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Lecture-28 Shock Wave Induced Phase Transformations 1

Hello everyone, so, in the previous lectures we discussed about shock waves, the basics of shock waves, the creation of state of shock waves, attenuation, interaction and reflection of shock waves. And also we have discussed about the basics of material science about crystal structure and the effects. So, now, we will talk about this a new chapter. **(Refer Slide Time: 00:49)**



That is Shockwave induce phase transformations and the chemical changes that means due to

shock waves. What are the physical and chemical changes happen in the material? (Refer Slide Time: 01:14)

Shock Wave Induced Phase Transformations and Chemical Changes

$$SW \longrightarrow physical 4 chemical changes in the
material
F.S. Mishall 1954
 $(polymerphic)$ phase transformation
 q iron at 13 hPa characteristics
 q multiple
 $rystal structure$$$

So, the shock waves as we know I write SW for shortcuts. It produce physical and chemical changes in the material. So, when it passes through the material. The material undergoes some transformations. So, first report on this was from a fresh Michelle in 1954. So, it first reported that kind of phase transformations which is Polymorphic phase transformation.

Volume of experience transmission of iron at a very high pressure. I think he reported 13 Giga Pascal. So, what he taught is the alpha item, which is FCC, a phase is transformed into gamma phase, I am sorry, the first one is the alpha iron. Which is a BCC phase, transforming to demo phase which is FCC. However, this was later corrected to actually the corrected transformation is alpha phase BCC to f7 phase which is a HCP hexagonal closed pen.

So, if you are wondering what is polymorphous transformation. Many of you I think, know about it. That is only polymorphic. Phase transformation is a characteristic of solid structure solid crystal and material, solid crystalline material. So, that can exist in multiple structures multiple especially multiple crystals structure. So, that is called polymorphous. And so, from one crystal structure to different crystal structure.

This kind of changes happen that is called polymorphic phase transformation. So, we will see this with a unary phase diagram, **(Refer Slide Time: 04:17)**



This is the unary phase diagram of iron unary as you know, that is one component unary means one component which is in this case is iron there can be binary phase diagram. That you know, binary Phase diagram example is iron carbon diagram, iron carbon phase diagram or you can say r1 sorry iron cement tight Fe-C Phase diagram. So, in this case for Iron the phase diagram, so, the y axis is temperature T and then x axis is preserved that is in Giga Pascal and then temperature is in degrees Celsius.

So, what happened is at very high temperatures. I do not know we will be in gaseous phase and then the above the 3000 degree Celsius, then it will be pounding liquid stairs. And then in this smaller portions, it will be in delta phase which is BCC and in this phase it will be in gamma see FCC. Here, in room temperature will get it as BCC which is called alpha phase and then a very high pressure. It will be epsilon phase HCP. So, what the earlier reports by F.S. Mishall.

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Stated that, is actually from the transformation from alpha do epsilon phase. So, this is the transformation what he reported. So, we can see clearly see it from unary phase diagram. (Refer Slide Time: 06:31)



After that probably one of the important publication from De Carli and Jamieson in 1961 reported a transformation of carbon to diamond. With the help of shock waves, that is a very

at highest shock pressure. So, that is still even in this daily use that this process of applying very high pressure that is the shockwave induced transformation from carbon to diamond.

And in this process, we can have very fine that means in micron level very fine. I will right micron level, fine range of diamonds. Diamonds can be can be produced and then Dremin and Breusov in 1968. That they have presented a summary of the of the material changes that happen under shock waves presented a summary of the material changes that happened under shock with. So, we know that the shock wave has very high energy and this energy is dissipated. When it when Shockwave passes through the material and this dissipation of Shockwave.

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Shock Wave Induced Phase Transformations and Chemical Changes High energy deposition in the material can lead to physical and chemical changes 1) polymarphic phase transformations 3 chemical decomposition 3 chemical synthesis (9) polymerization of monomers and 5 defect formation (point, line, interfacial defects)

That will that means the deposition of the energy into the material. So, high energy deposition in the material can lead to physical and chemical changes in the material. So, that can be summarized by Dremin and Breusov. So, these are the processes can be polymorphic phase transformations that means, changes from one crystal structure to the other.

