conductivity etcetera. These kind of things also you need to check in before you know making a decision about a given type for refractory needed for the construction of a given type of furnace with a certain applications ok.

So, let us start with chemical properties commercial refractories classified into acid, basic and neutral groups though in many cases sharp distinction is not possible. Why sharp distinction is not possible whether a given refractory is acidic or basic or neutral? Because, they are made up of several components composed of several components or compounds right.

So, that is the reason you know you cannot say it is completely acidic or basic something like that. For example, silica bricks are confirmedly acid refractories ok, likewise magnesite bricks strongly basic refractories. But, if you take fireclay bricks or commonly grouped as a neutral refractories, but these may belong to either of acid or basic group depending on the relative content of silica and alumina.

If it is having more silica more than 60 percent of silica, then you can say this is acid refractory kind of thing. If it is having less than 30 percent of silica, then you can say you know it is more like a basic kind of thing if it is a order of 40 to 60 percent silica and alumina combined then you can say this is a kind of neutral brick kind of thing.

That is the reason sharp distinction is not possible for a given refractory and whether it is acid or basic or neutral. Because these refractories are not made up of single component, but they are made up of multiple components and then one example of silica alumina is shown here ok. So, further it is inadvisable to use acid brick in contact with alkaline product or a vice versa.

If you are to handle alkaline products in a furnace, then that furnace should not be constructed with the acid brick ok. Both chemical reaction and physical property should be the criteria to decide selection of a refractory, but not any one of these two. Because, you know you see chemical nature so many issues are there. When physical nature it is coming about strength, porosity, heat, capacity, conductivity etcetera all those things you know so many properties are there.

So, when you decide to design a refractory for a given furnace construction so, then you should construct not only the physical properties, but also chemical properties. So, chemical properties we have seen now we will be seeing the physical properties also.

Now, as I mentioned the sources of chemical reactions in furnace may be due to contact with slag’s, fuel ashes and furnace gases in addition to contact with products such as glass or steel that are being produced in furnace. And then furnace is made up of this refractory so, then all these possible reactions are possible.

So, this chemical reaction does not mean that you know about the chemical nature of the refractory alone. How is it in contact with the slag’s, fuel ashes and furnace gases also like you know products like glass or steel etcetera that are produced in furnace all of them are coming into the picture. How these are interacting with the refractory materials in a chemical way that is essential here ok so, all these things should also be considered.

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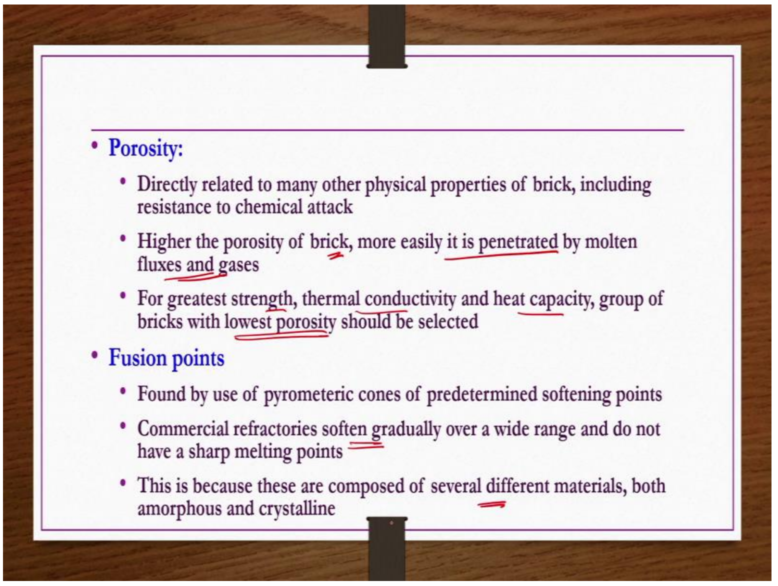

Now, we talk about the physical properties porosity, porosity is very essential part of the refractory, why it is very essential part of the refractory? Because any refractory that you are making you are going to take a 2, 3, 4, 5 raw materials depending on the type of refractory you are making. Some of the refractories may be having dozens of raw materials may be 1 or 2 may be predominant and remaining of them may be little components small amounts may be there right, but there may be.

So, when you mix together there should be some kind of plasticity so, that to combine the particles bind it together. So, for that purpose you know sometimes you use water to improve the workability or plasticity and then you mold them in a pressing molds and then you get a brick out of it out of it. After mixing this raw materials, water etcetera, you have a workable moldable slurry for mixture that you taking in a molding caseins and then you are getting a brick ware wet brick ware out of this one.

Now, so, much of water is there and then when you dry this brick this water would be evaporated dehydration will be taking place. When this water is being removed by the dehydration there will leave porous structure in the refractory. And then lot of porous structure if it is there in the brick then what happened and then such bricks if you are using for the construction of furnace.

And then during the reaction let us say glass you are making in that furnace and then refractories so much porous right. Then what happens the furnace gases and some amount of slag’s etcetera may also be you know going into the porous structure of the refractories.

So, once these gases and then other foreign materials getting into the porous structure or interstitial spaces of the refractories. Then the strength of those refractories with gradually decrease and then life of the furnace would be very less ok. So, for construction of any furnace you need to have a denser or least porous you know refractories are required.

If you are using refractories for insulation purpose, then there you can have a porous refractories but furnace construction if you are using refractories, then these refractories must be non-porous or least porous. Porosity directly related to many other physical properties of brick that including resistance to the chemical attack strength etcetera.

Higher the porosity of brick, more easily it is penetrated by the molten fluxes and gases. Once these are getting penetrated into the porous structure of the brick or refractory, the strength of the refractory is going to decrease gradually and then life of the furnace will substantially decrease. Thus, for greatest strength thermal conductivity and heat capacity, group of bricks with lowest porosity should be selected ok.

Next is the fusion points, fusion is important so, that to keep particles together, but that fusion should not occur during the operation. During the operation in the sense after constructing the furnace and then some product is being manufactured in the furnace glass or steel. And during the manufacturing of those glass and steel kind of products in the furnace these refractories should not undergo fusion ok.

So, fusion points found by use of pyrometric cones of predetermined softening points. Commercial refractories soften gradually over a wide range and do not have a sharp melting point that is one way good. This is because these are composed of several different materials both amorphous and crystalline.

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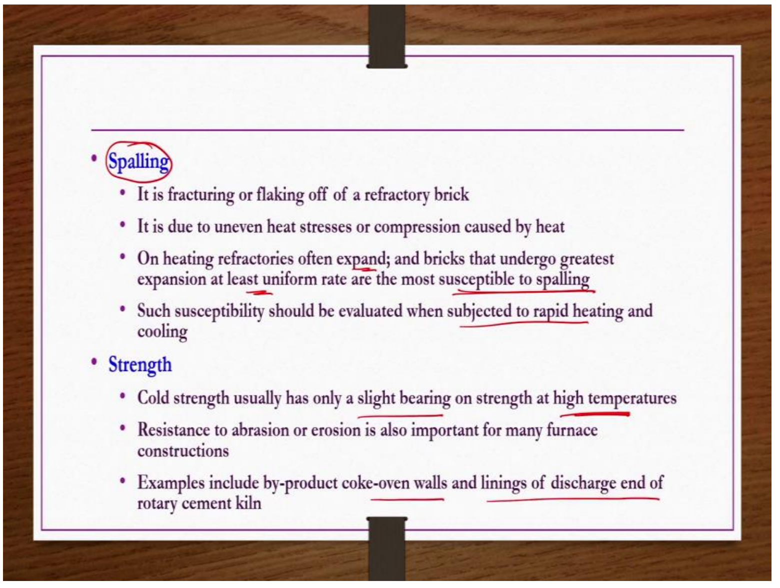

Next is the spalling, spalling is nothing but you know when you make a refractory or a brick which is a porous. And then when you allow it to affected by a rapid heating or rapid cooling and then that also at high temperature heating up to 1500 or 1600 degree centigrade and then heating at a very rapid pace. And then once the product has formed you know cooling it at the rapid pace.

If you do then what happens if the brick or refractory is not very dense enough, then what happen internal fractures may takes place inside the refractories or flaking of the refractories may also takes place. Such kind of fracturing or flaking of because of the rapid heating or cooling whatever occurs is known as the spalling.

It is fracturing or flaking of a refractory brick, it is due to uneven heat stresses or compression caused by heat. On heating refractories often expand and bricks that undergo greatest expansion at least uniform rate are the most susceptible to spalling ok. So, then you should have a construction material for the refractory which is having low thermal expansion coefficients, such susceptibility should be evaluated when subjected to rapid heating and rapid cooling.

