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Module - 2 Lecture - 3 Structure of Solids

This is the third part of the lecture on structure of solids until now we look that crystalline structures how crystals form and we look that the defects that can occurring crystal structures we look at point defects line defects surface defects and volume defects and then we started looking at amorphous, and structures which are materials which do not have any order in their microstructure that is they are not crystalline they could be glassy or amorphous will continue with amorphous structures.

(Refer Slide Time: 00:47)



Now, now one interesting type of amorphous state is in metallic glasses as we know what we have discussed until now metals generally have a crystalline structure because of the metallic bond they form crystalline symmetric structure we can have single crystal grains that can have varying sizes and these grains together make up the microstructure the crystal structure is form by nucleation growth of the crystalline phase from a molten material or molten alloy during the process of solidification; however, some researchers have developed multi component metal alloys which vitrify vitrify means they become amorphous with the same ease as it happens is silicate melts.

So, silicate-based glasses these bulk metallic glasses called b m gs have very unusual properties which make them interesting for engineering they are typically much stronger that the same material in crystalline form by a factor of two or three that is two are three time is stronger there also tougher that is the work to fracture is increased or rather the ability to resist cracking is increased more than in ceramics and there also more elastic or have a highest strain limit in the elastic range.

(Refer Slide Time: 02:29)



It is; however, not easy to make a metal in to a glass the trick or the technique is to make a metallic glass by cooling the melt for the metallic liquid very fast. So, that the disordered structure is maintained and there is not enough time for nucleation and an orderly structure or a crystalline structure to develop and it was not until the nineteen sixties that true or proper metallic glass was form it was done as an alloy of gold and silicon this was obtained by very rapid cooling in the order of two million degrees celsius per second.

(Refer Slide Time: 03:22)



So, very fast cooling rate more recently new alloys have been developed that become glasses at much lower cooling rates that is not. So, fast only in the range of one to hundred degrees per second though this is still very rapid it is slow enough to make pieces or bulk ingots this is this is a piece of one metallic glass here.

We see the difference in structure between crystalline zirconium and amorphous zirconium on the left you will see a more ordered structure in the zirconium this is now a zirconium glass or a amorphous zirconium on the right you see a metal glass which is an alloy now of zirconium titanium copper nickel and aluminum one thing that is common in the newly developed metal glass is that we have many different types of atoms together in the alloy this makes the nucleation get delay because to have an orderly structure with different types and sizes of atoms requires slower cooling. So, when you cool the material fast enough and alloy with many different types of atoms together as a higher chance of forming a metallic glass metallic glasses having magnetic.

(Refer Slide Time: 04:56)



Properties have also been developed they are typically high and rich amorphous solids with compositions such as ion boron and ion boron silicon, and these are formed into long metallic glass ribbons by a technique called melts spinning where a jet stream of molten glass is propelled it is short against a moving surface say cold rotating copper cylinder. So, when this jet hits the cold cylinder it cools down immediately.

(Refer Slide Time: 05:40)



And you see that here in this diagram. So, you have this copper wheel that is spinning this is kept very cold and then you have the jet of metal short impinging against this copper wheel. So, this is spinning at a fast rate and when this hits it cools down and forms this metal glass ribbon. So, here in this case the solid film of metal glass is spun off as a continuous ribbon.

(Refer Slide Time: 06:25)



So, this is the ribbon which is coming at a speed that can exceed kilometer per minute because of the fast spinning of this copper, wheel metallic glasses can be very strong as i said initially yet they can be highly elastic generally we find that strong materials are more brittle and have no elongation, but metallic glasses are interesting because they can be strong and elastic and tough; that means, they can resist fracture and cracking well also more interesting are the thermal properties for example, just like a in oxide glass in the metal glass is also there is a glass transition temperature this is the temperature above which a metallic glass become soft like what we see in other amorphous materials polymers and so on. So, above the glass transition temperature t g the metal glass becomes soft and flows easily we can take this material to temperatures higher than the glass transition temperature and mould it into different shapes.

