Experiment 5

X-rays Diffraction

Determination of crystal structure, grain size and phase characterization

Part I: Determination of crystal structure, grain size

Objectives

- To familiarize students with the components of XRD equipment and address safety and health issues when dealing with X-rays.
- To identify phase(s) present in a material.
- To determine the crystal structure and lattice parameter(s) of each phase.
- To determine the grain size of each phase.

Introduction

X-rays were discovered by W.C. Röentgen in 1895. The term **X-rays** refer to **electromagnetic radiation** with wavelengths between about **0.01** and **100 A$^{0.}$**

X-rays Production

One way to produce X-rays is to heat a tungsten filament with an electric current, which imparts sufficient thermal energy to drive electrons out of the filament.

These electrons are accelerated by an applied voltage towards a metal target Figure 1.1.

As the accelerated electrons approach the electrons in the target atom, they are decelerated.
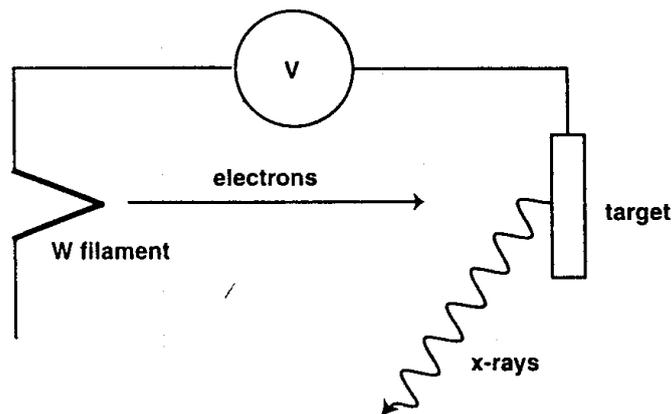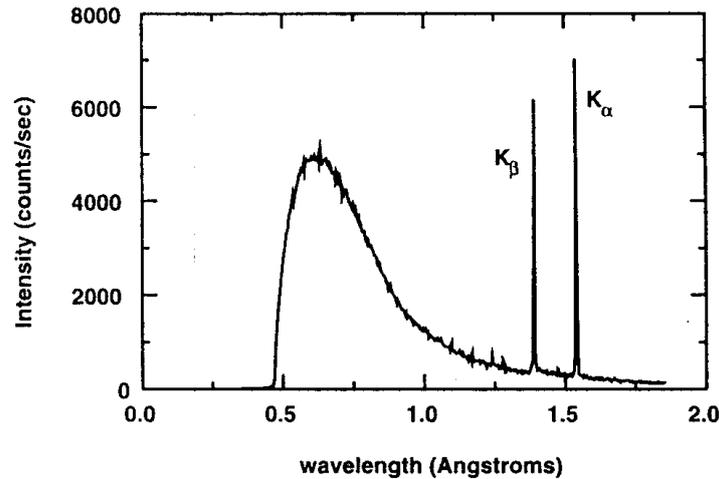

Figure 1.1 Production of X-rays

The loss of energy in this process is given off as X radiation and heat.

Only about 1 % of the total energy becomes X-rays, the rest being given off as heat.

An X-ray emission spectrum from electrons accelerated at 26 kV onto a copper target is shown in Figure 1.2.

Figure 1.2 The X-ray spectrum of copper (Cu) as a function of wavelength

There are **three** primary **features**:

- a **discrete wavelength cutoff**, called the short wavelength limit, below which no x-rays are produced.

- a **broad hump** of intensity in the low wavelength region.

- **sharp peaks** as characteristic peaks, in the high wavelength.

Continuous spectrum

The short wavelength, λ_{SWL}, represents the maximum energy loss ΔE_{max}, which is the transfer of all kinetic energy (= $\frac{1}{2} m_e v^2$) of an incident electron to photon energy, $e_e V$

$$\Delta E_{max} = \frac{1}{2} m_e v^2 = e_e V$$

where m_e is the electron mass, v is the electron velocity, e_e is the electron charge and V is the accelerating voltage.

The wavelength λ and the frequency ν of an electron of energy E are given by

$E = h\nu = hc / \lambda$ where h is Planck's constant and c is the speed of light.

$$\lambda = hc / e_e V = \frac{12.396}{V(kV)} \text{Å}^{0.}$$

The second future, the board hump, at the low wavelength end of the spectrum, results from the fact that ***accelerating or decelerating charge radiates electromagnetic radiation***.

