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ON-LINE X-RAY DIFFRACTION FOR QUANTITATIVE PHASE ANALYSIS: AN INDUSTRIAL APPLICATION OF THE RIETVELD METHOD

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Material properties and plant operations are governed by mineralogy not chemistry. However, they are most often controlled in production by simple measurement of bulk chemistry. If used at all, mineralogy is derived from chemistry through normative calculation. Methods of this nature are fraught with inaccuracy due to the necessary assumptions regarding the exact chemical formulae of each of the component phases. One example is the Bogue method which is the industry standard for Portland cement production. Using X-ray diffraction (XRD), Portland cement remains a notoriously difficult material to quantify due to (i) the number of phases present, and hence degree of peak overlap, (ii) the variable composition of individual phases, and (iii) the presence of polymorphism. Typical cement plant control relies upon intermittent (say, four-hourly) X-ray fluorescence (XRF) analyses of bulk chemistry from which mineralogy is derived.

These limitations in material characterization within the cement industry led to the design and construction of an on-line XRD instrument for direct minute-by-minute measurement of mineralogy. The complex nature of cement XRD patterns required that the instrument use the whole-pattern, Rietveld method for phase quantification rather than traditional single peak methods. The necessity for rapidity and stability of the analytical method required that the classical Rietveld approach be modified to a more restricted refinement strategy. Instruments incorporating these design criteria have now been installed in working cement plants. Preliminary results show that the rapid and direct measurement of mineralogy can be used in feed-back loops for plant control in real time and has the potential to be used in feed-forward loops for prediction of material properties.

Keywords: (ON LINE X-RAY DIFFRACTION) RIETVELD CEMENT

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IMPROVING THE ACCURACY OF SIZE/MICRO STRAIN ESTIMATION BY FIRST PRINCIPLES-MONTE CARLO RAYTRACED FUNDAMENTAL PARAMETERS PROFILES

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In the Monte Carlo raytraced FPA (Fundamental Parameter Approach), the true slit dimensions, their distances and other geometric features are used as input parameters to follow the beam paths inside the diffractometer. In a first trial, this model failed in describing the profile standard SRM 660 (NIST standard reference material) as measured using different devices and X-ray tubes. The reason could be addressed to the emission profile of the commercial X-ray tubes: 5%...30% of the X-rays do not originate from a proper rectangular X-ray focus. The intensity coming from both sides of the focus was called 'tube-tails'. In a second step, the raytraced FPA has been corrected by measuring the focus intensity distribution and including this measurement in the Monte Carlo raytracing algorithm. Now, SRM 660 gave a main micro grain diameter (size) of 725(8) nm and a micro stress of 0.000075(4). For the new SRM 660a a zero micro strain and 1164(13) nm size have been determined. However, the Rietveld plot of SRM 660a deviated significantly from a clean random difference curve. Additionally, a dynamic extinction/absorption correction to the diffraction profile was introduced. Now, a micro strain of 0.000075(4) and an insignificant large size of 11(-4+10) microns were calculated for SRM 660a. SRM 660 did not show a dynamic effect. The micro strains of SRM 660 and 660a are identical and may result from surface tension. SRM 660 has a clear micro size structure. SRM 660a seems to have a size value near to the macroscopic grain size.

Keywords: XRPD RIETVELD METHOD PROFILE ANALYSIS

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PRACTICAL APPLICATION OF THE RIETVELD TEXTURE ANALYSIS IN MATERIAL SCIENCE: PROBLEMS AND SOLUTIONS

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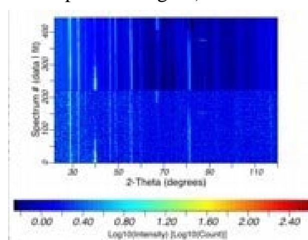
Rietveld Texture Analysis (RTA) is a relatively new methodology to analyze texture of complex materials. It is well known that quantitative texture analysis cannot be performed by traditional pole figures when the symmetries of the phase and sample are very low or the sample is a multiphase one. One solution is to substitute the usual data from traditional texture methods (few peaks, many pole figure points) with Rietveld like data (many peaks/data points, few pole figure points) and so we can obtain the Orientation Distribution Function (ODF) from global fitting of the spectra. Some advantages of this approach go beyond the texture analysis itself. Quantitative phase analysis and crystal structure refinements can be performed on textured samples.

To illustrate the method some examples will be given covering texture/quantitative phase analysis of ceramic matrix composites, multilayers and metallic materials. The spectra for each sample has been collected on laboratory X-ray diffractometers equipped with large position sensitive detectors as well as on neutron spectrometers. The data has been analyzed by a RTA program to obtain the ODF, quantitative phase analysis and crystal structure results. In all cases the analysis was impossible by the traditional methodology as the peak overlapping for some phases was preventing the texture analysis. In the particular case of the multilayer the combined analysis was necessary to obtain the texture and the crystal structure of the piezoelectric ceramic, as the phase was completely overlapped with the Pt buffer layer (2D plot of the measured/fitted spectra in figure).



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AN ACCURATE MOLECULAR STRUCTURE DETERMINATION USING CONVENTIONAL X-RAY POWDER DIFFRACTION DATA OF SMALL ORGANIC MOLECULE AND POLYMER MIXTURE

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An accurate determination of crystal structure and atomic positions of a small organic drug molecule in a mixture of the drug and polymer using conventional X-ray powder diffraction data is demonstrated. Polymer is used to control or release pharmaceutical substances from controlled release drugs or sustained release drugs. Crystal structure determination of the pharmaceutical substances in a drug-polymer mixture is necessary, although difficult, since the presence of polymer or the preparation method might cause changes in physical properties of the pharmaceutical substances; e.g. morphology, polymorphism, or intermolecular interactions to the polymer. Diclofenac in the matrix of chitosan-diclofenac was studied. The X-ray powder diffraction data were extracted using the Le'Bail method. The crystal structure was solved by direct methods from the extracted data and were refined using the Rietveld method. The results were compared with the crystal structural data obtained from single-crystal X-ray diffraction data. The differences in bond lengths are in the range of 0.30 Å and the differences in bond angles are in the range of 5.5°.

Keywords: RIETVELD METHOD CHITOSAN-DICLOFENAC MATRIX, POWDER DIFFRACTIN DATA