Advanced Materials and Processes
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Lecture – 15
Bulk Metallic Glass, Glassy and Amorphous Materials (Contd.)

Welcome to NPTEL, myself Dr. Jayanta Das from Department of Metallurgical and Materials Engineering IIT Kharagpur. I will be teaching you Advanced Materials and Processes. During last couple of classes we have discussed about the structure and the microstructures, glass forming ability of glassy or amorphous alloys, and we have also discussed some of the very basic aspects of mechanical properties. And today we will continue the same and try to learn how the idea evolved from a monolithic metallic glass to a composite microstructure.

What is the need of a composite microstructure? In case of a glassy alloy and so if you recall our last class discussion, we had talked about that shear band forms when glass deform plastically. On the other word if we go beyond the elastic regime, then definitely the shear transformation zone appear in the overall glassy structure, which ultimately lead to the formation of shear band. If we go beyond the elastic regime then definitely the shear transformation zone appear in the overall glassy structure, which ultimately lead to the formation of shear bands.

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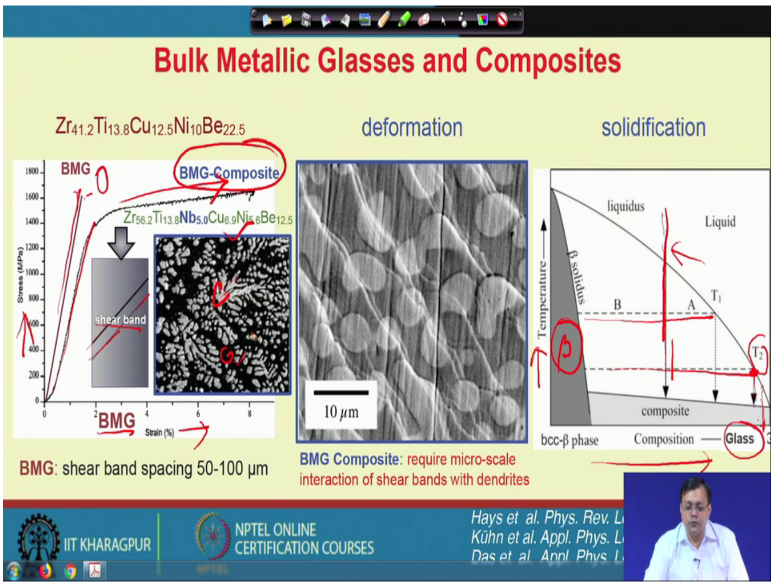

And definitely the shear bands at somehow linked with the thickness of the sample and so on. However, when we talk about bulk metallic glasses very bulk the separation distance between 2 shear bands is in the order of something like 10 to 50 or even 100 micrometer. So, if we take such a bulk metallic glass and compress it we will get a engineering stress strain diagram in that particular case we will get only the elastic deformation this is just a schematic deformation elastic deformation plot.

So, people get a idea that if we allow this shear band to fail catastrophically then we will 0 percent plastic strain. However, if we incorporate some second phase particle which will interact with those shear bands, then probably the catastrophic failure could be delayed and we will be able to get some amount of plastic strain. That was the idea behind the development of a composite microstructure.

So, along this line people tried to devitrify. A devitrification process means that glass is heated above glass transition temperature, near crystallization temperature and very fine crystalline precipitate appear inside the glassy structure. So, this is basically a solid solid type of transformation. However, we can also design the alloy very cleverly and what we can do, let us say in such a case, here is shown in a plot like a temperature versus composition, where glass forming composition are very close to the eutectic composition.

However instead of a composition choosing very near to the eutectic, if we go towards the terminal side and one of the terminal phase is like beta and if we cool down then there will be a partition in the liquid. So, in one hand this beta phase will evolve in the liquid and as we cool down the liquid composition will reach towards, the better glass forming composition and the matrix will solidify or vitrify into a glassy structure. It means that we will get such kind of microstructure.