(Refer Slide Time: 07:38)



So, there are a lot of opportunities for making metallic glasses into complex shapes here you see how the metallic glasses are glossy alloys are placed in the space of strength an elastic limit on the x axis you have the elastic limit at failure on the y-axis you have strengths and you see that polymers can be very elastic; that means, they have a very high elongation, but the strength is not very high metals on the other hand can have highstrength, but there elastic limit is limited on the other hand we have these metallic glasses which now have both high-strength and high elongation which makes it very interesting in terms of properties that we need in civil engineering; obviously, there are other materials which are in the other end of the spectrum like glass and brittle materials which have neither high elastic limit nor very high-strength.

(Refer Slide Time: 08:40)



One type is call liquid metal it is a patented product with a mixture of zirconium beryllium titanium copper and nickel and here just to give you an idea we put the different relative sizes of the atoms of this mixture and you see that the sizes of the atoms a quite different. So, for nucleation to occur an orderly structure to occur with all these different types of sizes of atoms there is slow cooling that is required to get a crystalline structure. So, when the cooling is fast this type of material can form metallic glass relatively easily.

(Refer Slide Time: 09:26)



So, as I said because of the varying sizes of these atoms atom sizes we saw a very, very different and the random arrangement in the solid it is very difficult for groups of atoms

to move fast one and other and because of this we have what is called atomic gridlock and this in parts a lot of hardness in the amorphous material slipping or sliding of the atoms against each other along planes is very difficult this is something that we discussed already when we look that alloys or point defects.

(Refer Slide Time: 10:12)



Another kind of a amorphous material is that which is caused by precipitation of solids precipitation is often to a disorderly structure and amorphous precipitates generally are a collection of individual particles which can be strongly stuck together, but still they do not have a orderly or a crystalline structure the precipitate then forms a solid matrix with packed particles these structures are generally severely defected that is they do not have very dense packing they have high concentrations of planar and volumetric defects defects such as crain boundaries and force can occur very easily in such precipitates.

(Refer Slide Time: 11:09)



Because of the defected nature these precipitates have high surface areas and because of this there is a lot of van der waals interaction between the adjacent particles which gives rise to gelling a gel you would remember is a material which has liquid between solid particles and this is called a gel and because these materials have a lot of surface and volumetric defects you can have a lot of gels being form due to precipitates.

(Refer Slide Time: 11:45)



One important gel in the area of civil engineering materials is the calcium silicate hydrate which is formed as an amorphous precipitate due to the reaction of portland cement and water and this is the blue that binds the hydrated cement paste and therefore, concrete together and the pictures at the bottom are taken from Taylor and mehta and monteiro where you see the gel structure of the calcium silicate hydrate you see the sponjee structure here with lot of particles put together lot of clumps of calcium silicate hydrated gel and within these layers, you have a lot of what are called the gel water and there is a lot of porosity outside also though this structure is very defected and porous it gives the strength required to make concrete very useful material.

(Refer Slide Time: 12:43)



This is a very interesting picture from soft x-ray microscopy from berkeley from the paulmonterous group where you see the initial hydrates forming when you have a cement grain in water. So, these are cement grains the dark yellow one's are the cement grains and this is in water and you see the gel forming this light brown structure that you find is the amorphous precipitates forming as the cement now reacts with water.

(Refer Slide Time: 13:20)



Now, we go on to a different type of material the polymer polymers are large molecules chain molecules which are made out of several repeating units call monomers. So, each of this is the monomer and together when they join together we call them polymer the monomers react chemically with each other the saw before that there is a covalent bonds which develop between the particles and form this molecular chains which can have several hundred to several thousand monomer units. So, it is a repeating units of this type which keeps reoccurring through the polymer chain. So, this is very different from this structures.

