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Pseudo-Plasticity of monoclinic Gd_2O_3

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Abstract

Monoclinic Gd_2O_3, when submitted to thermal and mechanical stresses, does not behave in a brittle manner. During the application of such stresses, twinned grains appear, especially on the surface of the samples; there is also the evolution of induced microcracks around the main crack. These two phenomena lead to the pseudo-plastic behaviour of the material.

1 Introduction

In a pressurised water reactor (PWR), gadolinia (Gd_2O_3) is used as a burnable poison; its function is to act as a neutron absorber whose effectiveness is progressively reduced during the irradiation. One configuration for the material in this application is in the form of a composite made of a UO_2 matrix and of Gd_2O_3 macrospheres,[1] It is interesting in assessing the performance of this composite to have a better understanding of the behaviour of monoclinic gadolinia when submitted to thermal and mechanical stresses. In the present work, the behaviour has been studied by means of two experimental approaches, namely, heating by an image furnace and testing in biaxial bend.

Gadolinia has been the subject of a limited number of publications in the last few years. Results in the literature now provide varied information concerning the crystallography,[1–4] the thermal expansion[5] and the elastic properties[6] of the oxide.

Gadolinia crystallises in a cubic structure (C) below 1200°C[2] and is reversibly transformed at higher temperature to a monoclinic phase (B). The kinetics of the C → B transformation is faster than its inverse B → C. High temperature X-ray diffraction observations of cubic gadolinia powders have shown that the cubic phase remains stable up to 1250°C and that it can only be considered fully absent from 1400°C.[2] After a thermal treatment at 1350°C, for a $^1/_2$ h period in an air environment, a major part of the system consisted of the monoclinic phase (> 80%).[1]

This material is difficult to sinter, as has been often mentioned in the literature.[7,8] The problem arises from polymorphic transformation which starts during the densification of the cubic form. An improvement in densification can be obtained by grinding the initial powder to obtain a finer particle size and by optimising the rate of temperature increase. However, it seems more promising to circumvent the effect of the polymorphic transformation by studying the direct sintering of the monoclinic form, first created by a thermal treatment of the original powder at 1350°C for a $1/_2$ h period in an air environment, followed by air quenching. Our results show that the sintering of Gd_2O_3 is significantly improved and that relative densities greater than 95% can be achieved (1700°C in $H_2 + 2$ vol% H_2O for a 2 h period) in comparison with the density of 75% obtained by the direct sintering of cubic Gd_2O_3.[1]

2 Experimental Procedure

The gadolinia used during these tests was taken from a homogenous batch of 'Nuclear Grade' quality (purity of the rare-earth oxides of 99·99%) manufactured by Rhône–Poulenc. The initial powder, of a cubic structure, was subjected to a thermal treatment at 1350°C, for 1/2 h in an air environment, in order to produce mainly the monoclinic form.

Before subsequent processing was carried out, a lubricant was added to the monoclinic powder [0·3% of $(C_{18}H_{35}O_2)Zn$] in order to facilitate the fabrication. The shaping was carried out by uniaxial die pressing at 300 MPa. The green pellets, with a diameter of 20 mm and an approximate thickness of 10 mm were sintered at 1700°C in a reducing atmosphere (H_2 + 2 vol% H_2O). The radial shrinkage was approximately 15%, giving a final diameter of 16 ± 0·2 mm. The relative final density was 95 ± 0·6%. The sintered cylinders were cut into discs 1 mm thick; these were then polished to remove surface defects resulting from the cutting. Therefore the samples used for our tests were sintered discs of monoclinic Gd_2O_3 which satisfied the condition for biaxial bending tests, namely, that the shape should obey the relation: 0·01 < thickness diameter < 0·1. Ten discs of gadolinia were subjected to biaxial bending under ambient conditions and to thermal gradient tests.

2.1 Mechanical stresses

The samples were tested in biaxial bend, where the specimen was placed on three balls made from tungsten carbide and loaded by an upper tungsten carbide ball.[9] The tests were carried out on a Mayes C Qual-50 kN press with a displacement speed of approximately 10 μm min^{-1}. The measured deflections were corrected for the stiffness of the support with an accuracy of better than 0·2 μm. The accuracy of the load cell was better than 0·2 N.

