

**Heat Treatment and Surface Hardening (Part-1)**  
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**Lecture Number 29**  
**Nucleation kinetics in solid state**

So this will be the last lecture on nucleation kinetics in the solid state. So far we have really looked at liquid to solid (tra) transformation and nucleation in liquid to solid systems. Now what happens in to the nucleation rate in the case of solid to solid transformation.

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Nucleation Kinetics in the solid state

- strain energy  $\alpha \rightarrow \beta$   
 $= \Delta G_s$

$$I = I_0 \exp\left(-\frac{\Delta G^*}{kT}\right) \exp\left(-\frac{\Delta G_s}{kT}\right)$$

$$r_{hom}^* = \frac{2\gamma_{\alpha\beta}}{|\Delta G_v - \Delta G_s|}$$

$$\Delta G_{hom}^* = \frac{16\pi \gamma_{\alpha\beta}^3}{3(\Delta G_v - \Delta G_s)^2}$$

$$\Delta G_{het}^* = \Delta G_{hom}^* \times S(\theta)$$

So here we are going to look at nucleation kinetics in the solid state. What things change mostly it remains quite similar to what we have done in liquid to solid. But there are going to be some additional terms that would come in.

For example in any phase transformation there is a volume change now this volume change gets accommodated in the case of liquid to solid. So if a solid let us say expands the liquid around it accommodates it. However in the solid to solid transformation if the nucleus that forms expands then it will tend to deform the surrounding parent phase.

As a result there would be a strain energy that would be introduced in the system. This strain energy as has already been discussed in earlier lectures (would) would be associated with positive

change in free energy  $\Delta G_S$ , where S standing for strain. And as a result what happens to the critical size of the nucleus in this case well the strain energy term would also get into the relationship.

And let us say we have transformation of alpha going to beta, so a beta nucleus is forming from alpha and there is a volume change as a result of strain energy term  $\Delta G_S$  comes in then the critical size in this case would be  $2 \gamma \alpha \beta$  upon  $\Delta G_V - \Delta G_S$ . Here, it is clear that the critical size when a strain energy term comes in would be bigger larger than in the case where the strain energy is negligible or 0.

And what happens to  $\Delta G^*$ , where here just looking at homogeneous case so let me also write it as homogeneous. Well this becomes  $16 \pi \gamma^3 \alpha \beta$  cube upon  $\Delta G_V - \Delta G_S$  cube. So the free energy associated with the critical size nucleus also goes up for the energy barrier is higher. So with the presence of strain energy one would expect nucleation to become little bit more difficult or would require further undercooling because of the transformation which takes place with the change in volume.

Of course strain energy is produced by from various factors one of them is just volume change the kind of interface that is formed whether it is a coherent interface or an incoherent interface that will also play a role in the strain energy. However I will not go into the details because in earlier lectures this has been delth in with quite some detail. If I look at the nucleation rate equation I is equal to  $I \exp(-\Delta G^*/KT)$  times  $\exp(-\Delta G_D/KT)$ .

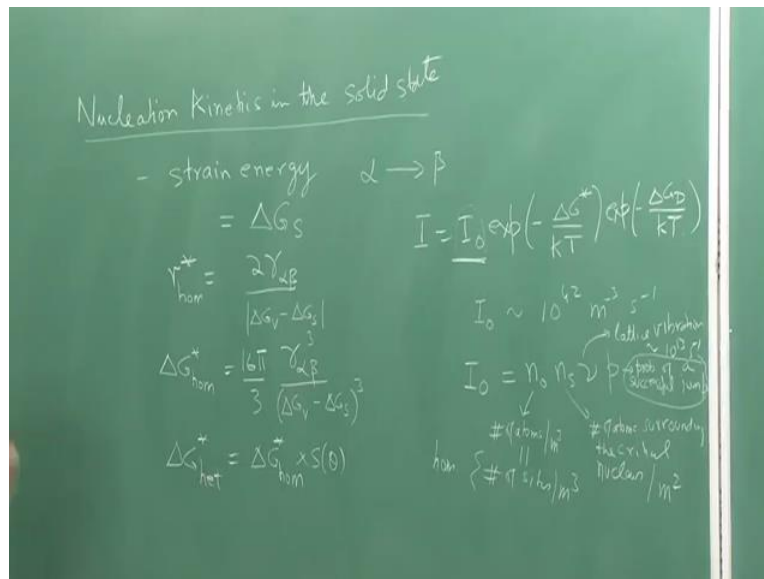
So what are the terms that are changing in this in the case of the solid transformation. So  $\Delta G^*$  would be somewhat different, so if it is larger than the nucleation rate will go down for the same amount of undercooling. In the last lecture we had also looked at  $I_{\text{not}}$ , what  $I_{\text{not}}$  in the case of homogenous nucleation would be of similar order that we have already got the order of  $10^4$  or so.

