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## Lecture - 49 Recrystallization (cont.)

So, we will be continuing our discussions again on recrystallization and we will today do some discussions on growth or other grain growths. As you know recrystallization kinetics is very important and that is why I will introduce a new topics in the last class that is the Johnson Mehl Avrami type of equations which can describe the growth nucleation growth both for different kinds of situations. And the fundamental equation which I have discussed in the last class is very simple it tells you the fraction transform Y.

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It can be any transformations whether its new grains from the deform grains or even a new product from a parent phase. So, it is equal to 1 minus exponential minus Kt to the power n say in which y is the fraction transformed K is a constant and t is a time and n is another exponent. So, K is normally given by very simple in a growth situation we have seen this is equal to pi by 3 N dot n dot is the nucleation rate G dot is a growth rate to the power q. This is the constant K, it can vary from different situations we will discuss 2 such situations and give you a detail list how K and n can be changed.

Now n is known as the exponent as you know here in this x equation exponent and for most of situation n is equal to 4, but it can be less than that value also. So, important aspects in understanding the kinetics of such a kind of equation or transformation are basically to determine the values of n and K as you know n is the time exponent. So, therefore, n has a stronger effect on these whole transformations as the n increases transformation rates transformations become faster. So, there are 2 important situations which we to deal with it give you example 1; I have already given another 2 example; I will give today I have listed down from this book.

Let us consider a situation very simple situation let us consider a situation in which in which you have a pre existing nuclei in the material, it can be pre existing nuclei of the re-crystallized grains already present its possible the recovery state these grains might have been nucleated just nucleation and then subsequent thing what happens is that is. So, increase the temperature the growth takes place. So, our predominant aspect is that growth happens from the basically at the beginning. So, growth happens from the time tau is will be 0.

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Time tau will be 0 and to the time tau is will be t so; that means, for the beginning itself growth happens and the such a situations is very simple to do that and also; we also assume that after they growth started there is no further nucleation so; that means, N dot is basically 0 after the time tau will be 0 obviously.

Because all the nucleating things nucleation events which was there nucleating if I nucleate nuclei they are already present they are not changing anymore so; that means, it is a completely growth control phenomena. So, in such a situations is very simple that the volume transform of the new phase beta which I have discussed in the last class also is basically equal to M 0 which is a constant I will tell a what multiplied the volume V, then G dot q t q and this has to be multiplied by 4 pi by 3 it is a constant term. So, why it is show here; M 0 is the constant nucleation rate it is not changing; it was a; it was there at the beginning of transformation; all the nucleation over there nucleation rate per volume and that is why you multiply by V.

G q is there remember t the exponent of t has reduced from 3 4 2 3 here that is because is very simple once you have a; I mean big list in nuclei it can grow all in 3 directions x, y, z. So, there has to be 3 components of the different growths and because of that it is only 3 as exponent in the time scale. That means, what in such a situation where your pre existing nuclei present already and the change of volume fraction of the phase or the volume fraction of the new phase form is directly proportional to the t 3; it equal to its all equal to t to the power q when these things actually normally constant M 0 is a constant volume is constant also G dot is normally constant when it is growing isotropically as say spherical manner into the phase the one picture is there all the on the slide you can see that.

So, this is one particular situation which is be there. Now y is; obviously, equal to 1 minus exponential you know that is basically equal to one minus exponential V B e by V where this is; these are the 2 different volumes one which is apparent volume another one is the actual volume and that is equal 1, 1 minus exponential minus you know is equal to minus K t to the power q and here K is equal to 4 per pi 4 pi by 3 M 0 V and G dot q.

So, this is one situation in which nucleation has no role to play that is why N dot is not present even anywhere in the equation there is only G dot which is determining the things now. Obviously, when you are talking about the growth it can be dependent on the transfer of the molecules from the product from parent phase to the product phase and that can be differing that can be different for different types of transformations.

If it is completely dependent on the get more of diffusion, then this one will change if it is completely depending on the volume diffusion it will change. So, those are all certain issues which can be dealt with separately, but fundamentally this is how things happens. So, this is how one can apply these things this is I write case 2 case; one I have already told you case one is basically where this is pi by 3 N dot b G dot t to the power 4 that is why I have discussed in last just now and case 3 is basically a situation in which both nucleation growth involve. So, case 3 is suppose you have a very small fine grain crystals; that means, you have a large number of grain boundaries.