So, here there is dendritic crystalline phases which appear in the liquid first and then the residual liquid which has a better glass forming composition will form a glassy phase. So, we will be able to synthesize a composite microstructure and now if we deform such a microstructure, then we will get both elastic as well as a plastic regime ok. So, this is one of the very beneficial effect of a composite this is called as a BMG composite, since it is a bulk or let us say a metallic glass matrix composite where we will get 2 phase one is the crystalline phase another one is the glassy phase.

However the question comes how to design such. So let us say this is a usual glass forming composition of vitriol ok, and here you can see zirconium, titanium, copper, nickel and beryllium is there and we intentionally add niobium into it so, that the zirconium or beta zirconium phase stabilized. It means that by adding niobium from a glass forming a fully glass forming composition, we are shifting the composition to this side by adding some extra niobium which will basically stabilize this bcc beta zirconium phase,

in this particular case. So this is beta zirconium phase or these are the particles of beta zirconium and this is a glassy matrix. Now after deformation we can look at the deformed microstructure and people have clearly observed that definitely the shear band will appear these are the shear band ok. However, this crystalline particles also deforming, so the deformation bands or the shear bands are interacting with this crystalline phases and dislocation is nucleated in this crystalline phases, which is delaying and avoiding the catastrophic failure by the single shear band. So, we will get multiple shear bands ok.

So, there are many shear bands in between also in this particular magnification we can see and this means we are designing the microstructure for the formation of the shear bands. So, that is why this composite microstructure evolves. However, so far there are many many composite has been discovered and all these composite we can classify and in a very simple way.

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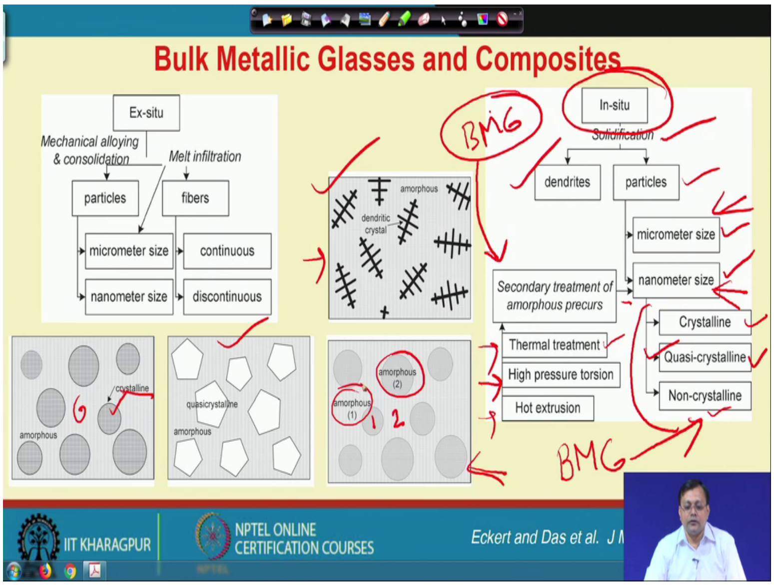

So, like a typical composite we classify into Ex-situ composite or In-situ composite in case of in ex situ composite we can go for some sort of melt in filtration process ok. Where we introduce externally some fibers and those fiber could be continuous fiber or discontinuous fiber. However, we can also go for some sort of mechanical alloying and some sort of consolidation and we incorporate some second phase into it ok. So, here we can introduce some particles which could be nanometer size or micrometer size, so this is different length scale.

So, these are since the second phase is added to the matrix externally we call them as an ex situ composition. Now in case of in situ composite we can go for solidification ok, or simply quenching process and if the alloy is designed properly then the primary phase will evolve as dendritic phase, the schematic microstructure is shown here, or we can also may get some sort of particles of the of the high melting temperature due to the addition of high melting temperature alloying element. Let us say something like a glass forming composition of zirconium if we add some tantalum into it ok.

So, those tantalum dissolve some part in the liquid however, some unmelted particles may remain in the liquid. So, this particle could be micro-meter size or would be nanometer size or otherwise we can simply take a BMG precursor. Precursor means as cause BMG and we can make some secondary treatment of the amorphous precursor, how we do secondary treatment simply we can anneal it or we can do some sort of thermal treatment.

