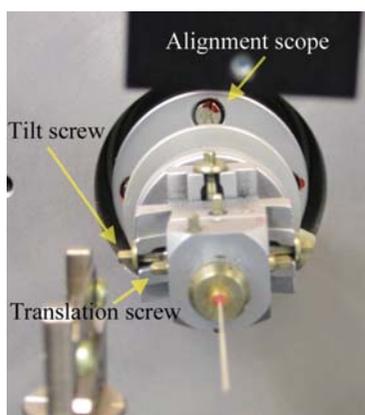


2. INSTRUMENTATION AND SAMPLE PREPARATION

**Figure 2.10.49**

Goniometer head position in relation to the goniometer-mounted alignment scope.

movement rather than any wobble from tilt misalignment. However, it can still take some time. For systems where the goniometer spinning is controlled by computer software a wireless computer mouse is a very good investment, as it allows the person performing the alignment to stop the spinning capillary without taking their eyes off the sample.

2.10.2. Neutron powder diffraction**2.10.2.1. Specimen form**

Large penetration depth and sensitivity to lighter elements (especially mobile species such as hydrogen, lithium and oxygen) in the presence of heavier elements make neutron diffraction a powerful and complementary technique to X-ray diffraction for structural studies. Because neutrons are highly penetrating and large sample volumes can be used, sometimes no specimen preparation is needed at all; sintered ceramic pellets, fish otoliths and renal calculi can be placed directly in the beam. However, the most traditional sample holder for standard neutron powder diffraction (Debye–Scherrer geometry) is cylindrical and is usually made of vanadium. If the diffraction instrument has reflection geometry, however, one has to use flat plates. Diffractometers built for the study of engineering materials can accommodate various shapes and forms because they can isolate small volumes within the sample.

2.10.2.2. Sample size

Traditionally, a large amount of sample was needed for neutron powder diffraction because of the limited flux available at various neutron sources. However, significant advances have been made in source power and detector technology, making it possible to do standard diffraction experiments with relatively small quantities of samples, both at reactor and spallation sources. There are multiple factors that have to be taken into account to determine how much sample is required. These include source power, detector coverage of the instrument, source-to-sample distance, the scattering power of the sample, beam size, available time and information sought from the measurement. Neutron powder diffraction instruments often have to trade intensity for resolution, and so often a larger quantity of sample is needed for high-resolution instruments. Sample mass can vary from milligrammes to several grammes, so it is always advisable to contact the scientists responsible for the particular instrument to determine the quantity needed for the proposed measurements.

**(a)****(b)****Figure 2.10.50**

Two examples of sample holders used in neutron powder diffraction. (a) A cell made of Inconel used for hydrogen absorption studies in Li_3N (Huq *et al.*, 2007). (b) Vanadium holders that were specially made for a sample changer built for the Powgen diffractometer located at Oak Ridge National Laboratory.

2.10.2.3. Specimen containment

The choice of materials for designing sample holders usually depends on the type of experiments, temperature or pressure conditions, the type of neutron source (constant-wavelength or time-of-flight), the presence or absence of fine radial collimators in the instrument and finally the sample. The scattering of vanadium ($\sigma_{\text{coh}} = 0.0184 \text{ b}$) or a TiZr alloy (a null scatterer, because of exact matching of the negative scattering length of titanium and the positive scattering length of zirconium) is almost purely incoherent, making it ideal for sample containment for diffraction measurements. Although the coherent scattering of vanadium is small, in careful work it should not be a surprise to find weak peaks from V (space group $Im\bar{3}m$, $a = 3.027 \text{ \AA}$) in the powder pattern. Examples of vanadium sample cans are shown in Fig. 2.10.50(b). At a reactor source aluminium is even better if low-angle (large d -spacing) reflections are of interest, as in the case of many magnetic structural studies, because the aluminium incoherent scattering cross section is three orders of magnitude less than that of vanadium. At elevated temperatures, vanadium easily forms oxides or hydrides in the presence of air or hydrogen, making the cell brittle, so its use is limited to low-temperature studies or in vacuum furnaces. At temperatures higher than 1273 K one often has to use boron nitride caps and molybdenum screws for vanadium sample holders to avoid eutectic formation (an example is shown in Fig. 2.10.51b). For

2.10. SPECIMEN PREPARATION



(a)



(b)

Figure 2.10.51

Two sample holders used for high-temperature studies. (a) A cell made of quartz with frits at the bottom to allow gas flow through the sample. (b) A holder on the right made of vanadium but using a boron nitride top with molybdenum bolt, nuts and washers to avoid melting due to eutectic formation. The fitting on the far left, which is made of stainless steel, is used to attach the boron nitride cap to the stick.

