Surface Engineering for Corrosion and Wear Resistance Application

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Lecture - 19

Strengthening of Non- Metals

Welcome to the 19th lecture of the course Surface Engineering, you heard already in the last lecture that we have cided to vote two lectures specifically on various strengthening mechanisms possible. Though these mechanisms are primarily mean for the bulk strengthening, but nevertheless they are equally applicable to the surface, but you do not necessarily do it only for the surface.

But what is important is we should know, how does how should interior of the solid, how does the bulk of the solid behave when it is subjected to mechanical formation or any amount of mechanical stresses and see if that could be changed or improved upon on to the surface. But in many cases the mechanism by which you actually strengthen the surface it’s not going to be very different than what is applicable to the bulk.

So, that is why we are voting these two lectures only on the strengthening mechanisms of the various possibilities of engineering solids. So, in the previous lecture we discuss only metallic materials and compared to that we will now discuss two other classes of engineering solids namely the ones which are.

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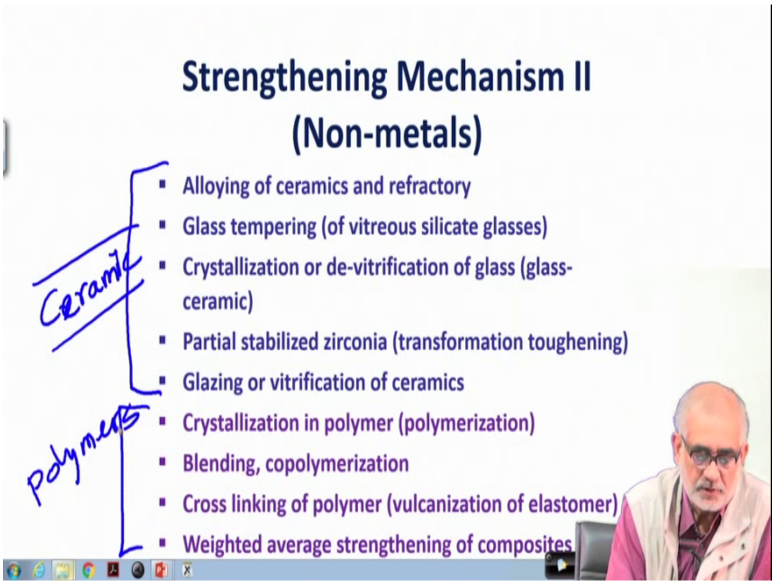

Strengthening Mechanism II
(Non-metals)

- Alloying of ceramics and refractory
- Glass tempering (of vitreous silicate glasses)
- Crystallization or de-vitrification of glass (glass-ceramic)
- Partial stabilized zirconia (transformation toughening)
- Glazing or vitrification of ceramics
- Crystallization in polymer (polymerization)
- Blending, copolymerization
- Cross linking of polymer (vulcanization of elastomer)
- Weighted average strengthening of composites

So, we will be discussing for example, a large extent on the ceramic materials. So, these are the various ceramic strengthening mechanisms applicable to ceramic materials, we will also be scribing the strengthening mechanisms applicable to polymers.

So, let us we I mean we will go one by one and then; obviously, we will have greater opportunity to discuss, but then this is not exhaustive I mean there could be certain strengthening mechanisms possible by some other meanings, but these are generally the more important and more widely used strengthening mechanisms ok.

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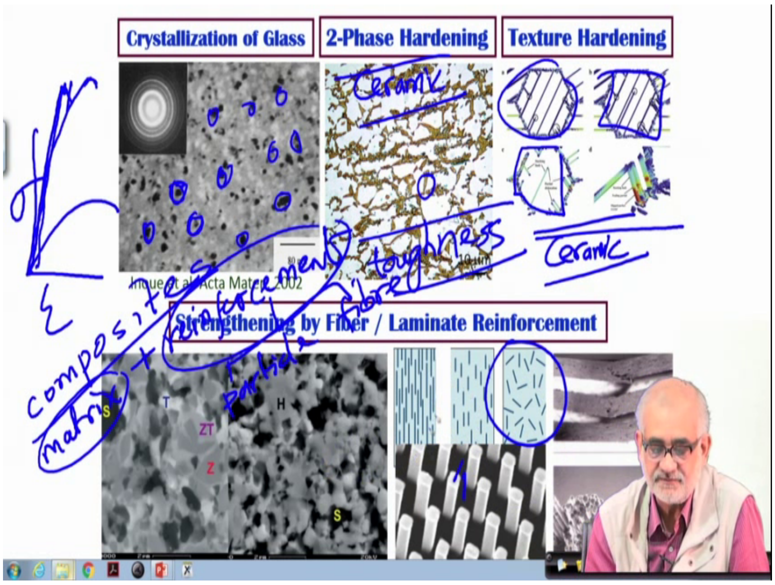

