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Structural Analysis of Nanomaterials
LECTURE-17
Quantitative Analysis by Diffraction
With
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Hello, in this Lecture, we are going to discuss about the Quantitative analysis by Diffraction, in our last lecture, we have discuss about the Qualitative analysis by diffraction, basically in our last lecture, we have discuss about that, suppose we are preparing any kind of materials, so just to know the presence of that materials means, what kind of materials are present inside that, composites or may be the alloys is, we can get the information's in this particular lecture, we are going to discuss about the quantitative analysis.

That, means that what is the percentage or presence inside the matrix or maybe composites or maybe the alloys, what kind of materials and what is the percentage of their presence so, basically quantitative analysis refers to analysis in which the amount

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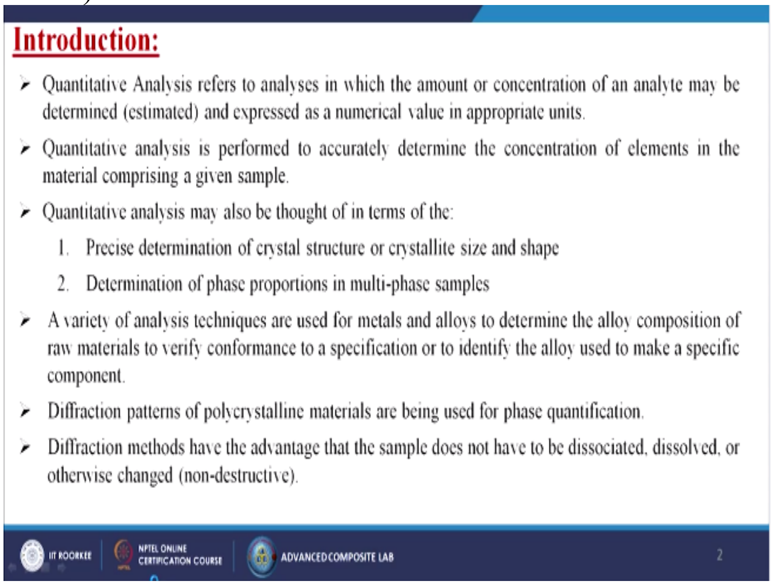

Introduction:

- Quantitative Analysis refers to analyses in which the amount or concentration of an analyte may be determined (estimated) and expressed as a numerical value in appropriate units.
- Quantitative analysis is performed to accurately determine the concentration of elements in the material comprising a given sample.
- Quantitative analysis may also be thought of in terms of the:
  1. Precise determination of crystal structure or crystallite size and shape
  2. Determination of phase proportions in multi-phase samples
- A variety of analysis techniques are used for metals and alloys to determine the alloy composition of raw materials to verify conformance to a specification or to identify the alloy used to make a specific component.
- Diffraction patterns of polycrystalline materials are being used for phase quantification.
- Diffraction methods have the advantage that the sample does not have to be dissociated, dissolved, or otherwise changed (non-destructive).

Or concentration of alloy or maybe analyte maybe determines and expressed as a numerical value in appropriate units. Quantitative analysis is performed to accurately determine the concentration of elements, that what concentrations whether it is three by percent, five by percent, or maybe the seven by percent, or maybe so on. In the material comprising eight given sample, generally quantitative analysis is maybe also be thought of in terms of the first is the presides determination of the crystal structure or maybe the crystallize size and shape.

Second is that, determination of the phase proportions in multiphase samples, a variety of analysis techniques are used for metals and alloys to determine the alloy composition of raw materials to verify the conformance of, to a specificification or to identify the alloy is used to make specific components.

Here some times, as per our requirement or maybe as per our requirement by any particular applications we are preparing the new materials or maybe the new composition where, where we adding the numeral elements and after that, what are the structure or maybe whatever the quantity, so if we are making it by our self easily get it, but if we are purchasing something or maybe we are getting something new materials so, simple by these techniques we, can calculate that what is the percentage present of that, particular elements inside the matrix or maybe the composites.

Diffraction, pattern of polycrystalline materials are being used for a phase quantifications, diffraction methods have the advantage that the sample, does not have to be dissociated, or maybe dissociated or maybe otherwise changed means, non destructive in nature. So, before we are going to start just let us know what is the atom fraction and what is the white fractions, so atom fractions, suppose before going to start just let us know that, we are working on a multi component alloy, containing the, in elements so, there are number of elements present.

Weight fraction,

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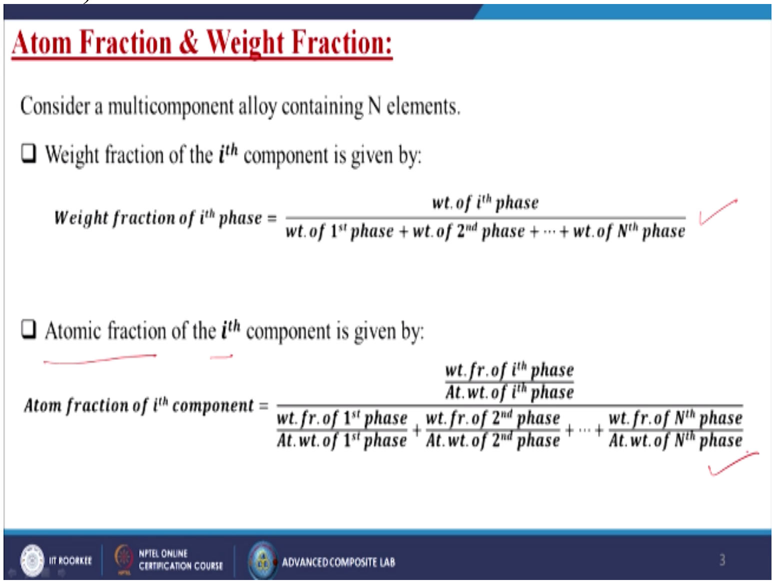

Atom Fraction & Weight Fraction:

Consider a multicomponent alloy containing N elements.

❑ Weight fraction of the i^{th} component is given by:

$$\text{Weight fraction of } i^{th} \text{ phase} = \frac{wt.of\ i^{th}\ phase}{wt.of\ 1^{st}\ phase + wt.of\ 2^{nd}\ phase + \cdots + wt.of\ N^{th}\ phase}$$

❑ Atomic fraction of the i^{th} component is given by:

$$\text{Atom fraction of } i^{th} \text{ component} = \frac{\frac{wt.fr.of\ i^{th}\ phase}{At.wt.of\ i^{th}\ phase}}{\frac{wt.fr.of\ 1^{st}\ phase}{At.wt.of\ 1^{st}\ phase} + \frac{wt.fr.of\ 2^{nd}\ phase}{At.wt.of\ 2^{nd}\ phase} + \cdots + \frac{wt.fr.of\ N^{th}\ phase}{At.wt.of\ N^{th}\ phase}}$$

Of the height component is given by, weight fraction of the i^{th} phase= weight of i^{th} phase/ weight of 1^{st} phase+ weight of 2^{nd} phase+…. Up to weight of N^{th} phase, when we are talking about the atomic fractions of the i^{th} component so, generally it is = weight fraction of i^{th} phase/ atomic weight of i^{th} phase/ weight fraction of 1^{st} phase/ atomic weight of 1^{st} phase+….or may be so on, + weight fraction of N^{th} phase/ atomic weight of N^{th} phase.

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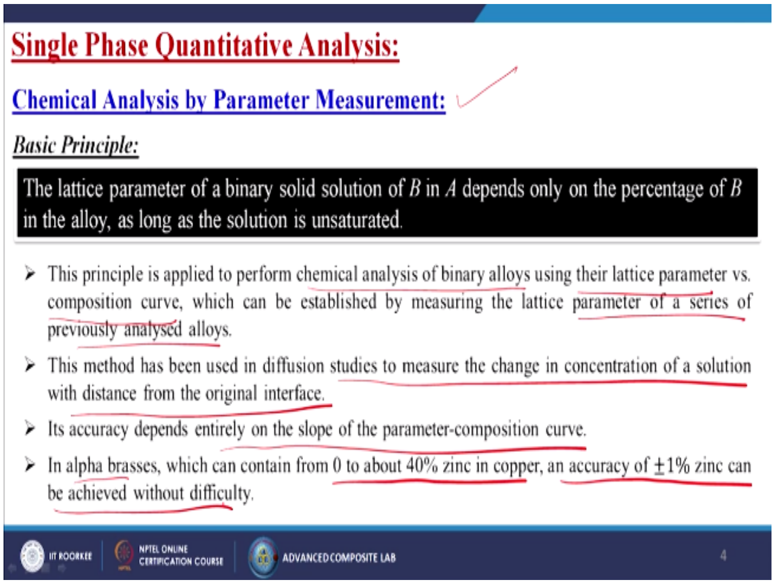

Single Phase Quantitative Analysis:

Chemical Analysis by Parameter Measurement:

Basic Principle:

The lattice parameter of a binary solid solution of *B* in *A* depends only on the percentage of *B* in the alloy, as long as the solution is unsaturated.

- This principle is applied to perform chemical analysis of binary alloys using their lattice parameter vs. composition curve, which can be established by measuring the lattice parameter of a series of previously analysed alloys.
- This method has been used in diffusion studies to measure the change in concentration of a solution with distance from the original interface.
- Its accuracy depends entirely on the slope of the parameter-composition curve.
- In alpha brasses, which can contain from 0 to about 40% zinc in copper, an accuracy of ±1% zinc can be achieved without difficulty.

