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The growth of crystals of erbium hydride

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Crystals of the rare-earth hydride ErH_2 have been produced with face areas greater than a square millimetre and corresponding volumes exceeding those of earlier crystals by orders of magnitude. The hydride, which was produced in bulk polycrystalline form by hydriding erbium metal at 950° C, has been examined by optical and X-ray techniques. For material of composition ErH_2 and $ErH_{1.8}$ the size of the grains and their degree of strain appears to depend more on oxygen contamination during formation and on the subsequent cooling procedure, than on the size of erbium metal crystals in the starting material.

1. Introduction

Interest in rare-earth hydrides was stimulated many years ago by the possibility of their use as reactor moderators and as target materials in neutron generators. Perhaps the most favoured target materials have been the tritides and deuterides of erbium of composition approaching ErT_2 or ErD_2. Studies of ErH_2 are clearly also of interest because of its chemical and crystallographic similarity and because it is more conveniently available.

Other workers have normally used these materials prepared in thin-film polycrystalline form or as a finely granulated powder [1, 2]. Recently, epitaxial growth of thin films of erbium dihydride has been achieved by Rahman Khan and Miller [3] by evaporation of erbium onto rock-salt substrates. We report in this paper the conditions for growth of the first millimetre-size crystals of ErH_2 and an initial assessment of the crystallographic quality of the specimens. The preparation technique was the hydriding of erbium metal.

Dissociation pressure isotherms were obtained by Jones *et al.* [4, 5] for the hydrides of many of the rare-earth metals, and it was concluded that erbium hydride was among the most stable of the rare-earth hydrides. It was also shown by Jones *et al.* [6] that dissociation pressure relations could be derived for tritides and deuterides from isotopic ratio measurements in the gas phase. Extensive pressure–composition–temperature data for erbium hydride has also been obtained by Lundin [7], who also studied the dihydride–trihydride region and found the trihydride to decompose to the dihydride above 383° C at 1 atm pressure. The data in this literature enabled appropriate conditions of temperature and hydrogen gas pressure to be selected for the hydriding in the present work.

Azarkh and Gavrilov [8] have reported an X-ray analysis of the phase changes occurring when hydriding erbium metal, itself of hexagonal structure. They determined the lattice parameter of the f c c dihydride lattice (fluorite structure) as 5.1254 ± 0.0003 Å.

Erbium metal has been noted to be resistant to attack by oxygen [6] and nitrogen [9], but has been shown to be a powerful getter for hydrogen even at low temperatures [9]. In X-ray and electron diffraction examinations of thin films of erbium metal by Gasgnier *et al.* [9], the hydride was always present but no evidence was found for the hydroxide, monoxide, nitride or carbide.

A mass spectroscopic examination was carried out on the polycrystalline erbium starting material used in the present work, which showed the heavy element content to be negligible but gave no information concerning oxygen, nitrogen, carbon or hydrogen. However, we would expect the oxygen

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content to be confined to a thin surface layer of oxide and the nitrogen and carbon content to be very small also [6, 7, 9].

2. Method of preparation

The hydriding was carried out with the metal starting material in a molybdenum boat inside a silica tube. Previously the latter had been outgassed at 950° C in conjunction with a liquid nitrogen vapour trap. The carefully weighed erbium sample was then transferred into the tube using a magnetic pusher. The volume above the metal was known and the temperature measured to an accuracy of 0.01° C. An adjacent reservoir was filled with very pure hydrogen to a pressure of about half an atmosphere by heating titanium hydride. To prepare a sample, a measured and appropriate amount of hydrogen was leaked very slowly and continuously from the reservoir into the silica tube over a long period of time (see Table I) while the material was held at 950° C. Initially the hydrogen was taken up to form the hydride at a pressure of 2 to 20 torr. Finally, with the pressure ~20 torr in the tube, no more hydrogen was supplied and the process of cooling to room temperature was begun. Various cooling rates were used, as indicated in Table I, which were interrupted by long anneals at constant temperature. The remaining hydrogen was taken up during cooling and the final residual pressure was $\sim 10^{-5}$ torr.