So, by that if the temperature is sufficiently high means a higher than glass transition temperature and close to a crystallization temperature, then we can evolve and some nano particles or crystalline particles could be evolve or we can also go for some sort of sever deformation, which may introduce some crystalline phase in the glassy matrix or maybe can go for some sort of hot extrusion.

However the second phase particle could crystalline in terms of structure or could be quasicrystalline this line or by simply a glass during solidification itself and spinodal decomposes and form basically a non crystalline or simply there is an existence of 2 different glassy phase, which is schematically shown here. So, this is a 2 phase amorphous amorphous 2 and amorphous 1.

So, there are 2 different glossy phase; however, quasi crystalline particle can also be incorporated in a amorphous matrix by some sort of thermal treatment or by directly cooling ok, or we can introduce some crystalline particle in different length scale means this crystalline particle could be nanometer size or it could be micro meter size. So, so in a in a glassy matrix, so these are typical 4 or 5 different microstructure people have so far observed.

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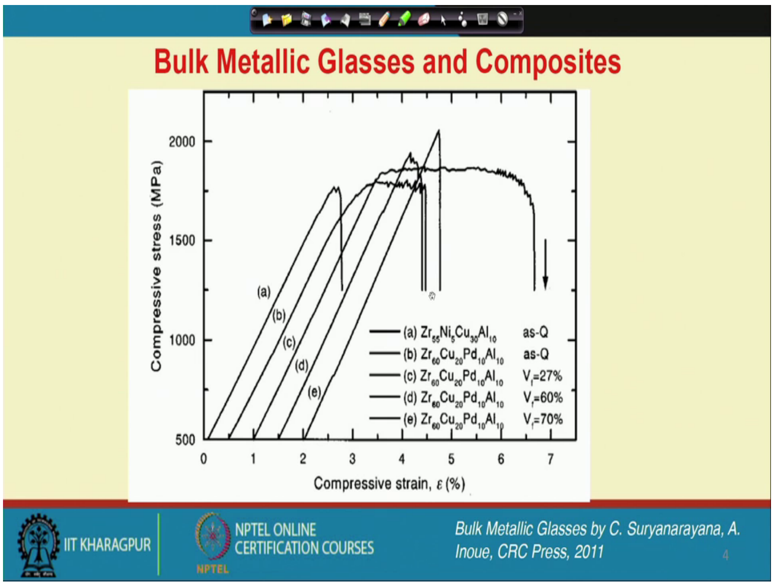

Now, along this direction as I said that people have also tried to incorporate some nano crystalline particles into a glassy matrix and you can see that the curve A which is from a zirconium nickel copper and aluminium very common glass, which is in the as quenched state or let us say a, b, b here is the is the palladium base glass, which itself show some plastic strain in the as quenched state.

However by annealing, people have incorporated some volume fraction of the particles and this palladium base glasses show some improvement. Let us say in curve (c) which has let us say something like 27% of crystalline phase has improved the compressive plastic strength. However, if we go for a higher and higher amount of a crystalline particle then there is a decrease in the compressive plasticity ok.

So, it is not necessarily that even if we incorporate some crystalline particle by a secondary treatment ok. So, higher the fraction of crystal will not all time increased the higher compressible plasticity this is not like that. So, some a particular amount of crystalline particle has been observed to improve some plastic strain. And later on, people have also observed that even though a monolithic glass does not show a plastic strain, which is a Vitreloy glass a monolithic glass.

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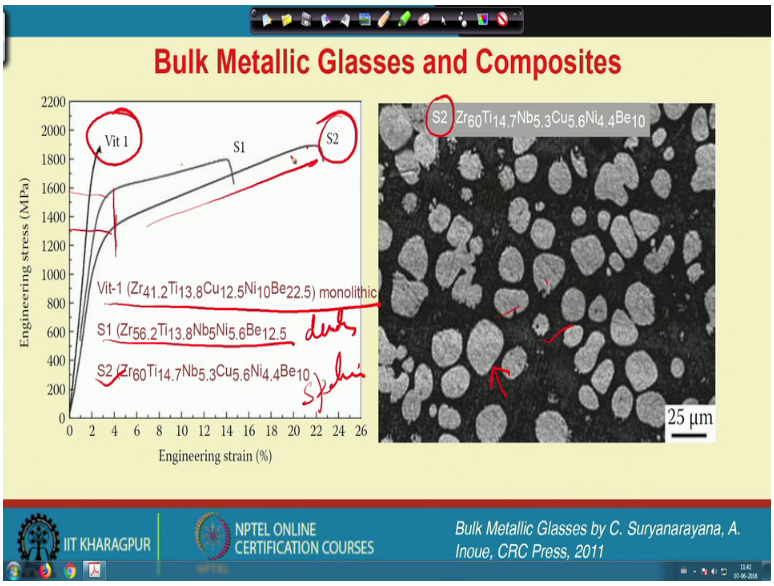

