Phase Transformation in Materials

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Lecture - 22
Types of Nucleation

So, in the last part of the discussions on the interfaces, I just like to take what is the effect of these interfaces on the stability of the system and I will take 2 examples on that which I have taken from another book and show you how things can be done.

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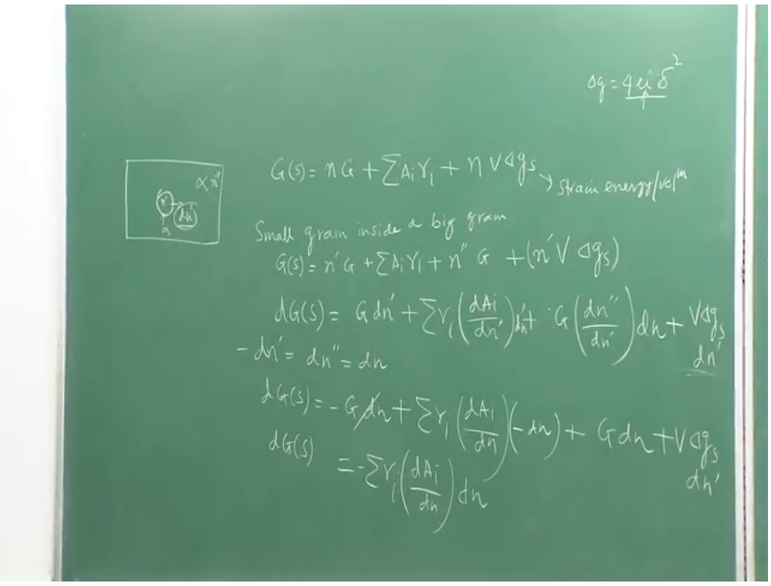

$\Delta g = 4\mu\delta^2$

$G(s) = nG + \sum A_i\gamma_1 + nV\Delta g_s$ → strain energy/vol^m

Small grain inside a big grain

$G(s) = n'G + \sum A_i\gamma_1 + n''G + (n'V\Delta g_s)$

$dG(s) = G\,dn' + \sum\gamma_i\left(\frac{dA_i}{dn'}\right)dn' + G\left(\frac{dn''}{dn'}\right)dn + V\frac{\Delta g_s}{dn'}$

$-dn' = dn'' = dn$

$dG(s) = -\cancel{G\,dn} + \sum\gamma_i\left(\frac{dA_i}{dn}\right)(-dn) + G\,dn + V\frac{\Delta g_s}{dn'}$

$dG(s) = -\sum\gamma_i\left(\frac{dA_i}{dn}\right)dn$

Let us suppose in the first example let us suppose I have a system which is a alpha phase and within this big alpha, there is a small grain and this is alpha; alpha remember because this is same grain and let us suppose the number of moles on of the alpha in this grain is basically n prime and in this case is n double prime let us suppose that this is a bigger matrix or bigger grain and within is a small grain.

So, we can write down the total energy of the system the free energy of the system is like that; obviously, is mole energy because these 2 are the same phase therefore, G will be same. So, I can write down this is as I know G mole and this normally mole energy of the system is written based like this because there will be boundary here. So, this is nothing but sigma A i gamma i that is you see this is the bulk energy bulk energy of the system which is small n; this is for the interfaces all the interfaces summation together plus it will have strain energy effects as and the effect will be n v delta delta G s.

What is this? This is again n is the number of moles, v is the mole of volume and G s is the strain energy; this I have already given you some formula 4 sigma and 4 mu square, it can be actually simple 4 mu square delta and something else, right; what was that some other parameter; I wrote something else was there anyway this is nothing but a strain energy, because this is your shear modulus and this is the misfit this can be calculated by many means by fact that there is a strain in these at the boundary between these and these because of the misfits you will have a x energy terms. So, let me just write down these this same thing for both and this is for volume remember this is the strain energy for volume on the other hand suppose energy is a per unit area and this is also per unit volume because this is the bulk energy.

