J. Appl. Cryst. (1993). **26**, 632–635

A Mirror Furnace for Neutron Diffraction up to 2300 K

BY G. LORENZ, R. B. NEDER, J. MARXREITER, F. FREY AND J. SCHNEIDER

Institut für Kristallographie und Mineralogie, Theresienstrasse 41, *D*-8000 *München* 2, *Germany*

(*Received* 21 *January* 1993; *accepted* 11 *March* 1993)

Abstract

This paper describes a mirror furnace that has been developed for neutron diffraction work at temperatures up to 2300 K. It is based on a reflecting rotational ellipsoid, in which the heating element, a halogen lamp, is placed at one focus and the sample at the other. It works in a normal, *i.e.* oxidizing, atmosphere, but can also be used in a vacuum. It has been developed for experiments of long duration. The stability and reproducibility of the temperature are better than 1% of the setting temperature. Further main characteristics are applicability to single-crystal and powder work, very low background, low power consumption and very easy and cheap handling. Several experiments have been carried out with the furnace.

Introduction

Structural work at (very) high temperatures is important. Many naturally occurring compounds, *i.e.* minerals, have structures or microstructures or, more generally, exhibit order/disorder phenomena that reflect the thermal prehistory of the rock-forming process itself. Therefore, *in situ* studies improve understanding of basic problems of geoscientific interest. In materials sciences, high-temperature studies of structures in relation to material properties are of importance for the practical use, and understanding and optimization of, the material processing itself.

Complementary X-ray and neutron scattering methods both have well known advantages that need not be discussed further. In particular, the relatively low absorption of thermal neutrons by most elements makes the use of neutron furnaces particularly easy, whereas high-temperature studies at, say, $T \geq 1300$ K with X-rays are usually cumbersome, at least if aimed at structure refinement. Different methods in X-ray and neutron high-temperature work are discussed by, for example, Adlhart, Tzafaras, Sueno, Jagodzinski & Huber (1982), Aldebert (1984), Ohsumi, Sawada, Takeuchi & Sadanaga (1984) and Peterson (1992). A neutron furnace for four-circle diffractometry with very high temperature stability has recently been reported by Kuhs, Archer & Doran (1993). A neutron-scattering furnace for very high temperatures, up to 2930 K, was developed at Harwell (Clausen *et al.*, 1984). It is clear from the literature and it has also been our experience that different types of heating are not equally well suited to different types of (single-crystal, powder) diffraction experiments. A particular type of furnace and specific method of temperature determination and control must be chosen for a specific scientific problem.

We report here on a neutron mirror furnace that was developed for use at weak- or medium-flux neutron sources, for weak diffuse scattering, for single-crystal or powder work and for use mainly in an oxidizing atmosphere (Lorenz, 1988; Neder, 1990) but also in a reducing atmosphere (Mursic, 1992). In consequence, relatively large samples must be heated, these must be oriented in the neutron beam and, last but not least, the spurious background scattering from the furnace should be kept at a very low level. The basic principle of mirror heating was developed for crystal-growth applications (Eyer, Zimmermann & Nitsche, 1975; Watanabe & Shimazu, 1976). For *in situ* scattering experiments, this furnace had to be redesigned. It should be mentioned that the same principle was also used for a new X-ray powder furnace (Schneider, 1992; Schneider, Frey, Johnson & Laschke, 1993).

