

A Mirror Furnace for Synchrotron Diffraction Experiments up to 1600 K

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An X-ray mirror furnace is described that has been developed for *in situ* diffraction experiments at a synchrotron source for temperatures up to 1600 K. It can be used in a reducing as well as in an oxidizing atmosphere. In this kind of furnace, the sample is located at one focus of a rotational ellipsoid and heated by the radiation of a halogen lamp located at the other focus. The furnace has been designed to work on a four-circle diffractometer with minimum restriction of the setting angles.

Keywords: furnaces; diffuse scattering; phase transformations.

1. Introduction

Phase transitions, disorder phenomena and kinetic problems in crystals are well studied by *in situ* high-temperature diffraction. In materials science, high-temperature work in relation to material properties is important for understanding and for practical use such as the optimization of material processing. Moreover, *in situ* high-temperature measurements are necessary, for example, for the study of ceramic materials under working conditions, such as zirconia used as an oxygen detector in hot fumes. Different methods of X-ray and neutron high-temperature work are discussed in the literature, for example by Adhart, Tzafaras, Sueno, Jagodzinski & Huber (1982), Aldebert (1984), Peterson (1992) and others. A neutron mirror furnace for four-circle diffractometry was reported by Lorenz, Neder, Marxreiter, Frey & Schneider (1993); a mirror furnace for X-ray powder work is described by Schneider, Frey, Johnson & Laschke (1993). The 'best' type of heating depends on the desired temperature range, the sample atmosphere and the type of diffraction experiment (single crystal, powder).

We report here on a mirror furnace that was developed for single-crystal diffraction work at conventional X-ray tubes or at a synchrotron source, in particular for the measurement of diffuse scattering. The furnace is designed for operation under an oxidizing as well as under a reducing atmosphere.

2. Design

The principal design feature of this furnace is a closed rotational ellipsoid that acts as a focusing mirror. The heating element, a low-voltage halogen lamp, is placed at one focus, the sample at the other one. The distributions of radiation in elliptical and parabolical mirrors are considered by Hart (1958) and allow one to find an optimum eccentricity of the ellipsoid for given experimental condi-

tions, *i.e.* the size of the lamp filaments or the shape of the sample. The aim of this work was to develop a furnace to be used on a Huber four-circle diffractometer (inner diameter of the χ circle 400 mm) for the measurement of diffuse scattering with minimal restrictions on the accessible angular ranges. This could be obtained by using one mirror. The rotational axis of the mirror ellipsoid is vertical to the scattering plane and coincides with the φ axis of the diffractometer. The furnace consists of three parts. One part is mounted directly onto the φ circle of the diffractometer containing connectors for thermocouples, cooling-water supply and vacuum tubes. The middle part is made up of a 0.3 mm-thick X-ray-transparent carbon cylinder (Anholt Technologies, USA). The inner surface of the cylinder is coated by a thin (<1 μm) aluminium film to improve the vacuum conditions. The X-ray absorption of this cylinder is about 9% for a wavelength of 0.7 Å (Coppens, Coppens, Li & Lee, 1993). This cylinder is stuck into the two other parts of the furnace. The connections are water cooled and sealed with vacuum grease. The third part contains the mirror and the halogen lamp. Two different variants of this part were checked:

(1) A water-cooled mirror body (Fig. 1) was built together with a 250 W halogen lamp (OSRAM HLX 64655). The lamp can be adjusted to position the filament exactly at the focal point. The lamp bulb is cooled by an air flow and protected against the vacuum by a quartz glass tube. The quality of the mirror surface is the decisive feature for achieving high temperatures. After milling, a tedious working cycle of polishing had to be carried out to increase the highest reachable temperatures further. The body is made of aluminium, an excellent material for high-quality polishing.

(2) As an alternative, a commercial halogen lamp including an elliptical reflector (OSRAM HLX 64635)

was used (Fig. 2). Evacuating the sample chamber means in this case operating the complete lamp in vacuum. We had no problems with this condition in our experiments lasting 3 days. Disadvantages of this variant are the lower power and the smaller distance between the focal points, which involves more restrictions on the setting angles. On the other hand, these lamps are cheap and can be changed easily. The different mirror parts are installed in the standard counterweight in the Huber 512 off-centre Eulerian cradle.

3. Sample mounting

Typical sample sizes used in X-ray single-crystal work are of the order of fractions of millimeters. In the case of neutron scattering experiments, sample mounting is easier due to the relatively large size of the crystals (Lorenz *et al.*, 1993). We have developed a sample holder that is a thin Al_2O_3 ceramic tube with the pearl of a Pt-Pt/Rh thermocouple on the top (Fig. 3). On top of the pearl, the sample is glued with a ceramic cement based on ZrO_2 or Al_2O_3 . The

wires of the thermocouple escape through two lateral holes in the supporting ceramic tube. The lower part of the sample holder is fixed to a normal goniometer head. In order to centre the crystal on the diffractometer optically, one must first mount the sample. Afterwards, the carbon chamber is positioned and, finally, the mirror part must be connected to the carbon chamber.