The maximum intensity in the hump occurs at the most probable energy loss.

Characteristic Spectrum

The third feature seen in Figure 1.2 is sharp peaks of high intensity.

They are known as characteristic peaks and are due to discrete electron transitions within the target atoms.

They occur via a two-step process:

-   the removal of K shell electrons from the target atoms.

-   Their replacement by electrons from L(K_α) and M(K_β) shells.

The energy released due to the intraatomic transition from an L or M shell to K shell gives rise the (K_α) (drop from L to K) and (K_β) (drop from M to K) X-rays (as indicated in Figure 1.3).

There are sub levels of the L shell that lead to doublet of transitions, and are very close in energy, known as $K_{\alpha1}$ and $K_{\alpha2}$.

The $K_{\alpha1}$ intensity is about twice that of the $K_{\alpha2}$ due to the respective transition probability. As a result the wavelength of the weighted K_α radiation is given

$\lambda_{K\alpha} = (2\ \lambda_{\alpha1} + \lambda_{\alpha2})/3.$ some elements also have multiple K_β transitions.
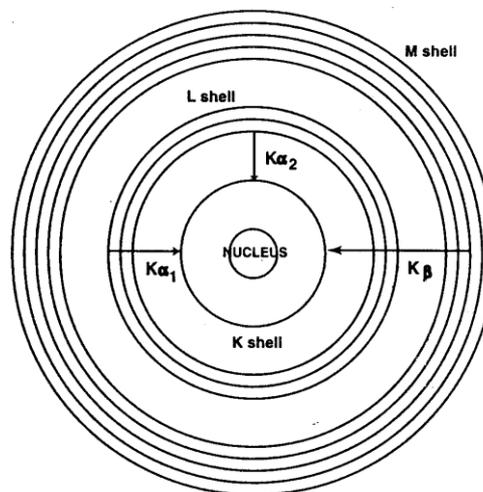
Figure 1.3 Energy level diagram indicating the atomic transitions for the emission of $K_{\alpha1}$, $K_{\alpha2}$ and K_β characteristic radiation.

X-rays Sources and detectors

A laboratory X-ray diffraction facility consists of the following.

-   An X-ray source.

-   A generator to power the X-ray source.

- A detector and associated electronics.

- A diffractometer, a mechanical system to hold and orient samples and enable the detector to measure scattered X-rays around a sample.

Sealed X-ray tubes are the **main laboratory source for X-rays**. The tube is vacuum sealed.

It has a cooling head to remove heat from the target, windows through which X-rays emerge, and radiation shielding.

The most common sealed X-rays tubes have Mo, Cu, Co, and Cr targets.

Accelerating voltage is around **40 to 80 kV** and corresponding maximum beam currents of **50 to 25 mA** respectively.

High-voltage generators are required to power X-ray tubes.

They supply current to the tungsten filament to cause thermoionic emission of electrons and high voltage to accelerate them to the target. **Operational voltages** are typically in the range of **20 to 50 kV** range.

The intensity of a characteristic K_α emission is given by:

$$I_\alpha = ki(V - V_k)^n \quad n = 1.5$$

V_k is the voltage at which the characteristic lines begin to appear, i is the electric current, and k and n are constants.

This value of V_k is the voltage for which all the kinetic energy of the accelerated electrons was converted to x-ray energy, the X-rays would have the characteristic wavelength.

For example for Cu K_α this voltage is 8 kV.

Detectors convert X-ray photons into current and then to voltage pulses that are electronically counted.

Ideally a **detector** would response only to the characteristic wavelength used and in linear fashion.

Bragg's law

It relates peak position (the diffraction angle θ), interplanar spacing **d**, and the wave length λ.

Consider a wave incident on rows of atoms, as shown in Figure 1.4.

The vector S_0 is a unit vector in the direction of the incident beam and the vector S is a unit vector in the direction of scattered beam.

In the figure two portions of the wavefront are scattered. One at point A and the second at point C.

The angle of incidence of both portions of the incident wavefront to the atomic planes is θ, and the angle at which scattering observed is θ.

The vector $S - S_0$ is normal to the scattering planes.

The points A, B, C and D define two triangles.

