A HIGH-TEMPERATURE POWDER DIFFRACTION FURNACE

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ABSTRACT

A new high-temperature XRD instrument, utilizing multilayer optics and a custom furnace, has been developed to maximize sensitivity and minimize problems associated with sample displacement. This paper will describe the technical specifications of the new instrument, and will present temperature calibration with standard reference materials and measurement of phase evolution in an industrial glass batch as illustrations of instrument performance.

INTRODUCTION

High-temperature X-ray diffraction (HTXRD) is an extremely useful tool in many areas of scientific research, particularly in the development of ceramic materials. A reflection geometry high temperature X-ray diffractometer with divergent beam has been developed previously by this laboratory [1], and has proven to be a valuable instrument in a variety of ceramic processing applications.

The development of focusing optics has brought high intensity X-ray sources, and the associated benefits, into laboratory applications. Collimating multilayer optics can be used to provide parallel X-ray beams from sealed tube X-ray sources, with fluxes approaching rotating anode sources. The benefits of parallel beam multilayer optics in powder diffractometry have been evaluated and reported by [2-5]. Use of a parabolic multilayer optic, manufactured by Osmic Inc., was shown to increase peak accuracy, intensity, signal/noise ratio and resolution, when compared to an identical instrument with no beam-conditioning optic [3].

The objective of this project was to combine multilayer optics and a furnace assembly to create a versatile transmission and reflection geometry high-temperature powder diffractometer.

INSTRUMENT LAYOUT

The instrument, featured in Figure 1, can be discussed as two discrete systems: the diffractometer, and the furnace.

Diffractometer

The system is based on the Siemens D500 diffractometer, with the goniometer operating in the horizontal plane, and a sealed Cu anode X-ray tube. Front end optics consist of a Max-Flux® GO-13N model multilayer parallel beam optic from Osmic Inc., which conditions the divergent X-ray beam into an $\alpha_1, \alpha_2$-only parallel beam of 0.8mm width. The beam then passes through an...
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axial collimator to the sample, creating a beam height of 12mm. The sample is contained in a vertical capillary of a suitable amorphous material, rotated about the central goniometer axis. A goniometer head with angular and translational adjustment ensures constant capillary positioning (Figure 2). A variable voltage DC motor drives the goniometer head, at up to 50 rpm. Sample alignment is facilitated by a removable high-magnification scope. Capillaries of up to 1.5mm diameter can be used, depending on experimental requirements, sample density and grain size. Glass capillaries are suitable up to 600°C, fused quartz up to ~1000°C and sapphire at higher temperatures.

Use of a capillary for sample containment offers several advantages over theta-theta geometry: Constant instrument geometry is ensured, even with samples prone to dramatic volume changes, foaming or spitting. Capillary diameter can be varied to suit the grain size, quantity and density of material available. In addition, use of a multilayer optic enhances the photon flux, allowing detection of phases present in low concentrations and vastly improving instrumental resolution. All of the above advantages make this instrument suited to a wide range of high-temperature materials processing applications. In addition, reflection geometry is also possible for use where an ‘infinitely thick’ sample is required.

For rapid data collection, an mBraun position sensitive detector enables rapid data collection with a resolution up to 0.02°. For reduced background noise, a radial collimator can be placed preceding the detector.

**Furnace Assembly**
The furnace attachment can be seen in Figures 1 and 2. A cylindrical hot-zone of one inch diameter and 2 inches length is surrounded by almost three inches of insulating refractory and a
stainless steel cylinder. Platinum/Rhodium heating elements lining the central core are connected to a SCR power system with digital temperature control. A 180° window of 12mm height creates a clear beam path between source, sample and detector. In order to eliminate convection currents, the window is covered with Kapton film. For sample loading, the furnace is raised via an electric winch system. The furnace has the capability to heat to 1599°C at a maximum heating rate of about 400°C/min.