Next one is the strength cold strength usually has only a slight bearing on strength at high temperatures. Resistant to abrasion or erosion is also important for many furnace constructions. Examples include byproduct coke oven walls and linings of discharge end of rotary cement kiln etcetera.

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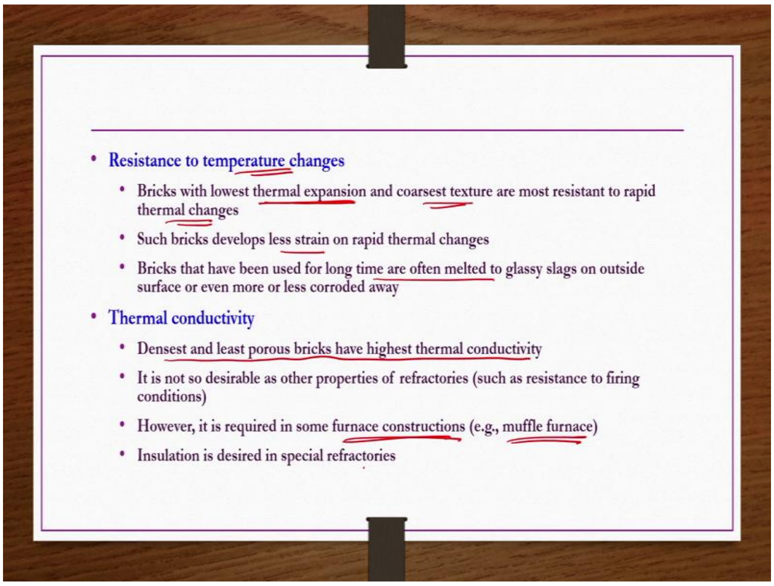

Now, resistance to temperature changes is another important physical property because temperature changes that is the heating rate, how rapidly temperature is changing while heating or while cooling is very much essential. The material should have resistance to such kind of temperature changes otherwise spalling may takes place. Bricks with lowest thermal expansion and coarsest texture are most resistant to rapid thermal changes right.

So, you should as I mentioned already you should have material which is having lowest thermal expansion so, that to make bricks also or refractories also with lowest thermal expansion. And then coarsest texture also another important thing is the porosity, least porosity is also the one which provide a resistance to rapid thermal changes.

Such bricks develop less strain on rapid thermal changes bricks that have been used for long time are often melted to glassy slag's on outside surface or even more or less corroded away anyway. Thermal conductivity is not that important however, densest and least porous bricks have highest thermal conductivity ok. But in the case of some furnaces, furnace construction like muffle furnaces then thermal conductivity is also very important to consider. Insulation is desired in special refractories only not for all.

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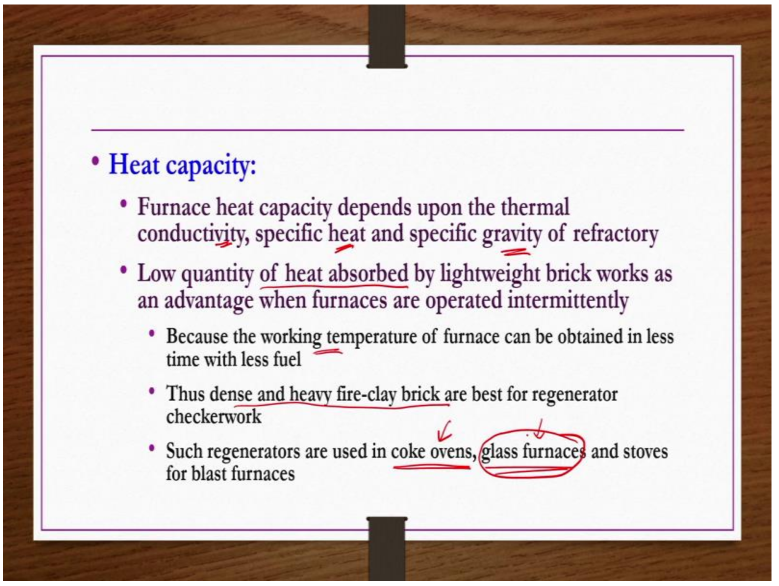

Now, the last important physical property of refractories is heat capacity. Furnace heat capacity depends upon thermal conductivity, specific heat and specific gravity of refractory. Low quantity of heat absorbed by lightweight brick works as an advantage when furnaces are operated intermittently, because the working temperature of furnace can be obtained in less time with less fear.

Thus, dense and then heavy fire clay brick are best for regenerator checker work refractories. Such refractories have been used for making generators which are used for coke ovens, glass furnaces and stove for glass furnaces steel making etcetera for those purposes. In fact, such checker work, regenerator we have seen in glass furnaces while discussing about glass industry now, we talk about manufacture of refractories.

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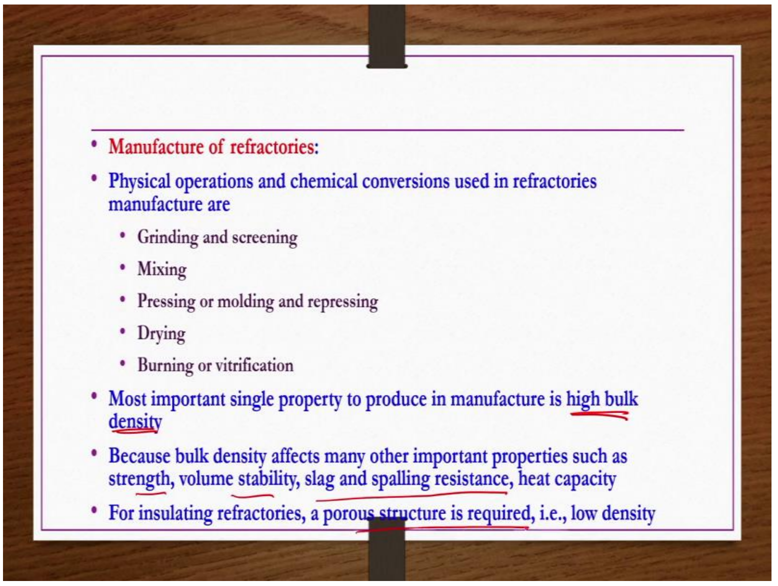

Physical operations and chemical conversions used in refractories manufacture are listed here. Most of them are common with any of the ceramic industries like something like you know grinding and size reduction, screening, mixing, pressing or molding and repressing drying and finally, burning or vitrification or firing.

So, what do you expect to have the most important property in the refractories as per the physical and chemical properties that we have seen is the high bulk density. If you have high bulk density most of the other physical properties are you know naturally maintained ok. So, because bulk density affects many other important properties such as, strength, volume stability, slag and spalling, resistance, heat capacity etcetera.

For insulating refractories anyway a porous structure is required that is low density material you can use, but for the furnaces definitely you look at it high bulk density refractories. So, we see individual steps of a refractory making, let us start with the grinding. Grinding is nothing but size reduction of the particles so, that you need to have a specialized or required size of the particles in the mixture.

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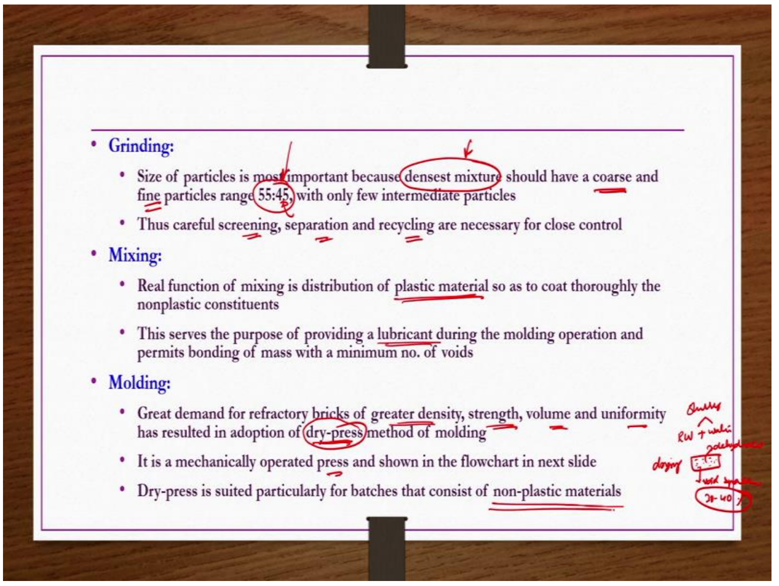

It has been found that you know if you have coarse and then fine particles in the ratio of 55 to 45 that is going to give a densest mixture right. So, you have to do the size reduction such a way that you get 55 percent of the material should be having coarse size and then 45 percent of the material having the fine size approximately ok. And then few intermediate particles are anyway unavoidable.

