6.1 XRF

X-Ray Fluorescence

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Introduction

X-Ray Fluorescence (XRF) is a nondestructive method used for elemental analysis of materials. An X-ray source is used to irradiate the specimen and to cause the elements in the specimen to emit (or fluoresce) their characteristic X rays. A detector system is used to measure the positions of the fluorescent X-ray peaks for qualitative identification of the elements present, and to measure the intensities of the peaks for quantitative determination of the composition. All elements but low-Z elements—H, He, and Li—can be routinely analyzed by XRF.

Since the 1950s XRF has been used extensively for the analysis of solids, powders, and liquids. The technique was extended to analyze thin-film materials in the 1970s. XRF can be used routinely for the simultaneous determination of elemental composition and thickness of thin films. The technique is nondestructive, rapid, precise, and potentially very accurate. The results are in good agreement with other elemental analysis techniques including wet chemical, electron-beam excitation techniques, etc.

Basic Principles

The fundamental principles of XRF can be found in the literature.[1-3] Briefly, X rays are electromagnetic radiation of very high energy (or short wavelength). The unit of measurement for X rays is the angstrom (Å), which is equal to 10^{-8} cm. When an X-ray photon strikes an atom and knocks out an inner shell electron, if the incident photon has energy greater than the binding energy of the inner shell electron, a readjustment occurs in the atom by filling the inner shell vacancy with one of the outer electrons and simultaneously emitting an X-ray photon. The emitted photon (or fluorescent radiation) has the characteristic energy of the difference between the binding energies of the inner and the outer shells. The penetration depth of a high-energy photon into a material is normally in the μm range. (Another method commonly used to produce X rays is electron-beam excitation; the penetration depth of an electron beam is about an order of magnitude smaller than that of X rays. See the articles on EDS and EPMA.)

Measurements of the characteristic X-ray line spectra of a number of elements were first reported by H. G. J. Moseley in 1913. He found that the square root of the frequency of the various X-ray lines exhibited a linear relationship with the atomic number of the element emitting the lines. This fundamental "Moseley law" shows that each element has a characteristic X-ray spectrum and that the wavelengths vary in a regular fashion form one element to another. The wavelengths decrease as the atomic numbers of the elements increase. In addition to the spectra of pure elements, Moseley obtained the spectrum of brass, which showed strong Cu and weak Zn X-ray lines; this was the first XRF analysis. The use of XRF for routine spectrochemical analysis of materials was not carried out, however, until the introduction of modern X-ray equipment in the late 1940s.

Instrumentation

The instrumentation required to carry out XRF measurements normally comprises three major portions: the primary X-ray source, the crystal spectrometer, and the detection system. A schematic X-ray experiment is shown in Figure 1. Fluorescent X rays emitted from the specimen are caused by high-energy (or short-wavelength) incident X rays generated by the X-ray tube. The fluorescent X rays from the specimen travel in a certain direction, pass through the primary collimator. The analyzing crystal, oriented to reflect from a set of crystal planes of known d-spacing, reflects one X-ray wavelength (λ) at a given angle (θ) in accordance with Bragg's law: $n\lambda = 2d \sin\theta$, where n is a small positive integer giving the order of reflection. By rotating the analyzing crystal at one-half the angular speed of the detector, the various wavelengths from the fluorescent X rays are reflected one by one as the analyzing crystal makes the proper angle θ for each wavelength. The intensity of at each wavelength is then recorded by the detector. This procedure is known also as the
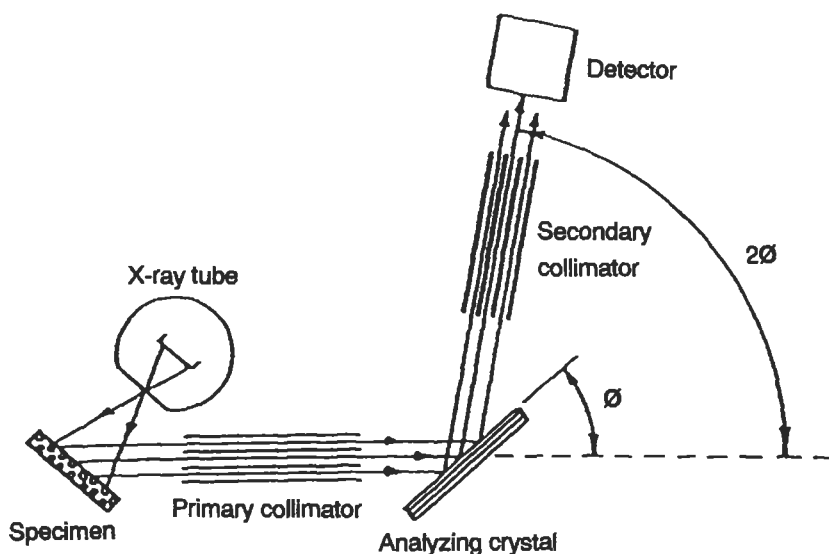
Figure 1   Schematic of XRF experiment.

wavelength-dispersive method. (The wavelength-dispersive method is used extensively in EPMA, see the EPMA article in this volume.)

