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Formation of very large ‘blocky alpha’ grains in Zircaloy-4

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ABSTRACT

Understanding microstructure and its evolution is very important in safety critical components such as cladding in nuclear reactors. Zirconium alloys are used as cladding materials due to their low neutron capture cross section, good mechanical properties and reasonable corrosion resistance. These properties are optimised, including grain size and texture control, to maximise performance in thin (<1 mm wall thickness) tubes in water reactors. Here we show that very large grains (>0.5 mm) can be generated systematically during controlled deformation and subsequent heat treatments. We observe that the texture of these grains is controlled either by twinning or prior texture, depending on the strain path. Their nucleation, growth and texture can be controlled through strain path and deformation level. This work provides detailed understanding of the formation of these very large grains in Zircaloy-4, and also opens up opportunities for large single crystal fabrication for mm scale mechanical testing.

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1. Introduction

Zircaloy-4 is dilute zirconium alloy used in nuclear power applications as fuel rod cladding due to its low neutron capture cross-section and good mechanical strength. At room temperature it is hexagonal close-packed (HCP) α phase, with a 0.5 % volume fraction of second phase particles around 100 nm in diameter [1]. The nominal chemical composition of Zircaloy-4 is Zr – 1.5 wt%Sn – 0.2 wt%Fe – 0.1 wt%Cr [2].

A typical Zircaloy-4 fuel tube in a pressurised water reactor has a wall thickness of 0.57 mm [3]. Tube walls are thin to minimise neutron absorption and maximise fuel efficiency, but need to withstand high stresses during operation. A fine, uniform grain size is desirable in order to optimise strength, minimise stresses from thermal expansion and irradiation, and ensure a relatively homogeneous strain state along the entire fuel tube. Understanding the evolution of grain size during service is important for component life estimations, and excursions of grain size towards very large grains, the so called ‘blocky alpha’ structure (grains >300 μ m with irregular and wavy grain boundaries) [4], need to be understood.

Since the tube walls are thin, blocky alpha grains could span the entire width of a fuel tube wall. These very large grains can cause issues, since zirconium is anisotropic due to its HCP crystal structure [5]. The texture spike from a single large grain can affect

anisotropic material properties such as yield [6] and thermal expansion [7]. An absence of grain boundaries can impact properties such as strength (as small grains result in a stronger product [6]) and change ageing regimes such as irradiation growth and creep [8]. Furthermore, the orientation of the blocky grains can affect degradation mechanisms such as hydride embrittlement, if the grain is poorly oriented for brittle hydride plates to form on near basal planes [9] or reorient along the principal stress direction [10], which is often a compressive radial stress for fuel cladding tubes [11].

This paper explores the formation of blocky alpha grains in Zircaloy-4. First, some terms relating to recrystallisation and grain growth processes will be defined. In the results section, observations of blocky alpha formation via strain-anneal processing using both uniaxial compression and three point bending geometries are reported. In the discussion section, a mechanism for blocky alpha growth and orientation selection during nucleation is proposed.

2. Grain growth and recrystallisation processes

Recrystallisation is the formation of a new grain structure in a deformed material by migration of high angle grain boundaries (>10 – 15°) to reduce stored strain energy. In plastically deformed materials the energy from plastic work is eliminated by nucleation and growth of new grains via **primary recrystallisation** [12].

Grain growth can occur on further annealing after recrystallisation. It is the migration of high angle grain boundaries where the

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driving force for grain boundary migration is the reduction of grain boundary interfacial energy. In **normal grain growth** the smallest grains shrink and are consumed by neighbours, so that the average grain size increases. Normal grain growth is a continuous transformation, which means that it occurs homogeneously and simultaneously throughout the parent structure [12]. **Abnormal grain growth** occurs if normal grain growth is suppressed, e.g. by pinning from second phase particles. A minority of grains grow rapidly and consume neighbouring grains. This leads to a bimodal grain size distribution until all the initial grains are consumed, then the grain size distribution is once again unimodal, with a much larger average grain size than the starting material. Abnormal grain growth is also known as secondary recrystallisation [13]. The driving force for both normal and abnormal grain growth is the reduction of grain boundary area [12].

Abnormal grain growth and primary recrystallisation are discontinuous transformations. In these transformations, there is a sharp interface between transformed and untransformed material which sweeps through the material as the transformation proceeds [12]. Discontinuous transformations generally are also termed 'nucleation and growth' transformations as these processes can be divided into two steps: the formation of a stable nucleus which is energetically favourable to grow, and then growth of that nucleus. For example, in primary recrystallisation, the nuclei are usually recovered subgrains; in abnormal grain growth, the nuclei are the pre-existing recrystallised grains [12].

Nucleation site limited primary recrystallisation [14], also known as 'abnormal' recrystallisation [15], is a recrystallisation phenomenon which can produce very large grains. Similarly to abnormal grain growth, a minority of grains rapidly consume neighbouring grains to form a very large final grain structure. 'Abnormal' and primary recrystallisation are mechanistically indistinct, and the difference in transformed grain size is due to the extreme sparseness of nuclei during recrystallisation.

Although abnormal grain growth and (nucleation site limited) primary recrystallisation can produce similar microstructures, the transformation driving force is different between them: the driving force for nucleation site limited primary recrystallisation is the lowering of stored strain energy in the material, whereas the driving force for abnormal grain growth is the reduction of grain boundary area.

Abnormal grain growth and nucleation site limited primary recrystallisation can be distinguished if the transformation driving force can be isolated, as has been studied by Chen et al. in a friction stir welded aluminium alloy [16], where pre-annealing was used to recover the deformed structure before further heat treatment to produce large grains. In addition, often the speed of the transformation growth front in metals is one order of magnitude faster for recrystallisation ($\sim 10 \mu\text{m/s}$) than for abnormal grain growth ($< 1 \mu\text{m/s}$), so the mechanisms can be distinguished if typical transformation kinetics are known [15].

Strain induced grain boundary migration (SIBM) is a nucleation mechanism for recrystallisation. A pre-existing grain boundary segment bulges into an adjacent grain, the driving force for which is to reduce local stored energy ahead of the bulging grain boundary segment. The stored energy can take the form of either residual elastic energy or a higher dislocation density [12,15,17]. SIBM provides a mechanism for a recrystallised grain to nucleate without the formation of new recrystallisation nuclei from e.g. recovered subgrains; hence, it is regarded as a nucleation process [15,18].

In SIBM, the bulging grain boundary migrates away from its centre of curvature, and increases the surface energy and line tension of the grain boundary. For SIBM to be energetically favourable, the volume ahead of the migrating grain boundary must have higher stored energy which can be swept away by the

migrating grain boundary [18]. The stabilisation of the bulging grain boundary segment is the limiting step in SIBM, leading to an incubation period in transformations which nucleate via SIBM [15].

The strain-free material created from the sweeping of the grain boundary takes on the orientation of the pre-existing grain behind the sweeping boundary segment. As a result, the recrystallised textures are generally similar to, or a subset of, the deformed textures [18]. This is not always true for primary recrystallisation via subgrain growth, where entirely different textures can form, such as in heavily deformed copper [12].

2.1. Prior observations of recrystallisation and grain growth in Zr

2.1.1. Primary recrystallisation and normal grain growth

Primary recrystallisation temperatures in reactor grade pure Zr range between 550 and 700°C after 10 – 50 % strain, and the recrystallisation temperature decreases with increasing cold work [19]. A finer grain size can be achieved by more cold work. Normal grain growth after primary recrystallisation is extremely limited.