Why this ratio because if you have coarsest particles so, the interstitial spaces are bigger. So, in those interstitial spaces or the void spaces the final particles will go and then stick there so, then occupy those interstitial spaces forming because of the coarse particles. So, then what happens, because of that one you know density or the void space in decreases.

So, what happens because of such occupying of fine particles in the interstitial spaces between the coarse particles that will reduce the void space. If the void space is reduced then obviously, density would be higher. Thus, careful screening, separation and recycling are necessary for close control. Next one is the mixing, mixing usually is done to mix the raw materials along with the water little bit of water so, that to have a required plasticity or workable conditions of the mixture.

So, real function of a mixing is distribution of plastic material so, as to coat thoroughly the non-plastic constituents. This serves the purpose of providing a lubricant during the molding operation and permits bonding of mass with a minimum number of voids. Next step in the manufacturing is the molding. Great demand for refractory bricks of greater density, higher density that is strength, volume and then uniformity has resulted in adaptation of dry press method of molding.

Because you know if the slurry which is you know mixture of raw materials after size reduction etcetera and then water you take it. And then if it is very wet then and then dry it by open drying or other kind of drying methods whatever we have seen. So, this water gets dehydrated and then removed while the drying process, but they leave void spaces so, leave the void spaces.

These void spaces you know if they may be up to 30 to 40 percent as per our fluid mechanic studies related understanding right. So, if such percentage of voids are there so, then you cannot have a dense brick. So, that is the reason people started new method dry press method where only nominal amount of water is only used for the you know mixing purpose and then only dry pressing is been done.

It is a mechanically operated press and shown in the flowchart in the next slide we are going to see. Dry press is suited particularly for batches that consist of non-plastic materials ok.

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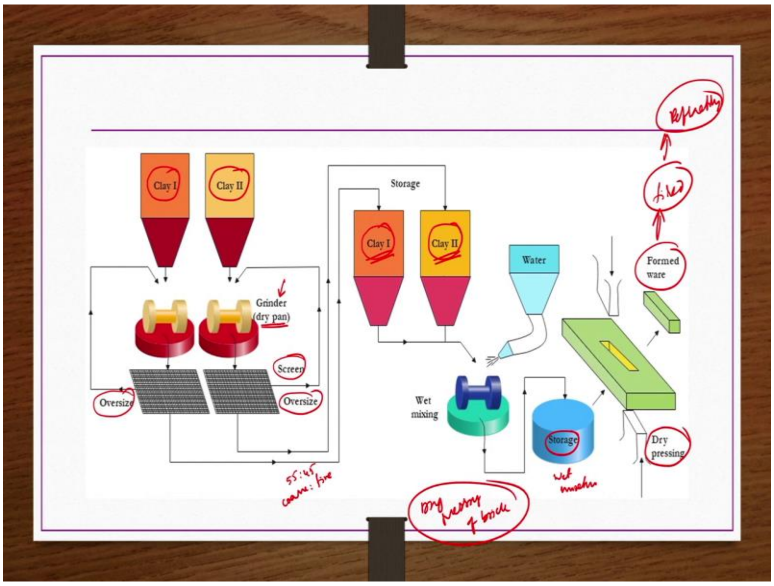

Now, this is the flowchart, the crude clay mixtures whatever clay 1, clay 2 etcetera are required for refractive materials. They are taken in halos or silos, then they have been grinded using dry pan grinders. So, that to get a particles of size 55 to 45 you know goes to fine particles and then such particles you separate out using the screen. If at all oversized particles are there you take back to grinding section ok. Whereas the particles of desired section they are taken to product particles storage.

These are not the product final product, in size reduction screening methods whatever the final particles of specified size as per the requirement are there they are also called as a product. So, that product particles are taken or the product clays are taken in separate you know containers in silos or hopper something like that. Then they will be you know mixed together along with some amount of water and then wet mixing would be done so, that a slurry can be made.

Slurry it is not it should not be slurry it is a kind of you know wet mixture just a wet mixture and then that is taken to a storage. And then that mixture is undergoes a dry pressing method to get a formed ware, this will be further fired to get a refractive. So, this is the dry pressing method dry pressing of brick or refractories ok, now, we see remaining steps of this refractory manufacturing.

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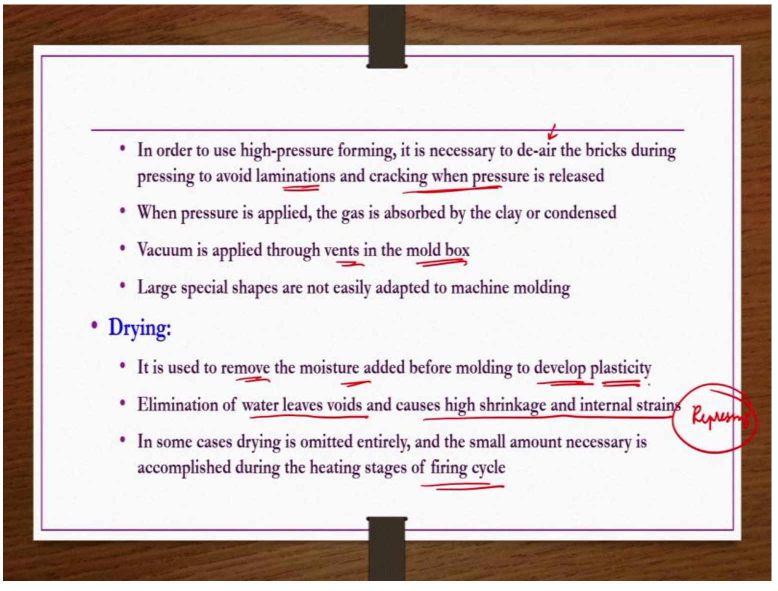

In order to use high pressure forming it is necessary to de-air actually you know the air is whatever are forming because of using little amount of water that is also should be removed. Actually whatever the wet mixture that you are taking so, in that one you know when pressing is done. So, still some kind of voids may be formed and then those voids may be occupied by the air.

So, those air gaps are you know voids occupied by the air you know should be provided in the deep pressing section itself and provision to remove that air as well that can be done by the vacuuming. So, that when you do the dry pressing along with the vacuum provision so, then you get a product or you know brick ware which is having as much denser as possible. This de-airing also helps in avoid laminations and cracking when pressure is released ok.

So, when pressure is applied the gas is absorbed by the clay or condensed. Vacuum is applied through vents in the mold box or in the dry pressing boxes that we have seen. Large special shapes are not easily adapted to machine molding in general so, next step is drying. It is used to remove the moisture added before molding to develop plasticity ok.

Elimination of water leaves voids as mentioned and causes high shrinkage and internal strains so, in order to avoid this one repressing is done sometimes right. In some cases, drying is omitted entirely and the small amount necessary accomplished during the heating stage of fire cycle or otherwise repressing is also done as per the requirement.

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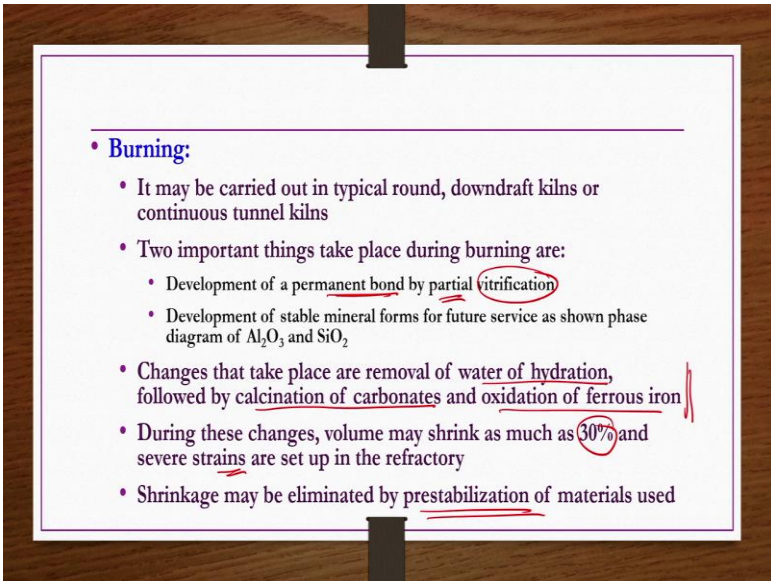

Last step of manufacturing of refractories is burning, here it may be carried out in typical round down draft kilns or continuous tunnel kilns as well. Two important things take place during the burning are development of permanent bond by partial vitrification ok. Vitrification is cannot be avoided because there are fluxes, but we had made sure that these fluxes are in minimum amount So, partial vitrification is taking place and then that cannot be avoided.

