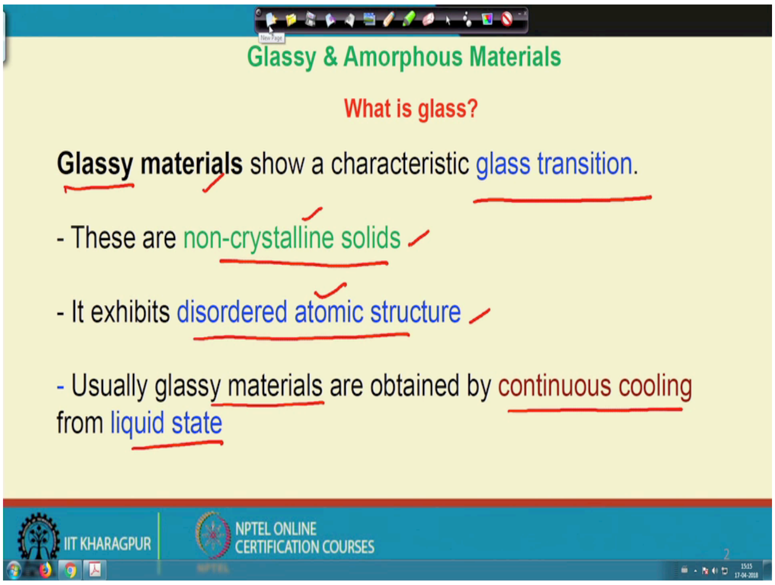
Advanced Materials and Processes
Prof. Jayanta Das
Indian Institute of Technology, Kharagpur
Department of Metallurgical and Materials Science Engineering

Lecture – 06
Bulk Metallic Glass, Glassy and Amorphous Materials

Hello, welcome to NPTEL, I am professor Jayanta Das from Department of Metallurgical and Materials Engineering, IIT Kharagpur. I will be teaching you Advanced Materials and Processes. Today we will start our discussion on Amorphous and Glassy Materials even though a very basic introduction has been given in the former classes, but today we will try to discuss a more a bit in detail.

(Refer Slide Time: 00:48)



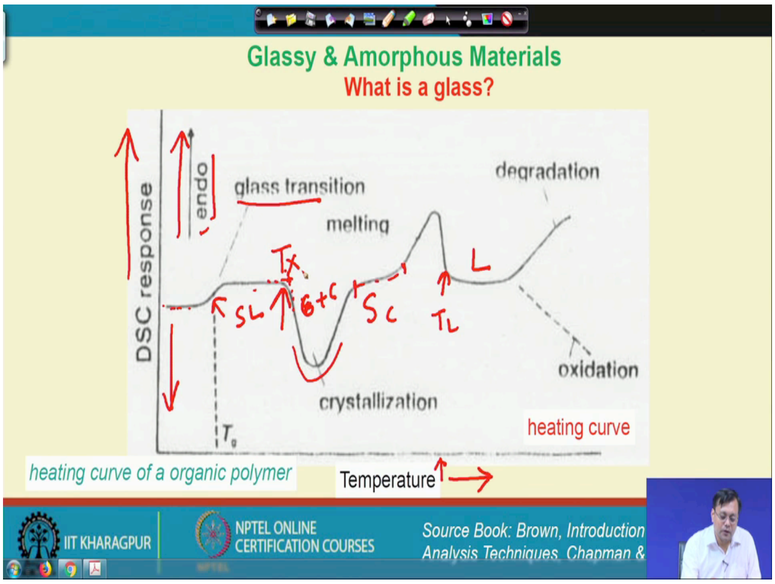
So, what really one mean by a glass? Like the glassy material shows a very characteristic glass transition and now the question will arise what do you mean by glass transition? We will come in detail do not worry; however, these are non-crystalline solids and they possess a disorder atomic structure or atoms are randomly organized in the glassy structure.

However, this glassy materials are obtained by continues cooling from the liquid state; one has to keep it in mind that this non crystalline solid, disordered materials and glasses; one should not confuse with because even though we often use the same terminology to express glassy material, but all the non crystalline solid, all the disordered atomic structure materials are not glasses.

So, glasses are only those material which has amorphous structure which are non crystalline, but it definitely should show a glass transition event which is basically a second order phase transition. And the glasses are usually obtained when we start with a liquid and continuously cool the liquid and below certain temperature, the viscosity reaches to such a high level; it appears as a solid and we call it as a glass and therefore, we need a little bit more discussion along this direction.

So, as I said that any glassy material definitely mean it has amorphous structure and it is non crystalline ok. And therefore, let us proceed with how really a glass transition event look like what one should understand and what we can learn out of it. So, we can take a glassy material and put it inside a differential scanning calorimeter and this is a device through which we can characterize different phase transition. So, let us have a look.