Some of the starting material was in the form of flat slices of metal. Since erbium softens at 950° C, the slices were laid flat on the molybdenum foil to minimize distortion created by volume changes in hydriding. Some loss of weight occurred due to evaporation of metal, but the hydride composition was not affected since all the metal remained inside the tube and a thin film of hydride was incidentally produced on the molybdenum. Possibly loss of material took place more readily from the sample surface away from the foil, as the resulting surface of the hydride had a matt appearance in contrast to the mottled appearance of the surface adjacent to the molybdenum.

In the last column of Table I, the values of final composition assume that all the erbium reacted with hydrogen. However, very small amounts of material of a different phase was also produced, as detected by optical microscopy, so that in the last three runs the actual composition of the hydride matrices was slightly closer to $Er_{2.00}$ than indicated.

3. Assessment of material

3.1. Assessment procedure

The aim of this investigation was to reveal the crystals so that they could be easily located in the matrix, to check their crystal structure and lattice parameter and to determine their crystallographic orientation and the degree of gross lattice disorder and strain.

The composition of the hydride material was identified using X-ray powder diffraction techniques by grinding random sections from all samples.

The crystal faces were revealed for visual observation by polishing the samples to a smooth surface and then etching using the etch of Dow *et al.* [2]: 2.5 vol% H_3PO_4, 2.5 vol% CH_3COOH, 2.5 vol% HNO_3 and 2.5 vol% H_2SO_4. A series of optical micrographs of the grains were obtained with the sample and incident light in different relative orientations. Once the grains had been revealed they were characterized using X-ray diffraction, either locally using the back-reflection technique or macroscopically using topographic techniques.

Back-reflection photographs were used to determine crystal quality and orientation of all the single crystals identified. In the larger grains, back-

TABLE I Hydriding conditions

Run	Form of starting Er	Hydriding time	Hydriding rate (of total charge per h)	Total cooling time	Cooling rate (intermittent)	Final composition
1	Bulk polycrystalline	20 h	$\ngtr$ 10%	6 h	–	$ErH_{2.09}$
2	Bulk polycrystalline	26 h	$\ngtr$ 10%	3 days	$\ngtr 100^\circ\ C\,h^{-1}$	$ErH_{2.00}$
3	Bulk polycrystalline	28 h	$\ngtr$ 6%	3 weeks	$\ngtr 1/3^\circ\ C\,min^{-1}$	$ErH_{1.96}$
4	Single-crystal disc	> 24 h	$\ngtr$ 6%	2 weeks	$\ngtr 1/3^\circ\ C\,min^{-1}$	$ErH_{1.98}$
5	Single-crystal discs	1 week	$0.3\text{–}2\tau\,h^{-1}$ *	1.5 weeks	$0.5^\circ\ C\,min^{-1}$	$ErH_{1.8}$

*Leak rate from reservoir initially at pressure of 330τ.

reflection photographs were taken at various points over the whole grain to check for uniformity of quality and orientation. Consistent results were obtained on some grains but by no means all. The overall quality of any grain was best ascertained by use of the Berg–Barrett X-ray topographic technique [10, 11] and topographs were taken of all grains of millimetre size.

Some representative material both in powder and bulk form was tested for thermal stability by heating *in vacuo* (10^{-4} torr), or in an ambient of pure dry nitrogen under controlled flow, to successively higher temperatures up to 700° C. They were then re-examined using X-ray techniques.

3.2. Quality of crystals

The material produced in all the runs was opaque and initially dark grey in colour, but after etching the samples were revealed to possess a bluish hue.

The variations in the conditions that were tried in producing samples are given in Table I and consisted mainly of differences in the starting material, in hydriding time and rate, and in cooling.