Development of stable mineral forms for future services something like you know mullite formation etcetera those things we have seen in phase diagram of alumina and silica. Changes that take place are removal of water of dehydration followed by calcination of carbonates and then oxidation of ferrous iron these are the common steps, any of the ceramics production as we have already seen in previous lectures also. During these changes volume may shrink as much as 30 percent and severe strains are set up in the refractories ok.

Shrinkage may be eliminated by pre-stabilization of materials used. So, whatever the raw materials that you are taking you do a kind of pre-stabilizations of such materials before making this wet mixture and then before undergoing these dry pressing steps etcetera. Ok. Now, we have seen the manufacturing of a refractories also after discussing about their properties now, we will see varieties of refractories.

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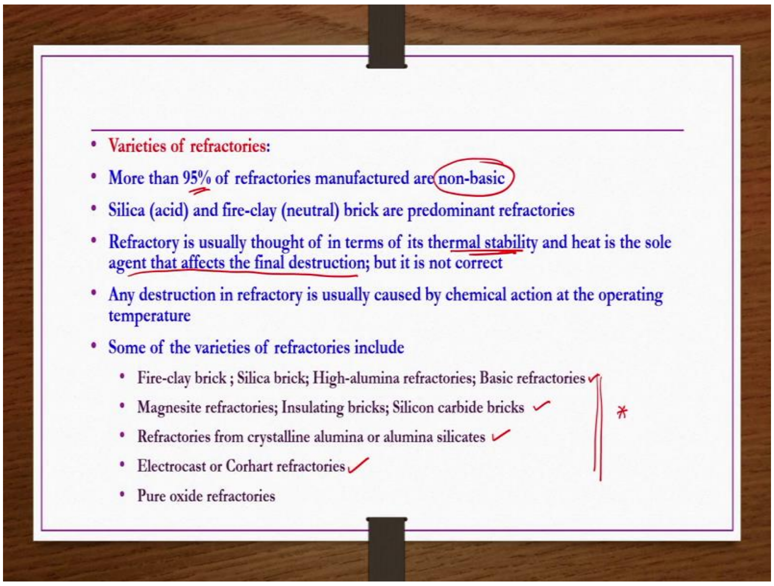

More than 95 percent of refractories manufactured are non-basic that is majorly acidic and neutral bricks are predominant as refractories ok. Refractory is usually thought of in terms of thermal stability and heat is the sole agent that affects the final destruction if at all occurring. But that is not true. It is the chemical reaction, chemical reaction between refractories and then slag's, glass slag's or steel slag's etcetera the furnace gases, furnace ashes etcetera with those whatever the reactions and this refractories are undergoing.

They are the main cause of any destruction of a refractories in the furnaces, but not the heat not because of heating at high temperatures ok. Some of the refractories include are you know fire clay brick, silica brick, high alumina refractories, basic refractories, magnesite refractories, insulating bricks, silicon, carbide bricks refractories from crystalline alumina or alumina silicates, electrocast or corhart refractories etcetera.

So, their manufacturing etcetera again specific to individual you know material that is being manufactured, but we are not going into the details of that one. As we have seen or we are discussing generalized aspects of any of the ceramic products given for other cases also.

So, here also a generalized approach of refractory making we have seen. We are not going into the details of a manufactured of any of the specific type of refractory. So, that is all about the refractories, raw materials, properties of refractories, manufacturing of refractories and then varieties of a refractories.

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Now, we discuss about the next topic that is specialized ceramic products, as the name suggests they are specialized, they are designed and constructed or manufactured for specialized applications only. So obviously, they will not be available in large amounts or large volumes.

However, their market value would be sufficiently high, because they have been designed and then produced for a specialized applications. So, these specialized ceramic products may be grouped as ceramic composites, ferroelectric and ferromagnetic ceramics and high alumina ceramics. We are going to discuss about each of these three types of specialized ceramic products.

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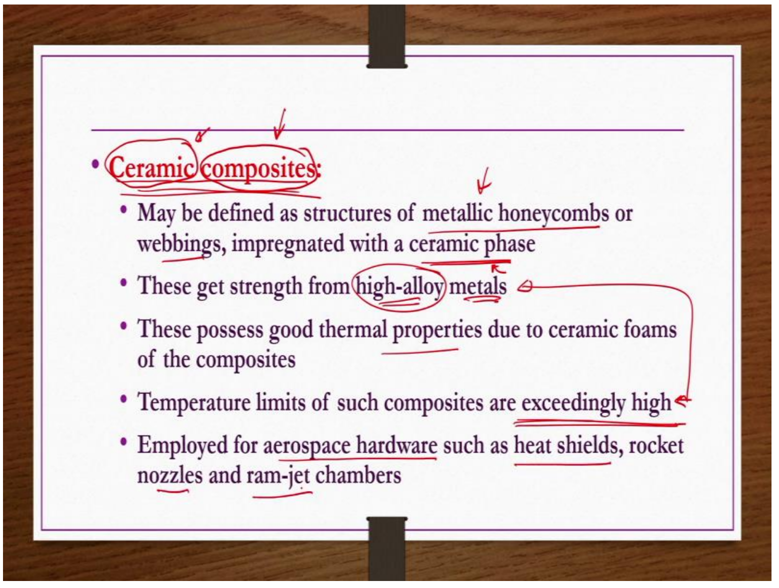

Let us start with ceramic composites, as the name suggests composites ceramic composites. So, then here you have the ceramic portion is anyway there and then it is being composited by adding some other material something like metal or metal oxides ok. So, these may be defined as a structures of metallic, honeycombs or webbings, impregnated with a ceramic phase.

So, we have a ceramic phase and then we have a metallic phase and then a kind of a composites are being formed. Similar like you know if you take a polymer, individual polymer if you take it might not be having the enough strength or you know properties of design or physical or mechanical strength right. But, if you make a composites of polymers then obviously, it has been found that their strength is better than individual polymers themselves right.

Similar concept maybe we can thought of here in ceramic composites also. However the ceramic composites were developed well before the polymeric composites. These get strength from high alloy metals, because when you have impregnation so, then strength may not be good. But strength may be coming here in the ceramic composites, because high alloy metals these metals and then also high alloy metals are there so, then they usually have the you know superior strength.

These processes good thermal properties due to ceramic forms of composites. Temperature limits of such composites are exceedingly high, why because these are made up of metals and ceramics and these metals are high alloy metals. These high alloy metals are having you know thermal stability of you know more than 2000 degree centigrade sometime or even higher also. Employed or developed for applications in aerospace hardware such as heat shields, rocket nozzles and ramjet chambers etcetera.

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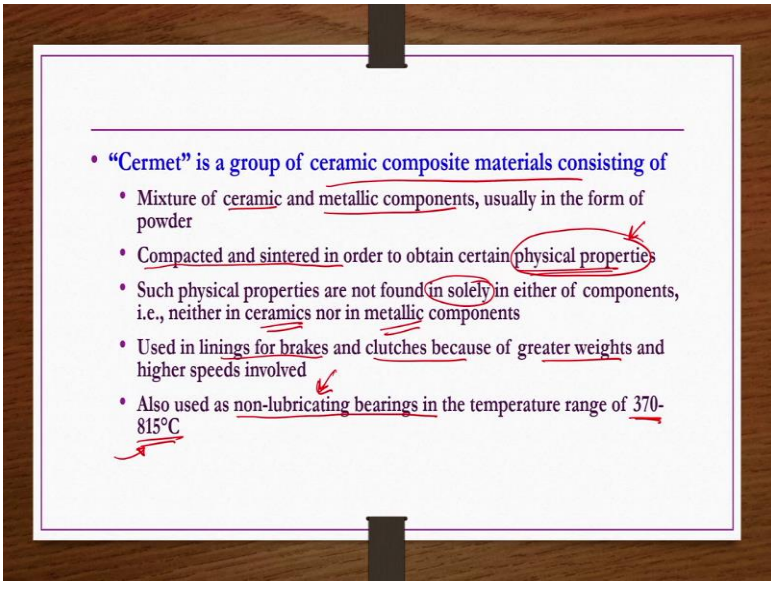

Now, we take a special type of a ceramic composite which is known as cermet. It is a group of ceramic composite material consisting of mixture of ceramic and metallic components usually in the form of powder. These mixture of a ceramic and metallic components in the form of powder whatever you have taken, they usually compacted and sintered in order to obtain certain physical properties of requirement of the consumer.

Such physical properties are not found in solely in either of the components neither in ceramics nor in metallic components. If you individually take ceramics whatever the physical properties are there and then if you take individually metallic components whatever the physical components are there you know then they may not be of certain importance.

