Techniques in Materials Characterization

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Module No # 14
Lecture No # 58

X-ray Diffraction Profile and Analysis (Continued)

Welcome everyone to this NPTEL online certification course on techniques on material characterization we are in module 12 and we are discussing about x-ray diffraction. So we are just starting understanding the x-ray diffraction profile and analysis from real specimen and in the last lecture we understood that what are the typical characteristics of an XRD profile from a real specimen where it is different from an idealized condition and ideal profile which you yourself can generate what could be the source of it and all.

And how to measure it in terms of FWHM that is Full Width and Half Maxima and we just understood one source of peak broadening that is a term we use that is the instrumental source or instrumental line broadening. So we understand that and we will be continuing this and we will be continuing this and we will try to understand some other factors which are responsible for this peak broadening.

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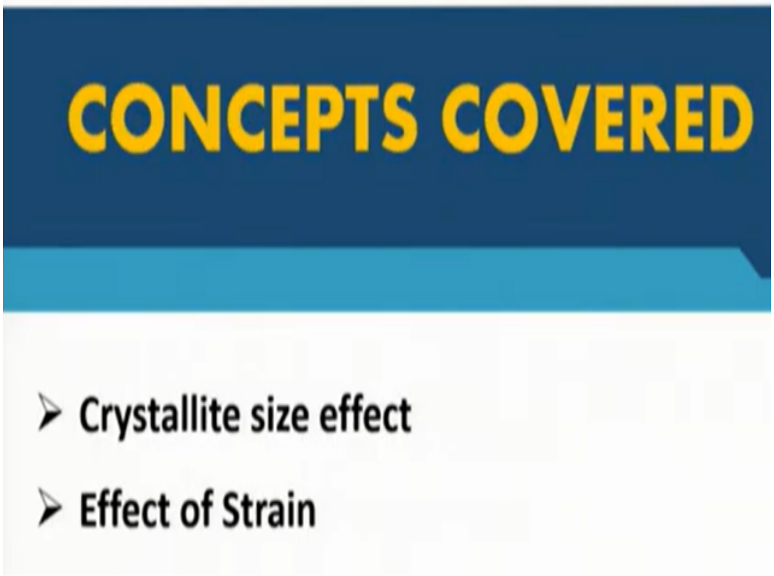

CONCEPTS COVERED

- Crystallite size effect
- Effect of Strain

So the concepts that we will try to cover in this lecture and in the up coming lecture in the last 2 lectures possibly. So one of them is the crystallite size effect and another one is the effect of strain in the material.

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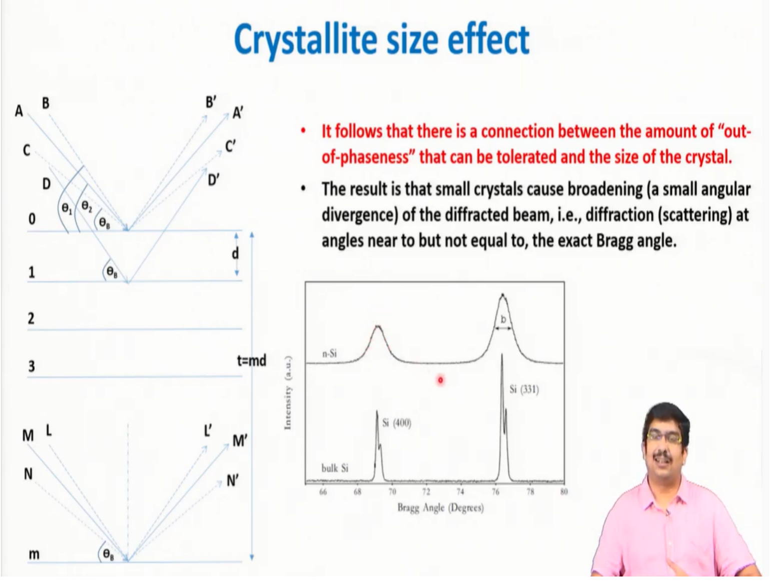

Crystallite size effect

- It follows that there is a connection between the amount of "out-of-phaseness" that can be tolerated and the size of the crystal.
- The result is that small crystals cause broadening (a small angular divergence) of the diffracted beam, i.e., diffraction (scattering) at angles near to but not equal to, the exact Bragg angle.

