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Lecture - 13 Bulk Metallic Glass, Glassy and Amorphous Materials (Contd.)

Hello. Myself Dr. Jayanta Das from Department of Metallurgical and Materials Engineering, IIT, Kharagpur, I will be teaching you Advanced Materials and Processes. We have discussed many different aspects on metallic glasses, amorphous alloys or bulk metallic glasses and today, we will continue the discussion and try to specifically emphasize on their mechanical properties. Now to understand mechanical properties, we must try to learn the physics of deformations in glassy or disordered solids.

In this particular aspects, there are some theoretical model has been illustrated quite long time back.

(Refer Slide Time: 01:28)



So, Professor Ali Argon from MIT was trying to create a model to explain the atomic scale mechanisms on deformation in disordered solid. So, he proposed the theory which is known as Bubble raft theory. In this particular theory, he tried to explain that the disordered solid could be deformed by some atomic scale rearrangement and this particular rearrangement could be two major types.

One is known as diffused shear because the atomic scale cluster must be rearranged by some shearing event. So, this is one part which is called as diffuse shear and the second one is the concentrated shears ok. So, in the left hand side, this model is shown here that there are several atoms which are randomly arranged and if you think about such a cluster and give us a shear strength, then upon application of the shear stress, some strain will be generated which is the gamma and here, this is the net amount of shear strength has been given to the cluster.

Now, please have a look to the right hand side of the slide, here, this is another same cluster which is shown here. We apply again the shear stress and the mostly shear is concentrated between these two; not really parallel, but somewhat like that is concentrated and it is known as the concentrated shear. Here also, the initial arrangement of the cluster is shown here and after the shearing event the arrangement or rearrangement is shown here.

So, here you see, the bottom part and the top part; this shear against each other and the shear is concentrated mostly in this two different let us say layer of atoms. Even though this layers are not very regular like a conventional crystalline lattice; however, whether it is a diffused shear diffused means the strain is almost distributed or where here, it is concentrated, this net strain to generate, there is a strain rate required. So, strain rate is explained with gamma dot, now it shows an Arrhenius type of relationship.

And. So, Arrhenius type of relationship means there is a constant and exponential and definitely, there is a delta G of shear which is the activation energy of the shearing process and this is a constant, I mean temperature at deformation and k is basically a Boltzmann constant. Now we need to learn something from here, we are talking about the shear strain and a stress strain rate is generated during a very short time in a very localized way.

However, this particular term which is the activation energy of this shearing event is linked with a constant which is C_S and τ_s is a critical stress that is required for the shear to occur. And this cluster of atom which get activated during shearing process it has a characteristic volume that is the net volume of this particular cluster that is Ω_S and it has been also proposed by Professor Argon that even though, we see this diffused or

concentrated shear, but at any temperature or deformation temperature the shearing event has two different component.

Both the component may be active. However, the relative contribution of this individual component could be different, like if the temperature is higher, here a higher temperature of deformation in case of glassy solid means the temperature close to glass transition temperature. In that particular temperature of deformation the diffused shear become more and more active, because all the atom get some activation energy and try to rearrange themselves or the net activation of the energy of whole cluster could shear.

Whereas concentrated share is mostly preferred at relatively low temperature. So, let us assume that for a particular glass forming composition, if that glass has a glass transition temperature of somewhat likes 400 °C. And if we try to deform at room temperature of 25 °C, then concentrated shear is mostly preferred or the contribution of the diffuse shear is less.

However, this is a bubble raft theory and which has been modified later on with the name of shear transformation zone or STZ theory by Langar and Professor Hull and there are several theoretician who keep on doing several modeling experiments and trying to explain this particular feature. So, it is not only valid for bulk metallic glasses, but also metallic glasses or any other solid which exhibit amorphous structure or disordered atomic structures.

And so, if we adopt such kind of understanding in case of a glassy solid then since we talked about shear strain rate.

(Refer Slide Time: 09:04)



So, temperature and strain rate both these parameter or external variables must be a very much important on the mechanism of deformation and a shear strain rate that is applied to a solid. However, a strain rate that is generated inside those atomic clusters which may not be same as the imposed strain rate and a along this direction. If we simply take a super cooled liquid even though the viscosity is higher than the conventional liquid, a super cooled liquid has a higher viscosity level, then the then the conventional liquid.

But we can think about a Newtonian or non Newtonian type of flow. So, in that particular aspect, we know that a strain rate; strain rate that is equals to $A\tau^n$. So, here this is the shear stress and n is a exponent if this value is n is equal to 1, then the strain rate that is inside the material is proportional to the shear stress and we can reach to a very high elongation level and if n is not equals to 1, then we get a basically and non Newtonian type of flow behavior.

And if you look at the same in a plot, it also explain the same feature that if we keep on increasing the temperature, then definitely we reached to a Newtonian flow where very large plastic deformation can be achieved. However, if the temperature goes down then in non Newtonian type of flow is activated. On the other hand, if we apply a very higher strain rate to solid, then the strain with be localized into some into some clusters and shear will be localized in those clusters ok.

