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IRRADIATION GROWTH IN ZIRCONIUM AND ITS ALLOYS

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The UKAEA Northern Research Laboratories (Risley) have recently completed an underlying research study on irradiation growth in zirconium and its alloys. During this study, irradiation growth measurements have been made on a range of well-characterized single-crystal and polycrystalline iodide zirconium, commercial alloys Zircaloy-2 and Zr–2.5 wt% Nb, and high-purity zirconium–tin alloys in different metallurgical conditions following irradiation in the DIDO reactor at AERE Harwell. Irradiations were performed in three rigs operating at irradiation temperatures between 353 and 673 K. An important feature of the experimental programme was the capability to perform repeat length measurements on individual growth specimens at intervals during their irradiation programme. This facility has allowed accurate monitoring of the growth phenomenon and changes in growth behaviour induced by the combined effects of irradiation temperature and accumulated fast neutron dose over large dose ranges.

This paper reviews the main experimental results from this programme and discusses them in terms of current understanding of the growth process.

Thus, it has been observed that, in annealed Zircaloy-2 at temperatures between 553 and 673 K, a transition from saturating growth to accelerating growth rates occurs with increasing dose. The dose above which this "growth breakaway" takes place is seen to be inversely dependent on irradiation temperature in this temperature range. The well-documented difference in growth behaviour between annealed and cold-worked Zircaloy-2 observed at relatively low irradiation temperatures, in which cold-worked material grows at a high linear rate over large dose ranges, is not observed at 673 K. Comparison is made with reported results on similar material irradiated in other irradiation facilities. The growth data are interpreted in terms of recent theories regarding the development during fast neutron irradiation of a cold-worked microstructure consisting of $\langle \boldsymbol{a} \rangle$- and $\langle \boldsymbol{c} \rangle$-type dislocations.

Irradiation growth behaviour of annealed polycrystalline iodide zirconium between 353 and 673 K contrasts strongly with that in annealed Zircaloy-2 with low irradiation growth rates being observed over a large dose and temperature range.

The influence of key irradiation parameters on the growth process have been examined in a series of studies initiated as part of a collaborative programme with AECL Chalk River Nuclear Labs. Final results from the studies on annealed and deformed single-crystal zirconium are reported here. They show that growth saturates rapidly at low dose in annealed single-crystal material irradiated at 353 and 553 K but that a gradual increase in growth strain is observed on irradiation to high dose at 553 K. Single-crystal specimens heavily swaged prior to irradiation at 353 K and given different pre-irradiation heat-treatments exhibit high near-linear or accelerating growth rates. These growth data are interpreted in terms of the importance of grain boundaries and twin boundaries as sinks for point defects which allow point defect separation and hence growth to continue to high dose.

Finally, the results of growth experiments performed on Zr–0.1% Sn and Zr–1.5% Sn alloys at 353 and 553 K are reviewed. These experiments confirm the important role played by alloying additions and impurities on the growth process in zirconium and Zircaloy-2.

1. Introduction

Irradiation growth under fast neutron irradiation is an important source of dimensional instability in zirconium alloy reactor structural components in water reactors. It is thought to result from the partitioning of irradiation-induced interstitials and vacancies between various point defect sinks, such as dislocations, grain boundaries and solute atom traps. Experimental studies [1] have shown that irradiation growth in zirconium and its alloys is influenced by material metallurgical conditions (texture, grain size, dislocation density, and alloy content) and by experimental conditions (irradiation temperature and fast neutron fluence). Dimensional changes associated with irradiation-induced relaxation of residual stresses can occur in materials deformed prior to irradiation, and, in materials given insufficient pre-irradiation stress-relieving heat treatments, these

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changes can make a significant contribution to the observed nett strain.

The UKAEA Northern Research Laboratories (Risley) (NRL(R)) have recently completed an underlying research study on irradiation growth in zirconium and its alloys. During this study, irradiation growth measurements have been made on a range of well-characterized single-crystal and polycrystalline iodide zirconium, commercial alloys Zircaloy-2 and Zr–2.5wt% Nb, and high-purity zirconium–tin alloys in different metallurgical conditions. Irradiations were performed in the DIDO reactor at AERE Harwell at temperatures between 353 and 673 K. An important feature of the experimental programme was the facility to perform repeat length measurements on individual growth specimens at intervals during their irradiation programme. This facility allowed accurate monitoring of the growth phenomenon and changes in growth behaviour induced by the combined effects of irradiation temperature and accumulated fast neutron dose over large dose ranges.

Several papers reporting the results of different parts of this programme have been published [2–15] in recent years. In this paper, the key growth results obtained on each of the zirconium and zirconium-alloy materials irradiated within the programme are reviewed. Recent unpublished data obtained on materials of high interest are presented and the results discussed in terms of current understanding of irradiation growth in zirconium and its alloys.

2. Experimental details

2.1. Materials

The single-crystal and polycrystalline materials referred to in this review are listed in tables 1 and 2 respectively along with data on material grain size, metallurgical texture, dislocation densities and irradiation temperatures. Typical chemical compositions of the iodide zirconium, Zircaloy-2, Zr–Sn and Zr–2.5% Nb alloys are given in table 3. Further information on the materials irradiated in this programme are given in the appropriate references described below.

Nearly all of the polycrystalline growth specimens were sectioned from the longitudinal and transverse directions of parent plate or tube material. Each of these specimens was 137 mm long (with gauge length 127 mm), 12 mm wide and either 2.40 mm, 3.7 mm or 4 mm thick depending on starting material thickness (fig.

Table 1(a)
Annealed zirconium crystals

Identity	Nominal orientation	Angle between specimen axis and *c*-axis	Dislocation density (m^{-2})	Irradiation temperature (K)
4 (iodide)	***a***	82	10^{10} to 10^{12}	353
3 (iodide)	***c***	27	10^{10} to 10^{12}	353
7 (iodide)	***a***	79	10^{10} to 10^{12}	553
6 (iodide)	***c***	26	10^{10} to 10^{12}	553
2 (zone-refined)	***a***	87	10^{10} to 10^{12}	553
5 (zone refined)	***c***	28	10^{10} to 10^{12}	553

Table 1(b)
Deformed zirconium crystals

Identity	Structure before deformation	Deformation mode	Microstructure after deformation	Irradiation temperature (K)
XI	***a***	Swaged 18% at 300 K	$\langle c+a \rangle$ ($1.1\times10^{14}/m^2$) large numbers of $(10\bar{1}2)$ twins	353
XII	***a***	Swaged 18% + 1h at 823 K	$\langle c+a \rangle$ ($2\times10^{13}/m^2$) grain boundaries, $(10\bar{1}2)$ twins	353
XIII	***a***	Swaged 18% + 1h at 673 K	$\langle c+a \rangle$ ($2\times10^{13}/m^2$) $(10\bar{1}2)$ twins	353
XIV	***c***	Swaged 18% at 300 K	same as XI	353

Table 2
Polycrystalline materials

Material	Basal pole texture coefficients			Grain size and shape (μm)	Dislocation density (m^{-2})	Irradiation Temperature (K)
	Long	Trans	Radial			
Poly-iodide Zr						
Annealed (material B)	0.16	0.40	0.44	40 isotropic	$<10^{13}$	353, 553
Annealed (material C)	0.16	0.40	0.44	5 isotropic	$<10^{13}$	353, 553
Annealed (material D)	0.30	0.44	0.26	75 isotropic	10^{13}	353–673
Annealed (CR1, CR2)	0.10			40	353, 553	
Annealed + pulled 5% (CR3, CR4)	0.09			40	1.6×10^{13}	353, 553
Zircaloy-2						
Annealed plate	0.10	0.15	0.75	20 isotropic	$<10^{13}$	353–673
Annealed tube	0.10	0.20	0.70	20 isotropic	$<10^{13}$	353
25% cold-worked pressure tube	0.10–0.12	0.47–0.50	0.36–0.41	5–8 elongated	8.10^{13}	353–673
Zr–2.5 wt% Nb						
Annealed tube	0.03	0.59	0.38	1, 5–7 elongated		353–553
Zr–Sn alloys						
Zr–0.1% Sn, Zr–1.5% Sn	0.05			20		353, 553

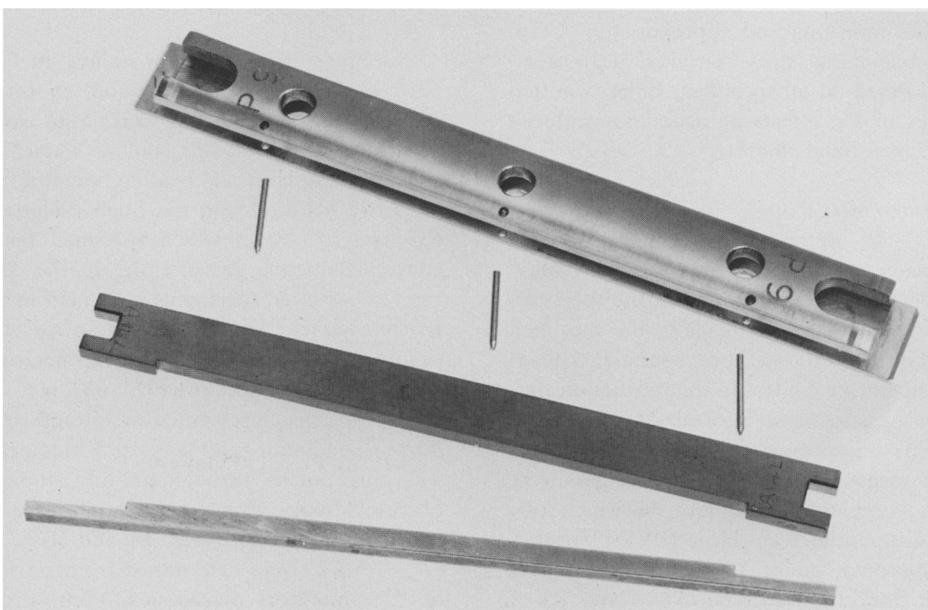

Fig. 1. Growth specimen and cassette.

