Phase Diagrams in Material Science Engineering
Prof. Krishanu Biswas
Department of Materials Science and Engineering
Indian Institute of Technology, Kanpur

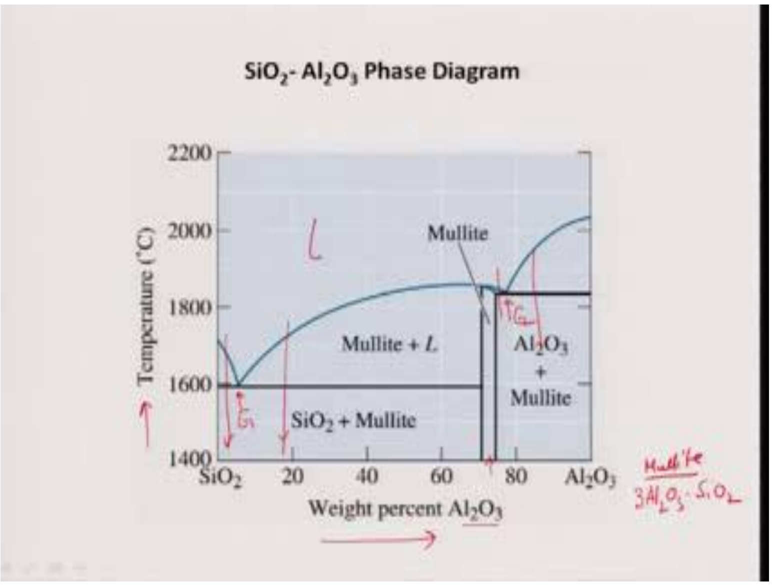
Lecture – 42
Phase Diagram of Ceramic

So, students we are going to discuss today on ceramic binary phase diagrams, and this is the last lecture on binary phase diagrams. Next onwards I am going to talk about tannery.

So, ceramic phase diagrams are also very important, in the sense that many of the important ceramic phases or I could say various ceramic components, starting from the bone china clay to even cutting tool. They are all based on basically the understanding of the phase diagrams. So, in this lecture I am going to tell you few examples of these phase diagrams, for the sake of your completeness or that for the sake of understanding, because discussing this phase diagrams will require much more time than specified for this course. As you know the ceramic phase diagrams will be more important as a tannery system, because like the glass, normal window glass which you see, is basically made up of three components silicon dioxide, sodium oxide, and calcium oxide.

So, they are more like ternary or quaternary systems than binary systems, but there are few binary systems we require discussions. I do not know how many of you heard about mullite. Mullite is an aluminum silicate this is three a l 2 o 3 s I o 2 is is composition. Three moles of aluminum oxide, and one mole of silicon dioxide for some mullite, in unlike metals where each of the components or the phase diagrams are pure metals. Here the components of the phase diagrams are not pure metals or pure material, but they are an oxide that is obvious, because ceramics are basically talks about oxides, carbides, nitrites, borides etcetera. So, they are all compounds. So, any of two compounds, as a two components the phase evolution in the phase diagrams are little bit different, but they have most many similarities, which I am going to begin to you. First phase diagram which I am discuss is, the silicon oxide s I o 2 and a l 2 o 3 phase diagram.

(Refer Slide Time: 02:46)


SiO$_2$- Al$_2$O$_3$ Phase Diagram

So, this is you see this is temperature axis, and this is the compositional axis which tells you weight percent of aluminum oxide a l 2 o 3. temperature basically start from fourteen hundred goes up to 2000 degree Celsius temperature, because aluminum actually oxide has a very high melting temperature its about 22000 degree Celsius temperature, and silicon dioxide also melts pure silicon melts about 1750 degree Celsius temperature. So, therefore, these temperatures are quite highest as compared to metals now if you look at this phase diagram, this is very simple phase diagram, and basically there are 2 eutectics; one here, and other one there, and in between the 2 eutectics, we have a compound called mullite just now I said. This is a silicon dioxide aluminum dioxide compound; composition is approximately about three a l 2 o 3 and s I o 2.