In the first three runs, the starting material consisted of polycrystalline lumps of erbium (of approximate dimensions 15 mm x 7 mm x 3 mm), which had a maximum crystalline grain size of the order of one millimetre. Run 1 produced a fragmented polycrystalline dihydride along with a few per cent of trihydride, as evidenced by X-ray powder diffraction. The dihydride crystals were generally less than 100 μm across. The trihydride component disappeared when heated above 400° C, in agreement with the findings of Lundin [7]. The samples from Runs 2 and 3 revealed only the dihydride diffraction pattern, and the lattice parameters were consistently of value $a_0 = 5.1267 \pm 0.0004$ Å. After heating to 700° C for 30 min very little effect was observed and the lattice parameter did not change at all. These results are in good agreement with the work of Azarkh and Gavrilov [8].

The first three runs gave rise to progressive improvements in dihydride single-crystal size and crystalline quality. The crystals of Runs 2 and 3 were strongly embedded in roughly rectangular-shaped polycrystalline slabs. Crystals produced in Run 2 often had faces ~ 0.25 mm^2, despite the hydriding temperature being about 100° C lower than intended due to a fault on the temperature recorder, whilst Run 3 material contained crystals with faces $\gtrsim 1$ mm^2 (see Fig. 1). The progressively slower rates of cooling appear to have resulted in the growth of larger grains and in the removal of strain from the crystals. Fig. 2 is an example of a back-reflection photograph indicating the crystallographic quality of a typical grain for Run 3, showing a certain amount of strain. A typical X-ray topograph is shown in Fig. 3 together with an optical micrograph of the same grain. The overall similarity in shape and uniform intensity of the topograph reveals a fairly uniform orientation, but there is evidence of strain and some slight defect structure. This is characteristic of most of the grains present in the bulk samples.

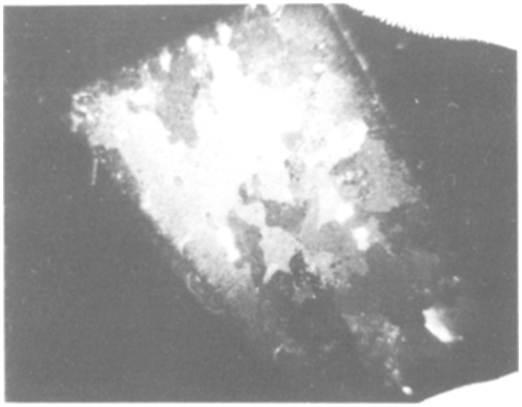

Figure 1 Optical micrograph of crystalline grains of ErH_2 produced in Run 3 (X 5).

An X-ray fluorescence examination was carried out on the hydride produced in Run 2, but no impurity was detected. However, the method was not sensitive to elements with Z-number less than about 16.

The phase transformation from c p h erbium to f c c dihydride involved very small shifts of the

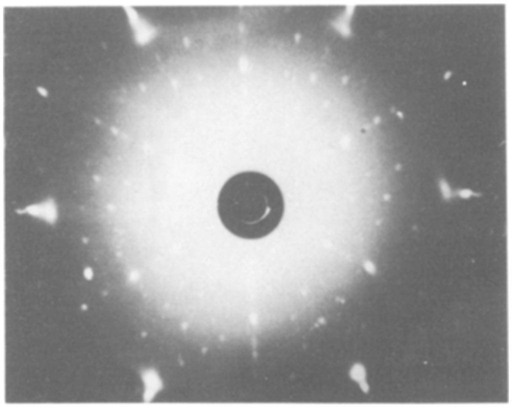

Figure 2 X-ray back-reflection from typical mm² size grain of ErH_2.