I. Design

The mirror furnace uses the geometrical properties of a closed rotational ellipsoid. With a heating element, a halogen lamp, at one focus, the sample is placed at the other. Radiation distributions in elliptic and parabolic mirrors are considered by Hart (1958) and allow one to find an optimum eccentricity of the ellipsoid for the specific experimental conditions (sizes of filaments, sample *etc.*). A more homogeneous temperature distribution at the sample position and a reduced maximum load of the lamp can be provided by the use of two coaxial ellipsoidal mirrors positioned in such a way that the sample is at one common focus of both mirrors (Fig. 1). The rotational axis is vertical to the scattering plane, which is defined

by the incoming and the outgoing (diffracted) neutron beams. If relatively large samples have to be used for intensity reasons (see the *Introduction*), it is advantageous for some axial defocusing, *viz* two displaced foci of the two mirrors, to be tolerated. For this reason, the furnace is made of three parts; the upper and lower main-mirror parts and one central part. The height of the latter matches the correct spacing of both foci at the sample position. The three parts can quickly be assembled after a change of sample without the need for further alignment of the furnace. The body of the furnace is made from aluminium. This represents a good compromise between ease of manufacturing and reflecting properties (see §V for further comments). The central part covers the scattering plane. Therefore, the aluminium walls of this central part are as thin as 1.5 mm to avoid any significant absorption and the diameter is as large as 140 mm to keep as low as possible spurious scattering from the walls that might enter the detector. Note that, except for these thin walls a long distance from the sample position, no part of the furnace is in the path of the neutrons. Both lamps may be inserted and adjusted from outside through axial holes at the top and bottom. A crucial point is the cooling of the lamp jackets. The glass bodies of the light bulbs become mechanically unstable only at relatively high temperatures. As mentioned, the lamps can and must be adjusted in the focal position of the ellipsoidal mirror body. There are, however, no important requirements for accuracy of lamp positioning. Owing to the desired extension of the focal image, some misalignment of the extended filaments is of minor importance. A further important concern is the quality of the reflecting mirror surfaces. This is also a question of material. Fortunately, aluminium is an excellent choice, allowing for high-quality polishing. After experiments with volatile samples, it is advisable to repolish the mirrors. Essential improvements can, however, be made if some advanced and sophisticated methods of mirror surface treatment are used (see Mursic, 1992). If necessary, the mirror bodies may be cooled by simple water cooling. As may be concluded from this design, there are no fundamental restrictions with respect to the ambient atmosphere, in other words, a normal 'oxidizing' atmosphere is as good as vacuum conditions.

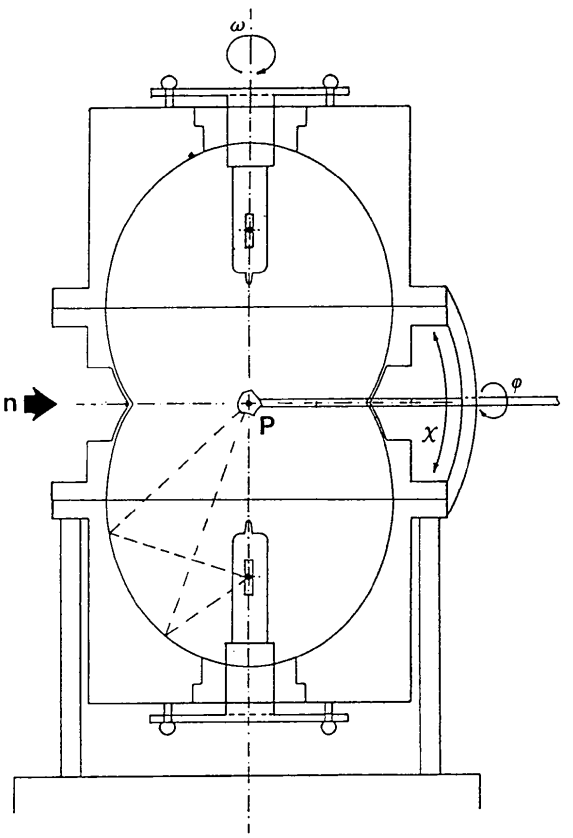

Fig. 1. Schematic drawing of the mirror furnace.

