

Some Observations on the Deformation Characteristics of Bulk Polycrystalline Zirconium Hydrides

Part 2 *The Deformation of ϵ -hydrides*

C. J. BEEVERS, K. G. BARRACLOUGH

Department of Physical Metallurgy and Science of Materials, The University, Edgbaston, Birmingham 15, UK

Received 20 December 1968

The compressive deformation of polycrystalline ϵ -zirconium hydride has been investigated within the temperature range 22 to $\sim 400^\circ\text{C}$ and over the composition range $\text{ZrH}_{1.71}$ to $\text{ZrH}_{1.92}$. The observed deformation modes included slip, creation of new lamellae of different orientations to those of the main transformation lamellae, and movement of lamellar boundaries. The results are considered in terms of the contribution of these three processes to the overall deformation behaviour.

1. Introduction

The cubic δ -phase in the zirconium-hydrogen system transforms to the tetragonal ϵ -phase at room temperature hydrogen contents in excess of $\sim \text{ZrH}_{1.66}$ [1, 2]. The extent of the ($\delta + \epsilon$) phase field at room temperature has been variably reported and is considered in some cases to extend up to $\text{ZrH}_{1.75}$ [3-6]. The crystal structure of ϵ -zirconium hydride is based on the CaF_2 type structure [7]. Sidhu *et al* [5] have suggested that the hydrogen atoms occupy some of the tetrahedral sites of the *fc* tetragonal zirconium lattice which has $c/a < 1$.

Metallographic observations of room temperature structures have indicated that the banded or lamellar structure formed in the $\delta \rightarrow \epsilon$ transformation occurs as a result of a martensitic mechanism [1, 8]. Using the Wechsler, Lieberman and Read [9] relationship, Chang [10] showed that the cubic, δ habit plane in the $\delta \rightarrow \epsilon$ transformation should be 3° from the (011). He also concluded that the twin interfaces correspond to the {101} type planes of the tetragonal lattice. From these observations it would appear that the $\delta \rightarrow \epsilon$ phase transformation can be explained in terms of a double shear model, as was originally proposed

to explain the morphology of polycrystalline, tetragonal indium-thallium alloys [11]. The large bands in polycrystalline, tetragonal indium-thallium alloys were explained in terms of a first shear on a cubic {110} plane in opposite $\langle 110 \rangle$ directions in neighbouring bands; the fine bands (which are actually tetragonal {101} twins) were interpreted as manifestations of a second shear on {110} planes at 60° to the undistorted {110} planes of the first shear.

The purpose of this paper is to present the results obtained from compression tests on four ϵ -zirconium hydrides. These observations will be considered in relation to their structures, as outlined above.

2. Experimental

Compression specimens of four ϵ hydrides, $\text{ZrH}_{1.71}$, $\text{ZrH}_{1.77}$, $\text{ZrH}_{1.88}$ and $\text{ZrH}_{1.92}$ were prepared and tested as described in Part I.

3. Results

3.1. Deformation of $\epsilon\text{ZrH}_{1.71}$ and $\text{ZrH}_{1.77}$ Hydrides

The nominal stress/strain curves of $\text{ZrH}_{1.71}$ and $\text{ZrH}_{1.77}$ specimens are shown in figs. 1 and 2*. The room temperature stress/strain curves

*Specimens were unloaded to facilitate structural examination and the termination of a test in fracture only occurred where indicated by the letter F.

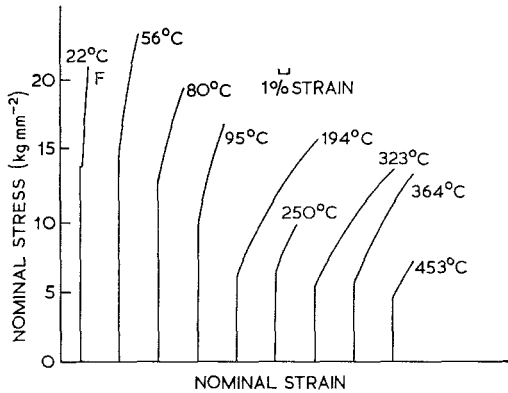


Figure 1 Nominal stress/strain curves for specimens of $ZrH_{1.71}$ tested in compression over the temperature range 20 to 453°C.