So, now we are going to discuss about the single phase quantity analysis so, generally we are doing it by the chemical analysis by parameter measurement, what are the basic principles? The lattice parameter of a binary solid solution of B in A, depends only on the percentage of B in the alloy, as long as the solution is unsaturated, yes off course, suppose I have making one kind of alloys composites, am having one phase materials, and am adding some constant through hence,
Whatever the constant through ends is adding, it should not go up to the saturation level.
This principle, is applied to perform chemical analysis of binary alloys using their lattice parameter verses the composition curve, which can be established by measuring the lattice parameter of a series of previously analysed alloys, this method has been used in diffusion studies to measure the change in concentration of a solutions with distance from the original interface, it accuracy depends entirely on the slope of the parameter composition curve, in à brasses, for an example, which can contain from 0 to about 40% zinc in copper, an accuracy of + plasama-1% zinc can be achieved without any difficulty.
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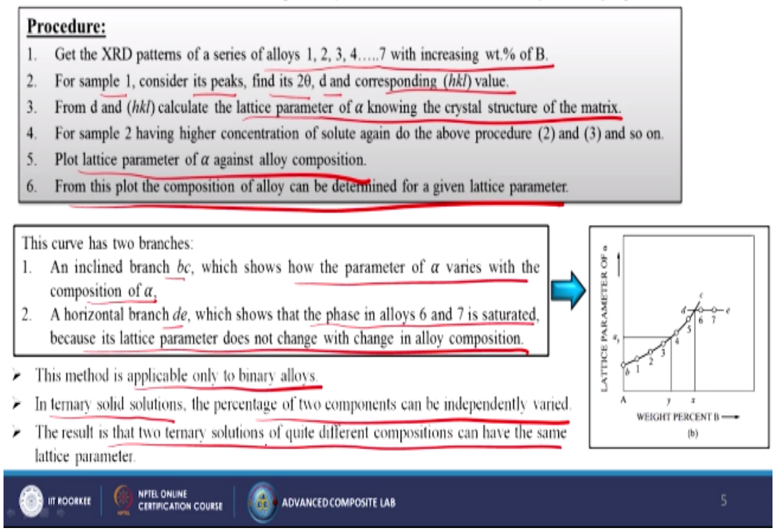

Assume that two elements A and B are partially soluble in the solid state to form single phase α.

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Procedure:

1. Get the XRD patterns of a series of alloys 1, 2, 3, 4.....7 with increasing wt.% of B.
2. For sample 1, consider its peaks, find its 2θ, d and corresponding (*hkl*) value.
3. From d and (*hkl*) calculate the lattice parameter of *α* knowing the crystal structure of the matrix.
4. For sample 2 having higher concentration of solute again do the above procedure (2) and (3) and so on.
5. Plot lattice parameter of *α* against alloy composition.
6. From this plot the composition of alloy can be determined for a given lattice parameter.

This curve has two branches:

1. An inclined branch *bc*, which shows how the parameter of *α* varies with the composition of *α*,
2. A horizontal branch *de*, which shows that the phase in alloys 6 and 7 is saturated, because its lattice parameter does not change with change in alloy composition.

- This method is applicable only to binary alloys.
- In ternary solid solutions, the percentage of two components can be independently varied.
- The result is that two ternary solutions of quite different compositions can have the same lattice parameter.

So, now through different examples, we are going to make you to understand about the quantitative analysis first as you that actual elements A and B are partially soluble in the solid state to form a single phase à, so what is the procedure, get the XRD patterns of a series of alloys, 1,2,3,4,5,6, up to 7, with increasing weight percentage of B, for sample 1, consider its peaks, find its 2 θ, d, and corresponding HKL value from, d and HKL value calculate the lattice parameter of à knowing the crystal structure of the matrix, then for sample to 2 also follow the same procedure.

Then, plot lattice parameter of à against alloy composition and from this plot the composition of alloy can be determined for a given lattice parameter, so this is the whole positive, this comes if you see this comes, it is having two branches, one branch from B to C, another G to E, what does it mean? So, an inclined branch BC, which shows how the parameter of à value varies with the composition of à, using it is in to the increasing order.

And then, after that it becomes a straight line, the horizontal branch DE, which shows that the phase in alloys 6 and 7 is saturated, because its lattice parameter does not change with change in alloy composition.

See, suppose I am adding one consequence or maybe the elements in to the matrix, so I will take one percent, 2 percent, 3 percent, 4 percent, like that then, after certain time, the whole matrix will became such saturated, that time if I am going to add more also, the lattice parameter is not going to be changed. This method is applicable only to binary alloys, in ternary solid solutions; the percentage of the two components can be independently varied.

The result is that, two ternary solutions of quite difference composition can have the same lattice parameter, now if we are having the multi phase, then for the multi phase, what we have to do? What is the basic principle? The intensity of

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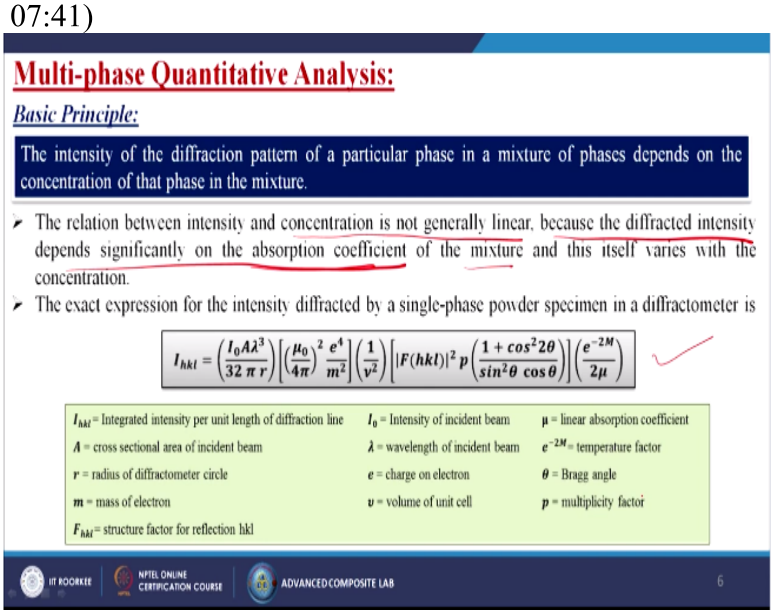

Multi-phase Quantitative Analysis:

Basic Principle:

The intensity of the diffraction pattern of a particular phase in a mixture of phases depends on the concentration of that phase in the mixture.

- The relation between intensity and concentration is not generally linear, because the diffracted intensity depends significantly on the absorption coefficient of the mixture and this itself varies with the concentration.
- The exact expression for the intensity diffracted by a single-phase powder specimen in a diffractometer is

$$I_{hkl} = \left(\frac{I_0 A \lambda^3}{32 \pi r}\right)\left[\left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^4}{m^2}\right]\left(\frac{1}{v^2}\right)\left[|F(hkl)|^2 p \left(\frac{1+\cos^2 2\theta}{\sin^2\theta \cos\theta}\right)\right]\left(\frac{e^{-2M}}{2\mu}\right)$$

I_{hkl} = Integrated intensity per unit length of diffraction line
A = cross sectional area of incident beam
r = radius of diffractometer circle
m = mass of electron
F_{hkl} = structure factor for reflection hkl
I_0 = Intensity of incident beam
λ = wavelength of incident beam
e = charge on electron
v = volume of unit cell
μ = linear absorption coefficient
e^{-2M} = temperature factor
θ = Bragg angle
p = multiplicity factor

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The diffraction pattern of a particular phase in a mixture of phases depends on the concentration of that phase in the mixture itself, the relation between intensity and concentration is not generally linear, because the diffracted intensity depends significantly on the absorption coefficient of the mixture and this itself varies with the concentration itself. The exact expression for the intensity diffracted by a single phase powder specimen in a diffractometer is, so, generally IHKL with these formula, where IHKL is the integrated intensity per unit length of diffraction line, A is the cross sectional area of incident beam, small r is the radius of diffractometer circle, M is the mass of electron, FHKL is the structure factor for reflection HKL, I_0 is the intensity of incident beam, λ =wavelength of incident beam, E is the charge on electron, V is the volume of unit cell, mu is the linear absorption coefficient, e^{-2m} is the temperature factor, θ is off course is the Braggs angle and row or maybe P is the multiplicity factor.

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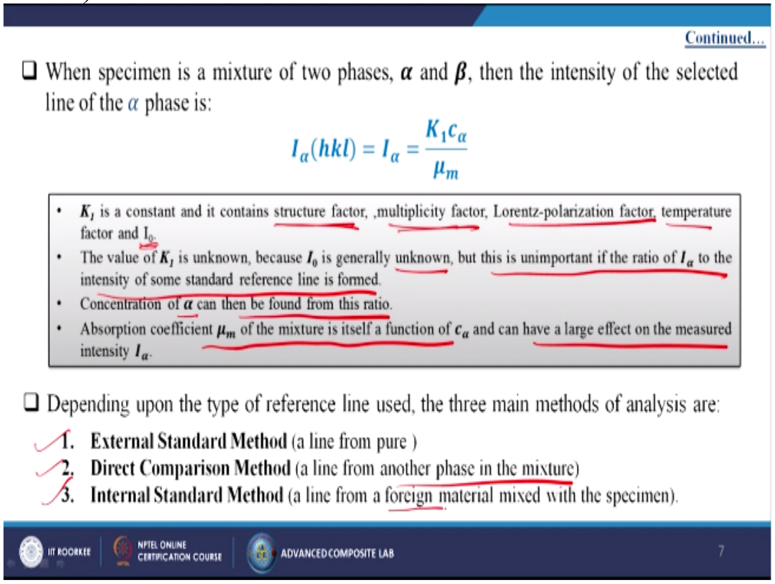

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- When specimen is a mixture of two phases, α and β, then the intensity of the selected line of the α phase is:

$$I_\alpha(hkl) = I_\alpha = \frac{K_1 c_\alpha}{\mu_m}$$

- K_1 is a constant and it contains structure factor, ,multiplicity factor, Lorentz-polarization factor, temperature factor and I_0.
- The value of K_1 is unknown, because I_0 is generally unknown, but this is unimportant if the ratio of I_α to the intensity of some standard reference line is formed.
- Concentration of α can then be found from this ratio.
- Absorption coefficient μ_m of the mixture is itself a function of c_α and can have a large effect on the measured intensity I_α.

