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EBSD CHARACTERISATION OF HETEROGENEOUS MICROSTRUCTURES IN ZIRCONIUM ALLOYS

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Declaration of Originality

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Abstract

This thesis explores heterogeneous deformation and grain growth behaviour in zirconium alloys using electron backscatter diffraction techniques. Zirconium alloys are widely used for nuclear power applications and controlling microstructure during manufacture of reactor parts is critical for safe operation of the nuclear reactor.

Mechanisms for the formation of abnormally large 'blocky alpha' grains in Zircaloy-4, which forms when annealing lightly deformed Zircaloy-4 within the alpha phase, have been explored using uniaxial compression and three point bending. The presence of blocky alpha is a known industrial problem, and adversely affects reactor safety, though there are limited studies addressing this problem. It was found that blocky alpha nucleates via strain induced grain boundary migration and grows via abnormal grain growth. In the presence of a strain gradient, blocky alpha grains nucleate in highly strained regions and grow towards lower strained regions. The final orientations of the blocky alpha grains depend on the pre-annealing strain state.

High resolution electron backscatter diffraction (HR-EBSD) has been used to characterise microstructures before and after annealing to produce blocky alpha. To validate observations of increased dislocation density near grain boundaries, the effect of pattern overlap near grain boundaries on accuracy of HR-EBSD measurements is quantified. It was found that HR-EBSD measurements do not produce significant artefacts in this case. A simple calibration model and experiment is described to enable the extent of pattern overlap to be measured in other set-ups.

Twinning behaviour in commercially pure zirconium was studied as a function of texture and strain rate. Twin types preferentially activated under high strain rate (10^3s^{-1}) and quasi-static strain rate (10^{-3}s^{-1}) were characterised using electron backscatter diffraction (EBSD) post-processing software. This software was written in-house and explanations of the algorithms used to identify twin boundaries and map intragranular misorientations have been included in this thesis.

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Glossary

CTF	Channel Text File
DIC	Digital Image Correlation
EBSD	Electron Backscatter Diffraction
FWHM	Full Width at Half Maximum
GND	Geometrically Necessary Dislocation
GOS	Grain Orientation Spread
GROD	Grain Reference Orientation Deviation
HCP	Hexagonal Close-Packed
HR-EBSD	High (Angular) Resolution Electron Backscatter Diffraction
IPF	Inverse Pole Figure (colour map)
KAM	Kernel Average Misorientation
MAE	Mean Angular Error
MATLAB	MATrix LABoratory
NaN	Not a Number
ND	(Sheet) Normal Direction
RD	(Sheet) Rolling Direction
ROI	Region of Interest
SEM	Scanning Electron Microscope
SIBM	Strain-Induced (Grain) Boundary Migration
SPP	Secondary Phase Particle
TD	(Sheet) Transverse Direction
TEM	Transmission Electron Microscope
XCF	Cross-Correlation Function

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1. Introduction

Zirconium and its alloys are used widely as structural materials in the nuclear industry. Zircaloy-4 in particular is used as fuel rod cladding in pressurised water reactors and fuel bundles in CANDU reactors. Zircaloy-4 nominally has a composition of Zr-1.5 wt%Sn-0.2 wt%Fe-0.1 wt%Cr [1].

These are load bearing structural parts operating at high temperatures and pressures in moderately corrosive environments. The Zircaloy-4 cladding tubes isolate the fuel pellets from the water in the primary circuit, so safety is critical and tubes need to be thick enough to maintain structural integrity, but over-conservatism can lead to other problems such as reduced neutron efficiency and higher levels of fuel enrichment required for the same output.

Thermal expansion of long tubes at 350°C operating temperatures is significant. Stringent dimensional tolerances combined with anisotropy between $\langle a \rangle$ and $\langle c \rangle$ directions in hexagonal α -zirconium require good control of texture and texture strength. Texture is also important for controlling other properties such as hydride formation [2].

A fine grain size is important for maintaining both high yield stress and toughness. Grain size distribution is also important as occasional large grains can lead to local stress concentrations in thin-walled tubes. If a grain grows to a very large size during processing, it could easily span the entire tube wall thickness. This compromises the structural integrity and increases the likelihood of tube failure in-service. Abnormally large grains known as blocky alpha are a known industrial problem [3]. Their formation is explored in Chapter 5.

Therefore, to optimise tube properties, we need to know the effect of microstructure on properties. Knowledge of the effect of hot and cold deformation on the material microstructure at various strain rates enables tuning of the microstructure (such as grain size distribution, texture, precipitate size and density) during tube forming, so that the tubes can maintain their structural integrity in-service.

Figure 1 shows the production process of Zircaloy-4 tubes. It involves hot extrusion of β -quenched ingot, then several annealing and tube-reducing (pilgering) passes with varying ratios of wall thickness reduction to diameter reduction, shown in Figure 1 as parameter q . The final pilgering step aims for majority wall thickness reduction (i.e. high values of q) to achieve the appropriate texture in the final product.

Twins in the starting tubes are unfavourable as geometrically necessary dislocation (GND) density hotspots build up ahead of the twin tip, which can act as failure nucleation sites [4]. Therefore tube processing routes which lead to the presence of twins in the final product should be avoided. This is particularly important in the second and final pilgering steps of Zircaloy-4 tube, as the final product after annealing is only partially recrystallised [5] so not all twins may be annihilated.

On the other hand, the same stress conditions which lead to crack propagation are also favourable for twin formation, which means there is competition between twin formation and crack propagation. Therefore, having a primary loading direction and texture combination favourable for twin formation could be good for blunting and deflecting cracks [6]. Since twinning reorients the crystal significantly, often into an orientation more favourable for slip, twinning also significantly increases the ductility of zirconium.

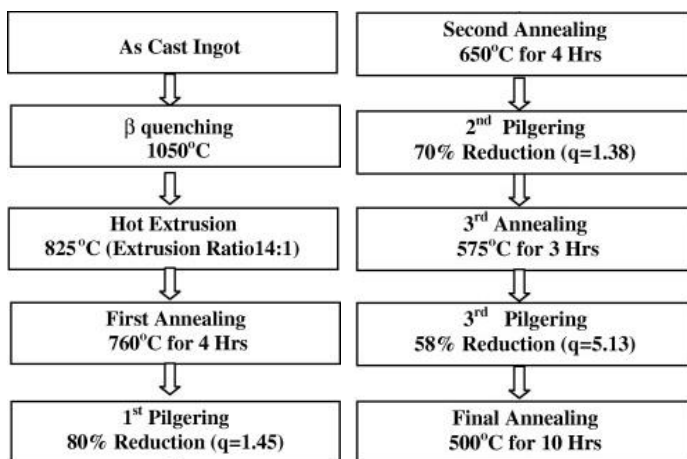


Figure 1: Steps in production of Zircaloy-4 fuel tubes (adapted from Reference [5] with permission from Elsevier). The parameter q is the ratio between wall thickness reduction and tube diameter reduction during pilgering.

Electron backscatter diffraction (EBSD) is a good technique to study large areas of microstructure quickly at high resolution (100+ frames per second for routine acquisition, with a maximum speed of 835 frames per second in 2012 [7], and a scan area of up to a few millimetres). Fundamentally, it obtains crystal orientation via electron diffraction in the scanning electron microscope (SEM), with a spatial resolution of $\sim 100\text{nm}$. The development of automatic indexing by Krieger-Lassen [8] enables large arrays of diffraction patterns to be analysed and indexed online via the greyscale Hough transform, and EBSD orientation maps to be obtained.

EBSD can be used to obtain information such as grain size distribution, texture, grain reference orientation deviation (GROD), grain orientation spread (GOS), and twin type and variant. These can be correlated with annealing temperature and time, strain path, and strain rate to derive fundamental materials properties. Therefore it is the main characterisation technique used throughout this thesis.

High angular resolution EBSD (HR-EBSD) employs cross-correlation of EBSD diffraction patterns to track sub-pixel shifts in crystallographic zone axes. In this way, residual surface strains and rotations can be mapped, and a lower-bound dislocation density, or GND density, can be estimated. HR-EBSD can be performed on bulk samples, and allows statistically significant numbers of grains to be studied, compared to transmission electron microscopy (TEM) techniques.

In many GND density maps obtained by HR-EBSD, GND density hotspots decorate grain boundaries, even in annealed, fully recrystallised grain structures. It has been unclear whether these GND density hotspots are real, or simply artefacts of increased measurement error near grain boundaries. Strain resolution has been well-characterised within grain interiors, and the effect of pattern overlap at grain boundaries on EBSD resolution has been explored by Wright et al. [9] for conventional, Hough-based EBSD. However, the effect of pattern overlap on residual strain and intragranular rotation measurement – from which GND density is calculated – has not been quantified in the literature, and will therefore be explored in Chapter 3 of this thesis.

Chapter 4 uses the quaternion representation of orientation to calculate intergranular and intragranular misorientations. From neighbourhood misorientation data, parameters such as grain boundary misorientation distributions, twin boundary types, grain average misorientation, and grain orientation spread can be calculated. It is not new maths, but has been written to overcome limitations of the current commercially available Bruker software.

Chapter 5 explores the formation behaviour and mechanisms of 'blocky alpha' grains in Zircaloy-4. Blocky alpha grains are very large ($>300\mu\text{m}$) and grow via an abnormal grain growth mechanism within a small-grained matrix (typically $<8\mu\text{m}$) in pilgered tubes. They have been recorded in literature to form either during alpha-phase annealing after small plastic deformations typical of straightening operations [10], or during alpha-phase annealing after beta-quenching [3]. The formation of blocky alpha has been linked to the dissolution of second phase particles in Zircaloy-4 [11], [12], though experimental confirmation of this has been limited.

Chapter 5 on grain growth uses optical microscopy and EBSD to characterise the dependence of blocky alpha structures on prior strain and annealing conditions. Both uniaxial compression and three point bending specimens have been studied – the former to characterise growth kinetics and equilibrium grain sizes, the latter to study blocky alpha nucleation and growth in the presence of a strain gradient, and also to efficiently test many strain states at once. The GND density measurements in Chapter 5 show dislocation debris being left behind as blocky alpha grain sweeps through the small-grained material. The validity of the GND hotspot measurements near grain boundaries in this section is confirmed by the results in Chapter 3, which allow confident interpretation of HR-EBSD measurements near grain boundaries.

In Chapter 6, the effects of strain rate and texture on deformation in commercially pure zirconium are studied using EBSD. The mathematical tools developed in Chapter 4 are used to identify the frequencies of different twin types activated under both quasi-static and shock loading conditions. GROD maps showing intragranular misorientation were qualitatively analysed to find the relative

Introduction

levels of constrained polycrystal slip. This analysis provides fundamental understanding of the rate sensitivities of different slip and twinning modes which could activate in normal operation and accident conditions.

This thesis aims to improve understanding of fundamental mechanisms such as abnormal grain growth and deformation in zirconium. This knowledge can be applied to controlling the behaviour of zirconium alloys during processing and informing modifications to processing routes. This will aid in maintaining good reproducibility of manufacturing safety-critical nuclear reactor parts.

2. Literature Review

The three themes explored in this literature review are: deformation behaviour in zirconium alloys, grain growth and recrystallisation processes in zirconium alloys and other alloy systems, and the resolution limits of high angular resolution electron backscatter diffraction (HR-EBSD) as a function of microscope settings during data acquisition and processing parameters. These topics are relevant for understanding the evolution of microstructure in zirconium.

2.1 Deformation of zirconium alloys

Understanding deformation mechanisms in zirconium and its alloys is important as they are used as structural components in the nuclear industry such as fuel rod cladding in a variety of nuclear reactor models. The presence of high thermal, mechanical, and irradiation stresses during reactor operation [13], [14] require a fundamental understanding of the deformation mechanisms preferentially activated under different loading conditions, in order to optimise the structural integrity of fuel cladding tubes in operation.

2.1.1 Elastic properties of zirconium

Zirconium exhibits anisotropic elastic properties due to the non-ideal c/a ratio of its hexagonal unit cell and directionality in bonding. The c/a ratio of Zr is 1.593, lower than the value of 1.633 for a hard sphere model [15]. Fisher and Renken [16] used an ultrasonic wave velocity technique to measure the anisotropic elastic constants of single crystal pure zirconium in different orientations at 20°C, which are shown in Table 1.

Schmid and Boas [17], [18] applied hexagonal symmetry to the measured elastic constants to derive the theoretical angular variation of the macroscopic Young's modulus in single crystal zirconium, shown in Figure 2. Only the angular deviation of the loading axis from basal plane is plotted as Zr is elastically isotropic within the basal plane. The isotropy within the basal plane means that ultrasonic

techniques for orientation or texture measurement such as spatially resolved acoustic spectroscopy (SRAS) , which makes use of elastic constants to calculate the surface acoustic wave velocity model, can only measure $\langle c \rangle$ -axis orientation and is insensitive to orientations within the basal plane [19].

Elastic constant	Value (GPa)
C_{11}	143.4
C_{12}	72.8
C_{13}	65.3
C_{33}	164.8
C_{55}	32.0
$E_{[10\bar{1}0]}$	99.1
$E_{[0001]}$	125.3
E_{min} (52.5° from $[0001]$)	89.0

Table 1: Elastic constants and Young's moduli for single crystal pure zirconium in different directions at 20°C [16].

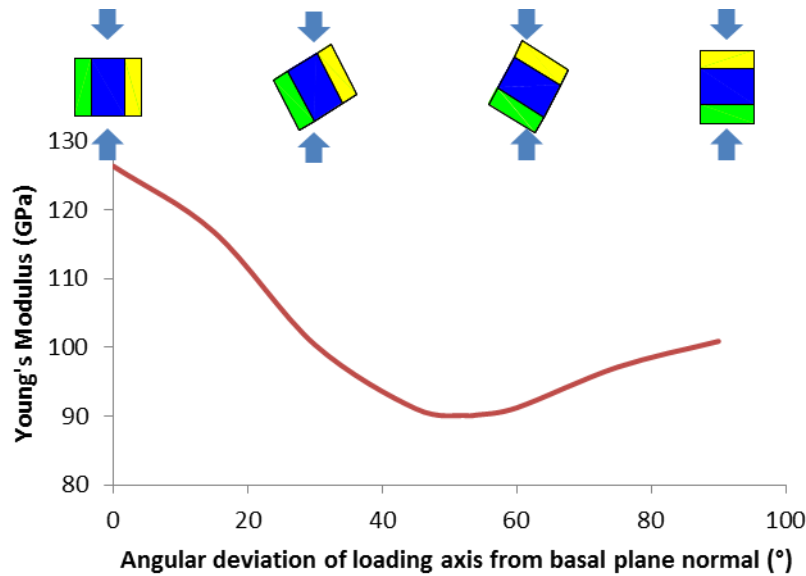


Figure 2: Anisotropy in Young's modulus of zirconium [16], [17].

Northwood et al. [18] measured the temperature variation of the dynamic Young's modulus of three zirconium alloys with different textures. The textures were measured by measuring differences in the ultrasonic velocities along the orthogonal sample axes [20]. The Young's moduli in dilute zirconium alloys decrease linearly with temperature between room temperature (95-100 GPa) and 800°C (45-50 GPa) [18], [21]. The exact values vary slightly with alloy content, but all follow the same trend. At 862°C, pure Zr phase transforms to body centred cubic β -Zr [22]. The transus temperature is dependent on alloy content [23] – for Zircaloy-4 the lower transus is around 820°C [24].

In elastic moduli measurements of polycrystals by Northwood et al. [18], there was good agreement ($\pm 5\%$ deviation) in the Young's modulus and shear modulus between directly measured values from bulk samples, and values calculated from combining single crystal elastic constants and texture measurements. This shows that the grains do not strongly interact in the elastic regime, and to a first approximation, a bulk polycrystal can be treated as an aggregate of single crystals.

A comparison of dilute zirconium alloys by Rosinger and Northwood [21] showed that the elastic properties are strongly dependent on texture and temperature, but only weakly dependent on alloy composition. They calculated the dynamic Young's and shear modulus from flexural resonance frequency measurements on unidirectionally rolled plate (with unit cell $\langle c \rangle$ axes pointing along the plate normal direction). The rolling directions have the lowest dynamic Young's moduli, the normal directions have the highest, and transverse directions lie in between. Niobium, tin and oxygen additions increase the elastic moduli slightly [21].

2.1.2 Plastic deformation in zirconium

Prismatic $\langle a \rangle$ slip is the dominant slip system in α -zirconium at temperatures between 77K (liquid nitrogen temperature) and 1075 K (near $\alpha \rightarrow \alpha + \beta$ transus temperature) [25], and has the lowest critical resolved shear stress to activate dislocation motion [26]. Figure 3 shows the main slip and twinning systems present in zirconium at liquid nitrogen and room temperatures [27]. The plastic behaviour of zirconium and its alloys is anisotropic because there are only two independent $\langle a \rangle$

prismatic slip systems available, fewer than the five independent slip systems required for arbitrary deformation. Also, $\langle a \rangle$ slip cannot accommodate deformation in the crystal $\langle c \rangle$ direction, therefore twinning on 1st and 2nd order pyramidal planes and $\langle c + a \rangle$ slip on 1st order pyramidal planes play significant roles in accommodating polycrystal deformation.

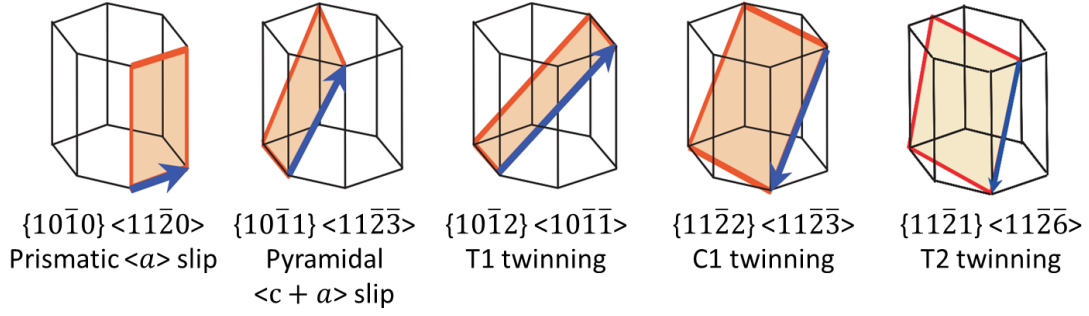


Figure 3: Dominant slip and twinning systems in zirconium at liquid nitrogen and room temperatures. The red planes show the slip planes and the blue arrows show the slip directions. Adapted from Reference [27] with permission from Taylor and Francis.

2.1.2.1 Slip

Zirconium has a ‘squat’ unit cell with a below-ideal $\langle c \rangle / \langle a \rangle$ ratio of 1.593 [15]. The shortest interatomic directions are the $\langle a \rangle$ type directions and the close-packed planes are the basal planes. $\langle a \rangle$ dislocations can theoretically glide on any plane containing the $\langle 11\bar{2}0 \rangle$ vector, as only the Burgers vector needs to be conserved during dislocation glide [28]. However, the primary slip system in Zr at room temperature is on $\{10\bar{1}0\}$ prismatic planes (with $\langle 11\bar{2}0 \rangle \langle a \rangle$ type burgers vector), whereas it is rarely seen in $[0001]$ basal planes.

Chalmers and Martius [29] argue that low energy slip systems tend to maximise the slip plane spacing, thus decreasing the Peierls barrier, whilst minimising the Burgers vector. At low $\langle c \rangle / \langle a \rangle$ ratios, the basal plane becomes less close packed, and the basal slip plane spacing decreases whilst Burgers vector $\langle a \rangle$ increases. This makes basal slip less favourable compared to prismatic slip, as prismatic slip plane spacing increases with decreasing $\langle c \rangle / \langle a \rangle$ ratio. This analysis still favours basal slip over prismatic slip as the easy slip system in Zr, albeit by a small margin.