Because of the fine grain crystal boundary area is large and the nucleation always happens of the grain boundaries we know that or grain edge corners or the grain edges or grain corners or the tipple points this is the places of heterogeneous nucleation is happens. So, nucleation will takes place randomly if the grain boundary characteristics are is random; that means, grain boundaries are not in a pestle type pestle type means if it had not sigma 3 type grain boundaries it has variables basically it had random grain boundaries in those cases nucleation also happened randomly as on the grain boundaries. So, once the nucleation actually happens out of the all grain boundaries and it is exhausted suppose all the grain boundary areas are filled with filled with these nuclei.

So, there is no further nucleation possible and the grain boundaries. So, only possible chances than having a nucleation inside the grain and there is very less likely because of the energetic of the system which you have discussed in many times in that earlier lectures. So, in this cases what will happen when a grain boundary of nucleation exhausted then growth will happens only now as you understand when such a situation happens in the growth actually is taking place on the from the nuclei along the grain boundaries grow is basically will be happening and in the direction perfected to the grain boundary that is obvious as you have seen it basically very simple suppose you have a grain boundary and you have a nuclei like this and this nucleus has a coherency along the on the grain boundary and incoherency along these.

So, this growth will happen perfectly to the grain boundary that is obvious. So, it is that is what you see in many cases these things form woodmen certain structures we have seen in the case of steels also and this is very common. So, therefore, if this grain boundary is completely filled by this nuclei and no further nucleation is possible the growth will only happen in the direction perfectly to the grain boundary correct; that means, go this one dimensional in such a case n become one because it is only happening in one directions. So, growth will be much slower. So, only thing only way it can actually grow is perfectly to this. So, if I draw this picture again. So, therefore, they will become they will become like that they will become bigger these crystals, but they are only growing along one directions although I have drawn little bit bigger in the direction, but mostly they are going along these direction.

So, many many such transformation like cellular precipitations or growth of woodmen certain plates happens by this mechanism. So, for these situation n is equal to 1 and very simple why because its one dimensional growth. So, you have seen when your 3 dimensional growth here on the pre existing nuclei 3 exponent of time become 3 so; that means, this exponent of time is basically telling you what are the different modes of the growth if the modes of the growths are actually multiple, then this becomes more than 1 if it become singular then this become one. So, that is is the difference you should you should very know very well in the literature and so, thus depending on different situations we can actually have a table and I will do that you should be very clear about it depending on the different situations these exponents can be changed.

So, let us put a tabular format because we have discussed many other transformations previously and we can make a table and tell you.

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So, I will tell you that different types of different types of situations nucleation and growth very early stage and late stage; that means, at the beginning and at the later and the. So, therefore, what I will do is that these are the different situations and values of n will be provide for these 2 to the early stage and very late stage. So, when you have homogeneous nucleation which is very rare first one is a homogenous nucleation which is very very small cases early stage, it is going to be 4 late stage also; it is going to be 4.

So, nucleation happens well inside the grain. So, it can grow in all directions; obviously, along with nucleation is not actually stopped see what happens as there nucleational growth takes place simultaneously many of the situation many of these transformations that is why n become 4 because we have 4 different things different other directions one is nucleation and other the other 3 are the 3 of the 3 growth directions that is why n become 4. Now, you have a pre existing nuclei already and they grow that we discussed. So, initially it will be 3 and let us say also it will be 3 because there is nothing about 3 dimensional growth along happen happening in the 3 directions x, y, z randomly we distributed it is in a nucleus nuclear randomly distributed.

This is the situation just I discuss the second one randomly distributed heterogeneous nuclei for that it can vary depending on 3 to 4 because either nucleation can happen together the growth or nucleation can happens and then growth takes place predominantly, but it can reach 3 at the later stage because nucleation is no longer happen at a later stage. So, it is only growth in 3 directions. So, situation 1, 2, 3; the situation 4, it is basically nucleation along grain boundaries. So, I simply write grain boundary. So, what will happen if it is along grain boundaries; obviously, initially both nucleation and growth can happen. So, that is why this 4.

But later stage it will be one that I told you when there all the grain boundaries will be filled by the nuclear no longer nucleation is possible and growth can only happen along partner to the grain boundaries. So, that is why is n become one this is a very special case and 5 is basically grain edge what is grain edge as you know that edge means the further meeting points of the grains and 6 is basically grain corner; it is all we discuss in nucleation; you should go back and see the lectures and this is will be 4 and this will be two; obviously, then growth can happening along 2 perpendicular directions because it is a edge. So, you have 2 perpendicular direction and here.