Crystallization of Glass

2-Phase Hardening

Texture Hardening

Inoue et al. Acta Mater. 2002

Strengthening by Fiber / Laminate Reinforcement

So, now for example, think of a glass now this glass could be a metallic glass also, but at the moment we are discussing oxide or silicate or various other kinds of inorganic glasses and which are non metallic in nature.

So, this is typically a glassy matrix where you do not expect any plasticity at all and in this kind of a situation since a glass is a subset of amorphous solids. In glass what you typically expect is that then it will have very high strength, but this strength essentially is going to be not without any penalty.

In other words if you draw the stress strain curve of this kind of a material compared to a metal which will show a very huge amount of plasticity, a glass essentially will give you very high strength, but will break immediately. So, there is no plasticity at all it's only you can have a very high elastic modulus, but you can bring in certain level of plasticity in glass by way of introducing small crystallites like this.

And this small crystallites actually essentially what it means is that you carry out vitrification and as a result of which there could be some amount of a crystallites or crystalline regions or pockets of three dimensional periodic arrays of a cations and anions, they appear into the matrix and these actually have a higher toughness than the rest of the matrix.

So, if there is a thermal shock or any amount of suddenly applied mechanical load, then these pockets actually can absorb some of these loads and as a result the material can behave in a slightly better than this completely brittle can actually show a slightly higher data and behavior.

So, partial crystallization can make a glass tougher and we will see that how this can be made use of in other examples. We also can create a situation in the ceramic materials I am not necessarily talking of glass. So, if you are aling with ceramic materials they can be single and they can be multi phase, in a ceramic material if we can have combinations of a very hard and a soft or a very or relatively smaller volume fraction of softer phases in hardened matrix, then also we can bring in certain amount of toughness.

So, we are not so much concerned with ductility what we want in ceramic materials is the property called toughness, which essentially means that when a certain amount of loading is applied the bulk actually is able to absorb certain amount of incident energy on it we did discuss little bit about texturing in the previous discussion.

So, the logic is exactly the same that if we can bring in a particular orientation specific orientation in the crystallites by way of certain thermally activated treatments, then the crystal as a whole the ceramic as a whole can behave in a slightly more stronger way. We also we with in case of a both polymer matrix or ceramic matrix, we certainly would like to introduce strengthening by way of the strategy called formation of composites.

And when we talk of composites essentially we are talking about a matrix phase and we are talking about reinforcement and when we talk of reinforcement these reinforcements can be particle, can be fiber or they may have even different shapes like laminates and so on. So, this reinforcement essentially they provide they are the agents of strengthening the matrix and these reinforcements can be discontinuous fibers like this, but aligned they can be non aligned or dis aligned.

So, randomly aligned or they can actually be fibers with the very high directionality and a very high aspect ratio. So, you are talking about several hundred micron length, but diameter wise cross section wise may be hardly one or two micrometers or even less. So, in all these such cases we actually create a situation where sharing of the matrix is impeded by the presence of these kind of reinforcements.

