

Heat Treatment and Surface Hardening (Part-II)
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Lecture - 01
Recap - 1

Hello everyone. Welcome back to the course Heat Treatment and Surface Hardening Phase-2. And in the introduction class as we have mentioned that in the first phase, we talked about some fundamentals. And today in the first two lectures, we will recap what we have discussed in our phase-1 and then gradually we will step into aspects of phase 2.

Now, if I go back and see our phase one lectures, you will find that the main thrust was on the finding of driving force of any phase transformation, which is very essential to get to the fundamental aspect of heat treatment, which is the overall transformation kinetics. And actually on that basis we have tried to find out TTT diagram, which is time temperature transformation diagram. And then gradually we moved into finding those equations which will be used for deriving TTT diagram. And the equation is nothing but JKMA equation which is Johnson Mehl Avrami Kolmogorov equation.

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Recap

1. Single Component System.

↳ $\Delta G_v \rightarrow$ Melting \Rightarrow Solidification

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$\frac{\Delta H_m \Delta T}{T_m V_m}$

ΔH_m - Enthalpy of melting
 ΔT - Undercooling = $(T_m - T)$
 V_m - molar volume
 T_m - Melting temperature

2. Nucleation rate = $I = I_0 \exp\left(-\frac{\Delta G^* + \Delta G_v}{kT}\right)$

$\Delta G^* = \frac{16\pi}{3} \frac{\gamma^3}{\Delta G_v^2}$ γ - Interfacial energy (J/m^2)
 ΔG_v - Gibbs free energy / volume (J/m^3)

Now, let us recap what we have done in our phase one. First thing we looked into a single component system mainly we looked into single component system though we

have covered a little bit on binary systems, but mainly concerned was single component system there we try to find out ΔG_v the expression for ΔG_v . Which in case of melting if we consider that time if it is melting or solidification that time if we try to find out the expression for ΔG_v , and that was our primary interest to find an expression for ΔG_v , which can be written in this form.

Where ΔH_m is enthalpy of melting, ΔT is under cooling; and this under cooling can be expressed in this form $T_m - T$, and this T is nothing but the point the temperature where we are having solidification. And T_m is basically the melting temperature. V_m is molar volume of that particular single component; and actually during derivation of this particular expression, we did not consider that what will be the change in molar volume from solid to liquid transformation or liquid to solid transformation. And T_m is melting temperature and interestingly this T_m is the melting temperature when the system is in equilibrium and the curvature effect is nil.

Now, this ΔG_v is later used to find out nucleation rate, and in case of again solidification, we started referring to solidification because single component solidification is little easy for treatment. Now, that time I , we try to find out expression for I , which is the nucleation rate and that time the unit is per unit per meter square per second which is a number of nuclei appearing per meter cube, which is the per unit volume per unit time. And that is expressed in this form, where I_0 is a constant, and that varies between 10 to the power 13 to 10 to the power 40 . ΔG^* can be expressed in this form square where γ is interfacial energy, which is joule per meter square ΔG_v is Gibbs free energy per unit volume, so that means, joule per meter cube.

So, this ΔG_v is Gibbs free energy per unit volume, and this is the driving force for solidification. And that time it is actually coming from G , temperature, which is the free energy temperature plot for single component, which varies like this. Where this is my T_m , and this is G_S , this is G_L . So, left to this we have solidification. And let us say if I am here, so that time this is my ΔG_v . And if we can take it as ΔG_v , G_v mode which is the volume free energy then this becomes my driving force for transformation from liquid to solid.

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ΔG_s - Activation energy for per atom jump across solid-liquid interface
 k - Boltzmann Constant
 T - Transformation temperature

Velocity expression

$$v = \frac{D}{a} \left[1 - \exp\left(-\frac{\Delta H_m \Delta T}{RT_m T}\right) \right]$$

D - Diffusivity of atom
 a - Atomic distance
 R - Gas Constant

The diagram shows a square representing an atom with arrows indicating movement. Below it, a vertical line represents an interface with 'S' (solid) on the left and 'L' (liquid) on the right. To the right of the interface, a series of circles represents atoms, with one circle at the interface and others further into the liquid phase.

A graph at the bottom shows the velocity v as a function of the interface velocity I_s . The curve starts at the origin and rises to a peak, then falls. The temperature T is indicated on the y-axis, and T_m is marked on the x-axis.