But when you make this cermet or ceramic composite called cermet then you get a ceramic composite which is having you know unusual physical properties ok. These are used in linings for breaks and clutches because of greater weights and then higher speeds involved. Further also used as non-lubricating bearings in the temperature range of 370 seventy to 815 degree centigrades.

Any lubrication if you take and then apply at such high temperature they will be dried up, but these provide such non-lubricating bearings. You know, you definitely you need bearings and then for those you need some you know lubrication, but when you use this thing you do not need any lubrications.

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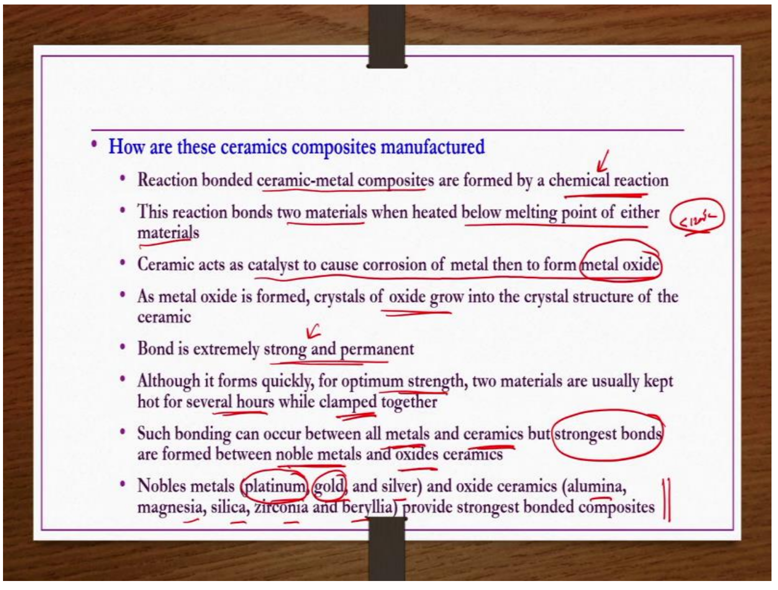

Then how are these ceramic composites are manufactured so obviously, natural intuitiveness tell us you have to make individually ceramics, you have to make individually metals and then you have to do some kind of thermal processing to get these ceramic composites so, but however, we see step by step. So, these are obviously, reaction bonded and then reaction is bonding ceramic and metal composites ok.

So, that whatever the bonding is there between the ceramic and metal composites are there they are formed by chemical reactions ok. This reaction bonds two materials when heated below melting point of either of the materials. Let us say ceramic is having melting point of a 1200 degree centigrades and then metal is having a melting point of a 1800 degree centigrades. So, you have to melt them at temperature less than 1200 degree centigrades ok.

Ceramic acts as catalyst to cause corrosion of metal then to form metal oxides. As this metal oxides forming, then what happens crystals of oxide grow into the crystal structure of the ceramic and then forms a ceramic composite ok. And then this bond formation whatever is there that is not only quick, but also it is extremely strong and permanent.

Once the bond is formed you cannot remove two materials individually, you have to break them destroy them ok. Although it forms quickly for optimum strength two materials are usually kept hot for several hours while clamping together chemically. This clamping is not physical it is a like just like a bonding like a chemical bonding.

Such bonding can occur between all metals and then all ceramics, but if you wanted to have strongest bonds it has been formed between noble metals and then oxide ceramics you can get a strongest bonds. Noble metals such as platinum, gold and silver, oxide ceramics such as alumina, magnesia, silica, zirconia and beryllia they provide strongest bonding it has been formed later.

However, you can take any metal any ceramic oxide right and then you can make a ceramic composite that is possible, but the bond has to be strong and then strength has to be higher so, then you have to opt for such kind of material ok. And then these are producing small quantity, small numbers because they are specialized ceramic products ceramic composite.

So, then they are developed for specialized application only so. Even if you are using you know noble metal like platinum, gold etcetera it is not going to be affecting economically. Because, you are getting money back, because they had developed or designed and then constructed for the specialized application purposes.

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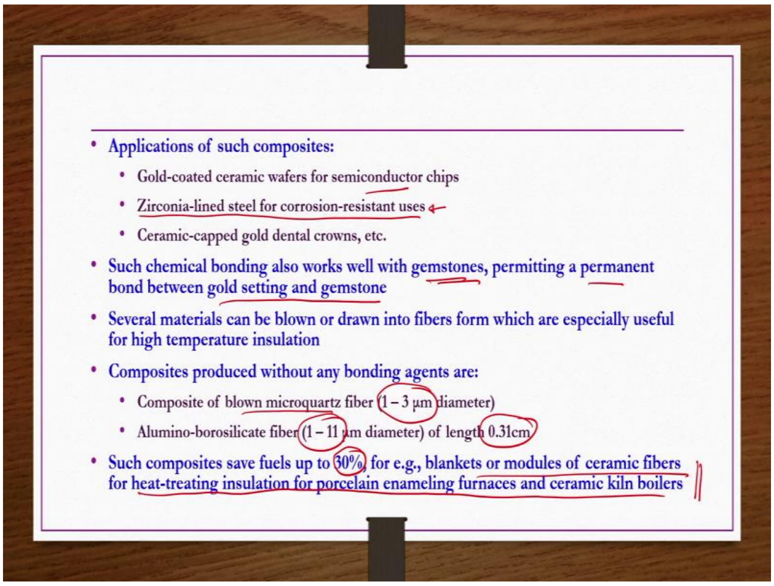

We see what are those applications? Gold coated ceramic wafers for semiconductor chips, then Zirconia-lined steel for corrosion resistant uses especially for a chemical plants then ceramic capped gold, dental crowns etcetera. Such chemical bonding also works well with gemstones, you might have seen several gold ornament with gems right. So, these gemstones are you know made as a composite along with the gold ok.

So, such kind of you know chemical bonding happens between these gemstones and then gold as well. They will be providing a permanent bond between gold setting and then gemstone and then you have a proper ornament and then you cannot remove them. They will not be detached at any time, it may be for years or decades. If at all you have to recover the gold from the gemstone then you have to melt it and then recover it, such strong and permanent is the bond between these metals and ceramics.

Several materials can be blown or drawn into fibers form which are especially useful for high temperature insulation. We can see that you know these are formed in a small small quantity, small small sizes, one or two examples we see now here. Composite produced without any bonding agents are composite of blown micro quartz fiber having just diameter 1, 2, 3 microns only. Similarly, Alumino borosilicate fiber having 1 to 11 micron diameter and then length you see only less than 30 mm ok.

Such composite save fuels also up to 30 percent fuel saving is done if at all if you let us say if you take a Zirconia lined steel for corrosion resistant such equipments you know in chemical plants if you use. So, then you know it saves fuels also for example, blankets or modules of ceramic fibers for heat treating insulation for porcelain enameling furnaces and then ceramic kiln boilers etcetera. So, if you have such kind of composite material for construction of these equipment you can save the fuel up to 30 percent.

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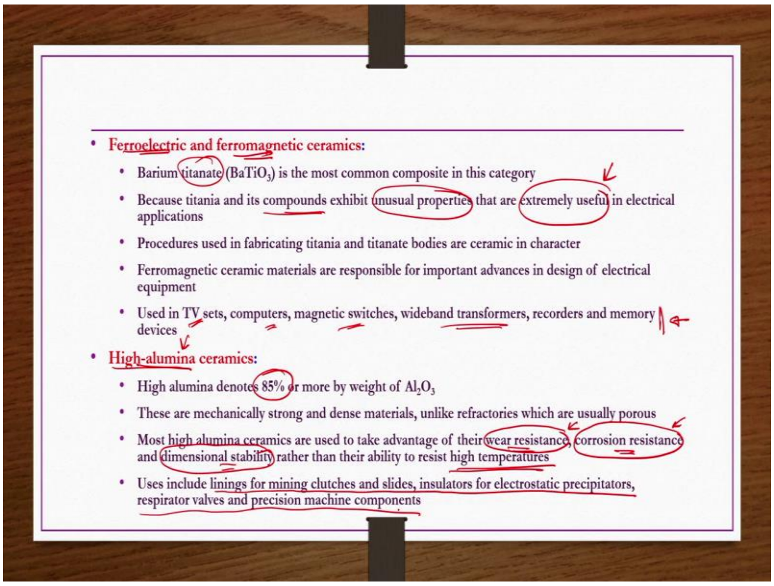

So, this is all about ceramic composites now, we go to the second category of the specialized clay products that is ferroelectric and ferromagnetic ceramics. Obviously you can see ferroelectric and then ferromagnetic titles. So, then that means, they are going to have or they must have been found at having great applications in electric design say equipment ok.