Akhtar and Teghtsoonian [30] suggest that prismatic slip occurs more readily than basal slip in Zr because of the low stacking fault energy of prismatic dislocations. This promotes dissociation of $\langle a \rangle$ prismatic dislocations into lower energy partials which stabilises the $\langle a \rangle$ prismatic dislocation, and promotes $\langle a \rangle$ slip. The dislocation reaction is $\frac{a}{3}[11\bar{2}0] = \frac{a}{9}[11\bar{2}0] + \frac{2a}{9}[11\bar{2}0]$. This is energetically favourable as the line energy ($\propto b^2$) of the two partials combined is smaller than the perfect dislocation. The stacking fault energy of this dissociation is 56mJm^{-2} , leading to an equilibrium separation of 3.35nm .

Titanium has a similar electronic structure to zirconium and also favours prismatic slip. Directionality and covalent character of the d-orbital electrons has been shown in titanium to stabilise prismatic dislocation core structures over basal dislocation cores. The d-orbital electrons lower the stacking fault energy of the prismatic dislocation core so that it dissociates into lower-energy partial dislocations on either the same or neighbouring prismatic planes [28], [31], [32]. This argument is supported by the fact that beryllium, also with a low $\langle c \rangle / \langle a \rangle$ ratio of 1.568, exhibits predominantly $\langle a \rangle$ basal slip, and has no d-orbital electrons.

Micro-cantilever studies in commercially pure zirconium at room temperature by Gong et al. [26] show that the ratios between extrapolated bulk critical resolved shear stress (CRSS) values of prismatic $\langle a \rangle$ slip compared with basal $\langle a \rangle$ slip and pyramidal $\langle c + a \rangle$ slip are 1.33 and 3.5 respectively. Therefore it is expected that prismatic slip would be favoured over both basal and pyramidal $\langle c + a \rangle$ slip. However, the absolute CRSS values for prismatic $\langle a \rangle$ slip span a large range: between 6.37MPa in high purity large-grained Zr containing 185ppm oxygen and measured using slip trace analysis [33], and 160MPa in commercially pure Zr containing 1000ppm oxygen and measured using micro-cantilever bending [26].

Although the CRSS values for basal and prismatic slip are both relatively low compared to $\langle c + a \rangle$ pyramidal slip, basal slip has rarely been experimentally observed to occur in bulk zirconium at room temperature. Rapperport [33], and Sokurskii and Protsenko [34] do not observe basal slip in slip

trace analysis of deformed high purity Zr. Rappaport reported the only slip system active at room temperature to be the $\{10\bar{1}0\}\langle 11\bar{2}0\rangle$ prismatic $\langle a \rangle$ slip system when observing slip traces in large-grained Zr. However, Bailey [35] observed small amounts of basal slip in zirconium of similar purity in the TEM. Basal slip occurred to eliminate jogs from prismatic $\langle a \rangle$ screw dislocations, which lie in the basal plane. However, basal slip was not observed for lower purity zirconium, since increasing oxygen content impedes basal slip, which also leads to prismatic $\langle a \rangle$ dislocation motion also becoming more difficult [35]. Clouet et al. [36] report that only prismatic $\langle a \rangle$ slip is activated during in-situ TEM deformation between 95K and 300K, for all sample orientations. They did not observe any cross-slip onto pyramidal or basal planes. This is attributed to the high stability of the glissile prismatic dislocation core compared with pyramidal dislocation cores as calculated by *ab initio* atomistic modelling.

In contradiction to this, Dickson and Craig [37] observe room temperature basal slip in slip trace analysis of deformed Zr single crystals. For high oxygen concentrations (1200ppm) the resolved shear stress required to activate basal slip is an order of magnitude higher than for low oxygen concentrations (140ppm). Although the CRSS values for basal and prismatic slip increase with oxygen concentration, the CRSS ratios between basal and prismatic slip remain similar.

Oxygen and nitrogen are interstitial impurities which can pin dislocation motion either as single atoms or in clusters, and the presence of oxygen dramatically increases the room temperature yield strength of high purity Zr [35], [38]. This is in agreement with the review by Britton et al. [31], who observe an increase in the CRSS for $\langle a \rangle$ prismatic and $\langle a \rangle$ basal slip as 'oxygen equivalent' interstitial content (summing weighted contributions from oxygen, nitrogen and carbon) increases.

Only two independent $\langle a \rangle$ type prismatic slip systems [15] can be easily activated during deformation, as significant basal slip at room temperature is generally not observed [25], [33], [34] and the CRSS for $\langle c + a \rangle$ pyramidal slip is several times higher than $\langle a \rangle$ prismatic slip. However, since five independent slip systems are needed to maintain grain compatibility during arbitrary

deformation, pyramidal $\langle c + a \rangle$ slip systems and twinning modes must play important roles in contributing to the room temperature ductility of polycrystalline zirconium. Furthermore, prismatic slip does not allow deformation with a $\langle c \rangle$ component, such that the texture of rolled Zr plate cannot be explained by prismatic slip alone. $\langle c + a \rangle$ dislocations have been observed by McCabe et al. [27] during room temperature compression in textured high purity zirconium, where basal poles predominantly point along the compression axis, and also by Jones and Hutchinson [39] after compression of strongly textured Ti-6Al-4V along the basal direction. Deformation with a $\langle c \rangle$ component are needed in these cases to accommodate the macroscopic deformation axis.

2.1.2.2 Twinning

Deformation twinning is a deformation mechanism which produces a coordinated shear transformation in a crystalline material. In zirconium alloys it is an important deformation mode as it allows deformation parallel to the unit cell $\langle c \rangle$ axis, which prismatic $\langle a \rangle$ slip cannot. Twin types can be classed as either contraction (C1, C2) or extension (T1, T2) twins, which accommodate strain either to contract or extend the $\langle c \rangle$ axis of the hexagonal close-packed (HCP) unit cell.

Twinning is crystallographically defined by its twin plane $\mathbf{K}_1$, the mirror plane in the twin and parent material, and $\boldsymbol{\eta}_1$ which is the twinning shear direction. The predominant twin type in zirconium is $\mathbf{K}_1 = \{10\bar{1}2\}$ $\boldsymbol{\eta}_1 = \langle 10\bar{1}1 \rangle$ (T1) twinning. Deformation twins in Zr are generally lenticular in shape, lengthening in the $\boldsymbol{\eta}_1$ direction and thickening along the $\mathbf{K}_1$ plane.

More generally, twinning can be described as a 180° rotation about an axis ($\boldsymbol{\eta}_1$ or $\mathbf{K}_1$ normal direction), or a mirror reflection in a plane ($\mathbf{K}_1$ or $\boldsymbol{\eta}_1$ normal plane). For $\{10\bar{1}2\}\langle 10\bar{1}1 \rangle$ (T1) twinning, there is no distinction between the four transformations as they are equivalent [40].

Unlike slip, twinning is asymmetric in tension and compression because the twin nucleation and growth mechanisms involve twinning dislocations, which only glide in one direction enables thickening of the twin. This means that twins in Zr can grow to accommodate shear strain, but when the sense of strain is reversed, the twins do not generally detwin. However, the crystal lattice is

significantly reoriented in twins such that different slip systems can be activated. In some cases, reversal of the load direction can cause a secondary twin of the same type and variant to nucleate inside a primary twin. This then reorients the twin back into the parent orientation, so appearing as a de-twinning or re-twinning [41] phenomenon which has been seen in Zr-1wt%Nb [42], high purity polycrystalline Zr [43], and high purity Mg [44].

Magnesium alloys behave differently and can de-twin by reverse movement of twinning dislocations when the loading direction is reversed [45]–[47]. Victoria-Hernández et al. [47] also observed thermal detwinning during annealing of Mg alloy AZ31 sheet at 250°C, where the twin tips were observed to shrink and shorten the twin. As there was no mechanical loading on the sheet during annealing, the driving force was not mechanical stress, but most likely a phenomenon similar to strain-induced grain boundary migration, to relax the stored residual stress at the twin tips.

2.1.2.2.1 Twin types and variants in Zr

The four major twin types in zirconium are listed in Table 2:

Twin type	Twin plane, K_1	Shear direction, η_1	Shear plane, P	Lattice rotation angle, ξ
T1	$\{10\bar{1}2\}$	$\langle 10\bar{1}1 \rangle$	$\{1\bar{2}10\}$	85.22°
T2	$\{11\bar{2}1\}$	$\langle 11\bar{2}\bar{6} \rangle$	$\{10\bar{1}0\}$	34.84°
C1	$\{11\bar{2}2\}$	$\langle 11\bar{2}\bar{3} \rangle$	$\{10\bar{1}0\}$	64.22°
C2	$\{10\bar{1}1\}$	$\langle \bar{1}012 \rangle$	$\{1\bar{2}10\}$	57.05°

Table 2: Major twin types in zirconium [15].

The twin plane, shear direction, and shear plane form the basis vectors of an orthogonal set. The axis-angle misorientation relationship between the parent and twin is a rotation of angle ξ about the shear plane normal direction P .

Due to symmetry in the HCP crystal structure, there are six crystallographically equivalent twin variants for each twin type. Different twin variants of the same type in a grain cannot be

distinguished by their misorientation to the parent, but by their orientation, and in some cases (depending on the sectioning plane) the twin boundary trace.

The primary twin type formed in any sample depends on the texture, temperature, strain rate, grain size, and loading axis and direction. Twin types present at liquid nitrogen temperature are predominantly $\{11\bar{2}2\}<11\bar{2}\bar{3}>$ (C1 twinning) and $\{10\bar{1}2\}<10\bar{1}1>$ (T1 twinning). Secondary twins of another type may form inside the primary twins as the crystal is reoriented with respect to the loading axis [27][48].

Rapperport [33], and Sokurskii and Protsenko [34] report a $\{11\bar{2}3\}<\bar{1}\bar{1}22>$ twin system in addition to the twins in Table 2. Tenckhoff [15], and Linga Murty and Charit [49] report that the C2 compressive twin system $\{10\bar{1}1\}<\bar{1}012>$ is only active at high temperatures.

2.1.2.2.2 Twin nucleation and growth mechanisms

Nucleation of $\{10\bar{1}2\}$ (T1) twins in magnesium, also an HCP system, has been studied using density functional theory simulations by Wang et al. [50]. A $[10\bar{1}1]$ perfect dislocation dissociates into two partial dislocations, one of which can further dissociate into a stacking fault on the $(\bar{1}012)$ plane bounded by two dislocation dipoles, which form the embryonic twin nucleus. However, this partial dislocation is sessile in the twinning direction.

Twinning dislocations, which have a Burgers vector in the direction of the twinning shear direction, can then glide along the plane of the stacking fault $<10\bar{1}1>$ to thicken the twin in the $\mathbf{K}_1$ normal direction $<\bar{1}012>$. Note that a twinning dislocation cannot glide by itself along perfect crystal, but only on a plane aligned with the twin boundary or the stacking fault of the twin nucleus. The twinning dislocations can be nucleated heterogeneously either from a grain boundary, from interactions between slip dislocations and the twin boundary [50], or from dissociation of slip dislocations [51].

Capolungo et al. [51] studied the nucleation of twinning dislocations from slip dislocations, and found that dissociation of prismatic dislocations cannot produce T1 twinning dislocations but only T2 and C1 twinning dislocations. They propose that in pure Zr very small basal dislocation pile-ups can dissociate into basal slip dislocations which in turn dissociate into T1 twinning dislocations. However, basal slip has only been observed in very high purity zirconium, but not its lower purity alloys [35]. This suggests that basal slip dislocations are not primarily responsible for triggering T1 twinning. Other mechanisms, such as $\langle c + a \rangle$ or $\langle c \rangle$ type dislocation dissociations, not studied in [51], may still operate.

After the twinning dislocation has glided through, the twinned volume undergoes minor atomic shuffles in different directions to occupy the correct lattice positions. The shuffles accommodate for varying interplanar spacings of the non-basal shear plane. This does not affect the macroscopic amount of shear due to twinning as the shuffles are in many different directions [15]. In zirconium, atomic shuffles are required for all of the twin types except for $\{11\bar{2}1\}\langle 11\bar{2}\bar{6} \rangle$ (T2) twins, where the twinning mechanism involves only shear [52].

To elongate a twin in the η_1 direction, the partial dislocations which form the twin tips propagate with the twinning dislocations along the twinning direction, as they are dragged along with the twinning dislocations. Although the partial dislocations on their own are sessile in the twinning direction, they can move in the twinning direction with the twinning dislocations as a single unit [50].

Once a stable twin embryo has formed, the twins thicken by successive twinning dislocations gliding along the twin boundary in the twinning shear direction. The formation energy of the twin boundary decreases with increasing twin thickness, making further thickening of a thicker twin energetically favourable [50]. Each subsequent thickening event requires production of new twinning dislocations. These are typically nucleated at grain boundaries or from interactions of slip dislocations with a twin boundary [50].

Abdolvand and Daymond [53] modelled the growth of a twin embryo into a successful twin ('twin inception') using a crystal plasticity finite element model. Plastic shear relaxation from twin nucleation is modelled in this work as a pseudo-slip mode, with crystal reorientation, i.e. twin inception, occurring once this plastic relaxation reaches a critical value. They found that due to compatibility stresses arising near grain boundaries, inception sites tended to be near grain boundaries. They also found that twin inception often occurs in grains which have low resolved shear stress with respect to the global applied stress state, suggesting that stress heterogeneity and load sharing between soft and hard grains play a more significant role than the global applied stress state. A better predictor of twin inception sites is the local stress state at each point, as calculated from the crystal plasticity model.

2.1.2.3 Influence of loading conditions on deformation modes

Deformation modes active in zirconium vary with sample texture and loading conditions. Here, slip and twinning are reviewed as a function of texture, strain rate, temperature, and grain size.

2.1.2.3.1 Deformation as a function of texture

Two typical Zr textures are considered in this review: where the 1st or 2nd order prismatic planes ($\{10\bar{1}0\}$ and $\{11\bar{2}0\}$) predominantly orient parallel to the compressive loading axes, here referred to as a prismatic texture, and where the basal planes predominantly orient parallel to the compressive loading axes, referred to as a basal texture. These are shown as a schematic in Figure 4.

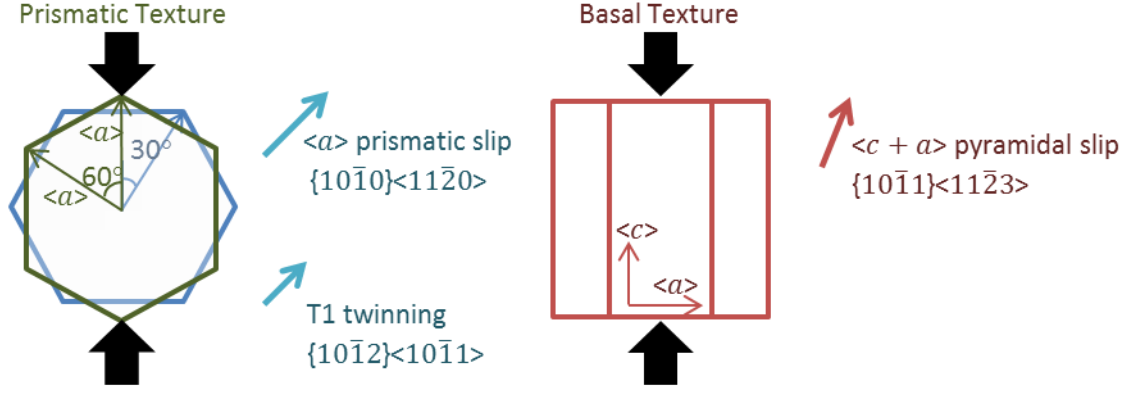


Figure 4: Cartoon schematic showing dominant unit cell orientations of two textures with respect to loading direction and the deformation systems active in each under uniaxial compression.

Kaschner and Gray [52] observed that prismatic textures yield at lower stresses than basal textures. In a TEM study of room temperature deformed zirconium, McCabe et al. [27] observed only $\langle a \rangle$ dislocations in samples with prismatic texture. In this work they assert that all $\langle a \rangle$ dislocations are prismatic, but this was not confirmed using $\mathbf{g} \cdot \mathbf{b}$ analysis or similar techniques. Both $\langle a \rangle$ (prismatic) and $\langle 11\bar{2}3 \rangle$ $\langle c + a \rangle$ ($\{10\bar{1}1\}$ pyramidal) slip were observed in samples with basal texture at room temperature, but only $\langle a \rangle$ (prismatic) dislocations were observed in the same sample at liquid nitrogen temperature.

Prismatic texture orientations have $\langle a \rangle$ directions around 30° or 60° from the loading axis (illustrated in Figure 4), which are favourable orientations for $\langle a \rangle$ prismatic slip. This is the ‘easy’ slip system with low critical resolved shear stress.

On the other hand, the basal texture orientation has prismatic planes perpendicular to the loading axis, which is unfavourable for $\langle a \rangle$ prismatic slip but favourable for $\langle c + a \rangle$ pyramidal slip. Since the critical resolved shear stress for $\langle c + a \rangle$ pyramidal slip is much higher than for $\langle a \rangle$ prismatic [26], $\langle c + a \rangle$ pyramidal dislocations do not glide as easily, and therefore McCabe et al. [27] observed a higher yield stress in the basal texture than the prismatic texture.

At quasi-static strain rates, McCabe et al. [27] only observed T1 twinning in samples with prismatic texture. They did not observe T1 twinning in samples with basal texture deformed to 25% strain.

Capolungo et al. [54] studied twinning as a function of grain orientation within a sample. They calculate a geometric Schmid factor using the macroscopic applied stress direction, and find the resolved shear stress on any grain without taking into account local intergranular interactions which may alter the actual stress state. They found that although the majority of twins occur in grains favourably oriented for twinning, around 30% of grains which were unfavourably oriented for twinning still contained twins. Likewise, the twins present were not always of the highest Schmid factor variant, with only 60% of twins twinning on the highest Schmid factor variant. This can be attributed to a strong dependence on the local stress conditions in grains or grain boundaries [53], which is difficult to measure experimentally.

2.1.2.3.2 Deformation as a function of strain rate

Kaschner and Gray [52] observe that yield stress increases with increasing strain rate in the range of 0.001/s and 3500/s, and the strain rate sensitivity in the yield stress is higher for prismatic texture than for basal texture. They conclude that the rate sensitivity of the flow stress is consistent with Peierls forces inhibiting dislocation motion in low-symmetry metals during slip-dominated deformation. This is valid in the early stages of room temperature deformation, which in Zr is usually slip-dominated [55].

Within the quasi-static loading regime ($0.001\text{--}0.1\text{s}^{-1}$), Song and Gray observe little strain rate sensitivity in the mechanical stress-strain response [55]. This is different to Kaschner and Gray [52], who observe a small positive strain rate dependence in the yield stress, but not the hardening response, in samples strained at rates of 0.001s^{-1} and 0.1s^{-1} . In both studies, texture and temperature effects are much greater than strain rate effects within the quasi-static regime.

Kaschner and Gray observe that deformation at high strain rates (3000s^{-1}) produces more twins than at quasi-static strain rates, but the twin types activated were not identified [52].

2.1.2.3.3 Deformation as a function of temperature

Song and Gray [55] observe that deformation in Zr is characterised by an initially parabolic stress-strain curve corresponding to slip-dominated work hardening. An inflection point marks the onset of twinning-dominated hardening, after which the stress-strain curve is linear. However, Kaschner and Gray [52] did not see an inflection point in stress-strain curves of similarly deformed Zr.

Song and Gray [55] observe that at 373K, deformation is dominated by slip up to 25% strain, and therefore does not show an inflection point.

At intermediate temperatures, the inflection point in the stress-strain curve marks the onset of twinning-dominated deformation; this inflection occurs at progressively lower strains as the temperature is decreased [55].

At 77K, twinning is dominant at all strain levels because there is insufficient thermal energy in the material to overcome the Peierls barrier to slip [55]. Kaschner and Gray [52] observe a sharp yield point with linear work hardening behaviour, whereas at room temperature the elastic-plastic transition is smooth and there is no defined yield point.