Now, I can write down because of the small grain; this is small grain inside, this is small grain inside. So, therefore, I can write down G s of the small grain is basically equal to n prime, G n prime is a number of moles plus summation of A i sigma; I remember the reason; I am writing a as sigma is because I do not know whether the all the interfaces of these small grain along all direction is same isotropic or not may not be, then we need to add up, because gamma will be varying depending on the crystallographic directions and plus; obviously, it will be n double small grain inside a big grain inside a big grain. So, that is for the small grain that is for the interface and that is for the G; G of the big grain plus there will be strain energy. So, n energy will be depending on this one v and delta G s.

So, for the sake of simplicity let I assume this strain energy is very small; this is not there at all, then it will be much easy to calculate, then we later on include that part. So, I can actually then take total differential like this; obviously, this will be G d n prime plus sigma gamma i gamma does not depends on this n. So, then this is d A i d n i sorry; d n prime not i plus n double G d n double prime by d l prime.

We have assumed initially that this part is not existing now what we can do let us suppose we have a transformation happening in which some d n prime moles are getting transferred from this small grain to the big grain what will happen then if d n small prime of these are getting transferred from small grain to big grain. And obviously, then we can write down that minus d n prime. Obviously, d n prime is lost by this grain this will be grain by the big grain it will be can mass cannot be destroyed so that any loss from this will be gained by that. And let us suppose these are all equivalent because grain loss is equal to gain.

So, in that case, we can write down d G s because of this is equal to minus d G d n plus sigma I basically we replace everything by d n that is what we do plus G something mistake I have done; yes, d n; d n here also d n, right. So, d n; now this d n will get cancel; obviously, loss of free energy by these because this is same phase it will be gain of that. So, you can clearly see d G s is nothing but sigma gamma i d A i d A n.

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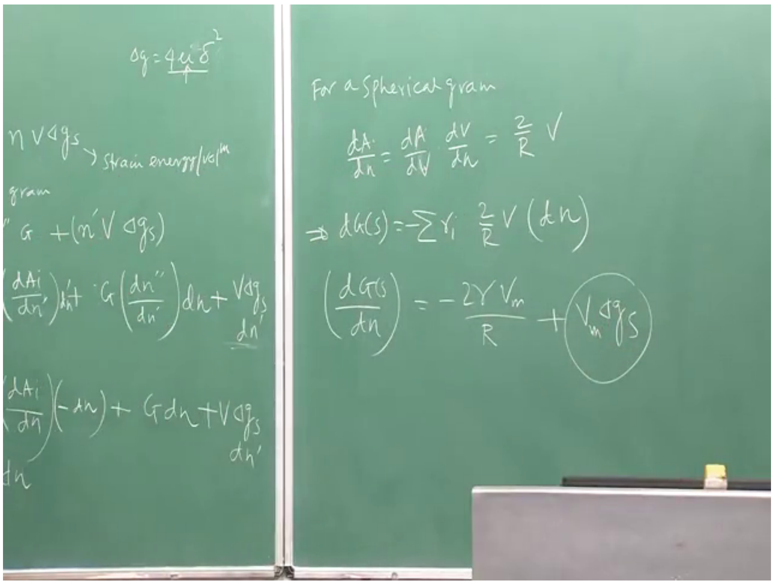

Now, if we assume; if we consider a spherical kind of a grain; let me do it here, if I assume a spherical kind of a grain as for a spherical grain we can write down d A by d n must d V by d A sorry d A by d V multiplied by d V by d n. Now for a sphere, we know area is equal to 4 pi square and volume is equal to fourth of pi R cube and if we do the mathematics perfectly; this will be coming like a 2 by R into V; V is the volume. Therefore, if I do it this is nothing but G d G s becomes sigma; sigma. So, sigma will be gamma i and this one which you have done recently that is what is your twice R by V say gamma is says one only one interface. And so this will be minus again why because somewhere we have done some mistake yes that is what is the case here. So, because this is a loss and that is what I was thinking.