(Refer Slide Time: 14:12)



That we have discussed before most of the monomers involved are organic compounds and the typical polymer is therefore, is characterized by a carbon chain backbone that backbone is the central structure of the polymer which is made up of carbon atoms what we see here in this diagram is how polyethylene looks hmm. So, these are the hydrogen atoms this is carbon and we have hydrogen on the other side. So, this forms a chain and you remember when we discussed about covalent bonds that long strong chains can form due to covalent bonding and the other thing is that the covalent bond was directionally. So, there is a certain directionality in how this monomers are bonded together.

(Refer Slide Time: 15:04)

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And this gives rise to a very interesting characteristic of polymers one of the important aspects of the carbon backbone is that there is a tetrahedral bonding configuration there is a tetrahedral bonding configuration hmm that is and this allows for free rotation of one segment of the carbon backbone relative to another. So, if you see this diagram you find that the rightmost atoms this atom can be anywhere on this dash circle for this angle to be maintained. So, if this is rotated on this circle why maintaining the hundred and nine degree angle you find that there is a lot of movement or strain obtained without breaking any bond. So, this leads to either change like this which can be relatively straight maintaining this angle or the same chain can be twisted into this and in this process we're not breaking any bond. So, there is a lot of flexibility that is obtain.

(Refer Slide Time: 16:24)



Because of this type of formation of the polymer chains consequently the single chains of polymers which are very long or capable of very large rotation and bending in three dimensions they can undergo lot of displacements lot of strains without braking also this long chains now get entangle they get cot among themselves and this entanglement prevents crystallization of the polymer reduces the possibility of of all these chains getting aligned in an orderly manner because they get entangle very easily you can see in this picture how the there is the polymer chain which is entangled by itself and you can imagine how difficult it will be for all these chains to be aligned in a orderly structure and this also gives rise to very high viscosity because as these chains get a entangle it is very difficult for the liquid to move easily these a chains get a entangle among themselves and with neighboring chains. So, that the material does not flow very easily. So, two of the very important consequences of the covalent bond within the polymer plate is that it gives rise to lot of ability for the chains to rotate and bend and this prevents crystallization the level of rationalization in polymer is reduced they are become more amorphous and very importantly they become highly viscous as the polymer chains are formed and are made to flow.

(Refer Slide Time: 18:19)



And this is a image taken from scanning probe microscopy from callister where you can see the chains entangled these are different chains of polyethylene which are here even though the chains are very large you see some sort of an orderly structure and this is how each of the chain is this is this chain here is shown here.

(Refer Slide Time: 18:56)



There are different types of molecular structures which occur the simplest structure is a linear polymer where you have long flexible chains with extensive van der waals bonds between the chains if you remember we said that within a polymer chain you have covalent bonds, but these chains bond with each other with a week van der waals bonds. So, this happens in many polymers that we come across such as polithene a polyethylene t v c polyvinyl chloride polystyrene polmethyl methacrylate and nylon. So, these are linear polymers.

(Refer Slide Time: 19:39)



You can have polymers with side change also these are called branched polymers where we have these branches occurring from the main chain. So, there are side reactions which cause these branches during polymerization and you can imagine that it will be now more difficult for such structures to be ordered and become crystalline. So, that is why we see higher degree of crystallinity orderliness in linear polymers then other type of polymers like branched polymers in branch polymers it will now become more difficult for an orderly structure to form because of this branches which will get in the way of the polymers being aligned and packed we also have crossed linked polymers.

(Refer Slide Time: 20:30)



Where we have covalent bonds between different chains instead of the covalent bonds only occurring along the chain now we have covalent bonds which are linking different chains together, so adjacent linear chains are joined to covalent bond and this is called cross-linking which is the feud by additive atoms or molecules that covalently bond with a chains, and one example of this is rubbery elastic materials which have a lot of elasticity and can undergo a lot of strain.