$Sin\theta = BC/d$ $BC = d \sin\theta = CD$.

For constructive interference, $BC + CD = n\lambda = 2d\sin\theta$

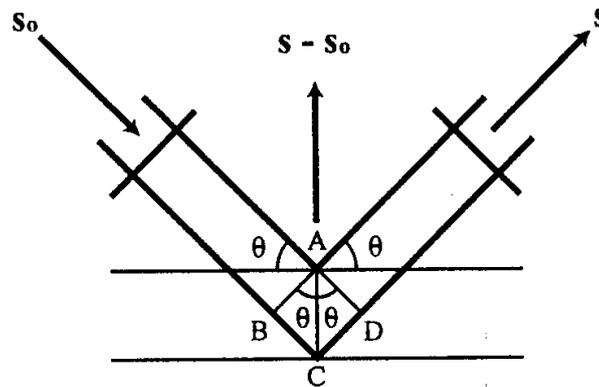By incorporation the integer n into d we obtain:

$$2d\sin\theta = \lambda$$

Figure 1.4

Grain Size Determination

The **positions**, **intensities**, and **shapes** of X-ray diffraction **peaks** are **related** to the **crystal structure** (peak position and intensity), and **physical state** (peak shape) of the material as well as to the **experimental measurement parameters** as shown in Figure 1.5.
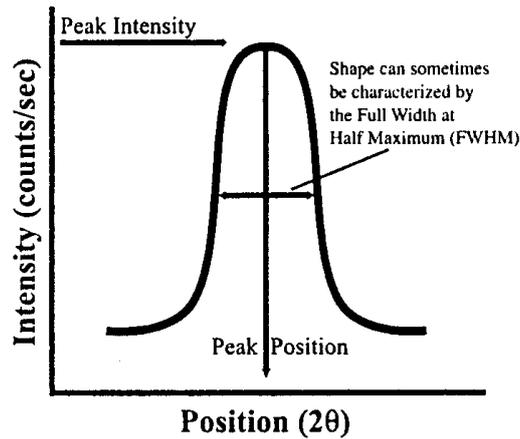
Figure 1.5

In a simple way the shape of powder diffraction peak can be characterized by the full-width at half-maximum (FWHM), as shown in figure 1.5.

It is defined as the width in degrees at half the peak height, I_{FWHM}

$$I_{FWHM} = (I_{peak} - I_{bkgd})/2$$

The peak height, I_{peak}, must be corrected for any background intensity, I_{bkgd}.

The measured width of a diffraction peak depends on factors such as:

- Slit dimensions.

- Detector resolution.

- Sample size.

- Metallurgical sources of broadening such as cold work.

The breadth and shape of a diffraction peak can be affected by a number of physical factors.

- Low angle grain boundaries.

- Very small particles of grains.

- Plastic deformation.

- Compositional homogeneity.

- Variation in large-scale or small scale elastic lattice stain.

The FWHM is related to the particle or crystal size (grain size) by the **Sherrer equation** as follows.

$$W_{FWHM} = (k\lambda) / (D\cos\theta) \times 180/\pi$$

Where W_{FWHM} in degree 2θ, D is the particle or crystal size and K is a constant usually evaluated as 0.94.

Experimental Procedure

You will be given a sample in powder form (a356 alloy). Carry out an XRD experiemnt, set the difraction angle 2θ range from 20 to 80^0, and the scanning speed at 2 deg./min.

Lab Report

The lab report shoud contain the following:

A) Introduction

B) Experimental Procedure

C) Results and Discussion

This part should contain the folloing:

i)   A printed table (2θ, d_{hkl}, relative intensity, integrated intensity, FWHM) and the XRD specter.

ii)   A printed PDF table for the phase(s) present in the sample.

iii)   Answers to the folloing questions.

1- What are necessary safety actions that should be taken when dealing with X-ray equipments?

2- List down the major components of the X-ray equipment available at your laboratory and briefly discuss the role of each component.

3- List all steps to operate the X-ray equipment.

4- Explain why a cooling system is required for X-ray equipment.

5- Determine the crystal structure of the phase(s) present in the sample.

6- Determine the lattice parameter of the phase(s) present in the sample.

7- Compare between the experimental results that you get and the data stored in the PDF files.

8- Determine the grain size of the phase(s)