samples that react with vanadium, a thin layer of a noble metal such as gold can be vacuum deposited inside a vanadium can to stop it from reacting with the sample (Turner *et al.*, 1999). If this approach is used, it should be remembered that the melting point of gold is 1337 K, and when it is irradiated by neutrons it becomes activated with a half-life of 2.7 days. For experiments requiring hydrogen pressure at elevated temperature, Inconel (Fig. 2.10.50a) is often the material of choice (Bailey *et al.*, 2004). However, in this case for diffraction measurements one has to either exclude the Inconel peaks or make use of radial collimators to reduce the signal from the vessel itself. In spallation sources with large detector area coverage one can also do an experiment where only detectors at a scattering angle of 90° are used. For gas-absorption experiments at low temperatures, however, vanadium is still the material of choice. For pressure measurement in anvil-type cells, TiZr is used for the gasket.

For opposed-anvil pressure experiments the anvil materials can be either cubic tungsten carbide or boron nitride. The latter is preferred as boron is highly absorbing and does not contribute anvil reflections to the sample measurement, so therefore effectively works as an incident-beam collimator. The use of tungsten carbide is reserved for techniques where a ‘through-gasket’ approach is required, such as furnace measurements with a graphite heater where the use of a null scattering alloy as a gasket material is not possible. A recent development in high-pressure neutron scattering is the use of sintered diamond anvils, also called PCDs (from polycrystalline diamond). They allow the accessible pressure range to be doubled at the cost of adding very strong diamond reflections to the pattern.

However, for gas pressure cells aluminium is often used, as it can withstand higher pressure and Al absorbs neutrons only weakly as the absorption cross section of aluminium, $\sigma_{\text{abs}} = 0.231 \text{ b}$ for a wavelength of 1.8 Å, is small. For high-temperature gas-flow experiments fused silica (‘quartz’) glass is generally used for sample containment. These holders can also have glass frits attached at one or both ends for easy flow of gas through the sample, as shown in Fig. 2.10.51(a).

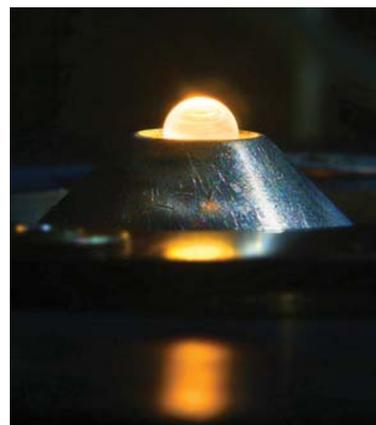


Figure 2.10.52

Aerodynamic levitation system to suspend melts at temperatures to 2773 K and beyond for neutron diffraction measurements.

A few very high intensity instruments are now able to carry out powder diffraction from milligram quantities of sample. For these measurements vanadium cans produce too much background, as there is more vanadium in the beam than the sample. The use of thin-walled silica/glass or Kapton capillaries may be more appropriate in those circumstances.

It is also important to remember that an exchange medium is used for low-temperature (heat transfer) and pressure (pressure transfer) measurements. Helium gas is generally used as a low-temperature exchange medium. Typically, cans are sealed with a flange and lid that supports an indium (or other soft metal) gasket. If the sample is air sensitive and has to be loaded in a glove box, one should try to use a helium-filled glove box. Argon- or nitrogen-filled glove boxes are more common but the freezing temperatures of argon and nitrogen are 84 K and 77 K, respectively. They will no longer work as exchange gases below these temperatures and, because of their rather large neutron-scattering lengths, new diffraction peaks will emerge at or below these temperatures. Similarly one should ensure that a pressure medium will remain hydrostatic for the pressure range for which it is being considered (Varga *et al.*, 2003).

It is also worth noting that cooling powder samples below 1 K relies entirely on thermal conduction through the walls of the sample holder and to the specimen itself. If great care is not taken, the specimen temperature may be far higher than that reported by a thermometer attached to the sample holder. At a minimum, the holder lid should be made from copper, as it is expected that the superconducting transitions in aluminium and vanadium would cause the walls of the sample holder to become thermally insulating and greatly reduce their ability to cool the sample. Of course, properly sealing the loose powder under an atmosphere of ^4He is equally important. It is essential that the indium seal be installed correctly, as ^4He undergoes a transition to a superfluid at 2.17 K and has effectively zero viscosity, and can easily escape from a poorly sealed can.

Levitation methods (*e.g.* gas flow, acoustic, electrostatic) as shown in Fig. 2.10.52 offer a containerless method, which eliminates altogether sample–container reaction problems and diffraction or additional background scattering from a sample container (Weber *et al.*, 2014). Levitated samples are typically used in conjunction with laser heating to achieve high temperatures, *in situ* melting of samples and prevention of heterogeneous nucleation.