Jedrychowski et al. [20] showed that recrystallisation in moderately (17 %) strained, textured commercially pure Zr (α -Zr) is likely to be via SIBM. SIBM is the bulging of a boundary segment ahead of a nearly strain-free subgrain into highly deformed grains in the heterogeneously deformed structure. It allows recrystallisation to nucleate without the formation of a recrystallisation nucleus, which has high formation energy. By comparing experimental textures with Monte Carlo Potts models, they showed that the SIBM model describes the texture evolution more closely than classical nucleation and growth models. This result is independent of texture component strained, which is important as texture has a strong influence on deformation systems activated in Zr.

2.1.2. Abnormal grain growth

Literature reports of abnormal grain growth in Zr are generally based on observations of very large grains in the final microstructure. This section is reported according to the conclusions of the cited literature, but it should be noted that similar grain structures can arise from either abnormal grain growth or nucleation site limited primary recrystallisation, even though the driving forces for these mechanisms are different.

2.1.2.1. Effect of prior strain. Washburn [21] observed significant grain growth in Zircaloy-4 plate after deforming in tension to strains between 2 % and 12 %, then annealing for different times at 800°C (Fig. 1(a)). Reducing the temperature to 700°C resulted in a suppression of grain growth, and after 167 h (10^4 min) some samples had grown slightly to an average grain size of around 50 μm (0.05 mm) (Fig. 1(b)). Annealing at 500 and 600°C produced no grain growth for up to 167 h (10^4 min) at strains between 2 % and 12 %.

Schemel [22] observed abnormal grain growth during annealing after 5–8 % cold reduction of zirconium alloys. This was reported to be common after straightening or forming operations.

Gray [19] observed abnormal grain growth (also called 'secondary recrystallisation') in reactor grade pure Zr. This was achieved by annealing 10 % and 50 % cold rolled Zr in 10^{-5} Pa vacuum at 800°C for 1000 min or longer. The largest grains were up to 2 mm in diameter, with wavy and irregular boundary traces between large grains. Small island grains, not consumed by the grain growth process, are also observed. The grain size increases with annealing time, with larger grains observed after four days than after one day. The 10 % cold rolled sample produced smaller grains than the 50 % cold rolled sample for the same annealing conditions.

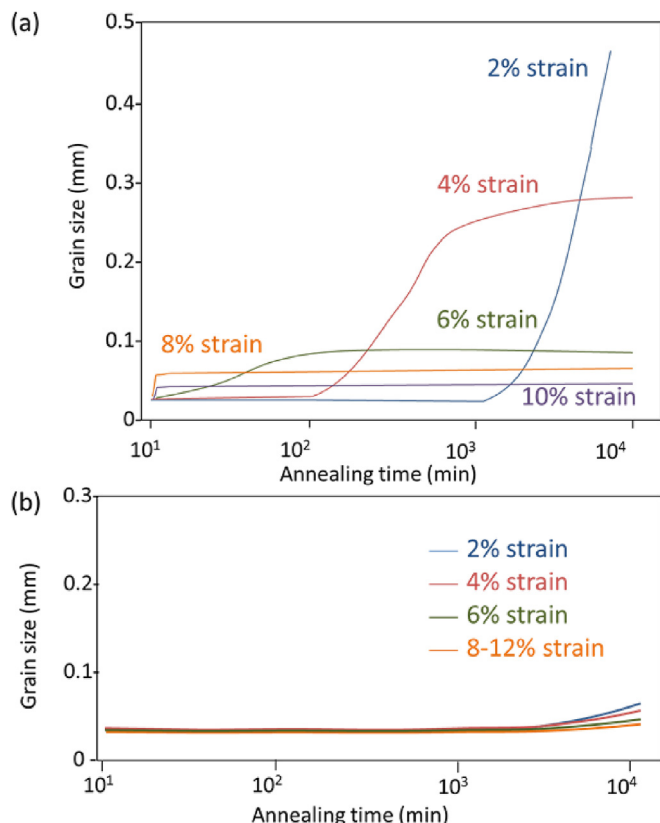


Fig. 1. Grain size in Zircaloy-4, as a function of time after annealing at (a) 800°C and (b) 700°C for a range of strains. Redrawn from Ref. [21].

2.1.2.2. Effect of second phase particles. In Zircaloy-4, second phase particles – ZrFe₂, ZrCr₂ and Zr(CrFe)₂ – are small intermetallic precipitates with diameter between 10 and 500 nm [1]. Washburn [21] speculates that the presence of SPPs may be the reason there is an incubation period for grain growth in Zircaloy-4 (see 2 % strain curve in Fig. 1), but did not demonstrate this.

Bozzolo et al. [23] observe abnormal grain growth in 80 % cold-rolled commercially pure Zr when annealing at 800°C for 100 min, but not with a shorter annealing time (10 min), nor at lower temperatures (700°C or 600°C). They state that second phase particles present in commercially pure Zr dissolve or coarsen over time at 800°C. Therefore, at 800°C it is probably dissolution of SPPs which allows abnormal grain growth in commercially pure Zr for longer annealing times of 100 min, but not for short annealing times of 10 min. High temperature differential scanning calorimetry experiments have indicated that second phase particle dissolution in low-tin Zircaloy-4 Zr - 1.2 wt%Sn - 0.2 wt%Fe - 0.1 wt%Cr occurs between 800 and 850°C [24].

In β -treated Zircaloy-4, Jeong et al. observe an increase in the volume fraction and mean diameter of second phase particles as the cooling rate decreases [25]. For Zircaloy-4 annealed at 780°C, Gros and Wadier observe that the modal second phase particle diameter increases from 120 nm to 330 nm after annealing for 50 h [1]. A high volume fraction of small, closely spaced second phase particles inhibits both normal and abnormal grain growth by Zener pinning. As a result, dissolution or coalescence of the second phase particles at high temperatures could trigger abnormal grain growth [13]. At 800°C second phase particles in Zircaloy-4 take 100–150 h to fully dissolve [26].

In Zircaloy-4, the second phase particle solvus is very close to the $\alpha \rightarrow \alpha + \beta$ transus at around 810–820°C [27,28]. Using

differential scanning calorimetry, second phase particle dissolution can be identified by a small endothermic thermogram peak, partially overlapping with the $\alpha \rightarrow \beta$ thermogram peak. The overlapped peaks span between 800 and 1000°C [24]. The overlap in thermogram peaks and the small volume fraction of second phase particles in Zircaloy-4 make specific identification of second phase particle dissolution very difficult to convincingly demonstrate. It is not possible to completely dissolve second phase particles and observe normal grain growth as single phase α -Zr, due to the overlap in second phase particle dissolution and β transformation temperatures.

As a comparison, abnormal grain growth in deformed Al-3.5Cu was observed to occur around the second phase particle solvus temperature. Below the second phase particle solvus, normal grain growth occurs slowly; above the second phase particle solvus, the material is single phase and the grains coarsen quickly, but the grain size distribution is narrow and the grain shapes are polygonal with straight boundary segments, which are features typical of normal grain growth [29].

Gray [19] observed that abnormal grain growth was present when annealing high purity Zr at 800°C in vacuum, but inhibited when annealing in helium or air. They attribute this to the formation of intergranular and intragranular precipitates which were visible after annealing in helium or air, but not after annealing in vacuum. The recovery, primary recrystallisation, and normal grain growth kinetics were not affected by annealing in air, helium or vacuum.