But in the solid state the heterogeneous nuclea nucleation case the situation would be similar in the sense that the free energy for the heterogeneous nucleation would be related to the homogeneous free energy multiplied by whatever shape factor that is there. So for example in in a in a in a polycrystal structure if the beta phase is forming on the grain boundary it might be

forming in a lens shape which also has been delth with in an earlier lecture we should have a somewhat different value of the shape factor than what has been considered earlier.

In the last lecture slightly different value by a factor of 2. So then what happens to the nucleation rate from all of this well the strain energy ofcourse changes this. If it is a heterogeneous nucleation that changes that again delta G star invariably in the solid state heterogeneous nucleation is the preferred route for formation of nuclei. In large number of systems for example in austenite to ferrite transformation in steels the proeutectoid ferrite tends to form on the grain boundaries of the austenite grains .

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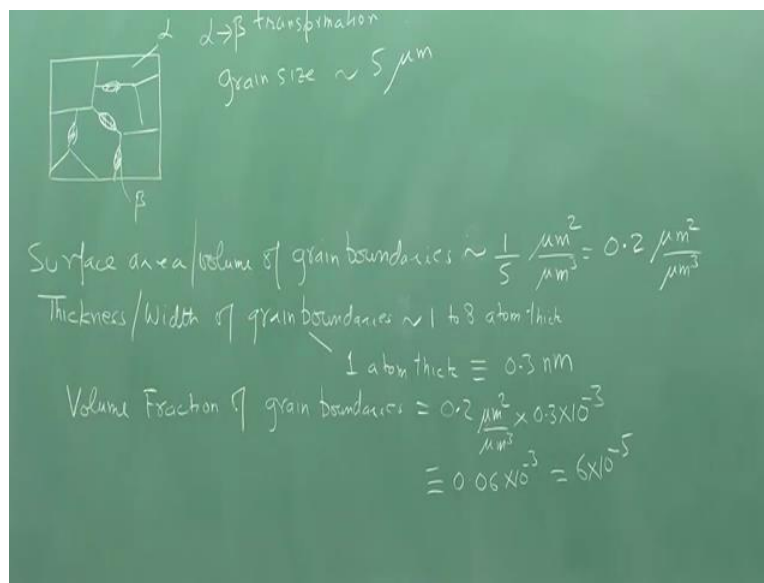
So what happens to the nucleation rate so delta G star has changed as we have already seen now I want to explore Inot what happens to the factor Inot in the nucleation rate expression. Well in in the homogeneous case Inot we have been taken as of the order of 10 to power 42 for metals, 10 to power 42 per meter cube per second. Now I want to explore how I0 will change in the heterogeneous case in the solid to solid transformation.

Remember that what is I0 from a previous earlier lecture I0 is n0ns mu times peak, n0 is the number of atoms per meter cube, these are the number of atoms surrounding the critical nucleus per unit area per meter square let us say. This is lattice vibration frequency which is of the order

of  $10^{13}$  per second and this is probability of a successful jump from an atom in the parent phase to the and the atom joins the nucleus so let me this.

Now in all these terms  $n_0$  the number of atoms per meter cube in fact this number of atoms per meter cube is taken in the homogeneous case as the number of sites for nucleation per meter cube, this is for homogeneous. Now, the number of sites in the heterogeneous case how are they going to change and let me consider two choices or rather let me consider two sites, two sites of heterogeneous nucleation.

