SYSTEMATIC ERRORS IN METAL STRIP DIFFRACTION FURNACES

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ABSTRACT

Requirements for accurate lattice thermal expansion measurements using Bragg-Brentano diffraction geometry are briefly described and results are shown for SRM676 aluminum oxide at temperatures up to 1000ºC. These data demonstrate that careful consideration of systematic sample displacement and temperature is necessary to obtain reliable results. A comparison of results with and without calibrations to remove the systematic errors shows that ignoring the errors produces unreliable and unreasonable results.

INTRODUCTION

High temperature diffraction measurements of polycrystalline and powder specimens using X-ray diffraction (XRD) is gaining popularity as commercially available diffraction furnaces become more widely used. Although the instrumental and sample-related errors for room-temperature measurements of interplanar spacings using Bragg-Brentano diffraction geometry have been well-characterized (Klug and Alexander, 1974; Jenkins, 1989; Wong-Ng and Hubbard, 1987; Jenkins and Schreiner, 1989; Payzant and King, 1993; Misture, et al., 1994) high temperature measurements lead to additional or exaggerated systematic errors. We consider the use of a commercially available diffraction furnace that incorporates two resistively heated metal foil strips, one acting as the sample support and the second surrounding much of the sample holder to provide volume heating. A photograph of the system is shown in Fig. 1.

Sample displacement away from the ideal focusing point on the diffractometer is generally the largest error found on well-aligned instruments, and, if left uncorrected, will result in incorrect d-spacings and thermal expansion coefficients (CTE). Most diffraction furnaces are prone to introduce sample displacement errors because of thermal expansion of the furnace materials.
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Resistively-heated metal strip furnaces are especially problematic because the metal strip heater, which is also the sample mount, may bend toward or away from the focusing circle of the instrument.

Accurate temperature measurement is difficult when using metal strip furnaces because temperature gradients normally exist through the thickness of the sample, but the temperature is commonly measured at the surface of the strip heater. Wang and Payzant (1999) have used infrared imaging to show that extreme gradients occur along metal strip heaters. A further complication is the reactivity of samples with the heater metals; samples often must be isolated from the heater strip using a non-reactive substrate, leading to even larger temperature inaccuracies. Although the temperature transducer, usually a thermocouple or pyrometer, can be calibrated, temperature calibrations using phase transformations of certified calibration materials are preferred because temperature gradients in specific sample mounting arrangements can be quantified.

A widely used method for removing instrumental errors in a room temperature XRD pattern is the internal standard method (Wong-Ng and Hubbard, 1987). A ‘standard’ material with certified peak locations is mixed with the specimen, which allows one to generate a Δ2Θ vs. 2Θ calibration curve for the standard. All systematic peak position errors are then removed from the XRD pattern of the sample by applying the calibration curve to the peak locations of the sample. This method can be used for high temperature measurements if an inert standard material is chosen with well-known thermal expansion coefficients.

More modern approaches for calibration of peak positions, which do not require an internal standard, analytically model the instrumental errors and remove their effects from the diffraction pattern. However, for brevity and clarity, this paper reports only the results from the traditional and well known internal standard calibration method.

**EXPERIMENTAL PROCEDURES**

High temperature XRD measurements were made using a Scintag Θ-Θ diffractometer with a Buehler HDK2 high temperature attachment and Cu Kα radiation. Pt/30% Rh heating elements were used for all experiments, and temperature measurements were made using a type S thermocouple welded to the bottom of the primary heater strip at the center of its length.

The HDK2 diffraction furnace contains two resistance-heating elements; a primary heater strip, which is also the sample holder, and an environmental heater that surrounds the primary heater strip with an opening for the X-ray beam. The diffraction furnace can operate in two different configurations. The standard configuration, which uses both the primary and environmental heaters and can reach 1600 °C, was not used in the experiments. Instead, the measurements were made using only the environmental heater to heat the specimen, which limits the maximum temperature to ~1000 °C. Wang and Payzant (1999) used thermal imaging with an infrared camera to show that using only the environmental heater does not reduce temperature gradients because the primary heater is water cooled on both ends. However, the combination of using the environmental heater and a substrate is expected to reduce temperature gradients.

XRD patterns were collected using an mBraun position-sensitive detector. Continuous detector scans were used in all cases, with a digitization step of 0.02 °2Θ covering an angular range of 20 – 130 °2Θ. The time-temperature profiles included heating the samples at 5 °C/min,
equilibrating the sample at temperature for 5 min, collecting the XRD pattern, ramping the temperature to the next setpoint, equilibrating, etc.