So, barium titanate is the most common composite in this category, because whatever the making of titanium and its components. You know its going to have a unusual properties that are extremely useful in electrical applications, whatever the titania and its components there they exhibit unusual properties. We may not be knowing from electrical engineering point of view, but it has been found that these unusual properties are extremely useful in electrical applications.

For that reason, these ceramic products or ceramic composites are placed in specialized ceramic products. Procedures used in fabricating titania and titanate bodies are ceramic in character. Ferromagnetic ceramic materials are responsible for most important advances in design of electrical equipment. These are used in TV sets, computers, magnetic switches, wideband transformers, recorders and memory devices etcetera.

Now, you see how much important these application these you know. They are not produce in tons and tons, they are produce in small quantities, but their application you see very much essentially in a present day's context view point of view. In present day's context point of view, these are very much important applications ok.

Last category of this specialized ceramic products is high alumina ceramics. High alumina in the sense alumina is present in the high quantities, but how much is high, more than 85 percent you know by weight if you have in the ceramics. Then that refractory whatever or that ceramic product whatever you are having that you can call it as high alumina ceramics.

These are mechanically strong and dense materials unlike refractories which are usually porous. Most high alumina ceramics are used to take advantage of their resistance, actually advantage of this high alumina ceramics are you know not their resistance to the high temperature, but their wear resistance. Their resistance towards the corrosion and then dimensional stability, in all three dimensions they almost remain stable at the applied temperatures or at the operating conditions ok.

So, they do have high thermal resistance, but these are known for the other properties. Because, other ceramics etcetera may be having the thermal resistance much better than this high alumina ceramics, but these high alumina ceramics are good at other properties like wear resistance, corrosion resistance and dimensional stability.

Uses include linings for mining clutches and slides insulators for electrostatic precipitators, respirator valves and precision machine components etcetera. So, this is all about the specialized ceramic products, now, the last topics of ceramic industry that we are going to discuss is vitreous enamel.

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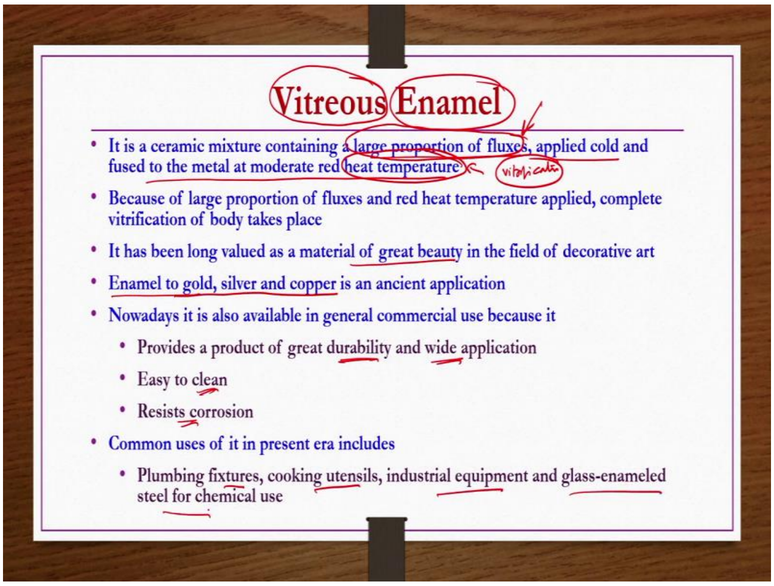

When the name indicate vitreous that means, fluxes would definitely be there and then vitrification must be taking place ok. So, we have to see how much important vitrification is required and then how this enameling is being done those things we are going to discuss. It is a ceramic mixture containing a large portion of fluxes applied cold, but fused to the metal at moderate red heat temperatures.

So, when you have large proportions of fluxes ok and then heating it moderate red heat temperature that means, high temperature. Then obviously, what will happen? Vitrification takes place, high vitrification or complete vitrification may takes place. Because, if the fluxes present in the large proportions, if the fluxes are there definitely vitrification takes place. If they are present in the high proportion and then heated at very high temperature then complete vitrification definitely will take place ok.

And then such vitreous enamel has been long valued as material of great beauty in the field of decorative art. In ancient days enamel to gold, silver, copper is found to be you know very precious kind of material ok so, that is one of the oldest application you can see ancient application of this vitreous enamel.

Nowadays it is also available in general commercial use because of a it is durability and then wide applications. In addition, it is easy to clean and then it resists corrosion which is very much essential. Common uses of it in the present era includes plumbing fixtures, cooking utensils, industrial equipment and glass enameled, steel for chemical use etcetera.

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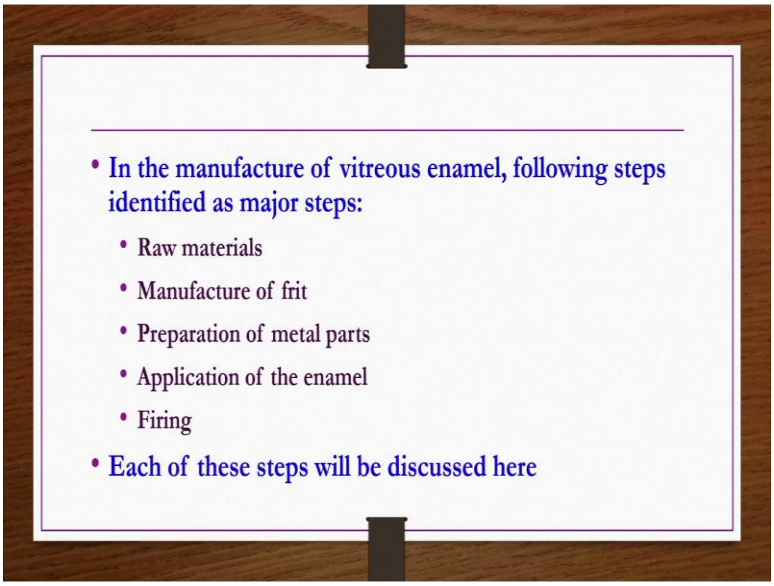

Now, we see what are the important steps in the manufacturing of this vitreous enamels. Raw materials are the very important steps, we understand that clay, feldspar and then sand, flint etcetera are anywhere raw materials, but important raw materials. But in addition to that one there are some other raw materials which are specifically required for either enameling or for you know vitrification. So, those what are they we are going to discuss in the part of raw materials.

Then manufacturing of frit, preparation of metal parts, then application of the enamel to the metal parts and then finally, firing.

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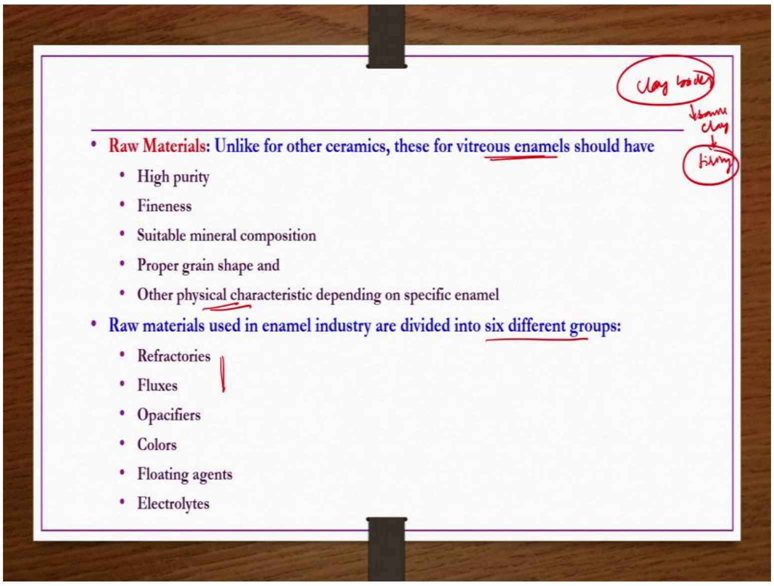

So, let us start discussing about each of these five important steps of a vitreous enamel making. First one is the raw materials, unlike for other ceramics these are vitreous enamel should have. When you are doing the vitreous enamels, then you know they should be fine enough, they should be high purity like let us say, you know clay bricks you are making.

So, directly from the bank you can take clay and then fire it in the setup so, then you get the bricks. But if you wanted to make vitreous enamels you know high purity is very much essential and then fineness is also very much essential and then suitable mineral composition is required. Composition something here and there, then gone you do not get the required material that is having proper corrosion, resistance etcetera ok.