(Refer Slide Time: 21:14)



We have network polymers polymer that linkup together to form a three-dimensional network and here because of the covalent bonds you can have a very strong material. So, here we have tri functional mer units with active covalent bonds you see that each has three active bonds and you get a three-dimensional networks such as in an epoxy and all of us have huge plastic which are hard and strong in many applications such as in epoxies two.

(Refer Slide Time: 21:53)



Major classes of polymer can be made depending on how they function under hightemperature first is called the thermoplasts thermoplasts polymers are homo polymers when we have the same type of polymers in the in the chain they could be a mixed called a copolymer this is called a statistical copolymer where we have a random mix of two polymers or we have a block polymer where some part of the chain is of one polymer another part of the chain is of another polymer. So, whenever we have different monomers used in synthesis of a polymer its called a copolymer and both of these can be thermoplasts thermoplasts means that the polymer will melt and the high temperature and when you cool the material it will go back to a solid state. So, that is what is called a thermoplasts.

(Refer Slide Time: 22:56)



These thermoplasts polymers can occur in a amorphous state here disordered entangle chains or it could be crystal and to some extent the say this part this part is orderly there are the chains which are closely packed together and through see here that this is a crystalline part the rest could be amorphous. So, that is why it is called semi-crystalline that is partly crystalline. So, we find that the crystalline state may exist in polymer materials and as for as polymers a concerned we say a polymer is crystalline when there is an orderly packing and you have an array of the chains.

(Refer Slide Time: 24:05)



So, in the same polymer you can have an amorphous region and you can also have a crystalline region and the proportions between these two will tell us what is the degree of crystallinity of the polymer. Thermoplasts also have a viscous behavior when they are polymerizing initially when you have just the monomers you have a lot of slow possible in the material the viscosity is low the monomers do not entangle they are all separate and the material can flow easily as the monomers now start to linkup and form chains as the chains become longer there is more and more stickiness or entanglement, and you find now that the liquid material does not flow that easily or the viscosity is now higher now this increases as the polymer chains become longer and longer they reaches state where they become totally entangle and even though the individual chains are flexible the whole mass does not move because the chains get entangle and you can reaches state that it will not even come out of a vesile here the viscosity is very high here the viscosity becomes very very high.

(Refer Slide Time: 25:20)



The other class of polymers a call thermosets thermo sets are those which will not melt, but will only decompose at very high temperatures and these are generally cross-linked polymer there are not the chain polymer that will look that in the case of thermoplasts and here what happens is the thermoset polymer is generally plastic in the primary states initially it is, but once molded or set once the cross-links have been form they cannot be resoften you cannot make it in them into liquid again by reheating like we could in the case of a thermoplasts. So, once they are set these stay that way and they cannot be reheated to soften and to the remolded and this is because of the covalent bonds between the chains in the case of thermoplasts we had only van der waals bonds between the chains. So, these van der waals bonds could be broken easily the chains could move around and then when the temperature is brought down again the van der waals bonds as strong enough to keep them in place here between the chains we have covalent bond which are not. So, easily to break and when they are broken they do not form again.

(Refer Slide Time: 26:41)



So, this is a comparison of what i have explained in thermoplasts we have these chains usually linear polymers and between the chains we have van der waals bonds between the chains we have Van der Waals bonds and with heat these van der waals bonds are broken and the chains can move around easily. So, this is what happens in melting this is what happened when the thermoplasts is melt it the chains are separated and when there are cooled again the Van der Waals bonds will keep them together; however, when we look at a thermoset you have the chains bonded to each other by covalent bonds and when the heat is apply these covalent bonds do not break and join again then they cool, but we have the chains disintegrating we have degradation of the chains. So, the chains breakup and when the cool back they do not join again or they do not go back to the same way linear thermoplasts we can go back when we cool, but. So, when we cool we go back here, but in this case we can do not go back that is why it is called a thermoset.