So let us understand what exactly is the crystallite size effect? So, crystallite size effect before that we must understand and we discussed this in the last class also. That the periodicity of any material is responsible for the constructive inference and Bragg's law is all about the constructive interference in the matter. Because it is separate atom that is scatter the X-ray beam in all possible direction now because of the periodicity of the atomic arrangement in a crystalline material regular arrangement of an atom in a crystalline material.

We tend to get the constructive interference along the particular directions and similarly because of that periodic arrangement itself we will be getting destructive interference along certain particular direction. If it all depends whether the part difference as the function of wave length of X-ray and that in sense is also the phase or the phase difference between the waves that is coming out from 2 different planes.

So it is all and interplay of these 2 and that is why we will be ultimately getting constructive interference along certain directions and destructive interference along certain other direction. For example, now let us consider this case of a crystalline material where we are considering few atomic planes. So let us imagine this is one atomic plane this is another atomic plane and so on this forth.

So this has M number of atomic planes all the way up to the crystal we have M number of some atomic planes itself. So this is first thing we understand we discussed it in the last class that this idealized conditions. So Bragg's law is valid for idealized condition were we are imagining the crystal planes to be extended all the way to the infinity. But here we are now assuming a real specimen where they crystalline planes are not extended upto infinity and it is structs somewhere in between all the way up to n number of plane that is the difference.

So now if I imagine this X-ray beam AA' so this is one is coming here and this one is falling and this one is getting scattered along A dash let us say. And making an exact theta behind which is the angle so, obviously this will be the direction for constructively that is fine. And what will happen is that the next plane from the next plane we will gave obviously another beam.

And that beam will be something like DD' which will be having a path difference exact integral multiplier all or in this case just one lambda part difference with this A A' B. So like that if we go through the entire crystal so if we can imagine that there is they should exist another beam in the this M' beam which will make a construct interference with this A' beam and it will have a path different which is sort of M lambda integral M + 1 lambda and integral multiple of this lambda.

So the path difference there will be M + 1 lambda so this one the path difference between this beam and this beam is 1 lambda. So, similar way the path difference between these beams and this Mth plane beam will be M + 1 lambda. So fine that is over now let us imagine that here getting some 2 other beams which are slightly away from theta beam condition slightly away. So that beams is this one BB'1 and CC1 is have the another one is having this theta 1 angle slightly differing from the Bragg's condition.

And the other beam is also theta 2 slightly differing from Bragg's condition basically then what will happen is that these 2 beams will have a corresponding beam from next atomic plane. But their the path difference between this beam will not be an integral multiple of lambda there will be a slight difference that is why this will not have a constructive interference along this directions.

But instead of that they will be having a partial interference from this beam and similarly we can imagine 2 other beams here also from Mth plane. Which will again have certain relationship with these beams slightly out of phase beams and they will have a partial interference. So obviously this out of phaseness will definitely increase as we are moving form this plane.

So this next plane will have slight little out of plane this 2 beams and then if we go to the next plane there will be some little more out of phaseness. Then if it goes further, we will be getting some out of phase beams the out of phaseness or that path difference between the beams will be increasing and what will happen is that somewhere in middle we will get a beam which is exactly half wave length out of phase with this first beam.

And another beam which will again be exactly half wavelength out of phase with this CC' wave length. They definitely that will cause a destructive interference and these beams will be then completely canceled out. Now in this process in this entire process what will happen if we imagine that this goes to infinite up to infinite level then we will have for every such beam which slightly out of phase from this exact Bragg condition.

For every such beam we will be having a corresponding beam from somewhere within this specimen somewhere we will have a beam which will exactly out of phase by 1 half of the wave length and that will completely cancel away this slightly out of phase beams. That means that if we get some how we get an infinite array of this planes and it extends up to infinity.

Then except for AA‘beams all other beams will have a complementary plane somewhere over here deep within this crystal which will exactly cause and distractive difference here. That means we will not get other than this AA' beam we will not get any kind of interference between them except constructive interference they will be complete destructive interference.

