[SQUEAKING]

[RUSTLING]

[CLICKING]

JUEJUN HU: OK, so in this lecture, what we'll do is we'll focus on a unique class of amorphous materials basically, metallic glasses. So metallic glasses is pretty much not included the reference text I recommended at the beginning of semester, so that's why I have included a few, I think, very nice papers here that discusses about structural or mechanical behavior of these metallic glasses as references.

All right, so to start with, this slide basically summarizes the historic timeline of the development for amorphous metals or metallic glasses. For a long time, people do not believe that you can actually prepare metal in an amorphous form, because they tend to crystallize very, very quickly. So it's very hard to prevent essentially a crystallization of this material.

It's only until like 1960s, where people actually start to discover that you can actually prepare essentially a very thin membrane form of metallic glasses or amorphous metals in this binary gold silicon alloy. So for that particular alloy, the critical cooling rate you need to actually prevent crystallization is of the order of 1 MIG degree Celsius per second. So you still need very, very fast cooling in order to be able to actually amorphize it. And you may also recall that this kind of fast cooling rate essentially also corresponds to a very small thickness, where you can get efficient thermal extraction from the interior to prevent essentially crystallization.

So that's why in the early days, these metallic glasses can only be prepared in a thin film or thin membrane form. The technique that people actually use to actually prepare them is mostly so-called the melt spinning. I have briefly mentioned about it earlier before, but the whole idea is that you have a big drum that's essentially rotating. You keep it at a low temperature. You then put the crucible on top. At the bottom of crucible, then the melt of the metal comes out. So then when it comes into contact with this cold drum, it then quickly cools down. And then due to the centrifugal force, it essentially comes out as like a continuous ribbon.

So starting in the 1970s, people started looking into applications for these kinds of amorphous metals. Their first area where they get commercial adoption is in the field of magnetic applications, mostly to use as essentially the core for transformers or generators. So the reason they have become attractive is because in amorphous metal, unlike crystalline metal, you have no crystalline boundaries.

So when the magnetic domains, they try to move around, they have much less resistance in amorphous metal compared to crystalline metal. So magnetically, what they correspond to is that the magnetic coercivity for amorphous metal tends to be very, very low. So in other words, they tend to be very good soft magnetic materials. There's very little residual magnetic polarization or magnetization once you remove the magnetic field. And that kind of characteristic is actually quite useful for things like transformers.

On top of that, the other advantage is that these amorphous metals tend to be electrically a bit more resistive compared to their crystalline counterpart, basically, because when the electronic carriers, when they are moving around because of amorphous structure, you basically get more scattering because of the lack of long-range order. So that leads to a reduced mobility and therefore higher electrical resistance.

Now higher electrical resistance is beneficial for these kinds of magnetic applications because electrical current, or eddy current, basically is a parasitic current that's getting generated if you have an oscillating magnetic field, they can actually dissipate energy, leading to unnecessary power consumption. So that's why people were interested in looking at them for soft magnetic materials essentially.

In 1980s, people start to discover that they can actually make what's called a bulk metallic glasses, BMG, with a much better glass forming ability. Now going to the range of maybe like a few hundred Kelvin per second, critical cooling rate. For that kind of critical cooling rate, you can start to make macroscopic size pieces of this kind of metallic glasses, with millimeters or even thicker, centimeter thickness.

1990s, that's when you start to get more and more companies start to jump into this field. There's a very famous group in Caltech. They actually developed this Vitreloy amorphous metal series. They actually get quite a bit of commercial traction. And then in they also get a lot-- I put a quotation mark "cheap." Cheap, this is a relative term, right? The Vitreloy is actually still pretty expensive. The little piece of Vitreloy I showed you in the last lecture, that one cost me $200.

But still, in terms of cost, this is much lower compared to a lot of the amorphous metal in early days because they tend to contain a noble metal like gold. So yeah, they are at least relatively low cost. And that's why we start to see some commercial adoptions there. Besides magnetic applications, they are mostly used because of their superior mechanical properties. So they're used in things like high-end sports gears like skis, golf clubs. They are also used in critical components like in sensors or automotive applications, where you need high temperature stability, minimal amount of degradation and plastic deformation. So that's where they see a commercial options there.

In this next slide, I'm showing you a table of different metallic glass composition or metallic glass compositions people have developed. This table, horizontal axis is basically the normalized Gaussian tradition temperature for various compositions here. Vertical axis, I have two vertical axis here. Left-hand side is basically critical cooling rate. We know that the critical cooling rate corresponds to the maximum thickness. You can prepare a sample while still staying in amorphous form. So we can see how this material is actually evolved from the ones that actually have a high critical cooling rate, small thickness, all the way down to essentially on this end, where we have actual bulk metallic glasses that can be centimeters thickness.

So what I will do in this lecture is I will divide it roughly in two parts. I will start by talking about structural model. How do we actually engineer the constitutive atoms so you maximize the glass forming ability. And then in the second part, I will then based on structural model let's discuss a little bit about their mechanical behavior, which is the main attribute that draws most of the commercial interest.

So in terms of structure of metallic glass, there are two key things I want to mention here. One is that the chemical bond in them is essentially metallic bonds. Metallic bonds, unlike covalent bonds that you find in other inorganic glasses, they are nondirectional. And also in order to stabilize metallic glass, the criterion is also a little bit different.