And then some may undergo chemical decomposition that means, the reaction in which the once substances decomposed into two or more substances, and then the opposite one is chemical synthesis, which means a two or more substances react together to form a more complex substance and then polymerization of monomers polymerization of monomers molecules but it means more normal molecules to form a polymorphic chain.

And then the last but not the least one is the defect formation that is the crystal defect formation. As we have learned the defect can be point defect or it can be line defect or it can be interfacial defect like tuning. As you know the line defects are mostly dislocations. So, these are the changes these are major changes that can happen due to Shockwave propagation

in a material. So, there are some other features like. $(D - f - S)^2 + (D -$

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They can be the local gradient of temperature development of local temperature gradient due to this is due to collapse of voids. So, voids which as you know happen because of the high velocity flow of material. So, that can create the development of local temperature gradient and that can this development of temperature gradient can lead to melting of in interface.

This can lead to melting of any interface present in the melting interface. And then also the relative motion of the powders produce severe friction. So, that produce severe friction Shockwave can produce very high pressure and high temperature and also it can produce high shear stress and strain, high stress and also string. So, these can be both maybe it is it may be local rise or it can be rising the entire body and entire body or it can be a global rise.

And these effects even get can be more pronounced even more pronounced. When the material is either a porous material or a mixture of powders. Powders like, it can be mixture of different powders of different elements or different compounds. So, what we have learned is so, these are the some different features characteristic of Shockwave propagation. **(Refer Slide Time: 15:23)**

Shock Wave Induced Phase Transformations and Chemical Changes

R.A. Graham and co-authors 1986, 1989, 1993 Summarized () configuration charge monthslogy & porosity change men mining: metainds from neighbouring particles forced together & forced to under go relative motion
 activation: high denvity defects may increase the reactivity of poorders
 (4) heating: SW produces intense temperature fluctuation.

Regarding the physical and chemical changes and some of the earlier publication also include one from a few from RA Graham and he is a co-authors that was like published at different times 1986, 1918, 1989 and 1993. These publications are summarized some of the processes see, one is configuration change. So, these are the processes that happened you do Shockwave and then mass mixing and then activation.

I will let you know what are these processes, activation and maybe heating. So, these happened due to shock waves country recent changes can include morphology or and porosity chains and mass mixing means materials from neighbouring particles forced together and also forced to undergo relative motion.

And then activation means the high density of defect formation may lead to defect means, that crystal defects high density of defects may lead to increase the reactivity of the powders also Shockwave produces high temperatures and that we know that he actually produces intense temperature fluctuations. So, these are the points summarized by from the early researchers. So, as we know (Refer Slide Time: 18:42)

Shock Wave Induced Phase Transformations and Chemical Changes

Fast process -> Application of SW -> short duration (1-10 MS) -> not enough time for significant diffusion -> different mechanisms involved -> P decreases the diffusion coefficient & it is difficult for foreign atom to penetrate into the other element.

This Shockwave propagation is a very fast process. So, it is the application of Shockwave is very has very short duration. It is in the order of microsecond application of Shockwave is has very solid duration. It is 1 to 10 microsecond in most cases. So, it is does not have enough time for diffusion to take place for significant diffusion. And so, and we know that different mechanisms are involved of doing involved in the formation and the completion of different features or compounds.

And also the pressure on right before pressure decreases the diffusion coefficients. And so, this lead to difficulty for the foreign atom to penetrate into or move inside the other element the element or compound. We will talk about the thermodynamics of phase transformation called phase transformation. (Refer Slide Time: 21:17)

Shock Wave Induced Phase Transformations and Chemical Changes Thermodynamics of phase transformation Duvall & Graham 1977 Therprodynamics Kinetics , Tromoformation of solids enternal factors phase slability (P, T) internal factors (composition, internal stresses due to adefects)

So, most of the part of the discussion in the mark May as book taking our premier references that is Duvall and graham 1977. That is one of the early publications in this area. So, the

transformation of solid depends on or controlled by one is thermodynamics and kinetics. That, mostly as you know means deals with rates of reactions and also we will talk about phase stability.