(Refer Slide Time: 03:29)



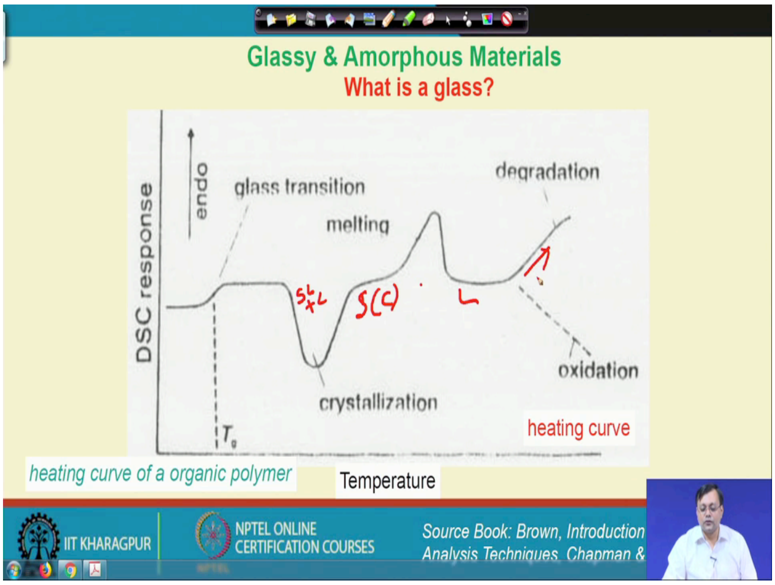
So, here you see this is a plot of temperature versus DSC response and if we look it very closely then along this direction the event represent; it is a endothermic event here it is written endo it means endothermic.

Similarly in the opposite side it is a exothermic event; now if we take a glassy material and put it inside DSC and simply rise the temperature, then we will get such kind of straight line response where there is almost 0 differences; however, there is a slight endothermic event can be noticed and after that it again become flat and again there is another event.

So, this first event is linked with the glass transition, which is a second order transformation and definitely it is endothermic in nature. So, endothermic event means the system takes the heat from the DSC, and exothermic means the system, the material releases the heat. So, here this is an exothermic event is shown here this is often we call it as T_x; T_x means basically the onset of crystallization temperature and we measure here by drawing a tangent of this and this is a point which is the onset of crystallization event.

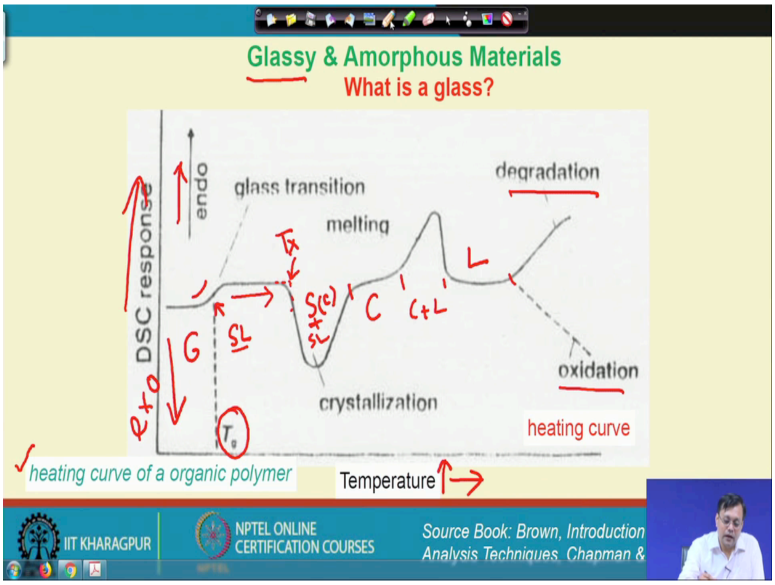
Definitely, here crystallization ends and those crystalline materials start melting from here and this is the liquidus temperature. So, T liquidus temperature is here and here we have liquid. So, here we have crystalline solid and here we have a glass plus crystal and here we have basically the super cooled liquid. So, here we have basically the super cool liquid now let us see once again.

(Refer Slide Time: 06:01)



So, super cool liquid plus crystal here we have solid which is in the crystalline state and here we have basically liquid. And this liquid basically keeps on degrading because of oxidation and so on. Let us try to understand if we take a glassy material and put it inside a differential scanning calorimeter; then how the DSC response looks like? So, DSC here means differential scanning calorimeter, a device that is used for studying phase transformation.

(Refer Slide Time: 06:44)



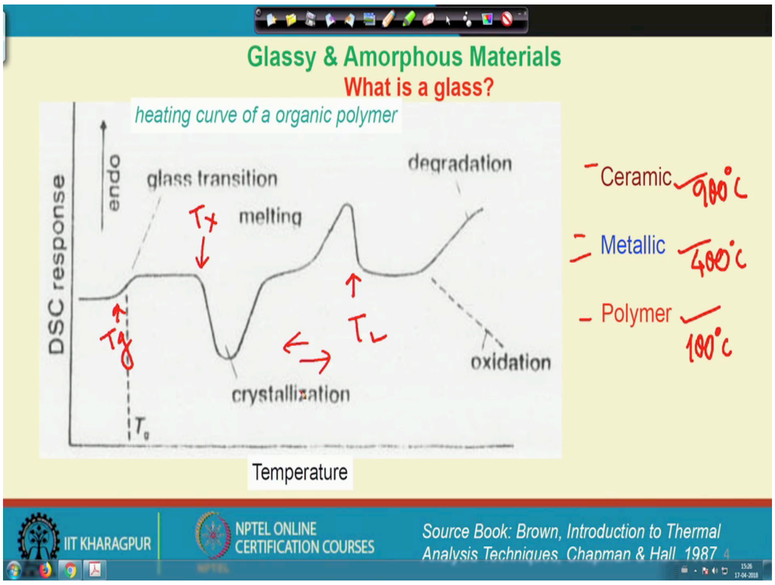
So, I show you here a plot of temperature versus DSC response. Now let us have a look that in this side that endothermic event is shown. So, the opposite this is an exothermic. An endothermic event means that a thermal event that consume energy from the DSC.