In organic network glasses we talk about essentially topology or the connectivity of the network being the key criteria that influence stability. In metallic glasses, on the other hand, what we are trying to do is we are trying to lower the Gibbs-free energy of the amorphous structure. To lower the Gibbs-free energy, you need to essentially lower the total energy of all the metallic bonds. And that's directly correlated with packing density.

If you can pack essentially atoms more close to each other, you get stronger interaction between the outer shell electrons and the atomic nuclei. And as a result, you reduce the overall energy of the system. So the key point I want to make here is that in order to get a stable metallic glass, you need to try to achieve structures that have as high density as possible.

So that's why Inoue, who is actually a pioneer in the area of bulk metallic glasses, when he actually summarized the three empirical rules here, you can clearly see the role that this close-packing structure actually kind of plays in dictating the glass forming ability in bulk metallic materials.

So I've already talked about this before. There are three rules. First one is that you need to have at least three constituent atoms or even more. And they also need to have significant size difference. Usually the size difference has to be greater than 15%. So that you can actually pack them together in a close packed manner without introducing structural order. The argument is quite simple. If you have all the atoms within the same size, you can easily achieve a close packing structure, go to FCC or HCP. It's very easy to look at form local structures like that. But then you are not able to realize amorphous stacking.

The first two points here, both actually has to do with the topology of metallic glass. The first two points that we have not talked about anything about the specific chemical properties of the constituent atoms. The only thing that really matters there is essentially size, which is a geometric parameter. The last point here, negative enthalpy of mixing, this is just to prevent essentially segregation of different compositions. They have to be thermodynamically stable. They need to be happy when they are actually staying together.

So these are the empirical rules. What I'll do next, I will give you a more quantitative description about the structural model for bulk metallic glasses. In this regard, if you think about the network in inorganic glasses, we talk about essentially Zachariasen's rules, the empirical rules. And then we talk about the topological constraint theory.

So in the world of metallic glasses, this Inoue's empirical rule plays the role of Zachariasen's rules And then what I'll talk to you about is essentially this topological model that allows us to achieve maximum packing density using different kinds of metallic atoms. Now, before I go to that, I just also want to mention that this theory, this is not just a speculation by scientists. This is something now people were able to essentially verify experimentally.

So this is actually one example. This is a paper published a few years ago where people were able to do essentially an electron tomography. So tomography essentially means that you're looking at 3D structures rather than these 2D sections or 2D images of materials. They were able to actually look at an amorphous metallic nanoparticle that actually determines the coordinates of all the constituent atoms within that nanoparticle, which then allows them to verify this kind of topological structural models. So if you actually go and read the *Nature* paper, what they spend a lot of time talking about is how they actually verified the topological local structures that people have predicted, and that eventually shows up in the experimental characterization.

All right, so now let's start by talking about topological theory. So the whole assumption is that we want to approximate all the constituent atoms essentially as hard spheres. So then the problem becomes a pure geometric construction. We want to find some hard spheres with different sizes and different fractions or different compositions, basically. We want to put them together so we can achieve maximum packing density. The hypothesis is that the glass composition that's most stable would also correspond to the compositions that gives us the highest packing density.

So let's start by looking at the most simple example here. Instead of looking at 3D packing, let's think about 2D packing. So a hard sphere in 2D basically means essentially a hard circle. And to make things even simpler, let's consider a binary 2D packing. We have only two kinds of circles that we want to put together. So what I'm showing you here, this is a local cluster where we have two kind of circles here. And the horizontal axis on this plot is basically a radius ratio of these two kind of circles.

Now if you only have two kind of circles, what you can imagine there is that there are some specific radius ratios of the two spheres. Once you meet those critical ratios, you can essentially put one kind of sphere right around the other without leaving any gaps in between. And what we argue is that that kind of configuration, or that kind of critical radius ratio, is what gives you the maximum packing density.

So that's what we are plotting on this plot here. The vertical axis, there are two vertical axes here. Let's look at the one on the right-hand side. So what's on the right axis is what we call the packing efficiency. I mean you can consider it as the packing density, the ratio of the actual packing density over the theoretical maximum packing density you can get. And for the right axis, the plot actually goes by these kind of dots.

And what you're seeing here is that you see this kind of a zigzag pattern. What happens is that when you actually hit one of these critical ratios here, you can fill one kind of sphere around the other without leaving any gaps. So this corresponds to a peak in terms of packing efficiency. You get unity packing efficiency. And as you deviate from that point, you start to get a decrease of packing efficiency until you go to the next point here where the coordination number essentially increases by 1, you can fit in one extra sphere. So again, the packing density peaks.

On the left-hand side this is basically coordination number. Coordination number actually goes essentially monotonically in a large 2D array there. It's talking about average coordination number. So take-away message, dense packing is only achieved at certain critical radius ratios.

So we can translate this conclusion into 3D. It's actually very, very similar. So the plot is exactly the same. We still have only two kinds of hard spheres now in 3D, horizontal axis radius ratio, this is packing efficiency. You see a very similar kind of zigzag patterns. Left-hand side is coordination number.

Now you do notice that for the average coordination number, there's a little discontinuity right here. That's actually because we have two different kinds of configurations here. On the left-hand side, one of the spheres is actually fitting into interstitial size between the other spheres. And on the right side, is basically going to a substitutional site. So because of change of configuration, that's why that little discontinuity there. Anyway, regardless of that detail, we see the very similar features here that if you want to achieve maximum packing density, the two spheres also need to fulfill specific critical radius ratios.