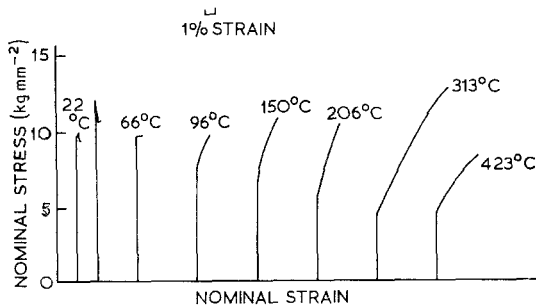


Figure 2 Nominal stress/strain curves for specimens of $ZrH_{1.71}$ tested over the temperature range 22 to 423°C.

revealed small discontinuities which were accompanied by audible clicks from the specimens. When specimens were unloaded immediately after the discontinuities, the previously flat surfaces were disturbed by the presence of a lamellar structure and cracks, some of which appeared to be in planes parallel to those of the lamellae (fig. 3). Surface slip traces were apparent within the lamellae when $ZrH_{1.71}$ specimens were unloaded after tests at temperatures above 80°C (fig. 4). However, surface slip markings were less evident on the $ZrH_{1.71}$ specimens tested above 100°C. The principal deformation mode in the $ZrH_{1.71}$ and $ZrH_{1.77}$ alloys at the higher test temperatures appeared to be the movement of the ϵ lamellae. Whilst many of the surface markings had the appearance of slip lines, the observations in figs. 5a and b show them to be fine lamellae. In fig. 6 the lamellae which were present in the as-grown specimens were partially destroyed by the deformation. In

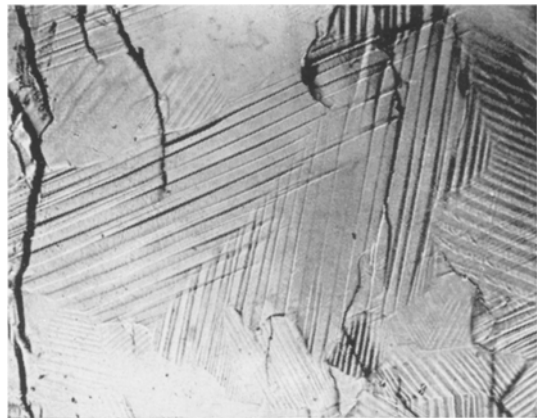


Figure 3 The presence of lamellae and cracks on an originally flat surface of a $ZrH_{1.77}$ specimen examined immediately after a load drop in the stress/strain curve during test at room temperature ($\times 60$).

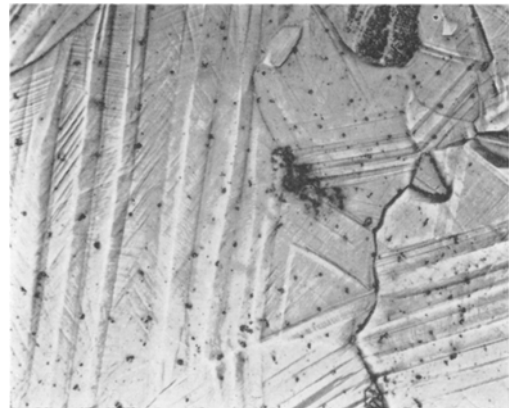
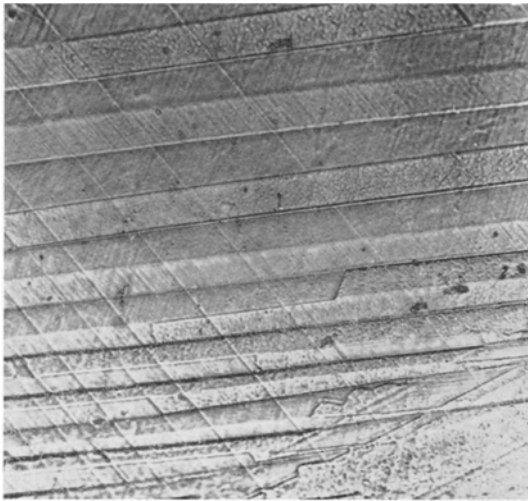