The maximum radial and hoop stresses are equal and are given by:[10]

$$\sigma_{max} = \frac{3P(1+v)}{4\pi e^2} \left[1 + 2\ln\left(\frac{a}{b}\right) + \left(1 - \frac{b^2}{2a^2}\right)\left(\frac{(1-v)a^2}{(1+v)R^2}\right)\right] \quad (1)$$

where P is the load, v the Poisson's ratio, e the disc thickness, a the radius of the circle of the support points, R the radius of the disc and b the radius of a fictitious region of uniform loading ($b \approx 30{\cdot}325\ e$).

In the same way, an estimation of Young's modulus is given by:[10]

$$E = \frac{3 - 2v - v^2}{4\pi} \frac{3Pa^2}{We^3} \quad (2)$$

where W is the central deflection.

2.2 Thermal stresses

The classic thermal shock tests do not produce the parabolic temperature profile which corresponds, to a first approximation, to the conditions in a PWR nuclear reactor. Consequently a device has been designed in order to reproduce the thermal gradients encountered in reactors.[9] The method consists of heating a sample disc at its centre while maintaining its edge at a low temperature. The samples are inserted into a support which cools their edges by means of circulating cold water. A good sample–support contact is ensured by using an aluminium thermal seal. The sample disc is heated in a controlled manner at its centre by radiation from two halogen lamps of 750 W focussed with ellipsoidal mirrors. The sample support is positioned in the mirrors' focal plane.

The procedure consists of increasing the voltage of the halogen lamps until a critical voltage is reached which results in material cracking. The device enables the measurement of the radial profile of temperature in the disc; cracking of the material can therefore be used to define the critical temperature difference between the core and the edge of the sample. This in turn allows evaluation of the stress field in the material.[9] The temperature profile, symmetrical with regards to the centre of the sample, can be approximated by:[11]

$$T(r) = a_O + a_2 r^2 + a_4 r^4 \quad (3)$$

where a_0, a_2, a_4 are constants established by the experiment.

The maximum stress resulting from the thermal gradient is given by:[11]

$$\sigma_{max} = \alpha E\left(-a_2 \frac{R^2}{2} - 2a_4 \frac{R^4}{3}\right) \quad (4)$$

where α is the thermal dilatation coefficient (°C^{-1}) and E the Young's modulus (MPa)

3 Results

3.1 Biaxial bending tests

The stress/strain curves (Fig. 1) show a clear departure from classical brittle fracture. The gadolinia samples do not display purely elastic behaviour up to fracture.

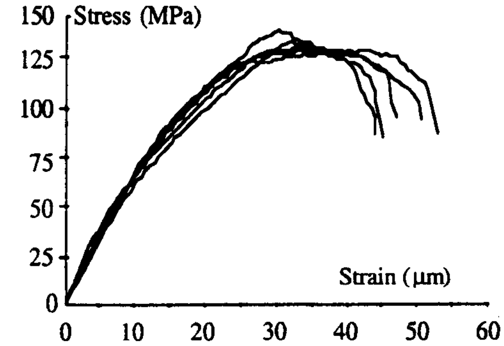

Fig. 1. Results of the biaxial test for five samples of monoclinic Gd_2O_3.

The application of Weibull statistic to the 10 samples gives a Weibull modulus of 24 and an average tensile strength of 139 MPa. The calculation of Young's modulus by means of formula eqn (2) gives an average value of 110 GPa.

After polishing and chemical etching (1 min in $2\,cm^3$ $H_2O_2 + 1\,cm^3$ $H_2SO_4 + 20\,cm^3$ H_2O solution) the samples reveal a microstructure consisting of twinned grains [Fig. 2(a)], especially for the large grains, as a consequence of the thermal dilatation anisotropy.[12] The same material, when submitted to a stress of mechanical origin, shows an increased density of twinned grains, especially around the edge of the sample where the tensile stress is maximum [Fig. 2(b) and (c)].