So now what we hypothesize, if we translate it into actual metallic systems, we expect to find pairs of atoms. If those atom pairs fulfill their critical radius ratio, you'll be able to maximize the atomic packing density. and we then postulate that those atoms will then give rise to the most stable binary metallic glasses.

So this is what they actually did in this paper here. So let me explain what they did. So horizontal axis, this is again the radius ratio of atoms in binary metallic glasses. The vertical lines here, each of these vertical lines essentially correspond to one of these critical radius ratios that give you the highest packing efficiency.

And the vertical axis here, this is basically a histogram. So what the authors did is they essentially survey all the literature published up to that time on binary metallic glasses, and then they essentially count the frequency of one particular atomic radius ratio that appears in literature. So if you see a peak, for example here, essentially it means that there's actually more literature reporting metallic glasses that are having atomic ratio right at this point there.

Now if you look at this line here, you clearly see the correlation. Whenever there's actually one vertical line that corresponds to one critical radius ratio, that tends to be a peak, meaning that there are more binary metallic glasses that assumes the particular atomic radius ratio.

OK, now one exception, you look at this line here. This line R equals 12 around R equals 12, you see that this actually corresponds like a local minimum. Why is that?

AUDIENCE: Because it's the atoms are the same size so they just form a crystal.

JUEJUN HU: Yeah, so essentially when I say the R12 here this is basically the coordination number nearest neighbor. So R12 corresponds to a what kind of structure?

FCC?

Exactly FCC or HCP. Both FCC and HCP have 12. So essentially what it says is like even though you can form close packing, but it will crystallize if they are exactly the same size. And that's why when the atomic radius ratio is close to 1, that's why despite you have a high packing density it's a poor choice for bulk metallic glasses.

So that's for binary metallic glasses. Now what we want to do is we want to actually extend the theory into a ternary, quaternary, multi-component bulk metallic glasses. Now for those, we will be looking at packing of hard spheres, but more specifically, we will be essentially looking at essentially this tiered structure.

We're looking at two structure tiers, first, by starting looking at clusters A cluster is defined, so what I'm showing here, this is a cartoon of the multi-component bulk metallic glass. Different spheres essentially correspond with different kinds of atoms. We are looking at essentially clusters, right? So a cluster is I will defined, is as you have a center atom in this case labeled as alpha. You then have some surrounding atoms. That's basically like the solute.

So each of these essentially is one cluster. These clusters then stack together to form the three-dimensional structure So there are two structures here. Now in order to maximize the packing density, we need to do two things. First thing we need to maximize the packing density within a cluster. And this is a problem we already solved.

We know that if the two atoms forming the cluster, they fulfill a certain radius ratio, then one kind of atom can surround the other without leaving any gaps. So this gives rise now to essentially a specific radius ratio between the two atoms, and also a specific competition ratio. Because once the specific radius ratio it also gives you the coordination number. If you know the coordination number, it actually corresponds to a specific composition ratio. So they can essentially form these clusters without leaving any atoms behind.

So that's how you maximize the packing density within a cluster. Now to maximize packing density between the clusters, the strategy what nature will actually take is you can actually fill in smaller atoms in between the interstitials between the clusters So you start by essentially packing the clusters. And then in the interstitial side in between the clusters, you're squeezing atoms with smaller sizes.

Now this strategy also specifies an optimal size for those interstitial atoms, right? So from crystallography classes you have taken, structured classes 3010, you know that all the interstitials have a specific size, right? There's a maximum radius where you can actually squeeze an atom into this particular interstitial, whether it's octahedral or tetrahedral. So if you have an atom that meets that critical size, it can be just squeezed into that interstitial. It will also maximize the packing density.

So then what this model essentially assumes is it basically assumes different kind of topological functions or topological roles to different kind of constituent atoms. They label it in different kind of letters. They have alpha, which is the center atom in the cluster. omega, as I said is maybe the solvent. It surrounds the center atoms to form the atomic clusters. And then beta is the interstitial atom that goes in between clusters to maximize packing density.

If you look at the original paper there, they actually also say there's some kind of atom called gamma. But gamma is basically equivalent as beta. Essentially, beta goes into octahedral like interstitial sites. Gamma goes into essentially tetrahedral interstitial sites, and tetrahedral interstitial is smaller [INAUDIBLE] interstitial site. So that's why there are two labels, but it's basically the same idea.

So what this theory predicts now is that it can predict, give you essentially the atomic radius ratio of all [INAUDIBLE] atoms. It also tells you what is the optimum composition. For example, if you look at cluster for optimal packing density for a given atomic radius ratio, the number of omega atoms you can fit around alpha is fixed. So it means that there's actually optimum composition. Same thing, once you determine the cluster, the number of interstitial sites around the cluster is also fixed. You want to have a sufficient number of beta atoms or the right number of beta atoms. So you fill in all those interstitial sites, but no more.

So this geometric theory essentially allows you to predict the optimal size and also the optimal composition for achieving maximum packing density. So then what we postulate is that these compositions and those kind of atomic size ratios correspond to the most stable bulk metallic glasses.