It can happen along 3 parameter directions because this is a corner in its 3 grains are met together; sorry, it can happen only thing can happen is that the nuclei will be having a detail essence with one of the grains other 2 maybe not having an eventual essence even they can go freely along these directions. So, these are the values of the ns along different situations possible in the different phase transformations depending on the nuclear and these are can be calculated using the; this can be used to apply the Johnson Mehl Avrami equation understand different phase transformation this is very important and you know this picture basically is a re-crystllization and you see here that the nucleus all most the nuclei has performed along the boundaries and again corners and edges normally.

So, that is this is very common and then this nuclei have grown and then they have reached a critical size now next thing which I will discuss whatever time I have next ten minutes is basically the growth as we know the these Johnson Mehl Avrami equation considers both nucleation and growth because it is talking about fraction transformations, but in recrystallization; how that growth actually happens suppose initially you have large number of grain boundaries because of the small grains and this boundaries are very large; so, because the area is very large. So, therefore, the energy of the boundaries are also large. So, therefore, it is obvious that these boundaries you know will the area will reduce and only way it can reduces by going the grains or.

By making the grains bigger and therefore, this process is very spontaneous this process is very spontaneous why because it is already small grains has large area. So, they will always try to reduce these things its simple like a; if you create bubbles in these. So, bubbles in a bucket you will see initially number of bubbles will be very small and then slowly they will try to reduce its surface energy by simply equalizing together whether such a thing happens in the grain growth or not the area this thing happens you know let us consider that a system in which the all about is has same energy. That means, boundary the boundary edge you can change depending on this characteristics of the boundary, but let us assume they are all same and there is a case then you know then what will happen as you know that the grain edges in the system will form by the 3 grains where the there are they meet.

Let me just show you the picture here.

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So, grain edges can easily form where the 3 boundaries meet these are the grain you can see that actually. So, and a equilibrium angle when the 3 of them meet 3 meets means what equilibrium angle when the 3 of them meets is basically you can see that is basically let me draw it properly this angle is basically must be 120 degrees that is a equilibrium angle and using Lamin's theory. One can show that that is because the energies of the boundaries must be at equilibrium and that is only possible when the angle is 120 degrees.

Now, question is this is only satisfied; this 120 degree is exactly. So, only satisfied when your number of sides of the grain is 6 6; that means, when it is in regular hexagon that is on then only the angle will be exactly 120 degrees and it is less than 6 sides angle will not be 120 degrees and in order to make the angle 120 degree. These will form what is known as they will curved the boundaries will get curved; what you see and this curved boundaries when it is less than 6 cur; 6 edges will be concave convex; we can clearly see they are like a convex boundaries, but then its number of sides are more than 6 and then still the 120 degree angle can be maintained again by you know making the boundaries curved, but the boundaries will become concave right you can see that. So, 6 is the critical number of sides a grain can have in which equilibrium angle of 120 degree can be maintained by simply making the boundary, but by making these grain boundaries curved and the curve in such way that they are radius of curvature.

Will be such that it looks like a convex, but only when its becomes more than 6 that number of bound number of sides of the grain and in this case is 1, 2, 3, 4, 5, 6, 7 still the angle can be maintained 120 degrees for equilibrium, but then the curved boundaries will be concave. So, now, what are happened when such that because in a random situation you can have boundaries starting from 3, 4, 5, 6, 7, 8 and may even more even if those who have looked at the grains properly you will see in optical micro scale; even if you look at iron grains and then an optical microscope you see the all kinds of grains; grains of different sides number of sides are possible. So, what will happen then let us look at that before I go into that I just wanted to discuss with you something that you know.

Let us take a situations the simple thermodynamics, let us take a situation that is a classical situation in which I have a alpha phase; the grain of alpha very big grain of alpha suppose and this is alpha.

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And suppose inside that I have a small grain and suppose this is also alpha; this is the alpha alpha and it has n prime number of moles and rest of the alpha has n double prime number of moles correct. Now, we are going to look at the situation in which the mass is getting transported from these small alpha grain to the outside and suppose if this much smaller mass d n number of molecules it transported.