And the exothermic event; that means, that the it releases the heat and therefore, we need to look at what are the signals we get when we increase the temperature of a glassy material. So, the first transition where there is a little change of the slope of the curve is noticed. And this is a signature of a glass transition, which is represented at temperature of T_g. Now at beyond this temperature beyond means above this temperature the glass transforms into a super-cooled liquid ok. Here, it is represented by SL and if we further increase the temperature, then at this temperature here there is another thermal event started.

So, here the crystallization starts. The onset of this temperature is called as T_x and here the event ends. So, here we basically get a solid which is in the crystalline form and beyond this temperature, we keep on heating then definitely in this temperature range it transform into liquid. So, here we get a complete liquid. On the other hand once again here basically 2 phases coexists which are super-cooled liquid and the crystal. And here everything is crystalline state here it is crystal plus liquid and here it is liquid; beyond this temperature level it has been observed that oxidation may start and degradation of the material may occur.

This is a typical DSC trace I have shown you which is a heating curve of an organic polymer; however, it really does not matter whether it is a polymer or a metal or a ceramic; the event and the fundamental principles are very same. So, we can clearly see that a second order phase transition which is a glass transition must be visible when the material is glassy. So, let us try to look at as I said that what are the different kinds of material are possible.

(Refer Slide Time: 09:39)



Which shows also glass transition and I said that ceramic, metallic or polymer. So, all different kind of materials whether the bonding is oxide or covalent bonding or metallic bonding, this material could posses a glass transition and we call them as glassy material.

So, in case of a metallic system we call it as a metallic glass or otherwise the window glasses that is often used in our home those of ceramic oxide glasses or let us say polymer, the tire which also content glasses. So, I am talking about the automobile tires. So, similarly all these glassy material will show such kind of phase transition event and these are very very characteristic event, this as liquidus temperature this is as T x and this one is T g, T g stands for glass transition.

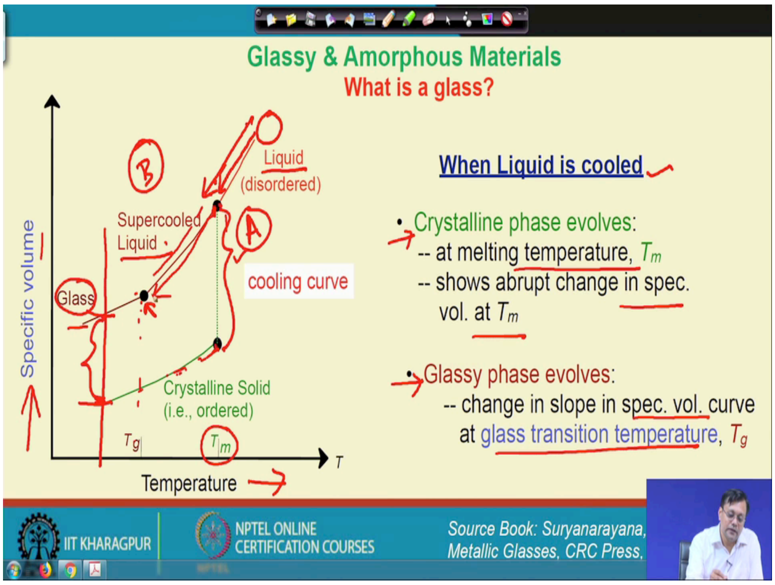
So, definitely one can think about then what is the difference between ceramic, metallic and polymer? Because it is the bonding nature of the martial. Whether they have covalent hydrocarbon bonds or they may have some set of ceramic or let say oxide bond and so on, but there is definitely a difference of the a glass transition temperature of this 3 category of material.

I can tell you as an example we simply take a borosilicate glass which is very common often used in our laboratory; they should have a glass transition around 800 °C to 900 °C below they are all solid; however, beyond that temperature; then we can see a glass transition event. In case of metallic system it is very common that around 400 °C there is a there is a one can notice a glass transition.

Whereas in case of polymer the glass transition is somewhat around let us say 70 to 100 °C where a the melting temperature of ceramic may be something around 2000 °C, in case of metallic system, let us say that the melting temperature is around 900 degree centigrade and in case of polymer may be it is 200 °C.

So, as the melting temperature of the material degreases the glass transition temperature is also decreases. So, that is a very link between melting temperate of a material whether ceramic metallic or polymer as well as their glass transition temperature. So, all this temperatures decreases or increases depending on which kind of material we are talking about.

(Refer Slide Time: 12:33)



So, so far we understood little bit about what we really mean by a glass transition and what are the signature event of a glass transition. Now once again if I simply start with a liquid simply measure its specific volume and then plot the specific volume with the temperature. So, here it is a temperature axis and this is a specific volume axis. So, I start from here that is a liquid and I keep on pulling a liquid then the specific volume basically decreases.