The cluster could be in a super cooled liquid or the clusters will be in a glassy state in a solid. So, it does not matter. So, there is some transition from a shear localization to a Newtonian type of flow. It depends on the parameter that is temperature of deformation and strain rate of deformation. So, this is a very good understanding we explore and on the other hand a non Newtonian type of flow is also lead to very low amount of plastic deformation that can be achieved in a solid.

And definitely if strain is localized, a shear is localized, then also we will get much or very very less strain like if we think about a conventional crystalline steel, and then if there is some necking is also a localized deformation just as an example. And so, let us try to proceed with this understanding and see that if we could categorize various type of deformation mechanism that is operative in a glassy solid.

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So far, we understood that the flow in a glass could be homogenous. So, this homogenous flow could be two major types. The first one is a steady state flow and the second one is non steady state flow. In case of a steady state flow, we could think about a viscous flow of the super cooled liquid.

So, why it is important? So, if the temperature is very close to glass transition temperature near T_g and definitely, it will help in shaping the bulk metallic glasses like conventional oxide glasses or window glasses, if we take, and if we can blow a glass then we can make different type of shapes like a bottle ok.

So, for a bottle making process in a glass blowing shop if you visit then you will see that there is a die and they put some oxide glass and they simply put some air pressure at a temperature very close to glass transition temperature where the viscous flow of this glass will occur and it will take the shape of that particular pattern and or a mold. So, that shaping of glasses could be also very much important or let us say, if you like to make a micro gear, a micro gear means a gear with the tip size somewhat in the scale of few micron, then you may not be able to directly cast or even if it is not possible, then you can go for shaping or micro forming ok.

So, working on a glass require such kind of flow and it should be homogenous otherwise if it is inhomogeneous, localized deformation of this, there will be a failure in the material and therefore, the steady state flow means there is some process goes on during the deformation of a solid.

Now if we look at the Argon's bubble raft theory or shear transformation zone theory, a atomic rearrangement can only happen when there is a local expansion of that particular cluster. So, that atom get a space to rearrange themselves and also the again the structure should be relax to come back to a more dense form ok. So, in that particular case, we may think about the local ordering or disordering process which goes on.

So, like a continuous process during deformation at a given temperature, there is some structural ordering or disordering goes on and there is some particular rate it goes on at a particular rate. So, steady state can only be reached when this rate is equal. So, we can also think about there are some excess volume in the glass and to rearrange a particular short range order or a short range order cluster with 100 of 1000s of atoms, then the free volume need to be increased so that atoms can be rearranged themselves to a different configuration under stress.

And therefore, the free volume creation is required. At the same time once this particular shearing event completed then there is also some localized annihilation process goes on, annihilation of the free volume ok, annihilation of the free volume or on the way, creation of the free volume means local dilation process means expansion as well as there should be some contraction.

So, this the same process, there is some they go on some rate during deformation and this rate if this rate is equal in a solid, then it can reach to some steady state flow where the

required stress to flow is almost constant, that is the understanding and this only happen when there is a localized redistribution of the stresses because once the stress is applied, some cluster where the stress concentration goes on higher and they rearrange themselves again in the stress will relaxes.

So, not only in terms of free volume, creation free volume annihilation their rate to be equal, we can reach to a certain steady state. So, we can mathematically express such steady state flow in terms of a shear transformation zone rate is this rate which is

$$\dot{s} = v_0 . \exp\left(-\frac{Q \pm \tau V}{kT}\right)$$

 \dot{s} equals to v which is some sort of frequency and that is some exponential Arrhenius type of term here Q is basically the activation energy and you can see here I wrote this volume is the activation volume and some stress with plus minus sign.

What I want to mean that the required activation volume could be modified by application of the stress, modified means it could increase or decrease. So, let us say a particular shear transformation zone may get favored or a atomic scale cluster may favour to undergo a shear transformation by the application of stress or it could be retarded by the application of stress.

So, in that case, the activation energy will increase which retard by the application of stress or it could simply decrease by the application of stress and that is why I put here a plus minus term means there are some phase shear transformation in some cluster which is favored by the applied shear stress and. So, we can get a mathematical expression in terms of such a steady state flow.

However, if all these explanation that we understood in terms of local dilation or relaxation, if they are not equal then definitely a non steady state flow can be seen where there is no balance between any of these processes and because of the rates are not equal and now like homogenous flow we have also inhomogeneous flow.

So, these are the two major types actually and in homogenous flow means that there is some localized deformation and localized deformation means the shear strain is accumulated in some specific sites in the glassy structure. So, the at that time the shear localization occur and it lead to the formation of some band because bands means some atomic or let us say some planes or some zones where the shear strains are more and more localized and they leave the stress at the surface and we can see such banded structure.