2.1.2.3. Texture following abnormal grain growth. Bozzolo et al. [23] observed abnormally large grains in 80 % cold rolled then primary recrystallised commercially pure Zr sheet with an initial mean grain size of 3.1 μ m. After holding at 800°C for 1.7 h (100 min) the microstructure showed a bimodal grain size distribution. The large grains had a different texture to the small recrystallised grains. No abnormal grain growth was seen at 700°C or 600°C for up to 1 h (60 min) holding times, or at 800°C for shorter 0.2 h (10 min) annealing times.

3. Method

The material was used as-supplied and consisted of fully recrystallised Zircaloy-4 plate. The as-received grain size was 11 μ m measured by a circular intercept method [30] and had a typical Zr rolled and recrystallised texture with basal poles oriented $\pm 30^\circ$ away from the plate normal direction (ND) towards the plate transverse direction (TD).

3.1. Uniaxial compression

Approximately 3.5 mm high cuboids of Zircaloy-4 plate were uniaxially compressed in a 10 kN Shimadzu AGS-X machine at 1 μ m/s to a known (engineering) stress, and in-plane strain distribution fields captured using digital image correlation (DIC). The DIC algorithm used has a displacement accuracy of 0.07 pixels for a known rigid body translation of 2 pixels.

The DIC imaging face and the faces in contact with the compression plates were ground to 10 μ m SiC paper after cutting. The DIC face was sprayed with white paint and a speckle pattern was applied using black copier toner. PTFE lubricant spray was applied to the compression plates to minimise friction at the sample edges. Although there was some barreling of the sample visible at high strains, the strain inhomogeneity in the sample is limited to around ± 1 % strain. [Supplementary material D](#) shows a strain distribution map and histogram of a typical compression sample, strained to 2 % along ND.

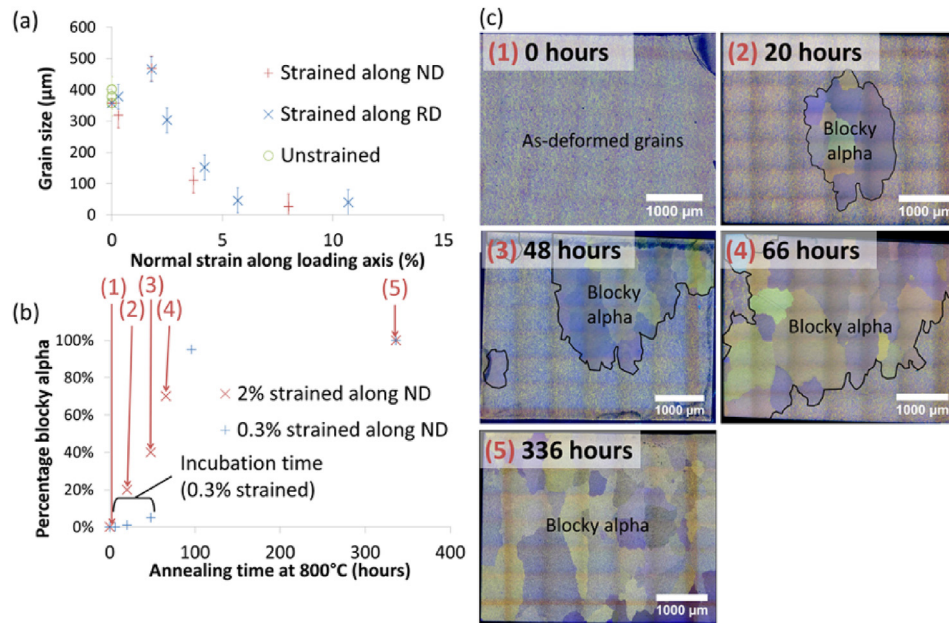


Fig. 2. Blocky alpha formation on annealing after uniaxial compression. Each data point in this figure is collected from a separate sample. (a) Grain size of Zircaloy-4 after annealing for 336 h at 800°C as a function of prior compressive strain. (b) Percentage of sample transformed into blocky alpha as a function of annealing time. (c) 'Time-lapse' optical micrographs of Zircaloy-4 annealed at 800°C for progressively longer times between 0 and 336 h, corresponding to points (1)–(5) in (b), with the blocky alpha regions outlined in micrographs (2)–(4).

3.2. Three-point bending

Three point bending was used to produce a well-defined strain distribution. Samples 29 mm long (TD), 2.8 mm wide (ND) and 2.9 mm high (plate rolling direction (RD)) were loaded at 0.8 μm/s (0.05 mm/min) to 550 N in a 2 kN Gatan Mtest2000E mechanical test frame. The central roller was displaced along ND and DIC imaging was performed on the face normal to RD to capture the tensile and compressive fibres during bending. The central and outer roller diameters were 4 mm and the distance between outer rollers was 26 mm.

3.3. Annealing heat treatment

At high temperatures, Zircaloy-4 transforms from a hexagonal close-packed α phase to a body centred cubic β phase. The $\alpha \rightarrow \alpha + \beta$ transus temperature in Zircaloy-4 is approximately 810–820°C [27,28]. To achieve maximum blocky alpha samples were held at 800°C for 336 h (14 days) in an encapsulated argon atmosphere, and air cooled. Two as-received samples were also pre-annealed at 300°C for 3 h before blocky alpha heat treatment to relieve surface stresses from machining or grinding that might nucleate blocky alpha grains. Comparisons of samples with and without pre-annealing showed negligible effect on blocky alpha formation.

3.4. Characterisation

Grain size was measured from polarised optical micrographs of mechanically polished samples using a circular intercept method following ASTM E112 Abrams Three-Circle procedure [30] scripted into MATLAB [31]. Since the grain size in annealed samples can be large compared to the sample size, the number of intercepts in the counting field can be as low as 40. The variation in apparent grain size was estimated by moving the circles used for intercept analysis, and a variation of ± 40 μm was found.

Samples for electron backscatter diffraction (EBSD) analysis

were electropolished for 90 s in a solution of 10 vol% perchloric acid in methanol at -40°C and 25 V, drawing a current density of around 1 A/cm². Electron backscatter diffraction (EBSD) data was acquired at 20 kV on either a Zeiss Auriga FEG-SEM or a FEI Quanta 600 FEG-SEM. For conventional orientation mapping, EBSD patterns were binned from a native resolution of 1600 × 1200 pixels to 320 × 240 pixels or 200 × 150 pixels, with exposure times of 20 ms or 8 ms respectively. High angular resolution EBSD (HR-EBSD) based geometrically necessary dislocation (GND) density analysis used 1600 × 1200 pixel patterns collected with an exposure time of 500 ms. In all cases the indexed fraction was at least 95 %.

4. Results

4.1. Uniaxial compression study

4.1.1. Transformation rate and transformed grain size

The equilibrium grain size after annealing was measured as a function of prior strain and strain direction. Fig. 2(a) shows increases in grain size (from 11 μm as-received) in all samples annealed for 336 h at 800°C. The grain size peaks at around 2 % strain and decreases sharply beyond this. The compression texture of the sample seems to have little effect on the final grain size (i.e. compression on the ND and RD faces produce a similar final grain size).

The rate of transformation was then estimated by compressing two series of samples to the same stress corresponding to 0.3 % and 2 % strain respectively, then annealing at 800°C for increasing duration. Fig. 2(b) shows that at 0.3 % strain, there is limited growth of a few grains after 48 h of heat treatment, whereas at 2 % strain, the same heat treatment time results in 40 % blocky alpha. By 96 h, the transformation is nearly complete. There is a ~50 h incubation period for blocky alpha formation in the 0.3 % strained sample, which decreases to less than 20 h when the strain is increased to 2 %.