So, which phase is stable and depending on that the phase transformation happens. So, these phase stability depends on either external factors controlled by external factors like pressure and right before pressure and T for temperatures. So, pressure temperature these external factors and there can be some internal factors which also control these phase stability. Internal factors which include Composition of the material and internal stressors due to defects.

Do we can write mostly crystal defects? Or, you can write simply defects as we know point line in interface and defects. So, there are internal stresses associated with these defects. So, that controls the phase stability whose phase will be stable. So, that debate and that will decide phase transformation. So, as we have already discussed. (Refer Slide Time: 24:13)

Shock Wave Induced Phase Transformations and Chemical Changes SW -> produce midden changes of P&T may result in generation of new phases

That shockwave will produce sudden changes of pressure and temperature that we already discussed many times. And we know that this will result may result in a generation of new Phase. That is why we are discussing these Phase transformation. So, the Phase transformation can be broadly have two types. I will use a new slide for this. **(Refer Slide Time: 25:03)**



Phase transformation can be broadly categorized into two categories. First one is diffusional phase transformation. Which involve diffusion and the second one is diffusion less phase transformation diffusion less phase transformations. So, diffusion less phase transformation includes this includes maybe different phase transformations like nucleation and growth of precipitation. And then Spinodal decomposition, financial decomposition and cellular transformation.

So, we will not discuss about these, so, we will just write 123. So, that we understand that these three are sub category of the diffusion less phase transformation. So, these type of the diffusion less phase transformation will not discuss much because during Shockwave propagation. They are not so important not important because the shockwave propagation involves very limited time because of limited time is very less limited time of shock wave propagation.

So, that means limited time to diffusion to happen that spends time is less diffusion cannot happen and there can be some post shock effects. Post shock means after the pitches after the shock wave passes through the material. Some effects can be there and that is that can be residual heating can induce precipitation, residual heating can induce precipitation.

The formation of precipitates precipitation so, this is post shock effects. However, we are more interested what happens during the shocker preparation not what happened after this shocker propagation. So, this is the post shock effects and not during Shockwave propagation, I will let SW for Shockwave. So, hence we will not discuss this the phase transformation much.

So, rather we will go to the diffusion less phase transformations that can be of different types. So, we will take number one else displacive transformations, one of the diffusion less information discipleship transformation then, second one is massive transformation and the third one is melting or solidification. As you know, both are opposite to each other. And then number four is order disorder transition.

Number five vaporization or condensation and number six is sublimation. Sublimation SUB sublimation. So, let us discuss the; so, this phase of transformation is essentially the due to displacement of atoms or irons from its regular positions. And all we can see that changing crystals symmetry or change in crystal structure. Which as a result of happens as a result of changing bone length or changing bone angles.

And then massive transformation is happens to an alloy without changing the composition. It may change from one phase to the other phase structure change without change of composition. We do not composition and this as the composition is saying that the fusion a long range diffusion does not need to take place for these. And it is a fast process and we can understand the number three the melting.

And solidification that order disorder transition is nothing but a transformation from order phase to disorder or disordered phase two or phase. And then respiration condensation which is also opposite to each other and sublimation is you know, the transformation directly from solid to liquid solid to gas sorry, solid to gas. That we call sublimation that you probably already know about that, sorry. I actually overlooked the spelling of sublimation. So, I am not sure how I overlooked that is failing. This is sublimation this is the correct spelling. So, **(Refer Slide Time: 33:09)**



That can be another classification. So, we had one classifications which is diffusion and diffusion list and there can be another classification of phase transformation. Which is we will discuss in details Here, So, phase transformations can be first order and second order transformations. So, this discussion will be based on thermodynamics. So, as we know from your thermodynamics classes.