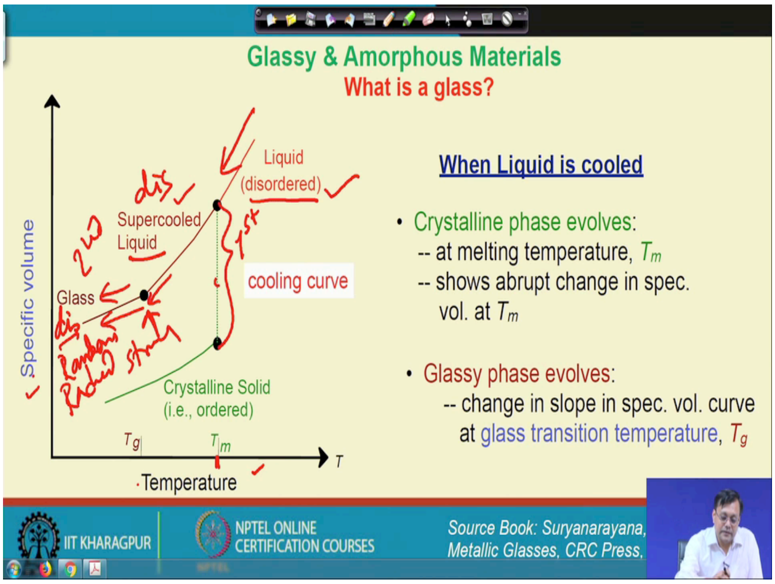
Now if the system choose or the liquid undergoes solidification and crystal nucleation occur; then definitely there is an abrupt change of the specific volume of. And then a crystal nucleate and definitely when solidification finish then below T_m or melting temperature; T m represent melting temperature then specific volume further decreases. However, if I take the same liquid and again cool it and cool it little bit faster than this case; so, let us say this case A and this is case B.

So, incase B I cool the liquid which also decreases the specific volume and I under cool it or super cool it ok, I still have the liquid state here. And below certain transformation temperature; the under cooled liquid or super cooled liquid transform into a glass because the viscosity basically increases in this range. And the viscosity here reaches the certain value that 10^{13} poise and it reaches and it transform into a glassy phase.

So, we can clearly see at any given temperature, the glass, the specific volume of a glass is much higher than a crystal. So, there is some extra volume extra enthalpy is already inside; some extra order of entropy is also inside. So, this is the excess volume which is inside a glass we often call it as an extra volume or free volume.

So, therefore, when we cool a liquid we learn that a crystalline phase evolve below melting temperature; when the system chooses or some crystal nucleation occur. And the abrupt change from here to here in the specific volume at melting temperature until and unless solidification completed. However, a glassy phase can evolve from here if we cool it down, then there is a change in the slope near glass transition temperature you can see here there is a change of the slope.

(Refer Slide Time: 15:41)

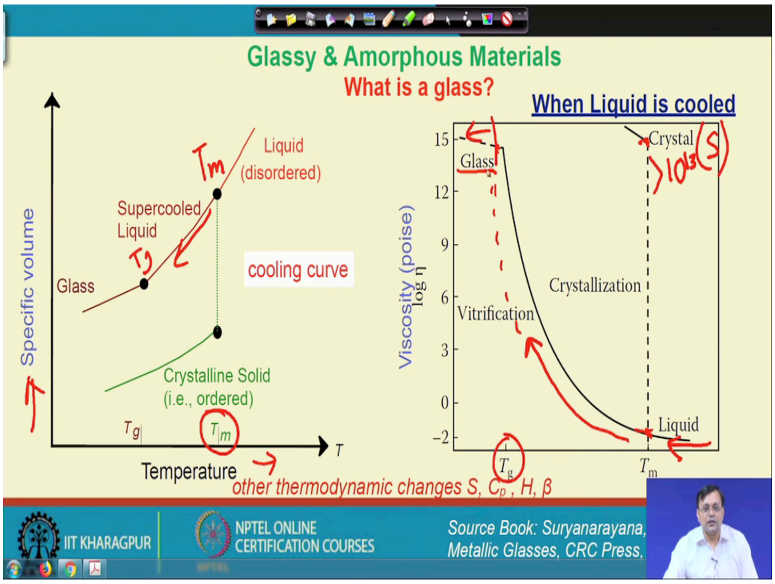


So, here during cooling the specific volume and temperature; here there is a change in the slope and therefore, it is characterize by a phase transition. Now you can also have a look from this, again a same plot of specific volume versus temperature then there is a discontinuity during solidification. Because we are cooling a liquid from higher temperature to a lower temperature; so, this is basically a solidification phenomenon and crystal nucleate here and we get a discontinuity in the specific volume axis.

However, here you see there is only a slope change and therefore, this basically a 1st order transformation and this is a second order transformation ok. And so, we learn here that what really a glassy phase evolve in a liquid, but definitely we need a to learn a little bit, but please try to remember that here liquid is disorder, here super cool liquid that is also a disordered phase and definitely the glass is also the disordered phase.

However, these are more random packed structure than the liquid phase or a super cool liquid phase ok. So, this is a more and more random packed structure. Let us try to understand once again and as I said how really the viscosity changes.

(Refer Slide Time: 17:24)



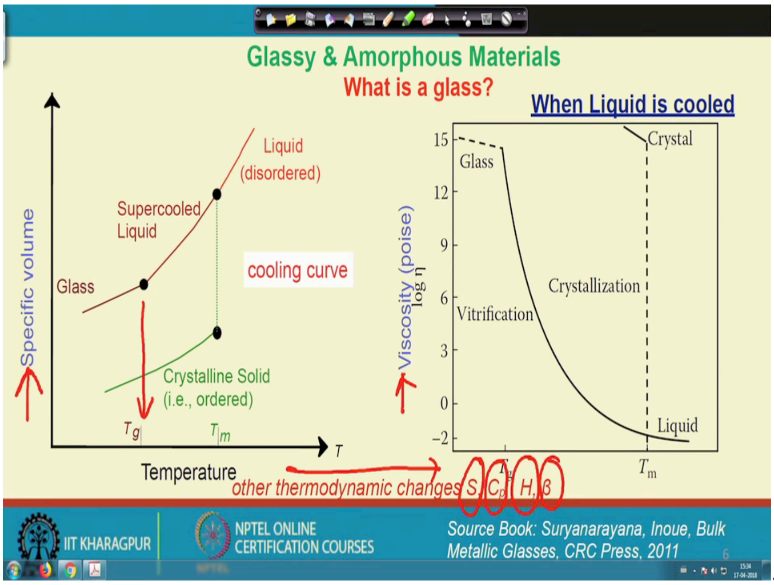
I took the same plot in the left hand side you can see this a specific volume versus temperature plot. And if we kindly have a look that what really happen at melting temperature when we start from a liquid, please have a look to the right hand side plot; here from a liquid phase if we cool it down and if the crystal nucleates and solidification begin with crystallization, then the crystal has a very high viscosity level and it is greater than 10^{13} ok.