But we can incorporate some particle in different different shape, so here it is a S2 glass which is this one and this one has a dendritic type of morphology ok. So, from a spherical spherical type of particle which is S2 is somewhat better and it shows a slightly lower yield strength then the dendritic phase, which is rather fine in the microstructure. So, by changing the morphology of this particles we can also alter the compressive plasticity and strength of the BMG composite.

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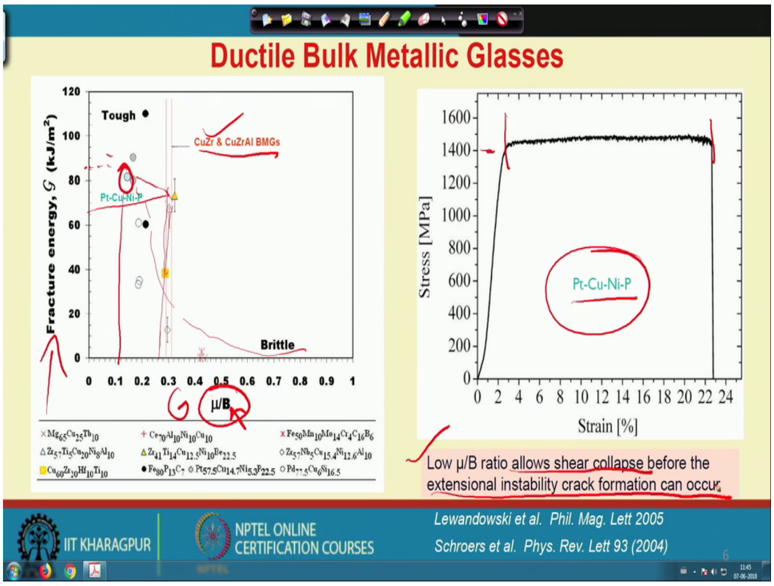

So, so far we have discussed about a a glassy phase with a micro meter or nanometer size a crystalline particles, but later on from 2005, there are many glasses which has been discovered which shows some inherent plasticity in the as quench state. So, I will try to show you some of the example of such very interesting phenomena. So, a platinum copper nickel phosphorus from a Caltech was discovered and they have shown that a compressive strength of 1400 and a large plastic strain can be achieved in a in a glassy phase.

In the same direction, there are also some copper zirconium or copper zirconium aluminum bulk glasses has been discovered. So, people were tried to link that so far from 2000, 2000 or 1993 onwards last let us say something like 20 years. There was no glass which shows intrinsic such large plasticity, but how suddenly this plastic strain appear in a glassy phase. So, people had looked at their elastic properties or elastic constants.

So, one of the elastic constant in the last class I also have discussed that is the μ/B, which is somehow linked with the fracture energy. Here mu means basically the shear modulus which can also be represented in terms of G and B is the bulk modulus. So, they have plotted all this fracture energy of different glasses and had a looked that platinum copper nickel phosphorus is lying, somewhere at a higher fracture energy size and a very very low μ/B ratio whereas copper zirconium aluminium glass also have shown such kind of large plastic strain and which is also lying somewhat in the boundary region.

So, it simply says that there is definite a link between this low mu by b ratio, which allows the shear because of what basically what shear band forms, a shear collapse before the extension ability of the crack formation can occur. It simplified that there is a competition between the shear band formation and a crack generation. It is for sure that more number of shear band we can generate the more plastic strain we can we can get.