At 77K, the only slip system present is $\langle a \rangle$ prismatic slip, as observed in TEM studies by McCabe et al. [27], and much more of the deformation is carried by deformation twinning. T2 and C1 twin types are activated in addition to T1 twinning, which is the only twin system active at quasi-static room temperature deformation. At higher strains (25% strain) there is also considerable secondary twinning, which are twins growing within twins, as the primary twins thicken and grow.

Song and Gray [55] report that the patterning of twinned grains is different at room temperature from 77K. At room temperature, twins nucleate and grow unevenly in bands across the sample, whereas at 77K they occur uniformly in all grains. This means that at 77K, twinning is dependent only on the global applied stress state, but at room temperature, local intergranular compatibility stresses play a large role in deformation twin nucleation and growth.

A TEM study by Song and Gray [55] shows dislocation cell wall structures in samples deformed to 20% strain at 423K and room temperature, but not at 77K. A low dislocation density in the 77K deformed sample means that dislocations can glide long distances without being blocked or tangling, which inhibits dislocation cell wall formation. The sharp yield point and linear strain-hardening rate in the mechanical behaviour for this sample confirms that most of the deformation at 77K is carried by twinning.

2.1.2.3.4 *Deformation as a function of grain size*

Song and Gray [55] observe large grained material to yield at lower stresses than small-grained material. This is consistent with Hall-Petch strengthening in polycrystals. Hall-Petch coefficients for zirconium at room temperature were measured by Keeler (1955) and reported by Armstrong [56] in Equation 1.

$$\sigma_D = 29.42 + \frac{7.85}{\sqrt{D}}$$

Equation 1: Hall-Petch equation for Zr [56]

σ_D is the 0.2% proof stress in MPa for a given grain size of zirconium, and D is the average grain diameter in mm, leading to a predicted yield strength of 85MPa if the grain size is 0.02mm. The texture and alloy content of the samples are not reported, though this can also affect the yield strength. Yield strengths from Equation 1 are somewhat lower than experimentally measured yield strengths: for comparison, ASTM standards require that the 0.2% proof stress of reactor grade pure Zr with a grain size less than 0.03mm at room temperature should be 140MPa when tested along the softest texture component, and higher along other texture components [57]. Most alloying additions or impurities strengthen the material and raise the yield point further [1].

Kaschner and Gray [52] observed no grain size dependence on twinning at either room temperature or 77K. This is in partial agreement with Capolungo et al. [54] in a statistical study of T1 twins in Zr. They found that the likelihood of a grain containing twins was not grain size dependent, but larger twinned grains contained more twins than smaller twinned grains. This is possibly due to a larger

grain boundary area, where heterogeneous twin nucleation is likely to occur [53]. The true twin thickness was independent of grain size, which means that twin growth is not affected by grain size. In contrast, twinning frequency in titanium was found by Ghaderi and Barnett to be grain size dependent [58], where larger grains were more likely to contain twins than smaller grains, and larger grains also contained greater numbers of twins than smaller grains.

However, Song and Gray [55] observe that larger grained material (75 μm compared to 25 μm) deformed at 77K promotes slip-dominated deformation at low strains, before transitioning to twinning-dominated deformation. In contrast, smaller grained material deformed at 77K shows twinning-dominated deformation at all strain levels. The grain size dependent behaviour is explained as being due to longer dislocation pileups being possible in larger-grained material, which increases the pile-up stress and allows slip transfer across grain boundaries. If the grain size is large enough, slip transfer occurs before the twinning critical resolved shear stress is reached and the deformation transitions to being twinning-dominated. The critical resolved shear stress for twinning is independent of grain size.

Note that there is a difference between the two definitions of grain size dependence. Kaschner and Gray [52] and Capolungo et al. [54] have studied the spread of grain size within a sample and concluded that larger grains do not twin preferentially, whereas Song and Gray [55] have studied materials with different average grain sizes and concluded that twinning is suppressed in large-grained material at low temperatures and strain levels.

2.2 Formation of abnormally large grains in Zircaloy-4

Zircaloy-4 tubes are used as fuel rod cladding in pressurised water reactors. A standard tube has 0.57mm thick walls and is 9.5mm tube diameter [59]. Tube walls are thin to minimise neutron absorption and maximise fuel efficiency, but thick enough 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 large grains, the so called 'blocky alpha' structure (grains $>300\mu\text{m}$ with a 'blocky' microstructure) [3], need to be understood.

Since the tube walls are thin, blocky alpha grains can potentially grow to span the entire width of a fuel tube wall. These large grains can potentially cause issues, since zirconium is rather anisotropic due to its HCP crystal structure [15]. The spike in texture arising from a single large grain can affect anisotropic material properties such as yield [56] and thermal expansion [60]. An absence of grain boundaries can impact properties such as strength (as small grains result in a stronger product [56]) and also change ageing regimes such as irradiation growth and creep [61]. 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 [2] or reorient along the stress direction [62], which is often a compressive radial stress for fuel cladding tubes [13].

2.2.1 Some theory on recrystallisation and grain growth

Recrystallisation is the formation of a new grain structure in a deformed material by migration of high angle grain boundaries ($>10\text{-}15^\circ$) to reduce the stored energy of a system. In plastically deformed materials the energy from plastic work is eliminated from the nucleation and growth of new grains by **primary recrystallisation** [63].

Grain growth usually occurs on further annealing after recrystallisation. It is the migration of high angle grain boundaries where the 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. Continuous transformations are also known as Gibbs II transformations [63].

Abnormal grain growth occurs only if normal grain growth is suppressed, e.g. by pinning from second phase particles (SPPs). A minority of grains grow rapidly and consume neighbouring grains. This usually 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 [64]. The driving force for both normal and abnormal grain growth is the reduction of grain boundary area [63].

Abnormal grain growth and primary recrystallisation are discontinuous transformations, which are also known as Gibbs I transformations. In these transformations, there is a sharp interface between transformed and untransformed material which sweeps through the material as the transformation proceeds [63].

There is another Gibbs I recrystallisation process which is less well documented in the literature, called nucleation-site limited primary recrystallisation, also known as **abnormal recrystallisation** [65]. Similarly to abnormal grain growth, a minority of grains rapidly consume neighbouring grains to form a very large final grain structure. The difference between abnormal recrystallisation and abnormal grain growth is this:

- In abnormal recrystallisation, few recrystallisation nuclei are present and therefore grain size is limited by the spacing between recrystallisation nuclei, and the grains ahead of the transformation front are not recrystallised. Abnormal recrystallisation and primary recrystallisation are mechanistically indistinct, and the difference in final grain size is due to the extreme sparseness of nuclei in abnormal recrystallisation. The driving force for abnormal recrystallisation is the stored strain energy in the material.
- In abnormal grain growth, the grains first recrystallise and then a few grains grow abnormally as normal grain growth is suppressed, and the grains ahead of the transformation front are fully recrystallised but have not grown [66]–[69]. The driving force for abnormal grain growth is not reduction of stored strain energy, but reduction of boundary area.

These two mechanisms can produce similar grain structures and dislocation densities if the deformed parent grains recover during abnormal recrystallisation. They can be distinguished if the recrystallisation texture is different to the deformed texture, such as in heavily rolled copper [66]. Alternatively, as has been studied by Chen et al. in friction stir welded aluminium alloy [67], the effect of stored strain energy can be isolated by first annealing to recover the deformed structure before further heat treatment to produce large grains.

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 the nucleus. In primary recrystallisation, the nuclei are usually recovered subgrains (small equiaxed volumes of low dislocation density bounded either by dislocation cell walls or low angle grain boundaries); in abnormal grain growth, the nuclei are the pre-existing recrystallised grains [63].

2.2.1.1 Effect of particle pinning on grain growth

The extent of secondary phase particle (SPP) pinning, assuming a uniform dispersion, can be expressed by the dimensionless constant $\Psi = \frac{3F_V\bar{R}}{d}$, where d is SPP diameter, F_V is SPP volume fraction, and $\bar{R}$ is mean grain size. A high value of Ψ indicates strong pinning, and $\Psi = 0$ indicates no pinning.

In single phase materials with no SPPs ($\Psi = 0$), normal grain growth will always occur to reduce interfacial energy. An ideal isotropic three-dimensional grain structure is always unstable and will grow indefinitely, as interfacial tensions at triple points and/or curved boundaries are inherently imbalanced [70].

The boundary growth pressure is inversely proportional to the radius of curvature of the boundary segment, such that large grains will grow more slowly than small grains and the size distribution remains narrow.

A positive value of Ψ slows down the growth rate of a grain structure by exerting a pinning pressure which retards or inhibits grain boundary motion. Zener [71] proposed a mean grain size limit in the presence of SPPs. Grain growth stops when the pinning pressure from SPPs equals the boundary growth pressure from reduction of grain boundary curvature and boundary energy. The process by which small particles pin grain boundary motion is also called Zener pinning.

If $\Psi > 0.25$, the mean grain size cannot increase by normal grain growth. However, individual grains may still grow if they are much larger than average. When $\Psi > 1$ all grain growth ceases and even abnormal grain growth is not possible as the pinning pressure will stop a planar grain boundary with infinite radius of curvature.

A detailed mathematical derivation of these results can be found in Chapters 10 and 11 of Reference [66].

SPPs only pin grain boundary motion if they are small, closely spaced dispersions. If the particles are large ($>1\mu\text{m}$) or much stronger than the matrix, deformation of the matrix material can localise around the non-deforming particle, creating a region or band of high dislocation density, where particle stimulated nucleation of recrystallisation nuclei can occur.

2.2.1.2 Strain induced grain boundary migration

Strain induced grain boundary migration (SIBM) is a mechanism by which recrystallisation can nucleate. It is the bulging of a pre-existing high angle grain boundary segment 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 [63], [65], [72]. 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 [65], [73]. SIBM was first observed as the dominant nucleation mechanism in recrystallisation of $<40\%$ strained aluminium [66], [73].

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. Therefore, 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 [73]. The stabilisation of the bulging grain boundary segment is the limiting step in SIBM, so there is usually an incubation period in transformations which nucleate via SIBM [65].

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 final textures are generally similar to, or a subset of, the deformed textures [73]. This is not always the case in primary recrystallisation, where new orientations can nucleate to form entirely different textures, such as in heavily deformed copper [63].

2.2.1.3 Grain growth in textured materials

A 'rogue' grain in material with strong texture is likely to exhibit abnormal grain growth, as the average grain boundary misorientation in textured material is lower than for a random texture. This gives any high misorientation (and therefore high mobility and energy) boundaries a growth advantage in abnormal grain growth [66]. A microstructure which has grown abnormally by this mechanism should have a very different texture to the starting material. Similarly, orientation pinning can prevent grains surrounded by low angle grain boundaries from growing, as low angle grain boundaries have lower energy and mobility than high angle grain boundaries [63].

2.2.2 Observations of abnormal grain growth and recrystallisation

There are a limited number of published studies on grain growth in zirconium alloys [10]–[12], [74], [75]. Therefore, abnormal grain growth and recrystallisation mechanisms in other metals have also been included in this literature review. These include electrical steels, and aluminium, nickel, and magnesium alloys.

2.2.2.1 Strain-induced grain boundary migration

Jedrychowski et al. [76] showed that recrystallisation in moderately (17%) strained, textured Zr702 (α -Zr) is likely to be via SIBM. In SIBM, a nearly strain-free subgrain grows into highly deformed grains in the heterogeneously deformed structure. 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.

Up to 40% strain, SIBM is the dominant nucleation mechanism for primary recrystallisation in high purity aluminium. [73]

SIBM is also observed in AZ31 Mg alloy sheet annealed at 250°C after equal channel angular pressing to 10% strain. The growth direction of abnormally large grains was observed to be towards regions of relatively high kernel average misorientation (KAM), corresponding to highly slipped regions. The stored strain heterogeneity in the deformed microstructure provides the driving force for SIBM [47], [77].

Abnormally large grains are often found in aluminium alloy friction stir welds after post-weld annealing [67], [78], [79]. This has been attributed to both abnormal recrystallisation and abnormal grain growth mechanisms. Chen et al. [67] found that abnormal grain growth cannot be avoided by pre-annealing to recover stored strain energy in friction stir welded aluminium alloy. Therefore, they conclude that the mechanism producing abnormally large grains in Al friction stir welds cannot be abnormal recrystallisation via SIBM, but must be abnormal grain growth, where the driving force is reduction of grain boundary energy.

Salinas and Salinas [80] studied microstructure evolution in Fe-0.5%Si-0.5%Mn-0.2%Al, a non-oriented electrical steel. There is a critical strain (3%) below which no grain growth will occur. At intermediate (8% - 12%) strains, abnormal grain growth during annealing takes place via SIBM, and at high (25%) strains, both abnormal grain growth via SIBM and primary recrystallisation via

nucleation and growth takes place at the same time. Preferential growth of Goss oriented grains was not observed at any strain level. The grains that nucleate growth via SIBM were found to have lower than average GOS than the consumed grains. On average, grains with low GOS have lower stored strain energy as intragranular orientation gradients (leading to high GOS values) in polycrystals arise from constrained plastic slip. Grains with low stored energy are shown to consume other grains with higher stored energy via SIBM, and therefore lower the total energy of the system.

Bennett et al. [81] characterised selective grain growth in Fe-1.5%Si using EBSD measurements of GOS, grain size, and grain neighbourhood. They found that grains which selectively grew were generally larger than average (with more than six neighbours [64]) and had lower GOS than their neighbours. The orientations of the growing grains were not reported in this study.

2.2.2.2 Secondary phase particles

In Zircaloy-4, SPPs – ZrFe_2 , ZrCr_2 and $\text{Zr}(\text{CrFe})_2$ – are small intermetallic precipitates with diameter between 10 and 500nm [82]. Washburn [11] 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 Figure 6), but did not demonstrate this.

Gray [75] observed that abnormal grain growth was inhibited when annealing high purity Zr in helium and air due to the formation of precipitates. Annealing at 800°C in air completely inhibited abnormal grain growth, and annealing in helium almost completely inhibited abnormal grain growth. As intergranular and intragranular precipitates were observed in Zr annealed in air and helium, but not for vacuum anneals, the inhibition of abnormal grain growth in air or helium was attributed to the presence of these precipitates. The recovery, primary recrystallisation, and normal grain growth kinetics were not affected whether annealing in air, helium or vacuum. Primary recrystallisation temperatures range between 550 and 700°C after 10-50% strain, and decrease with increasing cold work. A finer grain size can be achieved by more cold work, but normal grain growth after primary recrystallisation is extremely limited [75].

Lloyd [83] observed no grain growth after heat treating Zircaloy-4 for 24h at 830°C, but significant growth after heat treating at the same temperature for 100h. After the 100h heat treatment, the grains grow to 500µm but there are also large intragranular and intergranular precipitates present. They speculate that the SPPs may pin grain boundaries and inhibit grain growth for short annealing times.

Bozzolo et al. [12] observe abnormal grain growth in 80% cold-rolled Zr702 when annealing at 800°C for 100 minutes, but not with a shorter annealing time (10 minutes), nor at lower temperatures (700°C or 600°C). They state that SPPs present in Zr702 dissolve or coarsen over time at 800°C. Therefore, at 800°C it is probably dissolution of SPPs which allows abnormal grain growth in Zr702 for longer annealing times of 100 minutes, but not for short annealing times of 10 minutes. High temperature differential scanning calorimetry experiments have indicated that SPP dissolution in low-tin Zircaloy-4 occurs between 800 and 850°C [22].

In beta-treated Zircaloy-4, Jeong et al. observe an increase in the volume fraction and mean diameter of SPPs as the cooling rate decreases [84]. For Zircaloy-4 annealed at 700°C, Gros and Wadier observe that the modal SPP diameter increases from 100nm to >200nm after annealing for 50 hours [82]. A high volume fraction of small, closely spaced SPPs inhibits both normal and abnormal grain growth by Zener pinning. As a result, dissolution or coalescence of the SPPs at high temperature could trigger abnormal grain growth [64].

In weakly textured Al-3.5Cu deformed by equal-channel angular extrusion, abnormal grain growth was observed to coincide with the SPP solvus temperature. The grain size distribution is bimodal and small island grains are present inside the abnormally large grains. The grain boundary morphology of the abnormal grains is wavy. Below the SPP solvus, normal grain growth occurs slowly; above the SPP 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 [85].

A similar phenomenon is observed in primary recrystallisation of Al-1.3Mn [86], where samples annealed at lower temperatures (350-500°C) produce elongated grains with irregular grain shapes due to Zener pinning by prior grain boundary precipitates, but samples annealed at higher temperatures (550°C) produce a completely equiaxed grain structure characteristic of single phase material.

Island grains completely surrounded by a large grain are a common characteristic of abnormal grains. The island grain boundaries within abnormal Al-3.5Cu grains were found to have a higher than average SPP density, whereas the abnormally growing grain boundaries had a lower than average SPP density. These differences in density, and therefore Zener pinning strength, could explain the high growth rate of the abnormal grain, and also why the island grains were not consumed by the abnormal grains. [85]

In Zircaloy-4, the SPP solvus is very close to the beta transus. Using differential scanning calorimetry, SPP dissolution can be identified by a small endothermic thermogram peak, partially overlapping with the $\alpha \rightarrow \alpha + \beta$ transus peak. The overlapped peaks span between 800 and 1000°C [22]. Because of this overlap in transformation temperatures, it is not possible to completely dissolve SPPs and observe normal grain growth whilst still remaining in the alpha phase, as was observed in Al-3.5Cu [85].

2.2.2.3 Texture

Bozzolo et al. [12] observed abnormally large grains in 80% cold rolled then primary recrystallised Zr702 sheet with an initial mean grain size of 3.1µm. After holding at 800°C for 100 minutes the microstructure showed a bimodal grain size distribution, with the large abnormal grains showing significantly different texture to the small recrystallised grains. No abnormal grain growth was seen at 700°C or 600°C for up to 60 minute holding times, or at 800°C for short (10 min) annealing times.

In annealed folded nickel and steel sheet [87], the tensile, neutral and compressive regions in the as-folded sheet have different textures, due to the different slip systems preferentially activated in

tension and compression. The texture components in the deformed metal are preserved during annealing and grain growth, though in the steel sheet the texture strength is weakened by annealing.

In electrical steels such as Fe-3%Si, abnormal grain growth occurs when annealing at 1050°C, after primary recrystallisation (860°C) [88]. This produces a pronounced Goss texture, where {110} plane normals are parallel to the plate normal direction (ND), and <001> directions are parallel to the plate rolling direction (RD). The presence of a pronounced Goss texture improves magnetic properties of the material. Abnormally grown Goss-oriented grains typically have an irregular grain boundary front, and contain island grains completely surrounded by the abnormal grain. These island grains contain a high fraction of either low angle grain boundaries or $\Sigma 3$ twin boundaries, which have lower mobility than high angle grain boundaries. The strength of Goss texture increases with increasing annealing temperature [88].

Park et al. [88] propose a solid-state grain boundary wetting mechanism for the growth of Goss grains. In this mechanism, a grain at a triple junction, bounded by two low energy grain boundary segments, moves into the triple junction and penetrates along a high energy grain boundary. This is energetically favourable as it decreases the high energy grain boundary area and increases the low energy grain boundary area. Figure 5 illustrates the mechanism of grain boundary wetting and shows the direction of grain boundary motion.

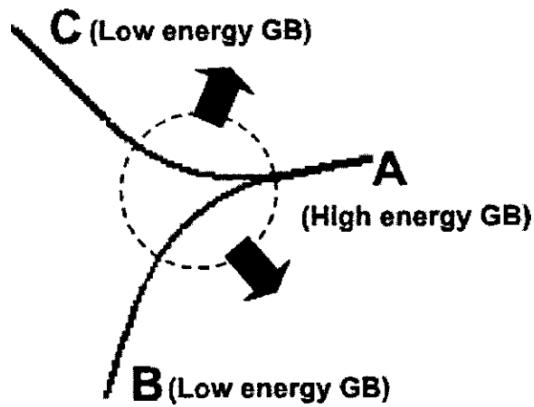


Figure 5: Solid state wetting of a high energy grain boundary at a triple point, showing decrease in high energy grain boundary area and increase in low energy grain boundary area. Reprinted from Reference [88] with permission from AIP Publishing.