Probably, you might know that the phase stability can be determined by gives free energy under a condition of constant pressure or constant temperature condition our first one is maybe constant pressure. But, I will just write p constant pressure or and constant temperature. Suppose, if you draw a plot like this sorry. So, how the D will vary with D because constant pressure mean the T will vary.

And here, how the D will use fear as he was sorry, I probably did not mention that. The group's free energy is capital G, that all of you know that we generally use that symbol Capital the in the second case of Constantine how the GU will vary with P. So, why it phase transformation happen or when it phase transformation happen transformation happens the uncertainties it.

Thermal dynamic system seeks to minimize the gives free energy seeks to minimize it wants to minimize the gives free energy. So, from the above two plot although not plotted just where I am showing G and T axis G and P and the second one, so, what we can, how we can determine is? So, we can plug these girls for different phases and from there, we know that for which is that the value of the gives free energy is less from that we can find which phase will be stable in that condition. So we will do some little bit of calculations. (Refer Slide Time: 36:36)



Will try to get some directions related to these determination of phase stability. So we know the gives free energy free energy exploration. Capital G is H minus TS You know, H is enthalpy which is equivalent to the total heat content of the system. And then these absolute temperature and right TMP sort in salt. So absolute temperature that means the reference is zero Calvin.

And then as is the entropy. I hope all of you learn these expressions, whatever we will discuss here in your thermodynamics class. And as we know, H can be expressed in terms of internal energy plus research into volume. So, E is the internal energy of the system. So then what we can do is we can write is like e plus PV minus TS which is equal to the game spinners EZ. So, what we will do here is we will take a differential of DG.

And that will give you differential of internal energy PDV differential and then VDP then the DS minus SDT. So, will now use thermodynamics first law and second law. So, first law is can be, we know can be written as differential of interlinked energy is released related to heat and work done. PDV and then second law from second law can be related SQ by T is equal to DS entropy.

So, if you combine these two explorations. So what we can get these DE equal to TDS minus PDV. So, if you rearrange it on only one side, so that will give you PDV minus TDS is equal to zero. So, this exploration if we use it here, if you see all the three terms are present here, So, in DR just cut it from here, so PDV and minus TDS. So, this will be zero, and then the resulting expression will be VDP minus SDT.

So, this is the exploration we get the differential of gives free energy. So, now we will consider two cases one is constant temperature constant T the case number one, so, which means DT is equal to zero. So that will give differential of DG is equal to VDP the volume p the presser as you all of you know, So, the sorry this will be partial generally our, the we as humans a function of P and T.

So it is a partial of G with respect to P as constant temperature, we will be equal to P and in the second case we have constant pressure Which means DP is equal to zero. So, that means your differential of DG is equal to minus SDT which can be written as partial of G. Which respect to P as constant pressure will be equal to minus S to what these statements what is exploration mean is when you increase the pressure for the first case the constant temperature. So, as pressure increases I will write the symbol as pressure increases, it favours, phases, phase of lower volume that you can understand that means, more compact volume. So, because we want to phase with lower gives free energy did you see that gives free energy very weak the presser that means a partial derivative of z which aspect to be will give it a VA equal is equal to p.

So, that means, if you increase the pressure, so, if you want to get a stable phase they will favour a phase with a lower volume and similarly, in the other case, as temperature increases, it favour a phase with higher entropy. So, these conditions we should remember and then, **(Refer Slide Time: 42:46)**



We will just draw this out. So, we have what is first order the transformation phase transformation and the second on the phase of transformations. So, what we will do we have some already drawn lines. Here, so just draw on top of them. So, we have this is we are having as these three energy on the y axis and the pressure on the x axis. So, we have two phases, the first one is let us say beta phase.

And which is we are having a solid line till this point and after that we will have a dotted line. So, this is phase beta and then we have an alpha phase which you were first drawing a dotted line and then we are having a solid line Okay. So, and then this line vertical line at the point of intersection of the two phases we are writing is PT. So, these are right here somewhere alpha beta phases, two different phases.

So, and P equal to PT, we have equilibrium. At PT, we have equilibrium or we can call PTS transformation temperature transformation from one phase to the other. So it is called transformation as I call it transformation temperature. This is transformation pressure, So,

what we are talking this is first order transformation, phase transformation. We will talk about second order transformation as well.

