Characterization of Engineering Materials

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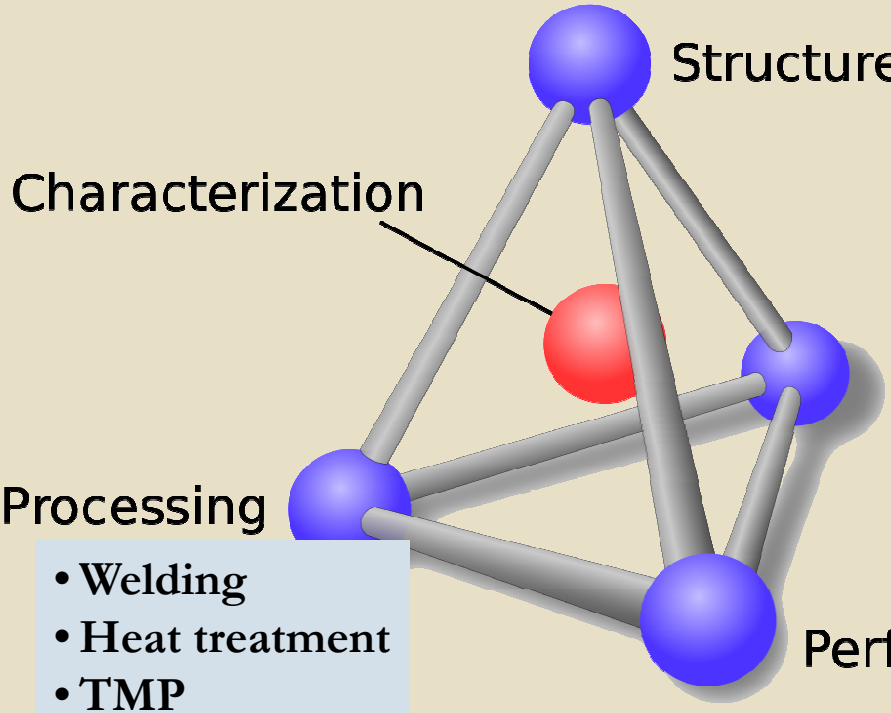
Need for characterization



- macro
- micro

- Mechanical
- Thermal
- Corrosion/oxidation
- Irradiation
- Magnetic
- Electrical
- Optical

- Welding
- Heat treatment
- TMP
- TCP

- Long life
- Safety

- Understanding materials behaviour
- Evaluation of products
- Life assessment and prediction
- Development of materials and processes

Materials Environment

Corrosive

High Temperature

Compressive stress

Residual stress

Tensile stress

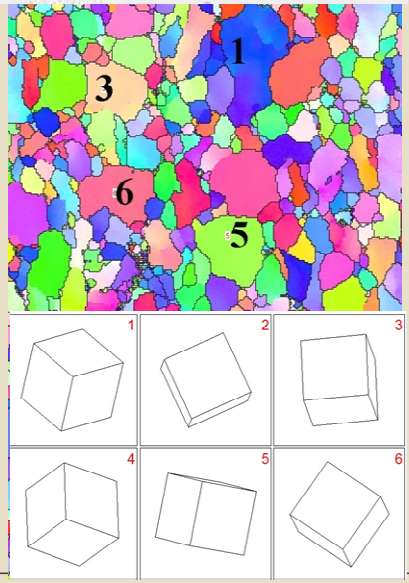
Ratchetting

Fatigue

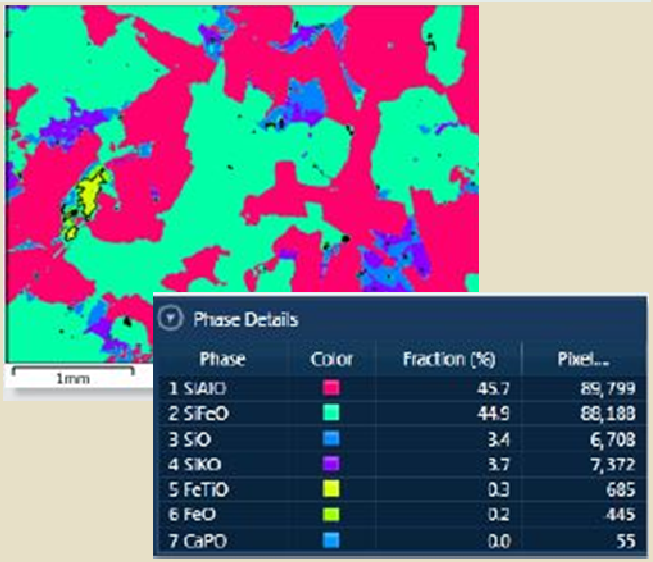
Deformation

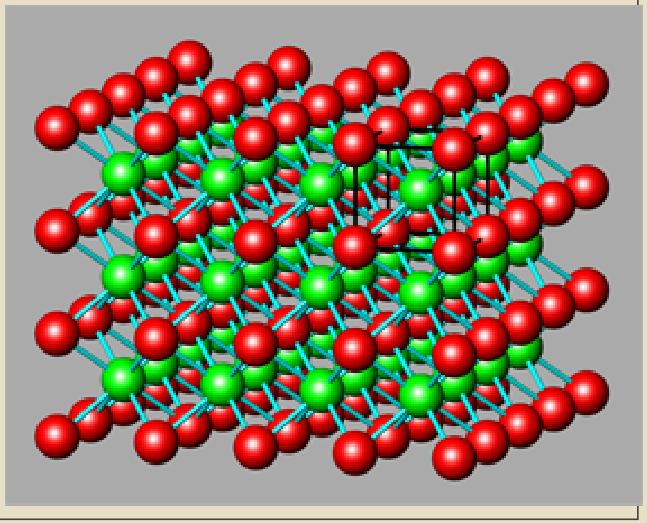
Microstructural defects

What is Microstructure?



- Morphology
- Microchemistry/ Composition
- Crystal structure
- Texture

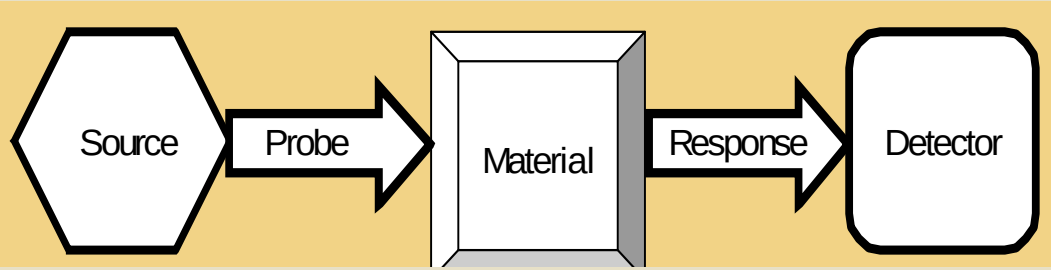




How do we characterize?

Nature of materials

- Crystalline, amorphous
- Metal,Semi-conductor, Ceramic/insulator
- Bulk or Surface



Techniques

Spectroscopy

- Optical
  - FTIR, Raman, …
- Mass
  - SIMS, ICPMS,..
- X-ray
  - XRF, XPS, …
- Nuclear
  - NMR, Mossbauer,…

Diffraction

- X-ray
- Electron
- Neutron

Microscopy

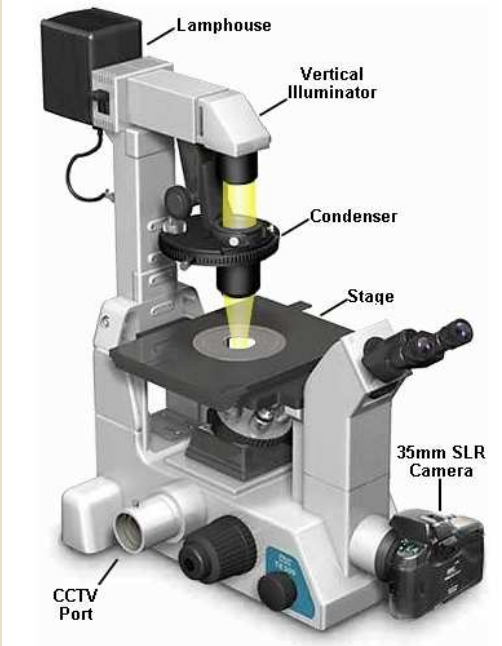
- Optical
- Electron
  - SEM, TEM
- Scanning probe
  - Tunneling
  - AFM

Optical Microscopy

- Resolution of human eyes is of the order of 0.3 mm.
- Features to be observed:
  - Grain shapes and size: from <μm to the cm regime
  - Precipitate size: mostly in the μm regime
  - Volume fractions and distributions of various phases
  - Defects such as cracks and voids: <μm to the cm regime

Compound Optical Microscope

- Visible light as illumination source
- Range of samples characterized - almost unlimited for solids
- Usually nondestructive; sample preparation may involve material removal



Optical Microscopy- Resolution

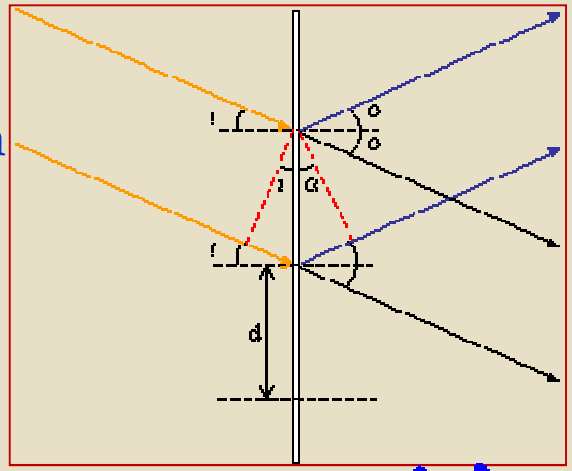
- **Transmitted OM** - transparent specimens like thin section of rocks, minerals and single crystals- *absorption*
- **Reflected OM** - opaque specimens like metals, ceramics, semiconductors - *reflection*

Inverted microscope - Materials science

Typical magnification in optical microscope is up to 1000x

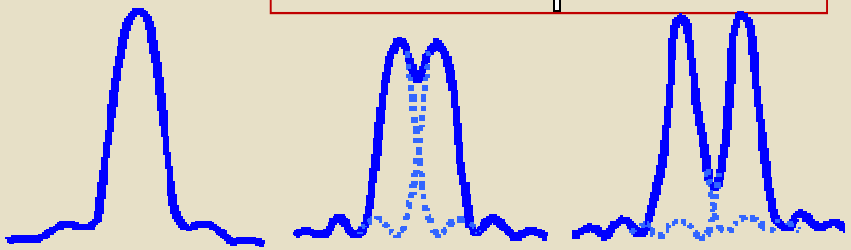
Resolution and Magnification:

d of two points is such that **central maximum** of one source falls on the **first diffraction minimum** of the other



$$d = \lambda / 2n\sin\alpha$$

d ~ 0.3µm for λ =0.55µm



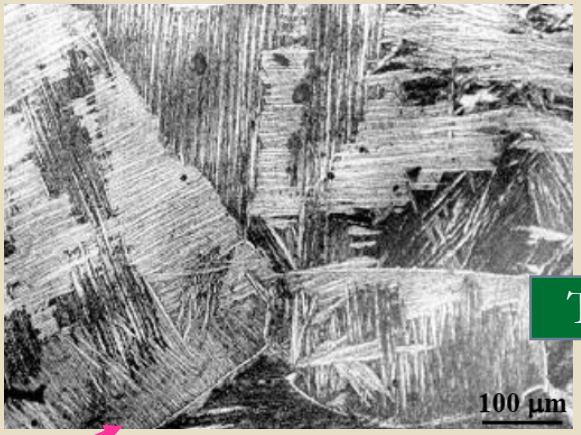
Useful magnification

= 0.3µm/ 0.3mm = 1000

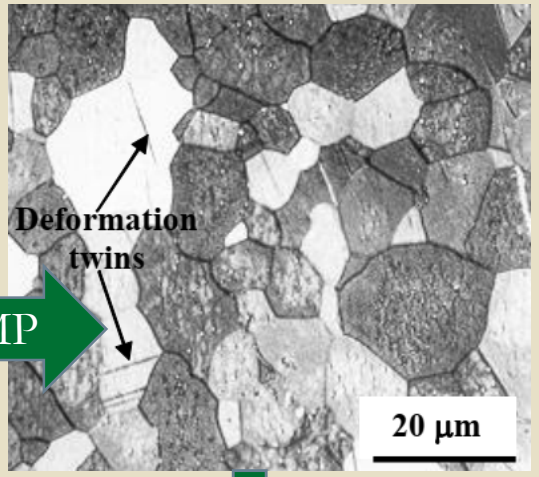
Any further zooming is of no use!

Morphology

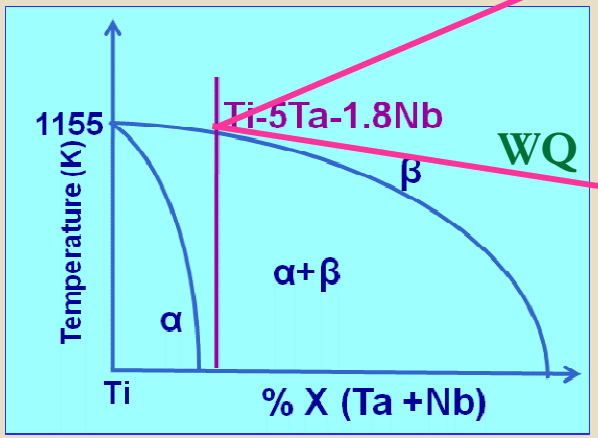
- Phase transformation
- Processing Route
- Volume fraction & size of phases

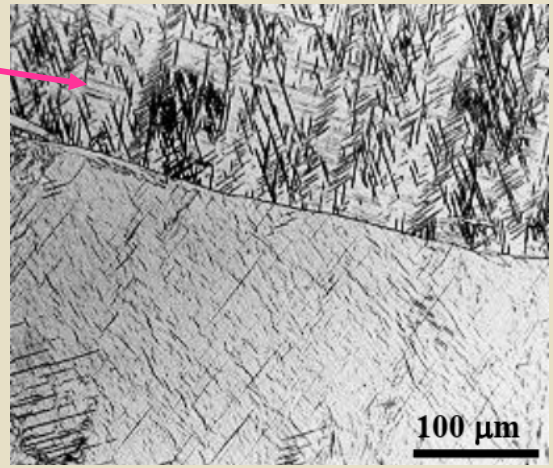


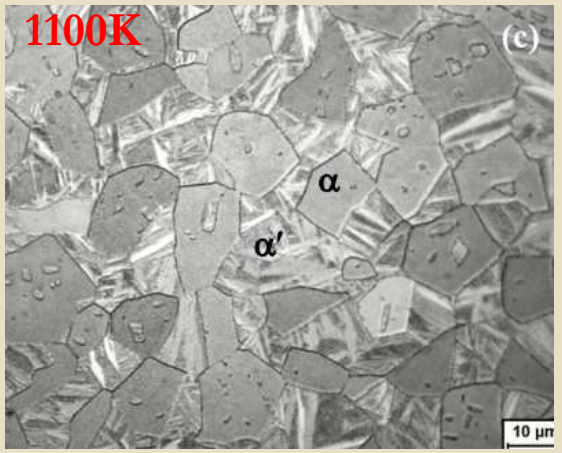
TMP



FC







Identification of phase regimes- 9Cr-1W-0.06Ta RAFM steel

Effect of cooling rate

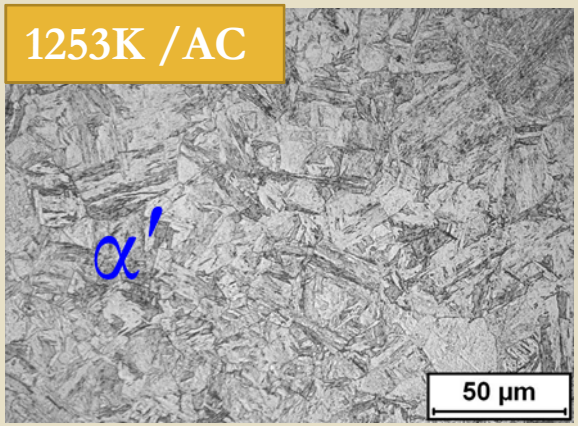
T_s=1253K → Water Quench, Air Cool, Furnace Cool