So now what you see here? This is a purely topological theory. We have not talked about any kind of chemical nature of the atoms. The only parameter that matters, just the atomic size. So then if you read the paper, they actually then there are many graphs like what I'm showing you on the plot here. It's actually examining many, many bulk metallic composition groups and compare the predicted composition with what you get experimentally.

So the plot essentially, for example, for this one, they are looking into a five-component bulk metallic glass-- zirconium, titanium, copper-nickel, beryllium. Now you notice that they group copper-nickel together. Because what happens is that copper and nickel, they have very similar atomic radius. So topologically, they essentially serve the same function. That's why they group them together

And then these four essentially correspond to essentially the omega, alpha, and then this is the beta and the gamma, the four kind of topological roles we talk about in the previous slide. And the closest are the predictions based on this kind of a topological theory that will achieve the maximum packing density. The square and the diamond symbols, these are actually the experimentally prepared bulk metallic glasses that people have actually commercialized, in this case Vitreloy 1 and Vitreloy 4.

So those actually correspond to what people have empirically derived, computations that give you the best stability. Now you see this kind of striking agreement here, the prediction and the actual competition. They are really quite close. Similarly, this is another one. This is calcium, magnesium, zinc, copper. Again, you see a remarkable similarity or remarkable agreement between the theoretical prediction and the actual competition your derive experimentally.

So I always find this paper being quite remarkable there because it essentially starts from this very simple assumption. You reduce this very complex problem of amorphous phase stability into essentially packing density of hard spheres. And in the end, you can get results that you can actually predict the most stable competition with external agreement with experiments. So that's why I always find this paper as a miracle, the fact that if you look at the last name of the author, it's also Miracle. So it is indeed a miracle, miraculous paper.

AUDIENCE: For the left-hand part, why is its prediction selection higher?

JUEJUN HU: This one?

AUDIENCE: Yeah, at [INAUDIBLE]. Yeah like, why is that one noticeably--

JUEJUN HU: Higher?

AUDIENCE: Higher, yeah.

JUEJUN HU: I don't have a good answer to that. I mean, I consider this already as a remarkable agreement, quite close to what you will get. But again, this is still, you can see that this is vastly simplified theory. Essentially you're treating-- the first thing, the atoms are not like hard spheres. The electron clouds can actually deform. They are more like squishy balls rather than hard spheres. So that's already one degree of error, even just looking at a simple topological model.

And two is that this model completely neglects any kind of chemical information, which should have at least some impacts on the final glass stability. Different atoms, how they form different chemical bonds, all those things, it impacts actually the glass formability. Again, that's completely ignored here. So the fact that they can achieve this agreement, I already consider as quite remarkable.

If you look, they actually predict two things. Essentially the atomic size ratio, which is the horizontal position of the crosses and the vertical position is the actual concentration. You see that the size almost agrees perfectly in this particular case. So yeah, I think that's already a miracle to me. It's such a simple assumption, already gives something that so closely agree with experiment. It's also similar to a topological constraint theory. So that's why.

I think bottom line here is that if you think about glass formation, topology really plays a very significant role here. OK. Any more questions?

OK, now let's switch gears a little bit. I want to talk a bit about essentially the mechanical properties of metallic glasses that derive from their unique structures. So in this slide, this slide I think I showed that in previous lectures. I'm just trying to summarize key structural differences of crystalline versus amorphous metals. For crystalline metal. We know that you can essentially induce plastic deformations. And most of the time plastic deformation in crystalline metal occurs through the motion of dislocations.

So this is what actually results in many phenomena such as essentially like work hardening. The more you actually drive plastic deformation, the more you generate [? dislocations. ?] You have the more interaction between them. Therefore, essentially, you impede the motion. Therefore, they actually become harder.

You also have crystalline planes. Those are the planes where you these [INAUDIBLE] can actually glide along those planes. So that also facilitates this kind of plastic deformation. Now all of those defects is absent in amorphous metal. So that's why we expect that amorphous metal tends to have much smaller plastic deformation compared to crystalline metals.

And that's why in the demo I showed you in the last lecture, the little steel ball, they will bounce back many, many times on the metallic glass sheet because you don't have essentially plastic deformation that actually absorbs this kind of mechanical energy. So this is what accounts for large elastic limit and the high-yield strength in metallic glasses. But the downside is that you cannot use a co-working as a way to actually shape this bulk metallic glasses because of this very poor, what we call, the global plasticity.

So metallic glasses, you cannot induce plastic deformation uniformly across the entire material. Instead, what happens is that there are always local regions for whatever reason. I mean, metallic amorphous structure network is not going to be homogeneous in the atomic scale. There are always certain regions that essentially initiates this kind of plastic deformation when you exceed your stress.

Now when that happens, this plastic deformation process always involves relative motion of atoms with respect to each other. So in that process, it inevitably results in the generation and redistribution of free volume. If you generate more free volume, you have more wiggle room for atoms and plastic deformation essentially becomes easier. So what that means is that when you actually have in some specific location where you already induce plastic deformation, it becomes softer. It becomes more amenable to further plastic deformation. So eventually, all the plastic deformation is going to get localized in the region where you already initiate some plastic deformation.

So this is a phenomenon known as shear localization. And that's why this is the image I showed you previously. You have a metallic glass rod. You try to compress it until it fails. What you see is that they tend to fail in some local region here, and you can clearly see this kind of shear bend actually forms, indicating large shear deformation occurs only in those kind of very narrow planes.