(Refer Slide Time: 28:02)



So, with this we have look that different types of material the different states of materials we have in the last lecture last part of this lecture we have look that how polymers are form we look previously at how amorphous materials occur and before that we look that crystalline materials; these are the different references some of this concepts could be difficult to assimilate you should go through this references.

(Refer Slide Time: 28:33)



There are several of this which will give a good background on how the material structures are form and what is very important for us to understand as civil engineer says

how the bonds leads to certain types of structure and how these structures go on to influence the behavior of different materials and this is also interesting when you look at a new material that you have not been taught how it behaves or you have not come across before knowing what is the type of material what is the family the chemical family that it comes from you can understand how it will behave, because there are a lot of materials which are being produced on a daily basis new materials, that are being introduced and to understand this materials are at least to predict what would happen in this materials it is good to know what is the structure of the material.

How the structure is being form and we have given you some basic in this lecture on structure of solid now in the lecture that follow. Now will go on to see how movement occurs in the solids and other properties link to the structure and later on will build up on this to take you want to look at different materials that we using civil engineering thank you will take some question on structure of solids from some of as to here yeah sujatha sir which type of polymer can elongate more linear or cross-linked polymer generally the linear polymers do not have covalent bond between the chains.

Since we have only van der waals bonds then they can elongate much more and you also know that when we have network polymers with lot of covalent bonds like an epoxies they are very brittle even though they are very strong and hard yeah sir, we know that the ionic bond is a strongest what about diamond crystals which we have in the those are based covalent once, but we still have them strongest material as diamond yeah see covalent bonds are also strong along the direction of the bonds and in the case of a silicon diamond. We have network which is formed entirely covalent bond and because of that you have a strong material generally covalent bonded materials are not very strong because we have the sheets and the chains which are linked only by Van der Waals bonds, but here in the case of diamond we have a network structure that is entirely linked with covalent bonds yeah, I wanted to also tell you one interesting anek dot I had student come to me after one of these lectures, and if you remember in this lecture that i talked about metallic glasses and the students brought me this mirror from a place call arenmula in Kerala.

So, if you're not familiar with in India Kerala is a one of a southern states and here we have something that is very typical of a certain town call Arenmula in Kerala where they make this mirrors and what you see in the middle is not glass it is not a glass mirror, but

it is a metal mirror and this is made after when alloy of copper with very high tin content and it is very well polished to become this mirror type surface what I have understood that it is also very brittle material and it retain its shiny surface, but if you drop it it can break very easily and we have one of us to students with from this place arenmula and maybe sunitha can tell us a little bit about the village and anything else you know about this mirror.

Arenmula is a village in pathenetita strict pathenetita is a where shabhari male is also situated. So, the main industry of this mirror manufacturing is around parthy saratyi temple where you have krishna and arjuna that is only temple in india which as arjuna's idol and this mirror has a importance that in kerala marries ceremonies we have something called ashtamangalyam where when the mirror marriage take place there are eight auspicious things that are kept on a on a plate and which is used to receive the bride and the bride group. So, this mirror belongs to one of the ashtamangalya things. So, it is considered to be very auspicious and also it brings in luck if you have it at home. So, that is the myth behind the mirror I do not know the much about the manufacturing because it is very kept very secretive it is belonging to only one family and they have been passing on through generations this secret good thank you thank you.

So, what we do know is that it is an alloy of copper with very high tin content and Sunitha said not much is known about the exact proportions and it is kept as a family secret, but also what we know is that it is it can be polished it can be made into a very reflective surface like what you see here, but it is also a very brittle material because we have introduced in this material. So, much of tin that it is basically become unstable in terms of the lattice because you have put a lot of more tin than it is stable for the lattice structure of copper and that is why it becomes a very brittle and it is not able to create the shearing or the slip planes within the material. So, if it if it is dropped it breaks very easily which is not typical of a metal, so going back to the question that the student ask me this is not the metallic glass, but it is a reflective surface particularly in this case it is a copper tin alloy thank you very much we will see you in the next lecture.