- Depending upon the type of reference line used, the three main methods of analysis are:

1. **External Standard Method** (a line from pure)
2. **Direct Comparison Method** (a line from another phase in the mixture)
3. **Internal Standard Method** (a line from a foreign material mixed with the specimen).

So, when specimen is a mixture of two phases à and beta, then the intensity of the selected line of the à phase is I à HKL=I à=K_1 C à/mu m, where K_1 is a constant and it contains structure factor, multiplicity factor, Lorentz polarization factor, temperature factor and I_0, the value of K_1 is unknown because I_0 is generally unknown but this is an important if the ratio of I à to the intensity of some standard reference line is formed. Concentration of à can then be found from this ratio, absorption coefficient mu m, of the mixture is itself a function of C à and can have a large effect on the measured intensity that is I à.

Now, depending upon, the type of reference line used, the three main methods of analysis are, first one is called the external standard method means, a line from pure, second one is called the direct comparison method, a line from another phase in the mixture, that is called the internal standard method, a line from a foreign material mixed with the specimen itself. Now first what is the external standard method, so, in this method?

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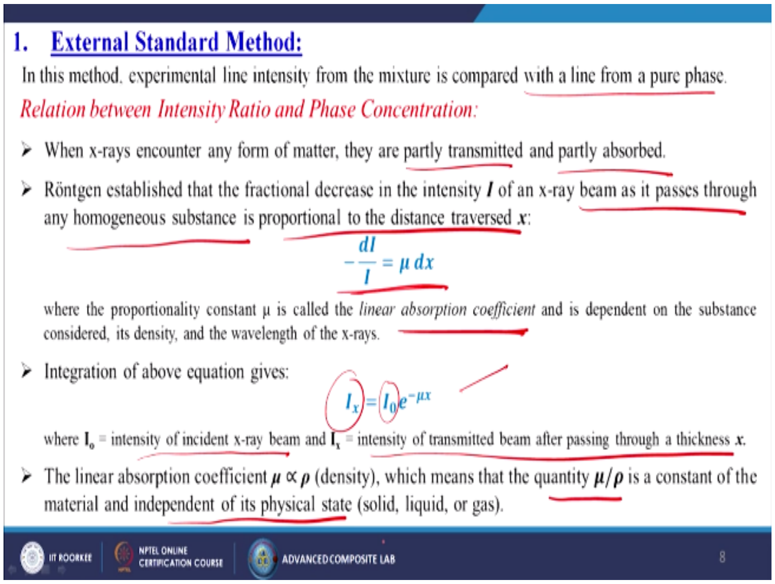

1. External Standard Method:

In this method, experimental line intensity from the mixture is compared with a line from a pure phase.

Relation between Intensity Ratio and Phase Concentration:

- When x-rays encounter any form of matter, they are partly transmitted and partly absorbed.
- Röntgen established that the fractional decrease in the intensity I of an x-ray beam as it passes through any homogeneous substance is proportional to the distance traversed x:

$$-\frac{dI}{I} = \mu\, dx$$

where the proportionality constant μ is called the *linear absorption coefficient* and is dependent on the substance considered, its density, and the wavelength of the x-rays.

- Integration of above equation gives:

$$I_x = I_0 e^{-\mu x}$$

where I_0 = intensity of incident x-ray beam and I_x = intensity of transmitted beam after passing through a thickness x.

- The linear absorption coefficient $\mu \propto \rho$ (density), which means that the quantity μ/ρ is a constant of the material and independent of its physical state (solid, liquid, or gas).

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Experimental line intensity from the mixture is compared with a line from a pure phase, relation between intensity ratio and phase concentration is when X-rays encounter any form of matter, they are partly transmitted and partly absorbed, already we have gone through, Rontgen established that the fractional decrease in the intensity I of an X-ray beam, as it passes through any homogeneous substance is proportional to the distance traversed X.

So, -d I/I=mu d x, where the proportionally constant mu is called the linear absorption coefficient and is dependent on the substance considered its density and the wavelength of the X-rays itself.

Integration of above equation gives, $I_x=I_0e^{-mux}$, so, where I_0= intensity of incident X-ray beam and I_x=intensity of transmitted beam after passing through a thickness X, the linear absorption coefficient mu is hollow, mu is direct proportion to the row, which means the quantity mu/row is a constant of the materials and independent of its physical state means, either it maybe the solid or maybe the liquid or maybe the gas

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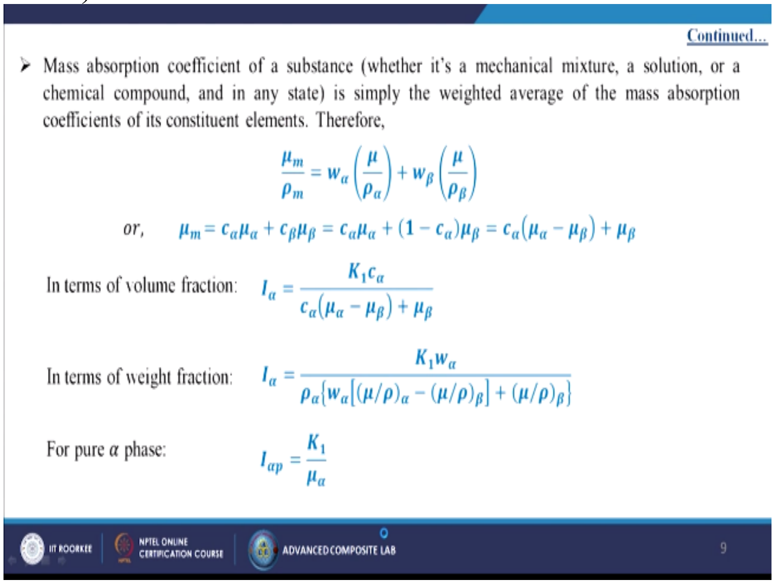

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- Mass absorption coefficient of a substance (whether it's a mechanical mixture, a solution, or a chemical compound, and in any state) is simply the weighted average of the mass absorption coefficients of its constituent elements. Therefore,

$$\frac{\mu_m}{\rho_m} = w_\alpha\left(\frac{\mu}{\rho_\alpha}\right) + w_\beta\left(\frac{\mu}{\rho_\beta}\right)$$

$$or,\quad \mu_m = c_\alpha\mu_\alpha + c_\beta\mu_\beta = c_\alpha\mu_\alpha + (1-c_\alpha)\mu_\beta = c_\alpha(\mu_\alpha-\mu_\beta)+\mu_\beta$$

In terms of volume fraction: $$I_\alpha = \frac{K_1 c_\alpha}{c_\alpha(\mu_\alpha-\mu_\beta)+\mu_\beta}$$

In terms of weight fraction: $$I_\alpha = \frac{K_1 w_\alpha}{\rho_\alpha\{w_\alpha[(\mu/\rho)_\alpha-(\mu/\rho)_\beta]+(\mu/\rho)_\beta\}}$$

For pure α phase: $$I_{\alpha p} = \frac{K_1}{\mu_\alpha}$$

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Now, mass absorption coefficient of a substance whether it is a mechanical mixture, a solution or a chemical compound and in any state, is simply the weighted average of the mass absorption coefficients of its constituent elements therefore, mu m/ row m=w à *mu/row à+ w beta*mu/row beta or simple with we can write the equations in these particular form. In terms of volume fraction, which is nothing but the I à =K$_1$C à/ C à *mu à-mu beta+ mu beta, in terms of weight fraction, so it's generally I à= K$_1$ W à/ row à* second bracket (w à *) third bracket, within first bracket, (mu/row à- row mu/ row beta) then third bracket closed + first bracket (mu/row beta), so pure à phase I à P= K$_1$/mu à.
Taking the ratio of intensity is from pure verses
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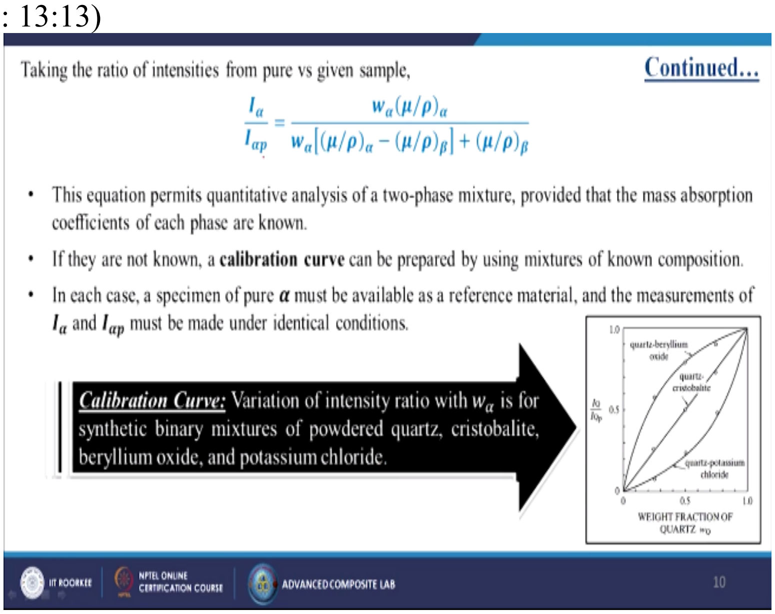

Taking the ratio of intensities from pure vs given sample,

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$$\frac{I_\alpha}{I_{\alpha p}} = \frac{w_\alpha(\mu/\rho)_\alpha}{w_\alpha\left[(\mu/\rho)_\alpha - (\mu/\rho)_\beta\right] + (\mu/\rho)_\beta}$$

- This equation permits quantitative analysis of a two-phase mixture, provided that the mass absorption coefficients of each phase are known.
- If they are not known, a **calibration curve** can be prepared by using mixtures of known composition.
- In each case, a specimen of pure α must be available as a reference material, and the measurements of I_α and $I_{\alpha p}$ must be made under identical conditions.