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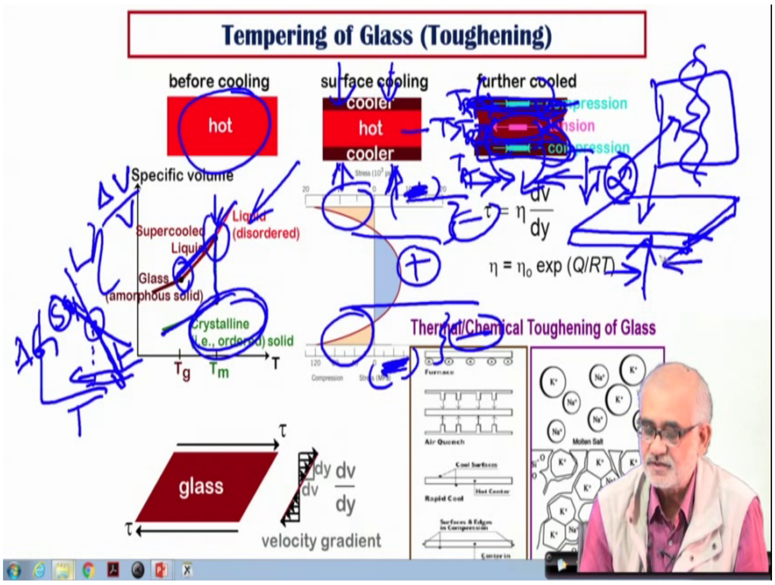

Tempering of Glass (Toughening)

Now, we think of another very widely used class of material called the silicate glasses, typically the window panes window glasses. So, they are nothing, but they are nothing, but glass which is the origin of which is actually silicates ok.

So, for example, if this is the piece of our glass pane and if there is a projectile which comes and hits the glass pane our common experience is that it is going to shatter in no time I mean it cannot take any formation it will break into pieces in a very brittle manner. In order to strengthen this kind of a glass sheet, so if this is the glass sheet that we are talking about which has a very thin section and, but is fairly wide in x and y directions.

So, we would like to make this sheet tough enough, so that any impact in the longitudinal direction oh sorry in the transverse direction will not immediately lead to such catastrophic failure. How do we do that? So, first of all we must realize that when we are talking about glass we are talking about a glass transition phenomenon, but we are not talking we are not expecting any sharp first order transition that is common of any crystalline material; that means, there is no fixed melting temperature only change in viscosity.

So, essentially this is how we are plotting for example, viscosity or specific volume as a function of temperature and as we cool like this in case of metals or all pure crystals we see a sharp change in specific volume across this temperature. And we call this melting temperature on melting phenomenon or solidification phenomenon which occurs across a particular point of temperature because we can easily explain in terms of the Gibbs energy that as we cool through like this.

So, we have for example, the two phases and there will be an intersection of the two phases. So, this is a liquid and this is solid and at this crossover point which is a melting temperature as we cool to lower and lower temperature as soon as we, so this is liquid. So, as soon as we move and reach this particular transition point, then because of the tendency for lowering of Gibbs energy the particular material will now follow this path instead of this path.

So, it will now move from liquid into solid and this happens across a specific transition temperature called the melting temperature. While this is possible in crystalline material this is not seen in glassy substances because they are amorphous there is no long range periodicity, they do not enjoy the same atom to atom distance of separation and not exactly the same forces of cohesion throughout.

So, what we see instead is a glass transition temperature, so these glasses actually are super cooled liquid in this region because they behave as solid as rigid solid simply because the viscosity is very very low, but they are not necessarily the same behave the same way as a crystalline solid.

So, for example, if you take a glass silicate glass this is the bulk of the glass in heated condition and now if you use some kind of a air stream to cool the surface faster than the bulk because you know conductivity wise silicate glasses a very poor conductivity. So, when you when you blow air from the surfaces the surface cools faster, but the center still remains at a slightly higher temperature.

So, very soon this comes at room temperature, this part comes at room temperature, but the core still remains at slightly higher temperature. So, the core is still at a temperature which is higher than the room temperature and then subsequently the core tries to come to room temperature to cool.

So, when it tries to cool already the surface is very rigid because it’s already come to room temperature this is a silicate glass. Now, they try to actually draw this material in because of the possibilities because of the tendencies of shrinkage, we all know that with creasing temperature most of the solids will have a positive coefficient of thermal expansion.