So, in case of BMG composite I have shown you those things that was the reason why we have incorporated particles or crystalline particles in to it. So, that the crystalline particle will deform by dislocation and the glassy matrix will be formed by shear bands ok. So, more number of shear band we can form in the glassy phase we will get more and more plastic strain. However to continue formation of more shear bands we have to somehow avoid the catastrophic failure by the cracks ok.

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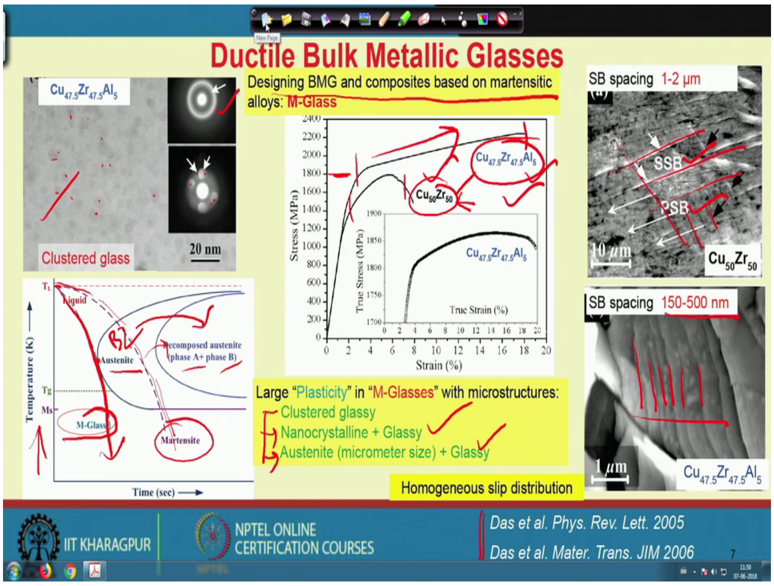

So, the extension ability of the crack can be easily suppressed by formation of such of such by tuning the tuning the elastic constant. Now, I show you another example of such ductile bulk metal glass and which is in a in a copper and copper zirconium aluminium system ok. It is for sure that aluminium addition enhances the glass forming ability of the copper zirconium glass, you can see this is a binary 50 50 composition, and this copper and zirconium and they basically is a good glass former and a people had a look on myself as well looked that the plastic strain is good enough and it improves with the addition of aluminium ok.

The strength is also very high of 1.8 GPa, so here the microstructure of these glasses does not show a very monolithic type of microstructure there is contrast in the bright field as well as dark field images. You can see also have some patchy type of type of a structures are available, which I itself called as a clustered glasses and even though most of the places shows you such kind of diffuse halo which represent a true glassy structure. But some of the region also show you some sort of crystalline spots in a in a micro beam diffraction or convergent beam diffraction.

So, it means that in true sense we cannot call it as a monolithic metallic glass, but rather I would say it is an inhomogeneous glassy microstructure. So, later on we find out that this 50 50 composition is a good composition for martensitic transformation, means a b 2 phase that appear in this 50 50 composition in a crystalline state, and then b 2 we will transform into a martensite phase.

So, probably this crystalline structure are some how linked with those kind of structure which could be easily deform. So, the crystalline phase itself maybe deformed easily and that is why this glass is showing such a high plasticity and. So, schematically we came up with this idea that if we take a liquid and if we simply cool very very slowly then we will definitely go to the crystalline region.

And in this particular copper fifty zirconium 50 system it is the austenite which is the b 2 phase and if we cool more and more slowly then this b 2 will decompose through a eutectoid transformation to do different phases. However, this b 2 if we do not allow then we can also get some martensite. However, if the cooling rate it of the super cooled liquid is much and much faster then we make a somehow go close to the nose of this TTT curve we will get a glassy phase.

However some quenched in nuclei or quench in clusters may be available in this glassy structure, which shows or which are somehow linked with such high plastic strain and therefore, we call them as a m glass or martensitic glasses. And so this large plasticity of these m glasses we have observed, whether it is in the glassy phase whether it is in the crystalline phase or it is in a composite microstructure all these glasses shows very good plasticity. So, there is a new era has evolve to design metallic glasses or composite in martinsitic alloys ok.