Proper grain shape is also required in addition to these properties depending on the vitreous enamel that is being produced there may be special other physical characteristics may be there so, all those things are important ok. So, raw materials used in enamel industries are divided into six different groups.

Two groups are very common for any of the ceramic product they are nothing, but refractories and fluxes. In addition to these two types of materials you also need to have opacifiers, colors, floating agents and then electrolytes.

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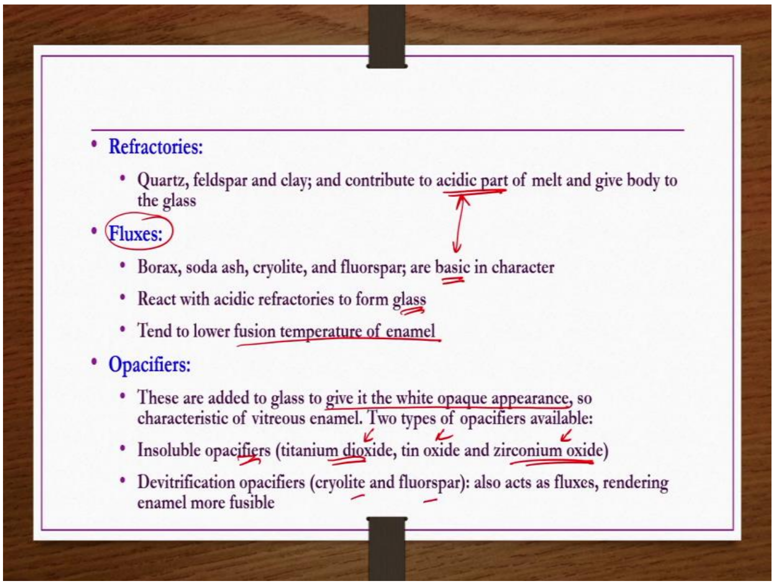

We see what are they? Refractories are same like whatever we had for other ceramic products like quartz, feldspar and clay and they contribute to acidic part of the melt and give body to the glass. Fluxes, borax, soda ash, cryolite and fluorspar etcetera these are the common fluxes and then they are also common for other types of ceramic products, but these are basic in nature.

So, then they interact with the acidic part of refractories and then form glass ok. These are also tend to lower the fusion temperature of enamel as the basic characteristics of the fluxes is the reducing the reaction temperature and then keeping the particles binded together. Opacifiers, these are added to glass to give it the white opaque appearance so, characteristics of vitreous enamel.

And then two types of opacifiers are available insoluble opacifiers like titanium dioxide, tin oxide, zirconium oxide. Now, see here zirconium oxide is also a flux right, titanium dioxide is also used as a color so, some of them are you know having multiple characteristics right. So, now titanium dioxide may be used for the color purpose as well as for the you know fluxing purpose as well as the opaque nature purpose.

Whereas the zirconium oxide they it can also be used as a kind of a not only opacifier, but also for the refractory purpose. So, some of these materials having more than one characteristics of requirement of final product. Other type of opacifiers are devitrification opacifiers, they are cryolites, fluorspars, they also act as fluxes which rendering enamel more fusible ok.

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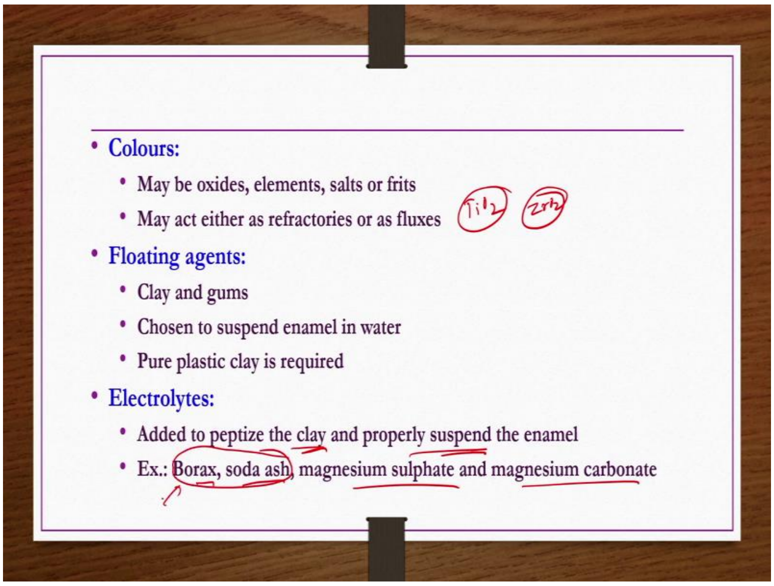

Colours may be oxides elements, salts or frits may act either as refractories or as fluxes. As I said titanium dioxide you, know it can be acted as you know colour as well as you know it can be acting use as fluxes also similarly, zirconium oxide etcetera these kind of thing. Floating agents, clay or gums are used as floating agents, chosen to suspend enamel in water, pure plastic clay is required.

Electrolytes added to peptize the clay and properly suspend the enamel example, borax, soda ash magnesium sulphate and magnesium carbonate. See now these borax and soda ash they are also fluxes they are also used for the electrolyte purpose as well ok. Now, we see the next step of a manufacturing of vitreous enamel first step is the raw materials that we have seen. The second step is manufacturing of frit.

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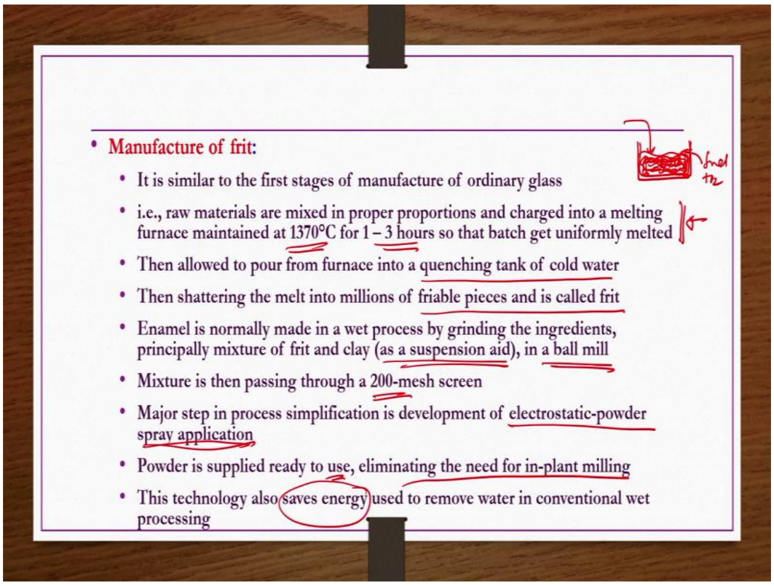

So, it is similar to the first stage of manufacture of ordinary glass. Ordinary glass what you do whatever the raw materials are there you take in a furnace and then you supply fuel and then oxygen. So, that the burning of fuel takes place and then heat would be supplied to these raw materials and then these raw materials would be melted.

And then this process you do for sufficiently higher time so, that the melting is uniform. It should not be like that melted at some location and then other locations it may not be properly melted. No, that can happen because in the furnace your temperature may not be uniform everywhere. It may be higher at the center at the walls it may be lower. There may be temperature gradients etcetera.

So, in order to have a proper uniform melting of the material, what you have to do? You have to allow them to melt for sufficiently longer time ok. So, here raw materials are mixed in proper proportions and charged into a melting furnace maintained at 1370 degree centigrade for 1 to 3 hours so, that batch get uniformly melted. Then allow to pour from furnace into a quenching tank of cold water, then shattering the melt into millions of friable pieces and is called frit.

Now, these steps whatever you know this melting all these things it is same like a glass making ordinary glass making like that only we are doing here also ok. Enamel is normally made in wet process by grinding the ingredients, principally mixture of frit and clay. Clay is used as a suspension aid only and then this is done in a ball mill.

Mixer is then passed through a 200 mesh screen so, that to see that size should not be more than 200 mesh screen ok. Oversize are sent back and then crushing all that process again, recycling process one has to go through. Major step in process simplification is development of electrostatic powder spray application ok. Powder is supplied ready to use eliminating the need for in plant milling etcetera. This technology also saves energy used to remove water in conventional wet processing.