2.2.2.4 Prior strain

Washburn 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 (Figure 6). Reducing the temperature to 700°C resulted in a suppression of grain growth, and after 10^4 minutes (around one week) some samples had grown slightly to an average grain size of $50\mu\text{m}$ (Figure 7). Annealing at 500 and 600°C produced no grain growth for up to 10^4 minutes at strains between 2% and 12%.

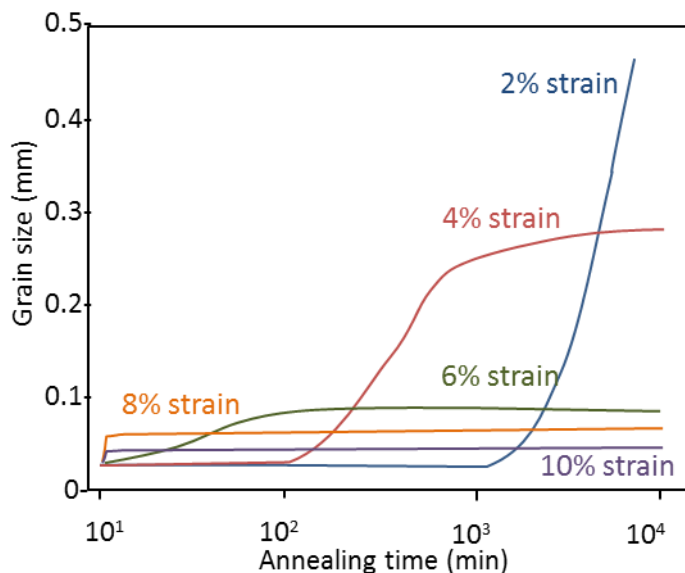


Figure 6: Grain size, as a function of time after annealing at 800°C for a range of strains. Redrawn from Reference [11].

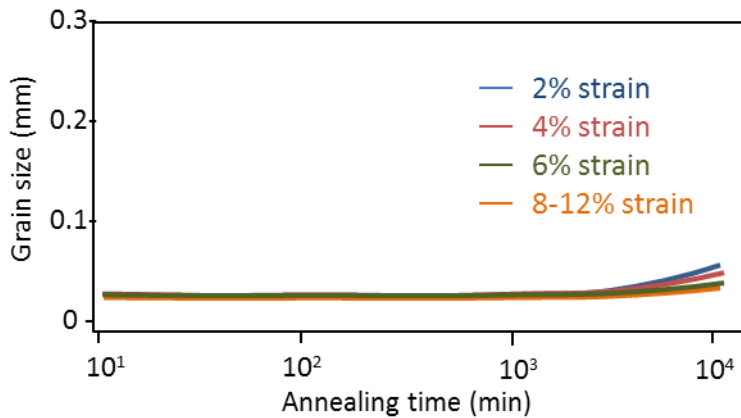


Figure 7: Grain size, as a function of time after annealing at 700°C for a range of strains. Redrawn from Reference [11].

Schemel [10] 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, but no indication of temperature, holding time or final grain size was given.

Gray [75] observed abnormal grain growth ('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 minutes or longer. The largest grains were up to 2mm in diameter, with wavy and irregular boundary traces between abnormal 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.

In folded Ni-200 sheet [87], recrystallisation starts from the highly strained regions and progresses into the lightly strained regions. Grains in the lightly strained regions then grow to form abnormally large grains, but grain growth is suppressed in the highly strained regions. In folded mild steel sheet [87], the trend is similar, apart from at regions of very low strain near the neutral axis of the fold, which did not recrystallise, so that the grain size remained small near the neutral axis of the fold. In folded Al-0.1%Mg sheet, there was significant grain growth on annealing, but the final grain size does not correlate strongly with prior strain [89].

Bozzolo et al. [90] observed abnormal grain growth during hot torsion deformation of a nickel-based superalloy (PER72) to 12% strain. Abnormal grain growth was not observed in an equivalent static anneal, and if the strain level was increased during hot deformation, dynamic recrystallisation was triggered and produced a homogeneous grain structure. The abnormally grown grains have lower than average SPP density, which probably allowed them to grow at the expense of other grains during hot deformation. However, stored energy from deformation was also necessary to provide driving force for abnormal grain growth, as shown by the stable microstructure during static annealing.

Salinas and Salinas [80] found that in abnormal grain growth of Fe-0.5%Si-0.5%Mn-0.2%Al, the average annealed grain size decreases with increasing prior strain, provided that the critical strain of 3% is first reached.

2.2.2.5 Relation of deformation twinning to recrystallisation nuclei

In a study of recrystallisation in 80% cold-rolled, low-alloyed titanium sheet, Bozzolo et al. [91] note that 25% of recrystallised grains nucleate and grow from orientations favourable for twinning in the deformed material; i.e. during primary recrystallisation of a twinned structure, the parent orientations are more likely to nucleate and grow to consume the adjacent twin orientations. A similar trend has been observed in zinc (also a hexagonal close-packed metal) where the twinned orientation texture component disappears whilst leaving the rest of the texture components unchanged [91].

The preferential consumption of twinned orientations in Reference [91] is attributed to a higher stored energy within the twins, leading to their consumption at the beginning of primary recrystallisation. However, Abdolvand et al. [4] note that in a study of twinned grains in Zircaloy-2, the residual stress is always lower in the twin than the parent. Therefore, if the preferential consumption of high stored energy regions applies to Zircaloy, it is likely that the twinned

orientations should preferentially nucleate and consume the parent to reduce the stored energy of the system.

2.3 Resolution of HR-EBSD

HR-EBSD [92], [93] is an SEM-based diffraction technique to precisely determine intragranular elastic strains and rotations by measuring small pattern shifts between EBSD patterns within a grain [93]. The analysis can be extended to measure GND density via Nye's tensor [94]. Provided that the dislocation types are already known, HR-EBSD can be favourable over TEM dislocation analysis as it enables statistically significant areas to be studied and correlated with material behaviour [95].

The potency and utility of HR-EBSD has been demonstrated in a variety of studies, such as: mapping surface morphology of silicon at nanometre resolution [96], strain accommodation during martensitic transformation in steels [97] and Co-alloys [98], [99], slip transfer at grain boundaries in Ti [100], [101], deformation near nano-indenters [94], [102], [103], stresses near inclusions in superalloys [104], [105], intragranular stresses in deformed Cu polycrystals [95], [106], stresses in Inconel-low alloy steel welds [107], in situ deformation of stainless steel [108], mapping stresses during *in-situ* micropillar compression testing [109], SiGe/Si heterostructures [92], [110], [111], stresses induced near edges of SiN layers on Si-on-insulator substrates [112], lattice strain and rotations in III-V nitride systems [113], c/a ratio variations in FeSeTe superconductors [114], residual strains near grain boundaries in Si [115], and elastic strains in 90 degree lamella domains in barium titanate [116].

In order to interpret HR-EBSD data confidently and link results to material microstructures, the resolution of the technique at each step should be known. During pattern acquisition, this includes detector signal to noise ratio from exposure time or binning settings, the geometry of the sample relative to the detector (i.e. the pattern centre coordinates), and the size of the electron probe, which is dependent on material, SEM focussing, probe current, and accelerating voltage [117], [118].

During HR-EBSD cross-correlation (which is typically a post-processing step), the noise floor of the image correlation method should be known. This is typically dependent on the upsampling algorithm used to measure sub-pixel shifts.

2.3.1 Brief theory of HR-EBSD

A fuller description of the HR-EBSD method for residual strain calculation can be found in [106] and [119], and the GND density analysis in [94] and [120]. For the purpose of this thesis a short description is given below.

Fundamentally, HR-EBSD measures intragranular residual strains and rotations. Cross-correlation of test patterns with a reference pattern in the same grain is used to measure shifts between zone axes and extract changes in residual strain and rotation. The zone axis shifts can be geometrically related to the deformation gradient tensor of that point, which is used to find deviatoric strains and rotations in the probed material. Using anisotropic Hooke's law and assuming zero out of plane stress ($\sigma_{33} = 0$) for a traction-free surface, the remaining hydrostatic strain component can be calculated. The strain and rotation can be optimised by measuring pattern shifts on more than four zone axes and using weighted least squares regression, as the equation relating pattern shifts and strains has an over-determined solution [121]. Figure 8 outlines the process of determining strains and rotations from EBSD data.

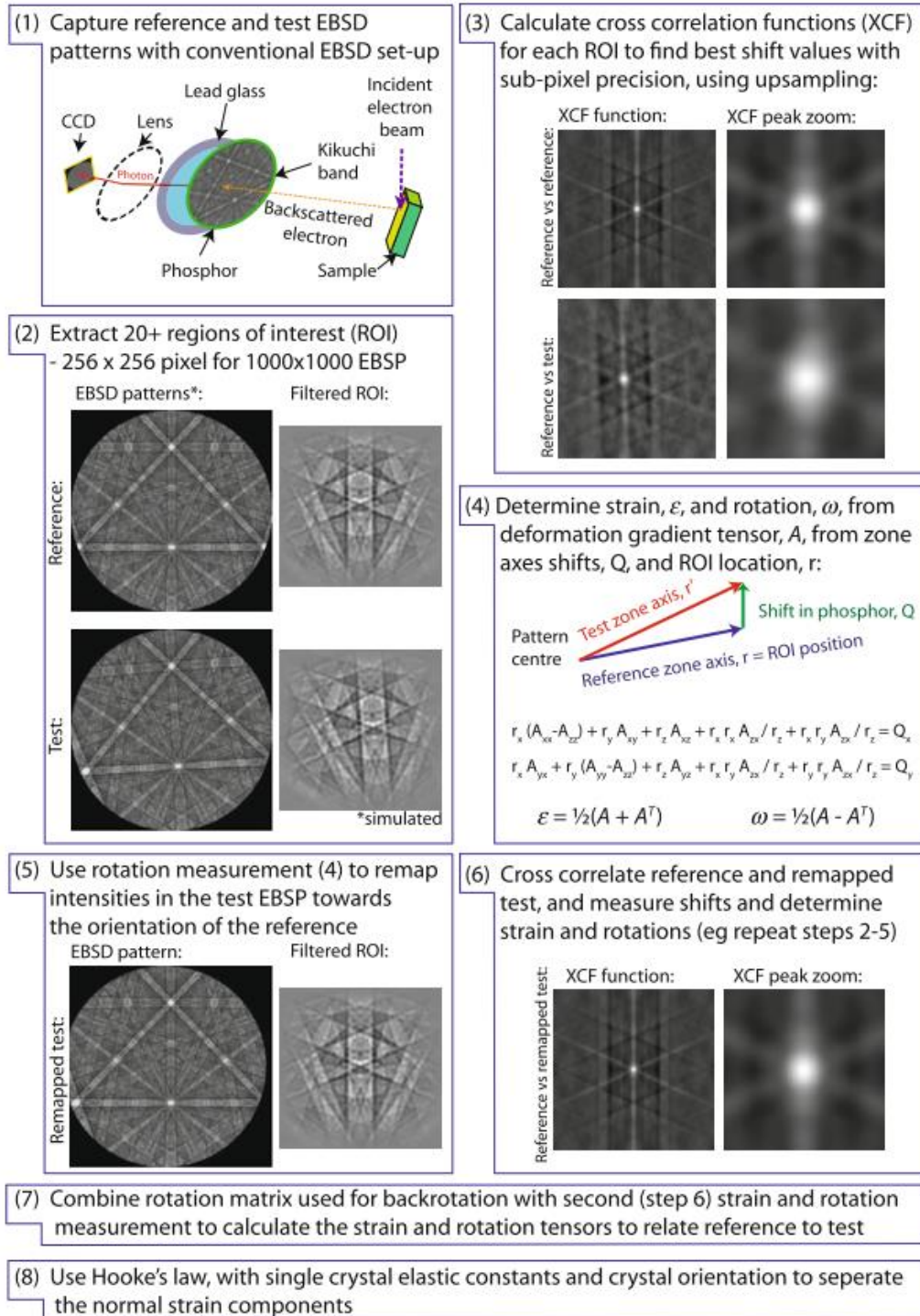


Figure 8: Process of calculating strains and rotations using HR-EBSD analysis. Reprinted from Reference [106] with permission from Springer.

Figure 9 shows that a residual strain or rotation gradient in a crystal must be supported by the presence of GNDs [122]. To quantify the GND content from the displacement gradient tensor mapped using HR-EBSD, the analysis in Reference [94] can be followed:

The displacement field is continuous, so the line integral of the measured displacement gradient tensor β around any closed surface loop C is equal to zero. Applying Stoke's theorem, this is equivalent to the curl of the displacement gradient tensor β integrated over a surface patch S bounded by the closed loop C , and equal to zero.

$$\oint_C \beta \, dx = \iint_S \text{curl}(\beta) = 0$$

Equation 2

β can be separated out into elastic and plastic displacement gradients $\beta = \beta^e + \beta^p$. As the surface integral term is zero, $\text{curl}(\beta^e)$ and $\text{curl}(\beta^p)$ must also sum to zero.

$$\iint_S \text{curl}(\beta^e + \beta^p) \, ds = 0$$

$$\therefore \text{curl}(\beta^e) = -\text{curl}(\beta^p)$$

Equation 3

β^e is the displacement gradient tensor accessible by HR-EBSD (via the deformation gradient tensor A), describing the residual elastic strain and rotation fields. It is equal to Nye's dislocation tensor α [123], which relates the dislocation types to the general lattice curvature.

$$A - I = \beta^e \text{ (where } I \text{ is the identity matrix)}$$

$$\alpha = \text{curl}(\beta^e)$$

$$= \begin{pmatrix} \frac{\partial \omega_{12}}{\partial x_3} - \frac{\partial \omega_{31}}{\partial x_2} & \frac{\partial \omega_{13}}{\partial x_1} & \frac{\partial \omega_{21}}{\partial x_1} \\ \frac{\partial \omega_{32}}{\partial x_2} & \frac{\partial \omega_{23}}{\partial x_1} - \frac{\partial \omega_{21}}{\partial x_3} & \frac{\partial \omega_{21}}{\partial x_2} \\ \frac{\partial \omega_{32}}{\partial x_3} & \frac{\partial \omega_{13}}{\partial x_3} & \frac{\partial \omega_{31}}{\partial x_2} - \frac{\partial \omega_{32}}{\partial x_1} \end{pmatrix} + \begin{pmatrix} \frac{\partial \varepsilon_{12}}{\partial x_3} - \frac{\partial \varepsilon_{13}}{\partial x_2} & \frac{\partial \varepsilon_{13}}{\partial x_1} - \frac{\partial \varepsilon_{11}}{\partial x_3} & \frac{\partial \varepsilon_{11}}{\partial x_2} - \frac{\partial \varepsilon_{12}}{\partial x_1} \\ \frac{\partial \varepsilon_{22}}{\partial x_3} - \frac{\partial \varepsilon_{23}}{\partial x_2} & \frac{\partial \varepsilon_{23}}{\partial x_1} - \frac{\partial \varepsilon_{21}}{\partial x_3} & \frac{\partial \varepsilon_{21}}{\partial x_2} - \frac{\partial \varepsilon_{22}}{\partial x_1} \\ \frac{\partial \varepsilon_{32}}{\partial x_3} - \frac{\partial \varepsilon_{33}}{\partial x_2} & \frac{\partial \varepsilon_{33}}{\partial x_1} - \frac{\partial \varepsilon_{31}}{\partial x_3} & \frac{\partial \varepsilon_{31}}{\partial x_2} - \frac{\partial \varepsilon_{32}}{\partial x_1} \end{pmatrix}$$

Equation 4

Nye [123] defines the dislocation tensor α in terms of dislocation density ρ_{ij} , Burgers vector b_i , and dislocation line direction r_j of each slip system active in the sample. Only nine sets of dislocations are required to generate an arbitrary lattice curvature.

$$\begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{23} & \alpha_{33} \end{pmatrix} = \begin{pmatrix} \rho_{11} \\ \vdots \\ \rho_{ij} \end{pmatrix} \begin{pmatrix} b_1 \\ \vdots \\ b_i \end{pmatrix} (r_1 \quad \cdots \quad r_j)$$

Equation 5

Only three out of nine terms in $\text{curl}(\beta^e)$ are fully known, as only surface strains and rotations can be measured by EBSD. The unknown terms in Equation 4 are shown in red. Two more terms can be recovered by ignoring the elastic strain terms, as they are usually negligible compared to the rotation terms in most metals. In addition, $\alpha_{11} - \alpha_{22} = -\frac{\partial \omega_{31}}{\partial x_2} - \frac{\partial \omega_{23}}{\partial x_1}$ can also be recovered if the elastic strain gradients are ignored [124]. For the GND density analysis, the unknown terms are set to zero.

The net Burger's vector of all the dislocation lines threading a patch, which is equal to the surface integral of the Nye tensor over the patch, can be calculated and decomposed into dislocation types corresponding to the slip systems in a crystal. From this a geometrically necessary lower-bound dislocation density can be determined [94].

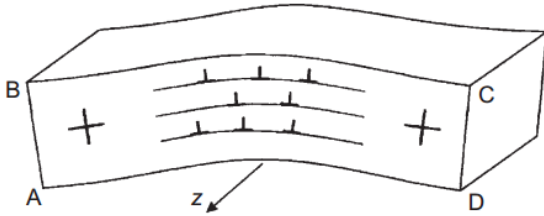


Figure 9: A lattice rotation gradient is supported by the presence of geometrically necessary dislocations of the same sign. Reprinted from Reference [122] with permission from Elsevier.

In most cases, this problem is under-determined, as there are more dislocation types than the six known terms of $\text{curl}(\beta^e)$. Therefore in most metals, the solution is non-unique and should be optimised to minimise total dislocation line energy [94]. The non-uniqueness of the solution means that in most cases individual dislocation types cannot be meaningfully recovered, although recent work by Ruggles et al. [125] has shown that the predominant dislocation type can be qualitatively identified in nickel by restricting the dislocation types activated under plane strain deformation. In

low-symmetry crystals with six or fewer dislocation types, simple least squares inversion can be used and the individual dislocation types can be recovered [126]. In HCP materials, the GND densities of $\langle a \rangle$ type and $\langle c + a \rangle$ type dislocations can be separated out, as the line energy for $\langle c + a \rangle$ type dislocations is much higher than for $\langle a \rangle$ type due to their different magnitudes of Burgers vectors. This means that $\langle a \rangle$ type will be strongly favoured unless $\langle c + a \rangle$ type dislocations are required to support the rotation field. This analysis where $\langle c + a \rangle$ and $\langle a \rangle$ type dislocations are separated out has been used to characterise dislocation content in a macrozone in HCP Ti-6Al-4V [127].

2.3.2 Sensitivity of residual strain and rotation measurement

The image cross-correlation method, when applied to clean patterns with limited noise, can measure sub-pixel shifts of ± 0.05 pixels or better with 256 pixel regions of interest (ROIs) dispersed within a 1000×1000 pixel image. This corresponds to an average strain and rotation sensitivity of 2×10^{-4} , which is sufficient to measure elastic strains in a material, which are up to 2×10^{-3} [128]. More recent studies have shown that optimising the capture geometry and maximising probe current and exposure time can result in a pattern shift sensitivity of up to ± 0.02 pixels, or strain sensitivity of 1×10^{-4} when using a 1000×1000 pixel detector [128].

Using simulated patterns, the theoretical noise floor of the technique can be found. The noise floor is 0.001 pixels for cross-correlation, which leads to a strain measurement noise floor of 3×10^{-7} in a 2000×2000 pixel simulated pattern [128].

2.3.2.1 High frequency noise

The maximum sensitivity decreases to around ± 0.2 pixels when artificial high frequency noise is added, but this can be partially compensated for if a low pass filter is used to optimise the quality of the cross-correlation function, so that a sensitivity of ± 0.1 pixels can be achieved [93].