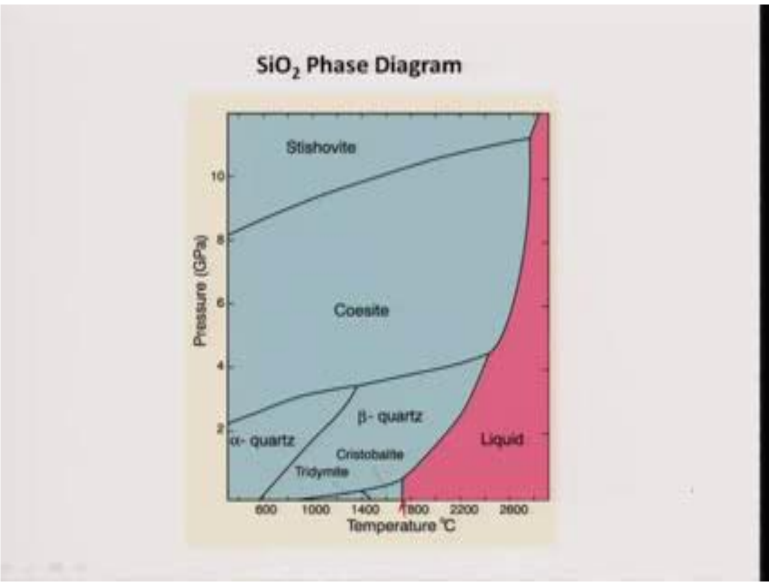
So, the 1 of the eutectics is between silicon dioxide and mullite, because mullite actually happens it remains at, you know how much about seventy five percent of a l 2 o 3; that is why is the 3 moles of a l 2 o 3, and one mole of s I o 2 this is what is the compositions of mullite. So, three moles of a l 2 o 3 and one mole of s I o 2 that is what the composition of mullite, is just like a n I 3 a l in the metallic phase diagrams. So, on the eutectic is basically between pure s I o 2 and mullite. And if you look at carefully, there is no primary, there is no actually terminal solid solutions on the both ends of the a l 2 o 3 and s I o 2; that means, what mutual solid solubility of aluminum oxide in silicon dioxide and vice versa are zero. So, that is why this eutectic exists, and another eutectic is between aluminum oxide and a l 2 o 3 and mulltite. This is more like element magnesium zinc phase diagram if you go back.

So, this compound in mullite is; obviously, we can call as intermediate compound in the ceramic phase diagram, as you have seen a lot of intermediate compounds in metallic phase diagram this is like that. So, the simple sense this is what is the phase diagram. Now as you know polite is the important material, it is used in many industries, cutting tool industry, biomaterials addition to you know (Refer Time: 05:33) sintering agents. So, that is a lot of huge (Refer Time: 05:37) application exist, and that is what this phase diagrams calls, you know importance in the in the ceramic phase diagrams. So, only difference I could see from the metallic is that as I told you, there is no terminal solid solubility of both of the silicon ends and aluminum oxide ends.

So, therefore, that is the only thing, now you can always there are 2 eutectic reaction that you can always have hypo and hyper eutectic for these first eutectic, similarly hypo and hyper eutectic for the second ones, which is same as like any metallic eutectic phase diagrams. So, either way mullite is going to be part of any of, you know any of the alloy composition you study; that is another beautiful part of it whatever alloy composition you study, mullite will be part of that; either as a eutectic phase mixture, or as a primary.

Primary for hyper eutectic for the first e 1 and hypo eutectic for the e 2, for e 1 e 2 are the eutectic compositions. So, that is the interesting part of it, and I do not need to discuss with you, because you have got enough knowledge to know what happened to the hypo hyper eutectic alloys, when you cool down from the liquid to solid. So, this is the liquid. So, that is what is the interesting part of it. Now as you go along you will see other phase diagrams.

(Refer Slide Time: 07:00)