So, then finally, if I consider d G for a single interface d G s by d n, it will be minus gamma twice v by R that is what you see this is v m v is v m is smaller volume. So, what you scale is see here whatever is the value of gamma v m are does not matter where basically R is the radius of this small grain the change of free energy with respect to the with respect to change of n is always negative so; that means, what this simple calculation tells you that this small grain will vanish very soon because transport of the atoms from this small grain to big grain is leads to reduction of the free energy or negative value of delta G and this negative value of delta G will make this small grain dissolve completely or rather small grain will be consumed by the big grain and it will be part of the big and a b; this mass will be part of the big grain and therefore, without considering this strain energy this is what is going to happen.

Now, if I consist an energy which is; obviously, positive suppose if I consider strain energy here let us do that now simple evaluating of terms what will happen just what you show you in simple calculation. So, this is nothing but V delta G s and so, therefore, I can write down this is v delta G s d n prime by d n prime; yes because this n prime and again this will be V delta G s d n prime.

So, clearly you can see there will be extra term here which is V delta G s and V. This is v m now because of this strain energy effect I cannot simply say whether the change of free energy will be all as negative it cannot be may not be actually depending on the value of G s the strain energy depending of the value of strain energy here in this term these value these things because of that the delta G s may might go to negative or might go to positive if it goes to positive these transport of atoms from small grain to big grain is not allowed anymore.

Therefore, interface has strong role to play depending on the type of interfaces whether it is the coherent semi coherent if is a coherent interface the delta G s is very small if it is a semi coherent interface still it is small, but not as small as coherent, but if it is a complete incoherent interface delta G s is very very high as a G s is very very high because of delta G s is very very high this negative term can be completely swamped or taken over by the positive value of the d V m delta G s and in that case this grain will remain inside this large alpha grain and you cannot remove it. So, that is the actual effect of strain energy on the whole mass phase transformation.

So, in actual reality real case we have to consider both the effect of these interface is because of the surface energy; energy of the interface plus the strain which is generated because of incoherency or semi coherency or partial sorry or you know coherency whatever is the situation all will lead to certain kind of a strain, but value of the strain will be varying depending on the type of interface you create. So, this is exactly I wanted to tell you that by simple thermo dynamic analysis; even free energy analysis; even one can prove that this is possible to actually create you know have different kinds of situations mathematically or theoretically possible why I; one can actually do as in a simple other analysis or let me just give you as a part of your home assignments.

Let us suppose I have a instead of this I have a matrix and I have a precipitate beta and therefore, I am asking the questions what will be this conditions of free energy process a numbers of moles transferred from here to there; when I transfer d n number of moles what will be the free energy function allow as a function of both case surface energy and the strain for such a thing to happen in the thermo dynamically possible way. So, you can actually do as a part of home assignments remember here both the phase are different.

Therefore, we cannot be consider G to be same for both the cases the bulk free energy will not be same and there and there here. So, G of alpha G of beta or G of beta and G of alpha one if you consider and one is to consider interface energies which will be beta and alpha plus the strain energy of beta and alpha. And finally, get an equation which will be much complicated than how much I have derived, but you can try.

So, in the last five six minutes I have in this lecture let me just introduce the new concept which we are going to deal with and that new concept is basically nucleation see we have thermodynamically dealt with the systems the surface energies and their strain energies. But the phase formation or generation of a new phase is also depends on how we whether we nucleate it or not in the system and that is why the nucleation becomes important. You know if you consider a solidification; suppose if I am solidifying as solid from a liquid simply what the different stages of solidification first thing what will happen is basically very schematic way is that you will have small clusters of atoms come together that is what is shown here small cluster of atom sorry small cluster of atoms which is shown as large number of sides this is the one.