All right, so more quantitatively we can describe this kind of a mechanical behavior of bulk metallic glasses using what we call the a deformation map, in this case. So for this deformation map, we have two axes. Horizontal axis is the temperature normalized against the glass transition temperature. Vertical axis is basically the normalized stress. So you see there are several regimes we can define in this kind of deformation map here.

So if you have a low temperature, you also have a smaller stress. This is the regime where the deformation is completely elastic. So there's no essentially permanent deformation in this region here. Now, if you exceed this point, this point basically is your stress. Above that, you start to get shear deformation. And more specifically, this is basically shear localization that actually takes place that lead to catastrophic failure. So that's why this regime is called inhomogeneous deformation, essentially indicating that this deformation is spatially inhomogeneous. They are localized only in certain regions.

If you go along the other axis, so that's actually what happens if you apply stress at relatively low temperature. So then you will introduce essentially shear localization. Now if you look at the stress strain plot, these lines indicate the behavior of this metallic glasses under low temperature. And low temperature, you see essentially elastic deformation. And then once you introduce shear deformation, it quickly fails because shear localization. So the curve abruptly terminates. So that's what the strain stress curve looks like in this region here, inhomogeneous deformation.

Now if you go along this axis, if you go to this part here, go to high temperature, if you go to higher temperature such that temperature becomes comparable to the TG, then the material essentially becomes viscoelastic. You have a lot more viscous flow contribution when it comes to mechanical deformation. So if you apply a small stress, then the material basically behaves like a Newtonian fluid. If it is a Newtonian fluid, the shear rate will now be proportional to the applied stress. OK?

So this is the regime that people like to use for thermoplastic forming to shaping this bulk metallic glasses. So if you look at all the strain stress curve, this curves at the bottom, this one. Forget about this one with a little bump. OK. Just look at this one at the bottom.

So this one is at the bottom is the Newtonian fluid ones. You see the curve start to come up and then eventually they plateau. The regime where they plateau, essentially it corresponds to a constant shear rate. So a constant stress correspond to constant shear rate. So that's why you see this strain essentially monotonically increases while you keep the constant stress.

So this is also a regime where you can essentially introduce a very large plastic deformation of bulk metallic glasses in a thermoplastic forming. So this is actually just one example on top what I'm showing here, there's essentially a little thin wire made of bulk metallic glass. You can actually introduce a very large strain. In this case, the deformation is actually more than 1,200, so huge deformation. You can introduce this very large elongation without actually breaking the material.

The reason this material doesn't break is because you have essentially uniform stress across it, which also in a Newtonian regime this is according to a uniform strain rate. So if it's uniform strain rate, essentially diameter across the whole wire reduces uniformly. And that's why you can essentially draw this kind of long wires here. It's similar to cane drawing in like inorganic network glasses.

All right, now last one, at high temperature, where you actually increase the stress, higher stress corresponds to higher strain rate. And this is where the nonlinearity would actually come into play. So now in this case, the metallic glass essentially behave like a non-Newtonian fluid.

On the strain stress curve, this curve with a little bump, this is indicative of non-Newtonian behavior. So you increase the stress. Strain rate starts to increase. And at some point, because the increase of the strain rate or the shear rate, the stress actually decreases because of the change of viscosity as a function of the strain rate. And that's why you see a little bump here, essentially indicating the variation of viscosity as a function of the stress or strain rate. OK, so this is the regime you probably don't want to perform your process at, because it becomes very difficult to control the process uniformly.

So that's about the high level overview of the deformation behavior. Now next we'll take a look at how the microscopic structure impacts their mechanical attributes. So starting from the simple elastic constants, for elastic constants, metallic glasses, they tend to be isotropic. Which makes sense, right? Because there's no particular grain orientation or crystalline orientation.

The elastic moduli in metallic glasses tend to be lower compared to a crystalline counterpart. So the bulk modulus typically is about 6% lower. Shear/Young's modulus is 30% smaller. The reason it's lower come from a few facts. One is that the packing density is lower. You have free volume, so the density of glasses is lower than crystalline counterpart. So that means on average the atoms are actually further apart from each other.

So this leads to a weaker interatomic interactions which then accounts for the reduced modulus. The modulus, essentially is the ability of a material to resist deformation. And it has to do essentially with stiffness of the chemical bonds in between the atoms. So low density means a low interaction, low stiffness.

Also, because you don't have this long-range atomic order, usually it reduces the directionality of the structure there. This also contributes to actually reduced stiffness of chemical bonds OK. And on top of that, because the local structure is essentially inhomogeneous at the atomic scale. If you look at one region of amorphous metal, atomically, it's going to be different from another region just because it's amorphous. So what that means is that there are always some microscopic region that tend to have less stiffness. They are softer.

So then when you try to essentially induce deformation in the material, those softer regions will then disproportionately contribute to a large deformation compared to other more stiff regions. So overall, essentially the elastic constants will become more dictated by those softer regions. And as a result, this will lead to reduce essentially the elastic modulus. So it's a combined effect coming from the lower packing density, coming from the structure inhomogeneity, and also coming from the lack of structural order which reduces stiffness of the chemical bonds.