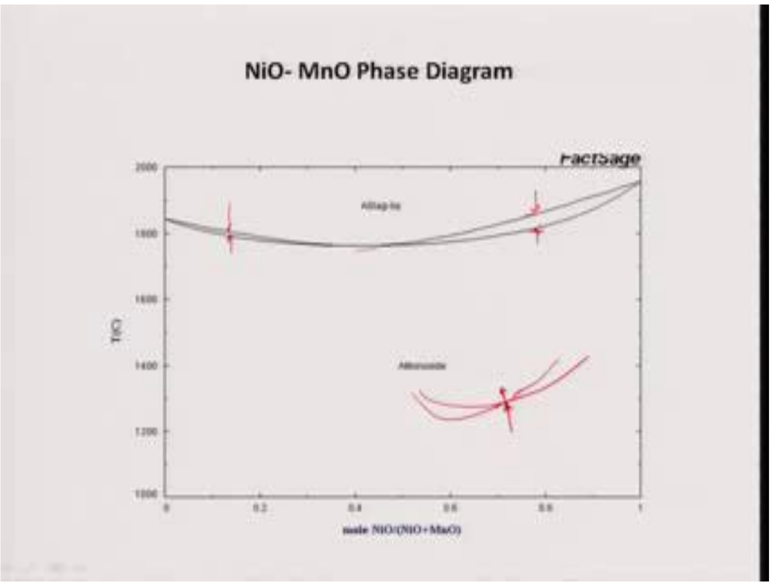


SiO$_2$ Phase Diagram

As you know silicon dioxide is also itself is a very interesting phase; why? Silicon dioxide has a phase diagram, which I will discuss in the very beginning of the course. Silicon dioxide and normally stable as the alpha quartz, and high temperature at about six hundred degree Celsius temperature, normal atmospheric pressure beta quartz forms. there are other phases; like tridymite cristobalite which forms at normal atmospheric pressure, but high temperature like thousand degrees or above 1500 degree Celsius temperature to the cristobalite forms and at a high pressure, you have coesite and stishovite forms, but you know normal binary phase diagram like the 1 I showed you, we do not know, we are not considering any high pressure effects.

So, here silicon dioxide you can exist in the alpha or beta quartz, as you see here, a temperature alpha and beta quartz, because I think alpha tridymite might also can exist, tridymite. So, which melts about 14 that is this is 1550 about 1617 (Refer Time: 08:12) temperature; that is what I told you this is the melting temperature of silicon dioxide. So, you can have all this crystal structure present in the silicon dioxide, but mullite is the stoichiometric compound. So, it will not have much effect of this change of crystal structure of the silicon dioxide.

(Refer Slide Time: 08:31)



NiO- MnO Phase Diagram

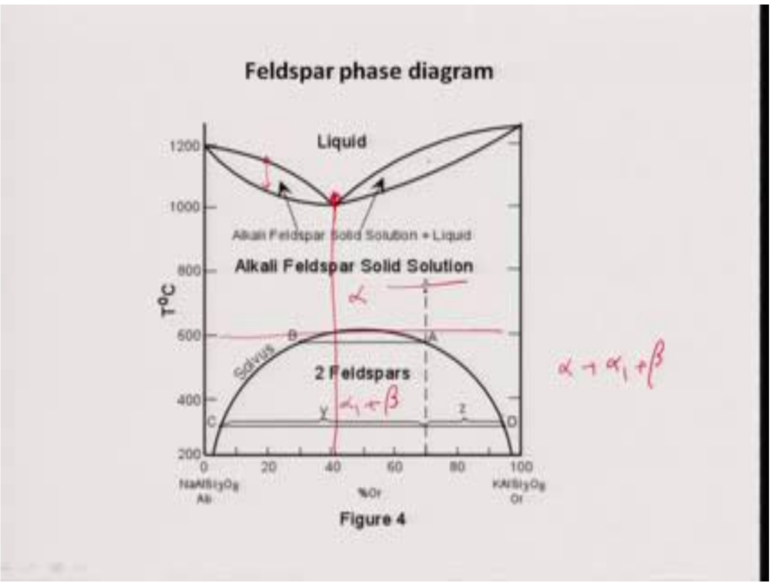
Second one is phase diagram which is very simple. It is just like as isomorphous phase diagram in a metal system like copper and zinc, copper and nickel is nickel oxide and manganese dioxide phase diagram. So, I am just showing you remember the examples of this phase diagrams which exists, which has similarities within some metals, these are the important one, and they are industrially it is important. You know this is you see this is a isomorphous type phase diagram, and this is what is known as liquid, and the mixture of two oxides.

Remember that nickel oxide and manganese dioxide lattice parameters also similar both of them are cubic. So, they are expected that they will form simple solid solution as per (Refer Time: 09:20) rules which I told you. The size depends of the lattice parameters should not be more than 15 percent, crystal structure be similar, electronegativity difference will be less, and also what is that called, the difference of the, these are the 3 main factors. So, therefore, these 2 components do satisfy these factors.