So, the crystal has a viscosity more than this value ok. So, there is a large difference between a liquid viscosity and a crystal. So, it is appear as a solid phase and now on the other hand if glass transform from liquid then definitely liquid if we cool it down then viscosity keep on increase; so in this region.

So, I am talking about from meting temperature to glass transition temperature the viscosity increases up to T g. And below this temperature below this temperature means this side the new phase as a glass which is also a amorphous structure appear inside a super cool liquid and with a viscosity level greater than 10^{13} power poise ok.

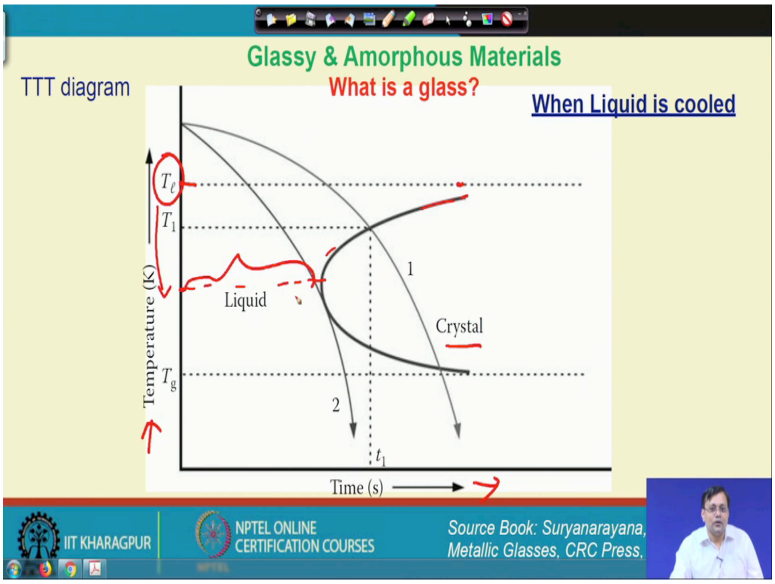
So, this is a distinction between a solid phase and a liquid phase. So, that is very clear distinction between a solid and a liquid, a solid may not have a crystalline structure, but if it has a viscosity level greater than 10^{13} and definitely; it appear as a solid and we call it as a amorphous because there is no crystallinity. And that solid if it shows a glass transition event, we call it as a glassy material whether it could be ceramic, it could be polymer or it could be metallic means metallic glass.

(Refer Slide Time: 19:47)



However one should keep it in mind that beside all these kind of viscosity changes or let us say the specific volume changes I have shown you this 2 different parameters of change. However, there are many other thermodynamic changes like entropy, like specific heat, like enthalpy and also the compressibility ok. So, there are many different changes occur during this glass transition event ok; those things we will discuss later on; however, let us continue with some other things.

(Refer Slide Time: 20:28)



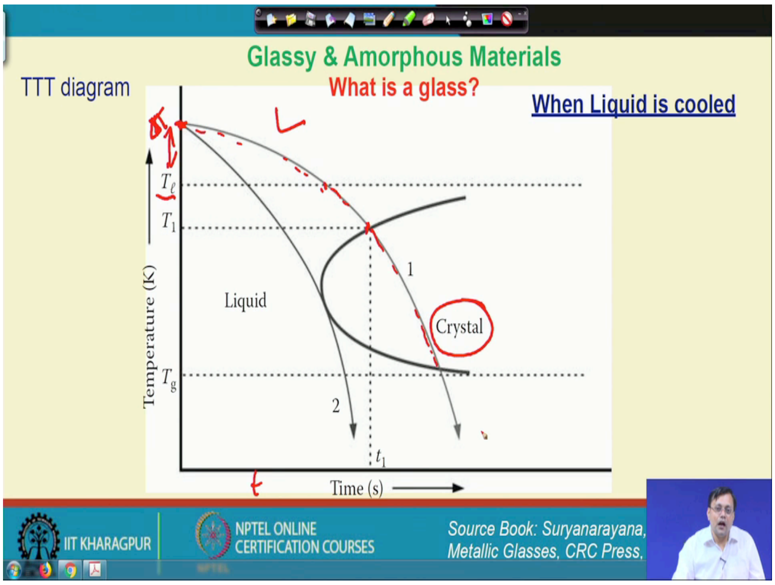
The question will arise, sir how you choose that in one case a crystal will appear and in the other case you think that the glassy phase will appear. Definitely to form a glass the trick here is to bypass crystallization, a crystallization event start with nucleation and growth of the crystals. So, nucleation if we can avoid nucleation of a crystal then we can retain that under plot super cool liquid and definitely if which will transform into a glassy phase.