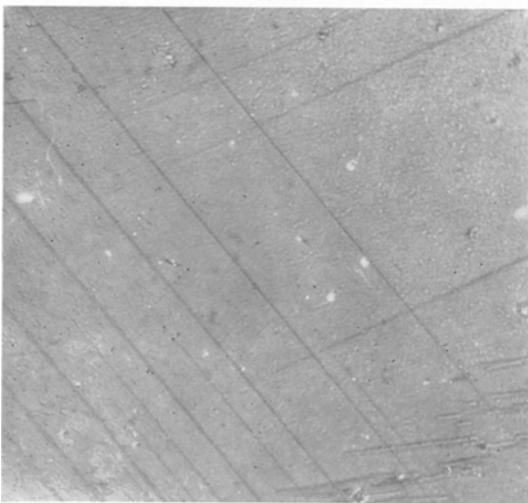
Figure 4 Slip lines on the surface of a $ZrH_{1.71}$ specimen after 2.5% plastic strain at 95°C ($\times 130$).

fact, the partial or complete removal of the original lamellar structure was a common feature of polished and etched sections of deformed specimens. This feature was directly attributable to the deformation, since heating to 400°C for 2 h and subsequently cooling to room temperature had no effect on the as-grown lamellar structure.

The deformation modes of $ZrH_{1.77}$ specimens were further investigated by carrying out the following experiments. The orientations of edge grains in $\delta ZrH_{1.66}$ specimens were determined to allow subsequent two face trace analyses. These specimens were transformed to the lamellar structure of $\epsilon ZrH_{1.77}$ (fig. 7a). Deformation of



(a)



(b)

Figure 5 (a) Fine surface markings cutting the lamellar structure in a $ZrH_{1.77}$ specimen after 2% strain at $150^{\circ}C$. (b) The same area as (a) after removal of a surface layer by mechanical polishing and chemical etching. Polarised light ($\times 270$).

the ϵ hydrides at $200^{\circ}C$ revealed the surface markings in fig. 7b. Analyses of the markings (fig. 7b) showed them to be parallel to $\{101\}$ planes of the cubic δ -phase and at 60° to the $\{101\}$ habit planes for the principal set of ϵ growth lamellae. Removal of a surface layer by mechanical polishing and chemical etching revealed the presence of the principal deformation markings (fig. 7c). Comparison of fig. 7a with fig. 7c also indicates that some of the as-

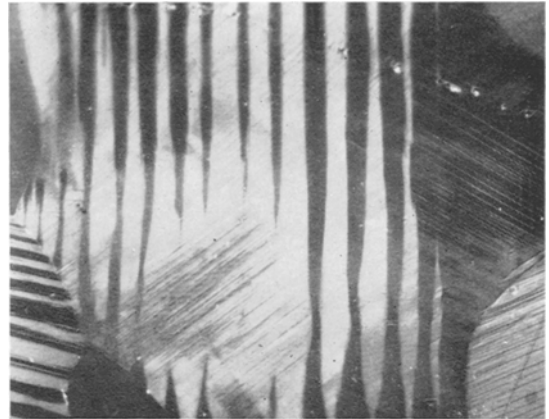


Figure 6 Partially destroyed lamellar structure in a polished and etched section of a $ZrH_{1.77}$ specimen after 2% strain at $150^{\circ}C$. Polarised light ($\times 285$).

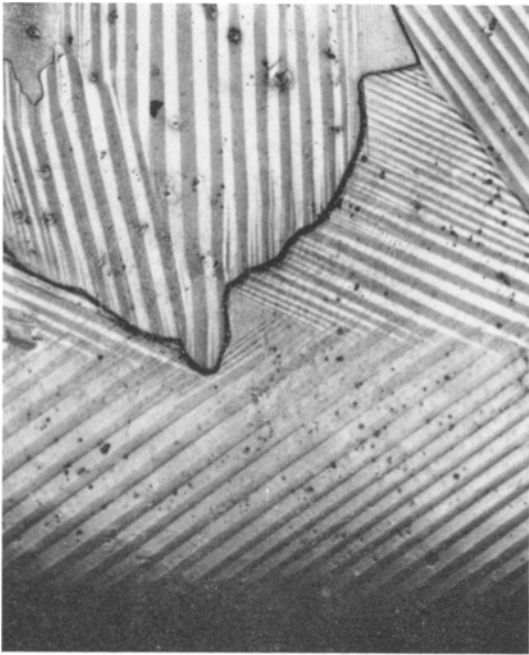
grown lamellae were destroyed during deformation. Some fine surface markings present in fig. 7b are not evident in fig. 7c and this indicates that these markings were slip traces.