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Let me consider one as grain boundaries as sites for nucleation. So what suppose I have a polycrystalline microstructure and I have these polycrystal in grains in the system. This is alpha and I am considering let us say alpha to beta transformation. So one way this beta phase can form or the beta nucleus can form is this nucleus at grain boundaries. So these are the lens shaped nucleus that is one shape that is possible for which the analysis has already been done.

Now the thing is for beta to form I have certain density of grain boundaries and that density of grain boundaries is going to determine what would be the number of sites at which beta can nucleate. So the density of grain boundaries is going to governed what is going to be the site of nucleation. So let us , let us try to estimate that how do we estimate that well what I need to know, I need to know what is the surface area per unit volume of grain boundaries.

So I need to know this, I need to know what is the thickness or width of grain boundaries. So that I can calculate what is the volume of grain boundaries or the volume fraction of grain boundaries in the material once I know this then I would be able to estimate what kind of a order of magnitude estimate for the density of nucleation sites.

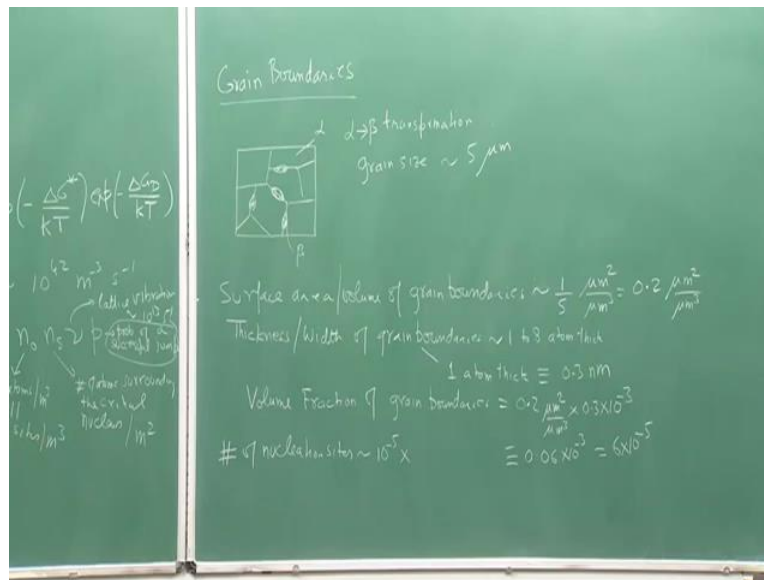
So let us consider, let us take in a case of any metal that grain size is of the order of 5 micrometer so obviously if I have small grain size I will have lot of grain boundaries, large density of grain boundaries larger number of sites nucleation. If I have coarse grains I will have less density of grain boundaries and hence less number of sites of nucleus.

So grain size let us assume is order of 5 micrometers then the surface area per unit volume or grain boundaries what is the surface area of these boundaries is and we are only doing an order of magnitude estimate is of the order of 1 upon 5, just a inverse of the grain size. And let me write the units as micrometers upon micrometer cube which is equal to 0.2 micrometer square upon micrometer cube.

What is the thickness or the width of grain boundaries well typically one can assume a width from 1 to 8 (ato) atom thick. Let us for our purpose is let us assume a grain boundary which is only one atom thick. So for example a metal like copper whose diameter is all the order of point 3 nano meters, which means the thickness of the grain boundary I can assume it to be 0.3 nano meters.