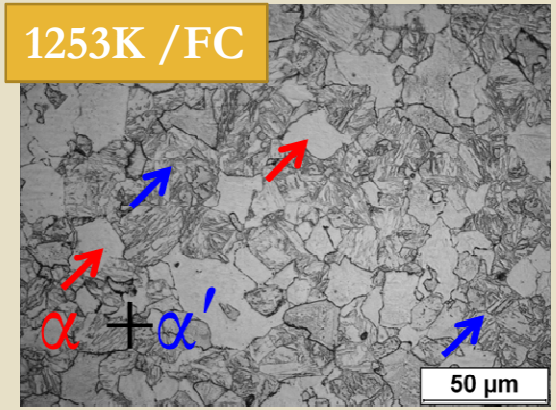
T_s=1323K → Water Quench, Air Cool, Furnace Cool

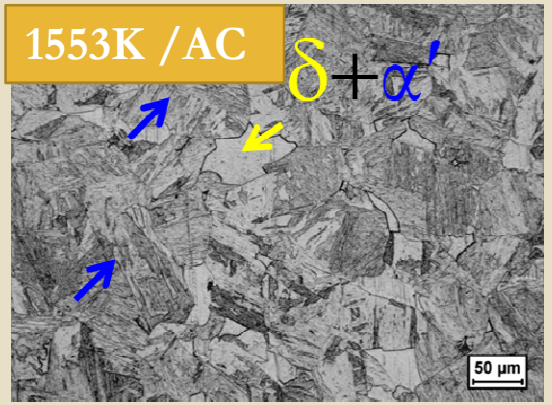
Effect of Ts

T_s=1453 K → Water Quench, Air Cool, Furnace Cool

T_s=1553K → Water Quench, Air Cool, Furnace Cool



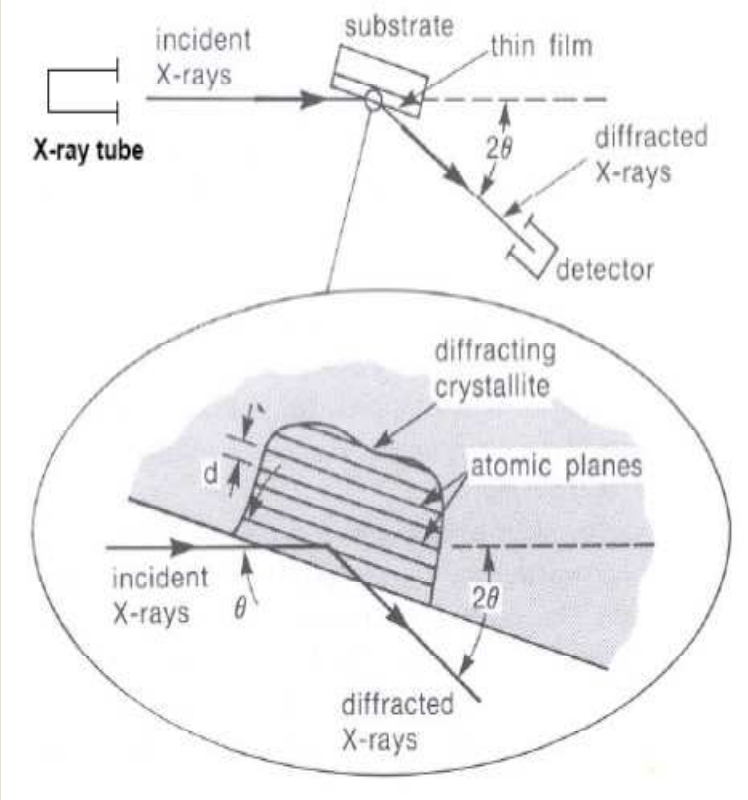




1253K >γ phase field< 1453K

1453K>T_δ <1553K

X-ray Diffraction



Bragg's law: $2d_{hkl}\sin\theta = n\lambda$

Source:

Monochromatic – Powder XRD

White- Single crystals

Mo Kα1	0.709300Å
Cu Kα1	1.54056Å
Co Kα1	1.788965Å
Cr Kα1	2.28970Å

Sample: Powder or bulk specimen with flat and smooth surface

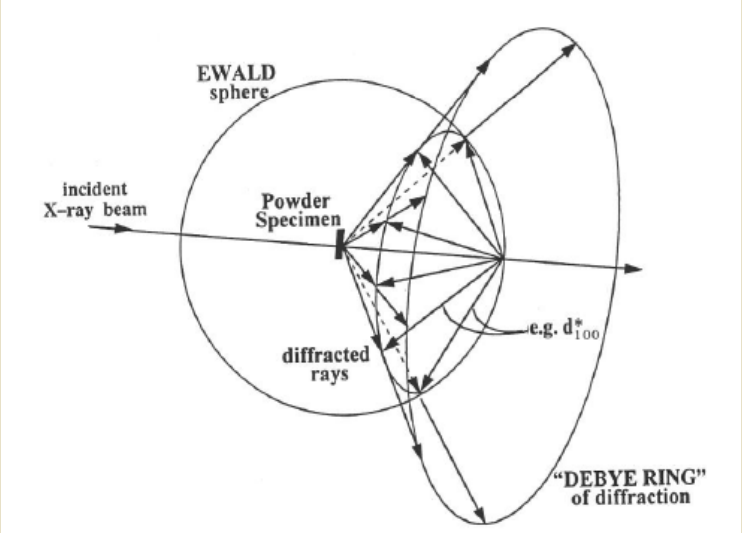
Geometry:

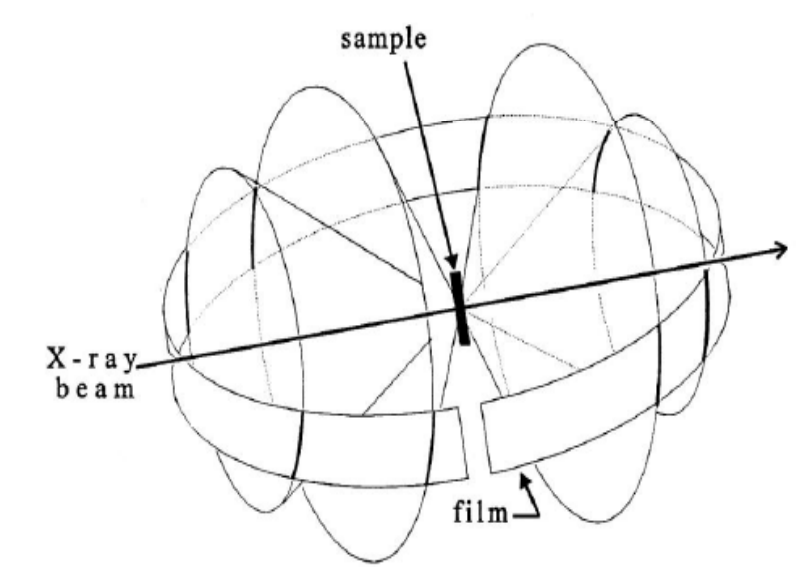
θ:2θ : tube is fixed, sample rotates at θ°/min and detector rotates at 2θ °/min.

θ:θ : sample is fixed and tube rotates at a rate of θ°/min and detector rotates at a rate of θ °/min.

Powder X-ray Diffraction

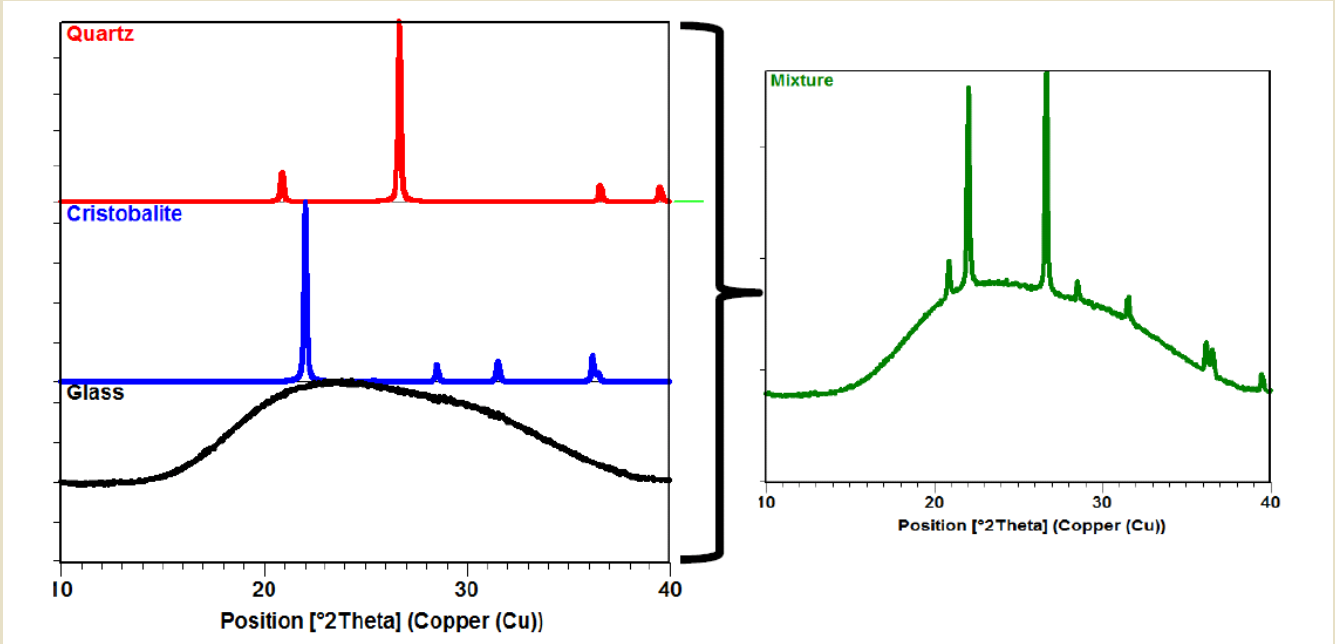
- Powder- collection of small crystallites oriented randomly
- X-ray beam falls simultaneously on many crystals and sees all the planes
- By varying the angle all the possible diffraction peaks detected





Au, FCC

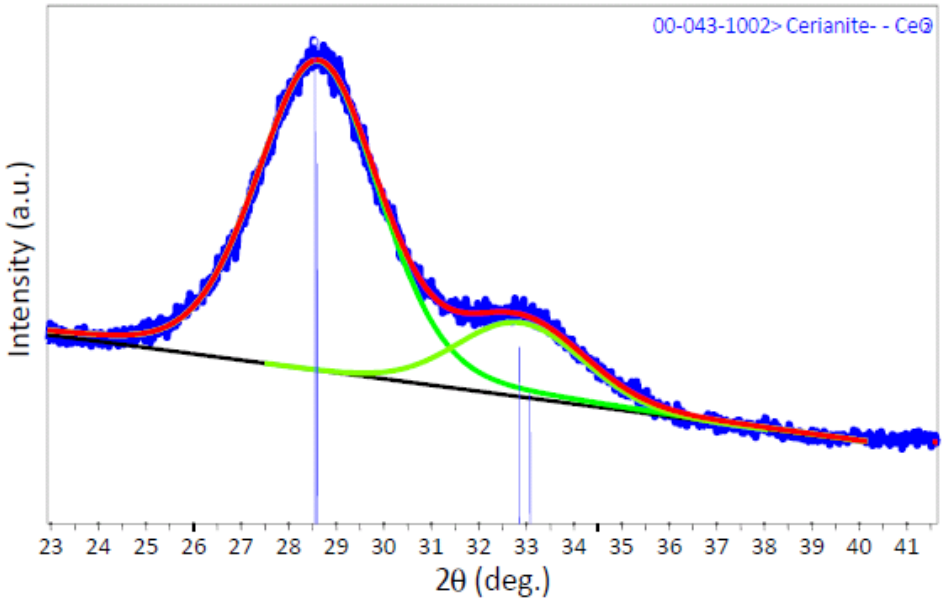
Powder X-ray Diffraction



■ peak position	➢	dimension of the elementary cell
■ peak intensity	➢	content of the elementary cell
■ peak broadening	➢	strain/crystallite size
■ scaling factor	➢	quantitative phase amount
■ diffuse background	➢	false order
■ modulated background	➢	close order

Crystallite size and microstrain

- Crystallites smaller than ~120nm create broadening of diffraction peaks
  - this peak broadening can be used to quantify the average crystallite size of nanoparticles using the Scherrer equation
  - must know the contribution of peak width from the instrument by using a calibration curve
- microstrain may also create peak broadening
  - analyzing the peak widths over a long range of 2theta using a Williamson-Hull plot can let you separate microstrain and crystallite size



