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2.6. Non-ambient-temperature powder diffraction

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2.6.1. Introduction

X-ray powder diffraction (XRPD) is a powerful tool for the *in situ* investigation of the evolution of a specimen during a non-ambient experiment and for studying structural changes such as lattice expansions and contractions, phase transformations, phase composition, material stability, and alterations in crystallite size. X-rays (and neutrons) are more penetrating than other analytical probes and thus are ideally suited to carrying out *in situ* studies. Many (if not most) polycrystalline materials undergo transformations under non-ambient conditions. If the aim of an experiment is to discover structure–property correlations, it is crucial that the correct structure be used; thus *in situ* diffraction experiments are almost mandatory. This chapter highlights the best ways to perform non-ambient experiments, describing the different equipment for slightly and heavily absorbing materials and the corresponding optical pathways.

The focus is on commercially available equipment for laboratory diffractometers and not on special equipment built at synchrotrons and neutron facilities.

2.6.2. *In situ* powder diffraction

The Latin phrase '*in situ*' literally means 'in position', but it is used in many contexts. In the field of X-ray powder diffraction there is no strict definition of this phrase. If the phrase is taken literally, all non-ambient experiments are *in situ*; the material stays 'in position' during the non-ambient experiment. The environment changes while transforming the sample by outside influences (Norby & Schwarz, 2008). Temperature changes give rise to many processes that can be monitored with or without different gas environments. The main processes that are monitored are the formation of new compounds, phase transformations, and structural changes such as lattice expansions and contractions. Increasingly, surface-layer properties such as stress and texture are studied. The characterization of variations in the crystallite size of nanomaterials is a more recent application.

In situ X-ray diffraction is still a growing research field owing to the introduction of line detectors and area detectors (see Chapter 2.5). These make it possible to measure a large part of the diffraction pattern at once, making the scanning time much shorter compared with a point detector. This speed significantly improves the data quality and reduces the risk of collecting uninterpretable data because of changes in the material under study during the measurement. Another advantage of these detectors is that static detector measurements can be performed, making time-resolved and/or temperature-resolved studies possible.

2.6.3. Processes of interest

Many applications of XRPD contribute to industrial and environmental process development. Some typical application areas are heat treatment and annealing, which are frequently used in the production of alloys, ceramics and polymers; the annealing process affects the strength and/or hardness of materials through microstructural changes. Calcination and sintering are used in the fields of catalysts, building materials and zeolites. Dehydration processes in pharmaceuticals are studied to determine the influence of local environment on the microstructure of drugs and how time affects the availability or preservation of the active pharmaceutical ingredient. These very important topics can be investigated in the case of hydration or dehydration with a humidity chamber. Such chambers control the relative humidity at the same time as the temperature, and are commercially available. Another important topic for the pharmaceutical industry (see Chapter 7.5) is the polymorphic transformations that occur under near- and non-ambient conditions. In nearly all fields from alloys to drugs, from building materials to catalysts, and from nanomaterials to single-crystal materials, structure and phase changes are studied during the operation of processes. Increasingly, non-ambient studies also include other parameters besides temperature and gas environment, for example pressure and humidity. Processes such as the charging and discharging of batteries (see Chapter 7.3) can also be seen as a non-ambient or perhaps better as an '*in operando*' process.

2.6.4. General system setup of non-ambient chambers

2.6.4.1. *Sample stage*

The main requirement for a good non-ambient chamber is that the specimen is cooled/heated homogeneously at a controllable rate. The temperature of the goniometer and other parts of the diffractometer should not be affected while operating the temperature stage. Different sample-stage designs are possible: direct heating/cooling *via* a strip or plate, or surround heating/cooling with an oven or gas convection for a capillary. The advantage of an environmental heater/cooler is the good temperature homogeneity, as there is heat transfer from all sides by radiation and gas convection around the sample or capillary. In contrast, when using a direct heater such as a heating/cooling strip or plate only one-side heat transfer to the sample is possible through the contact surface. An advantage of direct heaters/coolers is the ability to achieve very high and low temperatures and rapid temperature changes. Other differences are the more accurate sample-temperature measurement in an oven compared with a strip heater, where temperature gradients can be present in the strip and the sample attached to the strip heater. For high-temperature measurements with capillaries, the best choice is fused silica ('quartz') glass with a melting point of ∼1973 K; for low-temperature measurements borosilicate glass capillaries are used. A typical hardware setup for a non-ambient X-ray diffraction experiment is shown in Fig. 2.6.1.

2.6.4.2. *Temperature-control unit, process controller*

To control the temperature, a temperature controller with an integrated process controller is needed. For controlled heating/cooling it is necessary to continuously measure the actual temperature and compare it with the set temperature. Often, a standard industrial process controller is used to convert the signal from the temperature sensor into a temperature value, to display