Table 3
Chemical analyses

Material	Composition (wt%)						Impurities (ppm)		
	Sn	Fe	Cr	Ni	O	Nb	H	O	N
Iodide single crystal							1–8	80	25
Zone-refined single crystal							10	105	
Polycrystalline iodide zirconium							6	200	6
Zircaloy-2	1.53	0.14	0.10	0.05				1300	
Zr–0.1% Sn	0.13						25	120	10
Zr–1.5% Sn	1.6						18	117	10
Zr–2.5 wt% Nb					0.12	2.5			

Material	Impurities (ppm)									
	Fe	Cr	HF	Si	C	Sn	Pb	W	Ni	A
Iodide single crystal	54	Other substitutional impurities ~1000 ppm Other interstitial impurities ~1000 ppm								
Zone-refined single crystal	10–20	Other substitutional impurities ~ 250 ppm Other interstitial impurities ~ 250 ppm								
Polycrystalline iodide zirconium	170	< 10	170	< 40	260	15	< 5	< 25	< 10	
Zircaloy-2		120	85	70						50
Zr–0.1% Sn	12		70	50						
Zr–1.5% Sn	12		70	50						
Zr–2.5 wt% Nb	800	200	200	120	500	200	130	100		

1). Additionally, single-crystal specimens, polycrystalline Zr–Sn alloy specimens, and some polycrystalline iodide zirconium specimens were supplied by AECL, Chalk River Nuclear Labs, as part of a collaborative programme with the UKAEA. These were machined into cylinders 127 mm long and approximately 4 mm diameter. Post-machining stress-relieving heat treatments were performed on all specimens unless omitted to permit studies of the effects of irradiation-induced stress-relief on dimensional stability.

2.2. Growth measurement facilities

All specimens were enclosed in aluminium alloy cassettes (fig. 1) which prevented significant specimen bowing during irradiation and damage to the specimen during measurement operations. The cassette also aided the specimen temperature control in the irradiation rigs. Specimen length measurements were made in a fixture designed to keep the specimen flat and free of the cassette during measurement. Length changes were monitored by a comparator technique in which two linear variable differential transducer (LVDT) probes measured the specimen gauge length against master specimens made from a commercial alloy (Nilo K) of similar expansion coefficient to that of zirconium. A maximum measurement error of between 0.5 μm and 1 μm was obtained using this technique.

2.3. Irradiation facilities

Specimen irradiations in hollow fuel element positions in DIDO were carried out in three rigs; a rig operating at 353 K in which the specimens were immersed in the reactor coolant water; a helium gas-filled rig with electrical heating operating at 553 K; and a second helium/neon gas-filled rig operating at 573, 633 and 673 K in which specimen temperature was controlled by the gas mixture. In the 353 and 553 K rigs, 15 cassetted specimens were held in three banks of five in each rig. Three banks of four cassetted specimens occupied the third rig, each bank operating at a different specimen temperature (573, 633 or 673 K). Thermocouples near each specimen monitored rig temperatures during irradiation and a ± 10 K temperature control was maintained throughout the studies unless deliberately varied for experimental reasons. Mean fast neutron fluxes of between 4.1 and 10.8×10^{17} n/m$^2 \cdot$ s ($E > 1$ MeV) were determined from activation analyses of ^{54}Fe monitors placed near each specimen. A flux measurement accuracy and control of ±10% in each rig is estimated for the period of these studies.

Further details of the experimental facilities are provided elsewhere [16].

3. Review of growth results from the NRL(R) programme

In the following sections the key growth results obtained on zirconium and zirconium-alloy materials during the NRL(R) programme are reviewed and discussed in terms of the effects of different material and irradiation parameters on growth. A further general discussion is given in section 9.

4. Irradiation growth in single-crystal zirconium

4.1. Annealed single-crystal zirconium at 353 and 553 K

As part of the studies aimed at resolving the effects of different parameters on growth, Carpenter et al. [2] first reported growth data gathered within this programme on annealed iodide and zone-refined single crystals irradiated at 353 and 553 K upto a fluence of approx. 2×10^{25} n/m^2. Saturated growth strains of approx. 10^{-4} at fluences greater than 5×10^{24} n/m^2 were observed which were only weakly dependent on irradiation temperature. Whilst *a*-axis crystals expanded and *c*-axis crystals contracted, there was an overall volume increase of the order of the growth strain (approximately 10^{-4}). The rapid saturation of growth in single crystals contrasted with the high near-linear growth in irradiated polycrystalline material at low fluence and this was taken as evidence of the importance of grain boundaries as a sink for vacancies in polycrystalline zirconium.

Subsequently [3], irradiation of these annealed *a*-axis and *c*-axis crystals was continued at 553 K upto a maximum fluence of 7.1×10^{25} n/m^2. The high fluence growth data gathered on iodide and zone-refined crystals in these studies are shown in fig. 2. They revealed gradual acceleration of growth in *a*-axis iodide crystals and near-linear positive growth in *a*-axis zone-refined crystals above approx 2×10^{25} n/m^2.

This growth acceleration in *a*-axis single-crystal zirconium appeared similar to the growth "breakaway" reported [8] in polycrystalline annealed Zircaloy-2 at 553 K. Holt and Gilbert [17] have associated breakaway growth with the development of a $\langle c \rangle$-component dislocation structure at high fluence and have postulated that such $\langle c \rangle$-component dislocations might be generated by slip induced by intergranular stresses. However the absence of grain boundaries in annealed zirconium single crystals exhibiting breakaway growth

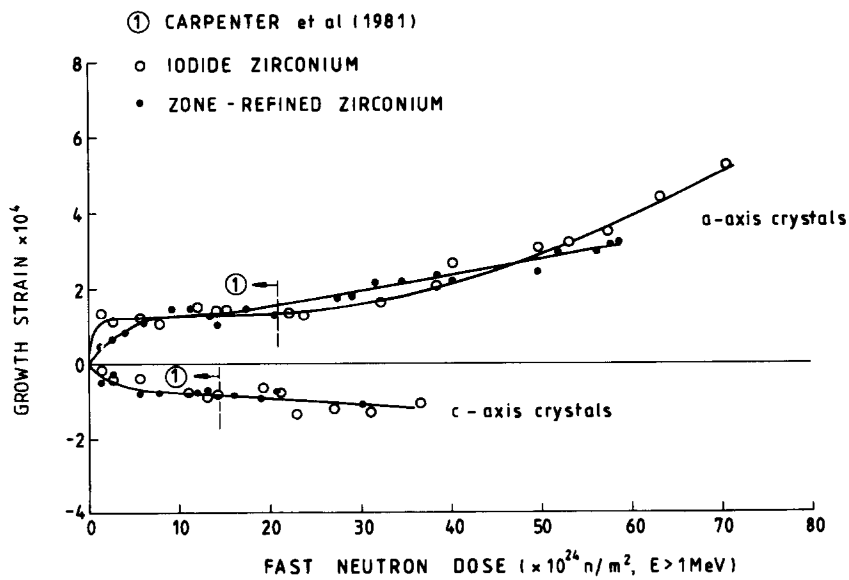

Fig. 2. Irradiation growth in iodide and zone-refined zirconium single crystals at 553 K.

in the NRL(R) studies favoured a different mechanism, possibly involving the rapid growth of submicroscopic ⟨*c*⟩-type vacancy loops under irradiation.

4.2. Deformed and annealed single crystals at 353 K

The effects of different deformation-induced structures on growth at 353 K have been studied within this programme in experiments performed on *a*-axis and *c*-axis crystals swaged 18% and given different stress-relieving heat treatments.

An *a*-axis single crystal (XI) swaged 18% elongated under irradiation at high rate as a result of the presence of massive aligned twins and ⟨*a*⟩-type and ⟨*c*⟩-type dislocations introduced by deformation [4]. It was concluded that the twin boundaries and ⟨*c*⟩-type dislocations acted as effective sinks for vacancies, thus allowing growth caused by absorption of interstitials at ⟨*a*⟩-type dislocations to continue at high rate. Similar high growth rates were observed in a swaged *c*-axis crystal (XIV) up to a fluence of 1.1×10^{25} n/m^2 when irradiation was terminated. The growth behaviour confirmed the conclusion from texture and microstructural analyses that swaging had eliminated any growth differences that might have arisen from the original *a*- and *c*-axis orientations of these specimens.