So either constructive interference if it is exactly on Bragg's condition or complete constructive interference for all other beams will happen if this has an infinite number of planes. If it extends infinite number but that is not the case we are getting a finite amount of number of planes n number of planes with a thickness. We can imagine that the thickness of this crystal is T some M into multiplied by D.

So this and this condition some beam will have some out of place some slight out of phase beam from the first plane will not get a corresponding or complementary plane here. Something most of the other beam may be it will have destructive interference but there should be some beam which will not get a complete construct complete destructive interference which will not get a complementary plane with which it can cause a complete active interference.

There will be a partial interference, similarly in the other side also the lower side one of this angles is higher than theta be exact Bragg angle. One of this, corresponding angle will be lower than theta B lower than the exact Bragg's angle. So these 2 particular angles there will be there definitely there will be 2 different angels for which there will not be a complete destructive in different there will be certain amount of partial derivative intervene will happen.

That means they will have certain amount of intensity so of course along the Bragg's angle theta B there will be complete constructive interference and that will have the highest intensity. But because of this finite size of crystal because crystal is not infinite it has a certain size because of that there will be some 2 other angles where the intensity will not be completely 0.

Above this theta 1 or below the theta 2 complete destructive interference will happen but this 2 within this 2 there will be some amount of partial interference will definitely will happen. And as we understand this is related to the size of the crystal finite size of the crystal and that is the crystallite size effect the y. That means the beam is now getting broadened X-ray diffraction profile is not getting broadened except a line function at theta B we are getting a finite width in that 2 theta access which is extended from theta 1 to theta 2.

Between theta 1 and theta 2 we are getting certain amount of intensity so this is the crystallite size effect or size broadened that is what it is called. So this definitely this is there so that means we get a relationship between this crystalline size effect this is because of out of phaseness and the size of the crystal. So this effect how it will seem for different size at all. So what the relationship is that the finer the size it will size is smaller if m is equals or the t the thickness of crystal if that thickness is smaller.

Then what will happen the theta 1 and theta b will be larger why? Because if this one is smaller if the crystal are very smaller the size of the crystals are very smaller then the chance of getting corresponding plane where the destructive interference will happen. The beam will undergo the destructive interference that chances will be lower. So we will be getting this theta 1 and theta b correspondingly increasing means there will be more deviation from the exact Bragg's condition.

Those beams so this there will not be a corresponding plane somewhere here which will be able to nullify this beam or this beam. So these 2 beams or these 2 angles will just go on and increase in the broadening will increase roughly saying if the size decreases crystallite size crystallite means? The entity which is responsible for causing diffraction phenomena if this size of the entity is decreasing then the broadening will increase and in extreme case you can imagine that.

As we have already discussed in the possibly in the last class that in extreme cases we can think the sizes to go all the way to like an atom for an liquid or for a mono atomic gases is almost in the size of atom, You can imagine and there we the broadening is so much we do not get any peak at all. But will come to that point after wards the other extreme or here real specimen this effect we can think if we go down with grain size or if we understand they are going from something like an nano materials then the peak are getting broadened.

Lower the size of the crystals the more broader the peaks will become so that is what it shown here. If you think this is bulk silicon and versus this is the nano silicon this is the bulk silicon where you are seeing a sharp crystalline peak corresponding to certain crystallographic planes. The corresponding nano crystalline material also shows this peaks and the intensity maxima is also coinciding with what we get for bulk silicon where the grains size is almost in the micron level.

But in the nano crystals this intensity is getting is decreased here and also we are getting a huge broadening now. The peaks are sharp at all the other here very broadened so if we go down with the size direction the peaks will get products. So this is the crystalline size effect.

