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On the Thermal Expansion and Crystallography of Cubic (C) and Monoclinic (B) Forms of Gd_2O_3 in the Temperature Range 20 to 900°C

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Thermal expansion coefficients of B-form (monoclinic) and C-form (cubic) Gd_2O_3 have been measured in the temperature range 20 to 900° C, by X-ray diffractometry. The thermal expansion coefficients of both cubic and monoclinic material are linear in the temperature range studied. The expansion of monoclinic material is, however, very anisotropic, and the minor axis of the thermal expansion ellipsoid is not parallel to the edge of the primitive cell to which Gd_2O_3 has been assigned. It is noted that the anisotropy in expansion behaviour of this material indicates that anisotropic growth probably occurs during irradiation.

1. Introduction

A limit is placed on the initial reactivity of the fuel in a reactor by the control characteristics of its design. In order to maintain criticality, it is necessary to replace the initial charge with fresh fuel of a higher reactivity, as the reactivity of the fuel decreases during irradiation. Hence the mean discharge irradiation of the initial fuel charge will be lower than that of subsequent charges.

One method of obtaining better utilisation of the initial charge is to increase the concentration of fissionable material in it and absorb the excess reactivity in a suitable material whose absorbing characteristics decrease with time. This is the so-called "burnable poison" concept. The nuclear properties of Gd make it an ideal material for this application. In its naturally occurring form, it has a very high thermal neutron absorption cross-section (in excess of 20 000 barns*). Higher isotopes, with much lower absorption cross-sections, are produced by the (n, γ) reaction during irradiation.

It has been proposed [1] that, in Advanced Gas-Cooled Reactors, the poison could be introduced in the form of Gd_2O_3-filled stainless-steel tubes, attached to the fuel-element assemblies. The detailed behaviour of the Gd_2O_3 under irradiation and the consequent performance of the component depends critically on the geometry and integrity of the stainless-steel tubes being maintained. This work is part of a materials evaluation of this type of system.

Goldschmidt, Olrich, and Barth [2] studied crystallographic modifications of rare-earth oxides and divided them into three main polymorphic groups, hexagonal or A-type, monoclinic or B-type, and cubic or C-type. There are two crystallographic modifications of Gd_2O_3, a low-temperature C-type and high-temperature B-type structure. Much conflicting evidence has been presented concerning the nature of this phase change [3-7]. It seems clear, however, that, like Sm_2O_3 and Eu_2O_3, the C-to-B phase change in Gd_2O_3 is irreversible and the transformation rate is a function of time and temperature [7].

2. Specimen Preparation

The nature of the C-to-B phase change in Gd_2O_3 means that the cubic phase can only be prepared by thermal decomposition of the metal, its

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*Unit of nuclear cross-section equal to 10^{-24} cm^2 per nucleus.

carbonate, nitrate, oxalate, or sulphate; all of which decompose completely below 1050° C. In the present work, a 0.5 cm diameter disc of Gd metal 0.003 cm thick was oxydised in a continuous stream of pure oxygen for 24 h at 800° C. This produced a white friable mass making grinding unnecessary. The measured weight gain of the sample was consistent with the formula Gd_2O_3. The metallic impurities present in the starting material are given in table I. Conversion to the B-type material was carried out simply by annealing the C-type material for 1 h in argon at 1600° C, no change in specimen weight being detected.

TABLE I The analysis of metallic impurities in Gd metal used in preparation of the oxides.

Other rare earth oxides	< 0.1 wt %
Tantalum	0.1 wt %
Other base metals	3.02 wt %

3. X-ray Diffractometry

Thermal expansion data of C- and B-type Gd_2O_3 were determined by X-ray diffractometry. A Philips wide-angle diffractometer was fitted with a MRC* high-temperature diffractometer attachment [8] and operated at scanning speeds of either $\frac{1}{4}°$ or $\frac{1}{8}°$ 2θ/min with 1° and 0.003 in. slits from 0° to 90° 2θ, and 4° and 0.006 in. slits for angles greater than 90° 2θ.† Unfiltered chromium $K\alpha$ radiation was employed; the diffracted radiation being detected with an xenon-filled proportional counter, coupled to a pulse-height analyser with chart-recording facilities. The diffractometer-detector-recorder system was calibrated using a silicon standard supplied by the manufacturer.

Measurements of 2θ values for B- and C-type Gd_2O_3 were recorded in the temperature range 20 to 900° C. The temperature was calculated from the variations in lattice parameter of 4N purity MgO powder which had been mixed with the Gd_2O_3 specimens (the relevant data for MgO was taken from an interlaboratory study reported by Campbell [9]). The lattice parameter of MgO, at each temperature, was calculated (by application of the Cohen method of least squares to the measured 2θ values of five reflections in the range $2\theta = 60$ to 140°), to an accuracy of 0.005 Å, and this corresponds to an uncertainty in temperature of 1° C.

4. Results and Discussion

4.1. Cubic Gd_2O_3

The thermal expansion of cubic Gd_2O_3 over a temperature range ΔT is given by

$$\alpha = \frac{\Delta a}{a \,.\, \Delta T}$$

where Δa is the change in lattice parameter from a, the value at the lower temperature of the range ΔT. Values of a were determined at eight different temperatures in the range 20 to 900° C, from a Cohen least-squares analysis of five measured interplanar spacings (in the range $2\theta = 50$ to 140°). Within the limits of the experimental accuracy ($T = \pm 1°$ C, $a = \pm 0.0005$ Å), the expansion is linear and a least-squares analysis yields the equation

$$a_T = a_0 \,(1 + 7.9511 \times 10^{-6}\, T)$$

where a_T is the lattice parameter at $T°$ C and $a_0 = 1.0821$.

