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Time Resolved Studies of Phase Transformations Using High Temperature Powder Diffraction

M.J. Kramer,^{*#} L. Margulies,^{*#} R.W. McCallum,^{*#} H.L. Zhao,^{*#} A.I. Goldman^{*^}, S. Kycia[@], P.L. Lee⁺ and D.R. Haeffner⁺

^{*}Ames Laboratory, [#]Department of Materials Science and Engineering, [^]Department of Physics and Astronomy, Iowa State University, Ames, IA 50011

⁺Advanced Photon Source, Argonne National Laboratory, Argonne, IL 60439

[@]Cornell High Energy Synchrotron Source, Cornell University, Ithaca, NY 14853

Abstract. A high temperature furnace (up to 1500°C) has been designed specifically for use with high-energy synchrotron radiation using Debeye-Scherrer transmission geometry. This allows for full bulk sampling and a low thermal gradient ($< 1^\circ\text{C}/\text{mm}$) and a controlled environment (inert to oxidizing). Unlike flat plate geometry, the transmission geometry allows for solid-liquid as well as solid-solid phase transitions to be explored. A comparison between image plate and charged-coupled detector (CCD) system will be discussed. The potential is to collect quantifiable powder patterns under a second. Data collected on the tetragonal to cubic transition in the RhTi systems demonstrate the capabilities for performing quantitative time resolved high temperature powder diffraction.

INTRODUCTION

Highly monochromatic synchrotron radiation provides an excellent source of photons for high-resolution powder diffraction.¹⁻⁵ With the advent of 3rd generation sources, the potential now exists to acquire data suitable for Reitveld refinement on time scale of seconds or less. This is well within the time scale of many solid state phase transitions. Being able to precisely follow crystallographic changes during phase changes, in particular transient metastable phases, would be an invaluable tool to Crystal Chemists, Condensed Matter Physicists and Material Scientists. Many of the important materials systems actively being studied involve multi-element, multi-component alloys that involve numerous intermediate reactions such as ceramic superconductors, high temperature alloys and permanent magnets. In materials processed by solidification, a succession of peritectic reactions is the norm for ternary and higher order systems. Current research in these alloys systems involves performing differential thermal analysis to identify the reaction temperatures followed by a number of high temperature annealing and quenches followed by x-ray diffraction (XRD) and electron microscopy to identify the phases. Being able to identify the crystallizing phases directly would greatly enhance the understanding of microstructural evolution in complex systems, in particular where metastable phases can not be quenched in. This is particularly a concern in peritectic systems where it is

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nearly impossible to cool a partial melt fast enough to prevent the liquid from crystallizing.

The primary concern with current high temperature XRD (HTXRD) systems is that they employ a flat-plate (Bragg-Brentano) geometry. During peritectic decomposition, the solid fraction, usually denser, can sink below the penetration depth of the x-rays. This is in addition to other errors introduced by this design; including large temperature gradients, sample shift from ideal focus during heating and inability to rotate the sample to achieve powder averaging. *In-situ* study of phase formation required overcoming these technical hurdles.⁶ High energy x-rays (> 20 keV) allow for a transmission geometry (Debye-Scherrer) to be used. This permits a sealed, cylindrical geometry of the sample to be used to prevent liquid/solid separation and incorporate sample rotation (Fig. 1). In addition, a tube furnace design with low thermal gradients across the sample could be used. A double crystal monochromator on the beam-line allows for selecting the optimal wavelength, particular to each system.

FIGURE 1..Schematic of the furnace used in the time resolved studies.

Obtaining time-resolved spectra requires a position sensitive detector (PSD). While there are a number of choices in this area, all have drawbacks. Wire based PSDs require an ionizing gas which, even for high z noble gases, have low efficiencies at high energies. The spatial resolution, particularly for curved detectors, was also of concern. Photo-diode arrays (PDA) have been used in HTXRD,⁷ but also have low efficiencies at high energies. Unlike PSD, appropriate phosphors could be used to enhance their efficiency. Charge coupled devices (CCD) also need a phosphor at high energies, but provide faster read-outs and a better dynamic range than PDAs. Image

plates have been extensively used at high energies.⁸ While there is some question to their efficiencies at high energies, their large area is very attractive for power diffraction. For this study, we primarily used image plates but we will also report on some promising results using a CCD coated with a Ag phosphor. There a number of technologies on the horizon which hold potential, such as energy dispersive diffraction and field effect transistors. However, this is beyond the scope of this paper. Here we wish to report specifically on the potential for doing time-resolved HTXRD using existing detector technology.