But more important here is the first order phase transformation. So, you can you can see that right here also this is beta and alpha. So, beta line is solid before PT solid before PT because, as you can see the dotted line sorry the dash line alpha has a higher gives free energy before PT before we reach that equilibrium point. So, that is why the lower the lower GIFs we and it will be the stable phase.

So, we can write it here below PT below means below lower pressure than PT below PT beta is the stable phase, and above PT solid phase alpha phase you can see from So, if you go on the right hand side of PT that means alpha has the lower gives free energy so that is why we are writing the solid line only for the stable part okay. So, before PT beta is stable and after PT after means above the phase are higher than PT.

So, we will have alpha phase a stable and also we can draw this the derivative of the z. So, partial derivative or do you just expect to be at a constant temperature. Whatever we pointing the last slide equation? So, what will happen is that you take this that that that curve will show for beta and then the other part will be again all right you are not it because that is not the stable phase.

So, let the stable phases the solid line. So, here it is alpha, the same beta line will continue till here and alpha line will continue to here. So, now as we have we have found that this partial of h with respect to p as a constant temperature is give V. So, this Plot actually is corresponding to the volume V and we can see that at PT at PT that is at equilibrium presser or transformation presser, so, we have a volume jump. So, there is discontinuity here.

So, this point is we have a discontinuity. And this is a will right is a delta V that is as we shown you that this is corresponding to a volume so, what we can say that the change in volume and Companies that transformation for all right here. So, change in volume during the transformation. So from, it because first order derivative, we got that there is a discontinuity and the discontinuity corresponds to a change in volume.

So, now we will see the second order phase transformation, second order phase transformation in the right hand side. So, we will draw a similar curve. So, beyond x axis z capital D on the y axis so, here we have little different phases are we are writing as that alpha phase and we have listed alpha line, we extend up to here and then let us see our stable phases on the right hand side of our transformation presser PT is alpha prime.

So, in this case, alpha and alpha prime has same slope add transformation pressure PT. So, and then if you we draw that. So, if we draw the first order derivative of DZ which has sorry this partial of z which has spread to at a constant temperature on the y axis and beyond the x axis, so, this will give us a car something like this and then this alpha prime will be Sorry please do not mind about any grey line which is already there.

So, that may confuse you only just take the red line, which I am drawing now. So, this is corresponding to PT and this is the solid line here is alpha prime and other correspond to alpha. So, basically this we can see that at transformation pressure there is no discontinuity in this case this is continuous at this point no discontinuity or it is continuous. Okay. So, that means no volume change because that first partial derivative of z which is spread to be at constant temperature gives us the volume.

So, no volume change in these table transformations. So, then what we will do is we will draw another co which is a second order of derivative. So, what we will do I will read somewhere here, it may look congested, but second personal of the which respect to P at a constant temperature. So, this is on along y axis. So, that gives us some curve like something like this is for alpha and above PT.

This are higher than PT this look something like this. So, the second partial derivative that is for alpha prime. So now, you can see there is a discontinuity at the transformation presser Discontinuity. So that means, the second or a derivative with discontinuous here for that is second order phase transformation, but we can see that we do not have any volumes change associated with it.

But in the case of the First Order phase transformation, the volume chain change in volume during the phase transformation is happening. So, we will see example of these two kind of his transformations. So, (Refer Slide Time: 52:42)



As we as you have discussed there are two kinds of transformations one is first order and second one is second order transformation. So, first order transformation can include number one, let us say Matristic transformation. I am sure most of you know that and we have discussed this Matristic transformation and which will okay then we will talk about the second one that is melting.

And the third one is solidification, these are some examples of first order transfers transformation. If you see all of them have some volume change. So the for the first case, matristic transformation volume generally will increase and then melting. Also, know that then increases the volume and solid integration will decrease the volume will decrease. So, in the second order transformations.