And because of which as a result of crease in temperature and phenomenon called thermal contraction due to crease in temperature we will expect the core which was still at a higher temperature now we will try to shrink. And when it tries to shrink that shrinkage is opposed by the already hard layer onto the surface and as a result they will try to pull in materials inside, but the force of reaction will be on the opposite side and as a result the surface will velop residual compressive stresses. So, this part will be under compression, this part will be under compression whereas, inside.

So, this is the cross section, so the surface will be at compressive force will experience compressive force and will be seeing the negative forces and the core will actually experience tensile stresses. So, this is inconsequential what is important is that up to a certain thickness you are experiencing residual compressive stresses.

So, now, when a projectile hits the surface of the glass first it has to overcome this residual compressive stresses and then only the crack and propagate. So, as a result the glass now acts tougher. So, this is how you can strengthen the silicate glasses. Now, we actually can apply a similar strategy not by so called thermal treatment, but by various chemical treatment.

So, this is how you can actually cool the glass sheets and make thermal tempering you can also do chemical toughening of glass by allowing the glass to be exposed to certain chemicals which will create certain chemical reactions onto the surface and then bring in certain ions and because of the reaction there will be some substitutional reactions as a result you will form a certain reactive layer or reaction product layer onto the surface which will have bigger ions bigger cations and hence there could also be the possibility of formation of a residual compressive stresses.

So, this kind of treatment chemical treatment can also make the glass tougher. So, both thermal tempering as well as chemical tempering or toughening of glass can make it more resistant to failure.

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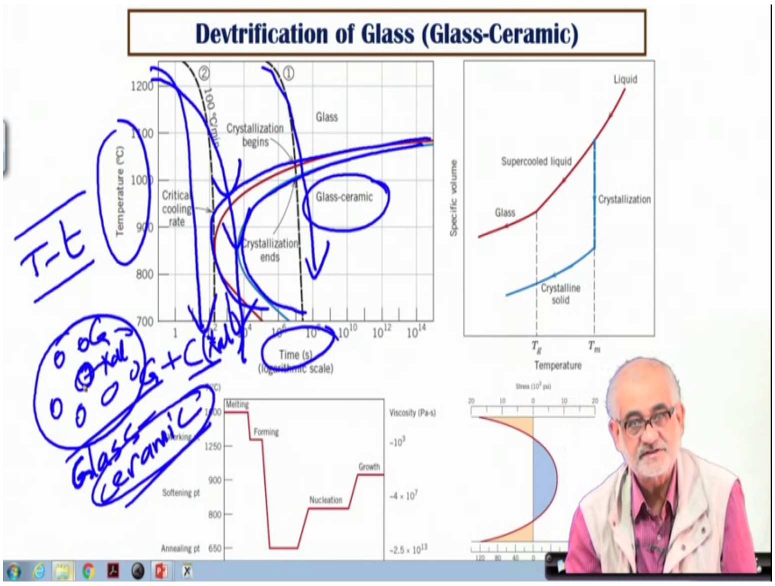

Devtrification of Glass (Glass-Ceramic)

Now, we saw glimpses of vitrification, but here you can understand it better that ah. So, if you have, so this is a kinetic diagram, so this is temperature and this is time. So, essentially this is a kinetic diagram where we are plotting the variation of a progress of certain transformations in this time temperature plot. So, this red line here is the beginning of a transformation, the blue line is the end of the transformation. Now, if you are able to cool following this path 1, then you are going to end up having practically the whole of crystal.

So; that means, you can vitrify the entire bulk of the glass, if you cool on the other hand relatively fast then from fairly less viscous liquid glass you end up forming a glass at room temperature which will be very rigid, but will remain completely glassy and non crystalline. But if you adopt a cooling rate which is somewhat in between, then you actually will start the formation of this crystallites.

But you may end in a situation where you will have both glass as well as ceramic or crystals by ceramic what we mean is that they are crystals or they have long range periodicity. So, we can actually end up having a situation where if this is a matrix and majority of the matrix region is all glass, then we can also bring in certain crystallites in between. So, these pockets of crystallites will be spread all over.

The advantage of having a matrix having an composite like this is that all of us are aware of the microwave volute cooking wares and we would have seen that those glass utensils they do not break whereas, if you place a normal glass; glass we use for drinking water.