So, not must to be discussed except that there is a point here, why the both the curves meet, it is just like this; this is the upper curve, and the lower curve means like this, like that, there is a meeting point. So, this is like a (Refer Time: 10:00) melting solid, when the solid melts it directly become liquid, the same composition there is no change of composition; that is what is the important aspects is to understand.

And another important aspect of this is that, the solidification range, the freezing range of these alloys are very small, although it varies from point to point composition, but this very small; a couple of you know tens of tens or 20 or 30 or (Refer Time: 10:34) fraction of 50 degrees. It is basically you see is about you know 70 degrees. So, that is another important that freezing happens for a very short temperature difference. So, compositional (Refer Time: 10:47) will be less. Although normally these kinds of alloys are not prepared melting rule they prepare by solid state rule, but even if it is prepared by liquid, from liquid rule the composition difference will be pretty low.

(Refer Slide Time: 11:03)



Feldspar phase diagram

Figure 4

Third one is the phase diagram which is known feldspar for phase diagram, you know feldspar is what; sodium, aluminum, silicate n a a l s I 3 o 8 or potassium k a l s I 3 o 8, you know this is called (Refer Time: 11:20) a b and o r orthoclase and anorthite I think. So, you see here there are 2 parts of these (Refer Time: 11:28) phase diagram this is like a two isomorphous phase diagrams sitting and joining together, but that is not the case. In fact, here actually they meet.

This is a concurrent melting solid, this 1 is a concurrent melting solid about a forty percent of orthoclase; that is what you see this is all taken from the book by Hummel; The Hummel Ceramic Alloy Phase Diagrams, Ceramic Phase Diagrams books which is very you know classic book, it shows all the phase diagrams mostly ternary, but sometimes binary is there. So, as you see here there is a liquid formation from the (Refer

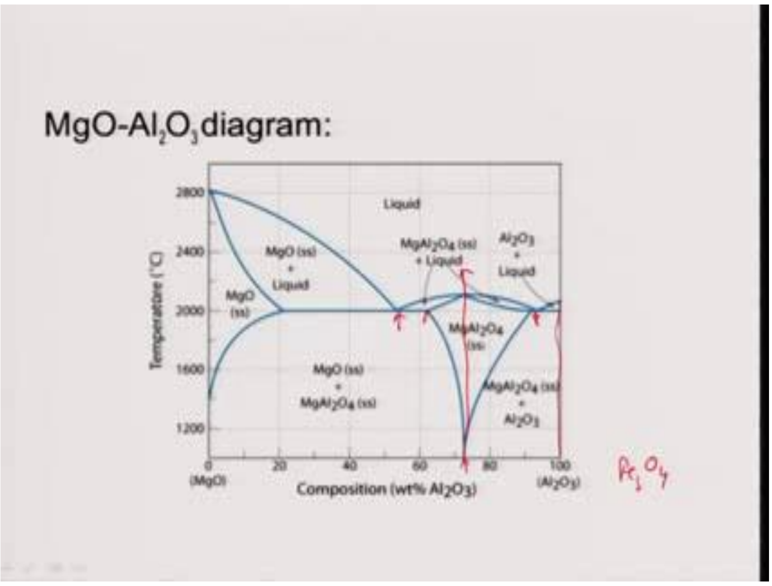
Time: 12:05) from the solid without changing compositions that is what it is called congruently melting solid.

On the left side or right side of that there is a (Refer Time: 12:12) of a phase diagram, and the physically it can be as (Refer Time: 12:15) couple of hundred degrees Celsius actually; 150 to 200 degree Celsius temperature. So, whatever way it forms is solid solution, solid solution with the liquid here, and this is solid solution; alkali feldspar solution, but most interestingly below 600 degree Celsius temperature, this solid solution undergoes what is known as spin order decomposition, or on separated into two phases, and this is what is this you know dome; dome like structure.

This is present in monotectoid phase diagram we will see. We have seen that, but this is also similar to monotectoid phase to (Refer Time: 12:56) phase diagrams, because 1 solid or let us say alpha separate in to alpha 1 plus alpha 2; two solids that is what you have seen right. So, alpha going to 2 alpha 1 and alpha 2, is basically are 2 solids, or not sorry alpha going to alpha one plus beta is what is monoeutectoid. So, here also it is similarly the case; that two alpha two solid phases form. And.