In specimens of $ZrH_{1.77}$ tested at temperatures in the region of $400^{\circ}C$, polished and etched sections had the appearance shown in fig. 8. Single face trace analyses of the fine lamellae in fig. 8 showed them to be parallel to $\{101\}$ planes in the ϵ matrix.

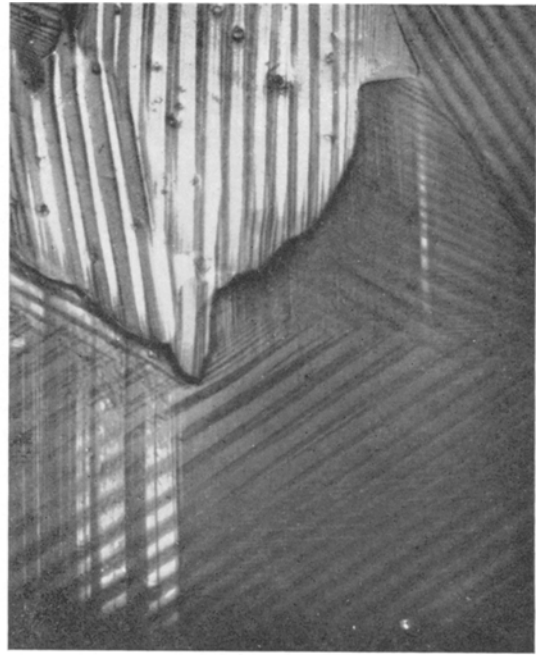
3.2. Deformation of $\epsilon ZrH_{1.88}$ and $ZrH_{1.92}$ Hydrides

The nominal stress/strain curves of $ZrH_{1.88}$ and $ZrH_{1.92}$ hydrides tested over the temperature range 22 to $200^{\circ}C$ and 22 to $150^{\circ}C$ respectively are presented in figs. 9 and 10. The equilibrium vapour pressure of zirconium hydrides approaching the composition ZrH_2 , increases rapidly with increasing temperature. Thus, it was considered appropriate to limit the maximum test temperatures of the $ZrH_{1.88}$ and $ZrH_{1.92}$ specimens in order to restrict the possibility of dissociation and subsequent changes in composition and structure.

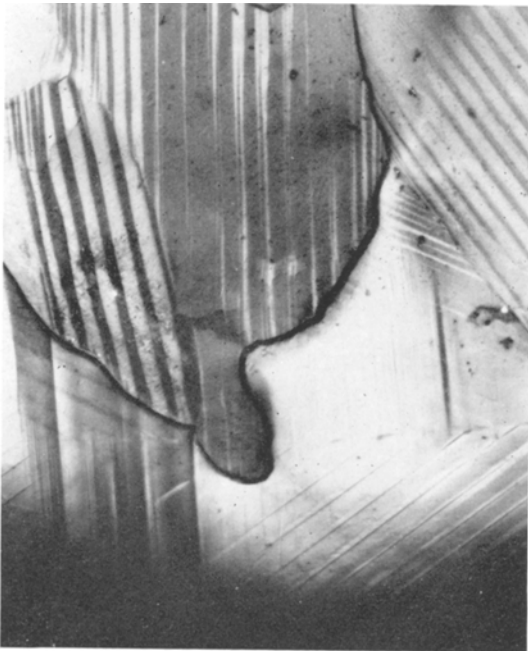
Stress/strain discontinuities were observed in the $ZrH_{1.88}$ specimens up to temperatures of $167^{\circ}C$. The extent of the load drops was not constant over this temperature range or even at one particular temperature (e.g. $22^{\circ}C$ fig. 9). The magnitude of the stress at the lower limit of the load drop, however, appeared to be relatively insensitive to test temperature. The nominal stress/strain curves of the $ZrH_{1.92}$ specimens



(a)



(b)



(c)

Figure 7 (a) Structure of an edge grain in a $ZrH_{1.77}$ specimen of known cubic orientation. Polarised light ($\times 158$). (b) Same area as (a) after 3% strain at $200^\circ C$. Polarised light ($\times 158$). (c) Same area as (b) after removal of a surface layer by mechanical polishing and chemical etching. Polarised light ($\times 158$).

exhibited similar characteristics to those of the $ZrH_{1.88}$ specimens.