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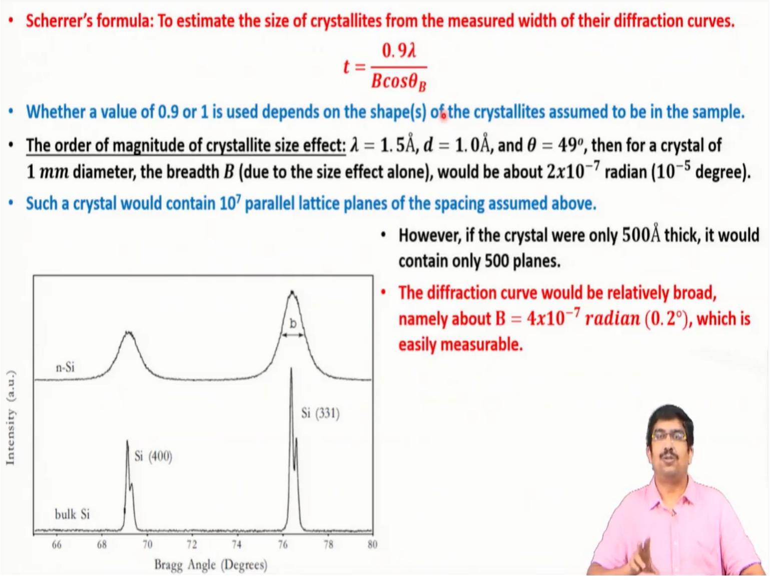

- Scherrer's formula: To estimate the size of crystallites from the measured width of their diffraction curves.

$$t = \frac{0.9\lambda}{B\cos\theta_B}$$

- Whether a value of 0.9 or 1 is used depends on the shape(s) of the crystallites assumed to be in the sample.
- The order of magnitude of crystallite size effect: $\lambda = 1.5\text{Å}$, $d = 1.0\text{Å}$, and $\theta = 49^o$, then for a crystal of 1 mm diameter, the breadth B (due to the size effect alone), would be about $2x10^{-7}$ radian (10^{-5} degree).
- Such a crystal would contain 10^7 parallel lattice planes of the spacing assumed above.
- However, if the crystal were only 500Å thick, it would contain only 500 planes.
- The diffraction curve would be relatively broad, namely about $B = 4x10^{-7}\ radian\ (0.2^o)$, which is easily measurable.

Now how to further understand this in terms of mathematically how we can understand this crystalline size effect. For that obviously what we understand is that these exists 2 different angle theta 1 and theta 2 so within this theta 1 and theta 2 after if we think of this extra peak if we take. So this is the peak for the ideal crystal where we have exactly at the theta B we are getting a intensity all other places there is a destructive interference.

So, this is for idea crystal which extends where the size of academic planes are extending from up to infinity. But because of this finite size what we are not getting is that the maximum intensity is of course happening at theta b the constructive interference is happening and then there exist to other angles theta 1 and theta 2 above theta 1 or below theta 2 we are getting complete destructive interference.

But within this 2 we are getting a partial interference so we are getting certain amount of intensity within these 2 angles. Now so width of this again so width means again full width of maximum where the intensity comes down to half so this full width at half maxima this we can now relate it by this and we know that this one width of this curve will increase as the thickness of the crystal decreases. So this will become broader and broader so this FWHM will increase as the size of the crystal decreases.

So basically the other way we can mean this is that this size this broadening we can explain or we can understand the broadening either in terms of the B or FWHM or broadening can also be think of the difference between theta 1 and theta 2theta 1 – 2theta 2. This also is the broadening this also is representing the broadening of the peak if we go by that concept where the after this destructive interference is happen within this range there is a partial interference is happening.

So the broadening is represented either by B or by 2 theta 1 – 2 theta 2 so the way we can these 2 that we are related B equals half of 2 theta 2 – 2 theta 2. Because we are measuring at the intensity where the intensity becomes half so this places intensity is 0 and we are now measuring FWHF at half with the intensity becomes half and that is coming out to be theta 1 – theta 2. So that is the relationship between FWHM and absolute broadening in the peak.

So now the path difference if we write the equations for path difference for these 2 angles at theta 2 and theta 1 angles what should be the path difference means, basically what should be the path difference between this theta 1 this one and the corresponding LL' coming out from this Mth plane. So what is the path difference between this BB' plane this one and this LL' path. Similarly this path difference between the CC' this ray this one and NN' here.

So if we write these equations this is coming out to be this much this will be the path difference between these 2 race. So for sing theta 1 what we can write t equals here t is basically the size of this entire crystal and the t is expressed in terms of MD. So D is the interline spacing and M is basically the number of planes that is present or inter atomic spacing or that is basically giving us the number of planes present within that finite site.