And also if you see ΔG_s , this is activation for per atom jump across solid interface; k is Boltzmann constant, and T is the temperature where transformation temperature. Now, this is the nucleation rate expression, which will be needed to find out overall transformation kinetics, there is another important aspect, which is the volume velocity expression. So, the rate at which this interface is growing into the parent phase that means, the product phase if we have a solid nuclei, which is a spherical, and remember this expression this particular expression is valid and this for spherical nuclei.

So, if the sphere is growing in all direction, then it is basically 3-D growth. And even it can grow specifically into one direction that time it will be 1-D growth or it can be 2-D growth in two dimension, it is growing and third dimension, it is not able to grow sufficiently. So, that it could be having a shape of disc, if it is a two dimension; if we have one dimension it can have a shape of needle, those shapes are possible.

Now, velocity expression if we write it that can be written in this form D by a 1 minus exponential minus $\frac{\Delta H_m \Delta T}{RT_m T}$, where D is the diffusivity of atom. And these atoms are basically jumping from this let us say this is the interface of liquid and this is the interface of solid. Then in these two interfaces, if we draw it those two interfaces, this is solid this is liquid two atoms are jumping like this from this end or from this end to this end and that time we see what is the diffusivity of the atom.

a is atomic distance, so that is if we have one layer of atom and then this if it is a solid and if this open spheres open circles are liquid atoms, so this distance between two is basically nothing but a . And as usual ΔH is the melting enthalpy, ΔT is the under cooling where the transformation is taking place. R is the universal gas constant gas constant.

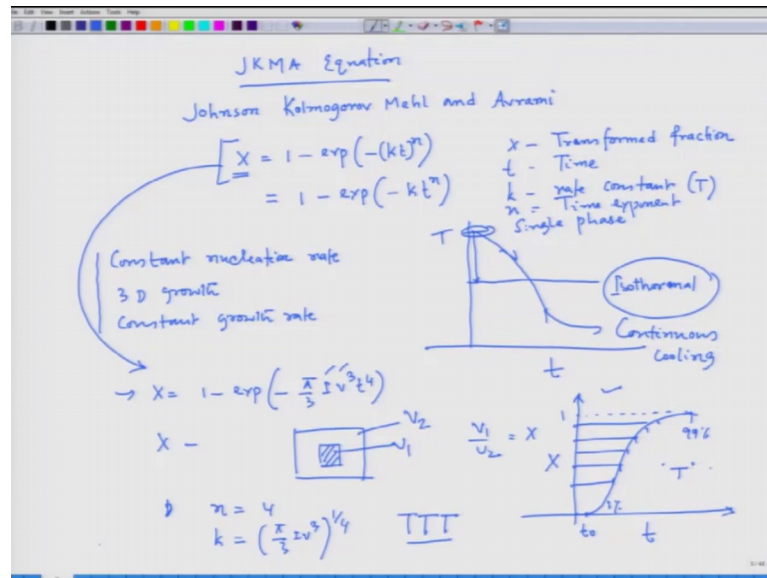
Now, if we try to see the way they vary, if we try to plot this axis is I and V , and this axis is T , and this is my T_m . Then I variation would be if we change the color, I variation would be like this, where there is a critical under cooling up to which there is not much of significant nucleation possible. And in the phase one, we have already discussed elaborately why there should not be any significant nuclei and then suddenly it starts appearing those nucleation starts appearing, because it is the main issue is the interfacial energy which prevents stable nuclei to appear, even if there are gradients which is a negative free energy change which are existing below T_m . But up to certain range we cannot have any significant nuclei.

And growth rate this is I and growth rate it is like this. So, this is my V . Now, from these two things, we have an idea that if we are having if we are operating at a higher temperature close to T_m , this is my T_m , then we see that growth rate is very high, but nucleation rate is low. And as we go down the temperature axis that means, this way that means, as we are increasing the under cooling we see that growth rate is gradually increasing and then going down, but the nucleation rates picking up. And around these zone, we see that that we have a comparable nucleation and growth rate. And as we go down further, we see that both the nucleation and growth rates are going down that it gives an idea that if we operate at a higher temperature, we have less amount of nuclei available for the growth. And that time if we operate there we will have coarse grain structure, because a smaller number nuclei as well as growth rate is very high. So, nuclei would start grow and then it will have a coarse grain structure.