Metallographic observations of $ZrH_{1.88}$ and $ZrH_{1.92}$ revealed similar characteristics. Specimens unloaded immediately after a discontinuity in the temperature range 22 to $167^\circ C$ showed surface cracks linked by broad lamellae (fig. 11); the presence of broad distorted lamellae can

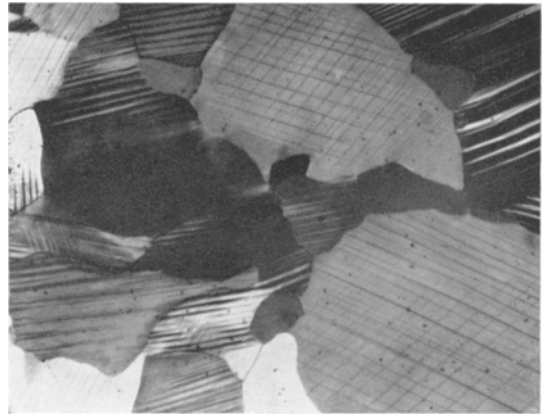


Figure 8 Fine lamellae in grains of a $ZrH_{1.77}$ specimen after 4% strain at $423^\circ C$. Polarised light ($\times 85$).

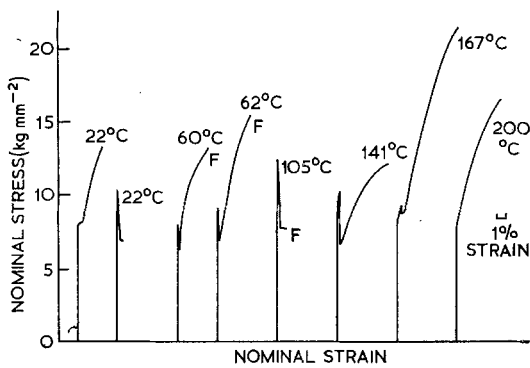


Figure 9 Nominal stress/strain curves of specimens of composition $ZrH_{1.88}$ tested in compression over the temperature range 22 to 200° C.

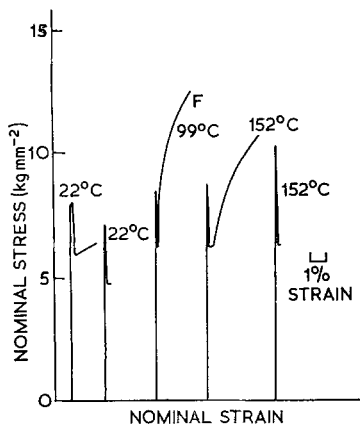


Figure 10 Nominal stress/strain curves of specimens of composition $ZrH_{1.92}$ tested in compression over the temperature range 22 to 150° C.

also be seen in this figure. Fine lamellae, intersecting the as-grown structure, and associated with surface cracks, were also evident (fig. 12).

The $ZrH_{1.88}$ specimen tested at 200° C exhibited distorted growth lamellae and new, deformation induced lamellae. Polished and etched sections of this specimen revealed structures similar to those of $ZrH_{1.77}$ specimens (fig. 8) in which the original banded structure was destroyed and fine lamellae extending across the homogeneous ϵ grains were evident.

4. Discussion

The deformation of polycrystalline ϵ -zirconium hydride is of a complex nature which can involve: (i) slip; (ii) creation of new lamellae of different orientation with respect to the as-grown banded structure; (iii) the movement of lamellar

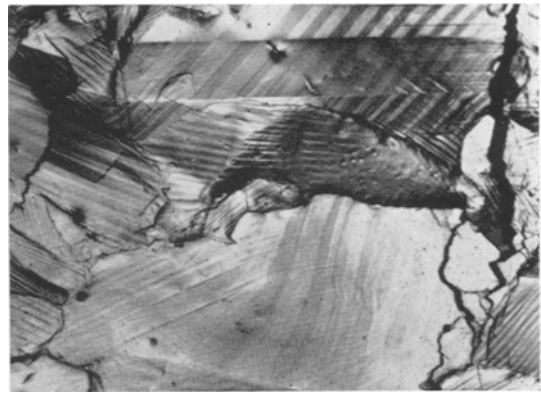


Figure 11 Surface of a $ZrH_{1.92}$ specimen examined immediately after a load drop at room temperature. Polarised light ($\times 110$).