PRELIMINARY DATA AND INSTRUMENT APPLICATIONS

High Resolution
The major benefit of a parallel incident beam is increased resolution. Figure 3 shows a comparison between this parallel beam, transmission geometry furnace and a divergent beam (1°), reflection geometry instrument, both with position sensitive detectors. Scans show typical E-glass batches containing silica and calcite. Increased resolution with the parallel beam system is obvious for the specific instrumental conditions used. Peak widths at half the maximum intensity are listed in Table 1, and show resolution to be more than twice that of the divergent beam system, with consequent benefits for phase-identification and lattice parameter refinement.

<table>
<thead>
<tr>
<th></th>
<th>Quartz</th>
<th>Calcite</th>
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<tr>
<td>1° divergent beam, reflection geometry</td>
<td>0.44°</td>
<td>0.52°</td>
</tr>
<tr>
<td>Parallel beam, transmission geometry</td>
<td>0.18°</td>
<td>0.17°</td>
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**Background Reduction**

Reduction in background radiation, and subsequent improvement in signal/noise ratio, is obviously desirable in any powder diffractometer. Background reduction is enhanced through two means: i) use of a radial collimator between sample and position sensitive detector and ii) lowering the furnace assembly, which acts to absorb much of the stray radiation. Figure 4 shows fixed-PSD measurements for quartz with furnace raised and no radial collimator, and for furnace lowered with radial collimator. The result is a background reduction of around thirty times the original background intensity. When the system is operated in fixed-PSD mode however, the axial collimator produces periodic signal reductions where the diffracted beam is physically blocked by the collimator blades. This can be observed in Figure 4, where a temporary reduction in intensity over a narrow angular range is observed on the quartz peak at around 26.5° 2θ. To ensure diffraction peaks are not blocked, the detector needs to be oscillated or scanned during measurements.

**Phase Transformation Studies**

The suitability of the new instrument to phase-transformation studies is illustrated in Figures 5 and 6. NIST (SRM8759) phase-transformation temperature standards have been employed in initial temperature calibration of the system. Figure 5 shows the phase transformation of NIST KClO₄. The onset of transformation can be observed at an indicated 290°C, and is complete at 295°, compared to the actual value of 299°C. Error at this temperature is therefore between 5 and 10°C.

Figure 6 shows phase transformation of K₂SO₄ to occur between an indicated 565 and 575°C, compared to the actual temperature of 586°C, suggesting an error of the order of 10° at this temperature also. An exhaustive temperature calibration up to the maximum operating temperature of this instrument allows measurements with fully calibrated temperatures and eliminates the need for a thermocouple attached to the capillary.
Glass Batch Reactions
One application for which this instrument is particularly suited is in the analysis of glass batch reactions. During heating, many glass batches evolve gas, causing foaming that can defocus reflection geometry furnaces. HTXRD has been employed previously to analyze these reactions [6,7] but have been restricted to near-equilibrium heating conditions due to insufficient X-ray flux and long counting times. Use of the Max-Flux® optic increases X-ray flux, therefore decreases counting time, enabling analysis of reactions at rapid heating rates.

Figure 7 shows fixed-PSD scans of a borosilicate glass batch heated at 50°C/min up to 900°C. Thermal expansion and melting (170°C) of boric acid can be readily observed. Calcite is seen to decompose above 800°C, however no CaO peaks can be observed. Small peaks representing CaSiO₃ (~29°) and Ca₂SiO₄ (~31°) can be seen at 800°C, but are not present at 900°C. Only quartz is present at 900°C. Such information is extremely valuable to the glass scientist when predicting possible defects in final products, and in devising thermodynamic models of glass batch reactions. The detail offered by this instrument enables detection of minor phases that would otherwise go undetected.

FUTURE WORK
The next phase of the project will involve the attachment of a scintillation detector with Osmic Inc. flat multilayer to accompany the existing PSD. This detection system will give much greater resolution than the PSD. This detector can be employed in instances where rapid data...
collection is not necessary, but where enhanced resolution is important. A comparison of the two detection systems will be presented at a later date.

SUMMARY

A high-temperature powder diffractometer has been constructed to take advantage of the latest multilayer X-ray optics available. The system offers high resolution and signal/noise ratio, and improved counting statistics over non-parallel beam instruments. The system is suited to a wide range of applications where in-situ XRD analysis is required.

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REFERENCES