In the next couple of slides, I will show how is the appearance of the shear band in a glass in solid and since the stress is localized, some part of the work must be converted into the temperature. And therefore, there is some heat evolution in the shear bands and these are some of the important aspect of today's discussion.



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Now, let us have a looked at some of the deformation curve of one zirconium based metallic glasses this is also one derivative of Vitreloy and the temperature is kept somewhere around 370 °C where you can see that the T by Tg is 1.03 and it means that the temperature is very very close to the glass transition temperature.

Now, let us have a looked at the stress strain plot which is very very important and during this experiment the strain rate has been kept at 10^{-3} /s and here, the stress increases and remain almost similar with increase of strain. So, this is something like 25 percent, there is no change in the flow stress level. Now it has increased, let us say 5 times. And so, in that particular case, the there is a slight overshoot of the stress and then again the flow stress remain constant with further deformation.

In this case, it is basically 10 times higher than the stress strain rate and so, almost one order magnitude higher strain rate is applied in that particular strain rate, we see a very significant overshoot of the stress initially occurred and then there is a under shoot and then again flow stress remain constant.

So, this under shooting or overshooting is somehow linked with non steady state flow. Non steady state occur when free volume creation and annihilation or local dilation and relaxation are not in the same rate. So, initially when deformation proceeds then free volume increases and the increase in rate is higher with increase of the strain rate level and once it reaches to a peak value. Then basically the undershoot occur due to the opposite process goes on and after some percentage of strain both the process come in a balance.

And due to that particular balance we get a constant flow stress and therefore, this is a region when steady state flow is there and here this is a domain when we can see the non steady state flow and this is a very clear and very common example of a disordered solid for particular this type of flow. Now let us take the same glass and deform it at this particular strain rate, we see such kind of flight overshoot and then there is a steady state is reach here.

And now only if I change the strain rate ok. So, definitely it will go here because these are somewhat in the same scale and then again between these two, there will be a under shooting and there will be some steady flow. And then again I go back to the initial strain rate which is lower than this particular one and then again, I can see that the steady state will be reached in that particular level. It means that the material flow stress is somehow linked with the given strain rate or material remember, the flow stress which is the function of a given standard and so it is something like a memory effect in a glassy solid. So, these are particular deformation mechanism people tried to understand by varying deformation temperature and strain rate.

(Refer Slide Time: 25:18)



Now, let us come to the inhomogeneous type of flow. So, here once again a derivative of Vitreloy glass was taken and they kept under compression.

So, for doing this compression, we basically take such kind of height which is the height of the sample and there are some diameter cylindrical samples you can take and we monitor the variation of the stress and strain ok. So, this is something like two percent level here. So, we can see that the material yielded showing a elastic strain of somewhat in the level of two percent which is almost two or three times higher than any conventional crystalline alloy; so, very very high elastic strain limit that can be achieved.

However, even though there is little plastic deformation of less than 1 percent, but if you magnify such deformation stress strain plot, you will see that there are some small serrations types of behavior. And this serration must be linked with the localized strain burst, means must be somewhere a sudden strain appear and that is linked with again some required some activation. And then again, there is some flow and there is a drop that is a undershoot again some overshoot.

Again some undershoot overshoot undershoot and so on ok. So, formation of such kind of serration clearly indicate that this is definitely not at all a homogenous flow, but it is a localized flow event or a inhomogeneous flow event that goes on in bulk metallic glasses. Now very similar types of behavior people have also observed in case of a nano indentation. So, there during nano indentation; since it is a instrumented indentation, a instrumented indentation means that we are capable of measuring the indentation depth with the given load or the strain rate.

So, we can vary the loading here, we can see if you see the unit it is basically mN Newton per second this means the loading rate has varied. So, load is a unit of mN Newton per second here is also mN per second. So, higher loading rate means a higher strain rate is expected. So, at very higher strain rate, the serrations almost like vanish than the lower strain rate. So, which is a a expected. So, a higher loading rate where I appears to be like a like a homogenous type of flow to a inhomogeneous. This is like a showing some sort of transition very similar way.

Here also this is a zirconium, aluminium, copper, nickel, aluminium, glass or let us say this is also one of the relative of that kind of glasses. Here is also another palladium type of glasses during nano indentation people observe such kind of serrations. And these serrations are called as pop in pop in event. And these pop in events are linked with the formation of some localized strain burst or the some shear bands or deformation bands in this glassy solid.

So, today, we tried to look at the atomic scale mechanism of glassy or amorphous or disordered solid, we tried to learn about the Argon's model on bubble raft theory, also the shear transformation zone theory and how the shear transformation get activated upon application of the shear stress or it may retarded. And we can simply think about the localized strain rate that evolve and we try to understand what is homogenous inhomogeneous flow and what is steady state can be reached and how a non steady state can be reached.

So, these are very fundamental understanding of any disordered solid. And the inhomogeneous flow and inhomogeneous deformation, we will discuss in the next class.

Thank you.