Annealing a swaged *a*-axis crystal (XIII) at 673 K for 1 h resulted in a much lower initial growth rate which correlated well with the reduction in dislocation density (from 1.1×10^{14} m^{-2} to 2×10^{13} m^{-2}) estimated from line broadening measurements. Annealing a swaged *a*-axis crystal (XII) at 823 K resulted in a smaller reduction in initial growth rate. As both swaged and annealed specimens had similar mixed ⟨*a*⟩- and ⟨*c*⟩-type dislocation densities, Zee et al. [4] associated the enhanced growth rate in specimen XII with the observed presence of grain boundaries which act as sinks for vacancies.

4.2.1. Recent data

Recent growth data on these deformed single crystals, together with the data reported earlier [4], are presented here in fig. 3 and in general confirm the trends observed in the earlier data. The abrupt cessation of growth above a fluence of 9.4×10^{25} n/m^2 in specimen XI, was caused by the specimen having outgrown the aluminium cassette in which it was housed and hence coming under restraint.

The growth data on specimens XII and XIII above a fluence of approx 8.2×10^{25} n/m^2 confirm that an acceleration in growth rate occurs in both specimens with increasing fluence, specimen XII exhibiting the larger acceleration. Breakaway growth, resulting possibly from either the density of ⟨*c*⟩-component dislocations in the swaged and annealed specimens increasing during irradiation or irradiation-induced relaxation of

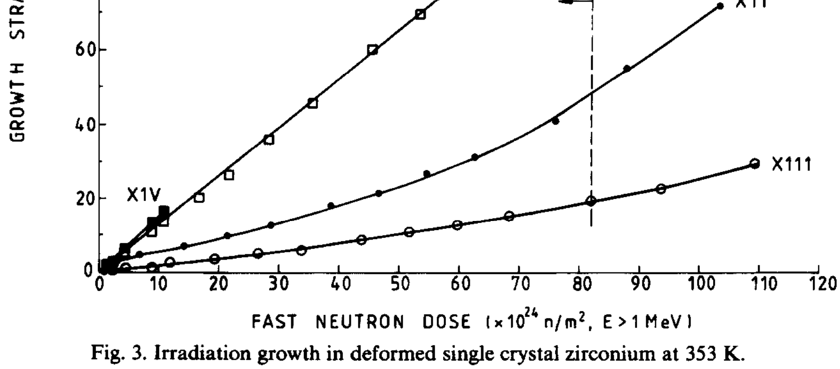

Fig. 3. Irradiation growth in deformed single crystal zirconium at 353 K.

residual stresses, could also account for the observed growth acceleration. In both cases, greater growth acceleration would be expected in the specimen annealed at 823 K (XII) since the higher annealing temperature would result in lower residual stresses and $\langle c \rangle$-component dislocation density.

5. Irradiation growth in polycrystalline iodide zirconium

5.1. Iodide zirconium at 353 and 553 K

The effects of grain size, basal pole texture coefficient (F_L), dislocation density, and irradiation-induced relaxation of residual stresses on growth in polycrystalline iodide zirconium have been studied [4,5] within the NRL(R) programme. In annealed materials at 353 K, growth was found [5] to be characterized by near-linear texture dependent growth rates at low fluence which saturated at fluences greater than approx 6×10^{24} n/m^2 and exhibited only weak grain-size dependence. At 553 K, the same materials showed much greater grain-size dependence with only the 5 μm material exhibiting significant texture-dependent growth. Growth in as-received cold-worked material at 353 K was dominated by irradiated-induced relaxation of residual stresses at low fluence and a rapid growth associated with pre-existing dislocation structure (6.5×10^{14} m^{-2}) at high fluence [5]. Growth data on other annealed and deformed polycrystalline iodide zirconium specimens irradiated at 353 and 553 K provided additional confirmation [4] of the trends seen in earlier studies [5] at these temperatures.

5.1.1. Recent data at 353 and 553 K

Irradiation of the annealed iodide specimens from Refs. [4] and [5] at 353 and 553 K has now continued up to significantly higher fluence. In figs. 4, 5 and 6 are presented the growth data obtained at 353 and 553 K on 5 μm, 40 μm and 75 μm grain-size materials of differing texture irradiated upto fluences of approx 11×10^{25} n/m^2 and 5.8×10^{25} n/m^2 respectively.

The 353 K data in fig. 4 confirm that low near-linear growth rates continue at fluences above the initial transient stage in all specimens. There is no discernible grain-size effect on growth rate above the transient stage at this temperature. At 553 K (fig. 5), the recent data indicate that near-linear texture dependent growth rates are established in 5 μm and 40 μm material above an initial transient stage. Again, whilst the transient growth strain is strongly dependent on grain size in this range the linear growth rates in 5 μ and 40 μm material are identical.

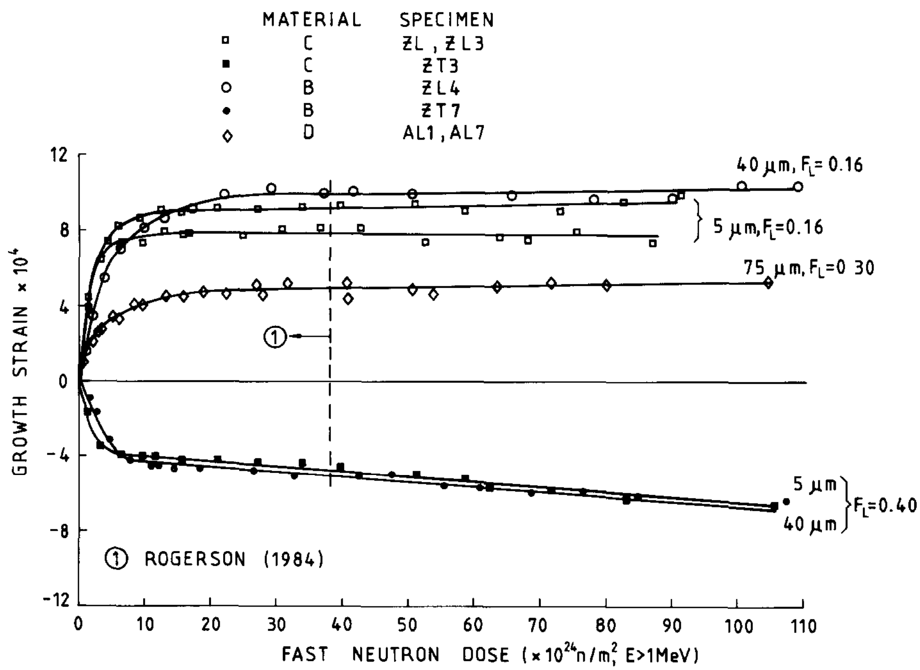

Fig. 4. Irradiation growth in annealed polycrystalline iodide zirconium at 353 K.

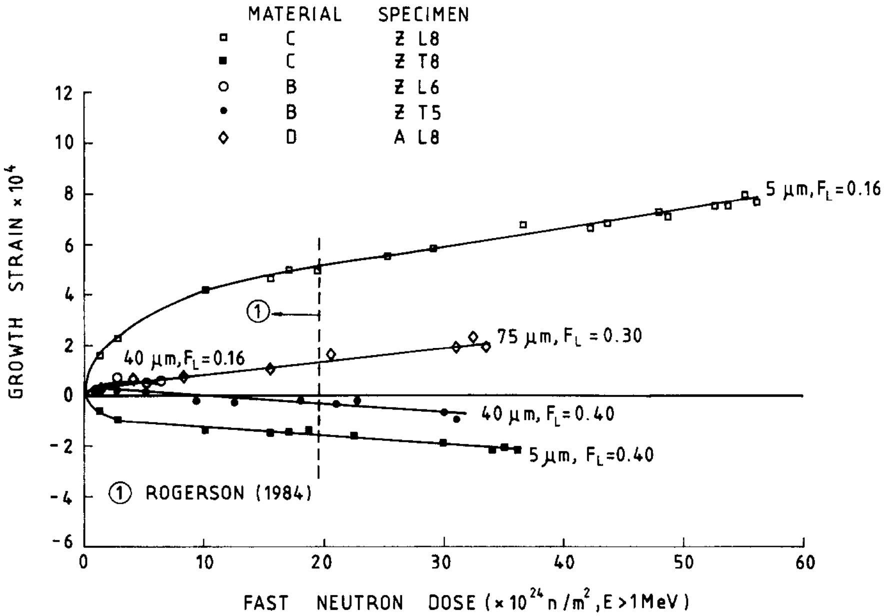

Fig. 5. Irradiation growth in annealed polycrystalline iodide zirconium at 553 K.

These results agree well with studies elsewhere by Cann et al. [18] over a higher temperature range. Their results confirmed the strong grain-size effect observed in the initial growth transient and indicated that growth rates were similar in different grain-size materials at higher fluence. Their results also indicated that the grain-size effect on growth saturated at grain sizes between 50 µm and 800 µm.