2.3.2.2 Region of interest size

Using smaller regions of interest (ROI) on clean patterns decreases the achievable sensitivity from ± 0.05 pixels (256 pixel ROI) to ± 0.15 pixels (64 pixel ROI) [93]. Sampling more ROI per pattern somewhat decreases the measurement error, but the placement of the ROI with respect to the pattern centre has a much larger effect on the error than the number of ROI [119].

2.3.2.3 Uncertainty in detector geometry

For any detector and sample geometry, the pattern centre (x^*, y^*, z^*) defines the relationship between the detector and the electron probe interaction volume. The pattern centre location (x^*, y^*) is defined by the position where the detector screen plane normal intersects the interaction volume, and the camera length (z^*) is the perpendicular distance between the detector screen normal and probed volume (Figure 10). It is invariant with strain and rotation and therefore the deformation gradient tensor in HR-EBSD is measured with respect to this location. A poor pattern centre measurement leads to phantom strain measurements [111], [129].

When measured by conventional iterative fitting to bands detected by the Hough transform, the pattern centre coordinates are known to a precision varying between 0.2% and 0.6% depending on pattern centre component [130]–[132].

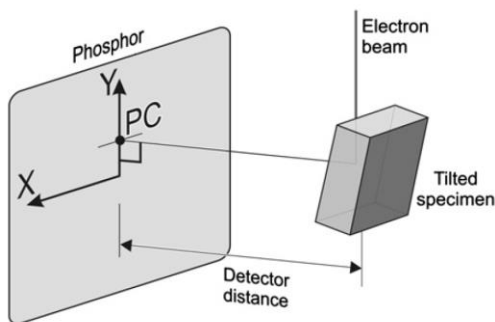


Figure 10: Pattern centre location in EBSD sample and detector setup. Reprinted from Reference [133] with permission from Elsevier.

Alkorta [129] quantified how errors in pattern centre measurement are carried into the strain measurement. They note that adjusting camera length increases the sensitivity of some terms in the

displacement gradient tensor and decreases the sensitivity of others, so the camera length can be optimised for strain measurement. Britton et al. [128] used a numerical simulation to find that the ideal detector position with respect to the sample. They found that in order to maximise the strain measurement resolution, the pattern centre should be $(x^*, y^*, z^*) = (0.5, 0.5, 0.25)$. This analysis is purely geometrical and ignores the changing signal to noise ratios at different camera lengths and back-scattering angles.

2.3.2.4 Presence of large lattice rotations

The presence of large intragranular lattice rotations increases error in both cross-correlation and the infinitesimal strain decomposition of the deformation gradient tensor. The errors in cross-correlation can be solved using a combination of using robust fitting algorithms to remove outlier points in the pattern shifts where cross-correlation has failed [121], and pattern remapping of individual regions of interest to refine the pattern shift measurement [134]. Errors arising from incorrect decomposition of the displacement gradient tensor can be minimised using finite instead of infinitesimal strain theory to calculate strains and rotations [119].

2.3.3 Sensitivity of GND density measurement

Jiang et al. [135] study the sensitivity of GND density measurement to EBSD detector binning and step size. Typically HR-EBSD measures sub-pixel shifts in the EBSD patterns to map residual elastic strains, therefore long exposure times and no binning are used. However, for GND density measurements in metals, often the rotation terms in the displacement gradient tensor are much larger than the strain terms and therefore produce larger zone axis shifts in the EBSD pattern. Therefore, there is an opportunity to use more detector binning, shorten exposure times, and enable larger areas of microstructure to be mapped. For no camera binning the GND density noise floor is 10^{13}m^{-2} [94], and this rises with increased binning to 10^{14}m^{-2} at 8×8 binning [135]. However, even when using up to 8×8 binned patterns, the GND density distributions in 10% deformed copper could be recovered sufficiently. Increasing the step size of the EBSD scan increases the sensitivity of

GND density measurement as lattice rotation contributions from more dislocations are summed over the step size. However, in heterogeneous polycrystal deformation, features in the dislocation patterning can be missed or become entirely different when using too large a step size.

2.3.4 Precision near grain boundaries (Hough-based EBSD)

Wright et al. [9] studied the precision of KAM measurement using conventional, Hough-transform based EBSD near grain boundaries. In conventional EBSD, linear band features in the EBSD pattern are detected via the greyscale Hough transform, and the orientation is indexed from a look-up table of interplanar angles for the crystal symmetry of a given phase. Interplanar angles can be measured directly from the angles between intersecting bands as the EBSD pattern is a direct projection of the orientation. Fuller descriptions of the conventional EBSD technique can be found in References [136]–[138]. The misorientation precision for this technique is around 0.2° [132].

Wright et al. [9] concluded that at a grain boundary, the KAM precision decreases from 0.2° to around 0.5° . The increased error arises from a combination of from long-range noise from extra bands present due to EBSD pattern overlap at high angle grain boundaries, and high frequency noise from statistically stored dislocations which do not give rise to a net misorientation. The size of the affected region is on the order of the interaction volume size of the electron probe.

In any given material, the interaction volume size depends on electron source, probe current, and accelerating voltage [118], [139]. The interaction volume size is smaller for field emission gun than a tungsten filament source, and increases with increasing probe current and accelerating voltage [118], [139]. For a field emission gun SEM operating at 10nA and 20kV, the lateral and longitudinal interaction volume size measured by Chen et al. [118] for twinned copper bicrystals are 40 and 120nm respectively.

2.4 Summary

Deformation in zirconium alloys is highly heterogeneous due to the low number of easy slip systems and inherent elastic anisotropy in the HCP crystal structure. $\langle a \rangle$ prismatic slip is the dominant slip system at room temperature and quasi-static strain rates. $\langle a \rangle$ basal slip has rarely been seen at room temperature and quasi-static strain rates, and $\langle c + a \rangle$ pyramidal slip has a high CRSS at room temperature. Twinning plays a significant role in supporting $\langle c \rangle$ -axis deformation, and is preferentially activated at low temperatures and high strain rates. Twinning significantly reorients the crystal lattice, and therefore contributes to texture evolution and work hardening behaviour during deformation.

The formation of abnormally large grains in zirconium alloys has been observed and reported in the literature. Recrystallisation and grain growth processes in metals are highly dependent on prior strain, the presence of small pinning particles and/or large particles to stimulate nucleation, and texture. The mechanisms for formation of abnormally large grains have been identified in other alloy systems such as nickel, copper, and steel. One potential mechanism is abnormal grain growth, also called secondary recrystallisation, where the driving force is reduction of boundary area. The other mechanism is nucleation-site limited primary recrystallisation, also called abnormal recrystallisation, where the driving force is reduction of stored strain energy.

HR-EBSD is a powerful technique to map residual elastic strains and rotations from small orientation changes. HR-EBSD can be used to characterise deformation and recrystallisation processes in zirconium, and therefore the measurement resolution both at grain interiors and near grain boundaries should be known. The pattern centre coordinates are coupled to the measured strains and rotations, therefore uncertainty in the detector geometry can lead to phantom strain measurements. The resolution of HR-EBSD can also be affected by low signal to noise ratio arising from either decreased exposure times, or pattern degradation either due to the presence of dislocations or pattern overlap at grain boundaries.

3. The effect of pattern overlap on the accuracy of high resolution electron backscatter diffraction measurements

(The work in this chapter has been previously published in Ultramicroscopy [140] and method, results, discussion and conclusions sections are reproduced verbatim.)

3.1 Motivation

There have been various studies on the accuracy and sensitivity of strain and rotation measurements in HR-EBSD [128], [141], [142], the dependence of accuracy on the pattern centre position [111], and the effect of high frequency noise on strain sensitivity [93], [128]. These studies are of experimental or simulated patterns all from grain interiors. Variations in strain and dislocation density near grain boundaries are often of interest [95], [100], [143], but the accuracy of HR-EBSD measurements near boundaries has not yet been quantified. Confidence in HR-EBSD results near boundaries is particularly important for studying fine microstructural features such as twins, where a fine step size must be employed to resolve features properly.

Approaching a grain boundary, the interaction volume samples two grains at once and results in an overlapped diffraction pattern. Broadly, the intensity contribution from each grain is approximately proportional to the fraction of the interaction volume in that grain. This phenomenon has been used to measure the spatial resolution of the electron beam interaction volume [118] and the inclination angle of the grain boundary plane [144]. It is well known that measurement near grain boundaries may cause some uncertainty in EBSD measurements, as highlighted recently with Hough-based EBSD by Wright et al. [9].

For HR-EBSD, pattern mixing may result in increased uncertainty or even entirely erroneous pattern shift measurements, which are then used to determine deviatoric strains and lattice misorientations

between test and reference pattern [93]. The degree of uncertainty is not well known. Understanding and reducing the causes of this uncertainty is very important, as features such as stress concentrations and crack nucleation sites are often near grain boundaries.

3.2 Method

3.2.1 Sample preparation and pattern acquisition

Zircaloy-4 plate was cut and ground to 4000 grit finish, then polished in a 5:1 solution of colloidal silica and hydrogen peroxide for 4.5 hours. This yielded a surface finish which showed grain contrast under polarised light. The sample was electropolished in a 9:1 solution of methanol and perchloric acid cooled with liquid nitrogen to -40°C , at 30V and $1\text{A}/\text{cm}^2$ for 60s in order to produce high quality EBSD patterns.

Full resolution (1600×1152 pixels, 12bit) diffraction patterns of Zircaloy-4 were captured from the interiors of distinct grains, on a Bruker eFlashHR detector mounted on in a Zeiss Auriga field emission gun SEM. The SEM was operated at 20 keV and delivered a probe current of 10.5nA measured using a Faraday cup, leading to an exposure time of 500ms per pattern, for an intensity bit depth of 11.5 (~3000 grey levels). The EBSD pattern greyscale intensities were linearly mixed at different fractions to simulate the effect of pattern overlap near a grain boundary (Figure 11).

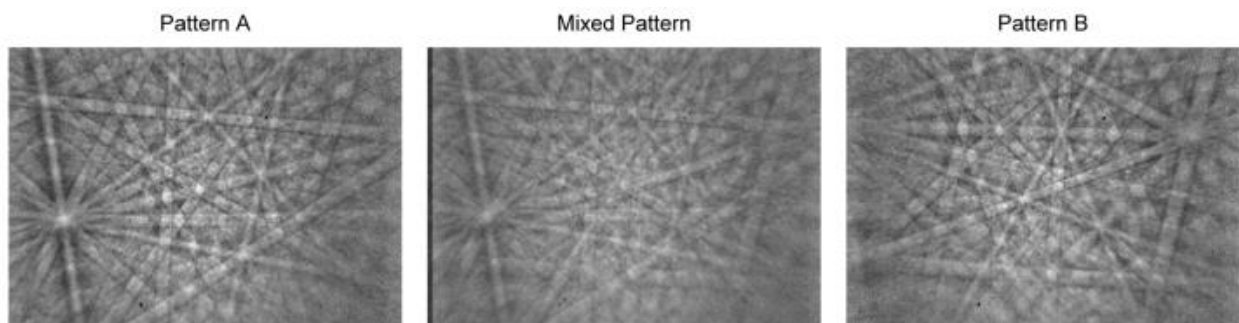


Figure 11: Greyscale intensities in diffraction patterns A and B are translated and mixed to form mixed patterns.

3.2.2 Spatial resolution of EBSD set-up

First, the physical spatial resolution of HR-EBSD for this EBSD set up is measured by determining the size of the interaction volume. This method measures the quality of cross-correlation on a line scan taken across a grain boundary, and has been used previously by Chen et al. [118].

Spatial resolution in EBSD can be defined in two distinct ways.

- The *physical spatial resolution* is linked to the size of the interaction volume, from which the diffracted signal originates. Zaefferer defines it as the distance between an electron beam and a large-angle grain boundary, within which backscatter diffracted signal from both grain orientations can be obtained [145]. This is equivalent to the radius of the interaction volume if it is modelled as a hemisphere, as illustrated in Figure 12(a).
In a typical EBSD setup for a copper sample at incident beam energy of 20keV and probe current of 10nA, this is about 40nm along the tilt axis, 120nm perpendicular to the tilt axis, and 60nm in depth [118]. The exact dimensions depend on accelerating voltage, probe current, and atomic number of the material.
- The *effective spatial resolution* [146] is based upon software algorithms used to discriminate one pattern from another. Here the limiting resolution is based upon where a mixed pattern cannot be indexed (in Hough-based EBSD), or cannot correlate well with the reference pattern to identify an image shift (in HR-EBSD). In practice, the effective spatial resolution is smaller than the physical spatial resolution, because it is possible to separate signal of one grain from another if one pattern has much higher intensity than the other pattern [146].

The physical spatial resolution, or interaction volume size, was measured using a cross-correlation method based upon the work by Chen et al. [118]. Figure 12(b) shows that a line scan of 20 patterns across a grain boundary was taken in 20nm steps aligned at 40° to the grain boundary, in order to avoid carbon contamination on the sample, which degrades pattern quality. This resulted in an

effective step size of 15nm normal to the grain boundary. The alignment of the grain boundary plane below the sample surface was unknown. Because the grain boundary is aligned 40° from the microscope tilt axis, the measured interaction volume radius lies between the spatial resolution parallel and perpendicular to the tilt axis. The resolution parallel to the tilt axis is up to three times smaller than perpendicular to it, so this measurement is moderately conservative.

Each pattern in the line scan was cross-correlated against the two extreme patterns and peak heights of the XCFs plotted. The peak heights were normalised to range between 1 and 0 and the values multiplied then normalised, producing a peak with a full width at half maximum (FWHM) of 59nm. Figure 12(c) shows the normalised cross-correlation function (XCF) peak heights of the line scan (red and black lines) and the normalised peak obtained from multiplying these values (blue line). The XCF peak height profile is relatively symmetric suggesting that the boundary plane was fairly close to normal to the sample surface.

A model of a hemispherical interaction volume crossing a grain boundary was used to relate the FWHM to the interaction volume radius. Volume fraction of the hemisphere in the reference grain was plotted as a function of perpendicular distance from the grain boundary. This produced Figure 12(d), a plot similar to the peak heights in Figure 12(c).

Figure 12(d) shows that the FWHM should be approximately equal to the interaction volume radius. The FWHM in the simulation was measured as 61nm, approximately equal to the 59nm interaction volume radius. This is different to the interpretation described in Chen et al., where the FWHM is described as twice the interaction volume radius. Since the FWHM measured in the EBSD line scan in Figure 12(c) is 59nm, our model indicates that the interaction volume is also approximated as a 59nm radius hemisphere.

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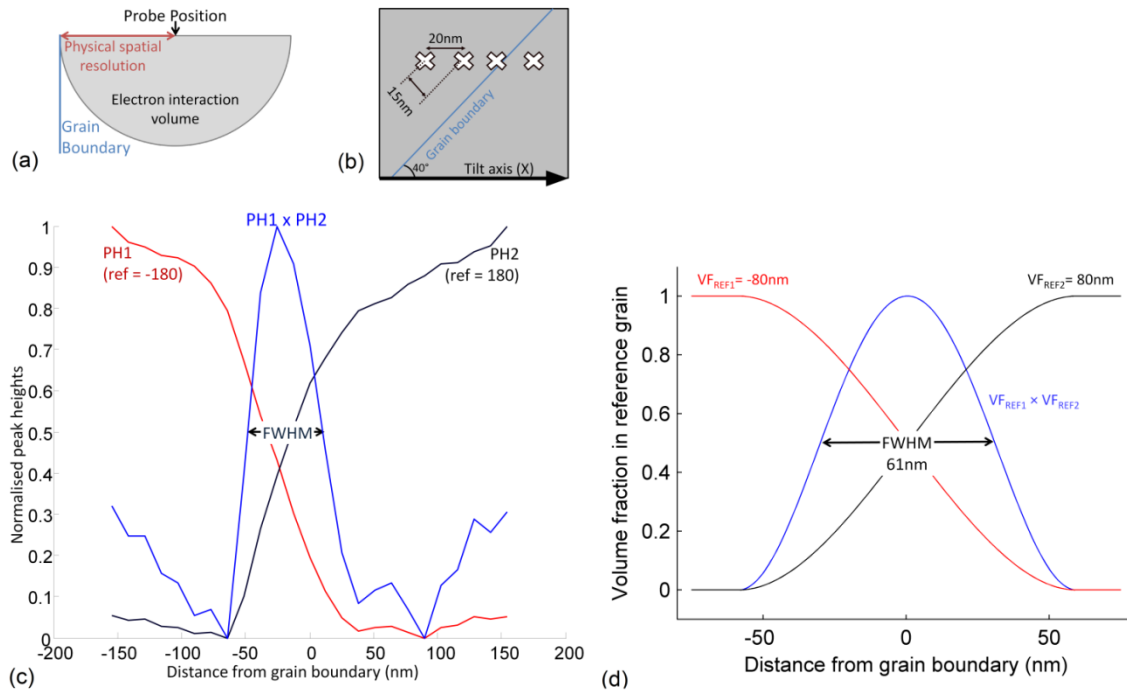


Figure 12: (a) Physical spatial resolution in EBSD (after Zaefferer [145]). (b) Microscope setup of grain boundary line scan. (c) Peak heights from XCFs of a line scan multiplied to calculate size of interaction volume. (d) Simulated line scan to relate the interaction volume radius to the measured FWHM.

3.2.3 Pattern mixing to mimic overlap near grain boundaries

From the size of the interaction volume, the link between artificial pattern mixing and pattern overlap can be established. A simple simulation has been used to describe the overlapping volume of sampled material and the corresponding mixed diffraction pattern.

The interaction volume was modelled as a 59nm radius hemisphere, corresponding to the interaction volume of this EBSD setup. The grain boundary is assumed to run perpendicular to both the free surface and the scan line. The distance from the centre of the interaction volume to the grain boundary was calculated for different mixing fractions, assuming that the intensity fraction is directly proportional to the volume fraction of the contributing grain within the assumed hemispherical interaction volume. This is a simplified model of the interaction volume which provides an indicative link between the proportions of mixed pattern intensity with a physical distance from the grain boundary; it is only meant as an approximate guide and would clearly vary

with beam conditions and sample type. Figure 13 illustrates the non-linear weighting of pattern mixing with distance from the grain boundary.

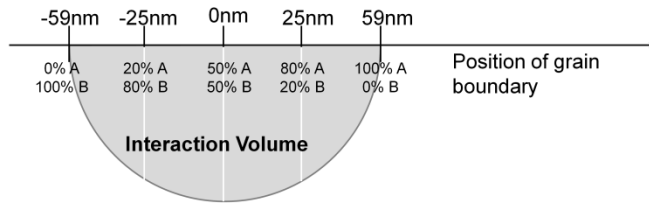


Figure 13: Different mixing fractions correspond to different positions of the grain boundary intersecting the interaction volume.

11 linearly spaced mixing fractions were used, corresponding to distances between the incident beam position and the grain boundary given in Table 3.

Reference Intensity	100%	90%	80%	70%	60%	50%	40%	30%	20%	10%	0%
Dist. from g.b. (nm)	59	36	25	16	8	0	-8	-16	-25	-36	-59

Table 3: Mixing fraction, or reference intensity, modelled as the distance from the grain boundary in a hemispherical interaction volume (shown in Figure 13).

3.2.4 Cross-correlation

One method of addressing noise from pattern overlap is by implementing a high-pass filter. The effective spatial resolution could be improved by considering that Kikuchi bands contributed from the less dominant grain effectively act as low-frequency noise which can be filtered in the Fourier domain.

Different filters are used to explore how filtering can reduce uncertainty and ideally improve accuracy of the technique. Filtering out low frequency components could attenuate features of the non-dominant pattern and improve cross-correlation measurements, increasing the effective resolution of HR-EBSD technique. A strategy for determination of optimum filter settings and errors is discussed.