In that particular case I have shown that the very good or very homogeneous very fine shear band spacing at a length scale of 100 nm we can evolve which people initially thought that something like 50 micrometer should be the shear band spacing ok. So, the more shear band spacing we can get out of such kind of microstructure, here SSB stands for secondary shear band or primary shear band means there is a shear direction and the opposite direction is called as a secondary.

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So, in both the cases we have shown that there is a large plasticity we can get out of such microstructure. And now let us come to some of the very critical application the glassy alloys are always at the top in competition with the conventional crystalline alloys. So, there is no other material which can show such kind of application areas.

So, let us have a look. So besides all are the properties some other engineering properties let us say corrosion which gives you a better surface protection and there are many glasses, which shows very good or iron based glasses shows good magnetic behaviour. Here good means specifically soft magnetic properties. The soft magnetic properties is linked with 0 hysteresis loss or 0 core loss ok. So, for making magnetic core or magnetic transformer which we often used in our home as a master circuit breaker, we can use in a very easily for those kind of magnetic properties.

Whereas for separation or let us say in a fuel cell those plates can be easily made out of a glassy alloy and they are very good in terms of fuel cell accessories. Now the major application areas where there is a definite demand as a pressure sensor because if a material shows you 2 percent elastic strain, that is very very high elastic strain ever achievable in any material ok.

So, we can use them as a pressure sensor here some of the example of pressure sensors are shown these are very small diaphragms, very thin diaphragms, of a thin plate of metallic glass, which are made and we will get a very good response out of those metallic glasses. Due to heavy high strain we can store very high elastic strain energy ok. We can use them for a basketball racket or tennis racket and so on as a sporting good or since the material has a very high strength we can use them as a energy kinetic penetrator.

And definite as I said the magnetic core as well as for shielding magnetic fluxes, we can also use these metallic glasses for this purposes. There is another new era has started for using metallic glass for bio medical implants for biomedical application, we have couple of a properties which are mandatory. So, first the material should have a low density there should be no cytotoxic metals in it is composition there should be very high strength which is already available in metallic glasses.

There are aluminium base glasses, which has a very low density and we can also make foam out of out of metallic glasses. So, you will get very low density. Now the very low Young’s modulus ok, we can either tune the Young’s modulus by manipulating it’s composition or we can make some foam structure or porous structure, which will also have low density and low young's modulus, that can be done, and a very good room temperature large plasticity they can be formed.

So, even though we cannot deform all the glasses at temperature way below glass transition temperature, but we can go to super cooled liquid region we can form the glass very easily ok. So, that can be always done and very good casting properties to make a defect free product. There is no doubt that the metallic glasses I have a very very good casting properties. So, we get almost all the good properties out of these glassy alloys. So, in this particular application areas, we can see that we have a large opportunity for using this glassy alloys.

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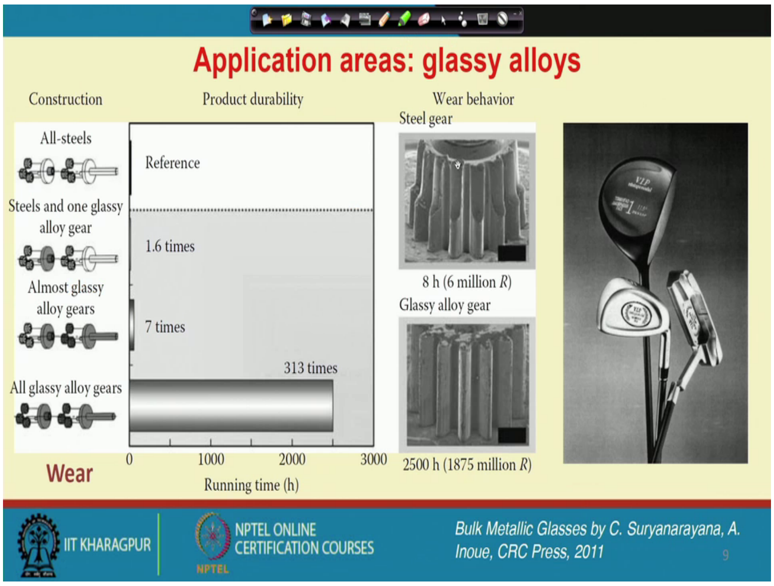

Now, that is another very good area where there is no competition with the glassy alloys. It is basically in terms of wear, wear and tear of glassy phases are very very low. So, let us say for using any or making any gear we usually use some hardened steels ok. So, in that case definitely these gears could be very large to a micro meter size and since glassy alloys or monolithic glassy alloys are isotropic in nature not like crystalline materials.