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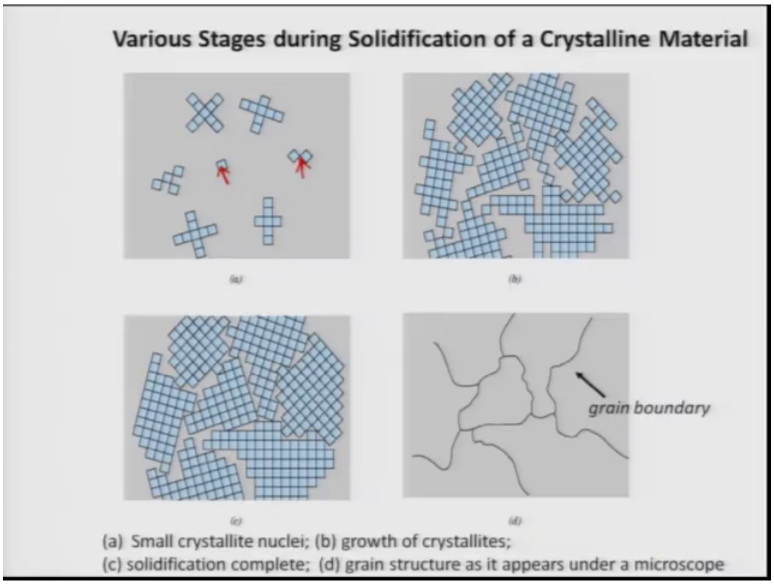
Various Stages during Solidification of a Crystalline Material

(a) Small crystallite nuclei; (b) growth of crystallites;
(c) solidification complete; (d) grain structure as it appears under a microscope

This is another one; 4 atoms cluster or may be 8 atoms clusters or may be 16 atom clusters will come together and from a emdrive; emdrive is the small you know that the first step of formation of nuclei; nucleus and then this small pieces like 4 atom things; they are getting added you can see here one (Refer Time: 15:46) 4 were added the some more added and when the size will become as critical one then only the nucleus will form. So, that is the first stage of liquid solid transformation; in fact this is first stage of solid to solid phase transformation also further more what will happen further more this atomic you know clusters will join in a systematic way to each of this nuclei there are 1, 2, 3, 4, 5 nucleus nuclei.

Therefore, that or be more and each of these atoms clusters of atoms will keep on joining with a nucleus and then they will become bigger, but there will be becoming the great going independent of each other, but they do not know whether the other things are existing in the liquid or not. So, therefore, when they will be becoming bigger that is what that they seeing this blocks are becoming bigger joining more and more clusters and finally, when they will meet they will form a boundary that is what they have been discussing for the last few lectures this is a grain boundary then.

So; that means, in a real solidification there will be nucleation growth and finally, formation of grains that is what actually happens. So, any phase transformation these are the 2 stages what happens one the nucleation of a new phase second one is the growth and we have to deal with separately as growth will be part of all the phase transformations will be discussing is separate cases whether it is a liquid to solid transformation or solid to solid transformation whether a single phase or multi phase will discuss separately for each of these different phase transformation, but nucleation is something which is generic all of them that is what nucleation has to be dealt with completely separately and will.

And you know analyze all the theories and tell you how we can apply the nucleation theories to determine the nucleation rate or the other factors which come in to picture. And as you know nucleation is nothing but a formation of tiny stable solid particles or solid phase not particle actually for the liquid or solid.

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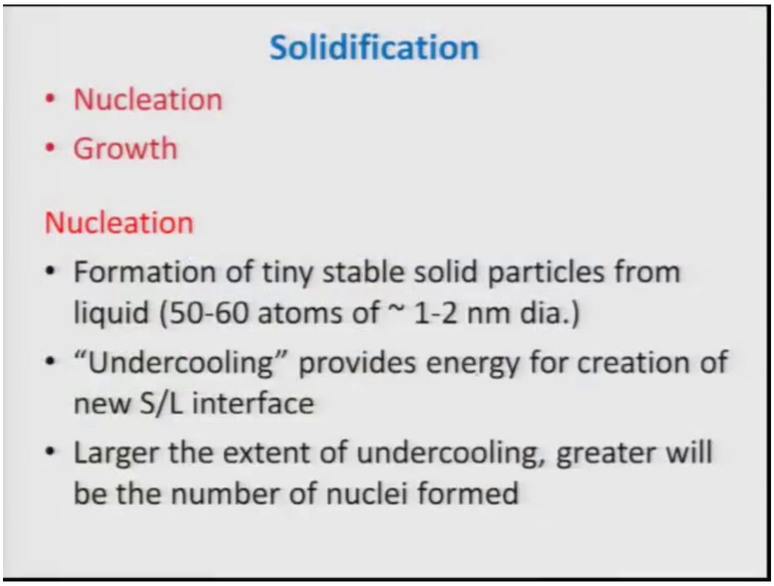