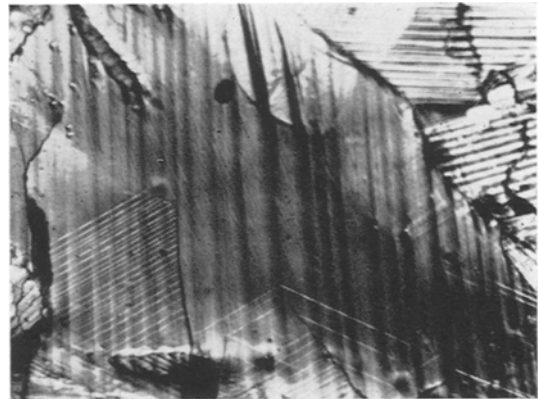


Figure 12 Fine lamellae associated with cracks on the surface of a $ZrH_{1.92}$ specimen after a load drop at room temperature. Polarised light ($\times 140$).

boundaries, which can reduce the number of different orientations of lamellae in a particular grain.

The observations of slip traces on the surfaces of deformed specimens were restricted to alloys of composition $ZrH_{1.71}$ and $ZrH_{1.77}$ tested above 100° C. Although the $ZrH_{1.71}$ specimens exhibited only tetragonal lines on X-ray diffraction powder patterns, the metallography suggested that the $\delta \rightarrow \epsilon$ transformation was not completed, and this is consistent with some reported values for the extent of the $(\delta + \epsilon)$ phase field [3, 6]. However, the $ZrH_{1.77}$ specimens were completely transformed to the ϵ structure and slip traces were observed in this alloy. Thus, it appears that, under certain conditions of composition and temperature, slip

can contribute to the overall deformation process.

The creation of new lamellae was a characteristic of the deformation process over the whole composition and temperature range examined. This feature is demonstrated by figs. 5a and b, 7a and b, 8 and 12. The crystallographic analyses of the habit planes of these new lamellae showed them to be parallel to the $\{101\}$ planes of the original δ matrix at 60° to the habit planes of the pre-existing lamellae. These factors suggest that new lamellae were a product of stress aided growth of twin orientations which did not predominate during the initial $\delta \rightarrow \epsilon$ transformation. If the close association between new lamellar formation, the stress/strain discontinuities and crack formation is also taken into account, it would appear reasonable to consider that the formation of new lamellae is analogous with mechanical twinning. Bolling and Richman [12] from their work on Fe-25 at. % Be alloys have shown that one of the characteristics of a deformation process which occurs primarily by continuous mechanical twinning is that the flow stress increases with an increase in temperature. Fig. 13 shows that the limit of proportionality decreases as the test temperature is raised for $\text{ZrH}_{1.71}$ and $\text{ZrH}_{1.77}$ alloys. It would thus appear that new lamellar formation does not determine the temperature dependence of the deformation characteristics of $\text{ZrH}_{1.71}$ and $\text{ZrH}_{1.77}$, above 100°C .

Twin boundary movement has been investigated in indium-thallium alloys [13, 14]. When single crystals of cubic, indium-thallium alloys were transformed to a structure containing fine, tetragonal $\{101\}$ twins and subsequently

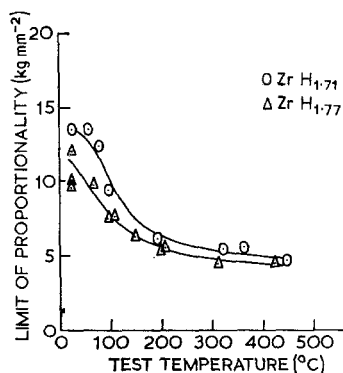


Figure 13 The temperature dependence of the limits of proportionality of $\epsilon\text{ZrH}_{1.71}$ and $\epsilon\text{ZrH}_{1.77}$.

deformed above 0°C , one of the twin orientations disappeared at the expense of the other until a tetragonal single crystal was produced. Chang [10], from an investigation of internal friction behaviour of $\epsilon\text{ZrH}_{1.92}$, interpreted his observations in terms of stress-induced twin interface motion and he concluded that the self diffusion of hydrogen was an important factor in determining the movement of the twin interfaces. If lamellar boundary movement involves hydrogen diffusion at the twin interfaces then the flow stress for this particular deformation mode would be expected to decrease with an increase in temperature. Thus, the temperature dependence of the limit of proportionality of $\text{ZrH}_{1.71}$ and $\text{ZrH}_{1.77}$ above 100°C (fig. 13) would appear to be related to the occurrence of slip and lamellar boundary movement as the primary modes of deformation.