If you just it away place it inside the microwave oven and try to heat up your milk it may crack and it does crack suddenly, that is because it is unable to withstand the pressure or the mechanical force is developed due to sudden heating and cooling and the associated contraction expansion and contraction forces associated with such heating and cooling.

But instead of such silicate all silicate matrix, if you have this glass ceramic. So, if you have this glass ceramic matrix or material or the particular utensil, then this ceramic oceans of these of the thickness will take care of the sudden rise in temperature and crease in temperature and be able to absorb the thermal shock.

So, in other words these agencies act as cushioning centers to absorb the high amount of surface high amount of stresses that this bulk can experience or is subjected to. So, in a situation like that we can, so by so in that very logic by going by that very logic vitrification not necessarily the hole, but a partial vitrification can actually give rise to formation of glass ceramic and so partially crystallized glass which actually will be much tougher than either a complete glass or a completely vitrified or a completely crystalline silicate glass.

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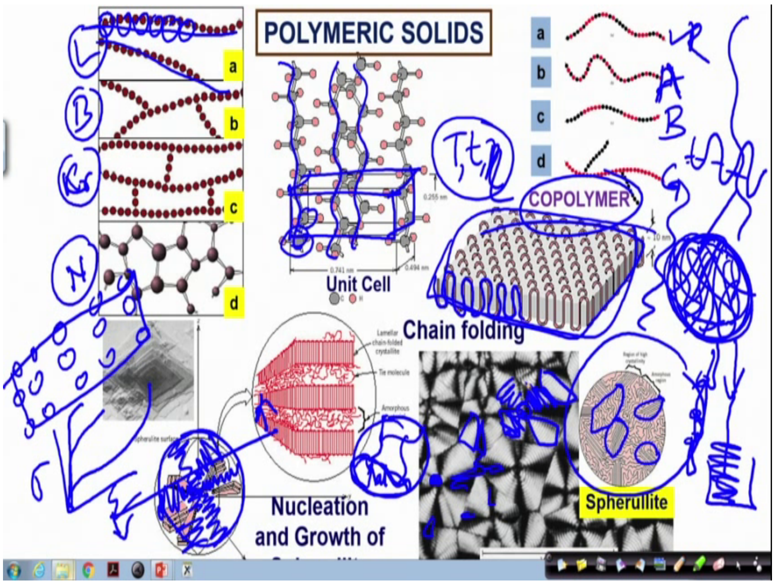

POLYMERIC SOLIDS

So, one other thing that we need to discuss little bit at this moment is the way the polymeric solids behave or how can we strengthen polymeric solids crystallization or partial crystallization is a possible strategy and in fact, there are many many polymers which actually undergo such kind of partial crystallization and in the process they offer you a higher strength than a normal in normal condition. But before we actually go into that lets quickly recapitulate we did discuss about the structure of polymeric solids and we said that they essentially are made by mars.

So, this little blobs here they are essentially the their individual mars. So, we just connect these mars through a thread and that is what is known as a polymer. Now, repetition of them can be linear, so we call it as a linear polymer, it can be branched, it can be networked or it can be cross linked.

So, we can have linear polymer branch polymer cross linked or networked, but if we the all these are like pure metal or a pure substance because all the mars have the same composition, but if we mix two or three different types of mars. So, we create what is known as copolymers and the copolymers can be random, can be alternate, can be block or can be graft.

So, either we have pure polymers or copolymers, and in one of these structural configurations, the polymeric solid that we see for example, if this is a polymeric solid all these chains basically are arranged randomly unless the fabrication process mands that they should be aligned. So, if this is a solid we simply call it solid because it’s rigid it has a particular volume and shape which it does not change unless it’s acted upon by forces.

So, this shape that we see of a polymeric object is because of the fact that we have millions of such threads inside which are all jumbled up, but because of the rigidity that they create because they are not able to move or not able to form very easily, so we call it a solid, but there is no long range periodicity in it. But if you take out one of these threads right like one of these long chains and if you make it actually undergo back and forth folding motion.