TIME RESOLVED STUDIES

In typical powder diffraction experiments, an analyzer crystal is used to focus the diffracted beam onto a point detector. The analyzer acts as an angular slit, avoiding resolution loss due to the sample size and eliminating secondary scattered photons, dramatically enhancing signal to noise. Use of an area detector precludes using the analyzer crystal, resulting in a dramatic loss in resolution since the sample cross-section is projected directly onto the area detector (Fig. 2). At high energies, this is problematic since reciprocal space is highly compressed. The only way around this is to either use very small samples, which would greatly reduce diffraction requiring longer counting times or place an area detector far back from the sample. For this reason, 20x25 cm image plates (Fuji) were employed. The instrumental resolution function for this geometry can be expressed as

$$\Gamma = [\phi_v^2(2\tan\theta/\tan\theta_m - 1)^2 + \delta^2]^{1/2} \quad (1)$$

where ϕ_v is the vertical divergence of the incident beam, θ_m is the Bragg angle of the monochromator, and δ is the convolution of the incident beam and the sample diameter.

$$\delta = (D_s^2 + D_d^2)^{1/2}/D_{sd} \quad (2)$$

where D_s is the sample diameter, D_d is the spatial resolution of the detector, and D_{sd} is the sample to detector distance.⁹

FIGURE 2. Peak width resolution of Si for 1.0 and 0.5 mm diameter samples using an image plate without an analyzer crystal compared to using an analyzer crystal

IMAGE PLATES

A number of image plate configurations were employed in three experimental runs, two at the APS (SRI-CAT 1-ID) and one at CHESS (A2), at nominal energies of 47 and 60 keV and distances of 0.7 to 1.3 m from the sample to the plate. There are a number of geometrical corrections that greatly increased the difficulty in analyzing the data. In addition to the obvious flat-plate correction, there are three orthogonal rotation corrections (Fig. 3). These rotations come about from imprecise mounting of the image plate stage while an additional rotation about X comes from feeding the plate into the image reader. Corrections for Y and Z rotations are performed using multiple scans of a standard (NIST Si) across the entire plate. The X rotation correction is

Figure 3. A schematic of the beam line showing the relative positions of the furnace to the shutter and image plate.

determined by only exposing a 1 mm strip of the plate and shuttering the beam while translating the plate. Furthermore, a higher degree of accuracy could be obtained by placing a Si standard into the beam after the sample to imprint a fiducial mark.

The phase transition of α to β -TiRh is an example of the high quality, but time resolved data that has been taken. There is some disagreement in the literature as to whether this phase transition is a first or second order. Ground powder of single phase TiRh was heated and cooled at 10°C/min. Each

Figure 4. A section of image plate showing the tetragonal to cubic phase transition in TiRh, area of transition marked by an arrow. The stripes are individual "snap-shots" taken every 8 seconds.

strip is an 8-sec. exposure (Fig. 4). The data clearly shows the coexistence of both phases over a narrow temperature range (Fig. 5). There are actually three phases, a low temperature monoclinic phase (P2/m) which converts to the tetragonal phase (P4/mmm) and finally to a cubic phase (Pm3m). All of these phases can be constructed out of a simple ordered cubic lattice with Rh atoms at the corners and Ti at the center. The phase transitions are diffusionless. The cubic to tetragonal occurs due to an elongation along the c-axis while the monoclinic distortion occurs due to an elongation along the {110}.

Figure 5. Cell parameters for TiRh on heating (closed) and cooling (open) showing that the phase transition is first order.

CCD

In order to evaluate the relative effectiveness of CCD detectors for taking time resolved data, we measured several standards (Si, CeO_2 and Al_2O_3) using various sample sizes (0.7, 1 and 2 mm diameter tubes). The CCD was a cooled 1K (6.25 cm x 6.25 cm) SMART 1000 Bruker AXS mounted on the Huber 2 θ arm and placed 30.3 cm from the sample. The front plate was coated with a Ag phosphor. While this was too close for reasonable resolution (see above section), the objective was to determine if higher S/N data could be obtained with shorter acquisition times than image plates. Unlike the image plate, each read-out contained the entire Debye ring since no slit was placed in front of the camera (Fig. 6). The data acquisition rate is limited to the readout rate, but this could be greatly enhanced by binning channels since only the central strip is needed. The sample was rotated through 20° during data acquisition. Powder averaging is confirmed by the uniform intensity of the Debye rings.

Figure 6. Representative CCD image of Si standard with 1 sec exposure. The solid lines indicate the region of integration in Fig. 7.

Figure 7 is a comparison of the integrated intensity along 10° arc length compared to a 1 mm strip of an image plate for Si using the same energy (60 keV) and sample tube diameter (1 mm). Ignoring the rather broad peaks for the CCD, note that the S/N is clearly superior for a 1 sec exposure compared to 5 sec for the image plate. In addition, the background is clearly lower and the peak intensities more representative of their calculated values for the CCD.

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Figure 7. Raw counts from a Fuji image plate and a CCD using a 1 mm capillary filled with Si.

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