Solidification

- Nucleation
- Growth

Nucleation

- Formation of tiny stable solid particles from liquid (50-60 atoms of ~ 1-2 nm dia.)
- “Undercooling” provides energy for creation of new S/L interface
- Larger the extent of undercooling, greater will be the number of nuclei formed

It can be like maximum hundred of atoms depends on the type of systems normally is 50 to 60 atoms or 1 to 2 milli nanometer diameter and near to form a nucleus you must have to have an under-cooling because we are creating an new interface random nature. They will be moving in the liquid randomly only few of them came and join and form a cluster. And therefore, only few of them actually are well ordered crystalline order is present in three of these atoms. So, thus the interface between this well ordered atomic clusters and the liquid is diffused.

So, because of the; that means, the atomic as mentioned the liquid atomic in this well ordered solids are distinctly defined because of that there is a this definite interface created between this clusters, and the liquid and because of the atomic, and atoms are different between this well ordered crystals and the liquid there will there will be energy associated with the interfaces. And this energy is positive just like surface energy I have just now gives you the mathematical examples of how the grain grows inside small grain grows inside the big grain, Similarly here is just basically small crystal forming inside a big liquid.

So, same situation the surface energy will come into picture and this surface energy is a positive in nature. Therefore, that energy must be supplied by the system and this supply of energy is possible only possible when I under-cool the liquid, because the free energy of the systems will be will be will has to be there positively available to the system to take care of that is why under-cooling is very much required. Now the larger the extent of under cooling greater will be nucleus form nuclei form that will see in the detailed calculations.

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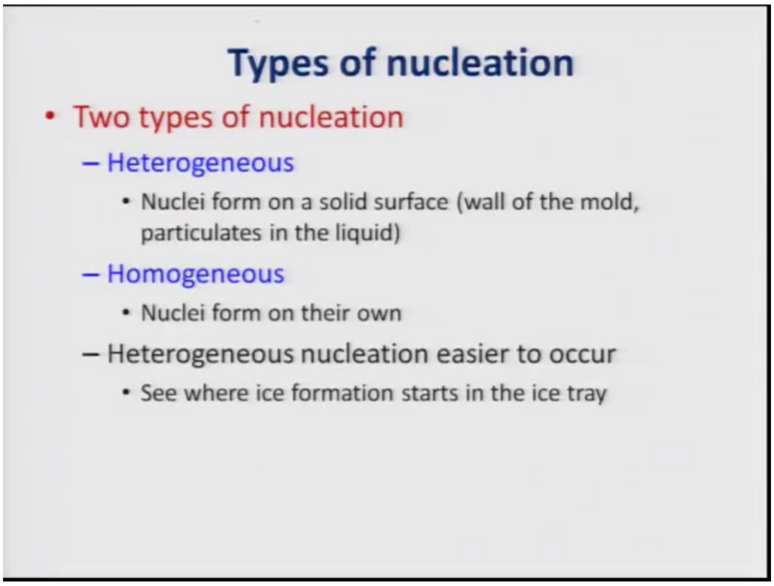

Types of nucleation

- Two types of nucleation
  - Heterogeneous
    - Nuclei form on a solid surface (wall of the mold, particulates in the liquid)
  - Homogeneous
    - Nuclei form on their own
  - Heterogeneous nucleation easier to occur
    - See where ice formation starts in the ice tray