So, just like as if you have a chain imagine us, a chain with multiple links. So if you have a chain with such multiple links. So, these are the links where they are attached. So, when you actually load this chain onto a particular vessel this whole chain essentially will fall and then will start under going back and forth motion.

So, the same way if you actually low this chains of polymers into a particular vessel by way of changing the temperature, time, viscosity and various other parameters, then they actually are likely to undergo such back and forth folding back and forth chain folding motion and as a result they can create.

For example, a two dimensional object wherein we may discover certain amount of periodicity occurring by coincidence because this is a long chain; this is a long chain, this is another long chain, but we happen to discover as if some of these molecules or these mars are getting repeated at some regular intervals. And if we trace more carefully we might even discover that there is a skeleton, there is a skeleton cell which is as if repeated in a given direction.

So, starting from a long chain; a long chain if we allow it to undergo back and forth motion folding motion, then we may discover that as we fold certain regions across the fold appear very similar and it’s very similar because they are they are made up of the mars of same composition and they are being repeated at exactly the same distances. So, in case of a normal crystal light you would expect one atom or one iron or one molecule to come and arrange themselves at regular intervals.

And this when repeated in 3 dimension we say this is a crystal and here what we are saying is that these chains they can arrange themselves such a way that a part of them actually can create an imaginary skeletal structure which resembles a particular unit cell. And this unit cell finitely will belong to one of the fourteen Bravais lattices and that is how we can connect even a polymer or a part of a polymeric solid as crystallite.

So, typically this kind of a chain folding motion can start from this point and let us say go along this direction, can go along this direction, can go in all possible direction and eventually. If this chain folding motion goes in all possible direction eventually you can end up making a complete sphere because they are allowed to grow randomly in all possible directions.

And if you have created such a sphere and now if you take a section out of this sphere, the section will show you something like this where the chain folding motion allows you to see a periodicity in this pocket, periodicity in this pocket, in this pocket, but in between lack of periodicity in this regions.

So, this is a cartoon whereas, this is a real time picture of such a change folded polymeric chrysolite formed wherein you can clearly see that maybe this was one particular region where the chain folding started and this is how one particular lamellae formed like this; this is how another lamellae formed this is how another lamellae formed.

So, essentially these are different chains radiating in different directions. So, this is a crystallite region; this is a crystallite region; this is a crystallite region and so on and so forth, but in between we also have dark regions and these dark regions are non crystalline regions. So, if you compare this with a metal typically in a metal or a complete or a ceramic crystalline ceramic you find 99 percent of the entire region of the bulk as crystal.

So, these are all crystals and we call them grains or crystallites, only a one or two percent of the area will be boundaries we call grain boundaries or phase boundaries, these are non crystalline regions. Whereas, in a polymeric crystal at best you can have something like about 70 80 maybe 90 percent at the most which are crystalline, but in between regions will be non crystalline. The so called boundary regions are much more here that is simply because the each of these chains also have certain amount of rigidity associated with themselves.

So, it's not always possible to make 100 percent crystal out of such threads or chains and behave make them behave, so periodically that the entire volume can be called a crystallite. So, this is how we can actually crystallize a polymer and when we can do that the advantage is that, now when you have such a crystallite, the formation when you try to form instead of having instead of showing a long um.

So, this is again stress strain instead of showing a fairly low strength, but a long plasticity plastic region, now partially crystallized polymer can actually show you slightly higher or even greater strength mechanical strength and this is not only possible in the bulk it's can be done even onto the surface.