In Fig. 2(b), the transformation rate was measured in terms of

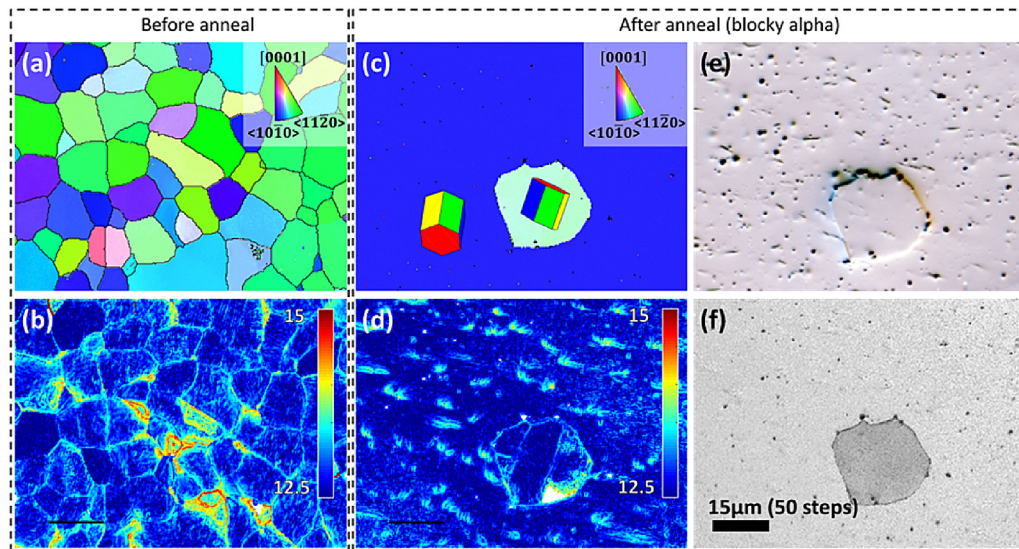


Fig. 3. Grain structure and dislocation density in deformed and blocky alpha samples mapped using HR-EBSD. All fields of view are the same size. EBSD step size in all maps is $0.3 \mu\text{m}$ (a) IPF map along RD of deformed sample. (b) GND density map of deformed sample (colour scale units $\log_{10} \text{m}^{-2}$). (c) IPF map along RD of annealed blocky alpha sample. (d) GND density map of annealed blocky alpha sample (colour scale units $\log_{10} \text{m}^{-2}$). (e) Forescatter electron image of annealed blocky alpha sample. (f) Pattern quality map of annealed blocky alpha sample. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

area fraction of sample transformed into blocky alpha. This metric was used as samples had a bimodal grain size distribution with clusters of large grains surrounded by small grains separated by a transformation front, as shown in the micrographs in Fig. 2(c).

The three green data points at 0 % strain in Fig. 2(a) are of samples which have not been compressed, and in addition, two of these three samples were pre-annealed at 300°C for 3 h to relieve machining stresses. Pre-annealing did not significantly affect the annealed grain size or morphology.

4.1.2. GND density of blocky alpha microstructure

The geometrically necessary dislocation (GND) densities in as-deformed and blocky alpha grains were analysed using HR-EBSD following the method reported by Britton et al. [32]. The step size used was $0.3 \mu\text{m}$ and the field of view sampled in both EBSD datasets was $90 \mu\text{m}$ by $67.5 \mu\text{m}$.

Fig. 3(a)–(b) show EBSD data for a deformed sample before annealing to produce blocky alpha. These samples were deformed to 0.3 % strain along RD. The deformed sample before annealing in Fig. 3(a) has an average grain size of $11 \mu\text{m}$. The GND density map shows heterogeneous deformation localised to some specific grains and also grain boundaries and triple junctions, whilst GND densities in most grain interiors remain relatively low.

Fig. 3(c)–(f) show maps of a blocky alpha grain surrounding an island grain. The blocky alpha grain formed on annealing after deforming to 0.3 % strain along RD. Island grains are a feature characteristic of abnormal grain growth in other material systems [29]. These island grains have a grain size of the same order of magnitude as the original grain size, and were observed in all the blocky alpha samples studied in this paper.

GND density hotspots, spaced 10–15 μm apart, are present within the large blocky alpha grain in Fig. 3(d). The spacing of the dislocation density hotspots is comparable to the grain size of $11 \mu\text{m}$ in the as-deformed sample in Fig. 3(a). Apart from one region (shown in white) which has not cross-correlated well, and two high dislocation density ‘walls’, most of the island grain has low GND density.

Pitting from electropolishing visible in the forescatter electron image can degrade pattern quality (shown in Fig. 3(e)–(f)) and

increase uncertainty in the GND density measurement. The positions of GND density hotspots correlate with pitting and reduced pattern quality. However, the higher dislocation density regions in the blocky grain are elongated and not round as the pitting artefacts are, and also extend far beyond areas of reduced pattern quality. Unlike small inclusions or precipitates which could potential induce longer range strain fields in the material, small surface pits cannot induce stress in bulk samples. The longer-range GND patterning cannot be only an artefact of reduced pattern quality from pitting. Pitting in this case is a sign of preferential chemical attack of high stored energy sites.

4.2. Three point bending study

4.2.1. Grain size variation and growth direction in three point bending

Strain variation has been shown to influence blocky alpha formation and therefore three point bending was used to impose a strain gradient on the sample. The three-point bend bar sample was bent to 550 N, heat treated for 336 h at 800°C , and subsequently metallographically polished. The surface strain field was measured using DIC and the ϵ_{TD} distribution (normal strain along TD, which is the bend fibre) is plotted in Fig. 4(a). The grain size distribution in the central region of the annealed sample was measured from EBSD data using the linear intercepts marked in Fig. 4(b).

Linear intercept grain size as a function of vertical distance from the central roller is plotted with the ϵ_{TD} measured from DIC in Fig. 4(c). The grain size distribution is approximately symmetric about the neutral axis and there is a step change around $\epsilon_{\text{TD}} = \pm 3\%$. The smaller ($\sim 100 \mu\text{m}$) grained regions will be referred to as ‘finer transformed grains’ and the large ($\sim 500 \mu\text{m}$) grained region will be referred to as ‘blocky alpha’. Fig. 4(b) shows that a single blocky alpha grain can span the entire length between the end of the transformed finer grained region and the neutral axis, where it meets another large grain.