So, one can always have look and develop a TTT diagram. Time Temperature Transformation diagram. A Time Temperature Transformation diagram means formation of a crystal or nucleation of a crystal inside a liquid at a temperature close to melting temperature required some incubation time. Because some number of nuclei should be stable enough and they should start growing due to a ΔT or under cooling level.

So, here I will show you a very interesting plot that we should keep it in mind that the temperature versus time. So, this is a time temperature diagram on the formation of a crystal phase and this is a temperature which is a liquidus temperature ok; liquidus temperature or let us say in a simplified way we can call it as a melting temperature. So, at a melting temperature if we keep the liquid for very very long time then definitely nothing will happen.

And also if we keep at very very low temperature and hold that temperature below melting temperature then there is a requirement of some incubation time ok. So, this is called incubation time for growing the crystal nuclei.

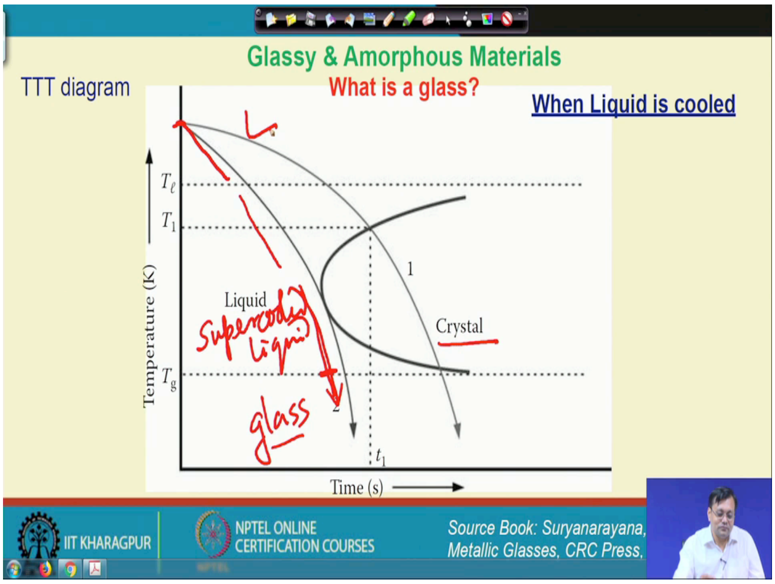
(Refer Slide Time: 22:41)



On the other hand on the other hand here; some amount of under cooling is required definitely to form a crystal.

Now, let us assume that we have taken a cooling curve and starting from such a temperature where we have given some super heat. Super heat means ΔT which is some amount of temperature rise above melting temperature or liquidus temperature and then I cool it. So, definitely cooling means there is a requirement of time and there is a drop of the temperature and then really here the nucleation actually starts grow and then we transform the liquid from a liquid phase we get a crystalline phase. However, all the crystal transform and there is no way that we can get any other phases except crystalline phase; however, if we can bypass this somehow then we may get some other phases how from here.

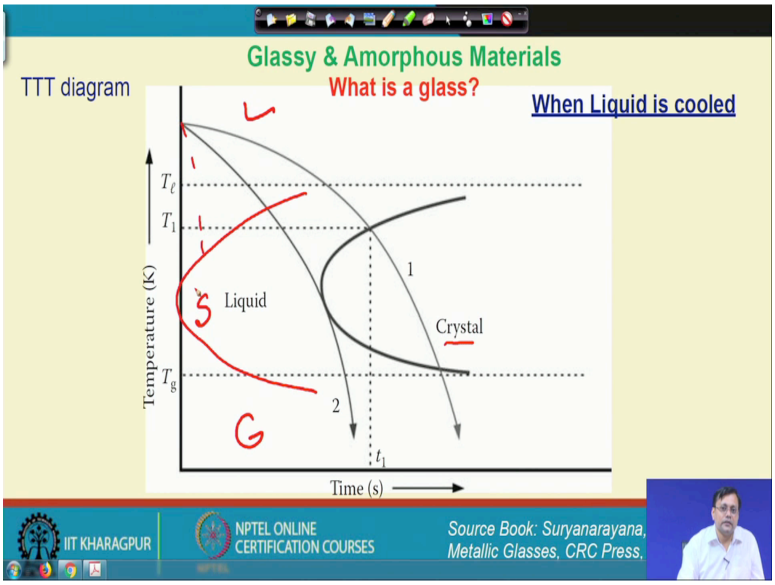
(Refer Slide Time: 23:43)



Again we started cooling; however, this cooling rate much more faster means the drop of temperature is much more faster than the other phase. So, here we bypass the nose of this TTT curve and then we cooled these super cooled super cool liquid. And this super cool liquid when there is a temperature it reaches to a temperature below glass transition temperature then we get a glass and this is a uniqueness.

So, here a slower cooling it may transform to a crystal where as in the other case we will get a glass when we cool the same liquid a little bit faster.