So, we can form these glass into a very good shape, so here I show you some example of such kind of gears. So, this is a gear which is made of a conventional steel that has been used. Now, in case of a glassy alloy gear even after long use of 2500 hour ok. So, we can still retain the shape of this and these are in the micrometer range, these are in the micro gear.

Now, all steel gear which is taken as a reference the running time is very very less as I said ok, and if we can the several components of the gear can be mixed with let us say steels and glassy alloy gear or let us say all glassy alloy gear then the whole cluster of this gear can give us something like 313 times ok. This is a revolutionary material that can be used for such kind of micro gear or let us say the sporting good these are the golf club that I said.

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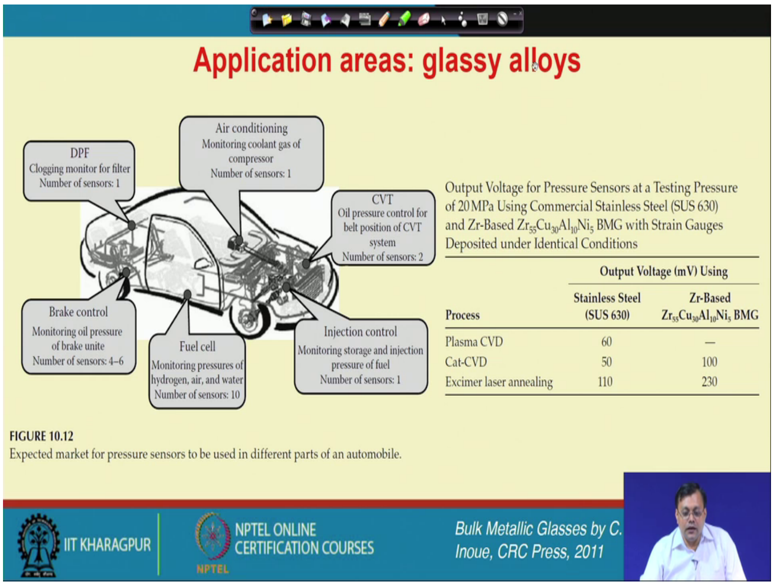

So, we have a large opportunity to use these advanced material for some novel application. Now, as a pressure sensor or different sensing application we can also use this glassy alloys in case of a different cars. So, there is a huge expected market for the pressure sensor where the sensor could be used for the, for let us say some sort of injection control and monitoring. Let us say for oil pressure control, for monitoring the coolant gas, for clogging monitor, for the filter, for the sensor or let us say for break control we can also use.

There are 4 to 6 sensors which are used these days, in case of a fuel cell also we have many different hydrogen air or water sensors used and this sensing not only due to very good elastic, elastic strain limit that metal glass shows, but you can see that a these are let us say the output voltage that appear from a pressure sensor, in case of a zirconium base glass which is almost 2 times higher than any of the conventional stainless steel ok.

So, the sensing and the output voltage both are very good or higher resolution or more precisely we can control. So, for a future generation car several sensor should be replaced. Now, for biomedical implants since I have discussed I show you some of the component how they look like this is a human teeth and the implant required some sort of fixing in the in a bottom part.