$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$

Texture analysis

- Orientation of Crystals is not random
- Preferred Orientation of crystals

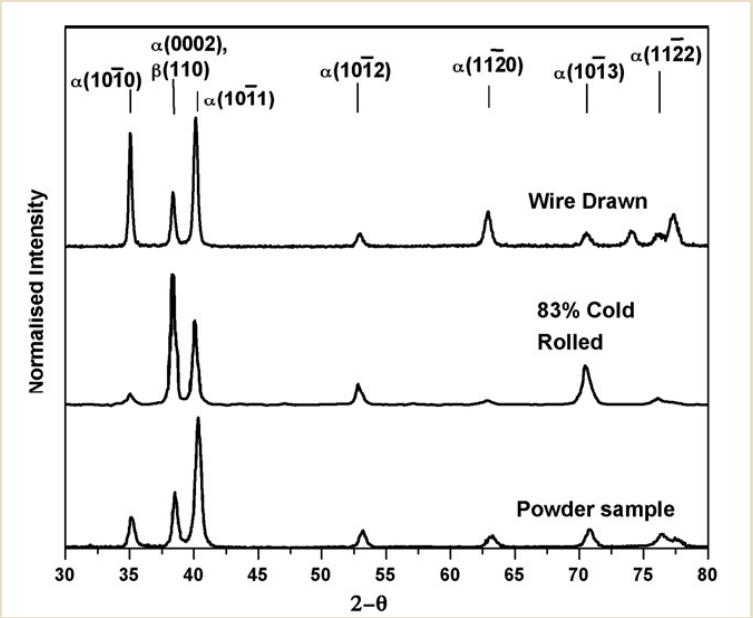
→ Anisotropy of properties

Macro texture: XRD

Micro texture : EBSD in SEM, OIM in TEM

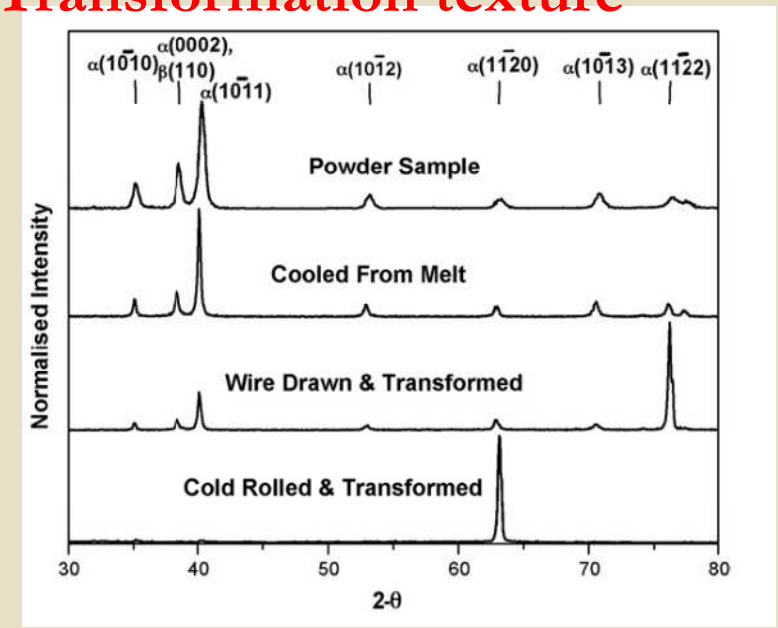
Types
- Deformation
- Recrystallisation
- Transformation

Deformation texture



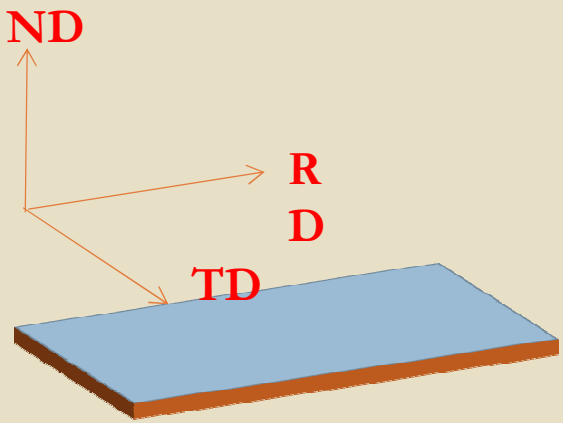
Ti-5Ta-2Nb alloy

Transformation texture



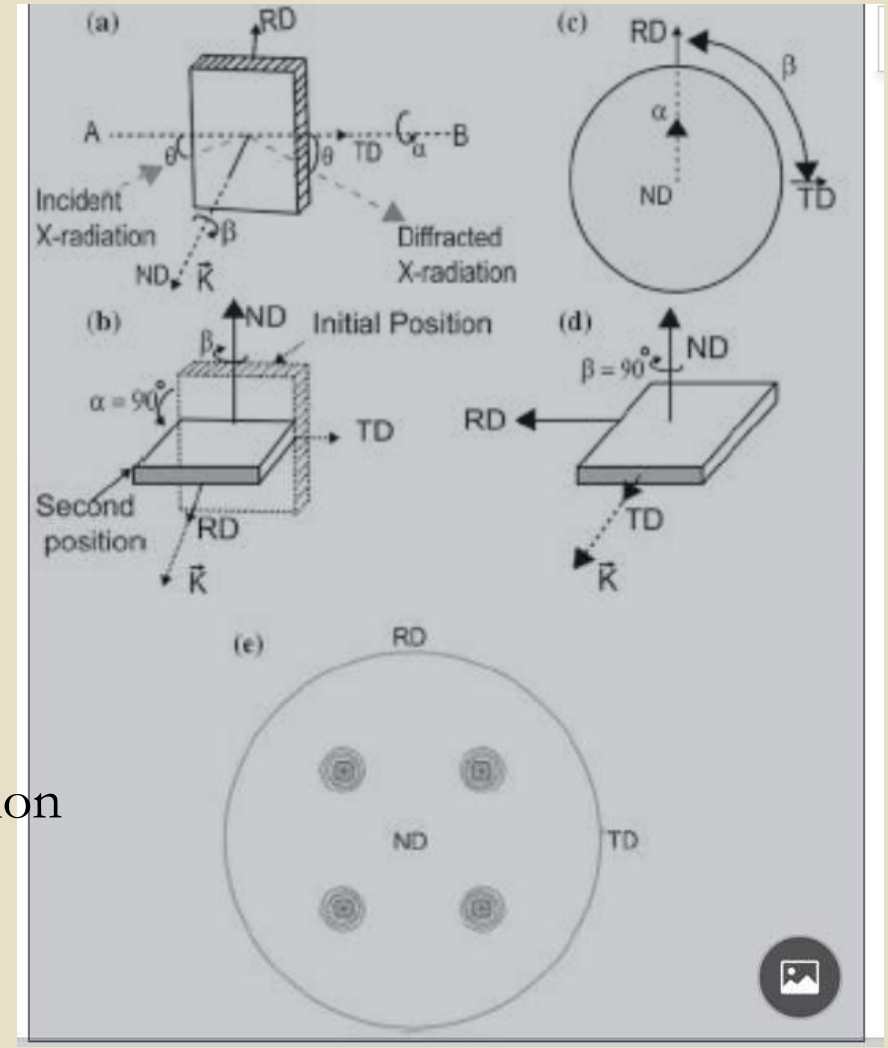
T. Karthikeyan et al. / Materials Science and Engineering A 485 (2008) 581–588

Texture Representation



Pole figures

Stereographic projection of distribution of crystallographic planes w.r.t the specimen co-ordinates



Electron Microscopy techniques for microstructural analysis

- **Optical**
- **Electron**
- **Ion**

❖Negative Charge - Beam Focus / Deflection by Electric Coils

❖Low Mass – Non destructive for most materials

❖Dual Behavior of Electron – Wave & Particle

Wave Behavior

❖Elastic Scattering - Images (phase / amplitude contrast)

❖Diffraction patterns – Crystallography

❖Shorter Wavelength– Better Resolution

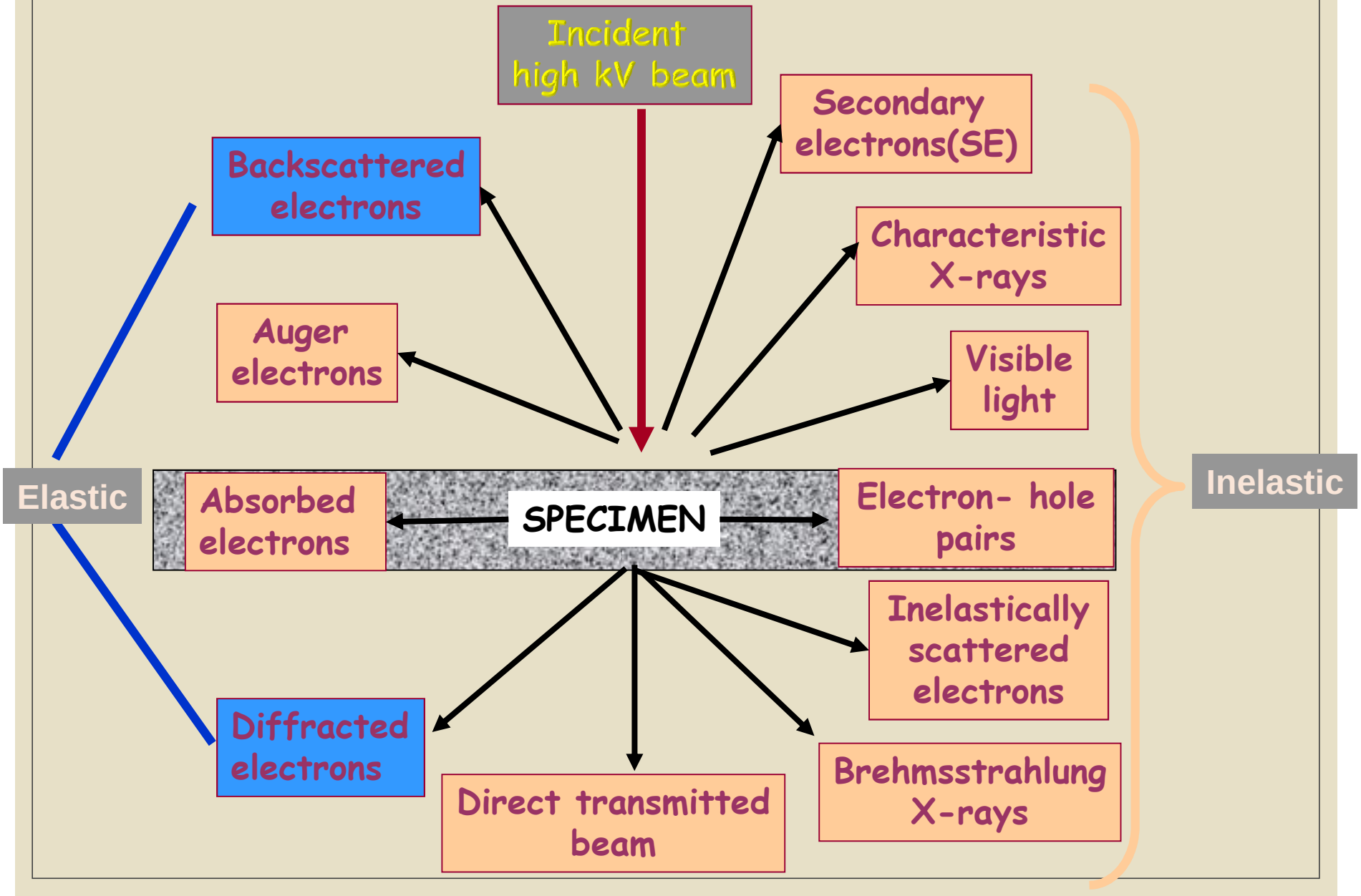
Particle Behavior

❖Electron specimen interactions

❖No. of signals generated - Inelastic scattering, Ionisation

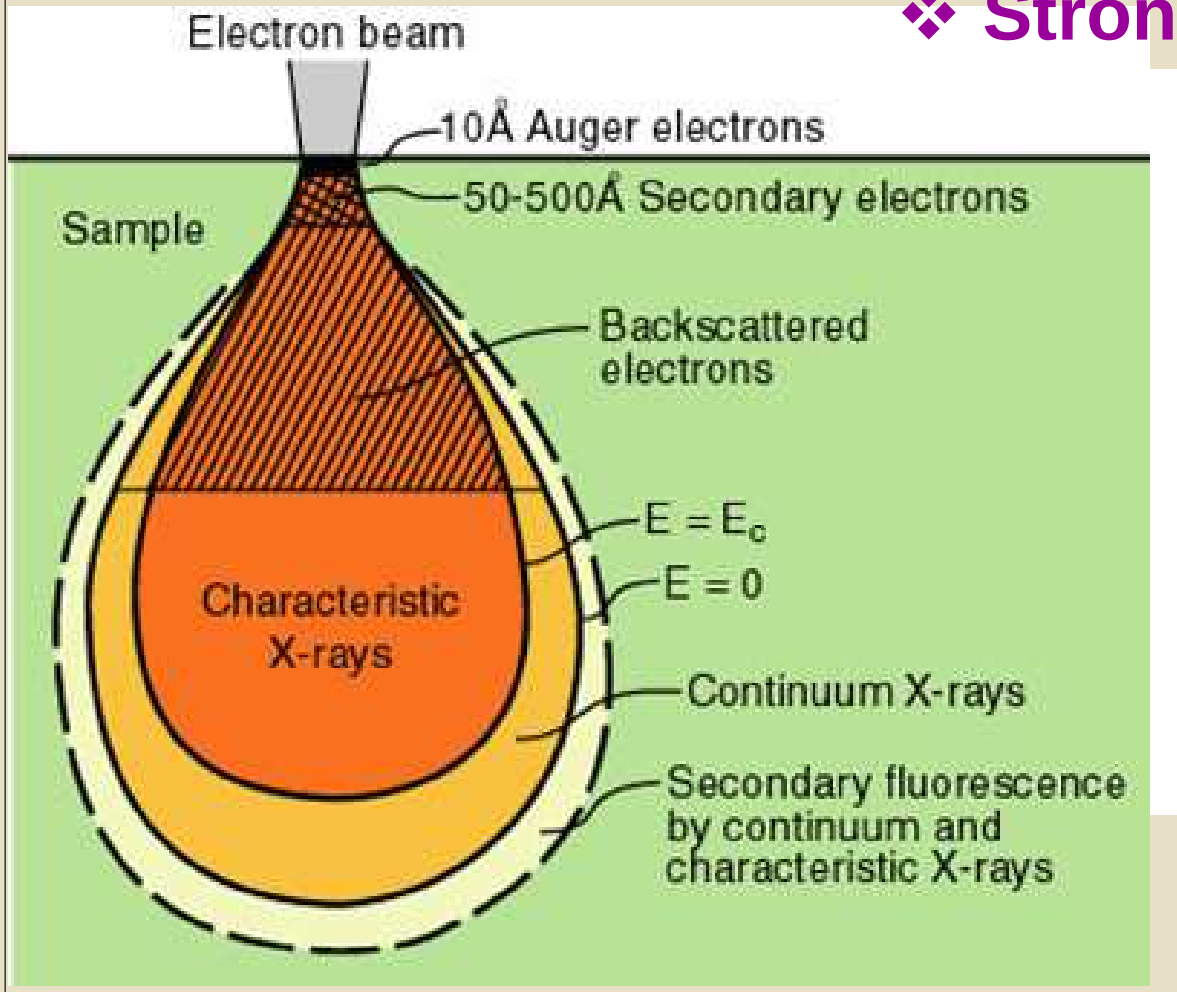
❖Wealth of information - Chemical information