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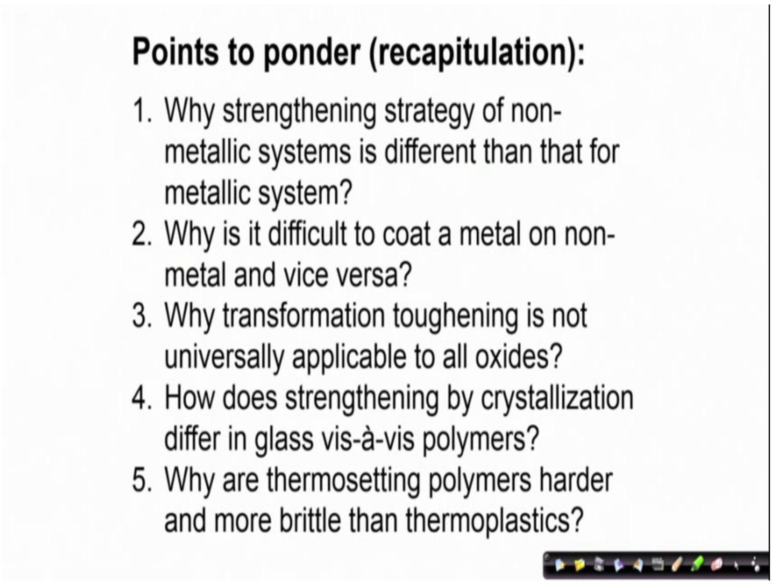

Points to ponder (recapitulation):

1. Why strengthening strategy of non-metallic systems is different than that for metallic system?
2. Why is it difficult to coat a metal on non-metal and vice versa?
3. Why transformation toughening is not universally applicable to all oxides?
4. How does strengthening by crystallization differ in glass vis-à-vis polymers?
5. Why are thermosetting polymers harder and more brittle than thermoplastics?

So, now we should try and come to we should try to summarize what all we have discussed so far. So, compared to metals first thing we must understand is that solids made up of polymers or polymeric solids will be primarily non crystalline.

So, the strengthening mechanisms are going to be very different and yet we can make them stronger by bringing in certain transformations or change in the structure one possibility as we saw was crystallization partial crystallization, we also saw that other non crystalline stuff which are not polymeric, but partially ionic predominantly ionic like a silicate glass can be made tougher either by partial with vitrification or crystallization or by glass tempering whereby we actually can bring in residual compressive stress onto the surface.

The question is that when we have composites when we have dissimilar combinations of metal with ceramic or ceramic with polymer or metal in polymer and so on, the biggest difficulty arises at the interface. Because they do not talk to each other they do not tend to talk to each other because a bonding characteristics are different.

But if we want a composite for particular applications made up of two or more number of materials of different origin like I said metal in polymer or ceramic in polymer, then we must find a way to modify the surface, so that these two dissimilar materials can bond well with each other and they do not undergo cohesion at the interface.

So, we need to understand the mechanisms, which actually allows us such kind of bonding to form and hence we need to understand strengthening mechanisms of the bulk and extend it to the surface.

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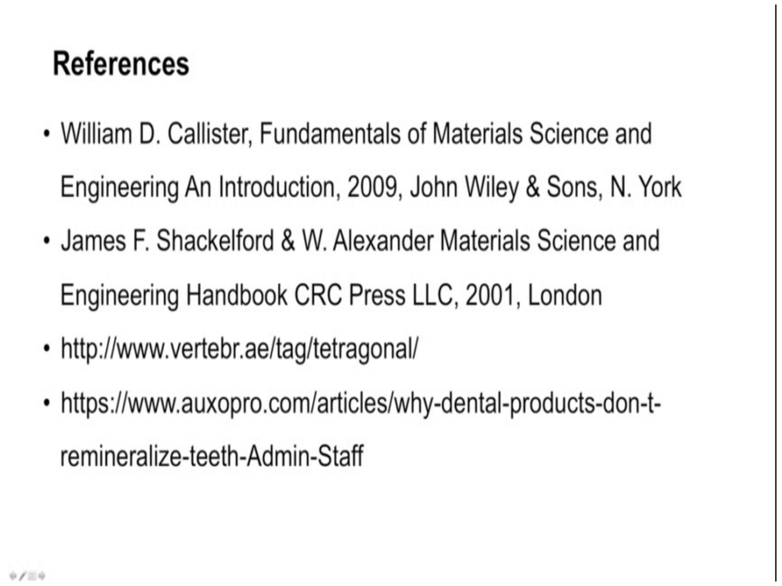

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So, so this is all we discussed and in the next lecture, we would like to take up the strengthening possibilities in steel because you all know that steel continues to be the second largest tonnage wise use materials for any kind of structural applications and there are multiple possibilities of application of steel for various purposes. So, we will be we will take it up in the next lecture.

Thank you very much.