phase characterization

Experiment 6: Qualitative and Quantitative Phase Analysis

There are **two** aspects of phase analysis:

Qualitative phase analysis: means the **identification of phases** that are **present** in materials, that *is, which* phase or phases are present, not how much.

The primary resource for the identification of unknown phases is the **Powder Diffraction File,** a database of more than 60,000 organic and inorganic phases.

Quantitative phase analysis means that the identity of phases is known but their quantities are not, for example, retained austenite or the production of carbides due to a heat treatment.

Diffraction is an important method in the determination of the amount of phases present in a multiphase mixture.

Quantitative Phase Analysis

The determination of the **amount of a phase** involves utilizing the **intensity expressions**, in particular, the expression for diffraction from polycrystalline material.

$$E(hkl) = I_0 A_0 \frac{e^4}{m^2 c^4} \frac{\lambda^3 p h w}{32\pi R^2 \omega_s V_{\mathrm{uc}}^2 \mu_l} F_{hkl}^2 \frac{1+\cos^2 2\theta}{2\sin 2\theta \sin\theta}$$

which includes (1) **physical** constants and **measurement** parameters and (2) **phase parameters**.

Let K_m represent the physical constants and measurement terms, and K_P represent the phase related terms:

$$K_{\mathrm{m}} = I_0 A_0 \frac{e^4}{m^2 c^4} \frac{\lambda^3 h w}{32\pi R^2 \omega_s}$$

$$K_{\mathrm{p}} = \frac{p_{hkl}}{V_{\mathrm{uc}}^2} F_{hkl}^2 \frac{1+\cos^2 2\theta_{hkl}}{2\sin 2\theta_{hkl} \sin\theta_{hkl}}.$$

$$E_{hkl} = K_{\mathrm{m}} K_{\mathrm{p}} \frac{1}{\mu_l}$$

where μ_l is the linear absorption coefficient. If α is one of N phases in a sample, then:

$$E_{\alpha,i} = K_{\mathrm{m}} K_{\mathrm{p},\alpha,i} \frac{V_\alpha}{\mu_{l,\mathrm{s}}}$$

where $E_{\alpha,i}$ is the intensity of the ith peak of the α phase, V_α, is the volume fraction of the α phase, and $\mu_{l,s}$, is the linear absorption coefficient of the total sample.

The mass absorption coefficient, $\mu_m = \mu_l/\rho$, of a sample.

For multiphase mixture:

$$\mu_{m,s} = \sum_j W_j \mu_{m,j}$$

where the subscripts refers to the sample as a whole, namely the absorption of the complete multiphase sample, and w_j is the weight fraction of the j1h constituent phase.

The volume fraction of α can be related to the weight fraction of a sample containing N phases by

$$V_\alpha = \frac{W_\alpha}{\rho_\alpha}\rho_s$$

where ρ_α and ρ_s are the densities of the α phase and whole sample, respectively, and the sample density ρ, is given by:

$$\rho_s^{-1} = \sum_{i=1}^{N} \frac{W_i}{\rho_i}$$

$$E_{\alpha,i} = K_m K_{p,\alpha,i} \frac{V_\alpha}{\mu_{l,s}} = K_m K_{p,\alpha,i} \frac{W_\alpha}{\rho_\alpha \mu_{m,s}}$$

The problem is to determine the weight (or volume) fraction of a phase in the presence of other phases each of which has, in general, a different absorption coefficient.

Two Phase Analysis

Use of Internal Ratios: We consider an alloy with two phases, α and β.

The phases and their structures are known, and all peaks are measured under the same conditions. Thus:

$$E_{\alpha,i} = K_m K_{p,\alpha,i} \frac{V_\alpha}{\mu_{l,s}}$$

$$E_{\beta,j} = K_m K_{p,\beta,j} \frac{V_\beta}{\mu_{l,s}}$$

$$V_\alpha + V_\beta = 1$$

A ratio is formed between the ith peak of phase α and the jth peak of phase β.

$$\frac{E_{\alpha,i}}{E_{\beta,j}} = \frac{K_{p,\alpha,i} V_\alpha}{K_{p,\beta,j} V_\beta},$$

$$\frac{V_\alpha}{V_\beta} = \frac{V_\alpha}{1 - V_\alpha} = \frac{E_{\alpha,i} K_{p,\beta,j}}{E_{\beta,j} K_{p,\alpha,i}}$$

$$V_\alpha = \frac{E_{\alpha,i} K_{p,\beta,j}}{E_{\alpha,i} K_{p,\beta,j} + E_{\beta,j} K_{p,\alpha,i}}$$

This result can be converted to weight fraction of α, W_α, using:

$$W_\alpha = \frac{\rho_\alpha V_\alpha}{\rho_\alpha V_\alpha + \rho_\beta (1 - V_\alpha)}$$

An **advantage** of this approach is that the **absorption coefficients** are the **same** for **each phase**, since the peaks come from the same physical sample.

This means that this parameter cancels out in the ratio.

Use of Pure Reference Standards: The idea is to form ratios between a peak from a phase of interest in the sample and a sample of pure phase.

$$E^{o}_{\alpha.i} = K_c K_m K_{p.\alpha.i} \frac{1}{\mu^{o}_{l}}$$

$$E_{\alpha,i} = K_c K_m K_{p,\alpha,i} \frac{V_\alpha}{\mu_{l,s}}$$

O refers to the pure material.

All constants now cancel and we get:

$$\frac{E_{\alpha.i}}{E^{o}_{\alpha,i}} = \frac{\mu^{o}_{l}}{\mu_{l,s}} V_\alpha$$

A potential problem is that the densities of the two samples may not be the same. Also the absorption coefficient of the unknown sample must be experimentally measured.

Experimental Procedure

Use XRD data obtained for A, B, C, D and F Powder samples to calculate the amont of the MgO phase present in the Al_2O_3-MgO Powder. You need to run another XRD experiment for Al_2O_3 powder.

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) and the specter for each sample i.e. Al2O3 and A, B,…. samples.

ii) Answers to the folloing questions.

1- Identify phases present in each sample.

2- Determine the volume fraction of the MgO phase present in A, B,…. samples.

3- Determine the weight fraction of the MgO phase present in A, B,…. samples