In fig. 6 are presented the recent growth data on annealed and deformed polycrystalline zirconium whose earlier results were reported by Zee et al. [4]. These recent data confirm the change in the direction of

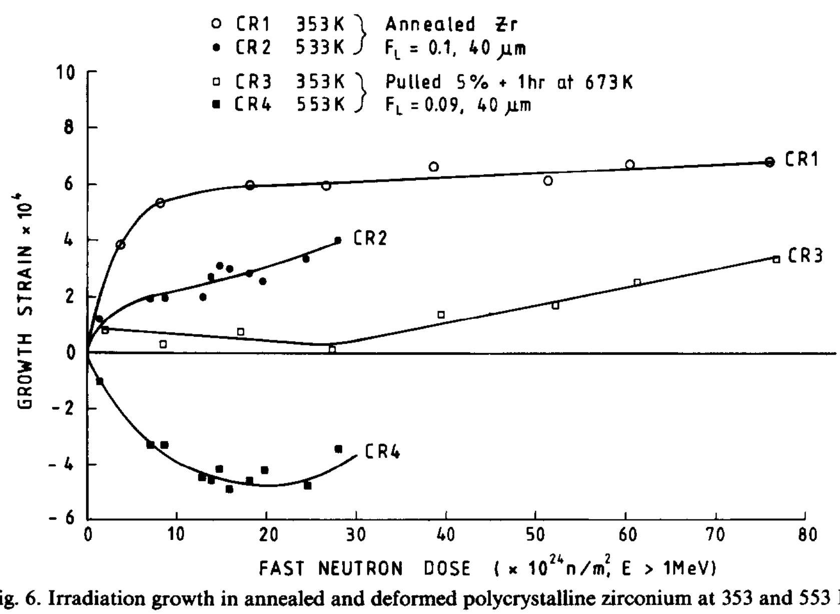

Fig. 6. Irradiation growth in annealed and deformed polycrystalline zirconium at 353 and 553 K.

growth in 5% pulled specimens at 353 and 553 K as the effects of irradiated-induced stress relief are exhausted. Also the high-fluence near-linear growth rates in annealed materials are now apparent.

These growth data in figs. 4–6 on polycrystalline iodide zirconium lend support to the view that, in this material at 353 and 553 K, growth occurs primarily by a volume-conserving process. For such a process, the texture dependence of growth should obey a $1-3F_L$ dependence, where F_L is the basal pole texture coefficient in the measurement direction. A $1-F_L$ dependence would occur for growth occurring solely by an isotropic volume increase. In fig. 7(a) and (b) the transient growth strains, measured at a fluence of 2×10^{25} n/m^2, and the mean high-fluence linear growth rates derived from figs. 4–6 are correlated with the growth coefficient, $1-3F_L$. Despite the scatter in these figures, the data confirm that growth occurs primarily by a shape rather than volume change as well as revealing the sensitivity of growth in annealed iodide zirconium to irradiation temperature and grain size.

5.2. Iodide zirconium at 573, 633 and 673 K

Annealed iodide zirconium (material D in figs. 4 and 5) has also now been irradiated at 573, 633 and 673 K. The growth data obtained on two specimens irradiated at each temperature are shown in fig. 8. The most striking feature of these data is the apparent upturn in growth rate in annealed iodide zirconium irradiated at 633 and 673 K above a fluence of approx 1×10^{25} n/m^2 and the absence of any significant positive transient strain below this fluence at the same temperatures.

Tucker et al. [19] and Cann et al. [18] have also observed high growth rates in polycrystalline zirconium irradiated at high temperatures, possibly associated with a volume increase. However this is the first observation of the change from negligible growth to accelerating growth rates with increasing fluence. This occurrence in material of near-random texture could also be interpreted as indicating a volume increase. If this is the case, it indicates a change from predominantly volume-conserving to non-volume-conserving growth in annealed iodide zirconium with increasing irradiation temperature. Unfortunately, uncertainties in measuring accurately the basal pole texture coefficient of near-random textured material prevent firm conclusions being drawn on this particular aspect from the present data. The positive temperature dependence of the high fluence growth above 633 K is consistent with studies elsewhere [18,19] on zirconium and its alloys and provides further evidence of a change in the nature of the growth process at high irradiation temperatures.

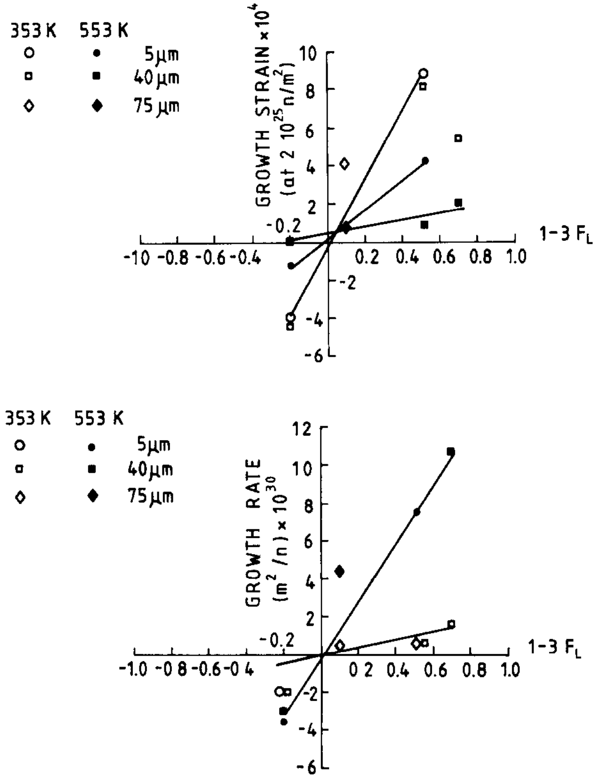

Fig. 7. Effects of texture and grain size on growth in annealed iodide zirconium.

5.3. Temperature cycling effects

The results on growth in annealed polycrystalline zirconium of changing the irradiation temperature between 353 and 553 K were reported in ref. [5]. They showed that rapid negative transient strains occurred on raising the irradiation temperature from 353 to 553 K whilst similar positive transients occurred on reversing the temperature change. These effects were interpreted in terms of the effects of temperature changes on the nucleation and dissociation of the small clusters and loops on prism planes.

5.3.1. Recent data

Whilst no further temperature cycling experiments on annealed zirconium have taken place within the NRL(R) programme, irradiation of a specimen at 353 K following initial irradiation at 553 K has continued to

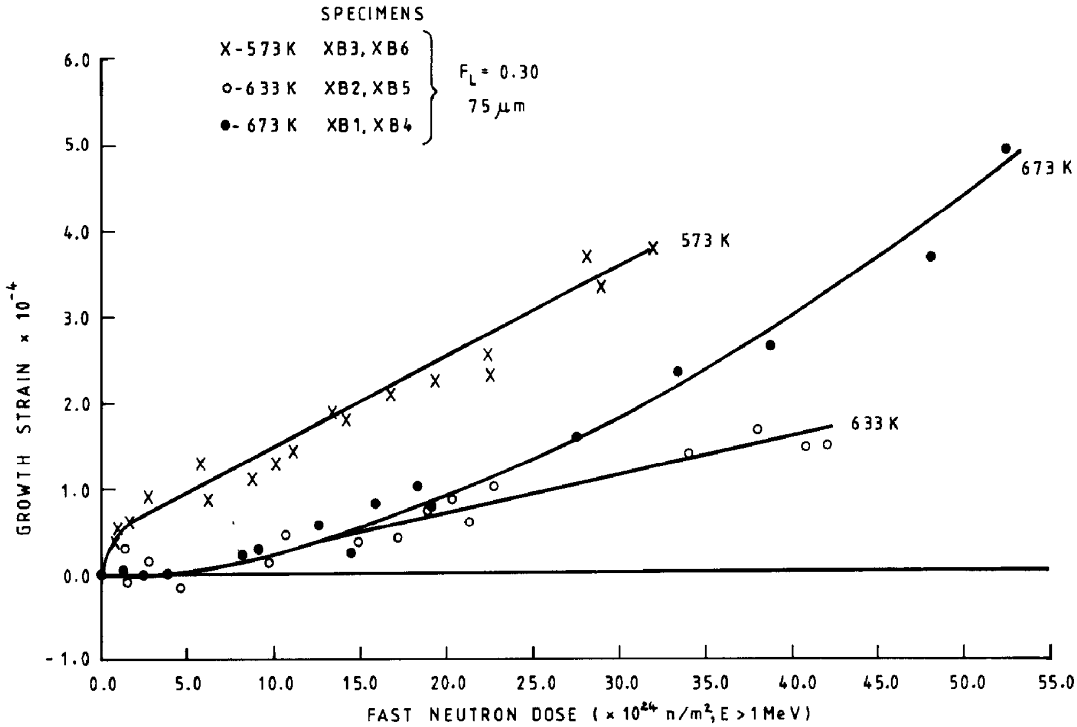

Fig. 8. Irradiation growth in annealed polycrystalline iodide zirconium at 573, 633, and 673 K.