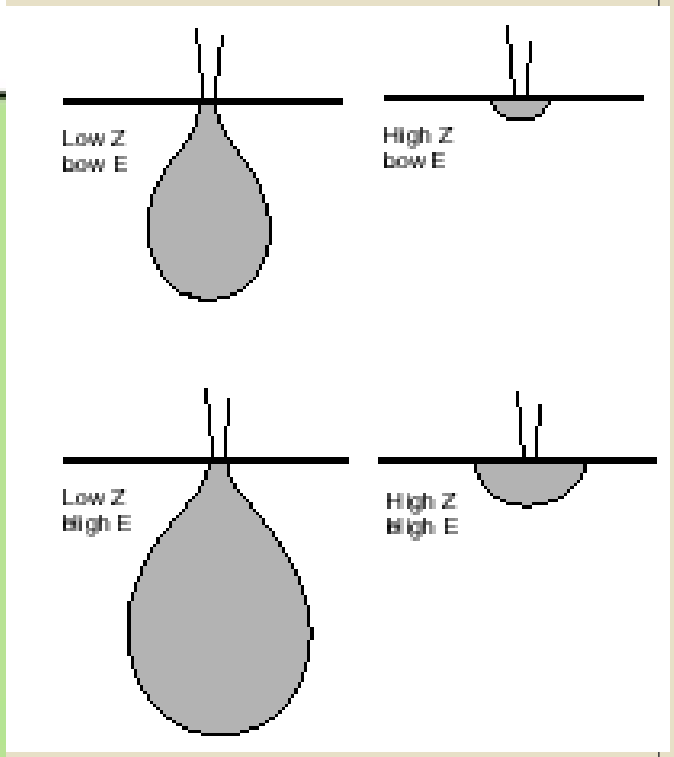
ELECTRON-MATTER INTERACTION



Volume of Excitation

❖ **Strong function of E, Z**





Surface analytical and bulk techniques

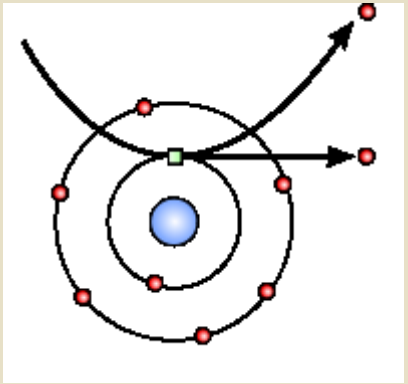
Spatial Resolution

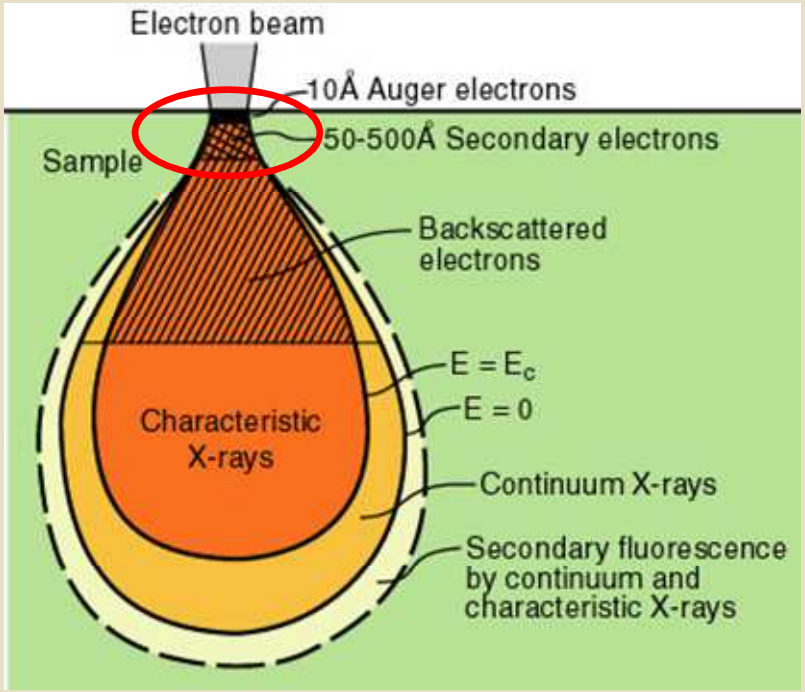
Comparing SEM and TEM

	TEM	SEM
Electron Beam	Broad, static beams	Beam focused to fine point; sample is scanned line by line
Voltages Needed	TEM voltage ranges from 60-300,000 volts	Accelerating voltage much lower; not necessary to penetrate the specimen
Interaction of the beam electrons	Specimen must be very thin	Wide range of specimens allowed; simplifies sample preparation
Imaging	Electrons must pass through and be transmitted by the specimen	Information needed is collected near the surface of the specimen
Image Rendering	Transmitted electrons are collectively focused by the objective lens and magnified to create a real image	Beam is scanned along the surface of the sample to build up the image

Secondary electrons (SE)

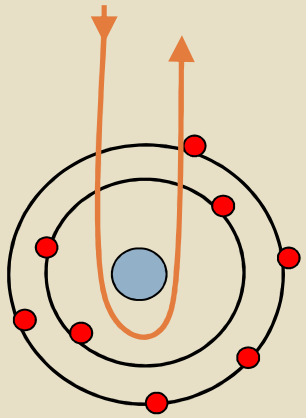
- Generated from the collision between the incoming electrons and the loosely bonded outer electrons
- Low energy electrons (~10-50 eV)
- Only SE generated close to surface escape (topographic information is obtained)
- Number of SE is greater than the number of incoming electrons



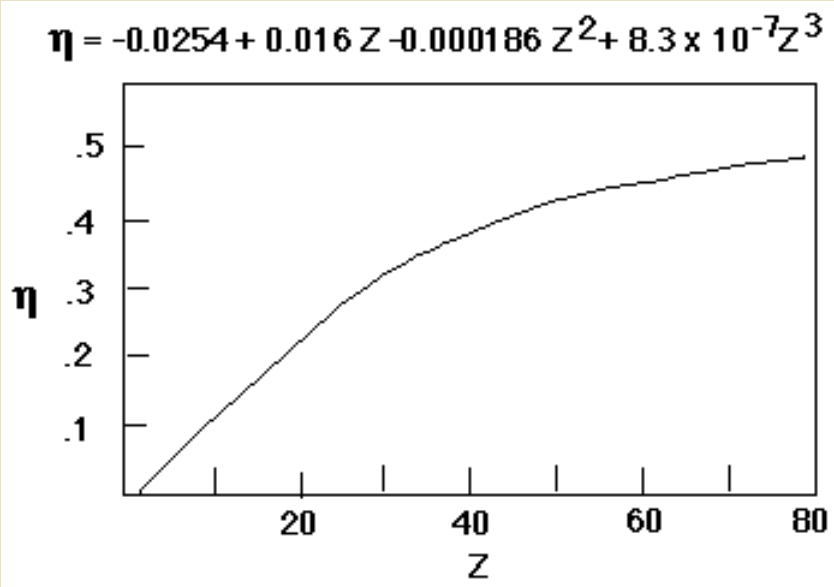


Backscattered electrons (BSE)

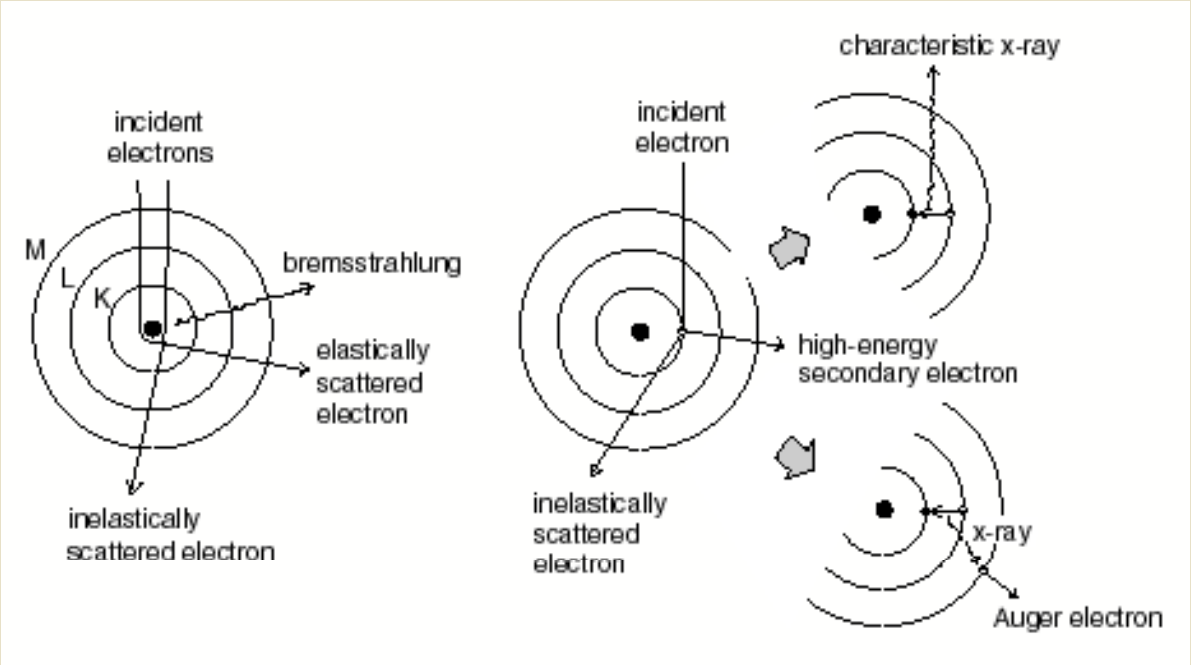
- A fraction of the incident electrons retarded by the electro-magnetic field of the nucleus and if the scattering angle >180° the electron can escape from the surface



- High energy electrons (elastic scattering)
- Fewer BSE tha $E_e \approx E_0$
- Probes higher depth than SE
- Depends of atomic number
- Undergoes Diffraction- EBSD for Crystallographic identity & microtexture



X-ray emission - Principle



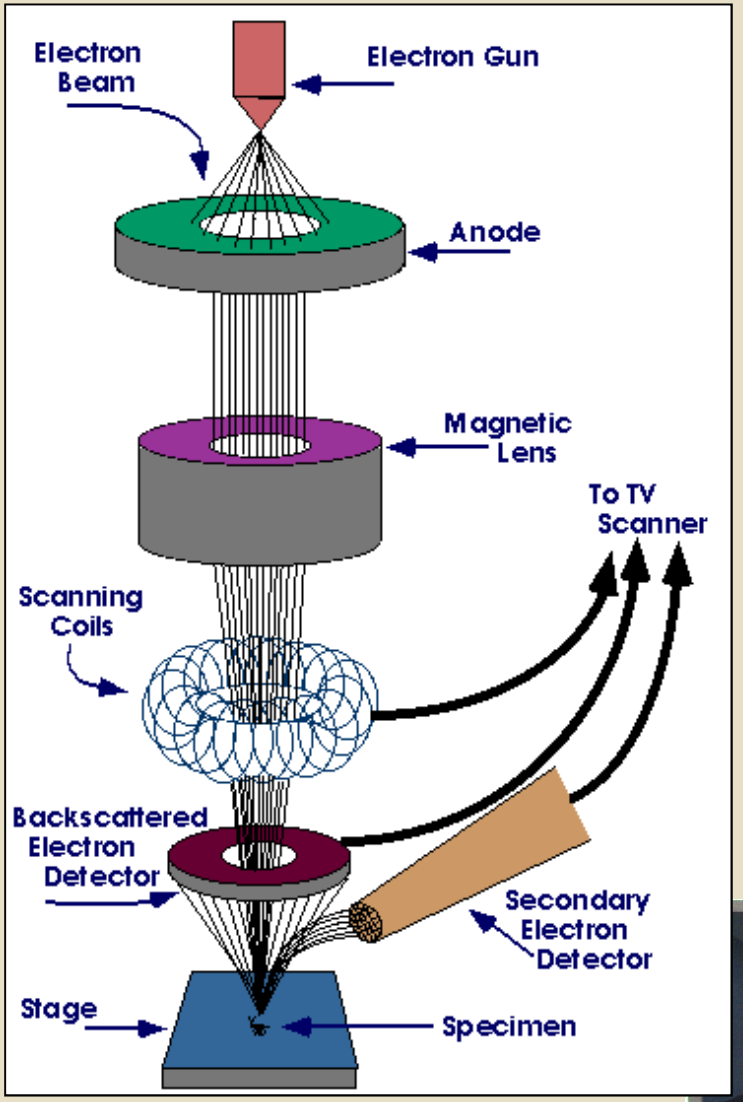
Inner-shell ionization => K-shell or higher-shell vacancies or heat depending on Critical ionization or excitation potential E_c

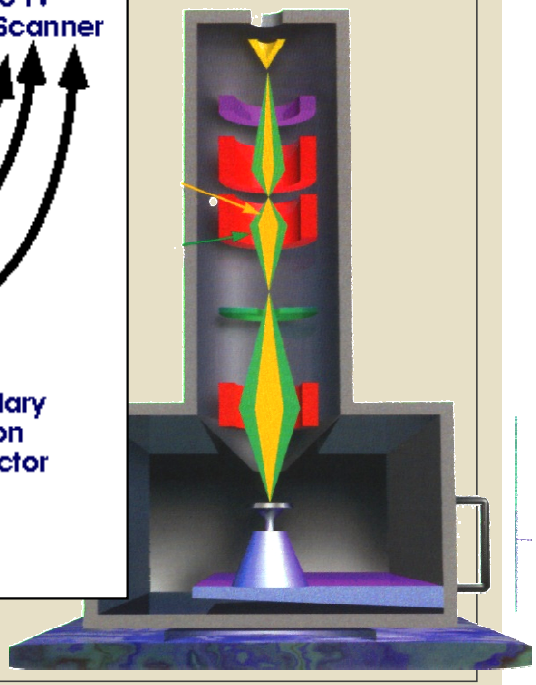
De-excitation => Characteristic X-radiation or Auger electron

- **X-rays emitted from the atom have a characteristic energy unique to the element from which it originated.**
- **These signals are collected and sorted according to energy or wavelength to yield elemental composition from micron size features of the specimens.**

Scanning Electron Microscope

- Gun
  - Filament
  - Wehnelt
  - Anode
- Electromagnetic Lenses
  - Usually three
- Spray apertures
  - At least one. More with higher resolution
- Scanning coils
  - Two sets X and Y deflection
- Stigmators
  - 1-2 sets
- Detectors
  - Could be several

