Chapter X: Characterization Techniques

Crystal structure analysis; microstructure and defects in crystal structure

Various instruments are necessary to examine materials at:
- millimeter
- micrometer
- nanometer
- Å

- microscopic defects
- grain size
- grain boundaries
- various phases
- internal damage
- crystal structure
- contaminations
- growth mode

Bibliography

**X-ray diffraction**
- Smith & Hashemi, Chapter 3.11

**SEM and TEM**
- Smith & Hashemi, Chapter 4.5.2-4
- Callister, Chapter 4.9-4.10

**STM and AFM**
- Smith & Hashemi, Chapter 4.5.5
- Modern Techniques of Surface Science, Woodruff and Delchar, 1994

**LEEM**
Probes of materials structure and properties

X.1 X-ray diffraction

Main method for determining crystal structure

Consider an X-ray of wavelength $\lambda$ hits a set of planes separated by $d$ under an angle $\Theta$
- some of the X-rays go straight through
- some are reflected (scattered), but only if specific conditions met

Consider a material to be a stack of planes at a constant separation - $d$

\[ 2d \sin \Theta \]

Some planes are in phase:

- \[ n \times \lambda \]
  - whole number
Bragg’s law

The diffraction (the coherent elastic scattering of waves by the crystal lattice) condition

\[ n \times \lambda = 2d \sin \Theta \]

where \( \lambda \) – wavelength of X-ray beam, \( d \) – spacing of reflecting planes, \( \Theta \) – angle of incidence and reflection, \( n \) – order of diffraction (for most of the cases we discuss \( n = 1 \))

The lattice plane spacing \( d \) depends on the crystal structure and indices \( \{hkl\} \) of the planes

\[ d_{\text{triclinic}} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]
\[ d_{\text{hexagonal}} = \frac{a \sqrt{3}}{\sqrt{h^2 + k^2 + h k + l^2 a^2 / c^2}} \]

\( d \) – set by the crystal
\( \lambda \) – set by apparatus (constant for a given setup)

Constructive and destructive interference

X-ray waves scatter in phase (constructive interference): \( \lambda, 2\lambda, 3\lambda, \ldots, n\lambda \) (\( n \) – whole number)

Out of phase (destructive interference): \( 1/2\lambda, 3/2\lambda, 5/2\lambda, \ldots \)

What about the other planes?
- if in phase condition holds for plane 1 and 2, it also holds for the plane 3, 4, etc.
- if plane 1 and 2 are out of phase, the 3rd will be in phase with the 1st, … but the 4th will cancel it out

Other planes are also important:

Unless constructive interference condition met (\( n \) – whole number), there is very little intensity at a given angle
Additional rules

- Consider diffraction from the (100) face of the fcc crystal

\[ 2d \sin \Theta = \lambda \quad (i.e., \ n=1) \]

but there is always another plane at (n=1/2)

⇒ no intensity…

Rules for determining the diffracting \{hkl\} planes in cubic crystals

<table>
<thead>
<tr>
<th>Lattice</th>
<th>Reflection present</th>
<th>Reflection absent</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc</td>
<td>(h+k+l)=even</td>
<td>(h+k+l)=odd</td>
</tr>
<tr>
<td>fcc</td>
<td>(h,k,l) all odd or even</td>
<td>(h,k,l) not all odd or even</td>
</tr>
</tbody>
</table>

Details of crystal unit cell are important

Different rules for different unit cells

Possible peaks for cubic structures

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}} \]

<table>
<thead>
<tr>
<th>(d_{hkl})</th>
<th>Family of planes</th>
<th>sc</th>
<th>fcc</th>
<th>bcc</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>{100}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Powder diffraction

- Use polycrystalline sample
  - All possible planes are at angle $\theta$ to beam
  - Only ones satisfying Bragg's condition provide diffraction
  - Need to change angle $\theta$ to detect all "Bragg peaks"

![Graph showing diffraction patterns with labels 110, 200, 211, 310, 321, 400]

Record of the diffraction angles for a $W$ (tungsten) sample obtained by the use of a diffractometer with Cu radiation

Experimental details (powder diffraction)

Use polycrystalline sample
- Source
- Collimator (slits)
- Sample holder (need rotation)
- Detector (moves in arc around sample; intensity vs $2\theta$ is recorded)
Q: A metal is known to have a cubic structure. An X-ray diffraction pattern (using wavelength $\lambda$ of the incoming radiation of 0.1542 nm) has its three lowest peaks at $\theta$ angles: 20.27°, 29.33°, 36.87°.

a) Determine the lattice constant of the element
b) Determine the crystal structure of the element.
c) Identify the element (use Appendix tables at the last slide)

Laue method

- If single crystal is illuminated with monochromatic X-rays $\rightarrow$ no intensity !!!
- White (not monochromatic X-rays) used
- Sample, detector (or film) are fixed

(a) Schematics for Laue-back-scattering-image: reflections from one zone are along a hyperbola on the film
(b) sample Al: reflections on the film
(c) sample Fe, zones and major reflections are indexed
X.2 Positron Annihilation