Fig. 5 shows EBSD grain maps of a three point bend specimen where the blocky alpha transformation has completed and another specimen where the transformation has been interrupted by annealing for the same length of time at a lower temperature

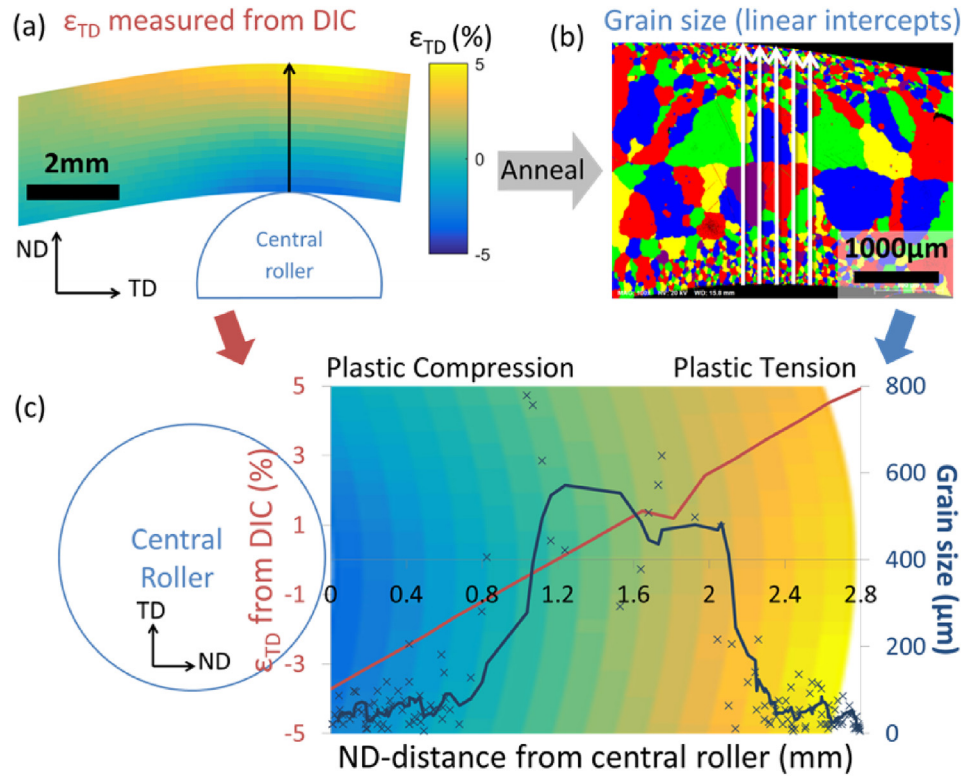


Fig. 4. Growth direction of blocky alpha and grain size distributions in three-point bend samples. (a) ϵ_{TD} (horizontal normal strain) distribution in deformed three point bend sample, measured by DIC. (b) Grain size distribution in central region of annealed three-point bend sample, measured using five linear intercepts shown by white arrows. (c) Grain size distribution plotted in central region of annealed three-point bend sample as a function of position on the sample, measured as distance from the central roller. New grains stop nucleating at less than $\pm 3\%$ strain and grow to large sizes towards the neutral axis.

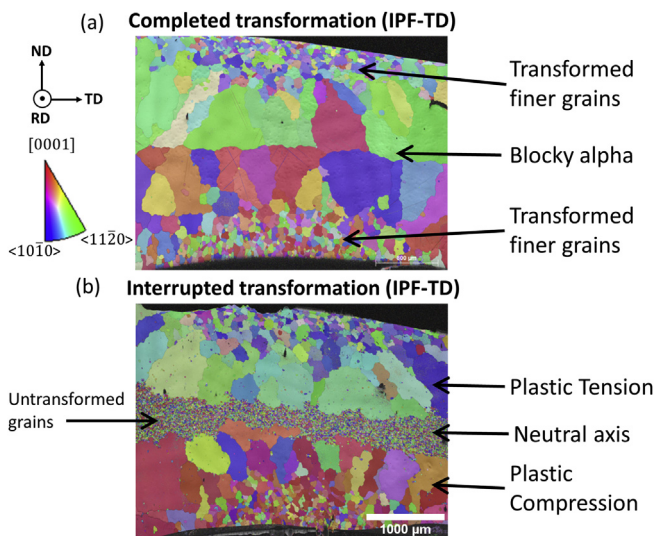


Fig. 5. Growth direction of blocky alpha. (a) EBSD maps (IPF-TD colouring) showing grain structures in annealed three-point bend samples where: (a) the blocky alpha transformation has fully completed, and (b) where the transformation has been interrupted. The growth direction of the blocky alpha grains is towards the neutral axis. The higher strained regions contain transformed finer grains and lower strained regions near the neutral axis contain blocky alpha after transformation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(750°C). The direction of the blocky alpha transformation front is inwards towards the neutral axis and therefore the large blocky alpha grains are elongated in this direction. (Note that the EBSD

data in Fig. 5 has been collected at the standard tilt angle of 70° and a very low magnification, with a horizontal field width of 4 mm. This introduces severe image distortions so that the left part of the map appears wider than the right. [Supplementary material B](#) shows optical micrographs of three bend samples which reflect the true geometry of the sample.)

4.2.2. Origin of blocky alpha texture in three point bending

An as-bent sample was characterised using EBSD to identify microstructural features with high stored energy which could provide driving force for blocky alpha nucleation. Slip and twinning are the main deformation modes in zirconium alloys. Twinning significantly reorients the crystal, whereas slip does not for the strain levels ($\pm 5\%$) explored here.

The texture variation along the as-bent beam section is low as the applied strains are low, though at the edges of the beam there are secondary peaks in the pole figure due to twinning. EBSD maps and pole figures for different regions along the beam bend section are included in [supplementary material E](#).

Twinning frequency was measured from EBSD maps in the as-bent sample. Fig. 6 shows the size and position of EBSD maps taken from a bent sample with a step size of $1\ \mu\text{m}$. Twin boundaries were identified using in-house developed post-processing software and twin interiors were flood-filled to identify twin area fraction as a function of ND distance along the sample (Fig. 4(a) shows the geometry of the three point bend test).

Only $\{10\bar{1}2\} \langle 10\bar{1}1 \rangle$ (T1) twins were observed, and the variation of twin fraction with position along the bend sample is plotted in Fig. 6. The step size used was $1\ \mu\text{m}$ so only larger twins could be identified; twin fractions therefore show indicative distributions.

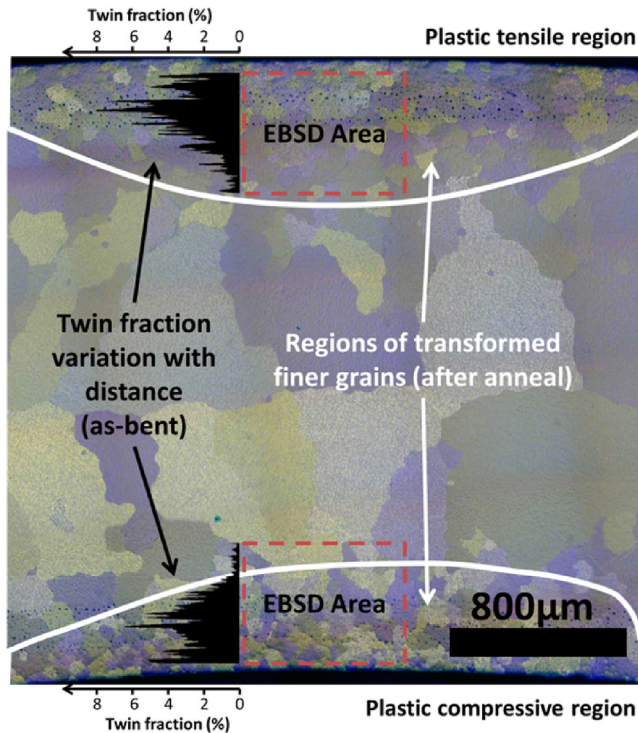


Fig. 6. Spatial distribution of twinning in the as-bent sample. Twin fraction is measured by EBSD in the areas indicated by the red box outlines in the as-bent sample, plotted as a function of position within the central region of the bend sample, and overlaid onto an optical micrograph of the annealed bend sample with the regions of transformed finer grains outlined in white. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The regions of high twin fraction loosely correlate with the transformed finer grained region in the annealed sample, outlined in Fig. 6 and labelled in Fig. 5.