Calibration Curve: Variation of intensity ratio with w_α is for synthetic binary mixtures of powdered quartz, cristobalite, beryllium oxide, and potassium chloride.

Given sample, so, I à/ I à P=w à*mu/row à/w à*mu/row à-mu/row beta+ mu/row beta, this equation permits the quantitative analysis of a two phase mixture, provided that the mass of coefficients of each phase are known, if they are not known a calibration curve can be prepared by using mixtures of the known composition, in each case a specimen of pure à must be available as a reference material, and the measurements of I à and I à p must be made under identical conditions.
So, what is happening in this case, so this side Y is the I cube / I cube P and X axis is the weight fraction of quads, that is in the WQ, so calibration curve, a variation of intensity ratio with W à is for synthetic binary mixtures of powdered quartz, cristobalite, beryllium oxide, and potassium chloride, though with different diffraction, we are getting the different graphs.
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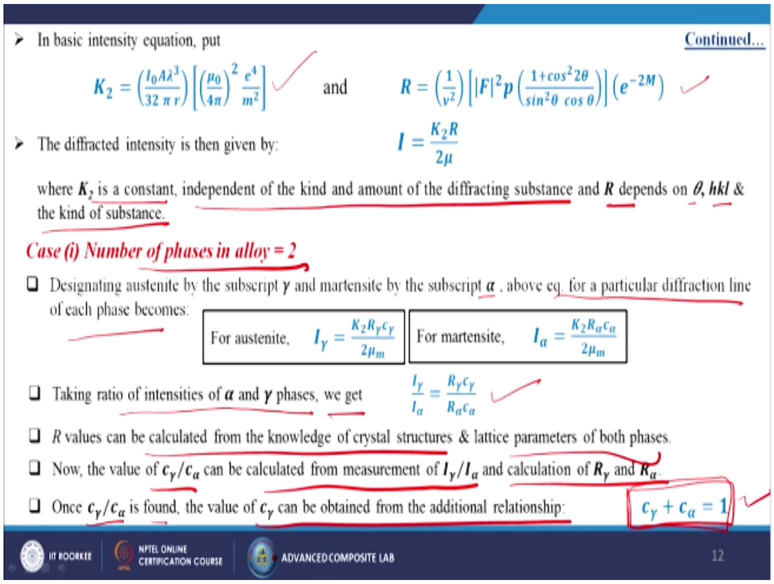

- In basic intensity equation, put

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$$K_2 = \left(\frac{I_0 A \lambda^3}{32\,\pi\, r}\right)\left[\left(\frac{\mu_0}{4\pi}\right)^2 \frac{e^4}{m^2}\right] \quad \text{and} \quad R = \left(\frac{1}{v^2}\right)\left[|F|^2 p\left(\frac{1+\cos^2 2\theta}{\sin^2\theta\,\cos\theta}\right)\right]\left(e^{-2M}\right)$$

- The diffracted intensity is then given by: $I = \frac{K_2 R}{2\mu}$

where K_2 is a constant, independent of the kind and amount of the diffracting substance and R depends on θ, hkl & the kind of substance.

Case (i) Number of phases in alloy = 2

☐ Designating austenite by the subscript γ and martensite by the subscript α , above eq. for a particular diffraction line of each phase becomes:

For austenite, $I_\gamma = \frac{K_2 R_\gamma c_\gamma}{2\mu_m}$

For martensite, $I_\alpha = \frac{K_2 R_\alpha c_\alpha}{2\mu_m}$

☐ Taking ratio of intensities of α and γ phases, we get $\frac{I_\gamma}{I_\alpha} = \frac{R_\gamma c_\gamma}{R_\alpha c_\alpha}$

☐ R values can be calculated from the knowledge of crystal structures & lattice parameters of both phases.

☐ Now, the value of c_γ/c_α can be calculated from measurement of I_γ/I_α and calculation of R_γ and R_α.

☐ Once c_γ/c_α is found, the value of c_γ can be obtained from the additional relationship: $\boxed{c_\gamma + c_\alpha = 1}$

Next, is the second one that is direct comparison method, this method does not require as a sample of the pure phase, whose composition is being determined, in this method, the experimental line intensity from the mixture is compared to a line from another phase in the mixture itself. The direct comparison method is of great interest because; it can be applied directly to the polycrystalline aggregates.

Most important applications is suppose to determine the composition of the mixture , when the two phases have the same composition but different crystal structure, examples, measuring the amount of retained austenite in the hardened steel. The external standard method cannot be used, because it is usually impossible to obtain a reference sample of pure austenite, off course or of known austenite content of the same chemical composition as the austenite in the unknown, quantitative microscopic examination is fairly satisfactory as long as the austenite content is fairly high, but becomes unreliable below about 15% austenite in many steels.

In basic intensity equations 2K to=I_0-Aλ cube/ 32πr) *(mu_0/4π)^2, e^4/m^2, and r value is this one, the diffracted intensity is given by I=K_2R/2 mu, so simple in this case we put the value of K_2 and we put the value of R, / 2mu, where, K_2 is constant, independent of the kind and amount of the diffracting substance and R depends on θ, HKL and the kind of substance, so now we are going first to see that K study, number 1 case, or maybe K^1, number of phase in alloys =2, designating austenite by the subscript γ and marten site by the subscript à, above equations for a particular diffraction line of each phase becomes for austenite I γ=K_2R γ, C γ/2mu m, and for marten site I à=K_2,R à C à/2 mu M.

Taking ratio of intensities of à and γ phases, we get I γ/ I à=R γ, C γ/ R à, C à, R value can be calculated from the knowledge of crystal structures and lattice parameter of both phases, now the value of C γ/C à, can be calculated from the measurement of I γ, I à and calculation of R γ and R à, once C gamma/ C à is found the value of C gamma, can be obtained from the additional relationship, that is C gamma+ C à =1.

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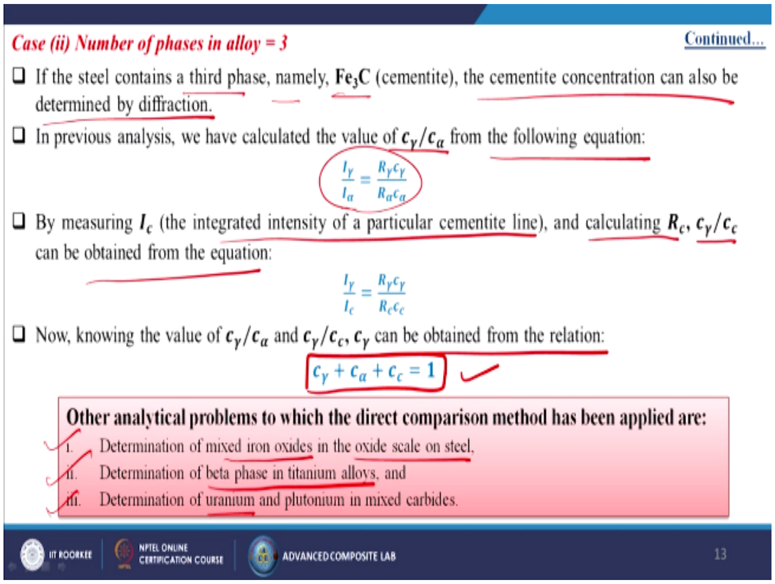

Case (ii) Number of phases in alloy = 3

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- ☐ If the steel contains a third phase, namely, **Fe_3C** (cementite), the cementite concentration can also be determined by diffraction.
- ☐ In previous analysis, we have calculated the value of c_γ/c_α from the following equation:

$$\frac{I_\gamma}{I_\alpha} = \frac{R_\gamma c_\gamma}{R_\alpha c_\alpha}$$

- ☐ By measuring I_c (the integrated intensity of a particular cementite line), and calculating R_c, c_γ/c_c can be obtained from the equation:

$$\frac{I_\gamma}{I_c} = \frac{R_\gamma c_\gamma}{R_c c_c}$$

- ☐ Now, knowing the value of c_γ/c_α and c_γ/c_c, c_γ can be obtained from the relation:

$$\boxed{c_\gamma + c_\alpha + c_c = 1}$$

Other analytical problems to which the direct comparison method has been applied are:

i. Determination of mixed iron oxides in the oxide scale on steel.
ii. Determination of beta phase in titanium alloys, and
iii. Determination of uranium and plutonium in mixed carbides.

Now, case number 2, number of phases in alloy, in this cases 3, so if the steel contains a third phase, namely Fe3C, which is known as the cementite, the cementite concentration can also be determine by diffractions, in previous analysis, we have calculated the value of C γ/C à from the following equations, so, by measuring I_C the integrated intensity of a particular cementite line and calculating R_C, C γ/C_C, can be obtained from the equation, that is I γ /I_C=R γ, C γ/ R_C,C_C, now knowing the value of C γ, C à, and C γ/C_C, C γ can be called obtained from the relation, that is C γ+ C à+ C_C=1.