3.2 Application of a radial thermal gradient

Up to a lamp voltage of 70 V, no detectable cracking occurs. For voltages above 73 V, which corresponds to an imposed flux of over 8·5 W mm^{-2}, a macroscopic crack appears. However, despite the cracking, all samples maintain their integrity. There is therefore no catastrophic propagation of the cracks. This result is consistent with those obtained in the biaxial deflection tests. Furthermore, calculation on the basis of eqn (4) shows that a main crack is induced for a stress above a value lying between 137 MPa ($a_2 = -2{\cdot}974$; $a_4 = -7{\cdot}02 \times 10^{-3}$) and 149 MPa ($a_2 = -2{\cdot}905$; $a_4 = -1{\cdot}073 \times 10^{-2}$).

As in the case of observations following the mechanical tests, the observations carried out by electron microscopy show the formation of a damaged zone around the main crack. The size of this zone, known as the 'process-zone' and normal to the plane of the main crack, is estimated at approximately 10 μm for a sample subjected to a flux of 9 W mm^{-2} [Fig. 2(d)]. Furthermore, as noted after the biaxial tests, a large number of twinned

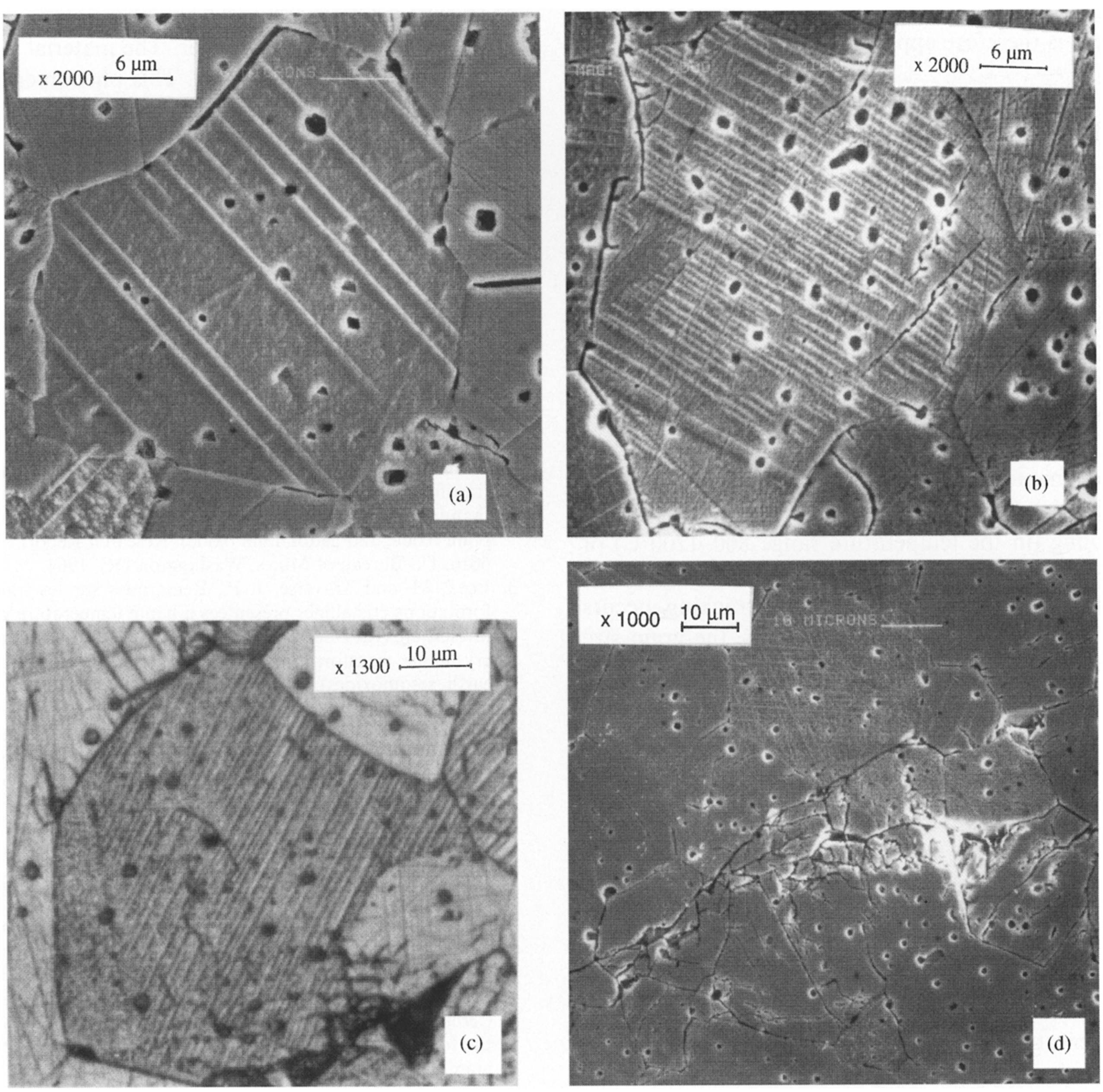

Fig. 2. (a) twinning in monoclinic Gd_2O_3 after sintering; (b) and (c) appearance of twinned grains after the mechanical or thermal stresses have been applied; (d) formation of a damaged zone around the main crack.

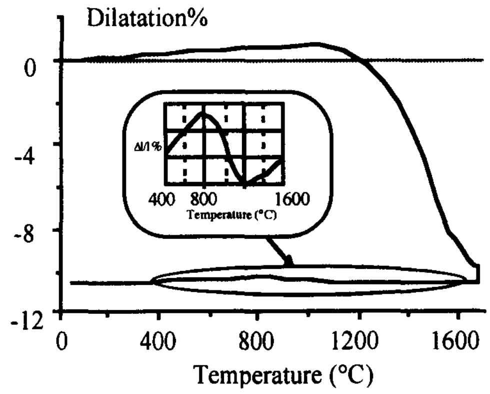

Fig. 3. Observation of spontaneous microcracking during dilatometry.

grains, especially around the edge of the sample, appeared following application of the thermal gradient.

The temperature difference between the edge and the centre of the sample, which corresponds to the appearance of an initial macroscopic crack, was estimated at 266°C. The critical temperature gradient is therefore approximately 32°C mm^{-1}.

4 Discussion

4.1 Young's modulus