II. Specimen mounting and alignment

Sample support and adjustment are usually provided by a thin ceramic tube or rod of Al_2O_3 or ZrO_2, to which the sample may be glued with a ceramic cement. Other possibilities are platinum cans for powder samples or platinum/rhodium wires sintered around a ceramic sample. Of course, some of this material acts as an additional source of background scattering. Minimization of background scattering can be achieved with single-crystal materials, like MgO needles, as supports for powder or ceramic samples. A particularly sophisticated sample holder for single-crystal work was used by Neder, Frey & Schulz (1990). There, a cube was cut from a large (sample) single crystal. On one side, a stem of the original material was left, which was fixed with ceramic glue to an Al_2O_3 rod. The ceramic glue was surrounded by a BN cylinder that acted as an effective neutron absorber. In this way, almost no spurious scattering obscured the diffuse signals to be recorded. In the case of powder or ceramic samples, only the correct position at the focus of the mirrors is needed. For work with single crystals, four-circle Eulerian diffractometry can be provided with some restrictions (Fig. 2). In the usual terminology, the crystal support (ceramic tube or rod) is at a $\chi = 90°$ position. Tilting around this position covers a range of $\pm 22°$ with an accuracy of $\pm 0.01°$. This tilting is performed by a stepping motor and is computer controlled *via* an encoder. The same holds for a φ rotation around the rod axis: here the whole range of $\pm 180°$ is accessible with an accuracy of $\pm 0.01°$. Because the whole furnace can be adjusted *via* translational operations and some tilt adjustments, the ω axis of the

diffractometer coincides with the vertical rotation axis of the furnace. The full range of the ω position can be utilized except for a 30° sector around the sample holder. No restrictions apply to 2θ. Thus, arbitrary sections from reciprocal space may be measured along various pathways. Approximately 80% of reciprocal space can be set into diffraction position (within the limiting sphere). Alternatively, the furnace can be placed in a large off-centre Eulerian cradle. This, however, further limits the χ rotation.

III. Temperature control

The temperature determination and control is usually provided by Pt–Pt/Rh thermocouples of various kinds, which can be used in an ambient atmosphere up to 2100 K, and a PID temperature controller. The thermocouples are placed in holes drilled in the sample or are even sintered within a ceramic sample. This procedure provides a precise temperature measurement, except for gradients within the sample. The accuracy of the temperature measurement is of the order of 1% of the nominal one, the stability over long time scales (of the order of 7 d) is ± 1 K and the reproducibility is ± 5 K. Gradients within the sample depend on specific factors such as the size or the thermal conductivity of the sample. As an example, the gradient within a ZrO_2 single crystal, an 11 mm cube, was about 30 K. It should be mentioned that reflections from the Pt/Rh elements cause some unwanted contamination of powder patterns, which might be cumbersome in the analysis of minority phases. In many cases, this influence may be ruled out by excluding regions from these diagrams. Further details and technical data are given in the Appendix.

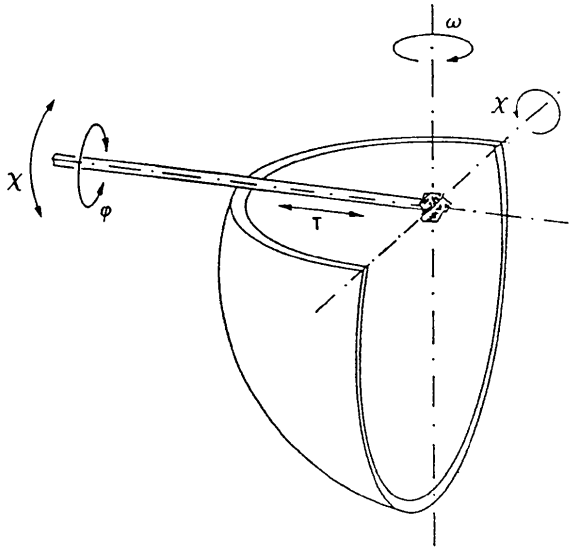

Fig. 2. Schematic drawing of the angular degrees of freedom of the sample within the furnace.