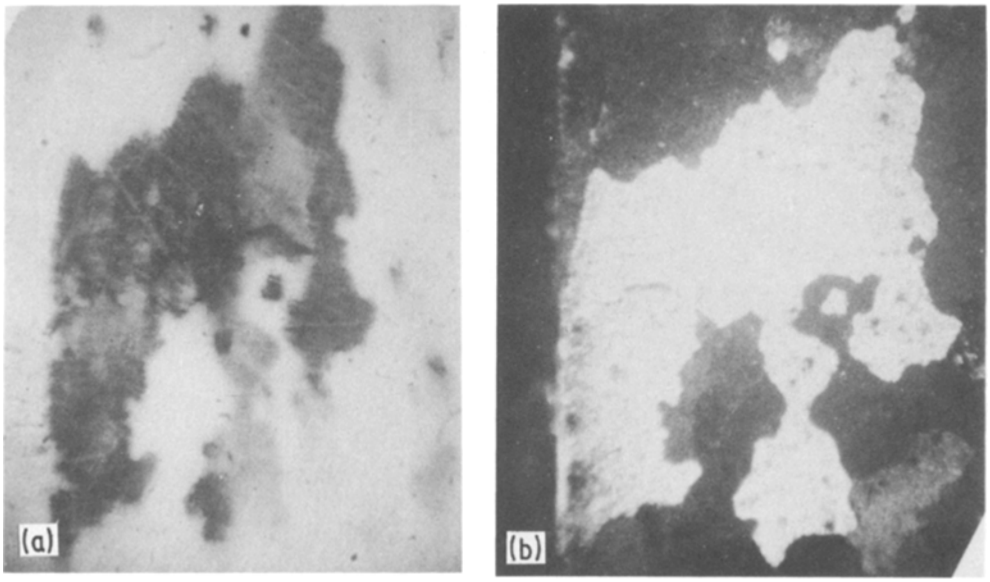

Figure 3 (a) X-ray topograph of largest grain of ErH_2, (b) optical micrograph of same grain as in (a) (× 17).

erbium atoms; an expansion of about 1% in the *a*-direction and 5% in the *c*-direction of the hexagonal lattice occurs in accommodating the hydrogen. It was felt, therefore, that larger hydride crystals might result from larger crystals of the starting erbium. Consequently, single-crystal erbium discs, of 7 mm diameter and thickness 1 mm, were used in the later runs. However, this did not result in larger or better hydride crystals. In Run 4, for example, the crystallite size turned out to be much smaller than in Runs 2 and 3. However for Run 4 the last trace of hydrogen was not absorbed, suggesting that the erbium had been contaminated. Before Run 5, the erbium slices were carefully polished to reduce any surface oxide present and then examined optically. The surfaces were excellent, without obvious oxide contamination, and X-ray diffraction showed the erbium to be of good crystallographic quality. During the subsequent run, the hydriding rate was even more carefully controlled, but the crystallites (see Fig. 4) were all less than 0.25 mm^2 in size and more strained than those of Runs 2 and 3. Again, possible trace contamination of the silica tube by unwanted reactive gases (probably oxygen) was suspected.

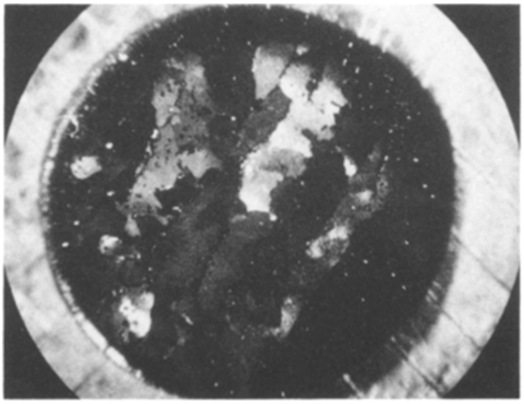

Figure 4 Optical micrograph of crystalline grains of $ErH_{1\cdot8}$ produced in Run 5 (× 7.8).

4. Conclusions

It is concluded from this work that crystals of ErH_2 with face areas greater than 1 mm^2 and volumes greater than 1 mm^3 can be grown by hydriding high purity erbium metal in bulk form provided contamination by reactive gasses, particularly oxygen, can be eliminated. The attainment of large crystals of good crystallographic quality depended more critically on the long and controlled cooling procedure and on slow and careful hydriding than on the size of the crystals in the erbium starting material.

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