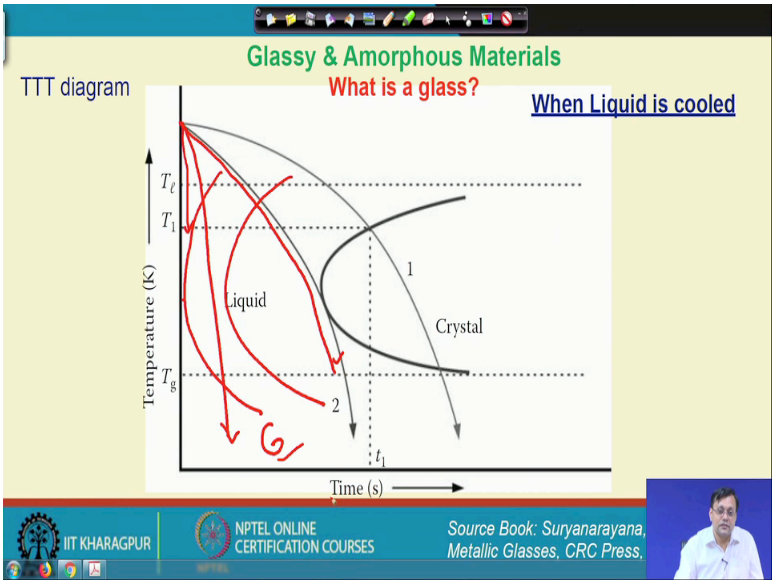
(Refer Slide Time: 24:46)



Now so, we will have a very very clear distinction between a liquid, a super cool liquid and a crystal and a glass.

So, let us start with this phenomena and then you can ask a question, sir whether any material we can transform into a glass from the liquid state? If so, may or may not how? It also depends on this TTT diagram. So, in a particular case this is a schematic I have shown you; however, it may be that in a in a different material the TTT diagram on the nose lies here, then the more and more faster liquid cool actually we can not get it ok.

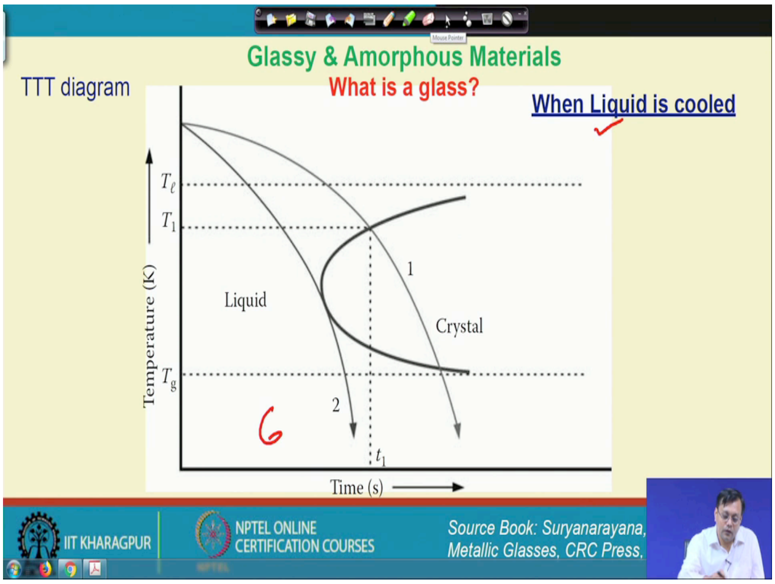
(Refer Slide Time: 25:32)



So, we can again draw it here may be this case or may be this case this is a TTT diagram. And then I really need a much faster cooling rate to transform this liquid into glass; however, in this case, may be there is no opportunity at all because it really need such a very very high cooling rate; then we really cannot reach up to this glassy phase.

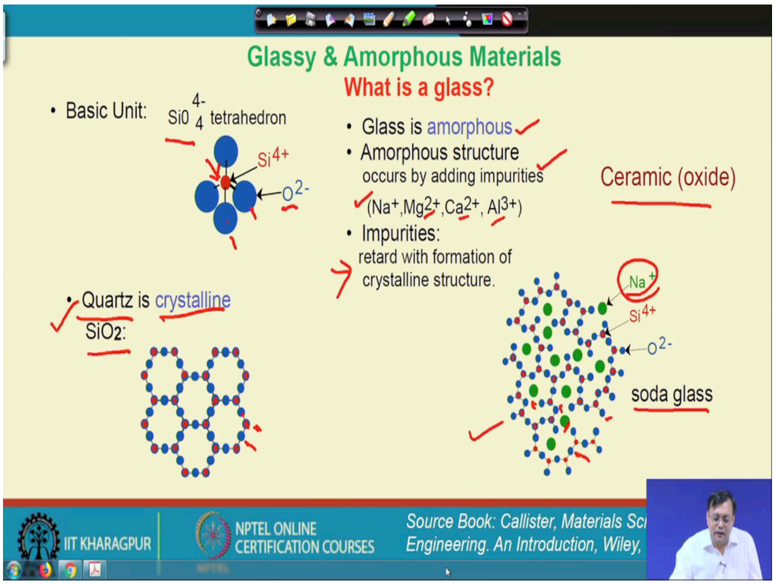
So, this critical cooling rate is very much important. So, this is a cooling rate that is required a definitely required to transform a under cool liquid or super cool liquid into a glass.

(Refer Slide Time: 26:18)



So, let us, we have tried to understand that when a liquid is cooled then how much really faster cooling rate we really need to transform into a glassy phase.

(Refer Slide Time: 26:32)



Now in case of a ceramic glass; let us think about what is the typical structure? So, let us say in case of a ceramic glasses or an oxide glasses here, the basic units are SiO_4 tetrahedrons. So, here these are Si^{4+} and O^{2-} atom; so, red color Si^{4+} atoms are shown here and O^{2-} shown as a blue color ok.