So that's for elastic deformation. Now for plastic deformation, we talk about essentially plastic deformation that essentially in this case always involves generation or redistribution of free volume. So what I'm showing on this slide here is actually the microscopic models where plastic deformation can actually take place in a bulk metallic glass.

There are in general two kind of ways to actually introduce plastic deformation. One is called diffusive atomic jump. This is a smaller scale deformation there. What we're looking at here is one atom may have two neighboring sites where you can locate it. If there's no applied stress, then the two neighboring sites may be more or less energetically equivalent. But once you start to apply a shear stress, you will energetically favor one side over the other. So then the system will then hop to one side where it can actually introduce this kind of plastic deformation. So essentially it leads to this directional diffusive flow of atoms that eventually lead to a plastic deformation.

So that's one mechanism where this kind of plastic deformation can take place. Now the other one, which is probably the more important one, a deformation takes place through what's called a shear transformation zone, STZ. Now simplistically, you can think of STZ as a local atomic arrangement where you have two clusters of atoms in contact with each other. The number of atoms involved in an STZ can really vary, maybe a few tens of atoms, maybe to a few hundred or thousands of atoms.

So when they come into contact with each other, this is initial configuration. There's an interface between these two clusters atoms. When you apply shear stress, at some point this atomic cluster group can essentially hop one interatomic spacing with respect to each other. So when that happens, essentially introducing a shear deformation that gives rise to essentially a one atomic spacing, horizontal one atomic spacing.

So then this process continues until you get macroscopic deformation. So one thing I want to mention here, this shear transformation zone is different from dislocations in crystalline metal. In a crystalline metal, you can go to a TEM. You can actually do atomic scale image. You can precisely pinpoint. We get one dislocation here. We get another distribution here. You know a priori whether it's dislocation states. They have very clear structure signature that tell you there's dislocation.

STZ is statistical. When you apply a shear stress on a metallic glass, you actually don't know a priori where the shear transformation is going to take place. Even if you go to a TEM, you are able to look at atomic scale image, you will not be able to predict where is the regime where the deformation is going to take place. It's statistical.

So you cannot consider STZ as a structural defect. It's not a structural defect. It's something we look at after the plastic deformation takes place. Then we know these local regions where you actually have the atomic transformation is where you correspond to STZs. So it after the fact.

Yes?

AUDIENCE: When you're looking at it?

JUEJUN HU: It's somewhat similar to dislocation, if you look at it. It's like edge degradation and moving around. But anyway.

AUDIENCE: You would see evidence that even if it's like moving one atomic spacing, but since both are shearing or jumping one small space?

JUEJUN HU: Yeah, there are a few ways you can tell this. I mean one way, suppose you were able to look at atomic scale image. You can do essentially time dependent imaging. You can see that initially it's like this. It becomes like this. You know that there's actually a shear transformation. That's one way to look at it.

The second way to look at it, you can actually look at the strain. We're going to talk about it. So once we actually introduce the atomic displacement, inevitably you are squeezing the atoms surrounding it. So this is actually introducing a local strain field.

AUDIENCE: And that strain would be larger for shear transformation than like a single diffusion?

JUEJUN HU: Oh, yeah, of course, I mean it's because there's more clusters. And also you only see the strain where you actually have essentially deformation. So now after the deformation takes place, you can actually do a post-mortem analysis and tell you where the STZs are. You just cannot tell it a priori before the deformation takes place, because it's statistical. OK? There may be certain regions that's more prone to plastic deformation, but there's no guarantee that those will be places that actually takes place. It's statistical.

OK. But as I said, this looks somewhat similar to edge degradation sweeping through. If your edge degradation is moving across, then you get this same kind of transformation there. But this is not dislocation OK.

All right, well, this is just another one that shows what actually happens when you have shear deformation zone. The way to look at it is that you can have two configurations. Initially, if you look at energy landscape, they have maybe a more or less comparable depth. So there's no preference of one configuration over another. But once you start to apply stress, you tilt the potential energy landscape, so that you're introducing directional flow. Then from one side to the other, you have [INAUDIBLE] once you can overcome the energy barrier in between.

So I'm quoting essentially Professor Schuh here, who used to be in DMSE. He basically says that the plastic deformation of metallic glasses on the macroscopic scale is an accumulated accumulation of local transformations coming from STZs which eventually lead to macroscopic deformation. And in the process, it's important to realize that in either case, you need free volume, which is quite obvious in the case of diffusive atomic jump. You need empty sites for it to hop into.

Same thing for this kind of shear transmission zone, if it's a very close packed structure such that no free volume, you don't have the wiggle room to move one cluster with respect to another. The resistance is going to be immense. So more free volume always facilitate this kind of plastic deformation. And once you introduce plastic deformation, you can see that you can generate free volume, for example, here. You're essentially moving free volume from this side to the other side. So there's generation and redistribution of free volume in the process once the plastic deformation takes place.

All right, so now with those concepts we can now explain why you have shear deformation by looking at how the shear transformation zone essentially impact each other during a deformation process. So let's see what happens. So what we are doing here, this is a very simplistic model of a bulk metallic glass. We have many, many local regions. Within each region, there could be one STZ that actually takes place.

So let's suppose when you apply the stress at some point one STZ pops up in the center. So when that happens, as I said, the atoms, because they are moving around, the class of atoms inevitably tries to squeeze only neighboring atoms there. So this would then introduce essentially a local stress, local shear stress, around those STZs.