IV. Performance

The furnace was checked in a series of powder and single-crystal experiments studying either Bragg reflections or diffuse phenomena. To check the background scattering by the furnace, an empty scan was compared to a scan without the furnace. 'Empty scan' means that the furnace was placed into the beam together with the sample support, *i.e.* an Al_2O_3 rod, and a thermocouple, but without the sample crystal. Fig. 3 shows an almost negligible smooth background and only very weak reflections from the Al_2O_3 ceramic. With a platinum can, correspondingly spurious platinum reflections become visible that do not affect the powder-data analysis in most cases. They can even be avoided by using sintered samples. High-temperature structural work with this type of furnace was very successfully carried out on zirconia single crystals (Lorenz, Frey, Schulz & Boysen, 1988; Neder *et al.*, 1990; Proffen, Neder, Frey, Keen & Zeyen, 1993) at different instruments at reactors and at the ISIS spallation source, and $ZrSiO_4$ single crystals were studied at temperatures up to 2000 K (Mursic, Vogt, Boysen & Frey, 1992). Powder and ceramic samples of, for example, ZrO_2 (Frey, Boysen & Vogt, 1990; Boysen, Frey & Vogt, 1991), CeO_2 (Berber *et al.*, 1991), $ZrSiO_4$ (Mursic, Vogt & Frey, 1992), $NiTiO_3$ (Lerch, Boysen, Neder, Frey & Laqua, 1992) have been investigated in recent years. Their great success with this type of furnace encouraged the ILL at Grenoble to rebuild and sell mirror furnaces of this type.

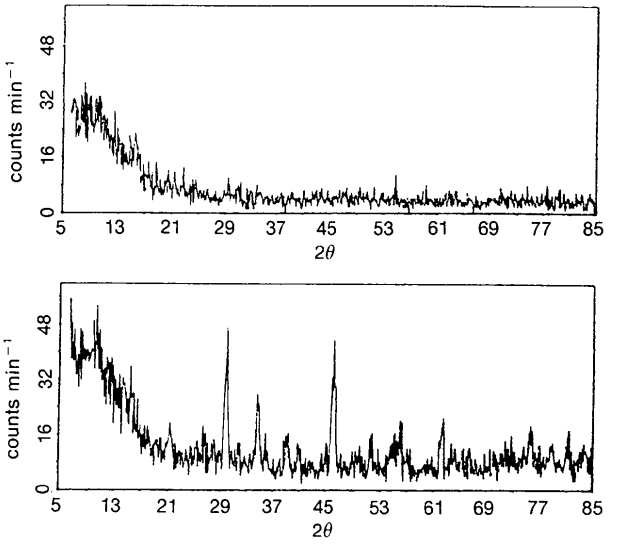

Fig. 3. Spurious background scattering at instrument MAN I/FRM. Above without furnace; below with furnace including sample support and thermocouple at sample position. Weak spurious reflections are due to the Al_2O_3 ceramic support.

V. Further developments

Further developments of the mirror furnace towards higher temperatures and various gas atmospheres were investigated recently by Mursic (1992) (see also Mursic, Vogt, Boysen & Frey, 1992). One essential concern is the quality and the tolerable heat load of the reflecting mirror surfaces. Coating with silver, gold or even SiO_2 is desirable. The main limiting factors towards higher temperatures are, however, the mechanical stability of the crystal support and the cooling of the glass bodies of the light bulbs. Ceramic refractory materials seem to be very promising. The bulbs may be cooled in an air stream, which may easily be realized in an ambient atmosphere. Another nontrivial aspect concerns temperature measurement at very high temperatures. In an oxidizing atmosphere, measurements by thermocouples are restricted to temperatures below 2100 K (PtRh30/PtRh6); higher temperatures can only be measured by pyrometric methods. Optical windows in the mirror furnace for this purpose are therefore foreseen. In vacuum, the temperature range up to 2500 K remains accessible by the use of thermocouples (WRe5/WRe26). Given this, it would be very interesting to carry out experiments under different gas atmospheres.