Two hundred ROIs of size 256×256 pixels were extracted from the reference and each of the mixed diffraction patterns, and cross-correlated using in-house developed MATLAB scripts using a single

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pass of cross-correlation and the Wilkinson, Meaden and Dingley strain and rotation analysis method [93] with a robust iterative weighting scheme [121].

To isolate the effect of filtering, a known pixel translation was performed to shift the positions of features within test pattern away from the reference before mixing. This translation in the diffraction pattern corresponds, effectively, to a known small rotation and elastic strain between the new test and reference crystal, and enables accuracy of the XCF peak determination to be measured. The translation was 2 pixels in X and 3 pixels in Y for the displacement gradient tensor calculations, and 20 pixels in both X and Y for the XCF peak shape calculations. If this translation is not imposed then ambiguity arises in interpreting any peak at the zero shift position in the XCF which could be generated by either a good registration of the diffraction information or by registration of undesired weaker contrast static background features when filtering has removed most of the diffraction contrast from the patterns. Figure 14 shows the way in which the test and reference patterns were combined prior to cross-correlation analysis.

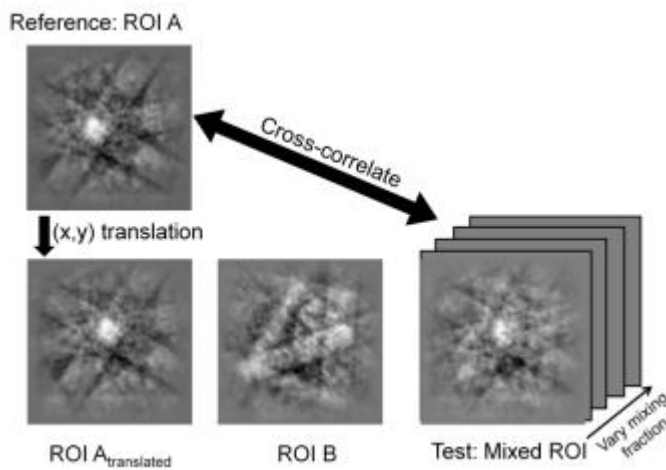


Figure 14: ROI A is first translated, and then mixed with ROI B to different fractions. The mixed ROI are then correlated with ROI A.

Band pass filters were applied in the Fourier domain to intensity normalised ROIs [93]. Band pass filters attenuate both high frequency noise (low pass component) and low frequency variation in the background (high pass component). The low pass component of the filter was set to

30 cycles/256 pixels, corresponding to the limits imposed by the detector optics [128]. Contributions at higher frequencies correspond to random noise and were removed by the filter. The high pass cut off frequency was varied between 0 (no filtering) and 14 cycles/256 pixels (severe filtering).

Figure 15 shows an example ROI near a zone axis and the power spectrum of its Fourier transform as the high pass cut off frequency is increased. Increasing the high pass filter cut off attenuates low frequency components at the centre of the power spectrum. The back-transforms of the Fourier transforms show how features are progressively removed from ROI, with and without pattern overlap.

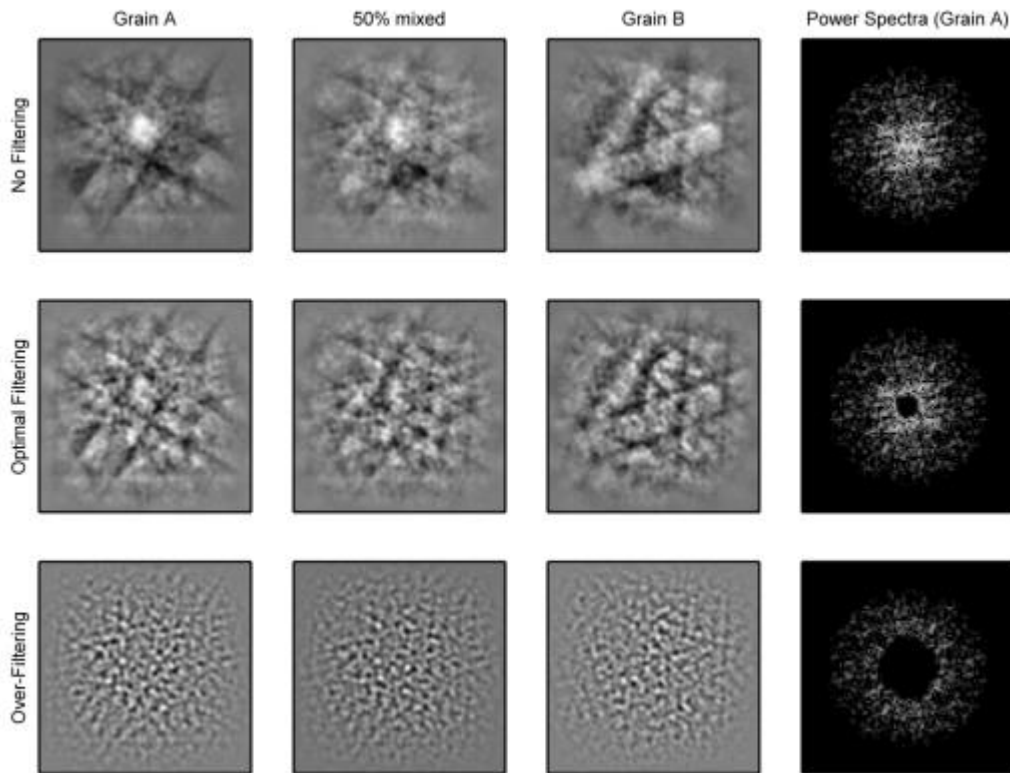


Figure 15: Effect of the high pass filter and pattern mixing on ROIs and power spectra. Optimal filtering: High pass cut off = 5.4 cycles/256 pixels. Over-filtering: High pass cut off = 14 cycles/256 pixels.

XCFs were computed for systematically selected combinations of filtering and mixing. The XCFs are normalised by the autocorrelation of the reference ROI, so an XCF peak height of 1 indicates perfect correlation. Displacement gradient tensors were calculated from measured X- and Y-shifts determined at each of the ROIs from the peak positions within their XCFs (using the Wilkinson,

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Meaden and Dingley infinitesimal deformation framework [93] with iterative robust weighting route [121]).

Two error metrics are presented: actual error and mean angular error (MAE).

1. Actual error is the difference between applied and measured values. Here the displacement gradient tensor can be calculated directly from the imposed translation to give the actual solution. The difference from the direct calculation and the XCF measurement enables probing of the accuracy of the method.
2. MAE is calculated using the mean deviation from least squares fitting to the WMD analysis route. The MAE describes how well the shifts fit the WMD model, but may not reveal some systematic errors, which are captured by the actual error metric.

1.1.1.1 Simulating statistical likelihood of pattern overlap

In practice, the exact distance of an EBSD point from the grain boundary can rarely be measured, and it is useful to know the statistical likelihood of pattern overlap occurring. This has been measured for a given interaction volume size using a simulated microstructure.

Voronoi tessellation is used to generate an exemplar microstructure (shown later in Figure 26a). A grid of EBSD points at varying step sizes is overlaid on the microstructure. The fraction of points near a grain boundary which would exhibit any pattern overlap, or sufficient pattern overlap to cause significant error in the strain calculations (following the method outlined in [93]), will be determined.

3.3 Results

3.3.1 Effect of pattern overlap on the XCF

3.3.1.1 Effects of high pass filter on XCF peak

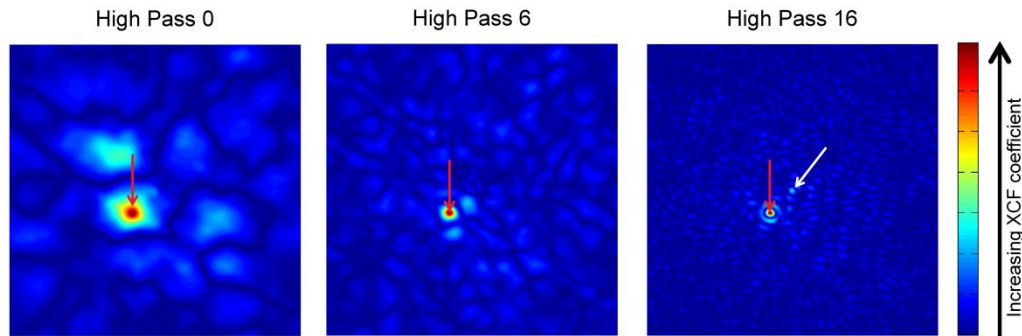


Figure 16: Effect of filtering on the XCF, 50% reference intensity, modelled as directly on the grain boundary. The white arrow indicates the peak at (0,0), and the red arrow the desired peak at (20,20).

Figure 16 shows the effect of filtering on the XCF peak shape for 50:50 mixed patterns. When no high pass filter is applied, the correct peak (indicated by red arrows) is broad and peak position is poorly defined. The peaks become rounder and sharper as filtering increases. Large high pass filter cut off frequencies cause a secondary peak to appear at (0,0) displacement (as indicated by the white arrow), and the correct XCF peak is very narrow, which makes upsampling for sub-pixel interpolation difficult.

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3.3.1.1.1 Onset of zero peak

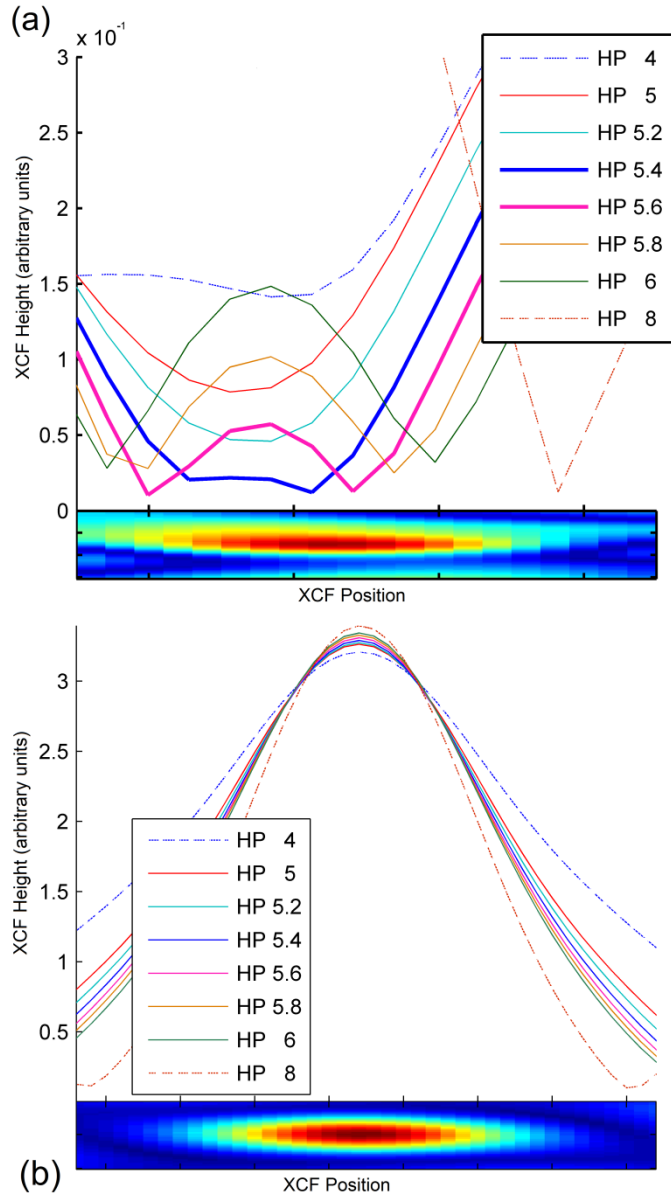


Figure 17: (a) Line profiles of the secondary peak at (0,0) displacement, 70% reference intensity, where the second peak begins to form at high pass cut off of 5.6 cycles/256 pixels (pink line). X-axis given as 2D profile of the peak centre showing the position of the second peak when high pass cut off is 14 cycles/256 pixels. (b) line profiles of the global XCF peak, with 70% reference intensity. X-axis given as 2D profile of the XCF peak showing peak position at a high pass cut off of 14 cycles/256 pixels. The legend boxes indicate the high pass cut off frequencies used in the line profiles.

The onset of the secondary peak at (0,0) displacement is shown in the XCF peak profile in Figure 17(a) to begin to form as the high pass filter cut off frequency is increased to 5.6 cycles/256 pixels with pattern mixing at 70% reference intensity (16nm from the grain boundary). This peak is not present at lower high pass cut offs (blue dashed line) and is very pronounced at large high pass cut offs

(brown dashed line). The shape of the correct global XCF peak at (20,20) displacement is shown in Figure 17(b) for comparison.

3.3.1.2 Effect of distance from grain boundary on XCF peak

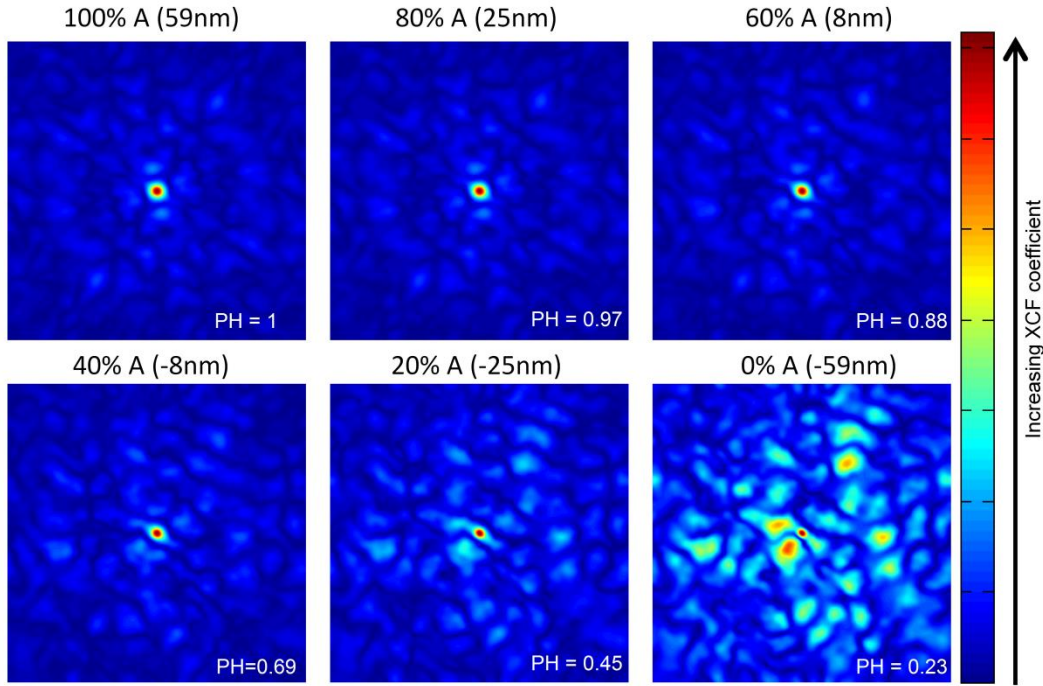


Figure 18: XCF as the interaction volume approaches and crosses a grain boundary with a high pass cut off of 5.4 cycles/256 pixels (optimal filter setting). PH = normalised XCF peak height

Figure 18 shows how the XCF varies as the pattern mixing is altered to simulate approaching a grain boundary with high pass filter of 5.4 cycles/256 pixels. The XCF shows a clear peak (but a lower peak height) at mixing down to 40% reference intensity, when the centre of the interaction volume is on the other side of the grain boundary (shown as negative distances). At 20% reference intensity, or 25nm on the other side of the grain boundary, other peaks begin to form, indicating poor correlation with the reference pattern.

3.3.1.3 Error in measured XCF shifts

Actual error in the XCF shifts is given by the length of the difference between the measured translation vector, $Q^{measured}$, and the imposed translation $Q^{imposed}$.

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Actual Error

$$= \sqrt{(Q_1^{\text{measured}} - Q_1^{\text{imposed}})^2 + (Q_2^{\text{measured}} - Q_2^{\text{imposed}})^2}$$

Equation 6

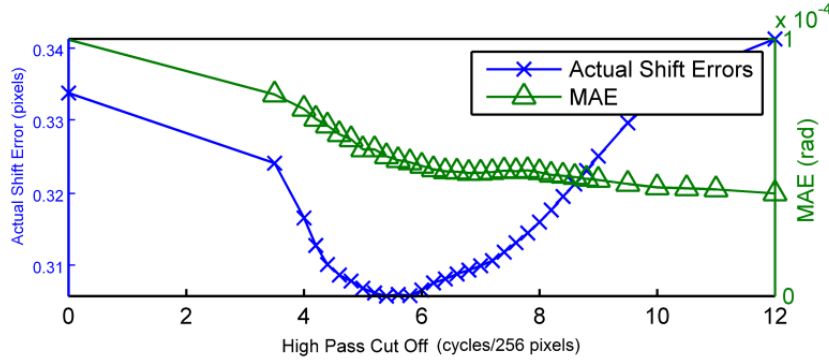


Figure 19: Actual error and MAE in the XCF pixel shifts, 70% reference intensity modelled as 16nm from grain boundary.

With the reference intensity at 70% the actual error in the XCF shifts has a minimum of 0.305 pixels at a filter high pass cut off between 5.4 and 5.8 cycles/256 pixels (Figure 19, blue line).

The MAE in the XCF shifts decreases with increasing high pass cut off and does not show a minimum (Figure 19, green line).

3.3.2 Effect of pattern overlap on displacement gradient tensor

3.3.2.1 Variation with pattern mixing fraction

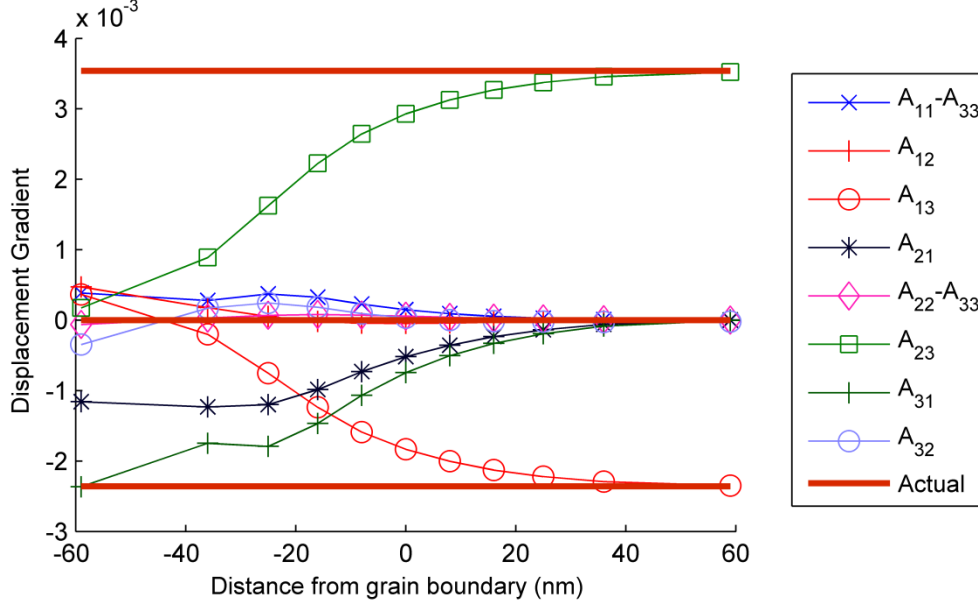


Figure 20: The displacement gradient tensor as a function of mixing fraction, modelled as distance from the grain boundary, for optimal high pass cut off = 5.4 cycles/256 pixels, with inclusion of the expected (Actual) displacement gradient values from the pattern translation – $A_{13} = 3.5 \times 10^{-3}$, $A_{23} = -2.4 \times 10^{-3}$, all other components of $A = 0$.