So, there are many ways 1 can create different microstructures; one can create you know solid solution, which can may not undergo this phase separation if you had rapidly cool it, one can create (Refer Time: 13:37) consisting of two separate phases alpha minus beta, or one can create (Refer Time: 13:42) consisting of very final lamellae of alpha one and beta. There are many such evidence exists, but we have to only look at. You have to know actually probably have got a lot of idea how to generate microstructure from my all the lectures of binary phase diagrams. So, you should think about it, and think about the different ways of generating microstructures from these phase diagrams. So, this is another one. And now another important phase diagram is a spinel, you know magnesium oxide and aluminum oxide from spinel.

(Refer Slide Time: 14:16)


MgO-Al_2O_3 diagram:

M g a l 2 o 4, and spinels actually a f c c based structure where both octahedral and tetrahedral (Refer Time: 14:24) are filled up. They have ratio of octahedral to tetrahedral (Refer Time: 14:28) is about one is to 2 in f c c. So, therefore, in a this kind of field structures so, but you what is interesting here is that, you know m g o if you look at from the left side m g o can accommodate a l 2 o 3 quite a bit it is, about twenty percent a l 2 o 3 can be accommodated at the eutectic transformation temperature; that is what you see here there's a terminal solid solution of at present at the m g o end, very easily you can see it can accommodate lot of aluminum oxide.

On the other hand there is a eutectic here; very clearly you see there is a eutectic here. This eutectic is formed between m g o solid solution and the spinel, and I know this eutectic point is very close to about 50 percent 55 percent of aluminum, weight percent of aluminum oxide and the component one of the important component for this eutectic is this spinel, and this can allow you to generate different kind of microstructures. on the other hand on the right side compared to, unlike the solid solubility of aluminum oxide in m g o, but you know in m g o does not have any solid solubility in aluminum oxide.

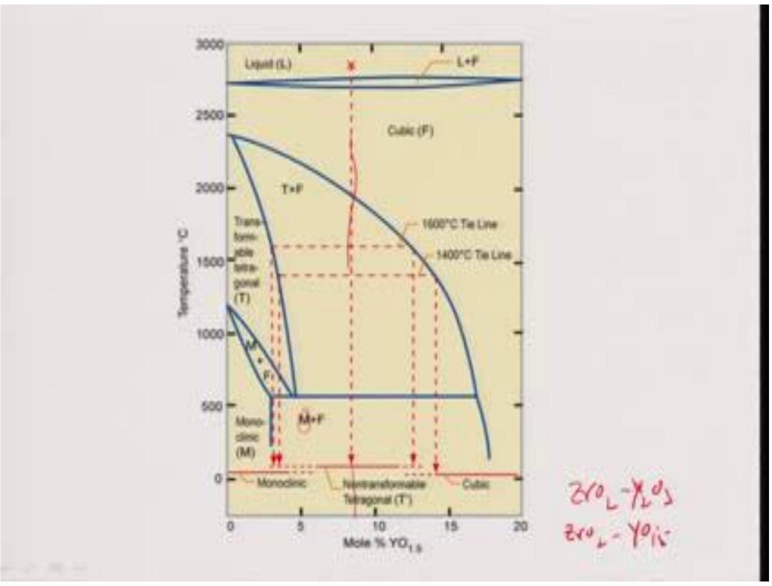
It is almost like a pure aluminum oxide end so; that means, what aluminum oxide is basically hexagonal (Refer Time: 15:48) structure alpha aluminum oxide, and that is the reason m g o which is cubic, will does not have any solid solubility exist at all, but on the other hand an m g o can accommodate a lot of aluminum oxide, that is the beauty of the this things. So, there is another eutectic between a m g a l 2 o 4 and a l 2 o 3. By the way this phase diagram also looks similar to silicon dioxide aluminum dioxide phase aluminum oxide phase diagram s I o 2 a l 2 o 3 type. difference is that here the m g o is basically a is line compound at low temperatures, but high temperature it has a stability range, which can be you know can vary from 60 to 80, 60 to 90 you can see here this is almost like 65, it is almost like 90.