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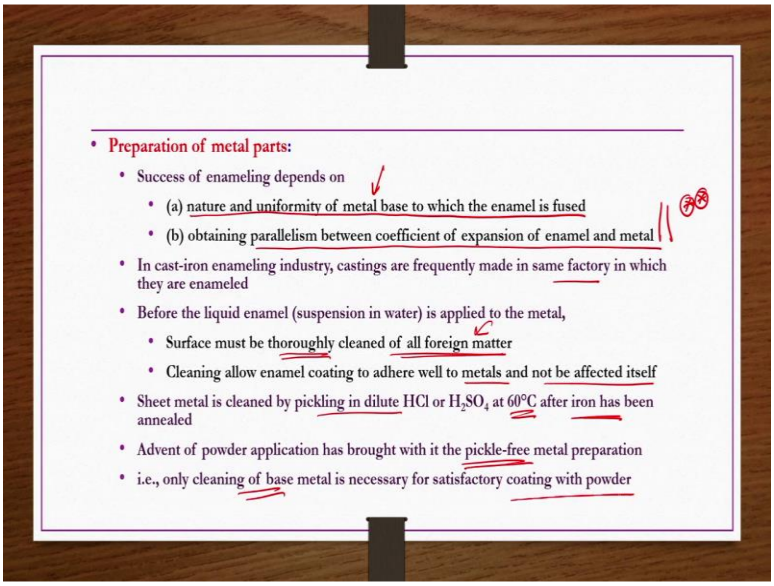

Next step of manufacturing of vitreous enamel is the preparation of metal parts, how do you prepare them. Success of enameling depends on nature and uniformity of metal base to which the enamel is fused. This metal base whatever is there that has to be clean enough, if it is clean enough then only enameling can be done properly ok.

Then second one is the obtaining parallelism between coefficient of expansion of enamel and metal. See the thermal expansion coefficient is very much important in any of the ceramic composites. Because these materials are having different thermal expansion coefficients then what happens? When you apply high temperature, they may not be attached or you know bonded together rather you know one of them may be flaking of kind of thing or shrinkage or internal strain formation may takes place.

That is the reason when you make a composite the material mixture whatever is there a basic constituents whatever you take they should have a thermal expansion coefficient of the same order ok. In cast iron enameling industry castings are frequently made in same factory in which they are enameled. Further before the liquid enamel is supplied to the metal, surface must be thoroughly cleaned of all foreign material then only proper bonding will take place.

Cleaning allow enamel coating to adhere well to metals and do not affected itself. Sheet metal is cleaned by pickling in dilute acids at 60 degree centigrade after iron has been annealed. Advent of powder application has brought with it the pickle free metal preparation method that is only cleaning of base metal is necessary for satisfactory coating with the powder.

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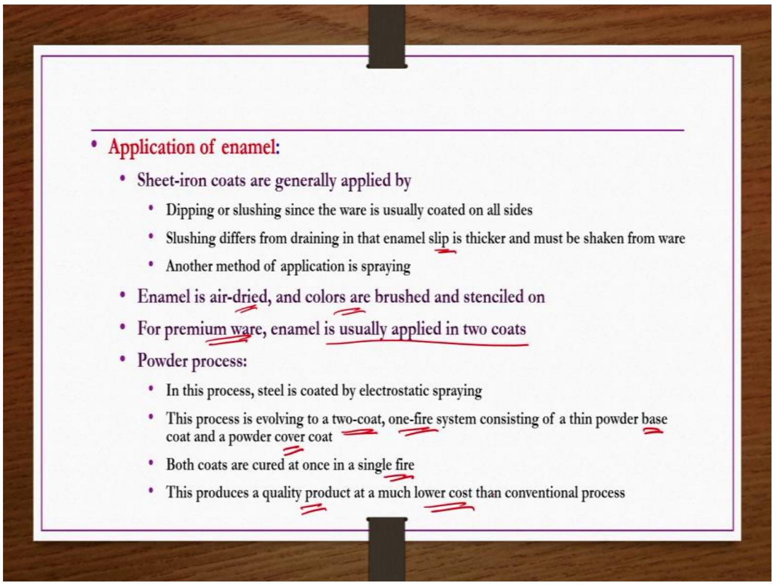

Next step of a vitreous enamel manufacturing is application of enamel. Sheet iron coats are generally applied by dipping or slushing since the ware is usually coated on all sides. Slushing differs from draining in that enamel slip is thicker and must be shaken from ware. Another method of application is spraying, enamel is air dried and colors are brushed and stenciled on.

For premium ware enamel is usually applied in two coats or even multiple coats as per the requirement. We have been talking about the powder process, what it is we will see in a few steps as well here. In this process steel is coated by electrostatic spraying, this process is evolving to a two coat, one fire system consisting of thin powder base coat and a powder cover coat as well base as well as the cover coat two coats.

And then these two coats are being fired in one single step that is the reason these are known as the two coat one fire system. Both coats are cured at once in a single fire. This produces a quality product at much lower cost than conventional processes.

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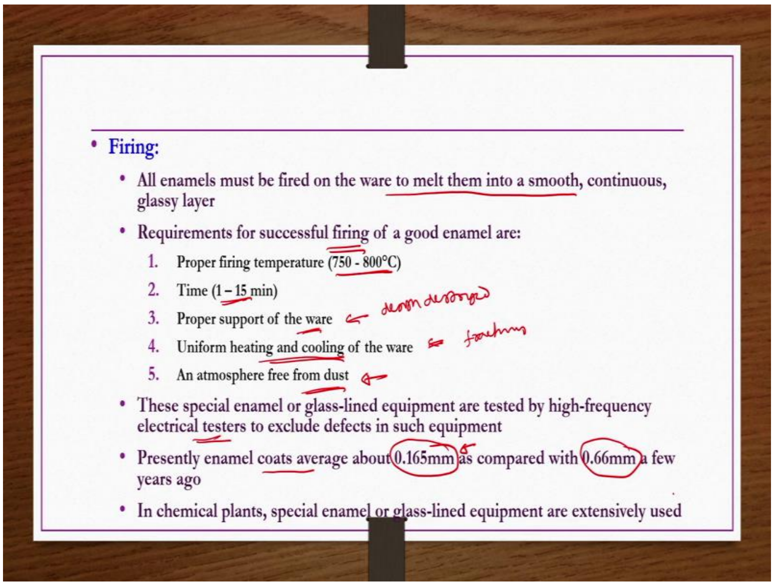

Final step of vitreous enamel making is the firing. All enamels must be fired on the ware to melt them into a smooth continuous glassy ware not only enamel any of the ceramic product that has to be properly undergo firing otherwise product will not be final. So, but however, firing is a very important step one has to do it carefully.

So, the following steps are very much essential to maintain in order to have a good enamel at firing stage, what are they proper firing temperature this temperature has to be maintained 750 to 800 degree centigrade. And then time also 1 to 15 minutes time, proper support of the ware, during the firing uniform heating and cooling of the ware otherwise you know fracturing may occur. If support is not there so, then you know design may be destroyed these kind of problems may be there.

Then atmosphere free from the dust, if the dust etcetera are there those will also be joined together with the vitreous enamel and then the product will not be fine enough. These special enamel or glass lined equipment are tested by high frequency electrical testers to exclude defects in such equipment.

Presently enamel coats average about 0.165 mm as compared with 0.66 mm a few years ago, you can see how much finer coats we are able to do nowadays. In chemical plants special enamel or glass lined equipment are extensively used especially in equipment like reactors etcetera. So, that is all about vitreous enamel manufacturing right so, with this we complete the ceramic industry's topic as well.

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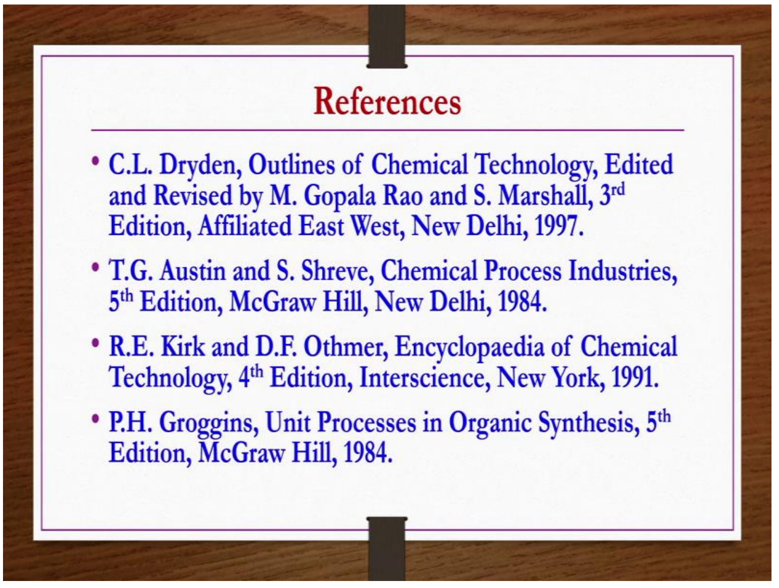

The references for this lecture are provided here however, this entire lecture is prepared from this reference book.

Thank you.