In Figure 20 and Figure 21, only the displacement gradient tensor components A_{13} (red circles) and A_{23} (green squares) should have non-zero values.

$$Q_1 = r_2 A_{12} + r_3 \mathbf{A}_{13} - \frac{r_1^2}{r_3} A_{31} - \frac{r_2 r_1}{r_3} A_{32} + r_1 (A_{11} - A_{33})$$

$$Q_2 = r_1 A_{21} + r_3 \mathbf{A}_{23} + -\frac{r_2 r_1}{r_3} A_{31} - \frac{r_2^2}{r_3} A_{32} + r_2 (A_{22} - A_{33})$$

Equation 7

This arises from the imposed (Q_1, Q_2) pattern shift to one of the diffraction patterns, which is used to determine accuracy of measurements. The values of Q_1 and Q_2 (pattern shift) are consistent for all the ROI. Any of the terms with an r_1 or r_2 component (which change depending on ROI position) must therefore go to zero. This leaves only A_{13} and A_{23} (terms marked in bold in Equation 7) which vary with Q_1 and Q_2 , as these are only dependent on the detector distance r_3 .

The effect of pattern overlap on the accuracy of high resolution electron backscatter diffraction measurements

For an imposed pixel shift of $(Q_1, Q_2) = (2, 3)$ with a pattern centre of $X^* = 0.46$, $Y^* = 0.57$, $Z^* = 0.53$ (where Z^* is measured as a fraction of detector x-axis), the displacement gradient tensor components are $A_{13} = 0.0024$ and $A_{23} = 0.0035$.

In Figure 20, the accuracy of the displacement gradient tensor decreases as the interaction volume approaches and crosses a grain boundary. For optimally filtered patterns, the deviation at 70% reference intensity, or 16nm from the grain boundary, is less than 5×10^{-4} .

3.3.2.2 Variation with high pass filter cut off frequency

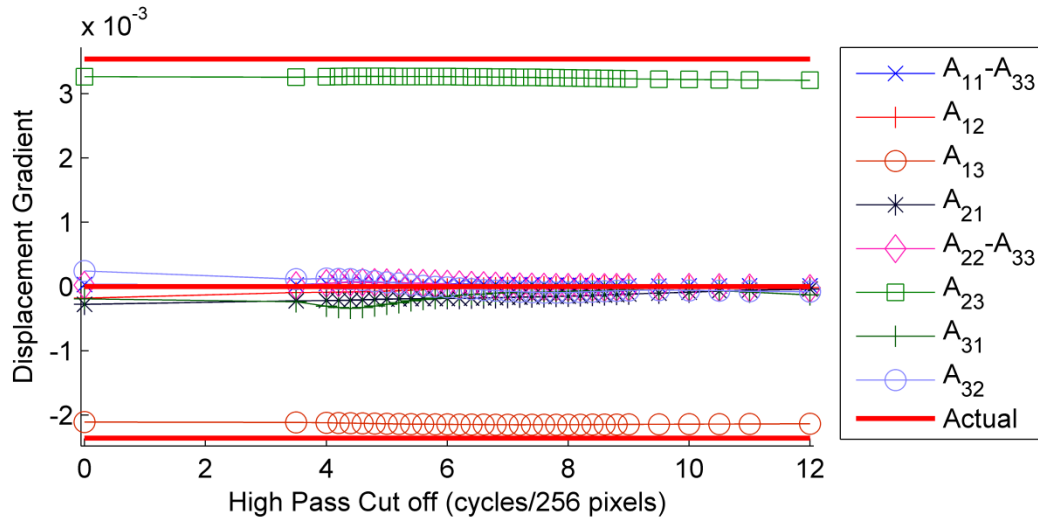


Figure 21: The displacement gradient tensor for a reference pattern correlated with a translated 70% reference pattern (i.e. 16nm from grain boundary) with varying high pass cut off filtering. The actual values are determined from the imposed pattern translation

Figure 21 shows the variation of the displacement gradient tensor at 70% reference intensity (16nm from the grain boundary). The two non-zero components A_{13} and A_{23} remain fairly constant despite large changes in the high pass filter cut off frequency. The systematic error from the actual solution in the non-zero A_{13} and A_{23} components comes from correlating a mixed pattern, which is shown in Figure 20 to increase with increasing mixing fraction.

All other components, which have an actual solution of zero, converge towards zero at large high pass cut off frequencies.

3.3.2.2.1 Error in the displacement gradient tensor variation with high pass filter

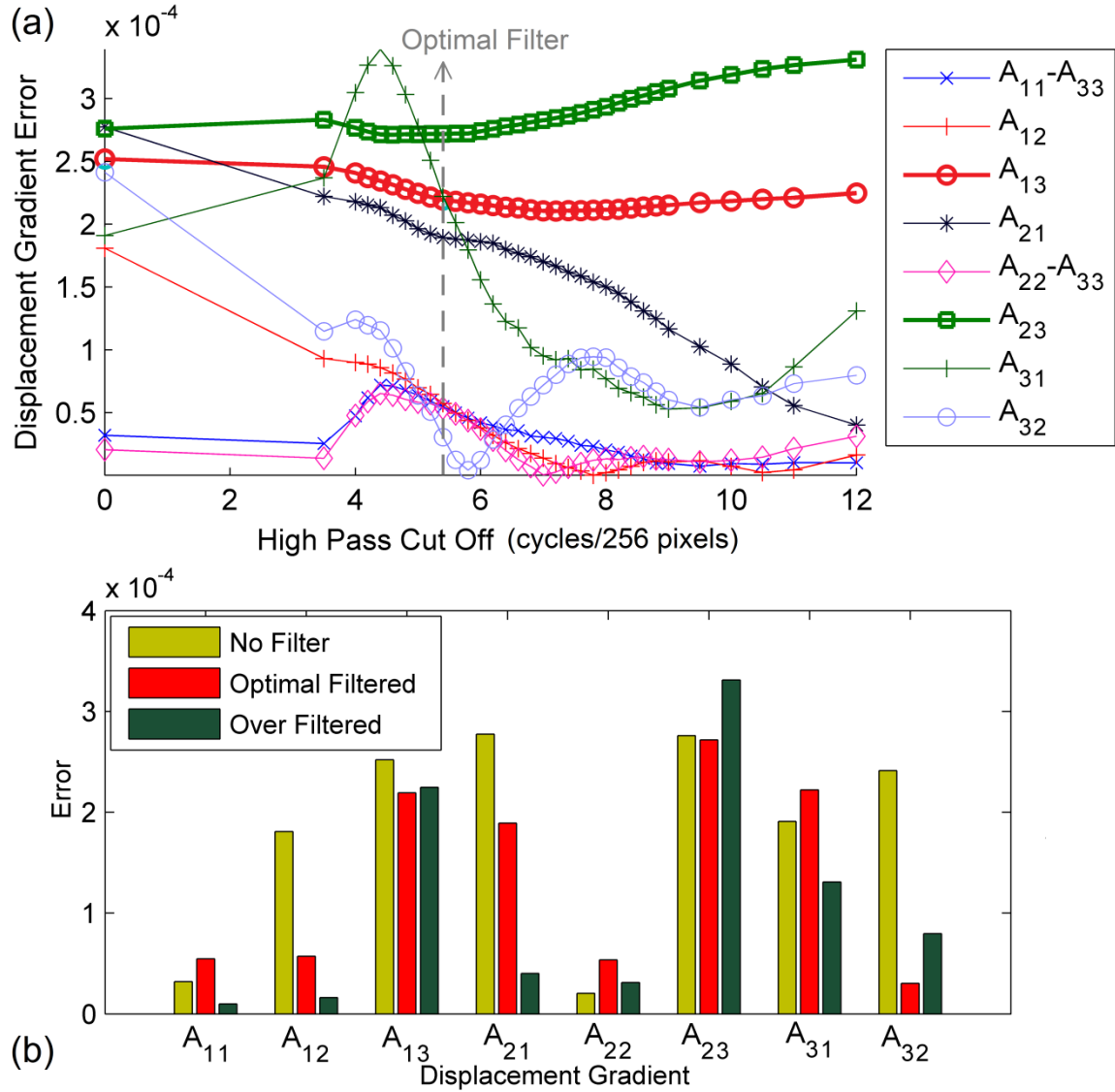


Figure 22: (a) Magnitude of error in each component of the displacement gradient tensor for different filters. Non-zero components are A_{13} (red circles) and A_{23} (green squares), marked in bold. (b) Bar chart of error in the displacement gradient tensor components for no filtering, optimal filtering, and over-filtering. 70% reference intensity modelled as 16nm from grain boundary.

Actual error in the displacement gradient tensor is given by magnitude of the difference between the measured displacement gradients, $A^{measured}$, and the displacement gradients caused by the imposed pixel shift $A^{imposed}$.

$$Actual\ Error = |A^{measured} - A^{imposed}|$$

Equation 8

The effect of pattern overlap on the accuracy of high resolution electron backscatter diffraction measurements

Figure 22(a) shows that for components of the displacement gradient tensor with an actual solution of zero, over-filtering generally decreases the measurement error. For components A_{13} (red circles) and A_{23} (green squares), which have a non-zero actual solution, the error is minimum at a high pass cut off between 4 (A_{23}) and 8 (A_{13}). This is the optimum filter set-up.

As seen in Figure 22(b), for all components the error in the displacement gradient tensor is below 3×10^{-4} at optimal filtering. For all components except A_{11} and A_{31} , appropriate filtering increases the accuracy of the displacement gradient tensor measurements, though the gains are sometimes rather modest.

3.3.2.2.2 Random error from ROI positioning

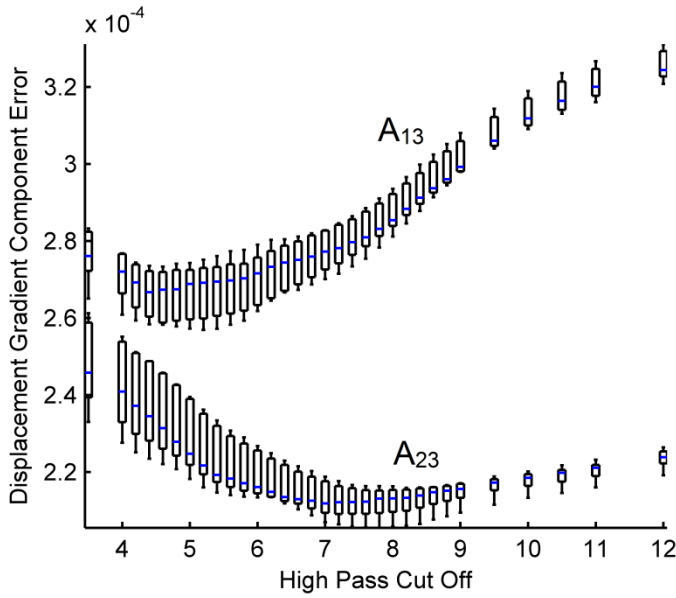


Figure 23: box and whisker plot showing the variation in displacement gradient error varying with ROI location (the box shows the mean, 75% and 25% range; the whiskers show the total range).

Even when using 200 ROIs, error in the displacement gradient tensor components can vary by up to 1.5×10^{-5} depending on where the ROI are placed (this problem is seeded always with 1 ROI in the centre, 19 in a ring in the EBSD, and the rest using the random number generator in MATLAB). Figure 23 shows the spread in error of the non-zero displacement gradient tensor components A_{13} and A_{23} , after five separate measurements. The minima in error are between 4 and 5 for A_{13} and between 7 and 8 for A_{23} , consistent with the minima in error shown in Figure 22(a).

3.3.3 Generalisation to many grain boundaries

The previous results have shown a detailed analysis of one particular grain boundary. The following section repeats the same analysis for different grain boundaries, simulated by mixing patterns from different grain interiors. The error metric used is the actual shift error as defined in Equation 6, and this is plotted as the blue line ('Actual error') in Figure 19.

Cross-correlation was performed on 210 simulated grain boundaries, and pattern shift errors obtained from the imposed and measured pattern translations. The mean pixel shift accuracy as the interaction volume approaches a grain boundary is given in Figure 24 for unfiltered patterns. The blue dashed lines (labelled $0.1\epsilon_y$ and 18nm) show the threshold for significant strain error in HR-EBSD measurements, or one tenth of the yield strain ϵ_y for most metals ($\epsilon_y = 2 \times 10^{-3}$, so $0.1\epsilon_y = 2 \times 10^{-4}$).

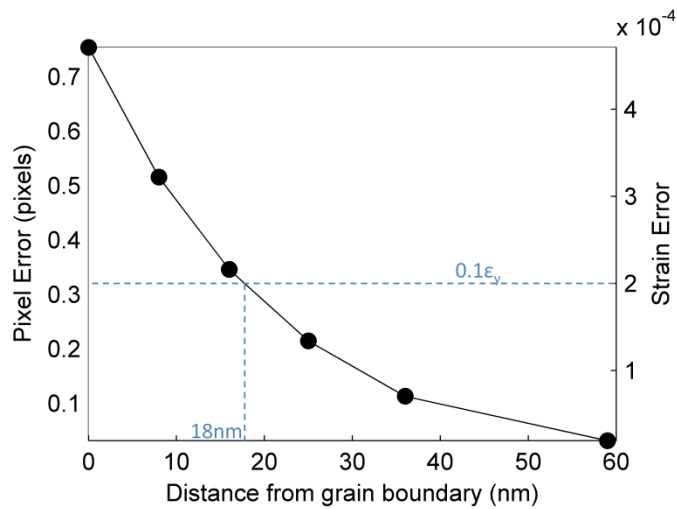


Figure 24: average pixel shift and strain errors as the interaction volume approaches a grain boundary (unfiltered patterns)

Figure 24 shows that the pixel shift error is small (0.03 pixels) when there is no pattern overlap and increases to 0.75 pixels at the grain boundary (50% reference intensity). The strain error can be linked to pixel error by Equation 9, from Britton et al. [128]:

The effect of pattern overlap on the accuracy of high resolution electron backscatter diffraction measurements

$$\text{Strain error} = \frac{m \times \text{Pixel Error}}{\text{Image Width}}$$

Equation 9

The resolution figure of merit m ranges between 0.4 and 1 depending on camera geometry, and a smaller value indicates better accuracy. Since m was not measured directly in this case, a conservative estimate of 1 was used and the image width here was 1600 pixels. Using these values, Equation 9 has been used to generate the second Y axis displaying strain error in Figure 24.

Histograms of the distributions of shift errors at 59nm (no mixing) and 16nm (70% reference intensity) from the grain boundary are shown in Figure 25.

Figure 25(a) shows the noise floor of HR-EBSD, obtained by correlating unmixed patterns. The mean value is 0.0313 pixels. Figure 25(b) shows the distribution of errors with high pass cut offs of 0, 5.4 and 12 cycles/256 pixels, corresponding to no filter, optimal filtered, and over filtered patterns respectively.

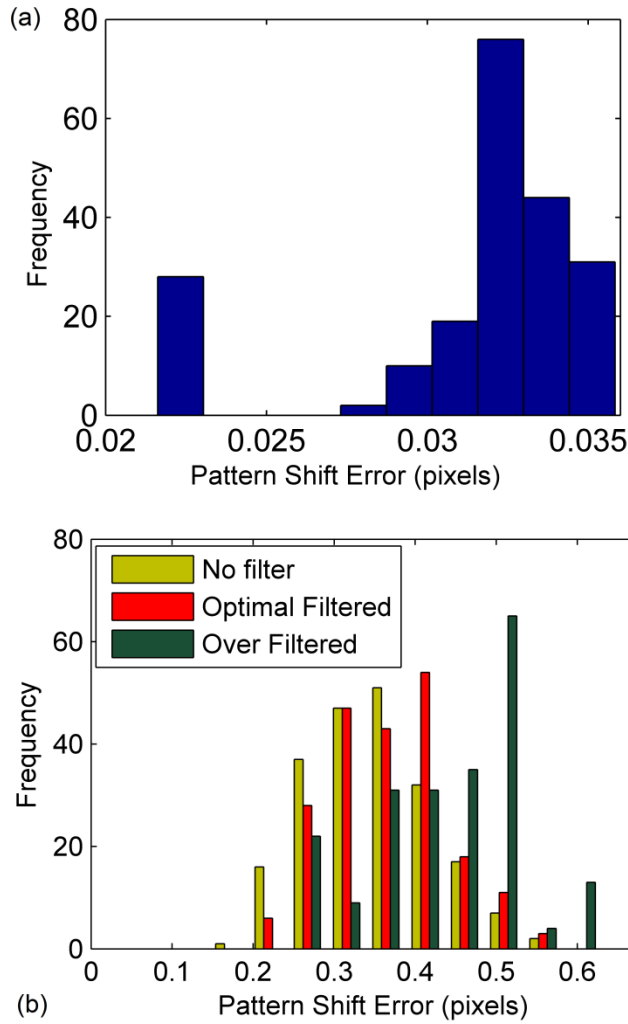


Figure 25: (a) histogram of pattern shift errors for patterns with no overlap – noise floor of HR-EBSD technique. (b) histogram of pattern shift errors for 70% reference mixed patterns (16nm from grain boundary) for different filters.

The histogram in Figure 25(b) shows that accuracy at 70% reference intensity, or 16nm from the boundary, is similar between unfiltered and optimal filtered patterns (any difference is around the noise floor of HR-EBSD, shown in Figure 25(a)). Over-filtering patterns significantly increases error.

3.3.4 Statistical likelihood of overlap

Now that the error associated with pattern overlap has been measured in Figure 24, it is important to consider how often pattern overlap occurs, and the degree of overlap when it occurs.

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Figure 26(a) shows a simulated microstructure of 50 grains in a 500 μm by 500 μm box constructed using Voronoi tessellation and seeded with the random number generator in MATLAB, producing a microstructure with an average grain size of 10 μm .

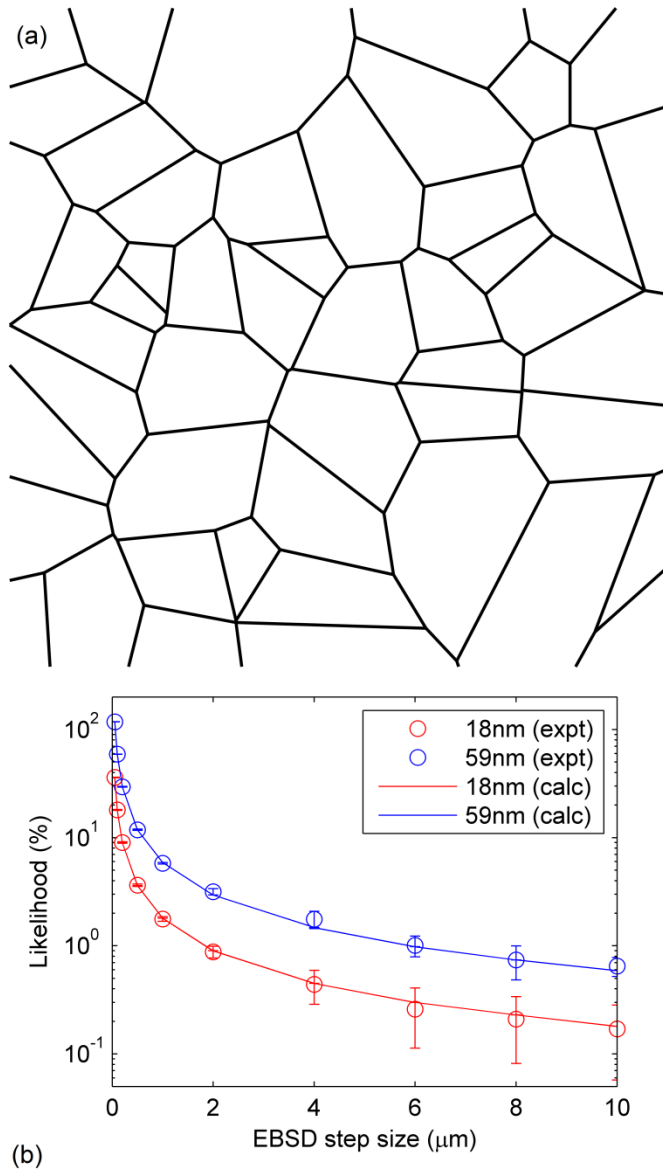


Figure 26: (a) test microstructure used to calculate the fraction of points near a grain boundary with pattern overlap. (b) probability of a point near a grain boundary with pattern overlap (blue) or significant strain error (red).