4. Temperature measurement and control

The temperature control is provided by the thermocouple and a PID temperature controller. Owing to the thermal contact between sample and thermocouple, the accuracy of the temperature measurement differs by up to 5% of the nominal one. It is important to mount the crystal near the middle of the pearl of the thermocouple. Otherwise, the measured temperature might depend on the φ position, because the crystal is centred and the thermocouple pearl oscillates around the focus during movement of the diffractometer circles. The temperature stability in a typical measurement time of 3 days was found to be about ± 5 K. A temperature gradient can be neglected due to the small size of the samples.

5. Background scattering

Test experiments with the furnace were made at the four-circle diffractometer at beamline D3, HASYLAB, Hamburg. The background scattering from the furnace is caused by the sample support and the carbon chamber. Scattering from the ceramic tube holding the sample or from the glue can hardly be avoided. In some cases, however, oriented cylindrical samples may be used, where the beam impinges only on the top of the crystal. The scattering caused by the carbon chamber appears as strong textured powder rings from graphite. Background scattering of the furnace is shown in Figs. 4(a) and 4(b). The scattering of the empty carbon chamber (Fig. 4a) was measured at $2\theta = 0^\circ$ at a wavelength of 0.7 \AA with a multiwire proportional counter. The strong peaks are of the same order as the intensity of weak diffuse scattering contributions. Therefore, one has to check for problems with this background in each experiment. An oscillation photograph of a CeO_2 sample at a temperature of 1260 K taken with an image plate can be seen in Fig. 4(b).

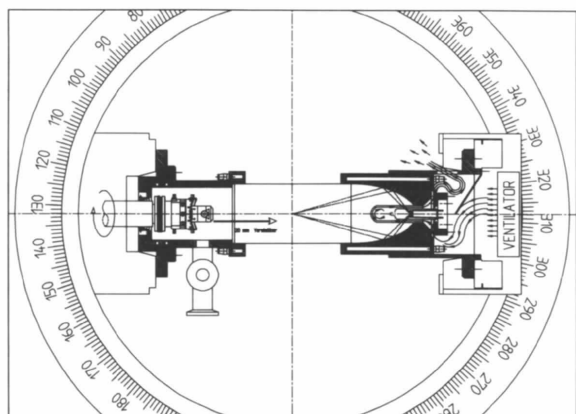


Figure 1
Furnace with self-designed mirror.

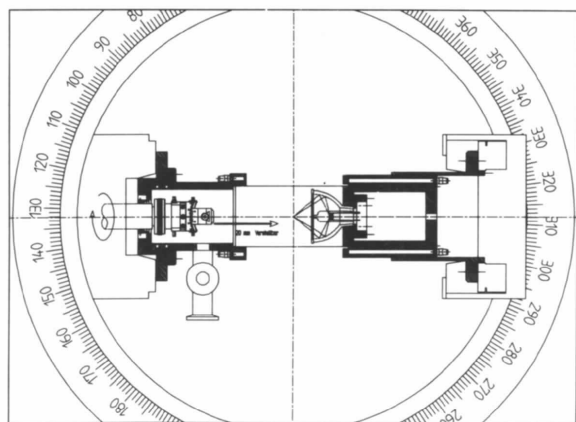


Figure 2
Furnace with the commercial reflector lamp (OSRAM).

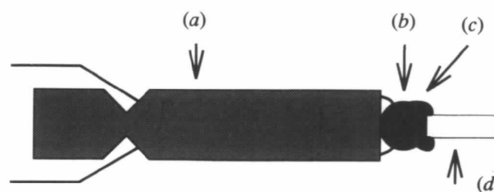


Figure 3
Schematic drawing of sample holder showing (a) the ceramic rod, (b) the pearl of the thermocouple, (c) the ceramic glue and (d) the sample.

For experiments using a single counter, this background can effectively be reduced by installing a beam collimator behind the furnace. As an alternative, a beryllium cylinder may be used; however, this is much more expensive as well as having well known hazards associated with it due to its toxicity.