So, last range of and a compositional range possible higher temperature. this is very important; that means, what we can form in all spinel at higher temperature at over 1600 or 1700 or 1800 degree Celsius temperature merge easily, because it can accommodate compositional change as compared to at lower temperature, lower temperature the solubility decreases, and it becomes exactly m g o a l 2 o 3 structure; that means, what; that means, that formation of any spinel structure, it depends on basically the exact composition of these 2 components m g o a l two o 3 at low temperatures, and this is the reason actually all the spinels, mostly aluminum (Refer Time: 17:17) oxide m g o spinels are (Refer Time: 17:19) at high temperatures which is easy. So, you know like many spinel structure possible, this is once such you have, even a f e 3 o 4 f e 3 o 4 is also a spinel is a inverse spinel actually. Similarly you have spinel on you know manga (Refer Time: 17:39) by various palladium oxides nickel (Refer Time: 17:41) is spinel structure.

So, there is a nickel oxide vanadium oxide, between nickel oxide and vanadium oxide. There also the phase diagrams exist where these kinds of spinel do form from these liquid states and it can get stabilized. Another important thing you can understand you can see here he said that at this composition, at this composition this spinel whatever forms is, and congruently melts in to liquid.

There is no separation to liquid, but just if you go out of the compositions you have a solid plus liquid formation composition change to occur that is the another difference, which is clearly see on this phase diagrams. So, all those features which you have studied in metallic phase diagrams are present in ceramic phase diagrams. You do not need to worry, only thing is changing here in the ceramic phase diagram, is the component itself, they are not pure metals. They are actually oxides, or carbides, or you know nitrites, or borides. The last phase diagram which I am going to talk about is, what is known as yttrium, the (Refer Time: 18:47) zirconium z r o 2, it y 2 o 3 or z r o 2 y o point o 0.5 this phase diagrams.

(Refer Slide Time: 18:45)



As you know z r o 2 actually you know has a polymorphic transformations, pure z r o 2. It is stable at room temperature as a monoclinic structure. At high temperatures at about say something like twelve hundred degree Celsius temperature it transform to tetragonal structure, than at a very high temperature, very close to twenty four hundred fifty degree Celsius temperature, it transform to cubic structure, but you know both monoclinic and tetragonal structures are basically brittle.

A zirconium oxide is a structural, is for structural application in ceramics, and these can be possible only when we can stabilize the Cubic phase at room temperature, and that is possible if we you add about 15 to 20 percent of weight mole percent of yttrium oxide. As you see here if we keep on adding the yttrium oxide more, the cubic phase get stabilized. Not only that a most important one will be this zones; central zone where both tetragonal and cubic phase is above.

As you know transformation transferring in ceramic is basically you know is a microstructural change, where tetragonal to cubic (Refer Time: 20:16) transformation happens, and then this tetragonal phase transform to monoclinic, and when it happens what actually happens suppose I take alloy composition of these, which is about say 7 percent or 7.5 percent of yttrium oxide, it will at higher temperature it will form cubic, but as you cool it down it will form it to a tetragonal plus cubic structure, but only when below this eutectic transformation temperature, this is a eutectic transformation close to five hundred degree Celsius temperature. This tetragonal phase transforms to monoclinic and when that does happen, there is a volume change, and this volume change leads to toughening of the matrix.

Basically it will lead to the (Refer Time: 20:59) compressive states, because of the transformation toughening, and time permits I will discuss this thing when ternary phase diagram will be coming, but what I mean to say is that, those of you who have little idea of transformation transferring in zirconium yttrium similar zirconium oxide, they know that this is. the bases the phase diagram is the bases for that, and I am not doing that you can if you see carefully at very high temperature of the liquid forms the phase diagram is like a isomorphous type. It is like isomorphous type.

So, therefore, important aspect from this phase the ceramic phase diagram we have to understood is that we can actually get similar information as we got from metallic systems, things are not varying much; that is the classical the similarity, between the binary ceramic phase diagrams and the binary metallic phase diagram. you do not need to worry about it, even if you are a metallurgist working on metals, you can clearly understands the ceramic phase diagrams like me, you do not need to worry much about it, because the phase formation micro evolution will be almost similar.

Only thing difference I told you instead of a pure metal components here you have oxide or carbides or borides or nitrites presents. So, will come back to this ceramic phase diagrams again, when you discuss about these phase diagram a ternary, by the ternary phase diagrams, and will probably bring in because time is there, because I have about a near about 20 25 lectures for the ternary phase diagrams. So, about twelve powers ternary, I will spend on ternary phase diagrams. So, I will get a lot of time to discuss with you about the different ternary phase equilibrium for ceramic systems. So, with this I conclude my binary lectures on the binary phase diagrams. Next lecture I am going to talk about ternary phase diagrams.