The twin fractions broadly decrease with distance from the edges, although twin fractions also decrease in the nearest 100–200 μm to the sample edges, probably because the strain is localised to a small region around the ‘hinge’ of the three point bend sample.

Higher spatial resolution (0.3 μm step size) EBSD maps were taken in highly strained regions of the bend sample to identify twin variants present in the as-bent microstructure, shown in Fig. 7(d) (plastic tensile region) and Fig. 7(e) (plastic compressive region). The IPF colouring is shown with respect to TD (the primary loading axis).

In addition to the maps shown, as-bent EBSD maps were taken from positions corresponding to the boundary between the transformed finer grains and blocky alpha regions. The twin types and variants activated in those regions are identical to the maps shown in Fig. 7, but the twin fraction is lower. EBSD maps from higher strained regions were used to ensure observation of statistically representative numbers of twins.

Although all twins are the same type, different variants are activated in plastic tensile and compressive regions. This is because T1 twinning shear accommodates only extension strain along the $\langle c \rangle$ -axis of the HCP unit cell, and the sense of loading is reversed above and below the neutral axis of the bend sample. Typical parent and twin orientations for the plastic tensile and compressive region are shown in the high magnification inserts in Fig. 7(a) and (b) respectively.

In Fig. 7(a), this region of the sample is loaded in primarily in tension along TD. Grains which twin have the [0001] direction

pointing along TD (red in IPF map). This orientation is poorly oriented for $\langle a \rangle$ prismatic slip, so twins substitute slip by accommodating strain parallel to the loading axis. In Fig. 7(b), this region of the sample is loaded in primarily in compression along TD. Grains which twin tend to have the [0001] direction nearly perpendicular TD (i.e. parent grains are near green or blue in IPF map). Twinning shear extends in directions perpendicular to the loading axis to accommodate Poisson contraction and intergranular compatibility strains.

Twins have a different texture to the initial untwinned microstructure. In T1 twinning there is an 85° degree rotation between the twin and parent basal directions [33]. Different orientations are favourable for twinning under each loading condition, so the individual parent grains also have a specific, and likely different, texture to the bulk material.

Fig. 7(c) shows the orientations of the grains after annealing. In the plastic compressive region, the texture is bimodal, consisting of ‘red grains’ and ‘blue grains’ in the IPF-TD map (see also supplementary material A). The $\langle c \rangle$ -axes of the red grains point along TD and the $\langle c \rangle$ -axes of the blue grains point along ND (see supplementary material C). The blocky alpha orientations in the plastic compressive region are largely inherited from the parent and twin grains, with the orientation of red grains corresponding to parent grains, and blue grains corresponding to the subset of twins where $\langle 10\bar{1}0 \rangle // \text{TD}$ (blue in IPF map). In the plastic tensile region, blocky alpha orientations are inherited from as-bent texture, but sharpened such that $\langle 11\bar{2}0 \rangle // \text{TD}$ (green in IPF map). One blocky alpha grain is most likely nucleated from a T1 twin (labelled ‘Twin’) and another grain from a T1 parent (labelled ‘Parent’), as their orientations correspond to these grains from the as-bent material. This can be seen from the summary of the as-bent and blocky alpha texture components in Table 1, where the ‘Twin’ grain and ‘Parent’ grain orientations match well with the T1 twins and T1 parents in the as-bent sample respectively.

5. Discussion

5.1. Driving force for blocky alpha formation

Stored strain energy provides the driving force for blocky alpha nucleation, demonstrated by the inverse relationship of annealed grain size with strain (Fig. 3(a)) due to increasing density of competing nucleation sites. The source of strain energy can either be anisotropic thermal expansion strain or applied during deformation. We argue that grains with low stored energy which have neighbours with high stored energy nucleate blocky alpha via SIBM, and progressively consume neighbouring grains to form a blocky alpha structure. The strain dependence of blocky alpha nucleation corresponds to a recrystallisation mechanism. Abnormal grain growth is typically dependent on annealing temperature [34], grain size distribution range, and particle pinning pressure at grain boundaries, but does not usually show this strong inverse dependence on prior strain [14].

In SIBM, orientations of nuclei are inherited from deformed grains so the annealed texture is expected to resemble the deformed texture [14]. The blocky alpha texture formed on annealing 2 % uniaxially compressed samples is inherited from the as-received plate texture (see supplementary material A), and therefore consistent with SIBM (though does not rule out a classical nucleation mechanism). SIBM characteristically has a lower activation energy than classical nucleation processes [14] and has been shown to dominate nucleation in primary recrystallisation of moderately (<20 %) deformed Zr [20]. It is reasonable to expect that

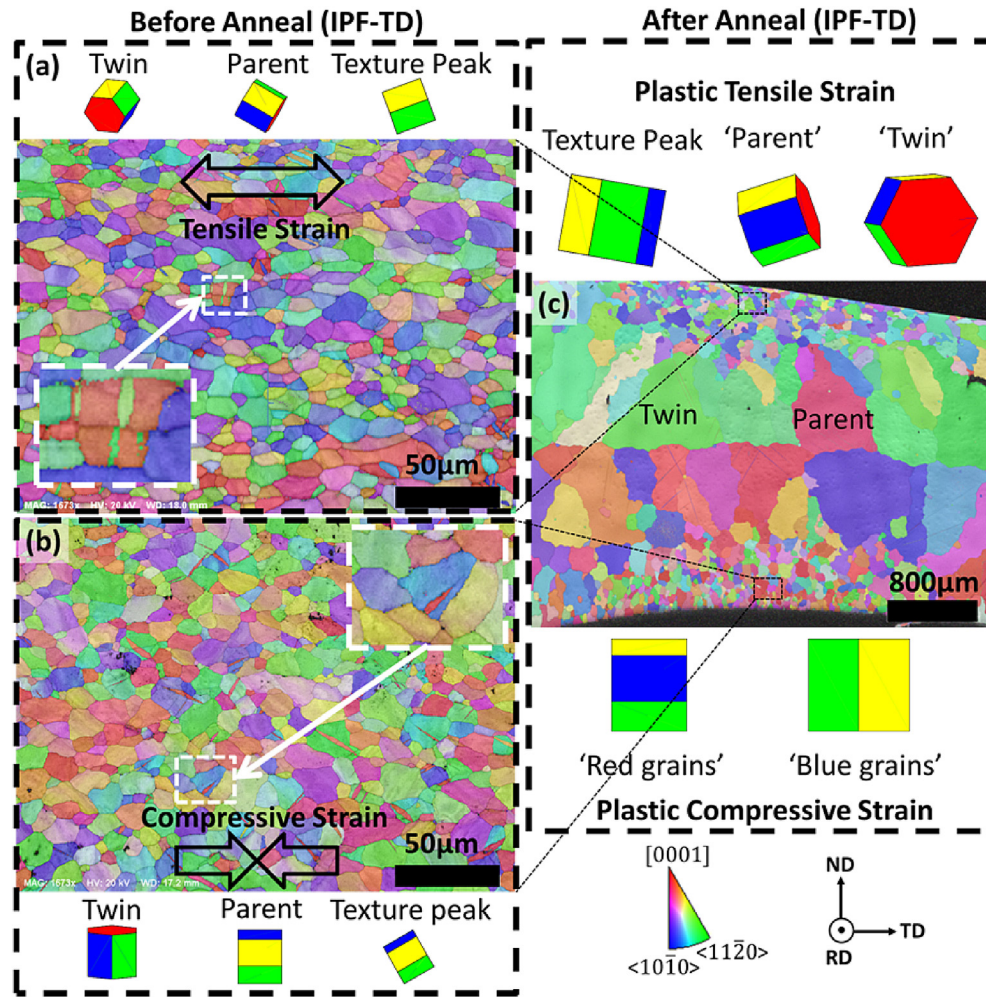


Fig. 7. Twin types and variants activated in as-bent sample, compared to textures in different regions of the annealed sample. (a) High magnification EBSD map (IPF-TD colouring) of plastic tensile region, showing twin types and representative orientations for a twin, parent grain, and the texture peak orientation of the field of view. Insert shows a typical twinned grain. (b) High magnification EBSD map (IPF-TD colouring) of plastic compressive region, showing twin types and representative orientations for a twin, parent grain, and the texture peak orientation of the field of view. Insert shows a typical twinned grain. (c) EBSD map (IPF-TD colouring) of central bend region in the annealed sample, with blocky alpha grains in low strain regions and recrystallised grains in higher strain regions, showing the texture switch above and below the neutral axis. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 1

Texture components of the as-bent and blocky alpha samples in the bend section.