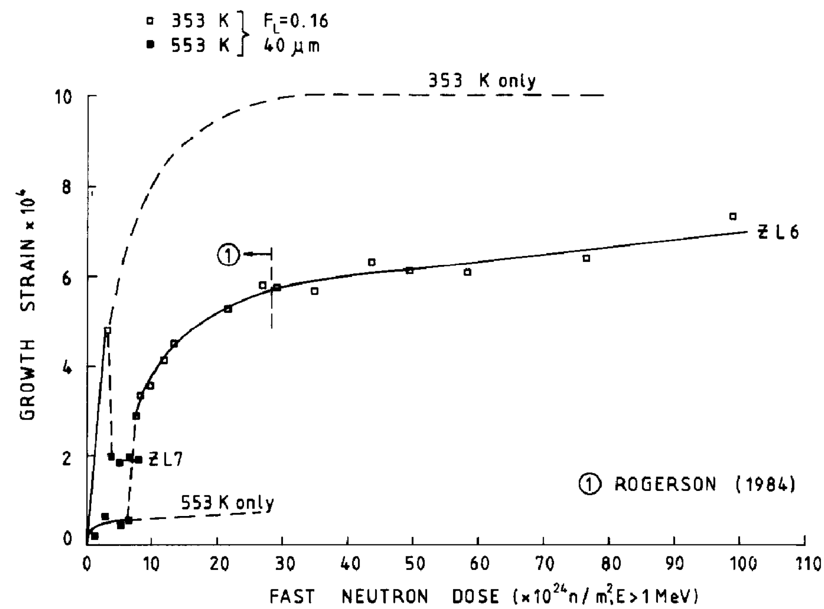

Fig. 9. Effects of temperature cycling on irradiation growth in annealed polycrystalline iodide zirconium.

high fluence. These data together with the earlier results are shown in fig. 9.

It is now apparent in the recent data on specimen ZL6 that the short period of irradiation at the higher temperature prior to transfer to the 353 K rig has significantly reduced the magnitude of the subsequent transient growth compared with that observed in material irradiated isothermally at 353 K. Additionally, the near-linear growth rate (1.71×10^{-30} m^2/m) beyond the initial transient stage is more than double the rate measured in material irradiated isothermally to high fluence. These effects suggest that, in annealed iodide zirconium, the presence of a damage microstructure characteristic of irradiation at the first temperature modifies the balance between recoverable growth, caused by loop nucleation, and non-recoverable growth, caused by dislocation climb, at the second temperature.

6. Irradiation growth in zircaloy-2

6.1. Annealed Zircaloy-2 between 353 and 673 K

6.1.1. Studies at 353 and 553 K

The majority of earlier publications [7–9,11] on growth in annealed Zircaloy-2 arising from the NRL(R) programme concentration on the effects of texture, fast neutron fluence, and temperature cycling on growth in the temperature range 353 to 553 K. At 353 K, growth saturation was observed at very low fluence following a rapid transient growth whilst at 553 K growth was initially less rapid but continued to higher strains. The onset of "breakaway" growth was reported [8] in annealed Zircaloy irradiated to fluences greater then 3×10^{25} n/m^2 at both temperatures.

In a recent paper [6], the present author has reported the continuation of growth acceleration at 553 K in annealed Zircaloy-2 irradiated upto a fluence of 11.1×10^{25} n/m^2. However, growth at 353 K was found to re-saturate at fluences greater than 4×10^{25} n/m^2. The recent data on annealed Zircaloy-2 are shown in fig. 10 together with similar data on 25% cold-worked Zircaloy-2 to be discussed in Section 6.2.

The 553 K data provided firm evidence of a change in growth behaviour in annealed Zircaloy-2 at high fluence linked to the appearance [17] of $\langle c \rangle$-component dislocations above the transition fluence. Acceleration of growth in annealed Zircaloy-2 as observed in fig. 10 lends strong support to models of growth in which interstitials and vacancies are absorbed at $\langle a \rangle$-type and $\langle c \rangle$-component dislocations respectively.

It was thought [6] that the re-saturation of growth in annealed Zircaloy-2 at 353 K indicated that minor alloying additions and impurities were restricting growth in annealed Zircaloy-2 at 353 and 553 K. support for this view came from the observed continuation of growth acceleration in high-purity Zr–1.5% Sn alloy specimens [14,15], to be discussed below.

6.1.2. Studies at 573, 633 and 673 K

Irradiation growth studies at 573, 633 and 673 K on identical annealed Zircaloy-2 to that studied at the lower temperatures were performed [6] in the NRL(R) programme to study the influences of these high-temperature irradiations on breakaway growth. Following an initial low-fluence saturating growth stage, sustained growth accelerations greater than that observed at 553 K were observed at each temperature. Marked differences in growth behaviour between nominally identical specimens became apparent at the higher irradiation temperatures as indicated by the growth data obtained at 673 K shown in fig. 11.

The high post-breakaway growth rates in annealed Zircaloy-2 at high temperatures were in good general agreement with the behaviour reported by Adamson et al. [20] and Tucker et al. [19] in their high-temperature, high-fluence irradiations in EBR2 reactor and by Willard [21]. Tucker et al. [19] also reported that growth at high temperatures was sensitive to minor microstructural and chemical differences between nominally similar Zircaloy materials. The NRL(R) studies indicated that such differences in growth behaviour can also occur in different specimens from the same batch of material.

6.2. 25% cold-worked zircaloy-2 between 353 and 673 K

6.2.1. Studies at 353 and 553 K

As with the annealed Zircaloy-2 growth studies, the majority of reports [7,9,10,12] on growth in 25% cold-worked Zircaloy-2 from this programme have concentrated on the effects of texture, fast neutron fluence, and temperature cycling on growth between 353 and 553 K.

High linear growth rates were observed [12] at both temperatures following an initial low-fluence transient growth of similar magnitude to that observed in annealed Zircaloy-2. The texture dependencies of these two stages of growth at 353 and 553 K in 25% cold-worked Zircaloy-2 are revealed graphically in the correlations of estimated low-dose transient growth strains and high-dose linear growth rates against the growth coefficient, $1 - 3F_L$ in figs. 12a and 12b. Also included in fig. 12b are data on annealed Zircaloy-2 [11] and

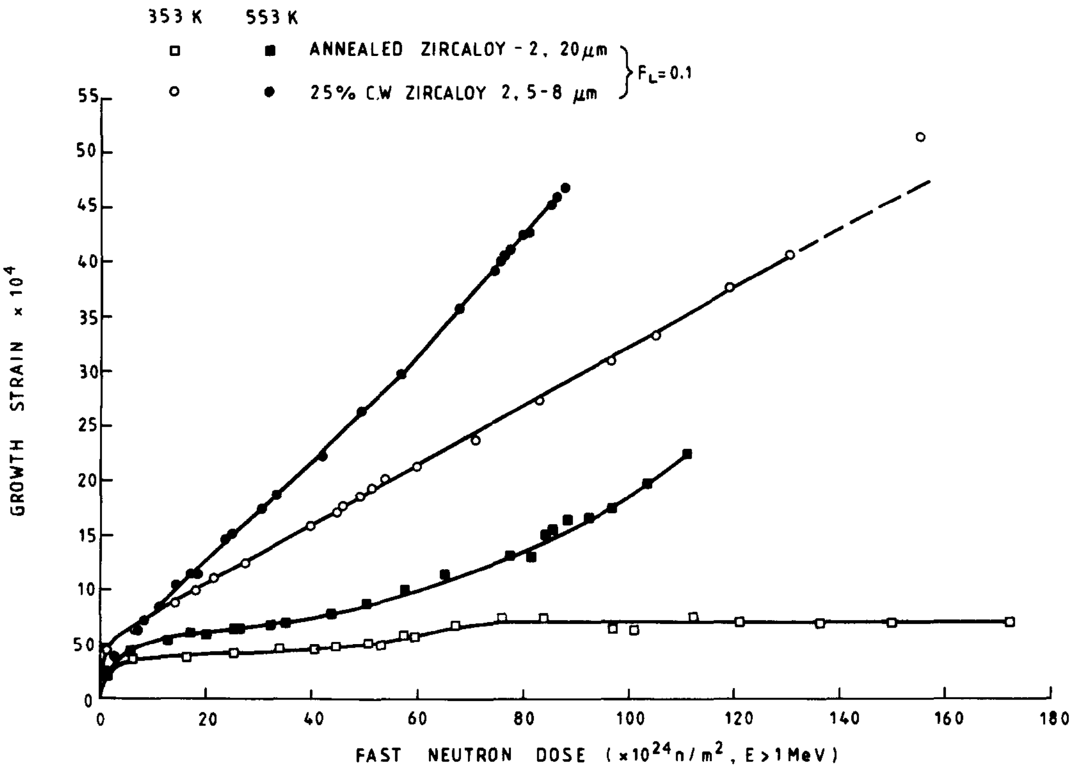

Fig. 10. Irradiation growth in annealed and 25% cold-worked Zircaloy-2 at 353 and 553 K.