Other analytical problems to which the direct comparison method has been applied are, determination of mixed iron oxides in the oxide scale on steel, determination of beta phase in titanium alloys and determination of uranium and plutonium in mixed carbides.

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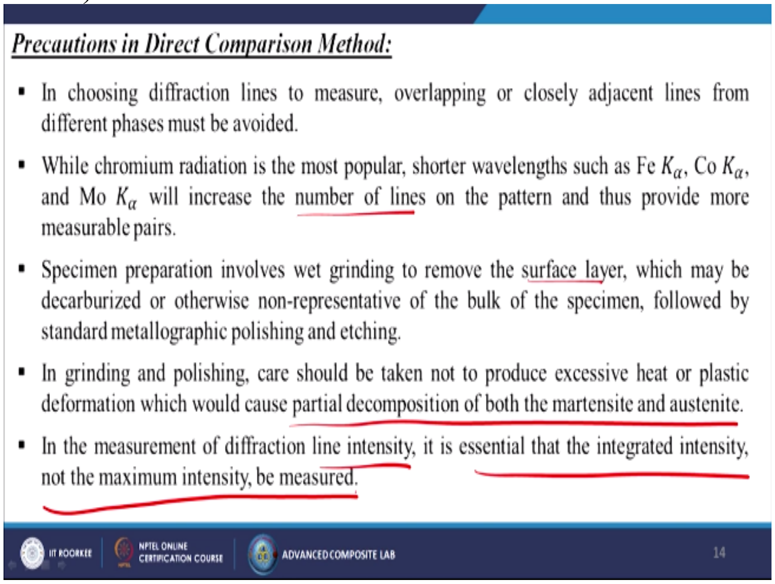

Precautions in Direct Comparison Method:

- In choosing diffraction lines to measure, overlapping or closely adjacent lines from different phases must be avoided.
- While chromium radiation is the most popular, shorter wavelengths such as Fe K_α, Co K_α, and Mo K_α will increase the number of lines on the pattern and thus provide more measurable pairs.
- Specimen preparation involves wet grinding to remove the surface layer, which may be decarburized or otherwise non-representative of the bulk of the specimen, followed by standard metallographic polishing and etching.
- In grinding and polishing, care should be taken not to produce excessive heat or plastic deformation which would cause partial decomposition of both the martensite and austenite.
- In the measurement of diffraction line intensity, it is essential that the integrated intensity, not the maximum intensity, be measured.

Precautions in direct comparison method, in choosing diffraction lines to measure, overlapping or closely adjacent lines from different phases must be avoided, while chromium radiation is the most popular shorter wavelengths such as Fe K à, or maybe Cobalt k à, and malign K à will increase the number of lines on the pattern and thus provide more measurable pairs.

Specimen preparation involves wet grinding to remove the surface layer, which may be decarburized or otherwise, non- representative of the bulk of the specimen, followed by standard metallographic polishing and etching.

In grinding and polishing, care should be taken not to produce excessive heat or plastic deformation, otherwise the structure will be changed, which could partial decomposition of both marten site and austenite. In the measurement of diffraction line intensity, it is essential that the integrated intensity not the maximum intensity be measured.

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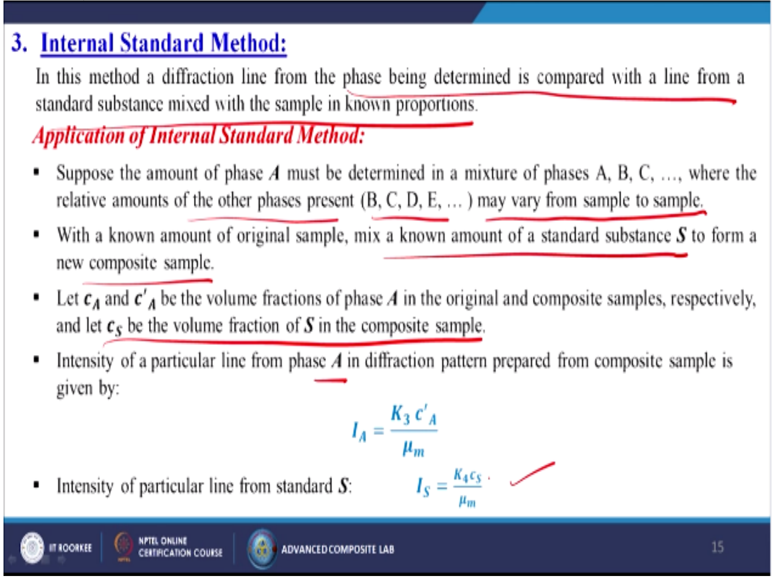

3. Internal Standard Method:

In this method a diffraction line from the phase being determined is compared with a line from a standard substance mixed with the sample in known proportions.

Application of Internal Standard Method:

- Suppose the amount of phase *A* must be determined in a mixture of phases A, B, C, …, where the relative amounts of the other phases present (B, C, D, E, …) may vary from sample to sample.
- With a known amount of original sample, mix a known amount of a standard substance ***S*** to form a new composite sample.
- Let c_A and c'_A be the volume fractions of phase *A* in the original and composite samples, respectively, and let c_S be the volume fraction of ***S*** in the composite sample.
- Intensity of a particular line from phase *A* in diffraction pattern prepared from composite sample is given by:

$$I_A = \frac{K_3 c'_A}{\mu_m}$$

- Intensity of particular line from standard ***S***: $I_S = \frac{K_4 c_S}{\mu_m}$

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Now, the third one that is called the Internal standard method, in this method a diffraction line from the phase being determined is compared with a line from a standard substance mixed with the sample is known proportions, application of the Internal standard method, suppose the amount of phase, A must be determined in a mixture of phases A,B,C or maybe so on, where the relative amounts of the other phases present like B,C,D,E , so, on, may vary from sample to sample, with a known amount of original samples, mix a known amount of a standard substance S to form a new composite sample.

Let see, C_A and C prime A, be the volume fractions of phase A, in the original and composite samples, respectively, and let C_S, be the volume fraction of S in the composite sample, intensity of a particular line from phase A, in diffraction pattern prepared from composite sample is given by IA=K_3 C prime A/mu M, intensity of particular line from standard S =I_S=K_4C_S/mu M

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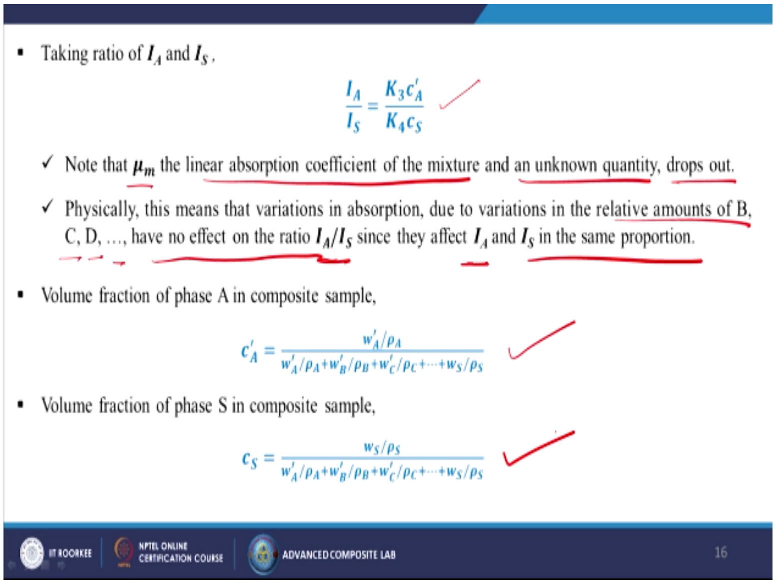

- Taking ratio of I_A and I_S,

$$\frac{I_A}{I_S}=\frac{K_3c'_A}{K_4c_S}$$

✓ Note that μ_m the linear absorption coefficient of the mixture and an unknown quantity, drops out.

✓ Physically, this means that variations in absorption, due to variations in the relative amounts of B, C, D, …, have no effect on the ratio I_A/I_S since they affect I_A and I_S in the same proportion.

- Volume fraction of phase A in composite sample,

$$c'_A=\frac{w'_A/\rho_A}{w'_A/\rho_A+w'_B/\rho_B+w'_C/\rho_C+\cdots+w_S/\rho_S}$$

- Volume fraction of phase S in composite sample,

$$c_S=\frac{w_S/\rho_S}{w'_A/\rho_A+w'_B/\rho_B+w'_C/\rho_C+\cdots+w_S/\rho_S}$$

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Taking ratio of I_A and I_S, so simple I_A/I_S, we will get K_3 C_A prime/K_4 C_S, note that, mu M, the linear absorption coefficient of the mixture and an unknown quantity, drops out, physically this means that variations in absorption, due to variations in the relative amounts of B, C, D and so on, have no effect on the ratio I_A/I_S, since they affect I_A and I_S in the same proportions. Volume fraction of phase an in composite sample, we can calculate by this formula, volume fraction of phase S in composite sample, we can calculate by this formula

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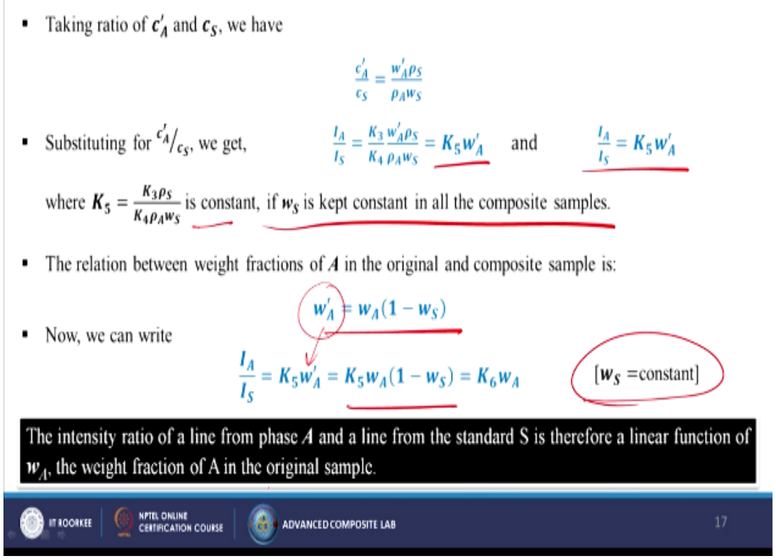

- Taking ratio of c'_A and c_S, we have

$$\frac{c'_A}{c_S}=\frac{w'_A\rho_S}{\rho_A w_S}$$

- Substituting for c'_A/c_S, we get, $\frac{I_A}{I_S}=\frac{K_3\,w'_A\rho_S}{K_4\,\rho_A w_S}=K_5w'_A$ and $\frac{I_A}{I_S}=K_5w'_A$

where $K_5=\frac{K_3\rho_S}{K_4\rho_A w_S}$ is constant, if w_S is kept constant in all the composite samples.