		Plastic tensile region		
		IPF-TD	IPF-ND	IPF-RD
As-bent	Texture peak	fibre	[0001]	$\langle 11\bar{2}0 \rangle$ or $\langle 10\bar{1}0 \rangle$
	T1 twins	$\langle 11\bar{2}0 \rangle$ or $\langle 10\bar{1}0 \rangle$	$\langle 10\bar{1}0 \rangle$ or $\langle 11\bar{2}0 \rangle$	[0001]
	T1 parents	[0001]	$\langle 10\bar{1}0 \rangle$ or $\langle 11\bar{2}0 \rangle$	$\langle 11\bar{2}0 \rangle$ or $\langle 10\bar{1}0 \rangle$
Blocky alpha	Texture peak	$\langle 11\bar{2}0 \rangle$	[0001]	$\langle 10\bar{1}0 \rangle$
	'Twin' grain	$\langle 11\bar{2}0 \rangle$	$\langle 10\bar{1}0 \rangle$	[0001]
	'Parent' grain	[0001]	$\langle 11\bar{2}0 \rangle$	$\langle 10\bar{1}0 \rangle$

if nucleation events are via SIBM even in <20 % deformed Zr, nucleating a blocky alpha grain from thermal strains only via classical subgrain growth is unlikely. Also consistent with a SIBM mechanism is the incubation time of around 50 h seen in the 0.3 % deformed samples in Fig. 2(b), which decreases to <20 h with 2 % strain. Incubation periods during SIBM are associated with stabilisation of the bulging grain boundary [15].

Blocky alpha formation occurs in the absence of macroscopic deformation, as shown by the three data points marked by green crosses in Fig. 2. These samples were not deformed prior to annealing (and two of the three samples had been pre-annealed to relieve machining strains) but still form blocky alpha similar to that of material deformed to 0.3 % strain. Nucleation could be from local intergranular strains from anisotropic thermal expansion. The

thermal expansion coefficients in zirconium are $5.5 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ along the unit cell $\langle a \rangle$ axis, and $10.8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ along $\langle c \rangle$ [7], leading to thermal strains of up to 0.4 % when heating to 800 °C in the case of neighbouring grains with perpendicular $\langle c \rangle$ axes. This occurs at T1 twinned grains where the $\langle c \rangle$ axes between twin and parent are 85° misoriented, or ‘rogue grain pairs’ with near perpendicular $\langle c \rangle$ axes (though the starting material is moderately textured so ‘rogue grain pairs’ are most likely sparsely distributed). In metallic systems there is a critical strain below which recrystallisation cannot occur [14,35]. For Zircaloy-4 annealed at 800 °C the critical strain less than 0.4 %.

When blocky alpha forms in the as-received samples, there is negligible long range strain field for the nucleated blocky alpha grain to continue to grow. The only possible driving force for blocky alpha growth in this case is the reduction of grain boundary energy, corresponding to an abnormal grain growth mechanism. To the authors’ knowledge, there are no literature reports of a separate driving force for nucleation and growth of grains during recrystallisation or abnormal grain growth, though this is what the results point towards.

A step change in grain size is seen between the transformed finer grained region and the blocky alpha region (Fig. 4). This is the threshold strain where recrystallisation nuclei stop readily forming. Below this strain, the final grain size is limited by the spacing of recrystallisation nuclei, and increasing strain refines the grain size. Above the threshold strain, the grain size is mostly independent of strain level.

5.2. Motion of the transformation front

The original grain boundary networks appear to be inherited by the blocky alpha grains as the transforming grain consumes individual as-received grains. This results in transformed grain boundaries with a convoluted trace (Fig. 2(c)) and island grains (Fig. 3) which are not consumed during the transformation, both typical characteristics of blocky alpha. This process is outlined in the schematic in Fig. 8. Convoluted grain boundary traces and island grains are typical features of abnormal grain growth. This

contrasts with normal grain growth of single-phase materials, where boundaries are straight and pinned at triple junctions to minimise surface energy [29].

GND density hotspots decorate grain boundaries and triple junctions in deformed samples (Fig. 3). The spacing of GND density hotspots in blocky alpha is similar, although the absolute GND density is much lower post-annealing (Fig. 3(d)), which suggests that GNDs decorating grain boundaries or triple junctions prior to annealing were retained after the transformation. The GND patterning seen here is significant, as dislocation densities of 10^{14} m^{-2} are observed compared to the noise floor of $<10^{13} \text{ m}^{-2}$ [36] for the EBSD acquisition settings used here.

5.3. Blocky alpha growth kinetics

Blocky alpha in Zircaloy-4 forms when samples are held at high temperatures for long times within the α phase field. This can occur both within as received samples and samples deformed to <3 % strain (Fig. 2(a)). The lower the annealing temperature, the longer the time required to form blocky alpha (see [supplementary material B](#)).

The inverse relationship of grain size with strain when the strain is >2 % can be attributed to the increasing density of competing SIBM nuclei in more highly strained material. Following this argument, the recrystallised grain size should be larger in as-received and 0.3 % strained samples than 2 % strained samples, but Fig. 2(a) shows that the grain size peaks at 2 % strain. Fig. 2(b) shows that the incubation time for blocky alpha growth is around 48 h for 0.3 % strain and decreases to less than 20 h for 2 % strain, consistent with literature [21] observations. The reduced incubation time would allow more time for blocky alpha grains in 2 % strained samples to coarsen after the blocky alpha transformation, resulting in larger grains than the 0.3 % strained samples, which have less time to coarsen.

5.4. Nucleation of blocky alpha

There is a significant texture switch between blocky alpha in the plastic tensile and plastic compressive regions of the annealed three point bend specimen, shown in the EBSD micrographs in Fig. 5. As blocky alpha grains are proposed to nucleate via SIBM, the texture switch may be caused by differences in the deformation modes activated, so that different subsets of grains are more likely to nucleate blocky alpha.

The main deformation modes in zirconium are slip and twinning. Twinning is tension/compression asymmetric and significantly reorients the crystal lattice. Slip is largely insensitive to the sense of the strain as dislocations can move in either direction along a slip plane, and for small strains, slip does not significantly reorient the crystal lattice (as compared to twinning). Although only the T1 twin type is observed in the entire as-bent sample, twinning activated in different subsets of grain orientations in the plastic tensile and plastic compressive regions of the bend specimen, leading to twin variants with significantly different orientations above and below the neutral axis.