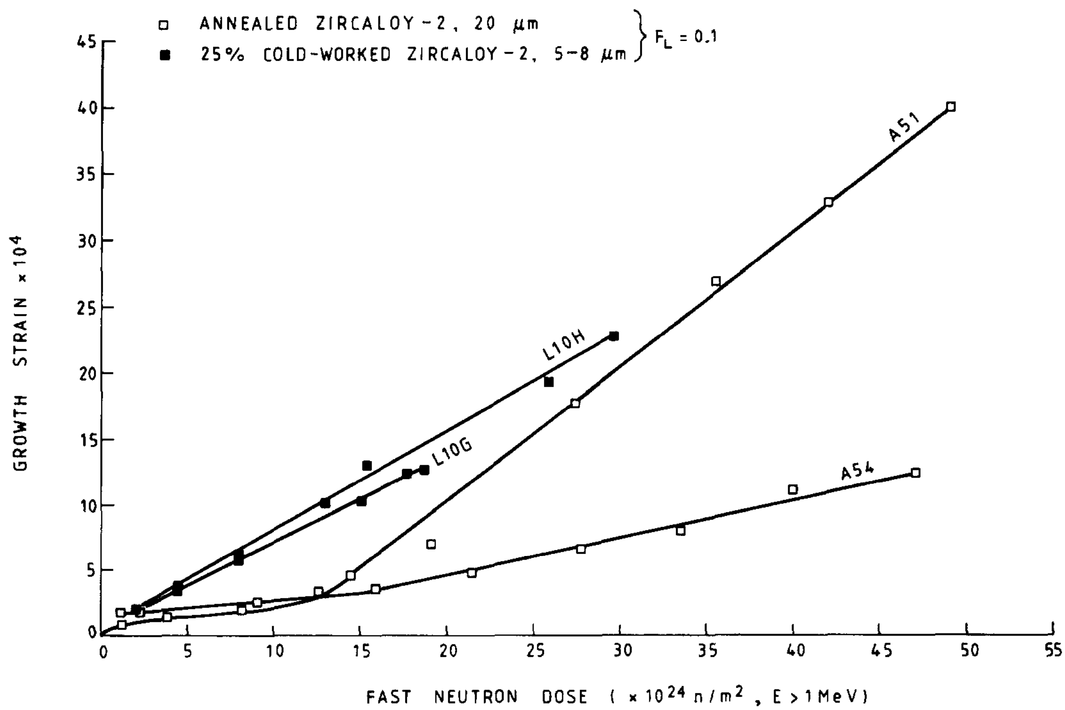

Fig. 11. Irradiation growth in annealed and 25% cold-worked Zircaloy-2 at 673 K.

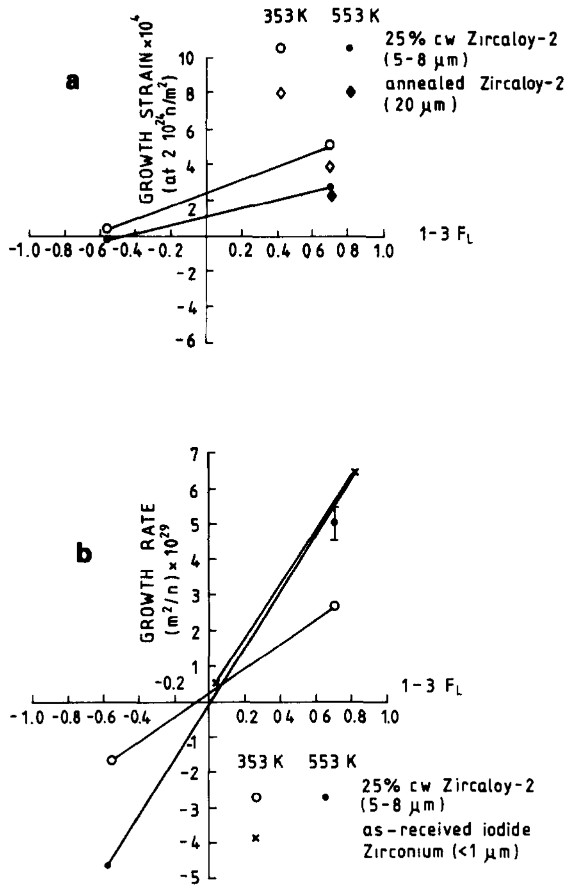

Fig. 12. Effect of texture on growth in Zircaloy-2 and cold-worked zirconium.

as-received cold-worked iodide zirconium [5]. It can be concluded [12] from these correlations that the low-dose transient growth strain occurring in cold-worked Zircaloy-2 at 353 and 553 K does not obey a $1-3F_L$ texture dependence, indicating that there was a volume change component associated with the low-dose transient growth behaviour in Zircaloy-2. Experimental confirmation of this in annealed Zircaloy-2 was obtained [9] in measurements which revealed a density decrease of $(5.2 \pm 1.0) \times 10^4$ in material irradiated to 5.7×10^{24} n/m^2 at 353 K.

Good agreement is found, however, between the ratios of the long-term linear growth rates in cold-worked material and those predicted by a $1-3F_L$ volume-conserving growth process.

The most recent growth data [6] on 25% cold-worked Zircaloy-2 specimens irradiated at 353 and 553 K are included in fig. 10. At both temperatures, the high near-linear growth rates continue to high fluence. The apparent small increase in growth rate in the 553 K data, although not significant in view of the 10% uncertainty in the flux rate over this long irradiation period, could indicate a slight further enhancement in growth in cold-worked material at high fluence.

Comparison in fig. 10 of the data on cold-worked material at 553 K with the data on annealed material at this temperature reveals that the growth rate in annealed material at high fluence is approaching that in cold-worked material. Such similarity in growth behaviour is consistent with the current view that growth at high fluence is dominated by climb of a pre-existing dislocation structure in cold-worked material and of an irradiation-induced dislocation structure in annealed Zircaloy-2.

6.2.2. Studies at 573, 633 and 673 K

Growth experiments on identical 25% cold-worked material to that reported above have also been performed [6] at 573, 633 and 673 K although up to much lower fluences.

Linear growth rates were observed at each temperature with good agreement between different specimens. These observed growth rates are correlated with those in annealed Zircaloy-2 over the same temperature range in fig. 13. A complex temperature dependence to the linear growth rate in cold-worked material was revealed with a

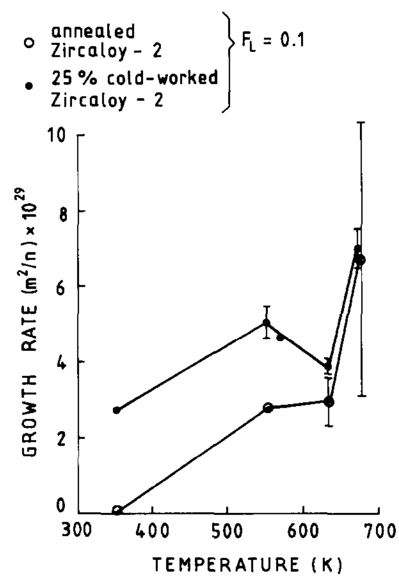

Fig. 13. Temperature dependence of growth in Zircaloy-2 at high fluence.

minimum occurring at 633 K. A strong positive dependence of growth on temperature was apparent above 633 K, with annealed and cold-worked specimens exhibiting similar high growth rates. The similarity in growth behaviour between annealed and cold-worked Zircaloy-2 above 633 K was consisted with results elsewhere [19,20].

6.3. Other Zircaloy-2 growth studies

6.3.1. Temperature cycling studies

Temperature cycling experiments on annealed and 25% cold-worked Zircaloy-2 between 353 and 553 K produced [11] rapid strain transients followed by growth at rates characteristic of the new irradiation temperature.

Various explanations of the Zircaloy-2 growth transients caused by temperature cycling have been put forward. Murgatroyd and Rogerson [11,12] originally considered that the observed changes might result from the dissolution and formation of interstitial clusters on prism planes as the steady-state vacancy concentration and vacancy mobility changed with temperature. Subsequently, Sn solute atom trapping and de-trapping of vacancies was suggested by Bullough and Wood [23] to explain the observed transients. Fidleris [1] has suggested that the transients may be due to the relief of intergranular stresses generated by the temperature cycle. Most recently, Fuse [24] has proposed that solute–interstitial complexes are candidates for the microscopic interstitial structure being modified during temperature cycling. The growth transients observed in annealed iodide zirconium (fig. 9) during temperature cycling would appear to case some doubts on the importance of Sn atom trapping in causing similar effects in Zircaloy-2. However the strong temperature sensitivity of growth in 40 μm grain-size iodide zirconium between 353 and 553 K further complicates interpretation of the observed changes. At present, therefore, the cause of this interesting effect in zirconium and Zircaloy-2 remains unclear.

6.3.2. Effects of small amounts of cold-work and irradiation-induced stress relief

During the early part of NRL(R) irradiation programme, it was noted that straightening operations on zirconium alloy reactor components could often introduce small amounts of cold-work and residual stress which might influence the dimensional stability of such components under irradiation. Experiments were initiated therefore to assess the effects on growth in annealed Zircaloy-2 of $\frac{3}{4}$% and 2% cold-work, introduced by pulling growth specimens in tension. Specimens were irradiated at 353 and 553 K in the as-received state and following stress relieving operations at 673 and 783 K.