So what we can get is from here is basically this is the path difference is for these 2 angles this similar but they are related to the thickness of the crystal rather to the distance between the adjacent plane meaning. This here if you look at this one this is also similar to the Bragg's equation except for the fact that we are replacing D by T, here. Because this phase relationship is related to the entire thickness of the crystals rather than the thickness or the distance between the planes themselves.

So we can write these equations for the 2 angles for this beams for this angle the BB' and LL' and we are taking a partial interference between them considering partial interference. So there we can write 2 T sin theta 1 equals M + 1 lambda that is this M + 1 lambda is basically the path difference. So this is the path difference and that is and M + 1 integral multiple of lambda and again we can write for theta 2 beam we can write M – 1 lambda.

Altogether if we subtract these what we can get is P = sin theta 1 – sin theta 2 equals lambda here from this most important relation that we can calculate how it is calculated I am not going. What we can calculate here is called Scherrer's formula basically gives us the relationship between size of the crystals with respect to the FWHM. And the exact Bragg's angle so we are taking a particular peak and then we can measure the D value or other we can measure the B value which is the FWHM and we can find out the size of the crystallite that is responsible that is causing this extra diffraction peak.

So that is the importance of Scherrer's formula which it is expressed here in terms of t – 0.9 Lambda by B cause theta B. B is the FWHM theta B is the exact Bragg's angle lambda is the wavelength of the x-ray source here. In this pre exponent point time this can become either 0.9 or 1 depending on the shape of the crystallite. So this is also telling you whether the crystallite are something like a equiseta one.

The crystallite are like extended pancake shape and so on and so forth so if we do not consider 0.9 if we consider some other exponent and try to determine the size of that exponent that will tell us what the size of the crystallite. So you can imagine the power of this analysis it can not only tell you the size of the crystallite it can also tell you what shape those crystallite are having. So if we try to plug in some values here and try to see the magnitude of this crystallite size effect.

Again we put it here lambda equals 1.5 angstrom and D is around let us say 1 angstrom that is which his very typical for most of the materials most of the elements. And theta again around 49 that means 2 theta is around 2 degree we are 2 theta is around 100 degrees. Then if we; imagine a crystal for 1 mm diameter that is the physical diameter this t. If t equals around 1 mm physical if you take single crystal and physically the bulk diameter or the size of the thickness of the crystal is around 1 milli meter.

Then the width the FWHM due to the size effect alone will be around 2 into 10 to the power -7 radiant or around 10 to the power -5 degree which is pretty small for a size. But here you can consider the size of this crystal for getting this small width increase of FWHM increase as a function of due to the crystallite size effect. In order to minimize the broadening due to the size to that extent 10 to the power -5 degree we have to take a single crystal of around this 1 mm diameter.

And this means that within this thickness this thickness will contain around 10 to the power 7 parallel lattice planes which is huge number. That means we are going to almost like an infinite array and that is why we are reducing we are able to neutralizing the crystallite size effect we are able to get a very much we can think very sharp peak. In this case we can imagine that this possibly the situation for this bulk silicon where the grains are in the micron or even in milli meter range the grains are in the milli meter range.

And correspondingly if we take this size the broadening due to size effect is almost negligible but if we consider this nano silicon case. Now we can imagine that these grains are becoming almost 500 angstroms thick. That means around 50 nano meter we imagine that the grain size or crystalline size is now only something like 50 nano meter thick. In that case the 50 nano meter grains will or the crystallites will have something like 500 planes 500 crystalline plane which is a pretty small number compared to 10 to the power 7 number of planes.

In this case if we calculate for the same condition lambda remains 1.5 angstroms D remains 1 angstrom and extra and for 2 theta or the 2 theta peak around 90 degree or around 100 degree. For that peak now we are getting a B value that is the FWHM or the peak broadening value is around 4 into 10 to the power -7 radiant which is around 0.2 degree quite reasonable. If you consider that this 2 theta width of the peak if you consider here 0.2 degree increase just because of the size effect is quite considerable.

So this also shows us the why we need to consider the crystallite size effect for this kind of material when we are dealing with nano crystalline material why we should take now consider the crystallite size effect. And also just by solving this crystallite or solving this extra diffraction profile we can measure this B value the width FWHM we can put it back here and we can try to find out the t that is also it is possible we can try to find out the crystallite size.