This work was supported by the BMFT, Germany, project no. 03-B02A04.

APPENDIX
Technical data

Size/weight: height 600 mm; diameter $\leq$250 mm; weight 7 kg.

Mirror ellipsoids: large/small half-axis 90/80 mm.

Central part: AlMg5, height 83 mm; diameter $\leq$140 mm.

Material: AlMg5.

Lamps: halogen type FEL, 2 × 1000 W, 120 V (Schahl Co., München, Germany); filaments 23 × 7 mm; life time dependent on temperature, 5 d at maximum load.

Cooling: mirror bodies and lamp jackets water cooled (1 l min^{-1}); maximum temperature of the jackets 555 K; maximum temperature of the light bulbs 1000 K.

Temperature measurement: thermocouples, *e.g.* EL18 (see text).

Temperature control: PID-thyristor equipped controller or Eurotherm 822 or 818; setting $\pm$0.1 K, reproducibility $\pm$1 K.

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.

BERBER, K., MARTIN, U., MURSIC, Z., SCHNEIDER, J., BOYSEN, H. & FREY, F. (1991). *Mater. Sci. Forum*, **79–82**, 685–690.

BOYSEN, H., FREY, F. & VOGT, T. (1991). *Acta Cryst.* B**47**, 881–886.

CLAUSEN, K., HAYES, W., HUTCHINGS, M. T., MACDONALD, J. E., OSBORN, R. & SCHNABEL, P. (1984). *Rev. Phys. Appl.* **19**, 719–722.

EYER, A., ZIMMERMANN, H. & NITSCHE, R. (1975). *European Space Agency Spec. Publ.* **114**, 241–244.

FREY, F., BOYSEN, H. & VOGT, T. (1990). *Acta Cryst.* B**46**, 724–730.

HART, P. J. (1958). *J. Opt. Soc. Am.* **48**, 637–642.

KUHS, W. F., ARCHER, J. & DORAN, D. (1993). *J. Appl. Cryst.* Submitted.

LERCH, M., BOYSEN, H., NEDER, R., FREY, F. & LAQUA, W. (1992). *J. Phys. Chem. Solids*, **53**, 1153–1156.

LORENZ, G. (1988). PhD thesis, Ludwig-Maximilians-Univ., München, Germany.

LORENZ, G., FREY, F., SCHULZ, H. & BOYSEN, H. (1988). *Solid State Ionics*, **28–30**, 497–502.

MURSIC, Z. (1992). PhD thesis, Ludwig-Maximilians-Univ., München, Germany.

MURSIC, Z., VOGT, T., BOYSEN, H. & FREY, F. (1992). *J. Appl. Cryst.* **25**, 519–523.

MURSIC, Z., VOGT, T. & FREY, F. (1992). *Acta Cryst.* B**48**, 584–590.

NEDER, R. B. (1990). PhD thesis, Ludwig-Maximilians-Univ., München, Germany.

NEDER, R. B., FREY, F. & SCHULZ, H. (1990). *Acta Cryst.* A**46**, 799–809.

OHSUMI, K., SAWADA, T., TAKEUCHI, Y. & SADANAGA, R. (1984). *Material Science of the Earth's Interior*, pp. 633–643. Tokyo: Terra Science.

PETERSON, R. C. (1992). *J. Appl. Cryst.* **25**, 545–548.

PROFFEN, T., NEDER, R. B., FREY, F., KEEN, D. A. & ZEYEN, C. M. E. (1993). *Acta Cryst.* B**49**, 599–604.

SCHNEIDER, J. (1992). 41st Annual Denver Conference on Applications of X-ray Analysis, Colorado Springs, USA, p. 134.

SCHNEIDER, J., FREY, F., JOHNSON, N. & LASCHKE, K. (1993). *Z. Kristallogr.* Submitted.

WATANABE, A. & SHIMAZU, M. (1976). *J. Appl. Cryst.* **9**, 466–469.