According to Haglund *et al.*,[6] for a porosity of approximately 4–5%, monoclinic Gd_2O_3 shows a Young's modulus of approximately 138 GPa; this compares, in our case, with a value estimated at 110 GPa. The difference between the two values seems to result from the spontaneous microcracking observed at the grain boundary [Fig. 2(a)] in the present studies. Indeed, this phenomenon can be observed by dilatometry (Fig. 3): a small expansion is observed during cooling (in the temperature range 800–1200°C) of a sample of monoclinic Gd_2O_3 with an average grain size of 20 μm. This microcracking occurs when, as in the present experiments, the grain size is larger than the critical grain size, 14 μm, estimated by Case *et al.*[13]

4.2 Tensile stress

Cracking of monoclinic Gd_2O_3 during thermal shock appears for a calculated maximum stress greater than a value between 137 and 149 MPa. This result corresponds well to that found directly in the biaxial bending test, namely, failure at a tensile stress of 139 MPa.

4.3 Microstructure

Observation of samples previously subjected to bending or to thermal gradient testing shows that the main crack is accompanied by a damaged zone (or 'process-zone') comprising a high density of induced microcracks which contribute to the fracture energy through the increased extent of fracture surface.

During the cooling, the thermal dilatation anisotropy of monoclinic Gd_2O_3 can result in microcracking in the polycrystal, especially at the grain boundaries,[14] and can also induce grain twinning. Furthermore, when the material is subjected to an external stress of a thermal or mechanical nature, grain twinning appears during deformation.

An interpretation of these observations is that the twinning, associated with the induced microcracking, is an essential element in the deformation process and thus in the pseudo-plastic behaviour of monoclinic Gd_2O_3.

5 Conclusions

This study has shown that monoclinic gadolinia when exposed to mechanical and thermal stresses does not fail in a brittle manner. The material presents pseudo-plastic behaviour. This phenomenon, which is relatively rare in monolithic ceramics, can be attributed on the one hand to the creation of microcracked zones around the main crack and on the other hand to the grain twinning which is observed in the highly stressed zone.

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