From nano material most of the cases the crystallite size is basically the size of the grain so if you interested to measure the size of the nano materials we were not able to do it by any other method we try to do it within this extra crystal extra diffraction method. Provided you are minimizing all other sources of peak broadening if you are able to do that like line broadening and what we are now going to discuss strain broadening we are able minimizing those effects.

Then just from the extra diffraction profile you can measure the size of the crystallites which is very much valid or which is very effective, for materials that are containing something like nano materials. And some other kind of material these days there are ultra-fining grain materials produce from metals by rigours mechanical processing for getting grain size you are bringing down. If not in the nano meters at least some micron level there also these methods extra diffraction method and measurement of size is very effective.

But all of these though this effect I just now discussed Scherrer’s formula 1 part of diffractions Scherrer’s formula is very much it is very crude one it depends on a lot of assumptions are involved in their. There are much more or much refined methods are available to calculate the grain size of the materials. So Scherrer's formula I would say once you try to apply Scherrer's formula for nano materials you should be very careful about it.

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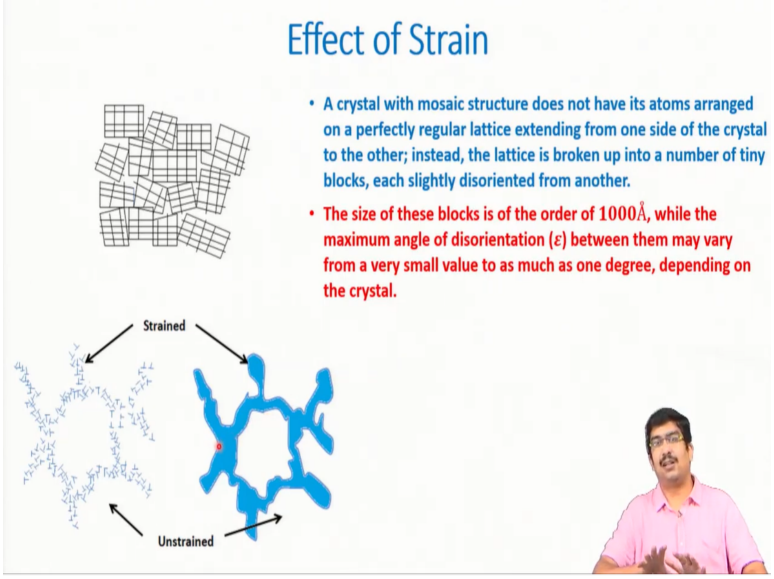

Effect of Strain

- A crystal with mosaic structure does not have its atoms arranged on a perfectly regular lattice extending from one side of the crystal to the other; instead, the lattice is broken up into a number of tiny blocks, each slightly disoriented from another.
- The size of these blocks is of the order of 1000Å, while the maximum angle of disorientation (ε) between them may vary from a very small value to as much as one degree, depending on the crystal.

So anyway so from there now we are moving towards another effect which can also produce this size broadening and that is known as effect of strain broadening or due to the dislocation substructure. The presence of substructure in the material so crystal size what we understand now crystal size we seen it as a type of a defect that means it is a deviation from the crystal from this idealized condition from where we imagine that this condition is like atomic planes or going all the way up to infinity.

And that itself says we assume a perfect atomic periodicity in the material and that periodicity how broken because of the finite size of the crystals there. So same approach now we can apply in case of a strain and in strain a most we discussed this in the last class the strain we can imagine the strain as in the form of dislocations which forms its own sub structure. When the amount of dislocation is very high in the material that can form a sub structure and that can further reduce the size of the crystallite in the first place.

So the dislocations will the effect of dislocations you can imagine will have pretty much same effect as the at least up to the crystallite level effect of the dislocations or effect of the strain will have very much same nature as the size effect itself. So it will be basically broadening in the same effect by dividing the structure into even smaller and smaller sub structure it will be creating an effect similar to the size effect.

So before the existence of dislocation was known dislocations basically was discovered something in 1950 experimentally or it was postulated time n 1930's and only in 1950's after the discovery of TEM it will started seeing the dislocation. So before the existence of dislocations the extra diffraction people they thought of some kind of a sub structure which they called something like Mosaic structure we call it a mosaic structure and what they imagine is that?

