

Materials IX

Techniques, Real Time *in situ* Reaction Chemistry

MS10.09.01 DYNAMIC CHARACTERIZATION OF CEMENT AND CERAMIC CHEMISTRY. Paul Barnes, Industrial Materials Group, Dept. Crystallography, Birkbeck College, London, UK

Elucidating reaction/structural pathways requires a complementary approach: Conventional diffraction/refinement techniques (e.g. Rietveld-powder) can yield high resolution "structural snapshots", but such information needs to be allied to that from other structural probes (EXAFS, neutron-scattering, computer-modelling, NMR, EM) as well as from dynamic *in-situ* diffraction. This approach will be illustrated with examples taken from three areas:

- (1) hydrothermal/autoclave synthesis of zeolites;
- (2) high temperature furnacing of tetragonal/monoclinic zirconia from the amorphous hydroxide precursor;
- (3) hydration of a variety of cements (Portland, calcium-aluminate, rapid) under conditions varying from ambient to autoclave.

In particular (3) will include a very recent dramatic example of a 3-phase scenario, anhydrous cement \rightarrow intermediate \rightarrow final hydrate, all occurring within 200 seconds.

MS10.09.02 IN-SITU X-RAY AND NEUTRON POWDER DIFFRACTION STUDIES OF PHASE EQUILIBRIA IN METALS AND CERAMICS. S.T. Misture and C.R. Hubbard, Oak Ridge National Laboratory, Oak Ridge, TN 37831

High temperature x-ray and neutron powder diffraction measurements of reaction chemistry, phase transformations and kinetics in ceramics and metals will be presented, with emphasis on data analysis methods. The capabilities of high temperature x-ray diffraction using conventional and position-sensitive detectors will be described using examples of phase evolution from amorphous precursors and solid-state and peritectic phase equilibria studies. The utility of position-sensitive detectors for time-resolved measurements will be demonstrated for systems including glass crystallization and order-disorder transformations. Rietveld refinement, profile fitting, and powder pattern calibration methods are applied to determine accurate lattice parameters and quantitative phase content, as well as for full structure refinements.

High temperature, high-resolution neutron powder diffraction experiments are critical for many systems where large sampling volumes are required or low-Z elements are of interest. Rietveld refinement for quantitative phase analysis and residual stress determination in metal matrix composites will be presented, as well as structure refinements of high temperature phases of oxide and carbide ionic conductors.

This research was sponsored by the U.S. Department of Energy, Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Transportation Technologies, as part of the High Temperature Materials Laboratory User Program, under contract DE-AC05-96OR22464, managed by Lockheed Martin Energy Research Corp. SM acknowledges the ORNL Postdoctoral Research Associates Program administered jointly by ORNL and Oak Ridge Institute for Science and Education.

MS10.09.03 HYDROTHERMAL CONVERSION OF ZEOLITES; AN IN-SITU TIME RESOLVED SYNCHROTRON X-RAY POWDER DIFFRACTION STUDY. P. Norby, Chemistry Department, Brookhaven National Laboratory

Using hydrothermal conversion of zeolites, new materials not obtainable by conventional synthesis may be obtained. By using *in-situ* synchrotron powder diffraction combined with *ex-situ* SEM, hydrothermal conversion of zeolite Na-LTA was followed. Using the equipment developed, hydrothermal conditions up to 260°C can be obtained using an applied pressure of 45 atm. Hydrothermal conversion with aqueous

solutions of LiCl and AgNO₃ were performed. The conversion zeolite LTA \rightarrow zeolite Li-A(BW) was followed in details using *in-situ* powder diffraction at temperatures from 200-260°C. Also, partially converted samples were prepared *in-situ* on the diffractometer, and investigated using Scanning Electron Microscopy. While the transformation process proceeds via dissolution, the zeolite-LTA crystallites serve as nucleation centers for zeolite Li-A(BW).

A Translating Image Plate System (TIPS) has been developed especially for time- temperature- and wavelength-dependent powder diffraction experiments. We are currently studying solid-solid, solid-gas and solid-liquid phase reactions with special emphasis on hydrothermal and solid state syntheses, ion exchange, phase transformations and chemical reactions. Information concerning e.g. kinetics of crystallization, transformation and chemical reactions, development of crystallite size, and occurrence and identification of intermediate phases have been obtained.

All reactions and syntheses are performed in .5-1mm quartz glass capillaries heated using a hot air stream. Hydrothermal conditions up to 260°C (45 atm.) are obtained by applying an external gas pressure to the reaction mixture.

This work was supported under contract DE-AC02-76CH00016 with the US Department of Energy by its Division of Chemical Sciences, Office of Basic Energy Sciences and by the Danish Natural Science Research Council.

MS10.09.04 TIME RESOLVED DIFFRACTION STUDY UNDER EXTREME CONDITION. T. Yamanaka, and T. Nagai, Department of Earth and Space Science, Faculty of Science, Osaka University, 1-16 Machikaneyama Toyonaka, Osaka, 560 Japan

Time-resolved diffraction studies and kinetic studies of the phase transition and solid reactions have been made by *in situ* observation under high pressure and temperature. Diffraction intensity measurement was made using X-ray from synchrotron radiation and rotated anode generator together with curved position sensitive detector (PSD). A streamer mode rather than proportional mode fulfills the function as an effective detector having an extremely high quantum efficiency. Dynamical range in full range of 120° and a maximum count rate are 10⁵cps and 5000cps, respectively. A delay line positioning system ensures the angular resolution of 0.06° in MoK α radiation using Kr (ethane 15%) gas with 4.2bar compression with high bias voltage of 9600V. A computer aided measurement and control (CAMAC) module enables us to make the time-resolved diffraction intensity measurement with an interval of 10 mil seconds under compression. A fast spectroscopy ADC with maximum of 16,384 channel having 450MHz converter and histogramming memory is installed in the CAMAC crate controller.

We designed a new oil-pressure control diamond anvil pressure cell (DAC) with heating system. A desired pressure was automatically regulated by pressure sensitive semiconductor and electromotive micro piston. A ring platinum micro heater with DC current supplier and thermocouple are installed in DAC. Sample temperature is controlled by PID system. Both pressure and temperature can be controlled from the outside of the station in SR facility.

The kinetic study of the structure transition from α -quartz (P3₂21, z=3) to rutile form (P4₂mnm, z=2) structure has been made by the above described diffraction apparatus. The transformation mechanisms of dehydration, melting and pressure-induced amorphization etc of monometal dioxides and hydrates have been also elucidated by profile analysis including size and strain effect. Their transformation rate were determined by intensity ratios with time between initial and final products. The kinetic study of the pressure-induced first order transition indicates five stages: initial process, inductance period, acceleratory period, steady reaction and deceleration period.