12.X-9 POWDER DIFFRACTION BASED ON SYNCHROTRON RADIATION X-RAY SOURCE.

by T. YAMANAKA, K. OGATA*, K. SUGIYAMA and M. TOKONAMI.
Mineralogical Institute, Faculty of Science, University of Tokyo, Hongo Tokyo 113, Japan.
* Production Engineering Research Laboratory Hitachi, Ltd. Yoshida-cho, Totsuka Yokohama 244, Japan.

Powder diffractometry is one of the most widely used and effective methods relevant to industries. Electron storage rings dedicated to X-ray synchrotron radiation (SR) researches have been constructed and the SR X-ray has become an attractive light source for the powder diffraction studies. X-ray emmited from the bending magnets or insertion devices (e.g. undulater, wiggler) offers the following outstanding properties for powder diffraction studies.

Extremely strong source. The SR X-ray having a great number of photons gives a brightness $10^4$ times as strong as the common X-ray sources and provides high resolution of peak profiles based on a large S/N and low background level; shortening time of the intensity measurement; detection of a very small amount of sample, which is an advantage for mixture, exsolution or contamination.

Highly collimated and polarized beam. The highly collimated SR X-ray ( about 0.2m rad) can be regarded as beam using X-ray tubes. The diffraction profile from the SR source gives a very small full width at half maximum.

The diffraction profile is basically expressed by the sum of the Gaussian and Lorentzian distribution function. The highly collimated SR X-ray gives a sharp powder diffraction profile having a large Gaussian component about 90%. Those profiles provide a high angular resolution and ensure an eccurate cell constant of the sample.

Broad and continuous energy range. The SR source composed of a continuous energy brings a polychromatic X-ray. A desired wavelength can be utilized by the monochromator (the shortest one is about 0.3A at PF). Diffraction studies based on the anomalous dispersion near the absorption edge are capable using a purely monochromated X-ray.

The polychromatic X-ray (white X-ray) having high and smooth intensities is advantageous for energy dispersive diffraction studies, especially for a fixed optical alignment of the assembly, for example, at high temperature and/or under high pressure.

The outstanding properties of the SR X-ray enable us to undertake many attractive powder diffraction studies, for example, time dependent studies regarding phase transformation, ( decomposition, chemical reaction and melt), and high temperature or high pressure experiment. Further, a high resolution of the diffraction profiles makes possible the Rietveld and profile analyses with a high accuracy. Structure refinement on the basis of the energy dispersive spectra has been also performed by the profile fitting with considering several corrections.

A powder diffractometer set in the Photon Factory at Tsukuba designed for molten salt, liquid, gaseous and polycrystalline substances is utilized by both angular and energy dispersive methods with monochromated and white X-rays. There are installed a single or double crystal monochromator and analyzer monochromator. The intensity measurement can be performed in the evacuated optical system and by the reflection or transmition methods with the sample spinner.

A Debye-Scharrer camera with a diameter of 229.2mm set on the monochromated beam line produced sharp powder lines with an extremely high angular resolution and gives accurate lattice constants of even mixed samples.

12.X-10 REAL-TIME NEUTRON POWDER DIFFRACTION

J. Pannetier & A.W. Hewat, ILL, 156X, Grenoble Cedex, France.

The use of large curved one-dimensional position sensitive detectors (PSD's) allows a complete powder diffraction pattern to be recorded simultaneously on a time scale of a few minutes or less so that transient phenomena such as chemical reactions in the solid state or first-order phase transitions can now be studied in real-time. Such measurements provide direct information on the progress of a reaction (kinetic law), but may also shed light on the transformations of structure and/or morphology which occur in the reactants during the course of a reaction. The instrumental parameters relevant to the design of time-dependent experiments are discussed. The applications are illustrated by four kinds of experiments: kinetic studies, thermodiffractometry, texture and stroboscopic measurements.

Static powder diffraction (either by X-Ray or neutrons) is a standard technique for the detection and identification of crystalline phases and for the quantitative determination of their volume fraction. Indeed, a diffraction pattern is determined by the exact atomic arrangement in a material and is like a fingerprint in that no two compounds give rise to exactly identical diagrams. In principle a proper measurement of a powder diffraction pattern affords the possibility to characterize the composition, structural arrangement (line positions and intensities) and morphology (line breaths and shapes) of any crystalline material.

Although X-ray diffraction is by far the simpler and less expensive method of powder diffraction (at least with traditional sources), neutrons may provide otherwise inaccessible information and some examples will be considered. Detailed comparison between X-ray and neutron diffraction is outside the scope of this lecture and can be found in most textbooks on diffraction methods (see, for example, G.E. Bacon). It is worthwhile, however, to draw attention to advantages of the low absorption cross-section of most elements for neutrons; this is obviously useful when the sample has to be contained in a controlled environment such as furnace, cryostat or reaction cell but, principally, means that neutron beams probe the bulk sample whereas X-rays often see only a thin layer at the surface. This (together with the almost random dependence of the neutron scattering amplitude on atomic number) clearly confers some advantages in the study of heterogeneous chemical reactions involving mixtures of heavy and light atoms reactants.

The use of neutron powder diffraction has increased rapidly over the last decade. This renewed interest is the result of the construction of high-resolution, high intensity powder diffractometers and of the development of data analysis methods such as Rietveld profile refinement, which allows precise structural information to be obtained from powder data. As a consequence, neutron powder diffraction is now often replacing single crystal methods and is expected to play a major role in various fields of chemistry and materials science; it is already the preferred method for studying the structure of materials which cannot easily be prepared as single crystals (for example catalysts, fast-ion conductors, zeolites etc.). However, it must be reminded that the intensity of the neutron sources, even at high-flux reactors, is weak compared to the intensity available with synchrotron radiation or even conventional X-ray sources; this implies that the data acquisition rates on the best neutron powder high-resolution diffractometers are still of the order of a few hours which clearly precludes their use in most studies of time-dependent chemical or physical phenomena.

In this lecture we will describe an alternative approach of neutron diffraction based on the use of high flux/medium resolution diffractometers equipped with position sensitive detectors (PSD's). This approach is believed to be of practical interest to investigate simultaneously the kinetic, mechanistic and structural features of solid state transformations in materials science.