The crystalline material at least they are divided from the grain structure they are divided into small mosaic so what is this mosaic is all about. So basically this mosaic structure means there the atoms is arranged in one single mosaic the atoms are arranged on a perfectly regular lattice that is extended all the way up to a certain level or certain size. And then each of this mosaic are basically disoriented within themselves this mosaics are disoriented by a certain level or certain angle.

So if we imagine this this one single grain that will grain itself is now divided within certain small mosaic. These mosaics are very small and they are misoriented themselves only certain angle and the size of this mosaics usually, they consider is around 1000 angstrom 100 nanometer on and the maximum angle of disorientation between them is that can vary some very small value to much as 1 degree that depends upon the crystal itself.

But this mosaic structure nowadays we know this almost similar to the dislocation of sub structure forms after invent of TEM we were able to see that is dislocation structure.

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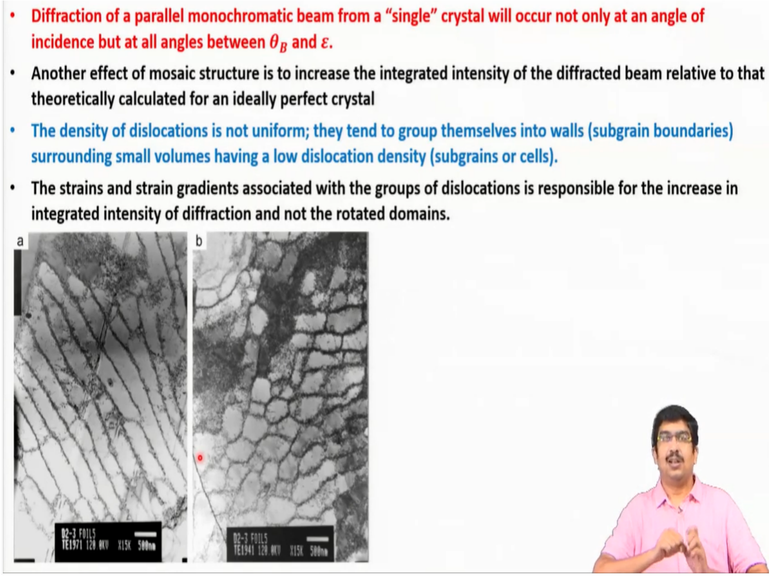

- Diffraction of a parallel monochromatic beam from a "single" crystal will occur not only at an angle of incidence but at all angles between θ_B and ε.
- Another effect of mosaic structure is to increase the integrated intensity of the diffracted beam relative to that theoretically calculated for an ideally perfect crystal
- The density of dislocations is not uniform; they tend to group themselves into walls (subgrain boundaries) surrounding small volumes having a low dislocation density (subgrains or cells).
- The strains and strain gradients associated with the groups of dislocations is responsible for the increase in integrated intensity of diffraction and not the rotated domains.

And this kinds of dislocation where you can see that it forms its own substructures and the size of the substructure is within the nano meter scale and the mis orientation between them is less than 1 degree. So this mosaic structure concept is very much valid even today and we can think of that this dislocations of structure is basically is a replacement earlier mosaic structure that people have imagined and they try to explain the effect of string one size broadened.

So because of this small amount of misorientation that exists between this mosaic structure or dislocation sub structure or this sub grains that is what it most. Because of the presence of slight amount of mis orientation between this sub grains structure what will happen is? The diffraction will now ideally if this is a single crystal or if it is a poly crystal and if this is with a grain if we imagine that this is a poly crystal and this is one single grain.

Now because of the dislocations ranging within sub grains we are now divided we are not getting this grain divided into smaller structure so what will happen is that if for the grain itself before the dislocation sub structure form. If the grain was oriented for exact Bragg's function now this substructure will have a very small misorientation within themselves. So the dislocation or so the constructive interference will not only happen at exact Bragg's condition.

But it will be happening with certain level of the Bragg's conditions will get relaxed up to a certain level and that relaxation will be exactly it will be related to the mis orientation between this dislocation substitute. So we will stop here and we will continue the discussion of this strain and micro stress and micro stress all of this in the next class thank you.