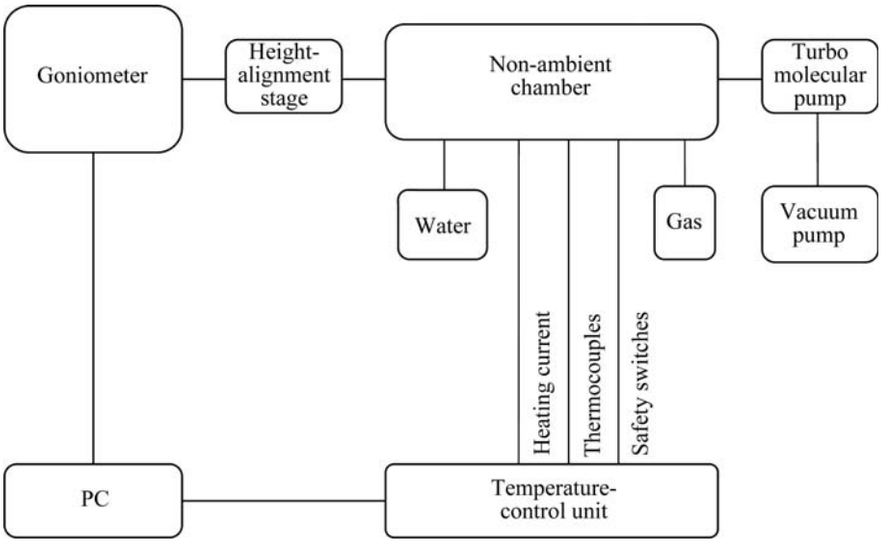

Figure 2.6.1
Typical hardware setup for a non-ambient X-ray diffraction experiment as described in Section 2.6.4; non-ambient chamber, temperature/process-control unit, vacuum/gas equipment, cooling water and goniometer with height-alignment stage connected to a PC.

the value, to send it to the control PC and to control the power for heating/cooling. In addition to controlling the sample conditions, the temperature-control unit (TCU) usually monitors other instrument components such as the cooling of the sample-stage housing and safety devices.

2.6.4.3. *Vacuum equipment, gas supply*

High-temperature X-ray diffraction measurements are often performed in vacuum or in an inert-gas atmosphere to avoid oxidation of the specimen or the sample support. Systems with a rotary pump typically achieve a vacuum of 10^{-2} mbar (where 1 mbar = 100 Pa); when adding a turbo molecular pump to the rotary pump, a vacuum of about 10^{-4} mbar can be reached. A low vacuum or a completely dry gas atmosphere, *e.g.* pure nitrogen (or helium, which has the advantage of a lower background in the diffraction patterns), is also needed for low-temperature experiments to avoid icing problems. Best practice is not to vent the flow of inert gas into the diffractometer enclosure or the laboratory atmosphere, but into the ventilation system (fume hood). Some local safety authorities may require such venting.

2.6.4.4. *Water cooling*

The housing of the sample stage must be kept close to room temperature to avoid heat transfer to the diffractometer and to ensure user safety. In most cases, water is used for this purpose, and the cooling water can be shared with the diffractometer.

2.6.4.5. *Diffractometer and height-compensation mechanism*

The non-ambient chamber has to be interfaced to the goniometer. Interfaces are available without and with a height-compensation mechanism; the latter can be manual or motorized.

When heating/cooling a specimen in an environmental heater, sample displacement is virtually unavoidable, mainly owing to the thermal expansion/contraction of the sample holder. It is possible to correct the temperature-dependent change of the sample position with a height-compensation mechanism (motorized z stage) or to model the displacement in the refinement software. When using a z stage that is controlled *via* software, the shifts in peak positions are only caused by the thermal lattice expansion/contraction of the sample under study. If no such mechanism is available, a parallel X-ray beam (which is not sensitive to sample displacement) can be used, but the resolution may be worse compared with measurements in para-focusing Bragg–Brentano geometry, and granularity may be significant. For strip heaters the displacement of the sample due to the strip is not so pronounced. If a peak of the material of the strip is visible in the diffractogram this can be used as a reference for height compensation if the thermal expansion of the strip material is also taken into account.

2.6.5. Specimen properties

In designing a non-ambient experiment the specimen properties must be taken into account; the holder material should not react with the sample. For flat sample geometry it is preferable that the specimen completely absorbs the X-ray beam. If the specimen is highly transparent, one can either use a thin specimen on a zero-background sample holder or use a capillary. For capillary measurements the X-ray beam must penetrate the capillary completely; if this is not the case, higher energy X-rays (such as Mo or Ag) can be used (Section 2.6.7.2). Every sample is unique, and a suitable solution must be devised.

2.6.6. High-temperature sample stages

A typical laboratory non-ambient setup consists of a non-ambient sample stage, often called a temperature chamber. The sample stage is mounted on a goniometer, preferably in a θ–θ configuration (Fig. 2.6.2). In this case the sample stays horizontal and there is no need to fear melting of the sample with the possibility of it dripping off/out of the sample holder.

A temperature-control unit, vacuum equipment, gas supply and water cooling have to be added to the system before it can be operational.

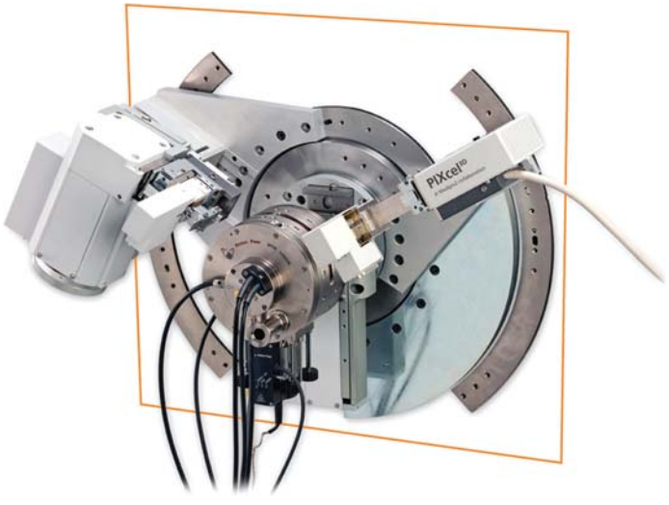

Figure 2.6.2
An Anton Paar HTK 1200N high-temperature oven chamber on a PANalytical Empyrean system equipped with a PIXcel3D detector.

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