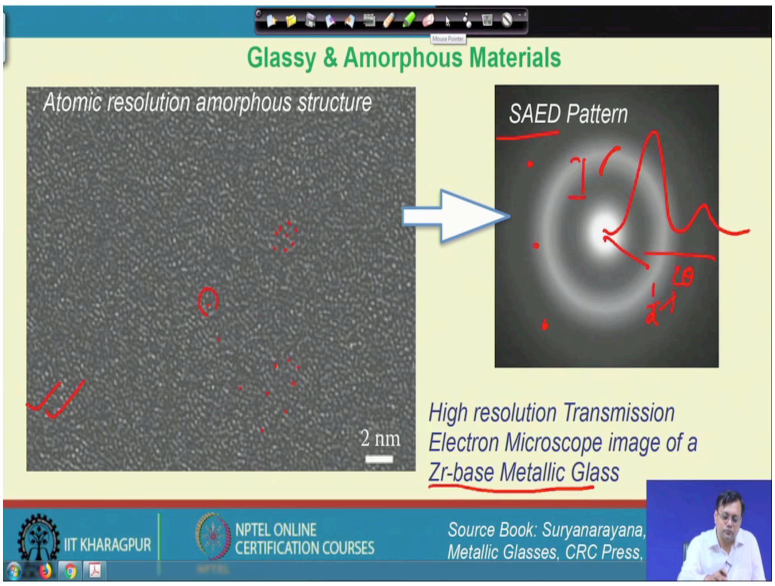
So, this a tetrahedron structure, this a basic unit and now quartz is a phase which is the crystalline form of silicon dioxide. So, in that particular case; you can see this red colors SiO_4 and the next one is O^{2-} they are arranged periodically in order to get this crystalline quartz structure. However, we can add some sodium or magnesium or calcium or aluminum ions which basically modified the structure of the glass.

And you can see that here in case of ceramic glass the glass is definitely amorphous and by adding some impurities we enhances the glass forming ability of the structure and the addition of impurities also help and it retards the formation of crystalline structure. And the same structure you can see here by comparing this 2 here there are in many broken bonds ok.

So, we have added these impurities actually to modify and tailor the structure of a crystal ok. So there are same tetrahedrons exists; however, they are distributed. So, the random packed structure really does not or close packed structure like crystalline material does not exists in case of a soda glass; so, this is called a amorphous structure.

So, we tried to understand that a glass is definitely should show a glass transformation or glass transition which is a phase transition and we can get such phase transition when liquid a super cooled and a new phase as a glass evolve there. And also we tried to understand that what is the meaning of such kind of amorphous structure or let us say a random atomic structures.

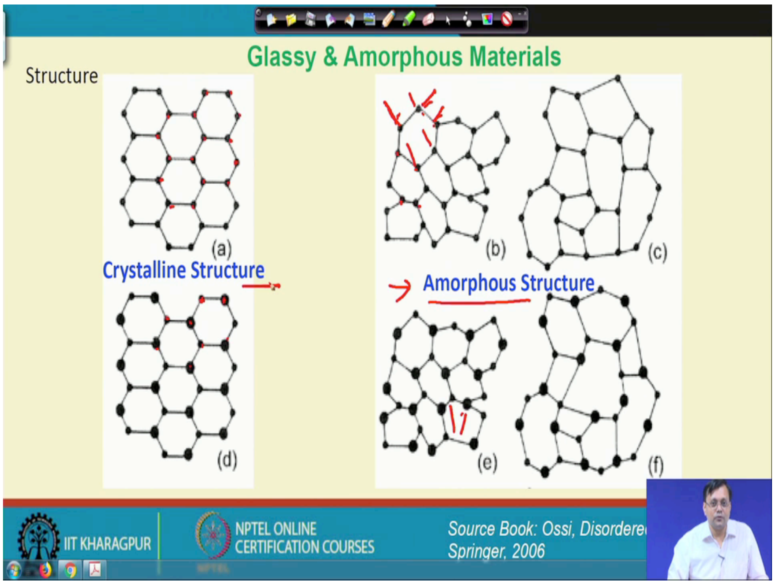
(Refer Slide Time: 29:17)



Now let us I show you one example of such a structure like this is a high resolution transformation electron microscopic image of a of a zirconium base metallic glass. So, you can see the atoms are arranged randomly. So, everywhere if you see that there are many atoms are surrounding one atom, you can take any of the atom; there are many atoms which are surrounded by its nearest neighbor.

And we take a selected area electron diffraction pattern and here this is in a reciprocal space. So, in real space in real space 1 by d actually; so, if we integrate this then you will get such kind of pattern which you can see here like a like a 2 theta versus intensity or if you transform from d to 2 theta ok. So, this is a amorphous halo where there is no sharp peak can be seen where as in case of crystal you will get very sharp spots.

(Refer Slide Time: 30:22)



Similarly, if you look at basic structure unit in case of a crystal where this is a different or the same type of atom position and different location there is a very clear symmetry exists.

However we can consists of 2 different element where this is a bigger this is a smaller element and they are also periodically arranged. But if we think about a amorphous structure, then definitely these structures are quite the atomic bonds are not at all equal. So, you can see the bond length here the bond length is different than the bond length here or here the bond length is different than here or may be here the bond length is different.

So, you can see that the amorphous structure is very different compared to the crystalline structure. So, we today learnt that glassy material are amorphous in structure and they show a very clear glass transition event and they are non-crystalline solid because the viscosity is greater than 10^{13} poise. And definitely when liquid or mostly the liquid cool to down, then they passes through a glass transition event and ultimately a glass phase evolved. We will further discuss these things in the next class, and will be continued.

Thank you.