The stress/strain curves of $\text{ZrH}_{1.71}$, $\text{ZrH}_{1.77}$ and $\text{ZrH}_{1.88}$ (figs. 1, 2 and 9) show that the extent of the yield discontinuities increased with hydrogen content at a particular temperature. Furthermore, the temperature range over which the yield discontinuities occurred increased with an increase in hydrogen content. The disappearance of the load drops with increasing test temperature appears to be associated with a decrease in the contribution of new lamellar formation to that of slip and lamellar boundary movement to the overall deformation process. With increasing hydrogen content the activation energy for self diffusion of hydrogen in zirconium hydride is expected to increase [15, 16]. Consequently, the temperature at which there occurred a significant contribution to overall deformation from lamellar boundary movement, would also increase. Thus, the stress/strain behaviour at yield appears, qualitatively at least, to be consistent with varying contributions from new lamellar formation and lamellar boundary movement.

In $\text{ZrH}_{1.92}$ new lamellar formation would appear to be the predominant deformation mode at temperatures up to 150°C . It is interesting to note that over this temperature range the stress immediately preceding the load drop shows a general increase with test temperature. A similar temperature dependence would be expected if the predominant deformation mode was analogous with mechanical twinning.

The observation of surface cracks in specimens unloaded at the stress/strain discontinuities (figs. 3 and 11) suggests that crack nucleation

was associated with lamellar formation. However, it is not possible on the basis of the present results to delineate the fracture nucleation mechanisms.

5. Conclusions

(i) The deformation of ϵ -zirconium hydrides can occur as a consequence of slip, creation of new lamellae and movement of existing lamellar boundaries.

(ii) The new lamellae which are created during deformation can form over a wide range of composition ($ZrH_{1.71}$ – $ZrH_{1.92}$) and temperature (22 to 400° C).

(iii) The limit of proportionality of $ZrH_{1.71}$ and $ZrH_{1.77}$ decreases with increasing temperature above 100° C, and this behaviour appears to be related to deformation taking place primarily by slip and lamellar boundary movement.

(iv) Discontinuities at yield in the stress/strain curves of ϵ hydrides were associated with new lamellar formation. The temperature range over which these discontinuities occurred, increased with hydrogen content from 22° C in $ZrH_{1.71}$ to 152° C in $ZrH_{1.92}$.

Acknowledgement

The authors wish to thank Professor G. V. Raynor, FRS, for the provision of laboratory facilities. This work was sponsored by the Metallurgy Division, AERE, Harwell, and the authors gratefully acknowledge financial assist-

ance and the provision of a studentship for K.G.B.

References

1. R. L. BECK, *Trans. ASM*, **55** (1962) 542.
2. K. G. BARRACLOUGH and C. J. BEEVERS, to be published.
3. S. TRZEBIATOWSKI and B. STALINSKI, *Roczniki Chem.* **30** (1956) 691.
4. E. A. GULBRANSEN and K. F. ANDREW, *J. Electrochem. Soc.* **101** (1954) 474.
5. S. S. SIDHU, N. S. SATYA MURTHY, F. P. CAMPOS, and D. D. ZAUBERIS, Non-Stoichiometric Compounds, *Adv. Chem. Ser.* **39** (1963) 87.
6. J. B. VETRANO and D. F. ATKINS, Nuclear Metallurgy (*Met. Soc. AIME*), **VII** (1960) 57.
7. R. E. RUNDLE, C. G. SHULL, and E. O. WOLLAN, *Acta Cryst.* **5** (1952) 22.
8. D. WHITWHAM, M. A. HUBER, and J. HERENGUEL, *Acta Met.* **7** (1959) 65.
9. M. S. WECHSLER, D. S. LIEBERMAN, and T. A. READ, *Trans. AIME* **197** (1953) 1503.
10. R. CHANG, *J. Nucl. Matls.* **2** (1960) 335.
11. J. S. BOWLES, C. S. BARRETT, and L. GUTTMAN, *J. of Metals* **2** (1950) 1478.
12. G. F. BOLLING and R. H. RICHMAN, *Acta Met.* **13** (1965) 709, 723 and 745.
13. Z. S. BASINSKI and J. W. CHRISTIAN, *ibid* **2** (1954) 101.
14. M. W. BURKART and T. A. READ, *Trans. AIME* **197** (1953) 1516.
15. J. F. HON, *J. Chem. Phys.* **36** (1962) 759.
16. B. STALINSKI, C. K. COOGAN, and H. S. GUTOWSKY, *ibid* **34** (1961) 1191.