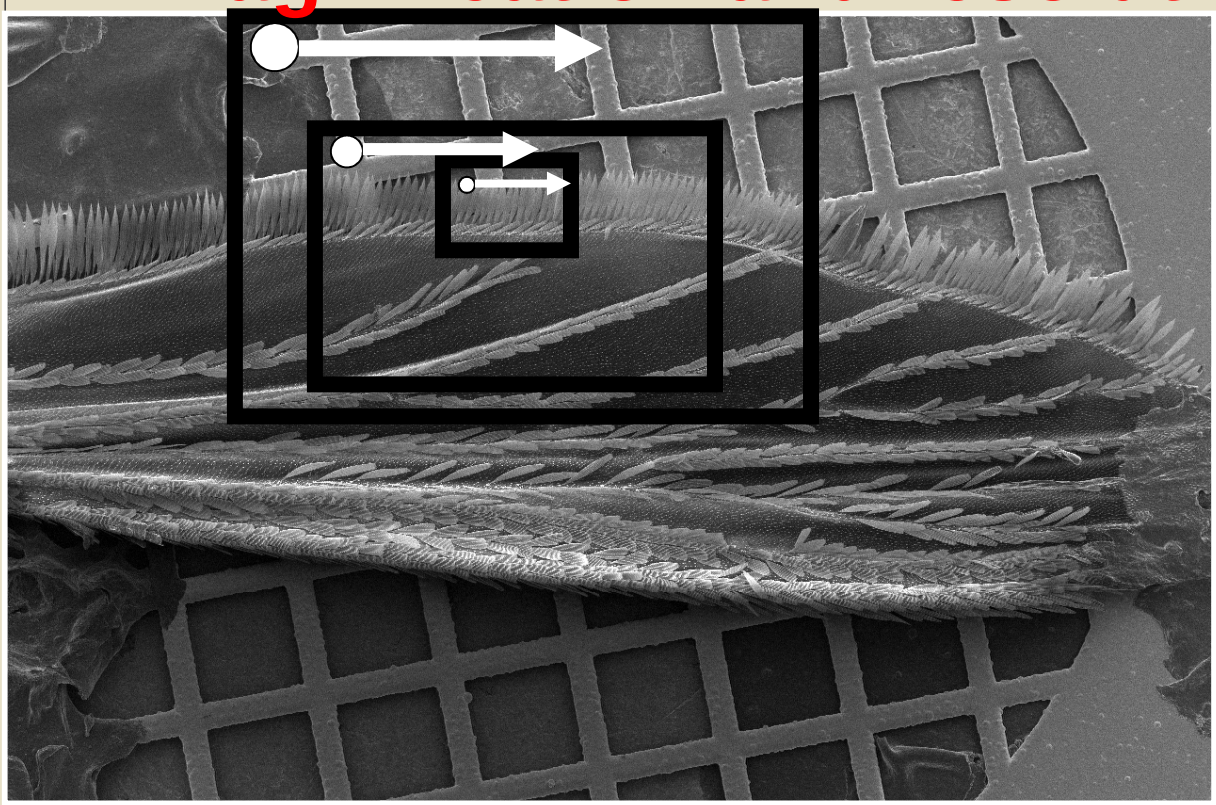




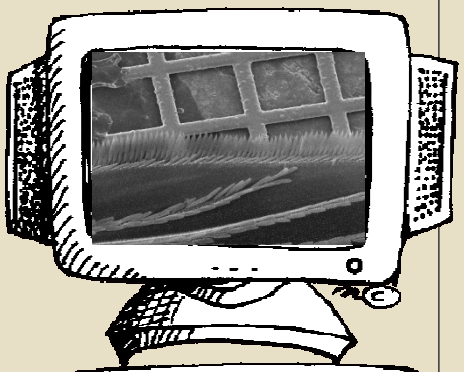
Samples

- Form: any solid or liquid having a low vapour pressure (10^{-3} torr, or 0.13 pa)
- Size:. Samples as large as 4-8 cm.
- Standard metallographic polishing and etching techniques are adequate for electrically conducting materials.
- Non-conducting materials are generally coated with a thin layer of carbon, gold, or gold alloy. Samples must be electrically connected to the holder
- Fine samples, such as powders, can be dispersed on electrically conducting film, such as a silver point that has been thoroughly dried. Samples must be free from high vapor pressure liquids, such as water, organic cleaning solutions, and remnant oil-base films

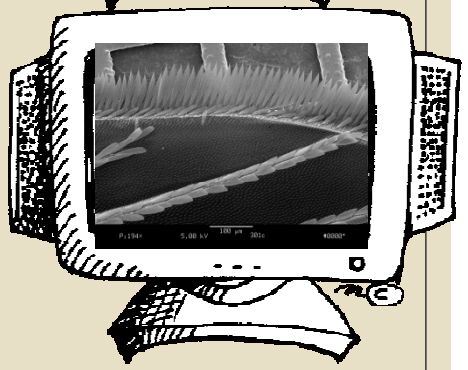
Magnification and resolution of SEM



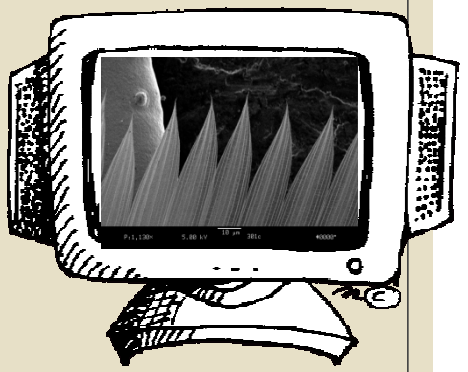
low



mid



high



Magnification increased by decreasing the area of scan on the specimen A virtual microscope!

Resolution is a function of the spot size

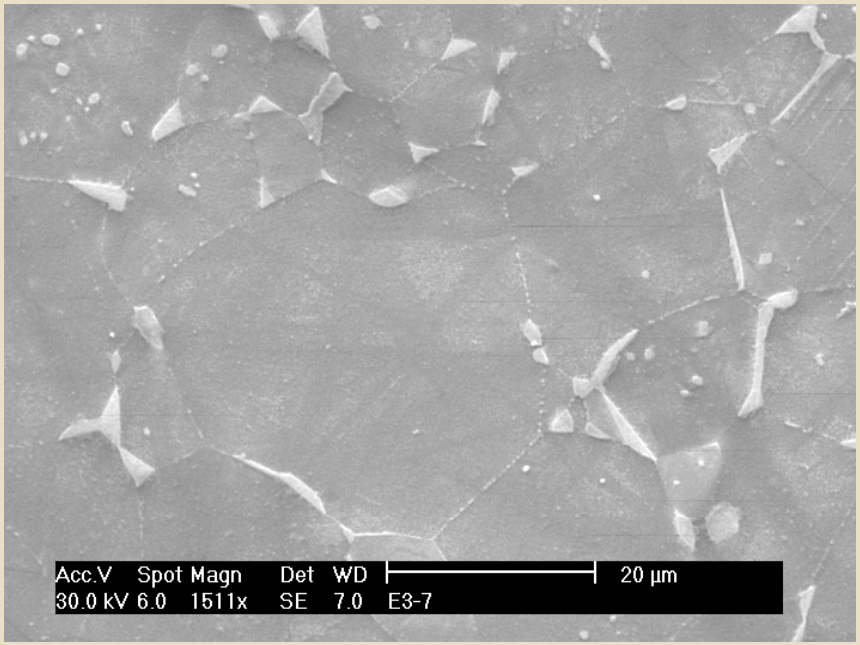
With a FEG gun the minimum spot size attainable ~1 nm

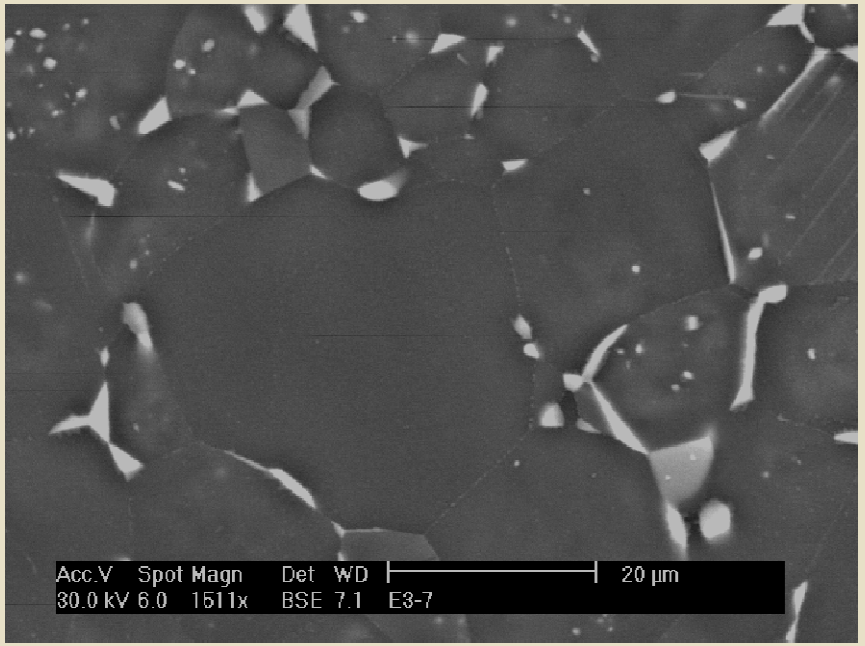
Maximum useful magnification = 0.2mm/1nm = 2,00,000

Decreasing spot size – Improves resolution ✓

Intensity loss ✗

Microstructure of a Ti-Ta-Nb alloy





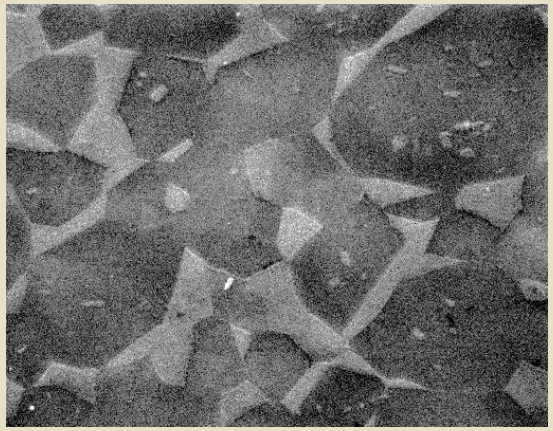
SE imaging ⇨ Morphology

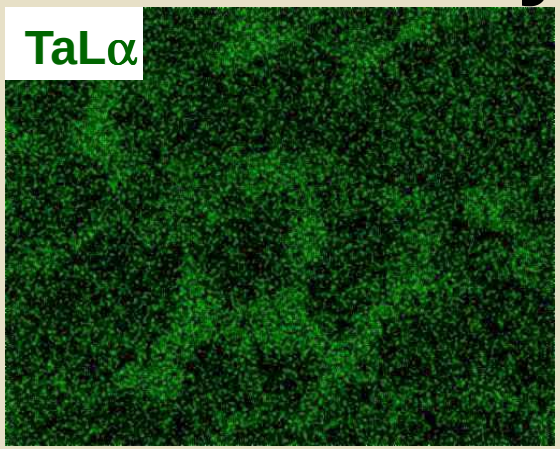
BSE imaging ⇨ Bright – High Z
Dark – Low Z

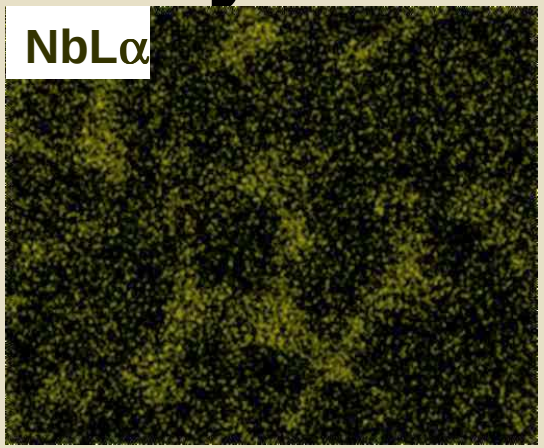
- **Grain Size**
- **Area fraction of phases**

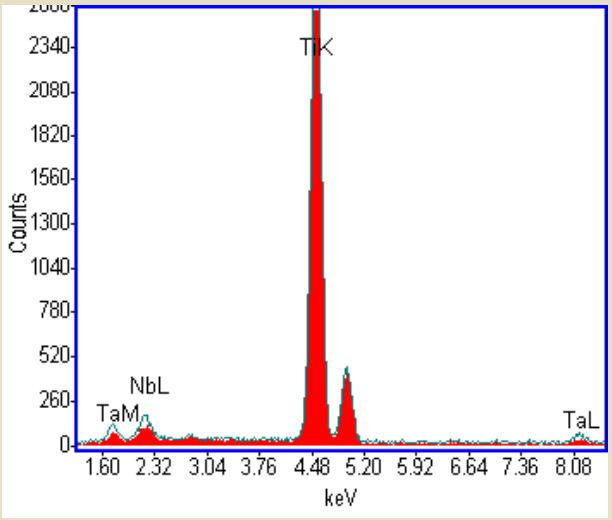
Chemical identity → EDS- X rays

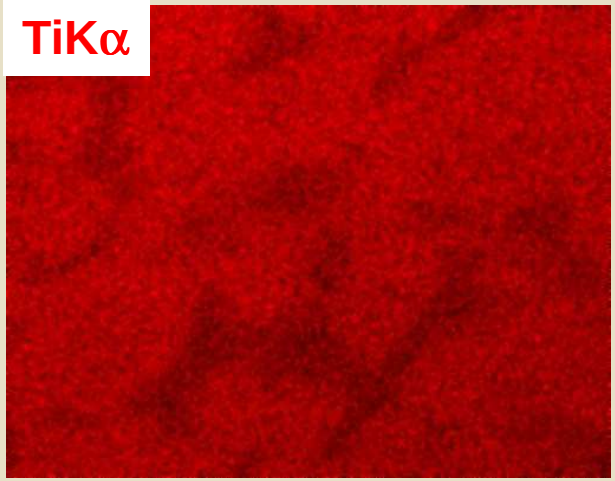
Energy Dispersive X-ray analysis











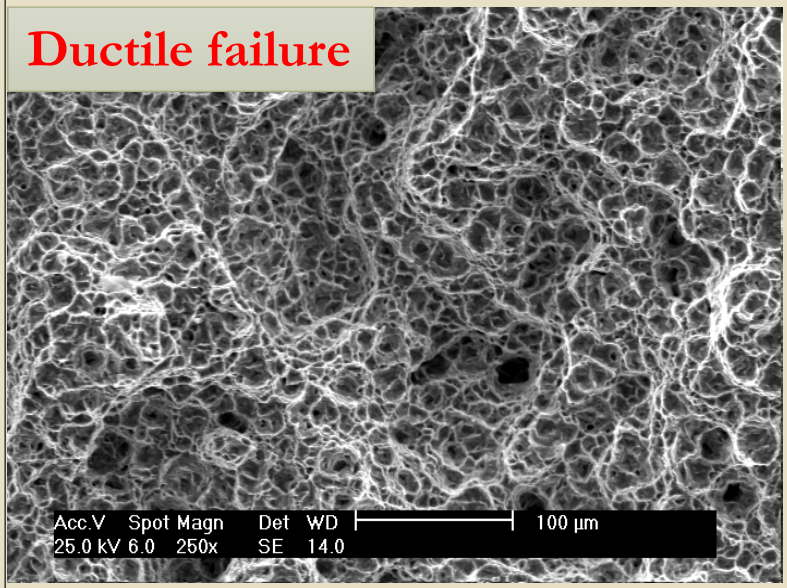
Higher enrichment of Ta and Nb in β phase than in α phase

- **Composition analysis from regions of a few microns size**
- **Spatial mapping of element distribution**