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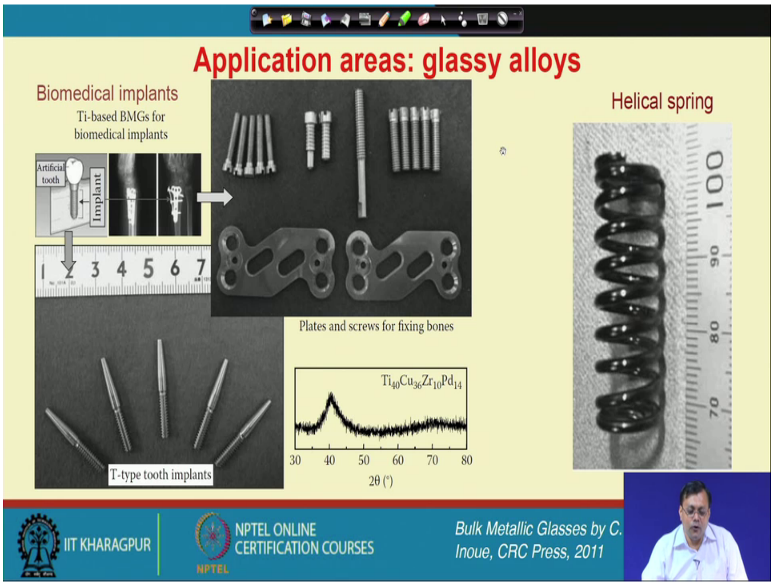

So, this screws are and the plates are made out of this bulk glasses or let us say some sort of t type of tooth implant could be made out of these titanium base glasses. So, that we can replace the titanium aluminium vanadium or let us say some of the helical spring which are very common mentionally used it has a very very high elastic limit and resilience. So, several times we can use the same helical springs means the durability will increase.

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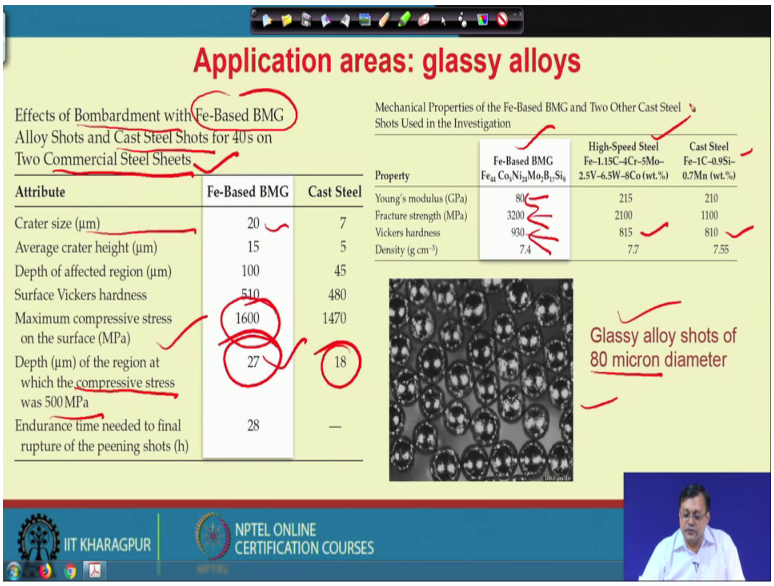

Now, there are another very large application areas we secondary process material the example is shot peening ok. We bombard sand particle on the surface of a metal in order to change a or in order to introduce some compressive residual stress and better surface finish or let us say the better surface for a good fatigue life. So, in those particular aspect we can use actually the glassy balls ok.

These are 80 micron diameter and how we compare with let us say the bombardment made out of a iron based BMG alloy shots or cast iron shots, cast iron is also has a very high cementite content it is also very hard. However, you see the crater size upon bombarding on a commercial steel sheet is higher and the depth of the region which is affected by this residual compressive stress is also quite high compared to the cast steel.

And maximum compressive stress that is introduced could also increase ok. So, we can simply change the material property we can use these glassy alloy shots for making them a better making steel as a better ok. So, so let us say, the typical iron base BMG shots where it has a young modulus of 80 and it has a fracture strength of 3000 ok. It has a Vicker's hardness which is 930 which is way above the cast steel or high speed steel.

So, so far we had a looked that the glassy alloys could be used, and exploited their properties could be exploited for various application and there is a very noble approach we can always adopt to replace some of the conventional engineering material and that is why these are the advanced material, and today is the is the is the we completed these bulk metallic glasses or a glassy alloys and we will start a new topic in the next class

Thank you.