• An accurate method to determine the **vacancy** concentration
• Positron (e+) has the same mass but the opposite charge of an electron (e-)
• Interaction of a vacancy with a positron increases the life time of a positron in a material
• Can be measured by the emitted $\gamma$-ray intensity

![Diagram of positron annihilation](http://www.physics.uwo.ca/~psimpson/)

X.3 Optical Microscopy

The ordinary light microscope

• **Advantages**: easy, cheap, direct
• **Disadvantages**: resolution only to ~0.3 $\mu$m (wavelength of light, can't see inside opaque samples, usually need sample preparation), max magnification 2000x

Typical sample preparation:

• cut, grind, and polish sample
• use chemicals to etch

• Shows grain boundaries! (Grain boundaries observed easily as they etch more rapidly than grains, chemical etching produces tiny grooves along grain boundaries which appear as dark lines (they reflect light less intensely)
• Can give different grains different texture (since different surface planes exposed)
Chapter X

Grain boundaries

Surfaces of polished and etched samples as revealed in the optical microscopy
(a) Low-carbon steel (100 x); (b) Magnesium oxide (225 x)

Measuring grain size (American Society for Testing and Materials (ASTM) method)

Grain size number is identified by: \( N = 2^{n-1} \)

where \( N \) is the number of grains/square inch, \( n \) – ASTM grain size number, integer (Table 4.2)

Ex.: what is the grain-size number of the metal if there are 64 grains/in² (as observed in microscope at a magnification of 100x)

\[
64 \text{ grains/in}^2 = 2^{n-1}; \quad \log 64 = (n-1)(\log 2); \quad 1.806 = (n-1)(0.301) \quad \Rightarrow \quad n = 7
\]

Chapter X

X.4 Scanning Electron Microscopy (SEM)

**Scanning electron microscopy (SEM)**

- Use electron beam instead of light
- records how many secondary electrons come out of sample at each spot
  - 30keV electron energy
  - field of view 0.1 - 100 µm
  - 5 nm resolution in plane
  - Magnification 15x – 100,000x
  - Typical operating pressure <1atms
  - build up image line by line

- **Advantages**: surface, common technique
- **Disadvantages**: need conductive sample to prevent charging

Schematic diagram of the basic design of a SEM
Chapter X

Applications

- Microscopic feature measurements
- Fracture characterization
- Failure analysis
- Quantitative and qualitative information – additional x-ray spectrometer (Energy Dispersive X-ray analysis, EDX)
  - lateral resolution

SEM of intergranular corrosion fracture near a weld

Chapter X

X.5 Transmission Electron Microscope (TEM)

**Transmission electron microscopy (TEM)**
- e-beam goes right through sample
- some areas diffract or scatter the beam
- record how much reaches a screen
- need thin samples (~ 100nm = 0.1 mm)
  - 100-300keV electron energy
  - resolution in plane 1nm (TEM)
  - 0.6Å (HRTEM, current record)
  - Need ultra-high vacuum

- **Advantages**: high-resolution
- **Disadvantages**: difficult sample preparation

Schematic diagram of the basic design of a TEM

Chapter X
Applications of HRTEM

Direct Determination of Grain Boundary Atomic Structure In SrTiO$_3$
McGibbon MM et al., Science 266, 102 (1994)

Impurity-Induced Structural Transformation of a Grain Boundary

Single Atom Spectroscopy

http://stem.ornl.gov/highlights.html

X.6 Scanning Tunneling Microscopy (STM)

STM used for direct determination of images of surface, with atomic resolution. Method is based on electron tunneling between tip and surface

- Was developed by G. Binnig and H. Rohrer (IBM) in early 1980
- Nobel prize in Physics (1986)
- Scanning Tunneling Spectroscopy (W. Ho, Cornell)

STM tip made from Pt-Ir alloy chemical etching

Get structural information by scanning tip across surface in constant height or constant current modes

Tersoff and Hamann developed a simple theory of STM: the tunneling current $I$

$$I = V \times \rho_{\text{tip}} \times \rho_{\text{sample}}$$

where $V$ - voltage applied,

$\rho_{\text{tip}}$ and $\rho_{\text{sample}}$ are the density states of the tip and sample.
**Piezoelectric Scanners**

- Scanners are made from a piezoelectric material that expands and contracts proportionally to an applied voltage.

<table>
<thead>
<tr>
<th>Voltage</th>
<th>No applied voltage</th>
<th>Extended</th>
<th>Contracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- V</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ V</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

**STM image Si(111) (7x7)**

- **Advantages**: atomic resolution on the surface, spectroscopic studies for a single atom are possible.
- **Disadvantages**: conductive samples, often need UHV, good vibration isolation is critical.