The in-reactor dimensional changes measured in these specimens during subsequent irradiation at 353 and 553 K are shown in figs. 14 and 15 respectively. At 353 K, the cold-worked and stress-relieved specimens show very similar dimensional changes to those observed in fully annealed material. In contrast, dimensional changes in the as-received material, after initial positive growth transients, appear dominated by the gradual shrinkage caused by irradiated-induced stress relief. The difference in dimensional stability of stress-relieved and as-received specimens is even more pronounced at 553 K (fig. 15). Both $\frac{3}{4}$% and 2% cold-worked material exhibit large negative strains which rapidly approach the strains measured during the pre-irradiation heat treatment of the stress-relieved specimens. These latter specimens exhibit an initial low-dose positive growth transient of similar magnitude to that in

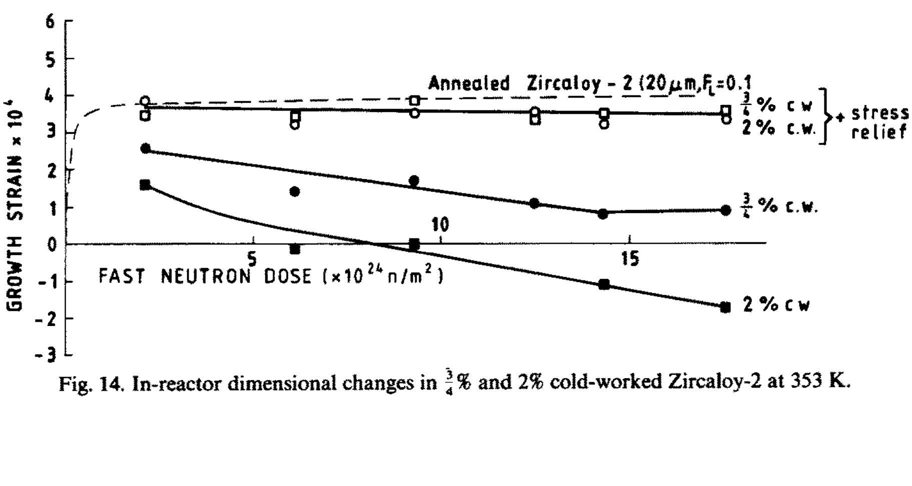

Fig. 14. In-reactor dimensional changes in $\frac{3}{4}$% and 2% cold-worked Zircaloy-2 at 353 K.

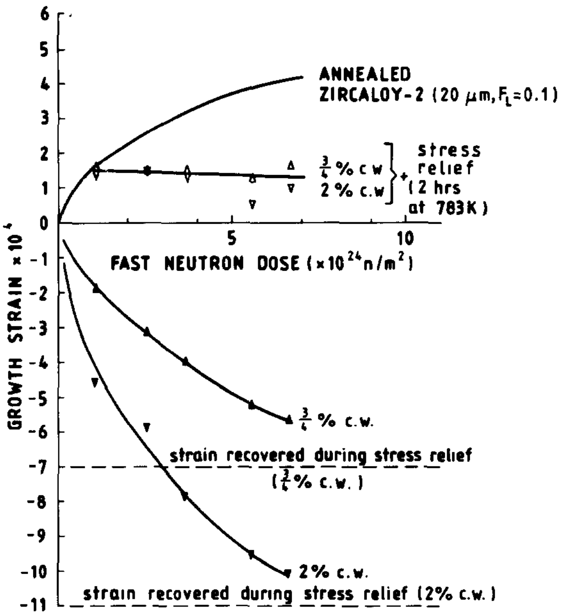

Fig. 15. In-reactor dimensional changes in $\frac{3}{4}$% and 2% cold-worked Zircaloy-2 at 553 K.

fully annealed Zircaloy-2. However they deviate from annealed Zircaloy-2 behaviour above a dose of about 1×10^{24} n/m^2 indicating that stress-relaxation effects are still influencing dimensional changes in nominally stress-relieved material at this higher irradiation temperature.

7. Irradiation growth in zirconium–tin alloys at 353 and 553 K

High-purity zirconium–tin alloy specimens containing 0.1% and 1.5% Sn were irradiated in the DIDO growth rigs at 353 and 553 K with the aim determining the effects of 1.5% Sn, the concentration relevant to Zircaloy-2, on growth at these temperatures.

Initial results from these studies upto a maximum fluence of 3.1×10^{25} n/m^2 showed that the growth characteristics of annealed Zr–0.1% Sn and Zr–1.5% Sn alloy specimens were in general agreement with those of annealed polycrystalline iodide zirconium [5] and Zircaloy-2 [11] respectively. The rapid attenuation of growth in Zr–1.5% Sn at 353 K after an initial rapid positive growth transient confirmed that similar behaviour in annealed Zircaloy-2 was consistent with enhanced point defect recombination caused by trapping of vacancies at solute Sn atoms. However, differences in detailed growth behaviour between Zr–1.5% Sn and Zircaloy-2 at 553 K had to be tentatively attributed to the effects on growth of minor solute elements and impurities in the latter material.

The results of further irradiation of these specimens at 353 and 553 K up to a fluence of 11×10^{25} n/m^2 have been reported recently [15] and are reproduced here in figs. 16 and 17 respectively. The key feature of these latest data was the breakaway growth observed in annealed Zr–1.5% Sn at 353 and 553 K above 3×10^{25} n/m^2. Comparison of these data with growth in annealed Zircaloy-2 and iodide zirconium appeared to support the view [15] that the additional minor alloying elements and impurities in Zircaloy-2 restricted the magnitude of the nett growth at 553 K and prevented growth breakaway completely at 353 K. Whilst the growth strains in annealed Zr–0.1% Sn and iodide zirconium were similar at both temperatures, the long-term linear growth rates in Zr–0.1% Sn were greater than those in iodide zirconium, indicating that the 0.1% Sn enhanced the growth rates in the Zr–Sn alloy.

8. Irradiation growth in Zr–2.5 wt% Nb at 353 K

Irradiation growth in nominally-annealed Zr–2.5 wt% Nb at 353 K has been studied within the NRL(R) programme and growth data reported [7] up to a fluence of 5×10^{25} n/m^2. In fig. 18 are presented the most recent data on specimens irradiated at this temperature. The growth rates observed in longitudinal and transverse specimens are in reasonable agreement with a $1 - 3\ F_L$ texture dependence. Line-broadening measurements [25] on Zr–2.5 wt% Nb sample material indicated that it had a dislocation density of 3×10^{14}/m^2 prior to stress-relieving heat treatments and irradiation in DIDO, possibly as a result of straightening operations performed on the original annealed tube. This could have contributed to the high near-linear growth rates observed in this material. However, data on specimens annealed for 2 h at 750 °C prior to irradiation (dislocation density 0.3×10^{14}/m^2) (fig. 18) showed similar behaviour to the stress-relieved specimens indicating that residual cold-work was not responsible for the observed growth.

9. Discussion

In this review, the important results from the NRL(R) irradiation growth programme on zirconium and its alloys have been reviewed and the opportunity taken to

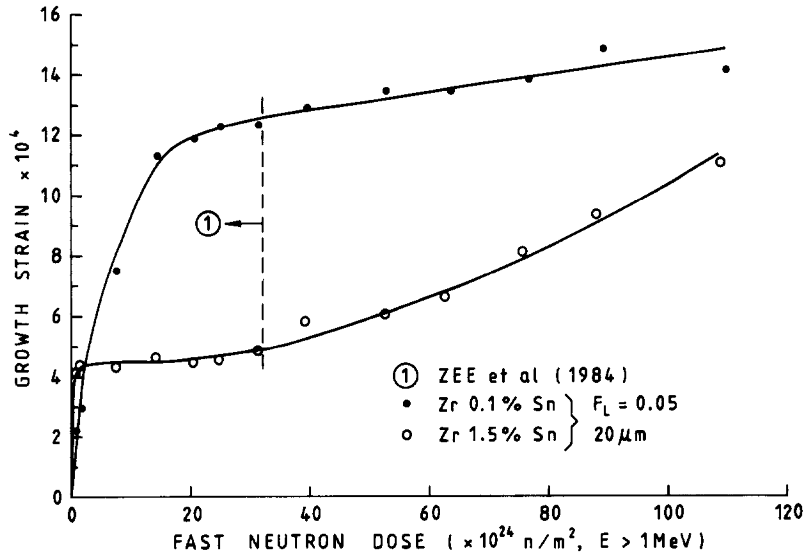

Fig. 16. Irradiation growth in Zr–0.1% Sn and Zr–1.5% Sn at 353 K.

publish the latest high-fluence data on material reported in earlier papers. It is inappropriate here to discuss further the detailed findings of the studies on each material as such discussion can be found in other references. A few general points can be made on the impact of the results of these studies on our understanding of the growth processes in zirconium and its alloys. In particular, it is useful to consider the influence of the material and experimental factors on growth and what future related studies should be performed.