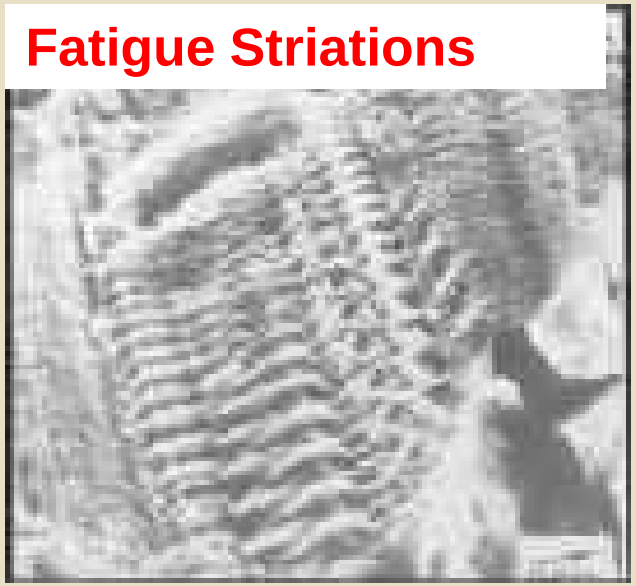
Fractography

- No sample preparation required
- High depth of field ⇨3D information

Ductile failure



Fatigue Striations

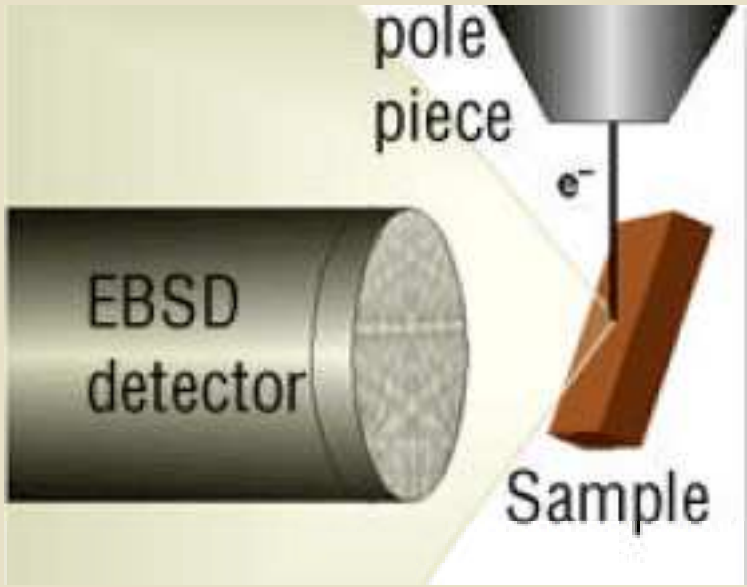


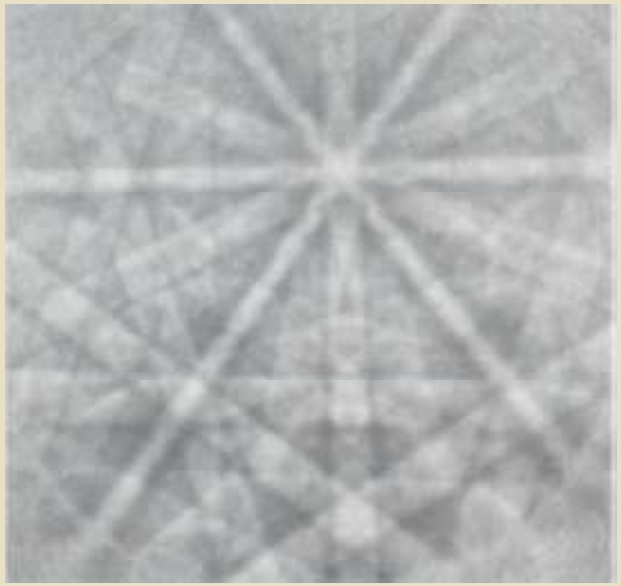
Intragranular

Intergranular

Identification of origin and mechanism of failure

Electron Back Scattered Diffraction





A typical EBSD pattern

- BSE undergo diffraction
- Diffracted electrons escaping from near surface produce Kikuchi bands imaged by film or a phosphor screen

- Symmetry of crystal lattice
- Width of bands are a measure of the interplanar spacing
- Angles between bands are related to the angles between planes in the lattice.

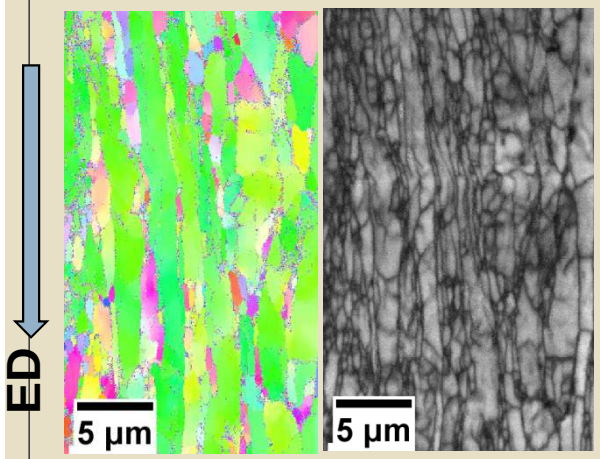
Fabrication of 18Cr ODS Ferritic Steel clad tube

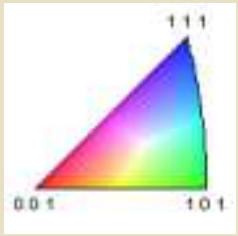
Extruded rod

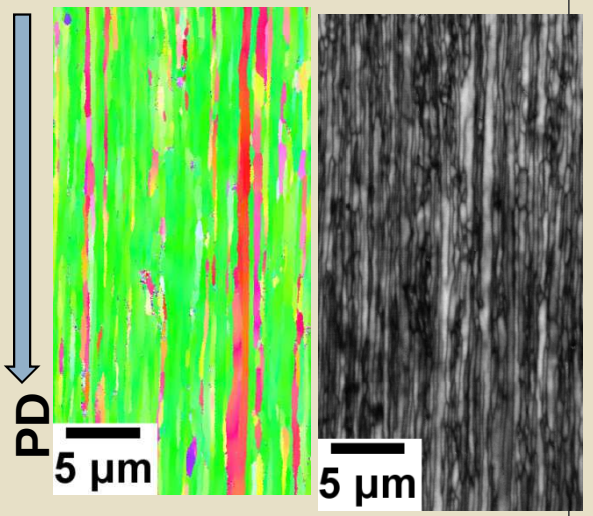
Pilgering

Clad tube

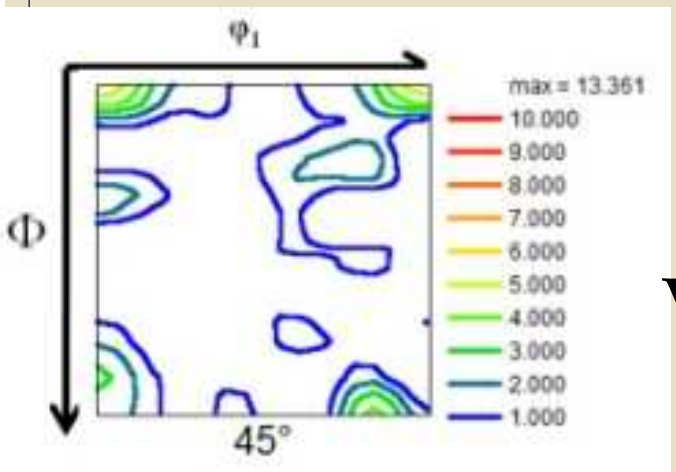
Double Int. annealing @ 1323 & 1423-1473K



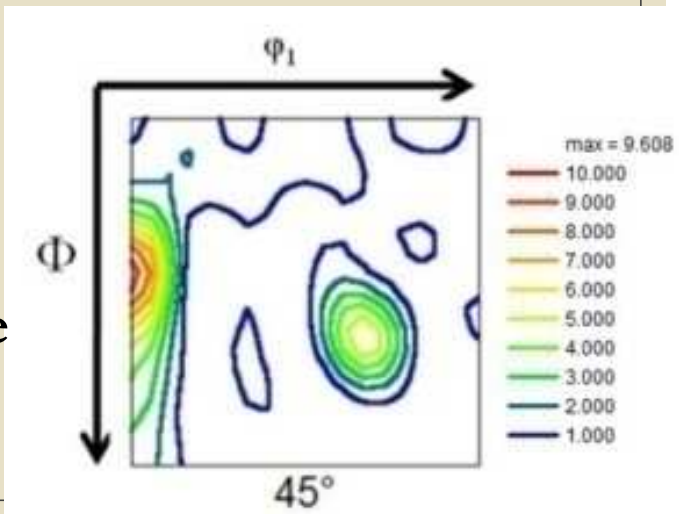




Elongated Bamboo like ferrite grains

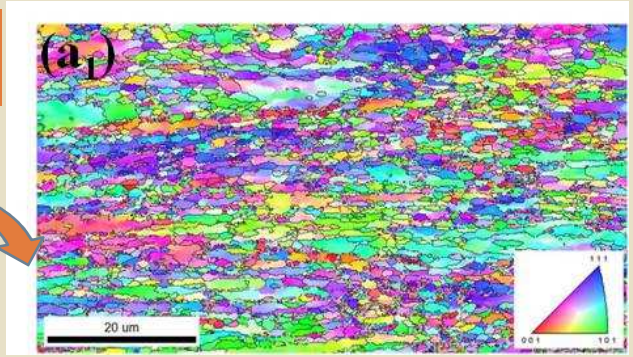


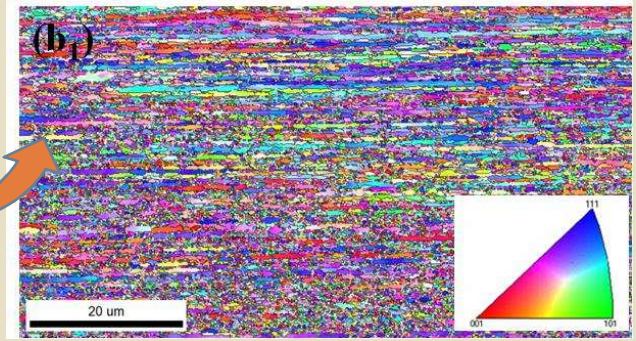
Very strong α texture (<110> || ED/PD)



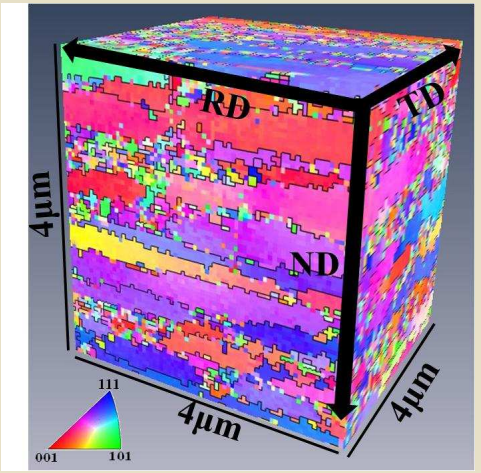
Recrystallisation in Mod.9Cr-1Mo steel

Cold Rolling (90%)

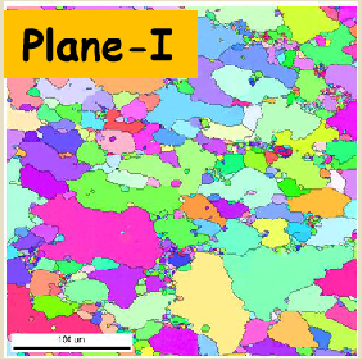


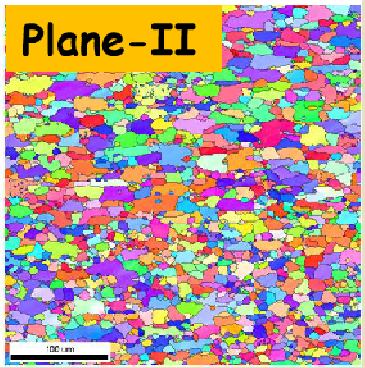


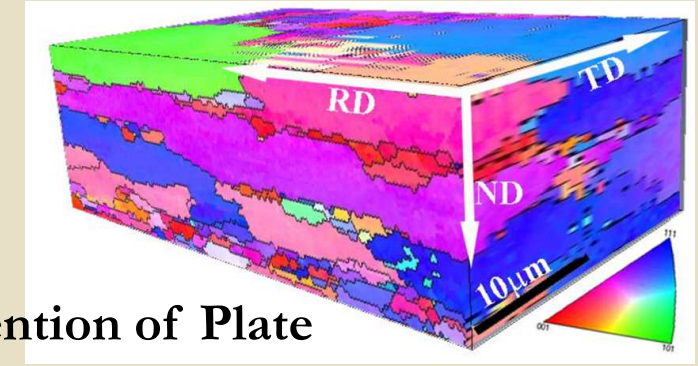
3D reconstruction



Recrystallisation @1023K







Retention of Plate like morphology

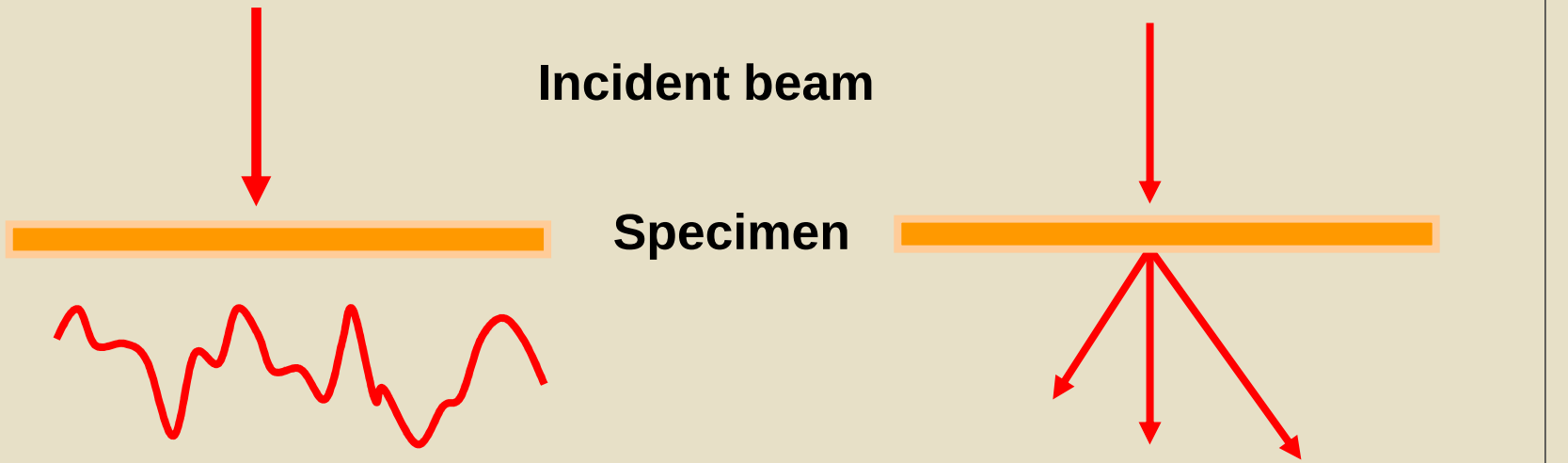
Partial recrystallisation

Pradyumna Kumar Parida et al, Trans IIM, Dec. 2018

Transmission Electron Microscopy

- Imaging of features at 1000 to 1000,000 X.
- Microstructural detail at resolution of <0.2nm
- Qualitative and quantitative elemental analysis of microstructural features as small as 10 nm
- Crystal structure and orientation determination of microstructural features as small as 10 nm
- Lattice imaging of crystals with inter-planar spacing > 0.12 nm
- Characterization of microstructure at very high magnification - metals, ceramics, geological materials, polymers, and biological materials
- Identification (composition and crystal structure) of inorganic phases, precipitates, and contaminants