See topmost atom layer (or electron density in the topmost layer)

http://www.omicron.de
X.7 Atomic Force Microscope (AFM)

- A very high-resolution type of scanning probe microscope
- was invented by Binnig, Quate and Gerber

- **Advantages:** > 1000 times better than the optical diff. limit, non-conductive samples
- **Disadvantages:** image size (max 150x150 µm), tip effects, and image artifacts

AFM Operation modes

- Contact mode
  - repulsive forces ~10^-9 N

- Non contact
  - attractive (van der Waals) forces regime

- Tapping (Intermittant contact) mode
  - cantilever is oscillated at its resonant frequency
  - repulsive force region, but touches the surface only for short periods of time
Chapter X

Contact Mode AFM

- Tip is in contact with the surface ⇒ the deflection of the cantilever or the movement in the z piezo required to keep the deflection
- Force constants for commercial cantilevers ~0.1N/m ⇒ a displacement of 1nm corresponds to a force 0.1nN
- high resolution, but wears out the tip
- high scan speed
- surface damage, if the surface is soft
- good for nanomechanical testing

Non-contact Mode AFM

- The cantilever is oscillated slightly above its resonant frequency.
- Oscillations <10nm
- The tip does not touch the sample
- A constant oscillation amplitude is maintained
- resolution is slightly worse
- useful for sensitive (biological soft) samples

http://www.quesant.com/Library
**Intermittent (Tapping) Mode AFM**

- A cantilever with attached tip is oscillated at its resonant frequency and scanned across the sample surface.
- A constant oscillation amplitude (and thus a constant tip-sample interaction) are maintained during scanning. Typical amplitudes ~ 20-100 nm.
- Forces can be <200 pN
- The amplitude of the oscillations changes when the tip scans over bumps or depressions on a surface

**X.8 Low Energy Electron Microscope (LEEM)**

**LEEM history**
- 1962 Invention by Ernst Bauer
- 1985 Operational LEEM instrument (Telieps and Bauer)
- 1991 IBM LEEM-I (Tromp and Reuter)
- 1998 IBM LEEM-II
- 2006 SPECS FE-LEEM P90
Chapter X

Phase contrast

Problems:

X.1 An x-ray diffractometer recorder chart for an element that has either the BCC or the FCC crystal structure showed diffraction peaks at the following 2θ angles: 40.663°, 47.314°, 69.144°, and 83.448°. (Wavelength λ of the incoming radiation was 0.15405 nm.)

a) Determine the crystal structure of the element.
b) Determine the lattice constant of the element.
c) Identify the element.

X.2 The distance between atoms in a crystal are ~ 1-2 Å, so waves with approximately this wavelength are required to explore the crystal structure. Using de Broglie law ($\lambda = \frac{h}{p}$), calculate the energies of (a) neutrons ($m=1.675 \times 10^{-24}$kg), (b) electrons ($m=0.911 \times 10^{-28}$kg) and (c) X-rays required for the structural studies.

X.3 Name and briefly describe three different AFM operation modes. In which mode separation between the probe and the surface is the highest?

X.4 What incident particles (X-rays, electrons, or photons (light)) do we use in (a) X-ray diffraction, (b) optical microscopy, (c) TEM, (d) LEEM. What particles do we detect in each of these techniques?

X.5 Why are grain boundaries easily observed in optical microscope?
### Appendix:

#### Table 3.2
Selected metals that have the BCC crystal structure at room temperature (20°C) and their lattice constants and atomic radii

<table>
<thead>
<tr>
<th>Metal</th>
<th>Lattice constant $a$ (nm)</th>
<th>Atomic radius $R^*$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>0.289</td>
<td>0.125</td>
</tr>
<tr>
<td>Iron</td>
<td>0.287</td>
<td>0.124</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>0.315</td>
<td>0.136</td>
</tr>
<tr>
<td>Potassium</td>
<td>0.533</td>
<td>0.231</td>
</tr>
<tr>
<td>Sodium</td>
<td>0.429</td>
<td>0.186</td>
</tr>
<tr>
<td>Tantalum</td>
<td>0.330</td>
<td>0.143</td>
</tr>
<tr>
<td>Tungsten</td>
<td>0.316</td>
<td>0.137</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.304</td>
<td>0.132</td>
</tr>
</tbody>
</table>

*Calculated from lattice constants by using Eq. (3.1), $R = \sqrt{3/4}a$.

#### Table 3.3
Selected metals that have the FCC crystal structure at room temperature (20°C) and their lattice constants and atomic radii

<table>
<thead>
<tr>
<th>Metal</th>
<th>Lattice constant $a$ (nm)</th>
<th>Atomic radius $R^*$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>0.405</td>
<td>0.143</td>
</tr>
<tr>
<td>Copper</td>
<td>0.3615</td>
<td>0.126</td>
</tr>
<tr>
<td>Gold</td>
<td>0.408</td>
<td>0.144</td>
</tr>
<tr>
<td>Lead</td>
<td>0.495</td>
<td>0.175</td>
</tr>
<tr>
<td>Nickel</td>
<td>0.352</td>
<td>0.125</td>
</tr>
<tr>
<td>Platinum</td>
<td>0.393</td>
<td>0.139</td>
</tr>
<tr>
<td>Silver</td>
<td>0.409</td>
<td>0.144</td>
</tr>
</tbody>
</table>

*Calculated from lattice constants by using Eq. (3.3), $R = \sqrt{2/4}a$. 