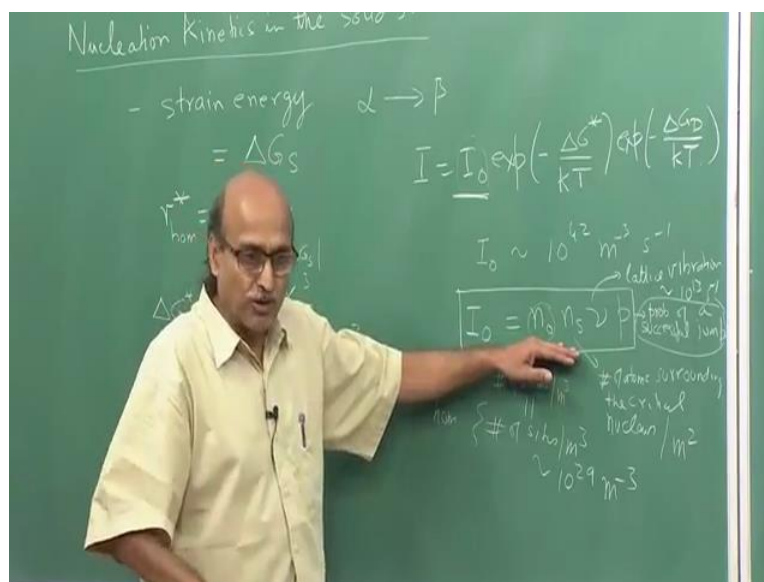
So what is the, now the volume fraction of grain boundaries in a material like copper which has a grain size of 5 micro meters. Well that would be simply surface area per unit volume multiplied by the thickness or the width of the boundary. So that is 0.2 micro meter square per micro meter cube multiplied by 0.3 this is a nano meters let me (con) convert this to micro meters.

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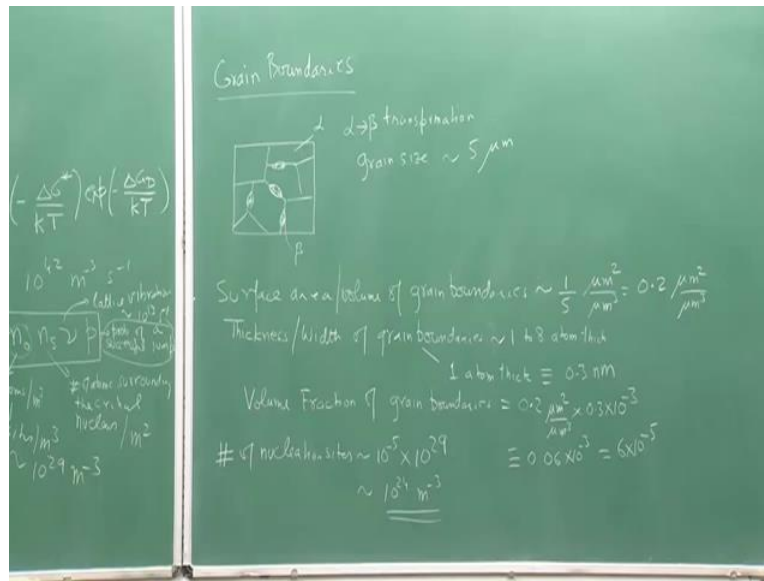
This turns out to be 0.06 into 10 to power -3 which is equal to 6 into 10 to power -5. That is a fraction of boundaries present in the material so what is the number of nucleation sites then on the grain boundary well that would be let us just take 10 to power -5 as an order of magnitude of estimate for the fraction in this case so it is 10 to power -5 multiplied by how many atoms are going to be there on the grain boundary each atom then is the potential site well that number is  $n_0$  which is of the order of 10 to power 29 per meter cube.

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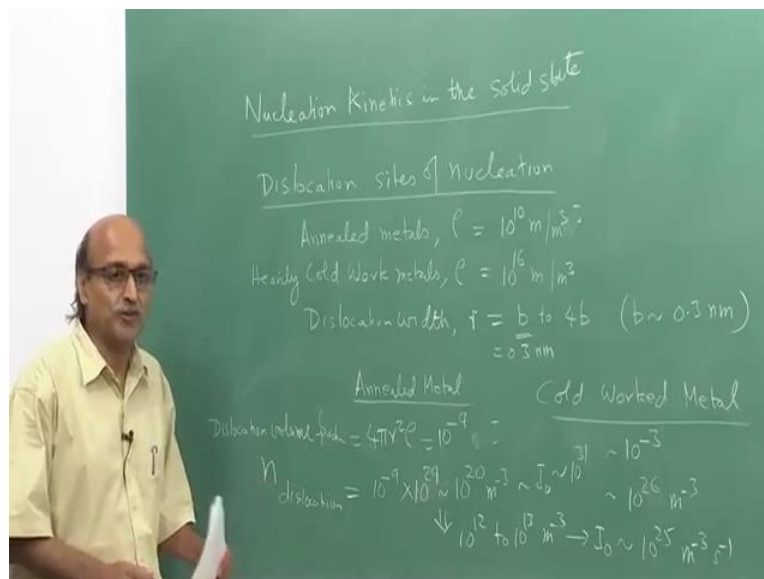
So all I have to do is multiply this with 10 to power 29 and I will get order of magnitude estimate of the nucleation sites on grain boundary as 10 to power 24 per meter cube. So therefore 10 directly where 10 is 10 is this will become several orders of magnitudes smaller as compared to in the case of homogeneous nucleation.