Diffraction and Imaging in TEM

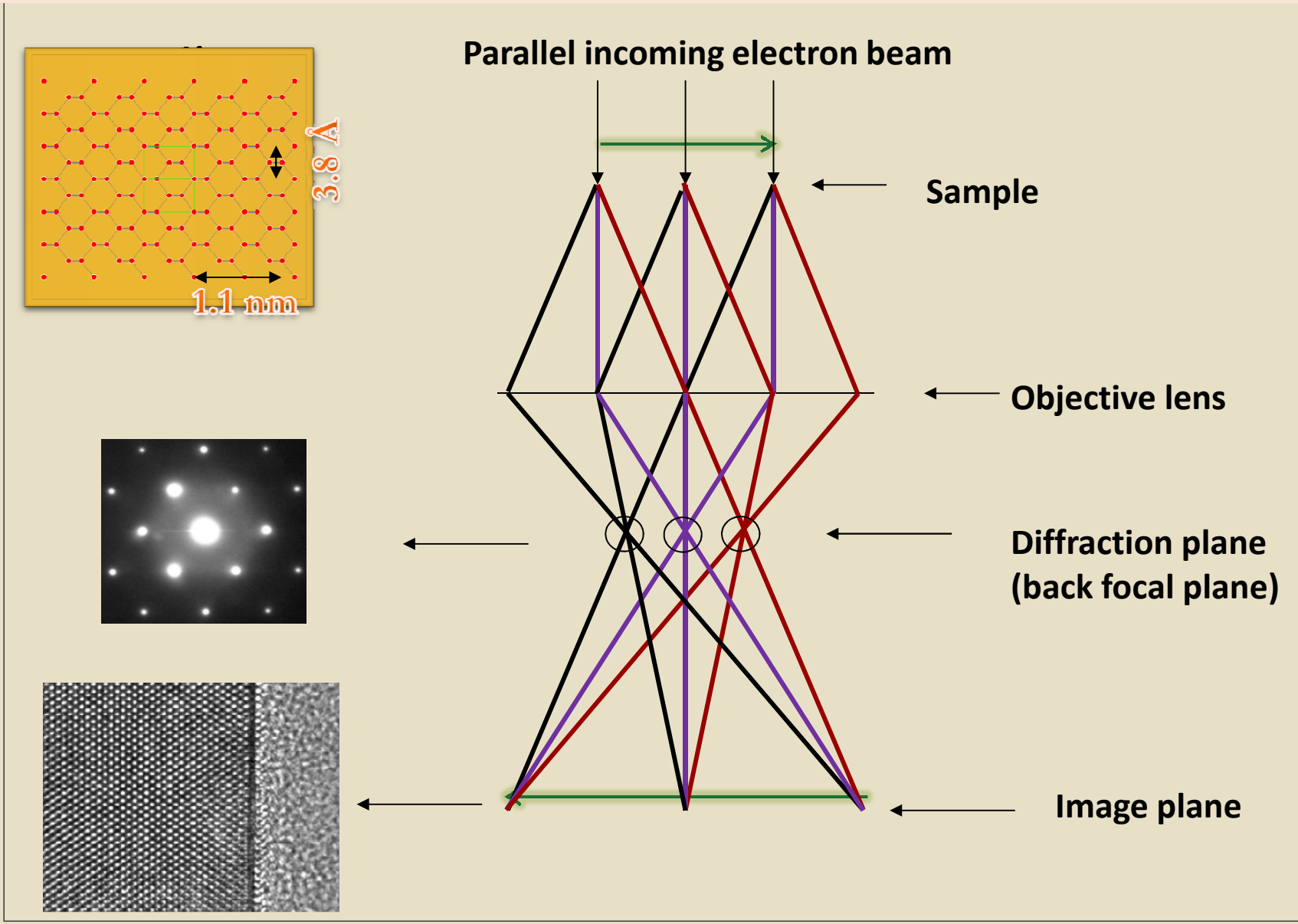


Spatial distribution-
Image : Real space image

Angular distribution - Diffraction
Pattern: Crystallography

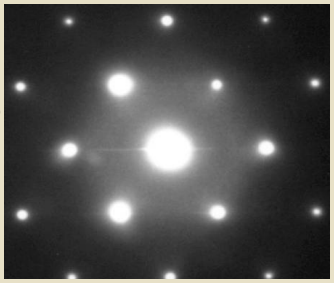
- Amplitude contrast
  - Mass-thickness
  - Diffraction
- Phase contrast

Simplified ray diagram



Electron diffraction

- Elastic scattered electrons
  - Only the direction of electron is changing (Bragg scattering)



- Elastic scattering is due to Coulomb interaction between the incident electrons and the electric charge of electron cloud and nucleus (Rutherford scattering).
- The elastic scattering is due to the average position of the atoms in the lattice
- Reflections satisfying Braggs law: $2d\sin\theta=n\lambda$

Electrons interact 100-1000 times stronger with matter than X-rays

- more absorption (need thin samples)

- can detect weak reflections not observed with X-rays

Electron Diffraction in TEM

- Consequences of small λ
  - Electron wave length at 200 kV = 2.508 pm
  - $1/\lambda \sim 400\ nm^{-1}$
  - $|g_{hkl}| = 1/d_{hkl} = 5\ nm^{-1}$ (typically)
- Very small Bragg angle (~1°)
  - Diffracting planes are nearly parallel to the primary beam

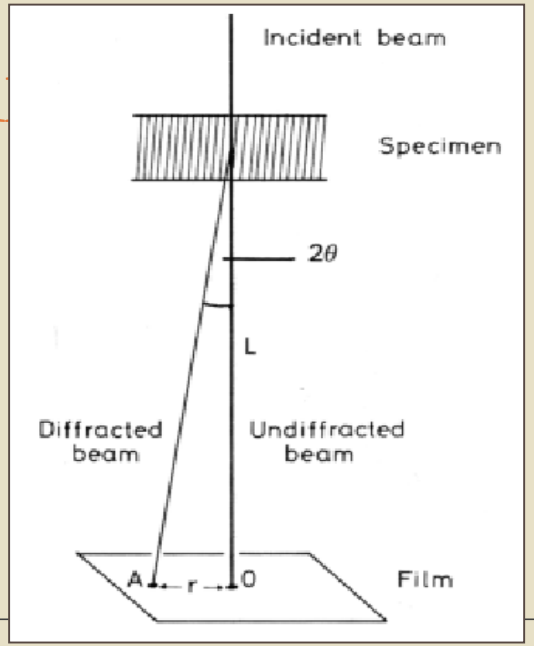
From geometry, noting θ smal

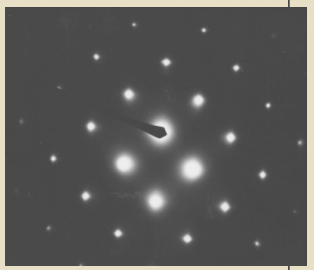
(Bragg law: $2d\theta = \lambda$)

$r = L\ 2\theta = L\ \lambda / d_{hkl}$

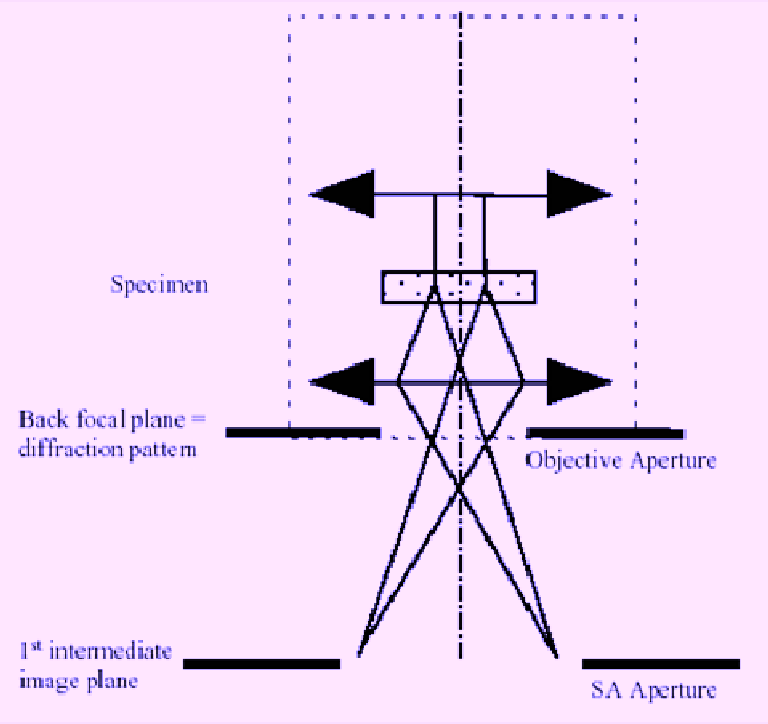
$r\ d_{hkl} = L\ \lambda$

$L\ \lambda$: camera constant



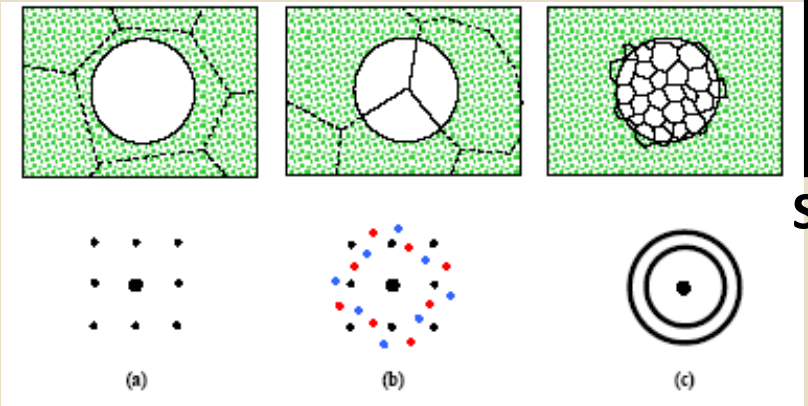


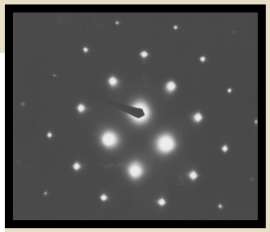
Selected area electron diffraction



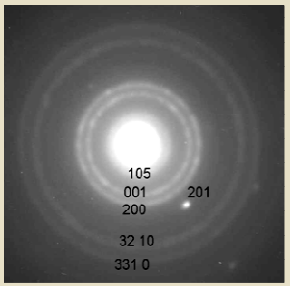
- A specimen which is crystalline will deflect incoming electrons in specific directions.
- For a parallel incident beam all electrons diffracted over the same angle will be focused at the same position in the BFP of objective lens.
- Area selected by aperture placed in image plane
- Virtual aperture created in specimen plane – demagnified !

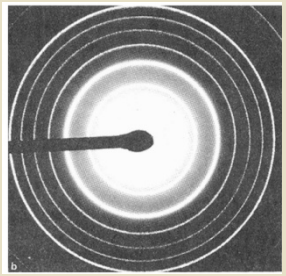
Changes in diffraction pattern – spots to rings