So those local shear stress essentially adds onto the existing macroscopic shear stress. And what that means is now if you look at the neighboring region here, the actual effective shear stress those neighboring regions sees becomes much greater than the global shear stress.

So now statistically, if you look at the probability of an STZ popping up across the entire bulk material, the probability for them to pop up becomes a lot higher near an existing STZ compared to somewhere that's far away from it. So as a result, it becomes more likely that you have more STZs right around it. And once that happens, of course, it further amplifies the local stress, and therefore, you become more likely to have more STZs right in the neighborhood. So in the end, this then lead to essentially the formation of the shear zone and the catastrophic failure.

So to some extent, you can think of it as like STZs, they are talking with each other essentially through strain or through stress. So there's a definitive positive correlation between STZs due to the existence of stress. Once you have one STZ popping up, it's more likely to have another STZ in the neighboring area.

So this is actually something that can actually be modeled. So what I'm showing you here, this is actually coming from this paper. The authors basically did a Monte Carlo simulation, a statistical simulation of the kinetics of plastic deformation in bulk metallic glasses. So it's a coarse grained model. So what they did is they divided up the entire material into many, many unit cells. Within each unit cell, there could be one STZ that actually takes place.

So then they run this statistical simulation. And in the simulation here then these STZs can initially randomly pop up. It can pop up anywhere. But as soon as one STZ comes up, the shear strain field essentially is getting modified. So in the next time step, they then again try to re-simulate. What's the probability of an STZ to pop up across the entire material? Initially it's uniform where there's no STZ.

But once you have one STZ coming up, the neighboring cells becomes more likely to have STZs. So as a result, they tend to essentially pop up right in this region here where we already have STZ. And this is where eventually you are going to lead to strain localization. Basically it's saying that this kind of strain softening or strain localization behavior is something you can predict quantitatively. It shows up naturally in this kind of a Monte Carlo simulation.

So what I'm going to show you here in this plot is actually just two SEM images. On the left-hand side, this is basically a metallic glass sheet. You bend it until you introduce a large plastic deformation. Now, unlike if you use a crystalline metal, when you bend it, you see essentially this curvature. You still see more or less a smooth surface. It just becomes curved. For metallic glass, one the other hand, you see the surface develop this kind of corrugated microstructure.

At each corrugation, you see this is actually where you have essentially a shear bend. So all the shear deformation essentially gets localized in one of these kind of shear bend here. So that's why it looks different compared to conventional metal during plastic deformation.

Now, what you can also imagine is that within this shear event, the shear deformation is actually enormous, right? So this very large shear deformation also corresponds to a significant energy release. It releases so much energy such that you can actually melt metal.

So that's what people did on this one here. So what they did is essentially on the cross-section of metallic glass, they coat a thin film of tin metal. Tin has a relatively low melting point. So when you're actually introducing this deformation, at the shear zone, there's actually so much heat generation that the tin metal actually melts into liquid. And once the tin melts into liquid, due to the action of surface tension, this film essentially breaks up into small droplets. So in the end, instead of a uniform film, you see these little tin droplets, which indicates the local temperature exceeds the melting point of tin.

They use it as a way to map the temperature distribution during this kind of a plastic deformation process. But what we can tell, this is a very dramatic process. It releases lots of local heat right at those kind of shear zones.

Now, another thing I also want to mention here, I've highlighted the fact that any kind of shear plastic deformation in metallic glass always involves the generation and redistribution of free volume. So when you generate free volume, what happens? If you generate free volume, the volume becomes bigger, the overall volume. Because overall volume is basically crystalline volume, which is a fixed number plus the free volume. So if you have more free volume, it must expand. So now if you actually apply compressive stress on the metallic glass, you are going to prevent or impede the generation of the free volume.

As a result, this will also impede plastic deformation. And vice versa, if you want to facilitate plastic deformation, you can apply a tensile strain. Tensile strain, of course facilitates generation of free volume and therefore, it should also facilitate plastic deformation. So in other words, people call this kind of shear deformation process in metallic glass as a dilatational process.

Essentially it means that the volume expands, dilatation. There's always volume expansion that accompanies this kind of shear deformation process. Diliational. I'm going to use this word as a spelling test for my daughters to see if they can spell it correctly.

So now as I mentioned, this should shear dimension also comes pressure dependent. If you apply compressive stress you impede this shear deformation. So that's why people also consider it as a frictional process. You apply stress, you essentially impede the deformation. On a phenomenological level, it appears like friction. OK?

I just want to mention that this kind of dilatational or frictional process occurs not only in atomic solids. It's actually a pretty general phenomena that's involving deformation of any kind of amorphous collections of particles. Where the particles does not have to be atoms. One example is sand.

So the packing of sand is actually an amorphous lattice or amorphous structure. On the beach, you probably all have the experience when you are in the wet beach, if you step on the sand, there's actually a region of dry sand that actually appears around your foot. So what happens there, is when you actually stepping on it, you are trying to introduce shear deformation.

When you introduce shear deformation, the volume must expand. So when you actually try to generate free volume, the sand essentially squeezes out the water in between to accommodate those kind of dilatational processes. And that's why the sand around your foot essentially becomes dry, basically because of the rotational process. The sand is trying to occupy more volume during this deformation process.