What will be happen to the equilibrium situation there is a very simple situation or difficult. So, initially the total free energy system is what total free energy system is;

obviously, equal to you know number of moles n prime rather let me write; let me see this equations are very simple, but needs to be written properly I should not make any mistake say this is the free energy G is the free energy are write in G alpha plus this interfacial energy interfacial energy means what because of the this interface between 2 alpha grains there is interface and I am writing in general. And I do not know the how many interfaces are there A i gamma i, but A i can vary from one to anything because you can have large number of such grains presence inside these big alpha grain that is what is that is how the grain growth happens and so, this is the total surface energy contributions plus n double prime multiplied by G alpha n double prime is the moles of the rest of the alpha the big grain and G alpha is the G free energy of the G this is the G of the system.

Now, very simple suppose if such a situation happens when dn number of dn prime number of moles is getting transported from inside these grain to the outside. So, what will happen to change of the free energy what will happen is very simple; obviously, G alpha is not going to change; it does not depends on that. So, what I am going to change is this plus summation that is what it is. So, this is the area dependent term and this is the basically them because of the big grains outside for that change now as we know mass needs to be conserve. So, therefore, dn must be equal to this must be equal whatever mass is getting transported there is a mass grain to the next grain we whatever is getting transported from small grain dn prime is basically is added to that. So, there is no mass loss.

So, therefore, whatever addition we are doing because there are changes of the molecules of moles of these big grain n double prime that is the change dn double prime that is must be equal to d prime or let us suppose this is dn. So, I can write down G d system is equal to nothing, but very simple nothing, but minus gamma i d A i by dn prime or rather dn into dn that is what I write down. Now, if we consider its pair here already we have considered as pair and you know the volume of this pair area of this pair volume is 4 third pi r cube if r is the radius and area is equal to 4 pi r square you can convert pi relationship between volume and areas very simple you can do that let us not do that. So, it is for this sake of the time I can write down this change we can write down in terms of delta G remember this is d; d is small and delta is big nothing, but it is n.

This is implication will small this is small. So, we can write you can see that this will be equal to twice gamma V by r multiplied by G n; it is very simple; if you consider one grain with this volume and this area. So, what does it say it says tells that free energy is changes is always negative that mean mass will be kept on and getting transferred from these small grain to the outside and slowly this boundary will be wiped out there were no such boundary. And it also tells you this change of delta G is negative why because gamma is the interfacial energy and this is positive volume is also positive r is also positive none of these are negative and because you have a negative sign at the at the front therefore, the whole change of the free energy is negative.

So, let me this process spontaneous you do not have to provide; you do not need to make it that process happen its only depends on these diffusion how fast you can do that because mass transport depends on the diffusion, but thermodynamically this tells you process is possible another important thing it tells you is small of the are higher this value of G so; that means, smaller the radius of curvature higher the value of G. So, now, let us use this chronology and to explain that explain the grain growth mechanism here it not very difficult to understand here as now I have given you the whole concepts so that means, what as you know if I have grains is less than num about the sides less and 6 and the these grains will slowly; it will have a convex curvature so; that means, what the grains will slowly sink why.

Because r has to be r will increase keep on if this bound is moved the centre then; that means, all the grains which is a side less than 6 will slowly vanish on the other hand these grains because in radia is centre of curvature is along these boundaries is move like that that is obvious and that is why in a grain growth situations the grains which is bound in less than 6. They are consumed by the system are they are simply vanished for the system and the grains which is the size sides more than 6 they grow. This is a basic aspects of the grain growth which you must please you must know this.

Because this is a very fundamental concepts that is why actually grain grains actually grow in the actual materials and that is actually the it will grow now one can actually look at the digital kinetics of the growth which we will do in a next lecture, but that is that is not very difficult that is also diffusional aspects. So, it is not extremely difficult to do that, but fact the fundamental things which you should know why a grain the side in less the number of sides will less than 3; 6 will grow and grains will not grow will get

strung and the grains which more than 6 sides will grow this is very important and this comes from the thermodynamics of the whole situations.

Remember one thing we have assumed here the gamma we are assumed in this equation is isotropic which is not the case. So, there will be some variations when the gamma is an isotropic that is what I said the grain boundary in nature dictates whether the grain will shrank or grow. So, depending on the type of things type of the nature of the grain boundaries because this gamma is I am not want to discuss with you gamma depends on many things depends on the crystal of orientation, depends on the double derivative of the gamma is pair to crystals of correlations. So, by that we can actually make the sign positive there are situations. Let us not get into that complex situations this happens when you are especially in grain boundaries. But normally normal grain boundaries whatever I said will valid.

Let us stop here and then basically I am going to start a new topics in the next lecture and, but I will discuss at the beginning of the lecture the kinetics of the gain growth little bit in fast 5 to 6 minutes, first 10 minutes and then we will start the next lecture.