9.1. Effects of metallurgical texture grain size, and dislocation density

The studies on annealed single-crystal and polycrystalline iodide zirconium at 353 and 553 K have allowed

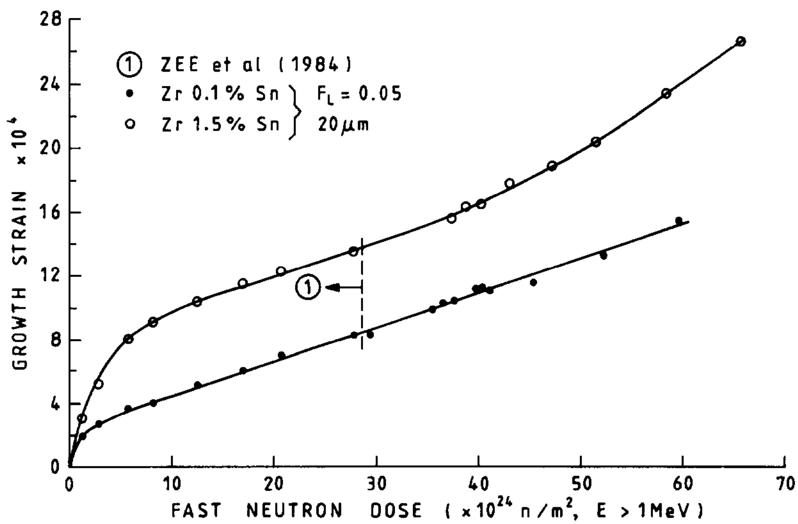

Fig. 17. Irradiation growth in Zr–0.1% Sn and Zr–1.5% Sn at 553 K.

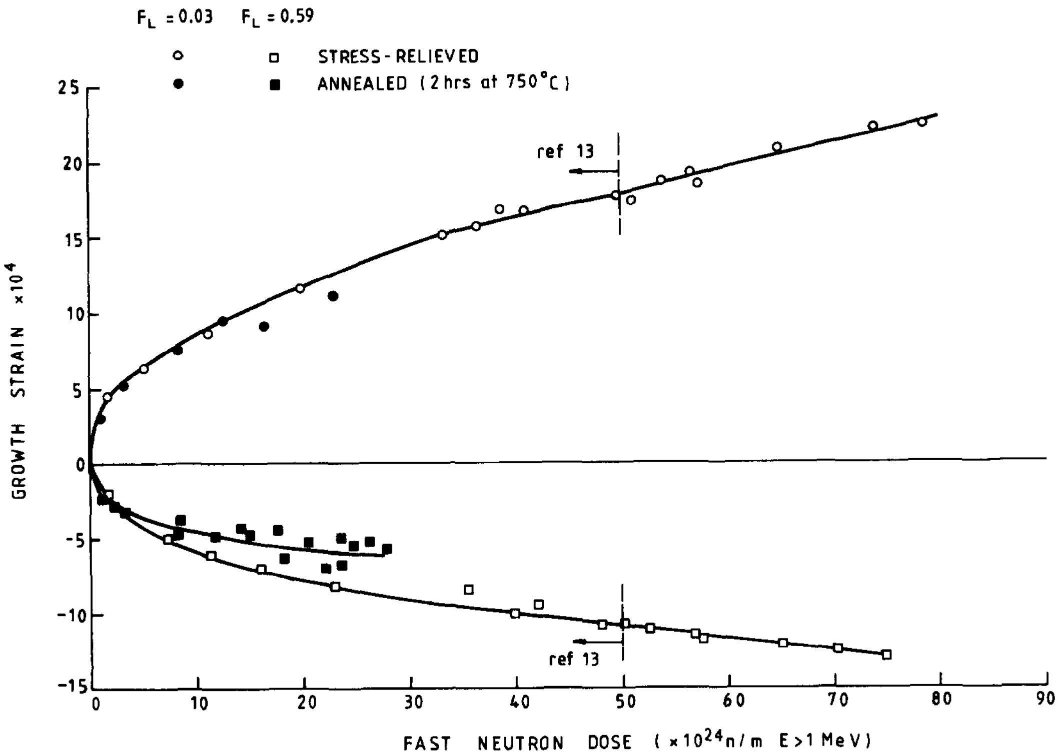

Fig. 18. Irradiation growth in stress-relieved and annealed Zr–2.5 wt% Nb at 353 K.

the importance of texture and grain size on growth to be clearly demonstrated. The results are consistent with a $1-3\ F_L$ volume-conserving growth process occurring in polycrystalline zirconium at these temperatures were an effective grain boundary sink for vacancies is also present.

A similar texture dependence of growth occurs at 353 and 553 K in cold-worked Zircaloy-2 above the low-dose transient stage and in cold-worked iodide zirconium where an enhancement in growth rate is evident due to the presence of a cold-worked microstructure. At these relatively low irradiation temperatures these observations are consistent with a modified Buckley model [28] of growth in which interstitials are absorbed at $\langle a \rangle$-type loops and dislocations, and vacancies migrate to $\langle c \rangle$-component dislocations and grain boundaries.

The limited range of materials irradiated at temperatures above 553 K in these studies prevents an assessment of material parameters on growth in this high-temperature regime. An unresolved question therefore is the importance of volume changes on growth at high temperatures. However studies elsewhere indicate that such changes account for a greater fraction of the observed texture dependent growth than at lower irradiation temperatures.

9.2. Effects of alloy content

The influence of alloy content on growth in zirconium alloys appears to be quite complex. The importance of solute Sn atoms in modifying the growth behaviour in annealed Zircaloy-2 at 353 and 553 K has been clearly demonstrated in the studies on Zr–Sn alloys. Sn appears to enhance or diminish growth relative to that in unalloyed zirconium depending on the irradiation temperature and fluence. This is thought to arise from the Sn–vacancy interaction which restricts vacancy mobility and thus affects point defect recombination and damage evolution. At 353 K, the volume increase associated with massive trapping of vacancies at Sn atoms would account for the non-volume-conserving texture dependence of growth in Zircaloy-2 during the low-dose transient growth.

The minor alloying elements (Fe, Cr, Ni) also appear to influence growth in zirconium and its alloys. Whilst experimental growth studies on zirconium–tin alloys [15] indicate that these alloying elements may restrict growth in Zircaloy between 353 and 553 K, recent microstructural studies by Griffiths et al. [26,27] have found a correlation between the onset of breakaway growth, the formation of *c*-component vacancy loops around intermetallic particles, and the extent of solute dissolution from these particles.

9.3. Effects of irradiation temperature and fluence

Transitions from saturating to accelerated growth rates have been monitored on a range of annealed zirconium and zirconium alloy specimens in these studies. In Zircaloy-2, an inverse temperature dependence to the fluence at which this breakaway occurs has been identified and a strong positive temperature dependence to the post-breakway growth rates observed (fig. 13). At the highest irradiation temperatures (633 and 673 K) there is evidence that significant differences in post-breakaway growth rates can occur in nominally identical specimens, possibly as a result of minor differences in microstructural or chemical compositions.

Based on the evidence of TEM studies performed elsewhere [17] on material exhibiting breakaway growth, these growth characteristics in the present studies have been associated with the development of a cold-worked microstructure in annealed materials at high irradiation temperatures and fluences. It remains to be confirmed, through post-irradiation examinations of these specimens, that this explanation is valid for all the materials exhibiting accelerated growth. There is a need to confirm that dimensional changes due to hydrogen pick-up remain negligible, as indicated in control experiments [16], throughout the long irradiations involved in these studies.

Finally, the large texture-dependent growth strains attained in materials irradiated above the breakaway fluence, should permit the fractional volume change associated with such growth to be determined accurately from density measurements on the irradiated specimens. Such studies would form an important part of the required PIE programme and help to resolve unanswered questions regarding the observed change in the high temperature dimensional stability of zirconium and its alloys.

10. Conclusions

(1) Under fast neutron irradiation, volume-conserving texture-dependent growth occurs in polycrystalline annealed and deformed zirconium, Zircaloy-2 (beyond a transient stage), and Zr–2.5 wt% Nb at low irradiation temperatures (353–553 K).

(2) The observed effects of texture, grain size and dislocation density on growth are consistent with growth caused by the absorption of interstitials at $\langle \boldsymbol{a} \rangle$-type dislocations and loops, and the absorption of vacancies at $\langle \boldsymbol{c} \rangle$-component loops and dislocations and at grain and twin boundaries.

(3) Sn-atom trapping accounts for the non-volume-conserving transient growth in Zircaloy-2 and the growth similarities in Zircaloy-2 and Zr–1.5% Sn at 353 K above 3×10^{25} n/m^2.

(4) Growth differences in Zircaloy-2 and Zr–1.5% Sn at 353 K above 3×10^{25} n/m^2 and at 553 K may reflect the influence of minor alloying elements and impurities on damage evolution.

(5) Transitions from saturating to accelerated growth rates are observed in single-crystal and polycrystalline zirconium and some zirconium alloys at high fluence. The growth behaviour is consistent with the development of a cold-worked microstructure in annealed material above the breakaway fluence.

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