- The relation between weight fractions of A in the original and composite sample is:

$$w'_A=w_A(1-w_S)$$

- Now, we can write

$$\frac{I_A}{I_S}=K_5w'_A=K_5w_A(1-w_S)=K_6w_A$$

[w_S =constant]

The intensity ratio of a line from phase A and a line from the standard S is therefore a linear function of w_A, the weight fraction of A in the original sample.

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Now, we are taking ratio of C_A prime, and C_S, we have C_A prime/C_S=W_A prime, row S/ row A/ W_S, substituting for C_A prime/C_S, we get simple $I_A/I_S=K_{3,}$ W_A prime row$_s$/ K_4/row A/ W_s= $K_{5,}$ W_A prime, and I_A/ I_S=K_5W_A prime, where K_5=K_3 row S/ K_4 row A, W is the constant, if W_s is kept constant in all the composite samples, the relation between weight fractions of A in the original and composite sample is W_A prime,=W_A(1-W_S), now we can write I_A/I_S=K_5W_A prime=K_5W_A*(1-$W_{S,}$), so simple we are substituting this one over here, which is nothing but the K_S W_A, so W_S is allows the constant, the intensity ratio of a line from phase A, and line from the standard S is therefore a linear function of W_A, the weight fraction of A in the original sample.

Mow we are going to give you the more clarity by giving an example, see suppose measurement

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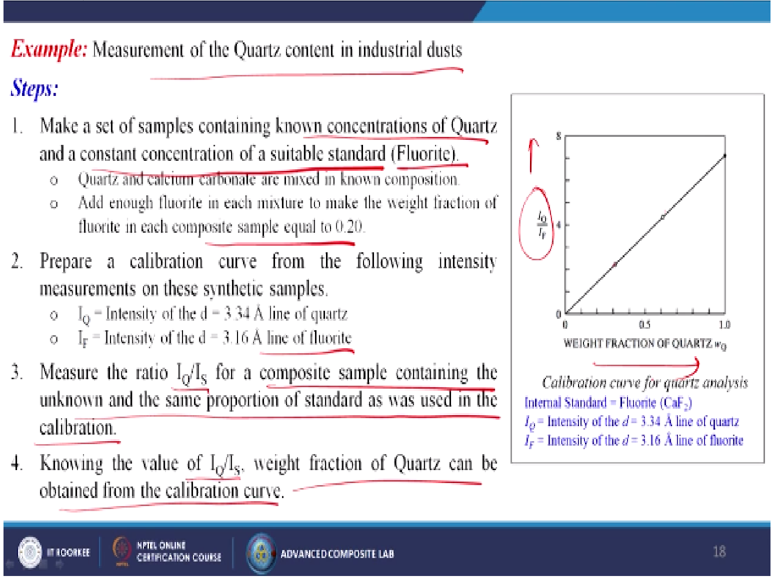

Example: Measurement of the Quartz content in industrial dusts

Steps:

1. Make a set of samples containing known concentrations of Quartz and a constant concentration of a suitable standard (Fluorite).
   - Quartz and calcium carbonate are mixed in known composition.
   - Add enough fluorite in each mixture to make the weight fraction of fluorite in each composite sample equal to 0.20.
2. Prepare a calibration curve from the following intensity measurements on these synthetic samples.
   - I_Q = Intensity of the d = 3.34 Å line of quartz
   - I_F = Intensity of the d = 3.16 Å line of fluorite
3. Measure the ratio I_Q/I_S for a composite sample containing the unknown and the same proportion of standard as was used in the calibration.
4. Knowing the value of I_Q/I_S, weight fraction of Quartz can be obtained from the calibration curve.

Calibration curve for quartz analysis

Internal Standard = Fluorite (CaF_2)

I_Q = Intensity of the d = 3.34 Å line of quartz

I_F = Intensity of the d = 3.16 Å line of fluorite

Of the Quartz content in industrial dusts, so what are the steps, first make a set of samples containing the known concentrations of Quartz and a constant concentration of a suitable standard fluorite, quartz and calcium carbonate are mixed in known compositions and enough fluorite in each mixture to make the weight fraction of fluorite in each composite sample equal to 0.20, second step prepare a calibration curve from the following intensity measurements on these synthetic samples like, I_Q = Intensity of the d= 3.34 angstrom, line of quartz, and I_F intensity of the d, where is =3.16 angstrom line of fluorite, measure the ratio I_Q/ I_S for a composite sample containing the unknown and the same proportion of standard as was used in the calibration. Knowing the values of I_Q/I_S, weight fraction of quartz can be obtained from the calibration curve, so, I am getting this point and this point, so internal standard of fluorite means, calcium provides generally, we are taking, so I_Q/I_F, in to the Y axis weight fraction of quartz in to the X axis

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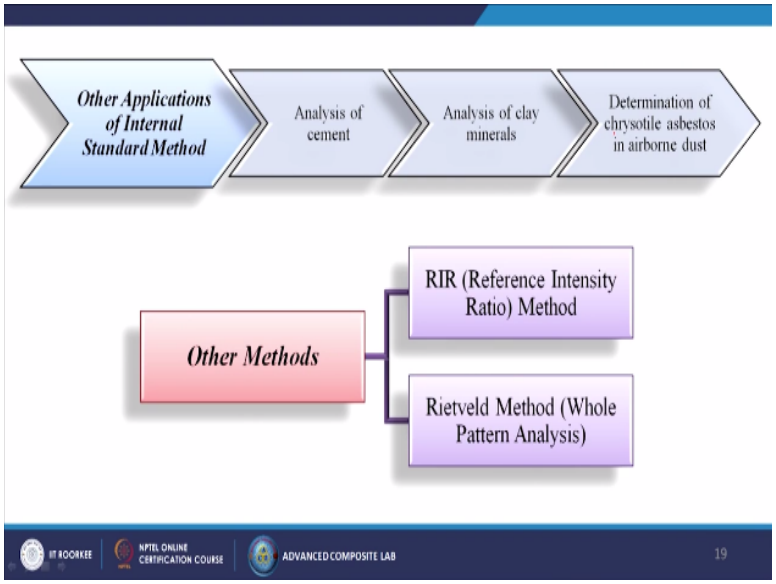

Other Applications of Internal Standard Method

Analysis of cement

Analysis of clay minerals

Determination of chrysotile asbestos in airborne dust

Other Methods

RIR (Reference Intensity Ratio) Method

Rietveld Method (Whole Pattern Analysis)

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Now, what are the other applications, so generally analysis of the cement we can do by this methods, analysis of clay minerals we can do by this method, determination of chrysotile asbestos in airborne dust, also can be done by these methods, off course there is some other method also, that is called RIR Reference Intensity Ratio method, another one is called the Rietveld method or namely other we can say it as a whole pattern analysis, so what is RIR? Or maybe the reference intensity ratio method, the RIR method

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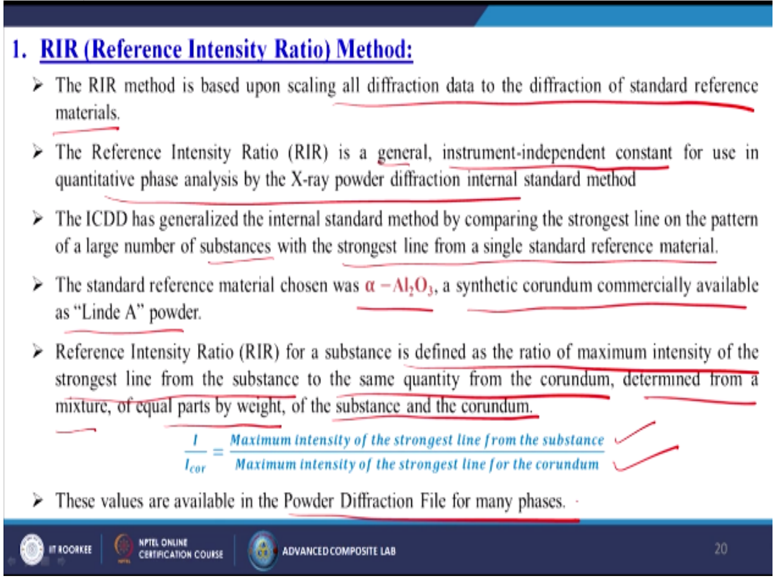

1. RIR (Reference Intensity Ratio) Method:

- The RIR method is based upon scaling all diffraction data to the diffraction of standard reference materials.
- The Reference Intensity Ratio (RIR) is a general, instrument-independent constant for use in quantitative phase analysis by the X-ray powder diffraction internal standard method
- The ICDD has generalized the internal standard method by comparing the strongest line on the pattern of a large number of substances with the strongest line from a single standard reference material.
- The standard reference material chosen was $\alpha - Al_2O_3$, a synthetic corundum commercially available as "Linde A" powder.
- Reference Intensity Ratio (RIR) for a substance is defined as the ratio of maximum intensity of the strongest line from the substance to the same quantity from the corundum, determined from a mixture, of equal parts by weight, of the substance and the corundum.

$$\frac{I}{I_{cor}} = \frac{\text{Maximum intensity of the strongest line from the substance}}{\text{Maximum intensity of the strongest line for the corundum}}$$

- These values are available in the Powder Diffraction File for many phases.