4.2. Monoclinic Gd_2O_3

The thermal expansion of monoclinic Gd_2O_3 is described by relationships of the type

$$\alpha_{hkl} = \frac{d_{hkl}}{d_{hkl}\Delta \mathrm{T}}$$

where α_{hkl} is the coefficient of expansion perpendicular to the $\{hkl\}$ planes with interplanar spacing d_{hkl}, at the lower temperature of the range ΔT. Δd_{hkl} is the change in the interplanar spacing which results from the change in temperature ΔT. Twenty-five interplanar spacings indexed by comparison with the data of Stecura [7], over the range $2\theta = 40$ to 144°, were measured at eight different temperatures between 20 and 900° C. Application of Cohen's method of least squares for a monoclinic crystal, with the aid of a computer programme [10], yielded values of the lattice parameters a, b, c, and β at each temperature. From these values, the thermal expansion of monoclinic Gd_2O_3 was tested for linearity and anisotropy. Within the experimental accuracy, the expansion is linear; but, as it is to be expected, it is also anisotropic.

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†2θ is the angle between the incident and diffracted beam.

Hence complete representation of the thermal expansion can only be given by a symmetrical second-rank tensor of the form [11]

$$\begin{vmatrix} \alpha_{11} & 0 & \alpha_{13} \\ 0 & \alpha_{22} & 0 \\ \alpha_{31} & 0 & \alpha_{33} \end{vmatrix}$$

where α_{11}, α_{22}, and α_{33} are, respectively, the coefficients of expansion along [100], [010], and [001], and α_{13} determines the orientation of the representation quadric (which is the geometrical representation of a symmetrical second-rank tensor). Simplification of this tensor is obtained if it is referred to its principal axes, when it takes the form

$$\begin{vmatrix} \alpha_1 & 0 & 0 \\ 0 & \alpha_2 & 0 \\ 0 & 0 & \alpha_3 \end{vmatrix}$$

where $1/\sqrt{\alpha_1}$, $1/\sqrt{\alpha_2}$, $1/\sqrt{\alpha_3}$ are the mutually perpendicular semi-axes of the representation quadric, which is an ellipsoid when α_1, α_2, and α_3 are all positive.

Neumann's principle dictates that one principal axis (conventionally α_2) must lie along the diad axis (conventionally b), while the other two principal axes must take some orientation that can be obtained by rotation of the orthogonal pair about b. To determine the magnitude and orientation of α_1 and α_2, it is first necessary to calculate the best (i.e. least-squares values) of α_{11}, α_{33}, and α_{13} from the measured thermal expansions perpendicular to the $\{h0l\}$ planes. Seven independent measurements were available yielding values of

$$\alpha_{11} = 9.9096 \times 10^{-6} \pm 0.027$$
$$\alpha_{33} = 11.83 \times 10^{-6} \pm 0.151$$
$$\alpha_{13} = -4.54 \times 10^{-6} \pm 0.031$$

These results give the following values for the principal axes of the thermal expansion ellipsoid (see fig. 1).

$$\alpha_1 = 9.74 \pm 0.22$$
$$\alpha_3 = 13.9 \pm 0.22$$
$$\Phi = 36^\circ\, 48' \pm 51'$$

where Φ is the angle between [001] and α_1 measured in a clockwise direction from [001]. The best estimate of the magnitude of α_2, the orientation of which is determined by symmetry (see above), is to analyse the thermal expansion coefficients measured perpendicular to the $\{0kl\}$ and $\{hk0\}$ planes. Unfortunately, only three measurements were possible in each set; however, an average of the two values of α_2 derived from this procedure is more accurate than a straightforward measurement of the expansion along the [010] direction and gives

$$\alpha_2 = (15.45 \pm 0.4) \times 10^{-6}/^\circ\mathrm{C}$$

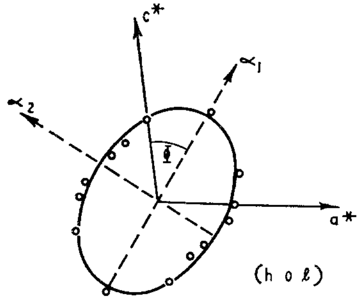

Figure 1 The thermal expansion ellipsoid of B-form Gd_2O_3 on the $(h0l)$ plane.

Finally, it is noted that the principal expansion direction α_3 is parallel to an edge of the primitive cell, which can be defined from the centred space group (C2/m) to which monoclinic Gd_2O_3 has been assigned [7], and α is, within the limits of the experimental error, parallel to the [101] direction. These facts may be useful if a structure determination of monoclinic Gd_2O_3 were to be undertaken.

The anisotropy of the thermal expansion coefficients of B-form Gd_2O_3 may well be important in relation to its nuclear application. The presence of irradiation defects in a crystal leads to changes in their shape and volume. The irradiation growth behaviour of graphite [12] and various metals [13] has been shown to be directly related to the anisotropy of their thermal expansion coefficients. It is therefore highly probable that anisotropic growth occurs in B-form Gd_2O_3 under irradiation.

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