And if we operate at a very low temperature growth rate as well as nucleation rates are low, that means, there also we have limited number of nuclei. But the since the growth rate is very low, it will also have a situation where we can have a situation like we can have a small number of nuclei since the growth is not taking place, there could be a possibility of parent phase being there. But if we operated at in between stage, we can have sufficient number of nuclei, but at the same time growth rate is also not low; it is

moderately high compared to this zone, then we can have a very good amount of transformation. So, that indicates that if we include time scale into it, we would get that at a different time range, what would be the fraction transformed, and that actually ends up getting an equation which is popularly known as equation which makes use of mix use of nucleation rate and growth rate expression.

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There are different conditions we have also explained; what are those conditions. For example, let us say we can have 3-D growth, we can have 2-D growth, we can have 1-D growth, this we can have constant nucleation rate, we can have transient nucleation rate, we can also have site saturation nucleation rate. For example, in case of site saturation, we are saying that during in the beginning of the transformation, all the nucleus what are possible in the system are there. And after that as the time relapses, we will not have any more nuclear formation. In case of constant nucleation is we are saying that at every time moment, we can have a constant number of nuclei appearing. Depending on that we can have different expressions for this JKMA equation, and this JKMA equation is termed is as Johnson Kolmogorov Mehl and Avrami.

So, this four scientists they all of them for example, three places it was being developed. So, finally, it is there they end up getting the same expression, and generally this is also popularly known as Avrami equation. The general form is x equal to one minus exponential minus $k t n$. Now, this some book, it writes as 1 minus exponential minus $k t$

to the power n . So, different forms, but actually it ends up getting the same form, where x is transformed fraction, t is time. k is rate constant specific to temperature, because these form is best suited for isothermal case, but later on it can be tricked a bit to include the non-isothermal form.

And in order to explain this isothermal and non-thermal case, for example, let us say you are at some temperature T and this is time axis, one can do jump to some other temperature below this temperature. And they are one can hold the sample like this, this is the treatment called isothermal. And then another experiment can be performed where the material is taken to this level, and then it is continuously cooled and this temperature where it is to be taken in case of solidification, it is to be taken to single phase.

In case of solidification, everything should be liquid. And in case of solid-solid transformation, we should reach to a point, where it leaves us single phase. For example, in case of phase transformation in steel, we generally take it to austenitizing temperature, where things would all transform into austenite, and then we will start transforming either we can go through this route or we can go through this route. So, this is basically nothing but continuous cooling. We have explained this part also in our phase one lectures, and whenever we talk about this x , and now one can plot x as a function of time at a particular temperature if we carry out the experiment in isothermal mode.

And now let us say if we consider constant nucleation rate that time and also a 3-D growth that means, the nuclei form is growing in all three dimension as well as constant growth rate. If we have these three conditions, then this expression takes a form like this x equal to $1 - \exp(-\frac{4}{3} I V t^3)$. If we go back to our lectures in our in the phase one, you will see how this thing has been derived. And this is valid in case of spherical nuclei and also spherical growth.

So, that time if we try to compare this one this equation with this, we can see that x which is the fraction transformed that means, if we have a particular volume, then if we have a particular phase forming, so this volume is v_1 , this initial volume is v_2 , so then v_1 by v_2 would be the x . So, this x is can be plotted with respect to time. And this I and V we know those expression at a particular temperature, we can calculate I and V , and if we put that thing in that expression, the graph we will get like this, where this is plotted with x versus time you will see a plot like this. And in this plot, this is one, it is touching one,

it can never reach completely one. But it is started transforming after some time delay that is called t_0 which is nothing but the incubation time.

Now at different locations; that means, if we consider to be one percent which is the measurable quantity for getting the idea of whether the transformation is taking place or not and if this is 99 percent, so at different points I can get the transformation part. And this is specific to at a temperature which is below the transformation temperature the equilibrium transformation temperature. And there if we compare this and this, I can get n to be 4. And remember here we miss this point n is basically time exponent which gives an idea that whether the system is growing in 3D or 2D or 1D those information it can give. And k can be related to π by $3 \pi V \text{ cube } 1 \text{ by } 4$.

So, this thing also we have elaborately explained and these particular graph at different other temperatures, if we plot and try to extend that graph on a temperature time diagram we can get a diagram which is called TTT diagram. Now, we will explain little bit on this TTT diagram in our next lecture. And remember this is all about recap of what we have done in our phase one.

Let us stop here. We will take it up in our next lecture.

Thank you.