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The RIR method is based upon scaling all diffraction data to the diffraction of standard reference materials, the reference intensity ratio is the general instrument independent constant for use in quantitative phase analysis by the X-ray powder diffraction internal standard method, the ICDD has generalized the internal standard method by comparing the strongest line on the pattern of a large number of substances with the strongest line from a single standard reference material. The standard reference material chosen was à $Al_2 O_3$, synthetic corundum commercially available as linde A powder.

Reference intensity ratio for a substance is defined as the ratio of maximum intensity of the strongest line from the substance to the same quantity from the corundum, determined from a mixture, of equal parts by weight, of the substance and the corundum, that means, the I/I corundum is equal to maximum intensity of strongest line from the substance/maximum intensity of the strongest line from the corundum, these values are available in the powder diffraction file for many phases.

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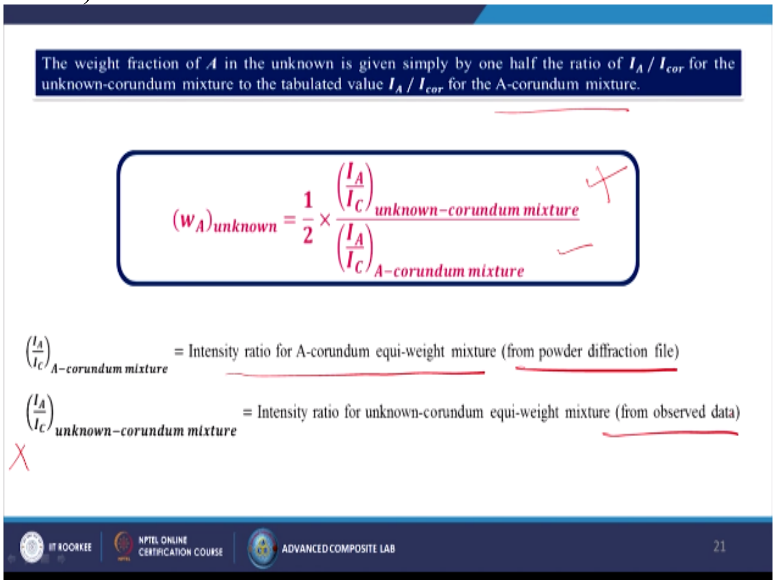

The weight fraction of *A* in the unknown is given simply by one half the ratio of I_A / I_{cor} for the unknown-corundum mixture to the tabulated value I_A / I_{cor} for the A-corundum mixture.

$$(w_A)_{unknown} = \frac{1}{2} \times \frac{\left(\frac{I_A}{I_C}\right)_{unknown-corundum\ mixture}}{\left(\frac{I_A}{I_C}\right)_{A-corundum\ mixture}}$$

$\left(\frac{I_A}{I_C}\right)_{A-corundum\ mixture}$ = Intensity ratio for A-corundum equi-weight mixture (from powder diffraction file)

$\left(\frac{I_A}{I_C}\right)_{unknown-corundum\ mixture}$ = Intensity ratio for unknown-corundum equi-weight mixture (from observed data)

The weight fraction of A in the unknown is given simply by one half the ratio of I_A/I corundum, for the unknown corundum mixture to the tabulated value I_A/I corundum, for the A-corundum mixture, so W_A unknown=1/2 * I_A/I_C, unknown corundum mixture/I_A/I_C A- corundum mixture, so where this first is the corundum mixture this one is the intensity ratio for the A corundum equi-weight mixture, from powder diffraction files, and this one is here, that intensity ratio for unknown corundum equi- weight mixture from the observed data.

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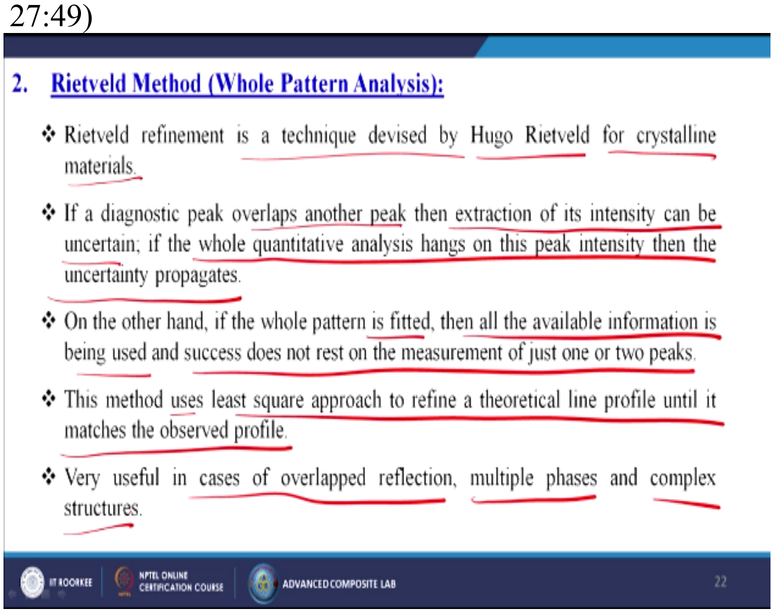

2. Rietveld Method (Whole Pattern Analysis):

- Rietveld refinement is a technique devised by Hugo Rietveld for crystalline materials.
- If a diagnostic peak overlaps another peak then extraction of its intensity can be uncertain; if the whole quantitative analysis hangs on this peak intensity then the uncertainty propagates.
- On the other hand, if the whole pattern is fitted, then all the available information is being used and success does not rest on the measurement of just one or two peaks.
- This method uses least square approach to refine a theoretical line profile until it matches the observed profile.
- Very useful in cases of overlapped reflection, multiple phases and complex structures.

Second is called, the Rietveld Method or maybe the whole pattern analysis method, so generally the Rietveld refinement is a technique devised by Hugo Rietveld, in his name just we are calling it as a Rietveld method, who has inverted this method, for crystalline materials. if a diagnostic peak overlaps another peak then the extraction of its intensity can be uncertain, if the whole quantitative analysis hangs on this peak intensity then the uncertainty propagates, on the other hand, if the whole pattern is fitted, then all the available information is being used and success does not rest on the measurement of just one or two peaks. This method uses least square approach to refine a theoretical line profile until it matches the observed profile, very useful in cases of overlapped reflection, multiple phases and complex structures.

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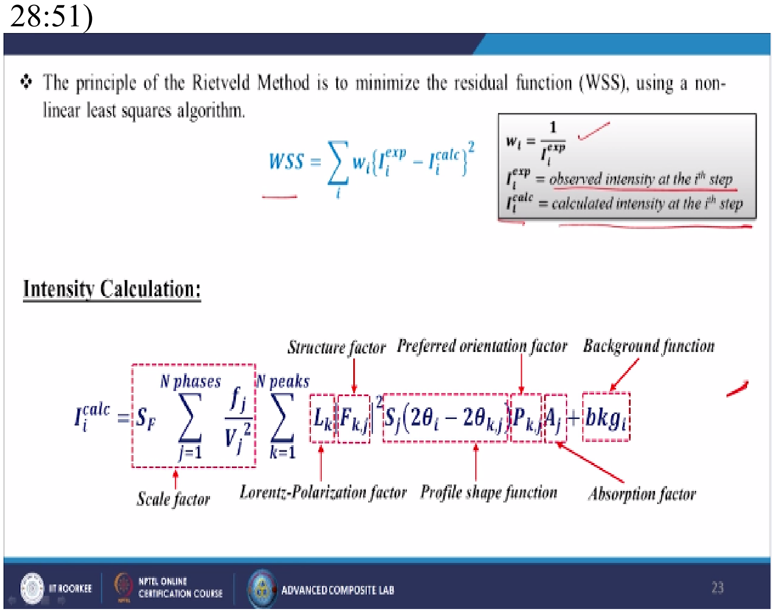

- The principle of the Rietveld Method is to minimize the residual function (WSS), using a non-linear least squares algorithm.

$$WSS = \sum_i w_i\{I_i^{exp} - I_i^{calc}\}^2$$

$w_i = \frac{1}{I_i^{exp}}$

I_i^{exp} = observed intensity at the i^{th} step

I_i^{calc} = calculated intensity at the i^{th} step

Intensity Calculation:

$$I_i^{calc} = S_F \sum_{j=1}^{N\ phases} \frac{f_j}{V_j^2} \sum_{k=1}^{N\ peaks} L_k |F_{k,j}|^2 S_j(2\theta_i - 2\theta_{k,j}) P_{k,j} A_j + bkg_i$$

The principle of the Rietveld method, is to minimize the residual function that is, WSS, using a non-linear least squares algorithm, so, what is WSS= Σ IW{I_I ^{exp}-I_I ^{calc}]^2, so, where W_I=1/I_I ^{exp}, I ^{exp}=observed intensity at the i^{th} step, I_I ^{calc}= calculated intensity at the i^{th} step, how we are going to calculate the intensity, so generally the I_I calculated we are following these whole equations, where this is known as the scale factor, then we are having the Lorentz –polarization factor, then we are having the structure factor, then we are having the profile shape functions, or maybe the preferred orientation factor, then we are having the absorption factor, and then we are having the background function, so like, this way we can easily calculate, so how we are going to calculate intensity calculations that is by these formula, so we are having the scale factor, we are having the Lorentz –polarization factor, we are having the structure factor, we are having the profile shape function, we are having the preferred orientation factor over there, then we are having the absorption factor and then we are having the background function.