So there's actually a lot of studies in the community of like colloidal solids, where they essentially use colloidal particles to essentially study the behavior of actual atomic solids. And many of this kind of behavior is quite analogous in those kind of systems as well.

All right. So one immediate consequence of this, it has to do with the angle where a beam breaks during compressive or during tensile test. So if it's a crystalline metal, when you apply essentially a tensile test or compressive test, we know that they tend to break. The fracture surface, tends to form a 45 degree angle along the axis where you apply the uniaxial strain. The reason it's 45 degrees is because 45 degrees is where you have the maximum shear stress. So if the material failed by shear stress, the angle it breaks is at 45 degrees.

For amorphous metal, on the other hand, this angle is not 45 degrees and it depends on the direction, whether you apply compressive or you or tensile strain. If it's tensile strain, then this angle tend to be larger than 45 degrees. So in other words, it tends to break, this fracture plane, tends to rotate. So it's surface normal is getting closer to the axis of the tensile stress.

Now that makes intuitive sense. Because if you try to rotate so that x is more aligned with tensile strain, you have more tensile strain contribution at the surface where it fractures. We have mentioned that this tensile stress is going to promote the formation of free volume and therefore promote the plastic deformation. So rotating this plane towards this direction essentially facilitates that kind of process. It increases the contribution of tensile stress.

Now vice versa, if it's compressive stress, compressive stress inhibits the rotational process of deformation. So in order to introduce fracture, the system will try to essentially rotate towards this direction, because the more you rotate towards this direction, the compressive stress contribution is getting smaller on the plane. It essentially it goes by like cosine. So if it's here, you have full contribution compressive stress. If you start to rotate, the compressive stress component on that plane, essentially decreases.

Does that make sense?

OK, we can look at it.

AUDIENCE: I guess my first question is so you have a thing--

JUEJUN HU: Essentially you have a rod. You try to break it by, for example, applying compressive stress on two ends. So if it fails by shear stress, if it's a crystalline material, don't worry about amorphous material. Then what happens is it's going to break at 45 degrees. This [INAUDIBLE] is going to be 45 degrees. Because the 45 degrees is where you have maximum shear stress. That's mechanics. That's really not within the scope of this class. OK? Go back to talk to Professor Chiang. That's his problem. OK?

So that's what happens to crystalline metal. Now for amorphous metal, as I said, you want to avoid compressive strain because during deformation you need to generate free volume. You need to expand. So you try to avoid this compressive stress. So if you have a plane that's vertical, for example, if it's vertical you have essentially full compressive stress exerting on it.

On the other extreme, if you have a flat plane like this, horizontal, that's basically no compressive stress. Because compressive stress essentially goes by essentially cosine theta. It's basically the component that exerted on the plane of the compressive stress scales by cosine theta.

So instead of breaking at 45 degrees, the system will try to break at this smaller angle here. At the smaller angle, you have a smaller contribution of compressive strength hitting the surface. So therefore, it will have less impedance on the plastic deformation. Yeah. And then vice versa. If it's tensile it will try to maximize that tensile stress that's exerted on the surface. That's why it rotates this way. So that's why you see this asymmetric behavior of the fracture angle with respect to the direction of the stress.

And I just want to highlight that this is actually universally observed in pretty much all kind of metallic glasses. So in this table, I'm just summarizing essentially the fracture surface angle for tensile and compressive test. You can clearly see that for tensile tests, the [INAUDIBLE] becomes bigger at 45 degrees. Compressive test, they pretty much all become smaller than 45 degrees.

Now another immediate consequence of this kind of asymmetric behavior between tensile compression is that the strength is also different for the material. We reflect with tension and with respect to compression. For compression, you tend to have a considerably higher strength, which makes sense. Compression, essentially, you are preventing the formation of free volume. Therefore, you're inhibiting this plastic flow. As a result, you should have higher strength.

I want to mention that this behavior is not unique just to metallic glass. For inorganic network glasses like silica, you also see that they tend to be a lot stronger under compression compared to compression. But the microscopic mechanism is completely different. For metallic glass, it has to do with generation of free volume to the rotational process. For inorganic network glasses, the mechanism that fails is through essentially opening of the cracks. If you do compression, this usually inhibits the correct opening. Versus tensile, this promote correct opening. So that's why for inorganic network glasses like silica, it's also stronger under compression than under tension. But the microscopic mechanism is different. OK?

So let me summarize what I talked about in this lecture here. We have essentially discussed about the structural model for metallic glasses. The key takeaway message for that is that this is a topological model. And the model essentially assumes that we want to achieve close packing of hard spheres. How do you engineer the radius as well as the atomic fraction to maximize packing density, which then allows you to lower the overall Gibbs free energy coming from the metallic bonds? That will stabilize the amorphous network. That's the whole assumption there.

And then this kind of amorphous packing and the lack of structural defects, it will indicate many of the mechanical behavior in amorphous metal here, such as large elastic limit, lower elastic moduli, and we also discussed about the plastic deformation mechanisms and the different kind of plastic deformation regimes.

I guess the key takeaway message is that the atomic scale deformation of bulk metallic glass takes place through this STZs, sheer transformation zones, and the sheer transformation zones they are not structural defects, but they can communicate with each other through stress, which is eventually lead to this kind of stress, shear stress localization.

All right. So I'm going to stop here for this lecture. Any more questions?