NIST standard reference materials (SRM) were used to evaluate the internal standard 2θ calibration method. NIST SRM 640b silicon was used as an internal standard, and SRM 676 Al₂O₃ was used as the sample. The Al₂O₃ was run from 27 to 900°C, and diffraction patterns were collected isothermally every 100 °C.

To prevent reactions between the Al₂O₃/Si powder mixture and the Pt/Rh heater, the powder sample was mounted on a full-density polycrystalline MgO substrate. Substrate dimensions were 10 x10 x 0.25 mm. Powder samples were loaded by grinding the powder in ethanol and applying a drop of the powder/ethanol slurry to the substrate. This sample mounting method produces a uniform powder mount approximately 30 μm thick after drying.

Temperature calibrations were made using differential thermal analysis standard materials certified by the International Confederation for Thermal Analysis (ICTA) and distributed by NIST as SRM numbers 759 and 760. The standards used and their transformation temperatures are summarized in Table I. XRD patterns were collected in 3, 5, or 10 K increments to determine the transformation temperature of the standards. Transformation temperatures were determined from the XRD patterns as the lowest temperature where XRD peaks of the high temperature phase grew out of background. The random temperature error introduced by mounting the samples was determined by measuring separate mounts of each standard material two to five times.

The powder patterns were analyzed using several software packages. Peak locations were determined using JADE+ (Materials Data, Inc., 1996). The peak search algorithm was a modified second derivative Savitzky-Golay method, and a smoothing filter length of 7 data points was employed.

Internal standard calibration required first calibrating the temperatures using the ICTA standards, then using the calibrated temperatures and the thermal expansion of Si metal to determine the correct peak locations for the Si. Each high temperature pattern was calibrated using the peak locations determined using JADE+ and a locally-modified version of INTCAL (Snyder, 1994) which incorporates the thermal expansion for silicon metal. The program INTCAL automatically calculates the peak locations for Si metal at the specified temperature and corrects all peak locations using a calibration curve of the form Δ2θ vs. 2θ; i.e. the typical internal standard calibration method is used after correcting for the thermal expansion of the Si standard. The thermal expansion of Si was the “best polynomial” in the compilation of thermal expansion data (Touloukian et al., 1977).

The calibrated peak positions produced by INTCAL were then used to refine the lattice parameters and calculate the thermal expansion as a function of temperature. Lattice parameter refinements were carried out using the Appleman code (Evens, et al., 1963) modified by Hubbard, et al. (1982) in MICRO-CELLREF (Materials Data, Inc., 1995).

RESULTS AND DISCUSSION

HTXRD patterns for the transformation of a K₂SO₄ slurry deposited powder on an MgO substrate are shown in Fig. 2. A temperature correction curve, determined using ICTA standard materials and HTXRD patterns similar to Fig. 2, is shown in Fig. 3. The temperature standards used were KClO₄, Ag₂SO₄, K₂SO₄, and SrCO₃, and cover the range of ~300-930 °C. Reproducibility between sample mountings, as indicated by the error bars in Fig. 3, ranges from
±2 to ±5 °C, approximately the delta-T between X-ray patterns. The difference between the measured and certified temperatures (shown in Fig. 3) changes sign between ~600 and 930 °C. This result is expected because the thermocouple is mounted under the specimen and therefore is shielded from heat loss that occurs from the top of the specimen.

Figure 4 clearly demonstrates that calibrated XRD patterns are essential for determining accurate lattice thermal expansion values. The data for the a axis shows drastic inaccuracy when using uncalibrated XRD data for cell refinements, with most points significantly below the ±3% error window. The uncalibrated data for the c axis show random error above and below the known values. Sample displacement is expected to shift both the a and c axis data in the same direction, which indicates that the inaccurate peak positions caused large correlations between the a and c axes in the refinement, producing unreasonable results.

As shown in Fig. 4, 2Θ calibration of the diffraction data generally brings the a and c axis CTE to within the uncertainty of the accepted values. The point at 100 °C remains outside the ±3% error window in the a axis CTE, while the points at 100, 600, and 700 °C are slightly outside the error window for the c axis CTE. Nonetheless, the CTEs determined using calibrated XRD patterns provide correct trends and reasonable accuracy as opposed to the uncalibrated data that show wild variations in expansion with temperature.
**SUMMARY**

Bragg-Brentano geometry XRD using metal strip heaters is an effective method for measuring lattice thermal expansion, but special care must be taken to eliminate systematic instrumental errors. Temperature corrections based on standard materials are recommended when using metal strip diffraction furnaces to account for temperature gradients between the location of the thermocouple and the irradiated sample surface. Diffraction pattern calibrations are critical for accuracy, and can be performed using the traditional internal standard method or using Rietveld refinement.

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