Now, nucleation which is very generic in all kinds of phase transformation are mostly heterogeneous; that means, nuclei forms on a solid surface it can in a solidification, it can form on the walls of the mold or in a particulate on a liquid or solid case it can form on a interface like grain boundary or dislocation or a twin or even any other interfaces inside a solid. So, with this is the most prevalent one which is observed in the real situation the one which is easy to deal with, but really observed in the literature or in the experiments is homogenous nucleation. That mean nucleation can form in everywhere in the system there is no preferential side for the nucleation it may not be there it has to form in a boundary or it has to form on a certain kind of a solid particle or notice ice formation starts in the ice tray when it happens. That is the case of heterogeneous nucleation those of you seen how the ice solidifies in a ice tray probably you have seen that ice starts forming around the ice tray surfaces and then grow. Therefore, homogenous nucleus is nothing but a theoretical process which allows us to understand how the nucleation happens.

So, our first discussion in the next lecture will be on homogenous nucleation and to build a theory of homogenous nucleation then slowly will move onto the heterogeneous nucleation, because that is more complex that is why it is better to start with homogenous nucleation to give an idea in a homogenous nucleation.

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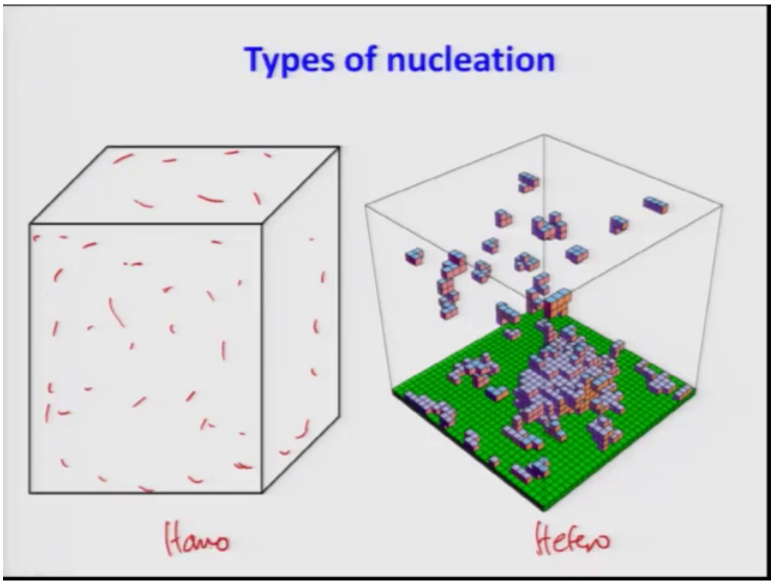
Types of nucleation

That is what is shown on the left side this is the big cube suppose or a system in which nucleation can happen anywhere any where it can happen there is no preferential things anywhere it can happen. That is what I have written it blank and I am all filling up with the nucleus. But on the other hand heterogeneous nucleation will be happening on you see on the surfaces or the boundaries or the corners whatever. So, this is hetero that is what we say and this is homogenous.

Finally, you know it is very easy that because there is no preferential side for the nucleation in the homogenous nucleation very easy to deal with it; it is much much easy all important factor is that we create an interface between the solid and liquid. So, therefore, you must take care of the interfacial energy fine. So, I have just introduced the subject and nucleation is very very you know generic in all the system whether solid solid or liquid solid phase transformations or even paper to solid phase transformation it is all as present, but theory of nucleation will be generic it will not change whether we having different type of transformation.

So, whatever you are going to learn in the next few lectures is very generic which you have probably learned in some other subjects it will be simply re-couple recapitulation of whatever you have learned in your others other you know is courses in material science engineering. But, still for sake of understanding or completeness of the understanding of the phase transformation this is important, because we will be doing calculations using this equation in your assignments or in your exams. Therefore, these equations or the theories of the nucleation must be known.