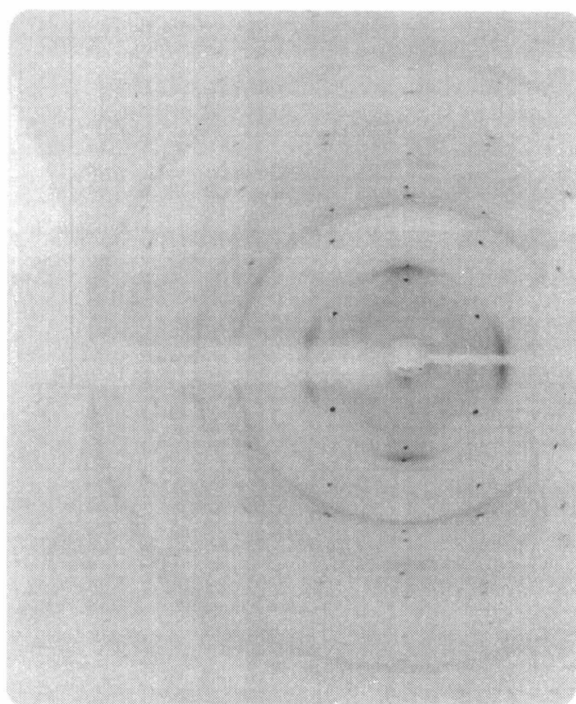
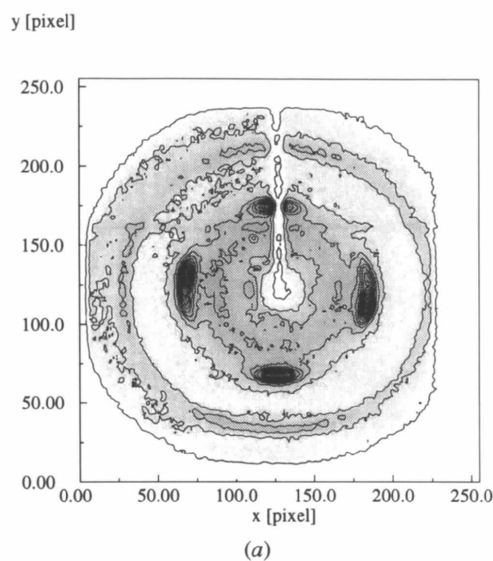


Figure 4

(a) Background, empty carbon chamber measured at $2\theta = 0^\circ$ with a multiwire area detector (Neder, Burghammer, Proffen, Schulz & Eichhorn, 1994) at the four-circle diffractometer of beamline D3, HASYLAB, Hamburg. (b) Diffraction pattern of a CeO_2 sample placed in the furnace, measured with an image-plate system (Proffen, Neder, Hradil & Frey, 1994).

6. Performance

Several high-temperature measurements in a reducing atmosphere as well as in an oxidizing atmosphere were carried out at the four-circle-diffractometer at beamline D3, HASYLAB, Hamburg. For the temperature dependence of the diffuse scattering, a quasicrystal ($\text{Al}_{72.5}\text{Ni}_{11}\text{Co}_{16.5}$) (Hradil, Proffen, Frey, Kek & Krane, 1994) and CeO_2 were studied in a reducing atmosphere. Measurements of the diffuse scattering of zirconia were made under an oxidizing as well as under a reducing atmosphere (Proffen, Hradil, Frey & Krane, 1994). Further experiments with this furnace at the diffractometer at beamline D3 (HASYLAB, Hamburg) are in progress.

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APPENDIX

Technical data

Temperature range

- ~400 K up to ~1300 K in oxidizing atmosphere
- ~400 K up to ~1600 K in vacuum

Size/weight

- ~300 × 80 × 80 mm, ~2.2 kg
- Can be accommodated to the larger Huber off-centre Eulerian cradle (400 mm inner diameter of χ circle)

Lamps

- (a) Halogen reflector lamps 15 V, 150 W (OSRAM HLX 64635); restriction of χ circle: $\pm 34^\circ$
- (b) Low-voltage halogen lamps 24 V, 250 W (OSRAM HLX 64655); restriction of χ circle: $\pm 58^\circ$

Cooling

- Connections between the carbon sample chamber and mirror are water cooled

Sample chamber

- Carbon cylinder (56 mm diameter, 110 mm length) manufactured by Anholt Technologies, Newark, Delaware 19713, USA

Temperature control

- Eurotherm 902 PID controller

References

- Adlhart, W., Tzafaras, N., Sueno, S., Jagodzinski, H. & Huber, H. (1982). *J. Appl. Cryst.* **15**, 236–240.
- Aldebert, P. (1984). *Rev. Phys. Appl.* **19**, 649–662.
- Coppens, D. D., Coppens, P., Li, R. & Lee, P. (1993). *J. Appl. Cryst.* **26**, 917–922.

- Hart, P. J. (1958). *J. Opt. Soc. Am.* **48**, 637–642.
- Hradil, K., Proffen, Th., Frey, F., Kek, S. & Krane, H. G. (1994). *HASYLAB Annual Experimental Reports*, pp. 537–538. HASYLAB, Hamburg, Germany.
- Lorenz, G., Neder, R. B., Marxreiter, J., Frey, F. & Schneider, J. (1993). *J. Appl. Cryst.* **26**, 632–635.
- Neder, R. B., Burghammer, M., Proffen, Th., Schulz, H. & Eichhorn, K. (1994). *Z. Kristallogr. Suppl.* **8**, 69.
- Peterson, R. C. (1992). *J. Appl. Cryst.* **25**, 545–548.
- Proffen, Th., Hradil, K., Frey, F. & Krane, H. G. (1994). *HASYLAB Annual Experimental Reports*, pp. 1025–1026. HASYLAB, Hamburg, Germany.
- Proffen, Th., Neder, R. B., Hradil, K. & Frey, F. (1994). *Z. Kristallogr. Suppl.* **8**, 296.
- Schneider, J., Frey, F., Johnson, N. & Laschke, K. (1993). *Z. Kristallogr.* **209**, 328–333.