5.5. Role of twinning

When a twin grows, regions of high residual stress are found at the twin tips and ahead of the twin boundary in the parent grain [37], and high GND densities are found ahead of the twin tips in the neighbour grains in Zircaloy-2 and titanium [38,39]. Local stored energy which could lead to blocky alpha nucleation come from either residual stress or stored dislocations. It is energetically favourable for grain boundaries to migrate, via SIBM, from regions

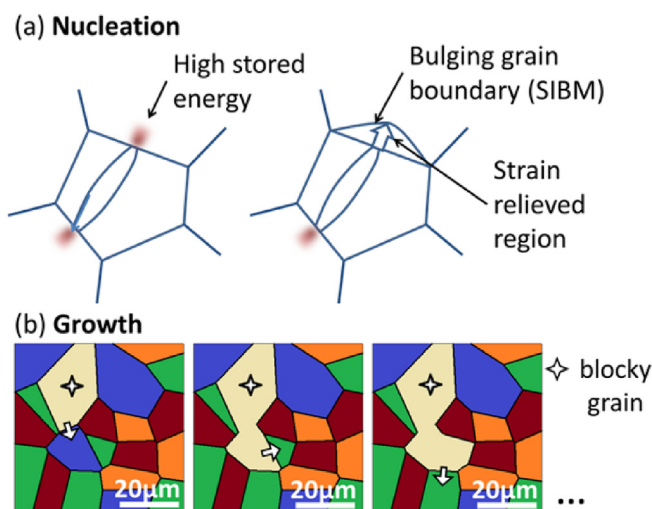


Fig. 8. Mechanism for blocky alpha nucleation and growth. (a) A grain boundary bulges via SIBM into local regions of high strain energy such as the region ahead of a twin tip. The reduction of strain energy provides driving force for blocky alpha nucleation. (b) When blocky alpha grain has nucleated, it grows into other grains by a whole grain consumption mechanism. The boundary trace is initially preserved. The driving force for blocky alpha growth is the reduction of grain boundary area.

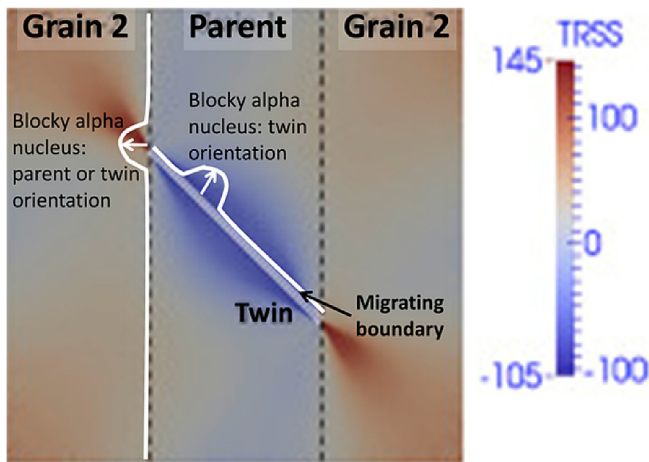


Fig. 9. Blocky alpha nucleation sites from a twinned grain via SIBM. The colour map (adapted from Ref. [37] with permission from Elsevier) represents twin resolved shear stress showing residual stress concentration ahead of the twin tips in neighbour Grain 2 and a backstress ahead of the twin boundary in the parent grain. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of low stored energy into regions of high stored energy. There are several potential nucleation sites present in the twin-parent combination that could contribute to nucleation of blocky alpha.

Fig. 9 shows two possible blocky alpha nucleation sites near a twinned grain growing via SIBM. The first blocky alpha nucleus is at a stress and GND density concentration near the twin tip. Here, the bulging grain boundary can inherit either the parent or the twin orientation. The second blocky alpha nucleus is along the twin boundary growing into the region of high elastic stored energy as a result of backstress on the parent grain. In this case, only the twin orientation is inherited.

5.6. Orientations of blocky alpha grains

Blocky alpha textures in uniaxially compressed material are inherited from the parent material independent of texture component strained (see [supplementary material A](#)). Although RD compressed material is in an orientation favourable for T1 twinning, at 2 % strain there are likely very few T1 twins in the RD sample and none in the ND sample [40]. Since the texture is broadly inherited from the parent plate, it can be concluded that arbitrary grains in the sample nucleate, and the heat treated texture is inherited directly from the parent material with no orientation selection.

In the plastic compressive region of the three point bend samples, twin and parent orientations dominate the final texture leading to a bimodal texture in the blocky alpha grains. Furthermore, only a subset of the parent orientations in the as-deformed microstructure (those with $\langle 10\bar{1}0 \rangle // \text{TD}$) grow into blocky alpha. Fig. 7(b) shows that the range of parent grain orientations have both $\langle 11\bar{2}0 \rangle$ (green in IPF map) or $\langle 10\bar{1}0 \rangle$ (blue in IPF map) pointing along TD, but Fig. 7(c) shows that only the $\langle 10\bar{1}0 \rangle // \text{TD}$ (blue) grains have grown into blocky alpha grains in the plastic compressive region.

In the plastic tensile region, neither twins nor parent grains selectively nucleate blocky alpha. Instead, the as-deformed orientations dominate the final texture, with the exception of two ‘rogue’ grains with T1 twin and T1 parent orientations respectively.

Analogous to the plastic compressive case, only a subset of orientations (those with $\langle 11\bar{2}0 \rangle // \text{TD}$) within the as-deformed grains grow into blocky alpha.

It is unclear why twinned grains in the plastic tensile regions do not selectively nucleate blocky alpha whereas in the plastic compressive regions they dominate the blocky alpha texture. Fig. 6 shows that the twin fraction is slightly larger in the plastic tensile region and their distributions are qualitatively similar.

6. Conclusions

Very large blocky alpha grains in Zircaloy-4 form via nucleation site limited primary recrystallisation as a result of annealing after low (<3 %) strains. These strains can be induced by either mechanical deformation or grain compatibility strains from anisotropic thermal expansion. There is an inverse relationship between prior deformation and final grain size due to the increasing presence of competing nucleation sites after deformation.

Recrystallisation is likely nucleated via SIBM, with dislocations debris left behind at the original grain boundaries in the annealed microstructure. The energy for SIBM at nucleation sites can arise from small (<3 %) amounts of applied strain before annealing, or anisotropic thermal expansion causing up to 0.4 % intergranular strain at 800°C. Below 3 % strain, the recrystallisation process is limited by the spacing of nuclei. Above 3 % strain, spacing of nuclei is no longer the limiting step in recrystallisation, and this transition is marked by a step change in the grain size of three point bend samples. As a result, grains at the edge of the transition strain grow inward towards the neutral axis. The magnitude of the strain is symmetric in tension and compression, so blocky alpha grains meet in the middle of the specimen and do not cross the neutral axis.

The nuclei selection mechanism which gives rise to the final texture is strongly dependent on the sense of strain in three point bending. Twinned grains dominate blocky alpha texture in the plastic compressive region of annealed three point bend specimens, whereas the blocky alpha texture largely inherits the as-deformed texture in the plastic tensile region.

This study enables grain size in Zircaloy-4 to be controlled during processing. To avoid blocky alpha in Zircaloy-4 components such as fuel cladding tubes, long duration heat treatments at temperatures approaching the β transus should be avoided after deformation to low strains. The range of achievable grain sizes also creates opportunities for near-millimetre scale mechanical testing of single crystal specimens, though care must be taken to account for island grains potentially present in large-grained material.

Data used within this paper can be retrieved from <https://doi.org/10.5281/zenodo.375797>.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.actamat.2017.03.002>.

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