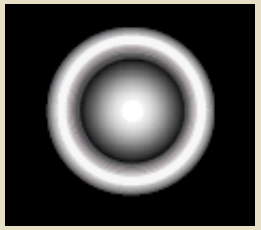


Single crystal





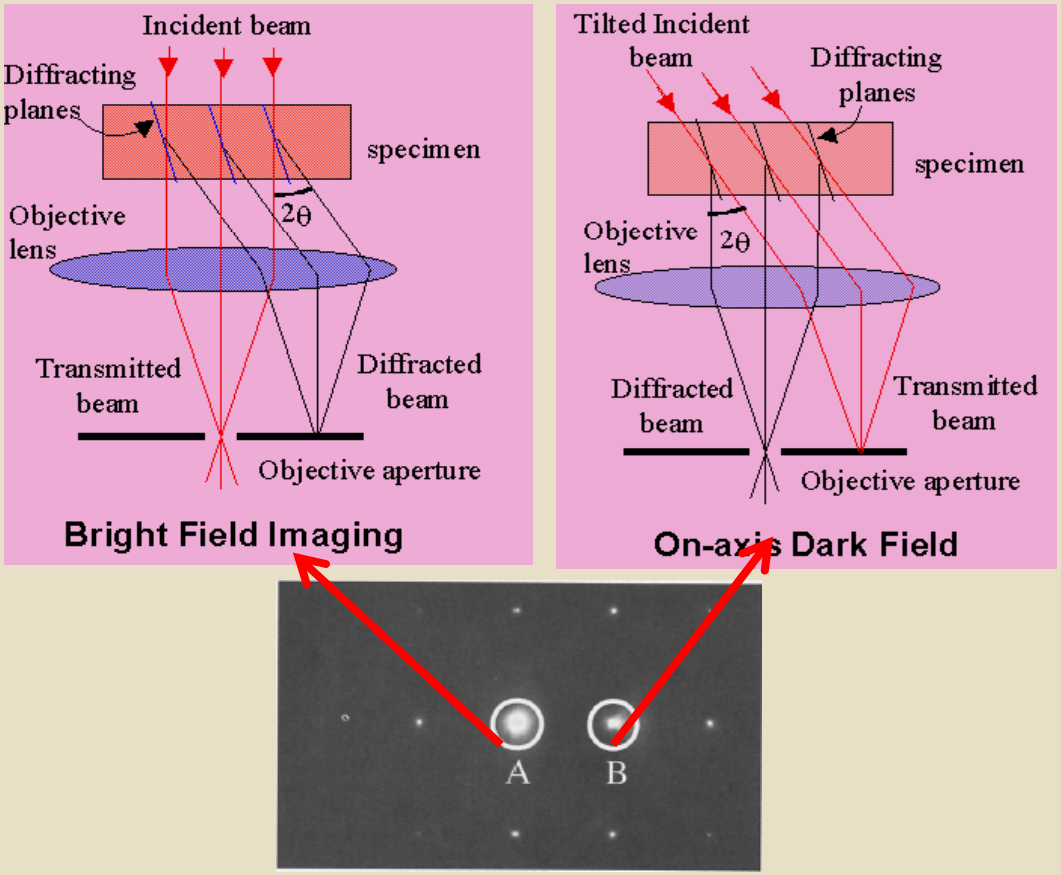
polycrystal



Amorphous

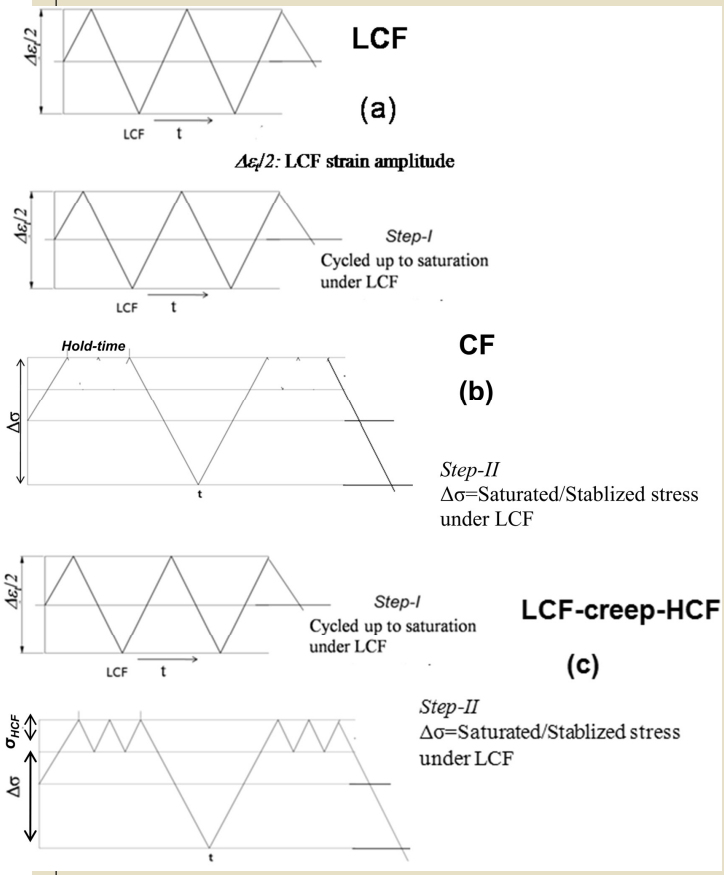
Bright Field / Dark Field modes

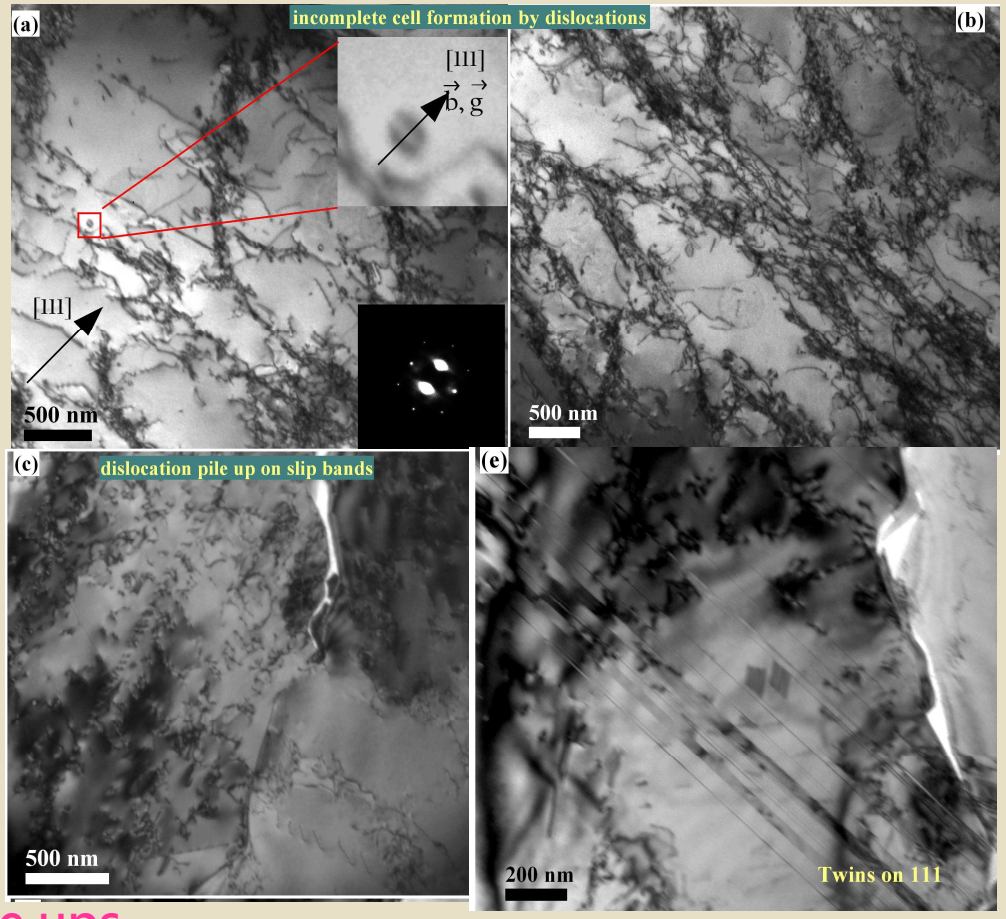
- Selective filtering of scattering that occurs at Bragg angles
- Dark-field image contains specific orientation information not just general scattering information as is the case for mass-thickness contrast



DEFECT STRUCTURE EVOLUTION IN SS316LN UNDER CYCLIC LOADING

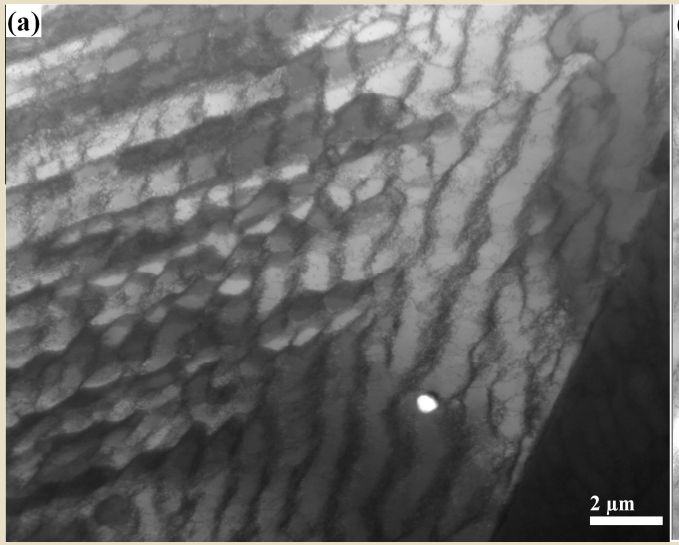
Strain amplitude ($\Delta\varepsilon t/2$) of ±0.25%, T= 923K

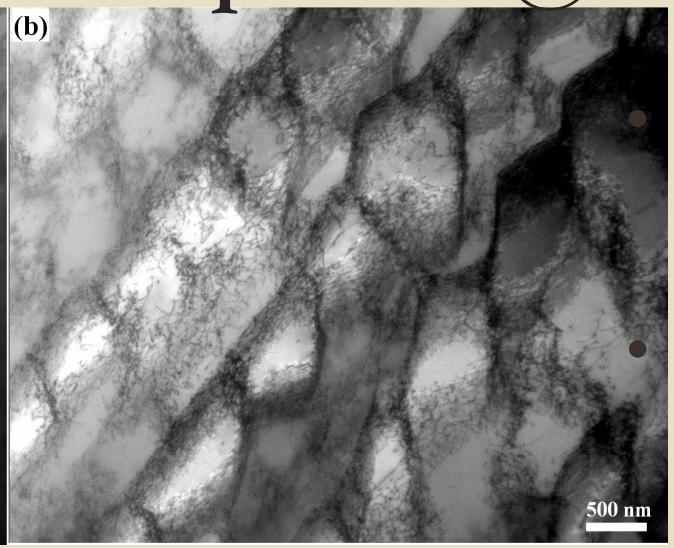


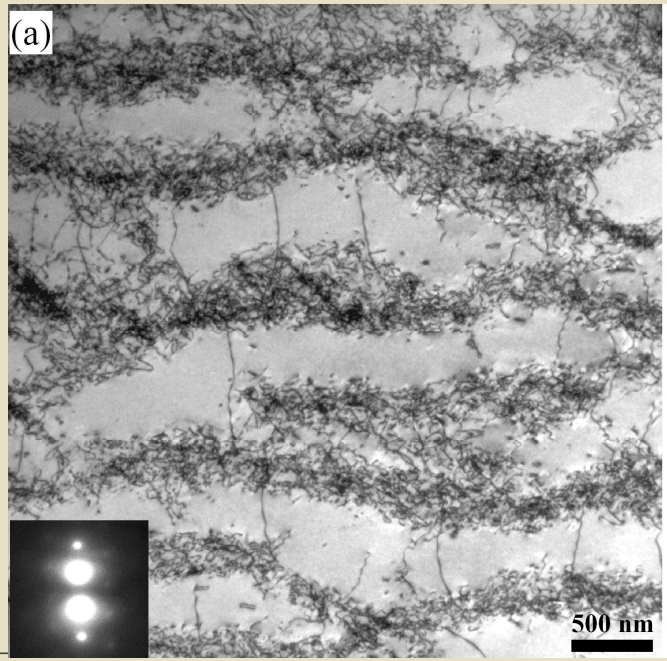


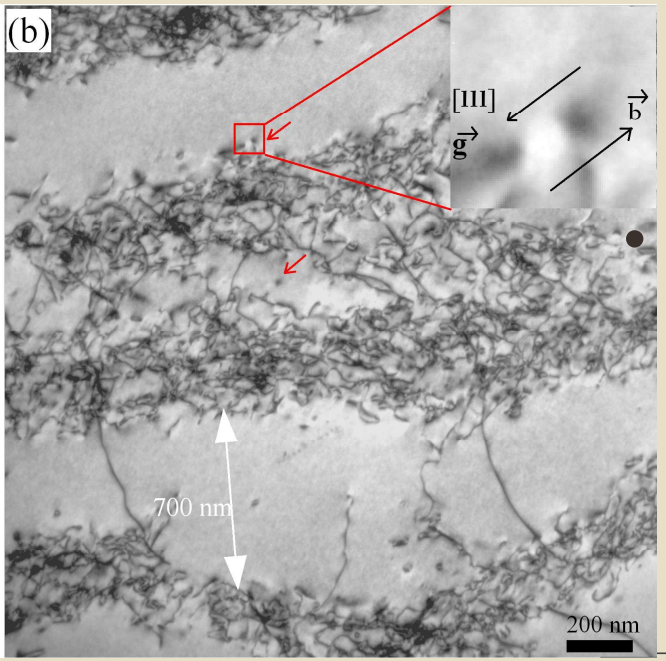
- Slip bands with dislocation pile ups
- Dislocation loops
- Fine Deformation twins (111)

SS316LN- LCF- Creep-HCF@ 923K



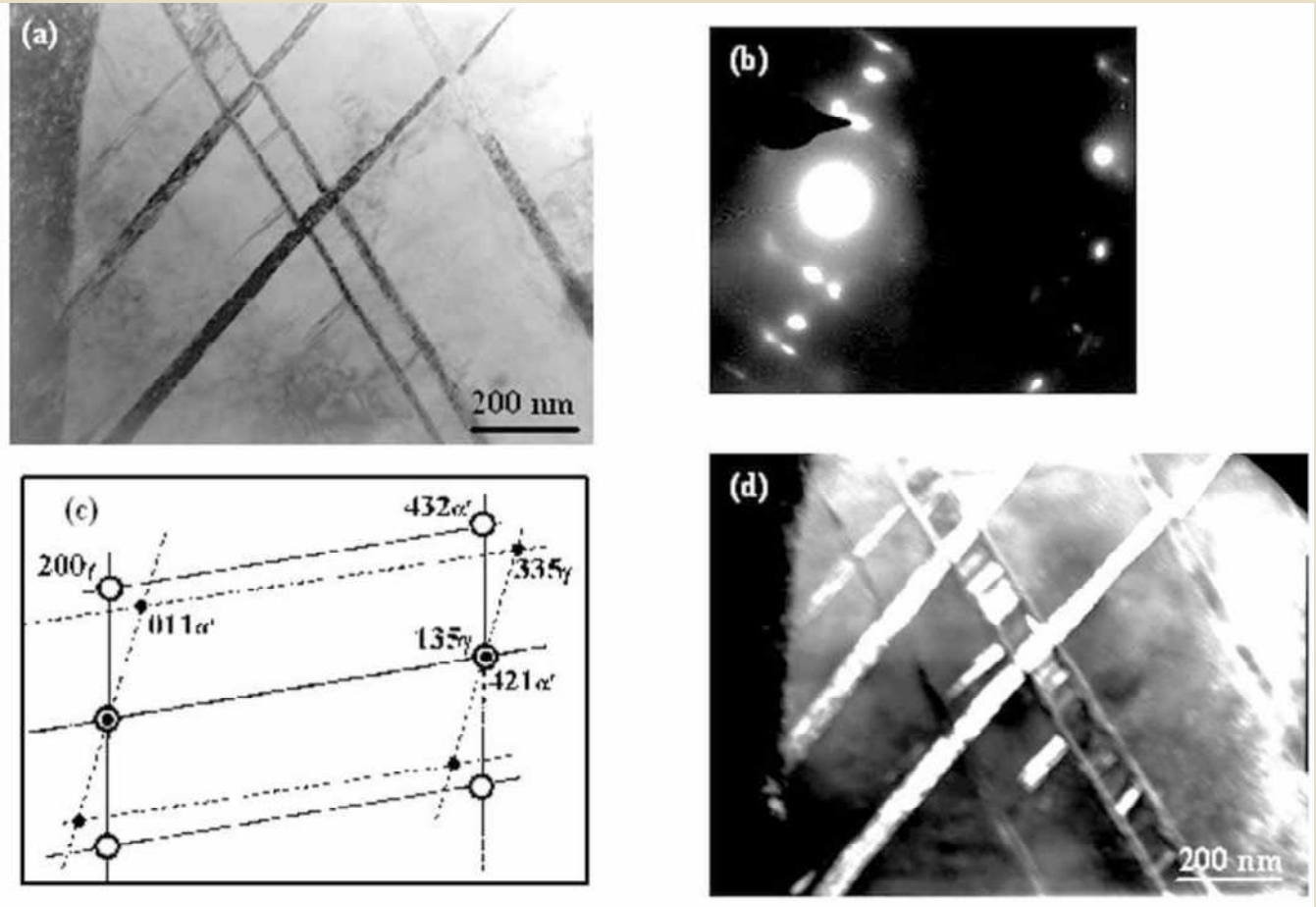






- Well defined dislocation cells
- Dislocation vein structure with high density dislocation walls
- Point defects like Frank edge-on loops

Ti modified 316 stainless steel bellow



- Partial conversion of $\gamma \rightarrow \alpha'$
- Strain induced martensite formed during fabrication
- Nucleation centres for α'

Summary

Characterization is essential for

- Understanding deformation mechanism
- Development of materials and processes
- Life assessment/prediction

Several tools available to study various aspects of characteristics of materials from component to atomic scale, with technological advancements!

- Morphology
- Crystal Structure
- Texture
- Composition

THANK YOU