The Relative weight function of the phase à

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That is à, W à in a mixture of n phases is given by W à= S à*(ZMV à/Σ I=1 ^{n} S_i (ZMV) I, where, S is the Rietveld scale factor, Z=number of formula units per cell, M= mass of the formula unit, in atomic mass units), and V is the unit cell volume in angstrom $A^{3,}$ so reilveld possible how to do that? First chose the appropriator software program, there are so many software by generally which we can do the reilveld method that is the expert high scored plus, GSAS, reitan, Maud program, fullprof, TOPAS and BGMN.

Then second load on input the phases in the sample obtain from qualitative analysis, and then third adjust manually some parameters like cell, intensities, background. Four refine overall intensities and background, peaks positions, peaks shapes and structures and the fifth access the results. Of course now there are certain practical difficulties generally what we are getting at the time of doing the quantitative analysis.

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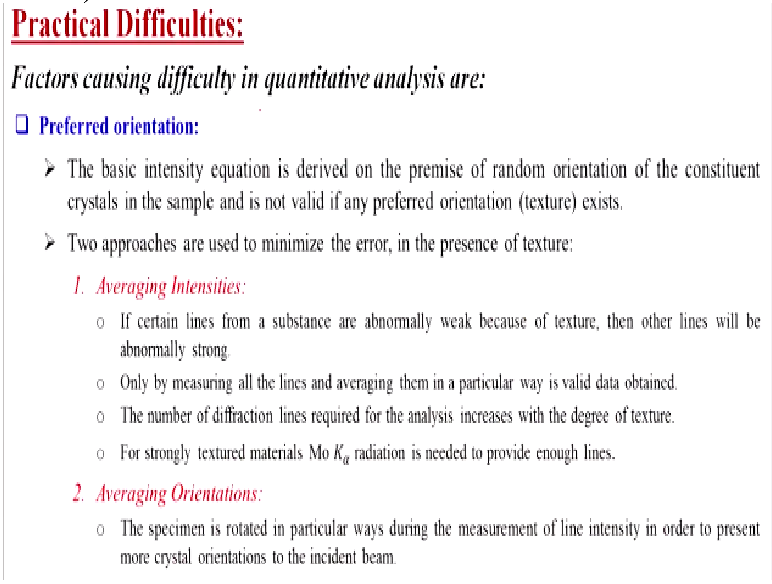

Practical Difficulties:

Factors causing difficulty in quantitative analysis are:

❑ **Preferred orientation:**

- The basic intensity equation is derived on the premise of random orientation of the constituent crystals in the sample and is not valid if any preferred orientation (texture) exists.
- Two approaches are used to minimize the error, in the presence of texture:
  1. *Averaging Intensities:*
     - If certain lines from a substance are abnormally weak because of texture, then other lines will be abnormally strong.
     - Only by measuring all the lines and averaging them in a particular way is valid data obtained.
     - The number of diffraction lines required for the analysis increases with the degree of texture.
     - For strongly textured materials Mo K_α radiation is needed to provide enough lines.
  2. *Averaging Orientations:*
     - The specimen is rotated in particular ways during the measurement of line intensity in order to present more crystal orientations to the incident beam.

So factors causing difficulty in quantitative analysis are first one is called the preferred orientation what is that? The basic intensity equations, is derived on the premise of random orientations of the constituent crystals in the sample and is not valid if any preferred orientation that means texture exists. Two approaches are used to minimize the error, in the presence of texture.

One is called the averaging intensities if certain lines from a substance are abnormally weak because of texture then other lines will be abnormally strong. Only by measuring all the lines and averaging them in a particular way is valid data obtained. The number of diffraction lines required for the analysis increases with the degree of texture for strongly textured materials molybdenum k α radiation is needed to provide the enough lines.

Second is that averaging orientations the specimen is rotated in particular ways during the measurement of line intensity in order to present more crystal orientations to the incident beam. Next is called the micro absorption.

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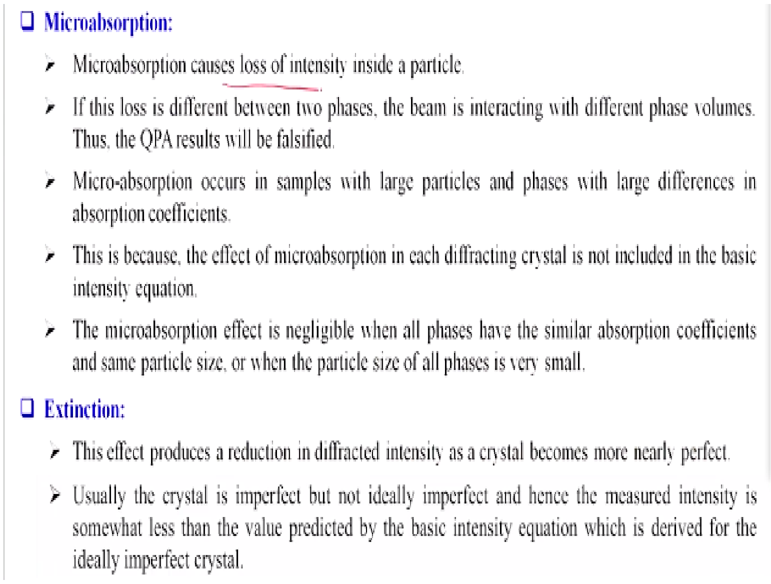

- **Microabsorption:**
  - Microabsorption causes loss of intensity inside a particle.
  - If this loss is different between two phases, the beam is interacting with different phase volumes. Thus, the QPA results will be falsified.
  - Micro-absorption occurs in samples with large particles and phases with large differences in absorption coefficients.
  - This is because, the effect of microabsorption in each diffracting crystal is not included in the basic intensity equation.
  - The microabsorption effect is negligible when all phases have the similar absorption coefficients and same particle size, or when the particle size of all phases is very small.
- **Extinction:**
  - This effect produces a reduction in diffracted intensity as a crystal becomes more nearly perfect.
  - Usually the crystal is imperfect but not ideally imperfect and hence the measured intensity is somewhat less than the value predicted by the basic intensity equation which is derived for the ideally imperfect crystal.

Micro absorption causes loss of intensity inside a particle. If this loss is between two faces the beam is interacting with different face volumes does the QPA result will be falsified. Micro absorption occurs in samples with large particles and phases with large differences in absorption coefficients. This is because the effect of micro absorption in each diffracting crystal is not included in the basic intensity equations.

The micro absorption effect is negligible when all phases have the similar absorption coefficients and same particle size, or when the particle size of phases is very, very small. Next last one is called the extinction. This effect produces a reduction in diffracted intensity as a crystal become more nearly perfect. Usually the crystal is imperfect but not ideally imperfect and hence the measured intensity is somewhat less than the value predicted by the basic intensity equation which is derived for the ideally imperfect crystals.

So now we have rest up to the last slide of this particular lecture so just we are going to summarize the whole lecture so first in this lecture so first in this lecture we have discussed about the x-ray diffraction.

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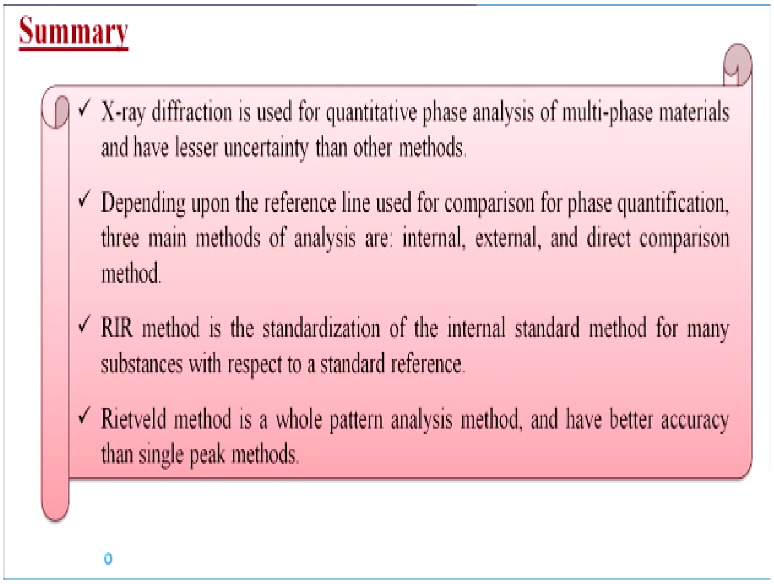

Summary

- ✓ X-ray diffraction is used for quantitative phase analysis of multi-phase materials and have lesser uncertainty than other methods.
- ✓ Depending upon the reference line used for comparison for phase quantification, three main methods of analysis are: internal, external, and direct comparison method.
- ✓ RIR method is the standardization of the internal standard method for many substances with respect to a standard reference.
- ✓ Rietveld method is a whole pattern analysis method, and have better accuracy than single peak methods.

Is used for the quantitative phase analysis of multi-phase materials and have lesser uncertainty than other methods. Depending upon the reference line used for comparison for phase quantification, three main methods of analysis are internal, external and direct comparison method. RIR method is the standardization of the internal standard method for many substances with respect to a standard reference. Rietveld methods are a whole pattern analysis method and have better accuracy than single peak methods, Thank you.

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