Which are not very important to us right now, the magnetic transition and number two is order disorder transformation. So, these are all the volume changes not involved in these type of transformations. So, all earlier plots in the previous slide are at constant temperature we know that these are all previous lights if you go back to the previous slide these all are constant temperature or I should tumble constant temperature goes all constant temperature curves.

So, we can have even constant pressure curves as well as I initially even told you, so, constant pressure ISO body drops also we can have. So, then we have the temperature on the x axis and the in the y axis. So, that will have a constant pressure Time goes and that we also we can determine the phase stability if it is a constant temperature curve, then we are having pressure in the wake of x axis and if it is a constant pressure curves we are having

temperatures in the x axis. But, as we know, the gives free energy is a function of both pressure and temperature. So, if you want to involve both pressure and temperature. **(Refer Slide Time: 56:08)**



So both we can include both P and D these blocks will be then surface not one coat. So, the surfaces that means okay all right this is a function of pressure and temperature. So, what we will do is similarly, like what we did now is we have that curves for different phases and then we found a point where both the phases exist or equilibrium point equal suppose in the in the earlier call.

So, I showed you the equilibrium price or transformation presser So, for this These kind of express when we express both the pressure and temperature which is surface that means gives you energy can be expressed with a surface then what we do is we tick the intersection of the two surfaces like we need intersection of the curves to curves as a the transformation pressure.

Here, what we will do is intersection of two surfaces that means, let us say surface one G1 you want G2 which is a function of PT and the two which is also a function of PT. We will get a career out of it. So that curve out of it and that is related to Clausius clip here on equation Clapeyron equation. So, we will do this now. So, we know that these three energy and a function of pressure and temperature.

Then, we will take the differential of G and that will give us partial of G with respect to P at a constant temperature and multiple by d p and then again partial of which respect to temperature the constant pressure by d t. So, these two surfaces will present the two phases. So, now, for two surfaces we have this two surfaces right. So, now for two surfaces what we can have is dh1 - dh2 to differential minus of the differential of the two surfaces.

That will give us differential of h which respect to p as constant temperature for surface one minus differential of z which aspect to be at constant temperature for surface one the entity multiplied by d p. Similarly, the other towns are differential of the which respect to temperature at a constant pressure for material one differential pressure sorry the partial derivative of z which respect to d t a constant pressure multiplied by d t.

So, we want to talk about equilibrium. Equilibrium we know these boulders surfaces that is intersection point intersection code will be DZ one equal to DZ two. So, that means, the left hand side will be equal to zero and, and then the right hand side what we can do is from our Alia equations as you know that I will write it somewhere here on the left hand side, what we got is partial of z with respect to be at constant temperature is V and partial of z which respect to T as constant pressure is minus S.

So, here what we will do is from now, we will replace those next on the partial derivatives. So, what will get is v one so, one is for the surface one minus v two multiplied by d p. So, as we have a in this exploration we have a minus here, this exploration minus. So we will have a not S one minus as to it will be s two minus s one deployed by DT. So, this will give us DP by DT differential of P with respect to t that is temperature is equal to we will write S1-S2 divided by V1-V2.

We can write like Del s can be divided by Del v sorry, Del v and also, we know that delta z is equal to delta H minus t delta S, which is now in this case we are taking a zero. So, delta H minus t delta S and that we give us delta is equal to changing and tell PY temperature. So, if we use this, so, that can be written as delta HT delta v. So, this equation will give us the effect of pressure on transformation temperature.

And this will be required for our later discussion. So, I made a mistake here. So, I should have wrote here, this one is true and similarly, in this case also I left out that this would be two. So, the first one is one this is one and this is too with this I will close the today's lecture. What we discuss today is we have discussed doubles phase transformation, especially the transformation that involves that occurs during the shockwave propagation and we discuss this from your point of view of thermodynamics.

And we have seen that how different factors can influence this phase transformation. Also, we discussed about the classification of this phase transformation, we have we got diffusion, phase transformation and diffusion less phase transformation and also classified as first order

and second on the phase transformation. So, we will continue this discussion in the next lecture. Thank you.