X-Ray Sources

A sealed X-ray tube having a W, Cu, Rh, Mo, Ag, or Cr target is commonly used as the primary X-ray source to directly excite the specimen. A secondary target material located outside the X-ray tube is used sometimes to excite fluorescence. This has the advantages of selecting the most efficient energy close to the absorption edge of the element to be analyzed and of reducing (or not exciting) interfering elements. (The intensity is much reduced, however.) X-ray sources, including synchrotron radiation and radioactive isotopes like ^{55}Fe (which emits Mn KX rays) and AM-241 (Np LX rays) are used in place of an X-ray tube in some applications.

Analyzing Crystals

Crystals commonly used in XRF are: LiF (200) and (220), which have $2d$-spacings of 4.028 and 2.848 Å, respectively; pyrolytic graphite (002), spacing 6.715 Å; PET(002), spacing 8.742 Å; TAP(001), spacing 25.7 Å; and synthetic multilayers of W/Si, W/C, V/C, Ni/C, and Mo/B$_4$C, spacing 55–160 Å. The lowest-Z element that can be detected and reflected efficiently depends on the d-spacing of the analyzing crystal selected. The crystals are usually mosaic, and each reflection is spread over a small angular range. It is thus important that the crystal used be of good quality to obtain intensive and sharp XRF peaks. The angular spread of the
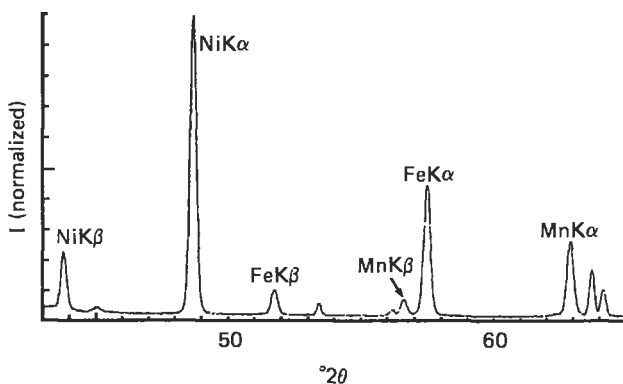
Figure 2　**XRF spectrum of MnFe/NiFe thin film.**

peaks, or the dispersion, $d\theta / d\lambda = n/(2d\cos\theta)$, increases with decreasing d. The dispersion thus can be increased by selecting a crystal with a smaller d.

X-Ray Detection Systems

The detectors generally used are scintillation counters having thin Be windows and NaI–Tl crystals for short wavelengths (above 3 Å or 4 keV), and gas-flow proportional counters having very low absorbing windows and Ar/CH_4 gas for long wavelengths (below 2 Å or 6 keV). A single-channel pulse amplitude analyzer is used to accept fluorescent X rays within a selected wavelength range to improve peak-to-background ratios and to eliminate unwanted high-order reflections.

The counting times required for measurement range between a few seconds and several minutes per element, depending on specimen characteristics and the desired precision.

A typical XRF spectrum of a FeMn/NiFe thin film is plotted in Figure 2. The $K\alpha$ and $K\beta$ XRF fluorescent peaks from the film are identified, and the remaining peaks are those from the spectrum of the X-ray tube. The experimental conditions included a Mo target X-ray tube operated at 45 kV, a LiF (200) analyzing crystal, and a scintillation counter with a single-channel pulse amplitude analyzer. The energy resolution of the Mn $K\alpha$ peak at 5.89 keV was 24 eV, compared to 145 eV for a Si (Li) solid-state energy-dispersive system (see EDS article). The high spectral resolution of the wavelength-dispersive method made possible the measurements of Ni, Fe, and Mn free of interference from adjacent peaks.

Analytical Capabilities

Elemental Depth Profiling

The X-ray penetration depth in a material depends on the angle of incidence. It increases from a few tens of Å near the total reflection region to several μm at large