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One can also see that if I let us say take a very coarse grain like 50 microns, so I increase a grain size on order of that density of nucleation sites will reduce magnitude by this simple calculation.

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Similarly let me pick up one more site where in solids nucleation takes place and which is on dislocations. So let us try to see what kind of an estimate one would get where heterogeneous preferred nucleation would be on dislocations. So dislocation sites of nucleation. Now in this case let us try again order of magnitude estimate. In annealed metals the density of dislocations is of the order of  $10^{10}$  meters per meter cube.

So dislocation density is measured as the total length of dislocations in a unit volume of material. So in this case  $10^{10}$  meters per meter cube. If I looked at heavily cold work metals, in heavily cold work metals the density can go up to as high as  $10^{16}$  meter per meter cube sorry this is meter cube. Now on these dislocations what would be the density of sites this could be calculated by considering that dislocations has a certain core width.

So we also have to have an estimate of the dislocation core width or the width of the dislocation you can imagine that this core is in the shape of a cylinder. So the dislocation core width radius  $r$  is of the order of 1 burgers vector to about 4 times the burgers vector. Now in a metal like copper we can (est) put the burgers vector to be of the order of 0.3 nano meters.

And let us just assume for purposes of order of magnitude estimation that the core width is just  $b$  which means 0.3 nano meters. Then let us do an estimation for, let me write down here annealed metal, cold worked metal, dislocation let us try to calculate dislocation volume fraction. So fraction of the material occupied by the dislocation core this is equal to  $4\pi r^2$  times the density which turns out to be  $10^{-9}$ . While in the case of cold work this would be the fraction of the material occupied by the dislocations is  $10^{-3}$ .

Therefore the number of or the site density number of nucleation sites on the dislocations in the case of annealed metal then is  $10^{-9}$  multiplied by density of dislocations in the annealed metal which I am taking it as a order of  $10^{10}$ , oh just a second what did I do no... sorry we have already taken this density. This is the fraction  $10^{-9}$  multiplied by  $10^{10}$  atoms per meter cube.

So this gives me an order of magnitude estimate of  $10^{20}$  sites per meter cube. What happens in the case of cold work metals we have much higher density of dislocations. This number turns out to be  $10^{26}$  per meter cube. So what we have seen is that in annealed



metals you can have if I look at it from the homogeneous case the number of sites for nucleation can drop down by as much as  $10^{20}$ .

And in fact it can even go down even lower if we specially make materials which have very low density of dislocations. Then it could even go down to the order of  $10^{12}$  to  $10^{13}$  per meter cube. So if I then look at what is the value of my  $I_0$ , well in this case for example grain boundaries  $I_0$  would be of the order of  $10^{35}$ . So in the case of grain boundaries value of  $I_0$  then would turn out to be the order of  $10^{35}$  per meter cube.

Here in the case of dislocations this will come down to  $I_0$  would come out to be the order of  $10^{31}$  and could go down to as low as  $I_0$  to be the order of  $10^{25}$  per meter cube per second. So we have seen in this lecture how the nucleation sites can change depending on what kind of heterogeneous site is available. With this we conclude our discussion on nucleation and nucleation rate. In the next lecture we will be talking about once a stable nucleus is formed what would be the rate at which it will grow. So will look at growth kinetics, thank you.