Grids of points at step sizes of 10, 8, 6, 4, 2, 1, 0.5, and 0.2 μm were overlaid on the microstructure and the Euclidean distances from each point to the nearest grain boundary calculated. If we consider only those points in the map that are within one step of a grain boundary we can then determine the fraction of grain boundary points that are within a threshold distance, sufficiently close for various

extents of pattern overlap to occur. When the step size is less than the chosen threshold distance from the grain boundary, then the region within 1 step of the boundary will always contain at least 1 point within the threshold distance.

Given the simple model of the interaction volume the pattern overlap begins when the incident beam is at 59nm from the grain boundary and the upper blue line in Figure 26(b) shows the likelihood of grain boundary points showing any degree of pattern overlap. Figure 14 shows that strain errors of 2×10^{-4} are generated by pattern overlap when the incident beam is 18nm from the boundary. The lower red line in Figure 26(b) shows the fraction of grain boundary points expected to fall within 18nm of the boundary and thus have sufficient pattern overlap to cause significant strain error. These fractions were found to follow the relation in Equation 10.

Each grid was displaced from itself ten times and the fraction of points within the threshold distances of 18nm and 59nm counted. This produced a spread in the results. Average values are plotted as circles in Figure 26(b) and error bars represent 1 standard deviation in the distribution.

$$\text{Likelihood}(d < x) = \frac{x}{\text{step size}} \quad \begin{array}{l} x = \text{threshold distance} \\ d = \text{distance from boundary} \end{array}$$

Equation 10

For a $0.2 \mu\text{m}$ step size, 30% of points that are already within 1 step of the grain boundary will have some pattern overlap, but only 9% of points will have significant strain error associated with the pattern overlap. This percentage varies with the step size according to Equation 10.

3.4 Discussion

Two diffraction patterns from grain interiors were mixed at different ratios to simulate pattern overlap, and cross-correlation was performed on the mixed patterns using the unmixed pattern as reference. The results show that a zero pattern shift peak develops in the XCF at large high pass cut off frequencies and the onset of this was used to determine an optimal filter. Pixel shift and strain

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accuracy of HR-EBSD were measured as a function of reference pattern intensity which was connected through a simple and approximate model to the distance of the incident beam from the grain boundary.

3.4.1 Effect of filtering

To optimise measurement of image shifts using cross correlation (i.e. for elastic strain measurement) typical upsampling methods require sufficient information within the peak to identify the 'best' shift with sub-pixel interpolation. This drives towards an optimal peak shape that is round and not too sharp. Figure 16 shows that the ideal peak shapes can be formed with appropriate high pass filtering, with cut off frequencies between 4 and 8 cycles/256 pixels. Less filtering results in blurry peaks and over-filtering results in very sharp peaks. Both of these situations are not ideal for interpolation of the exact peak position.

It can be difficult to determine the best filtering conditions, as in practice high-precision can be obtained through over-filtering where all useful information in the pattern is removed such that a prominent zero peak appears (Figure 16) and the mean angular error reduces (Figure 19) toward zero.

Figure 19 shows that accuracy is limited by over-filtering, even though precision improves at large filter cut offs. Therefore choosing an appropriate filtering condition to ensure accuracy, when the absolute strain between two patterns is unknown, can be explored using pattern translation. Here the optimal filter cut off is determined to be just before the onset of the zero peak in Figure 17, at 5.4 cycles/256 pixels.

3.4.2 Effect of mixing

Figure 20 shows that even for an optimal filter, accuracy is limited when the mixing fraction increases to less than 70% of the reference pattern, modelled here as 16nm from the grain boundary.

In practice, the presence of a clear XCF peak shape in Figure 18 does not necessarily mean that the correct XCF has been identified. Near grain boundaries, the XCF should be computed for both potential reference grains and the XCF with the higher peak height preferred. Care should be taken to use the same filter setting, since increasing the high pass cut off increases the peak height.

3.4.3 Errors

Only the non-zero components of the displacement gradient tensor have been used to determine the optimal filter (bold lines in Figure 22(a)). It is not helpful to include the zero components of the displacement gradient tensor in treatment of errors, since they generally tend towards zero when the ROI is over-filtered (Figure 21). These measurements tend towards the correct solution due to the false zero peak, even though accuracy of the XCF shift measurement at large high pass cut offs is worse.

The minima in error of displacement gradient components A_{13} and A_{23} are at high pass cut offs of around 8 and 4 cycles/256 pixels respectively. This confirms that an optimal filter cut off of ~ 5.4 is appropriate, since it is in between these two values.

MAE measures the internal consistency and not the accuracy of the displacement gradient solution. In the case of mixed patterns, Figure 19 shows that over-filtering decreases the accuracy, but increases the consistency only because the pattern shifts are drawn towards the false zero displacement peaks and hence towards a displacement gradient tensor with a smaller norm. Therefore, MAE is not a good error metric to determine the best filter settings (note that MAE is still indicative of whether the shifts relate to a consistent deformation gradient between the two patterns and is therefore useful).

Random errors in the displacement gradient tensor (Figure 23) are small ($< 1.5 \times 10^{-5}$), and decrease with increasing filtering to large high pass cut offs. In this case, they do not affect the choice of

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optimal filter (position of the minima in displacement gradient tensor components), and therefore multiple measurements are not needed to determine the optimal filter.

3.4.4 Likelihood of problematic overlap in a typical HR-EBSD scan

Although Figure 19 shows that the accuracy in XCF shift is in some cases improved by filtering, Figure 25(b) shows that this is not generally true. The accuracy can be improved in some patterns, as shown by the minima in the actual error in Figure 19. Therefore, high pass filters should not be used in HR-EBSD if the patterns are already background corrected. In the case where patterns are not background corrected, a high pass filter can be used to remove the background.

Figure 24 shows that strain error caused by pattern overlap 18nm from the boundary is 2×10^{-4} , and increases as the interaction volume approaches the grain boundary. The noise level for EBSD strain measurements within the grain interior varies somewhat with pattern acquisition settings but is typically at the $\sim 10^{-4}$ level. Thus it is only when the incident beam is closer than 18nm to the grain boundary that pattern overlap may appreciably affect errors in the measurement. The yield strain for most metals is 2×10^{-3} , one order of magnitude higher. Therefore, elastic strains can be measured accurately up to 18nm from the grain boundary.

The physical conversion of the intensity ratio in the overlapped region corresponds to 18nm in this material (Zircaloy-4) and the microscope settings used here. In this case, the volume has been conservatively approximated by scanning the beam at a 40° incident angle to the grain boundary and a simple hemisphere model has been used to extract the equivalent interaction volume radius. The backscattered interaction volume radius decreases with increasing atomic number. The equivalent extent of pattern mixing (72% reference intensity) is general and can be calculated for each material, using the pattern intensity mixing approach shown in Section 3.2.3.

In practice the quality of diffraction patterns may locally decrease due to increase in microstructural heterogeneity towards the grain boundary interface especially in plastically deformed samples. This

breaks the local symmetry of the crystal and blurs the diffraction bands, thus reducing the quality of the cross correlation process. Typical HR-EBSD studies include a normalised peak height measurement which can be used as a direct thresholding tool. In cases where accurate measurement of the strain and rotation gradients for particular grain boundaries is important, the effect of pattern overlap alone can be understood through simple mixing experiments as proposed here and as pattern simulation tools improve (taking into account full intensity distributions, optical noise and distortions from the capture system, as well as defect populations) it is likely confidence in these measurements will continue to improve.

Since the distance of a point from the grain boundary cannot be measured directly from the discrete sampling of an EBSD scan, points with large strain error cannot be identified. Therefore, the fraction of points <18nm from a boundary should ideally be as low as possible. Figure 26(b) shows that in an EBSD scan with a small step size of 0.2 μ m, only 9% of points within one step of a grain boundary are also within 18nm from the boundary, and therefore exhibit pattern overlap leading to significant strain error, and this percentage decreases with increasing step size.

There have been several studies using cross-correlation-based EBSD to measure stresses and lattice rotation near grain boundaries. Hotspots in geometrically necessary dislocation density distributions have been shown to occur near grain boundaries after plastic deformation of Cu [95], [143], and Ti-6Al-4V polycrystals [147]. Similarly a propensity for higher residual stresses near grain boundaries in deformed Cu has been observed [148], and more detailed analysis have been made of local stress intensities near grain boundaries that block slip bands in Ti [100], [101]. In each of these cases the step size was relatively large compared to the expected interaction volume dimensions and the local stress features typically persisted beyond just the nearest pixels to the grain boundaries. The work reported here confirms that pattern overlap does not significantly alter any of the results or conclusions drawn in these works. Work by Nacke et al. [115] has reported very fine scan step (5nm) measurements of lattice strains measured close to different boundary types in Si. The

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measurements they made at 10kV and 10nA in a region extending 50nm on either side of the boundary exhibited pattern overlap and so was excluded in their presented results. Our analysis suggests that data could have been included from regions somewhat closer to these boundaries despite the pattern overlap.

3.5 Summary

Pattern overlap affects elastic strain measurement accuracy within 18nm of the grain boundary for this EBSD setup (Zircaloy-4 sample, 20kV, 10.5nA beam, Zeiss Auriga field emission gun SEM with Bruker eFlashHR EBSD camera). It is likely that this will vary with material (atomic number, local boundary structure), and microscope settings (emitter type, voltage, probe current, and exposure time).

High pass filtering can have an effect on the XCF shape and generate false zero peaks when images are over-filtered. The high pass filter can sometimes improve accuracy but this is not generally true for background corrected EBSD patterns. Peak height and mean angular error are measures of precision but not accuracy. This work outlines how to determine the accuracy of HR-EBSD near a grain boundary using simple calibration tests.

Statistically speaking pattern overlap is unlikely to create significant artefacts in HR-EBSD measurements at grain boundaries, even at relatively small (0.2 μ m) step size. The use of HR-EBSD to measure residual elastic strains and GND density near boundaries has therefore been validated.

4. New software for EBSD data clean up and identifying special boundaries

4.1 Motivation: twin identification from EBSD maps

Twinning is an important deformation mode in zirconium alloys due to the limited availability of slip systems which allow deformation along the crystallographic c-axis. It is valuable to study slip and twinning behaviour as a function of loading conditions, and the role of stored energy from slip and twinning in nucleation of blocky alpha in Zr. These themes are explored further in Chapter 6 and Chapter 5 respectively. This chapter focusses on the mathematics and algorithms required to obtain this quantitative data about slip and twinning behaviour from EBSD orientation maps.

To study twinning, quantitative information about the twin fraction, shape, size, variant, and type must be obtained. Twins in a sample can be identified by their lenticular shape in polarised light optical or backscatter SEM micrographs, as the different orientation of the twins compared to the parent grains give contrast.

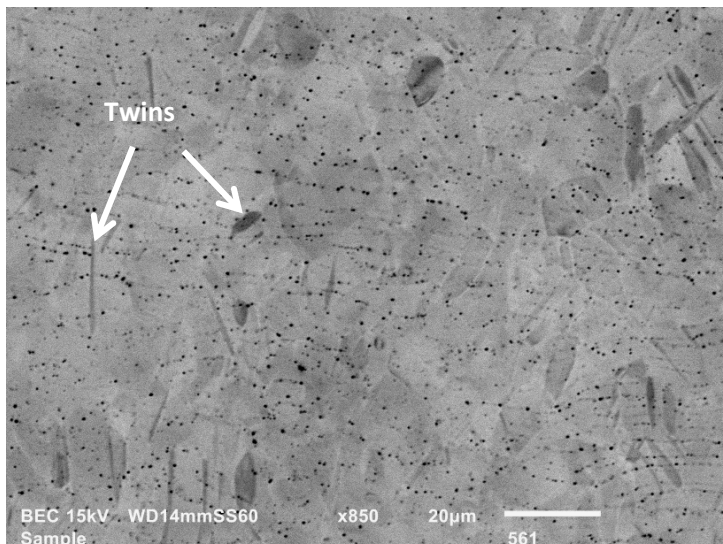


Figure 27: Backscatter electron image showing twins. Dark pits are artefacts from electropolishing.

EBSD allows further characterisation by mapping orientation at each point. Since twins are related to the parent grain by a specific misorientation relationship, the twin type can be identified in addition to the overall twin population. The number of variants of the each twin type activated in a grain can also be identified from the absolute orientations of the twins.

In order to obtain this information from EBSD data, the crystal orientations must be clearly defined, then post-processed to identify grains, grain boundaries, and twin boundaries. These post-processing tools are not available in the used Bruker Esprit EBSD software package [149], and so they are presented in this thesis and coded in 'Matrix Laboratory' (MATLAB) [150]. For this work, the crystal orientations are exported as a text file and manipulated within MATLAB, and care must be taken to describe the orientation correctly from the exported data. A tutorial outlining how to define and handle crystal orientations can be found in Reference [151].

This chapter outlines the mathematics of how to produce statistically relevant analyses of the twin populations, and intragranular misorientation maps to explore the effect of constrained slip in polycrystals, from a map of crystal orientations. Grain identification and data clean up algorithms are employed to correct noisy or missing data at grain boundaries. As this software is written in-house, it is valuable to describe the algorithms used explicitly, even though none of the maths is new and some of these tools may be available in software from other EBSD vendors [152].

4.2 Defining orientations in EBSD

4.2.1 Some representations of orientation

An orientation is a rotation with respect to a set of orthogonal reference axes, in the same way a position vector is a vector which starts at the origin. The reference axes usually align with either the crystal unit cell or the sample processing axes (e.g. normal, rolling, transverse directions in rolled plate). Misorientation between two orientations is the rotation needed to transform from one orientation to another.

All orientations are rigid body rotations with respect to the reference axes, belonging to the $SO(3)$ group of transformations. Any $SO(3)$ transformation has three degrees of freedom: one degree for the rotation angle and two for the rotation axis [153]. They can be represented in several equivalent ways, including Bunge-Euler angles, rotation matrices, axis-angle pairs, quaternions, and Rodrigues vectors.

4.2.2 Bunge-Euler angles

Euler angles combine three rotations about reference axes (x, y, z) to map an arbitrary rotation to new axes (X, Y, Z) . The reference axes (x, y, z) must be orthogonal and right handed. In the Bunge convention they are generally represented as $(\varphi_1, \Phi, \varphi_2)$. The order of rotation is important. First, the reference axes are rotated by φ_1 about the reference z -axis, then rotated by Φ about the reference x -axis, and finally rotated by φ_2 about the new Z -axis of the rotated orientation.

4.2.3 Rotation matrices

A rotation matrix $\mathbf{G}$ is an operator which, when multiplied to a vector, rotates a vector without changing its length or position. Therefore it must have a determinant of 1 (no volume change) and its inverse is equivalent to its transpose (orthogonal matrix).

The rotation matrix operator is pre-multiplied to a column vector for a passive rotation, and post-multiplied to a row vector for an active rotation. A passive rotation rotates reference axes about a stationary vector, whereas an active rotation rotates a vector about stationary reference axes. They are effectively the same rotation in opposite senses.

A passive rotation in two dimensions is shown in Figure 28. The reference (blue) axes (x, y) are rotated about the origin by angle θ to map unit vector $\hat{a}$ onto the new (red) axes (u, v) .

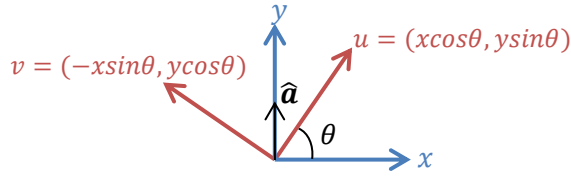


Figure 28: Diagram showing passive rotation of reference axes and a unit vector.

The relationship between (x, y) and (u, v) is the rotation matrix shown in Equation 11.

$$\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}$$

$$\mathbf{G} = \begin{pmatrix} \cos\theta & \sin\theta \\ -\sin\theta & \cos\theta \end{pmatrix}$$

Equation 11: Rotation matrix in 2D.

This can be trivially extruded to three dimensions, and the equivalent 3D rotation about z , were a right handed (out of page) z -axis to be added, is given in Equation 12. w maps directly onto z as the z -axis components do not change, and u and v do not contain a z -component.

$$\begin{pmatrix} u \\ v \\ w \end{pmatrix} = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$

$$\mathbf{G} = \begin{pmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Equation 12: Rotation matrix in 3D about the z -axis.

Different rotations about any of the three reference axes can be multiplied to create an arbitrary rotation, such as using Euler angles (see also Section 4.4.1). The order of operation is from right to left for a passive rotation, and left to right for an active rotation. This is important since matrix multiplication is non-commutative.

4.2.4 Axis-angle pairs

Another representation of a rotation or an orientation is a single rotation about an arbitrary axis, described as a unit vector. This is called an axis-angle pair (Equation 13). The rotation angle is related to the diagonal terms of a rotation matrix, and the rotation axis is related to the off-diagonal terms.

A more in-depth treatment, including the conversion between axis-angle pairs and rotation matrices, is given in Chapter 1.3.3 of Reference [153].

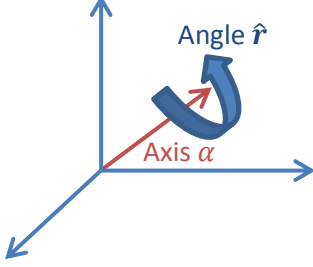


Figure 29: Axis-angle representation of a rotation.

The axis-angle pair represents a rotation R as:

$$R = (\alpha, \hat{r})$$

Equation 13: Axis-angle pair representation of a rotation.

4.2.5 Quaternions

Rotation quaternions (Equation 14) take an axis-angle pair $(\alpha, \hat{r})$ and scale the angle by $\cos \frac{\alpha}{2}$ and the axis by $\sin \frac{\alpha}{2}$. Quaternion representations of $SO(3)$ group are always of unit length, and can be written in vector-like notation using three mutually orthogonal basis quaternions $\mathbf{i}, \mathbf{j}, \mathbf{k}$. They have several other properties useful for orientation maths which are explored in more detail in Section 4.3 and Section 4.4.

$$q = [q_0; q_1, q_2, q_3] \equiv q_0 + q_1 \mathbf{i} + q_2 \mathbf{j} + q_3 \mathbf{k}$$

where

$$q_0 = \cos \frac{\alpha}{2} \text{ and } \begin{pmatrix} q_1 \\ q_2 \\ q_3 \end{pmatrix} = \hat{r} \sin \frac{\alpha}{2}$$

and

$$|q|^2 = q_0^2 + |\mathbf{q}|^2 = 1$$

Equation 14: Quaternion representation of a rotation and its relation to the axis-angle pair.

4.2.6 Rodrigues vectors

Rodrigues vectors (Equation 15) are similar to axis-angle pairs and quaternions, except that the scaling factor from the axis-angle pair is not by $\cos\frac{\alpha}{2}$ or $\sin\frac{\alpha}{2}$, but instead by $\tan\frac{\alpha}{2}$. A detailed explanation of Rodrigues vectors are given in References [154], [155].

$$\begin{pmatrix} RV_1 \\ RV_2 \\ RV_3 \end{pmatrix} = \hat{r} \tan \frac{\alpha}{2}$$

Equation 15: Rodrigues vector representation of a rotation and its relation to the axis-angle pair.

4.2.7 Advantages and disadvantages of different representations

Having defined each method of representing rotations and therefore orientation, the advantages and disadvantages for each of these methods are outlined in Table 4. Based on this, quaternions have been chosen as the main representation of orientation in the rest of this work.

Representation	Advantages	Disadvantages
Euler angles	Efficient to store – no information redundancy Computationally efficient - rotation of a 3D vector requires 27 scalar multiplication operations and 18 addition operations.	Difficult to visualise, interpolate or directly calculate misorientation, prone to rounding errors Gimbal lock – rotational degrees of freedom are lost with certain rotation combinations, when one or more of the rotation matrices in Equation 21 results in an identity matrix [156] Non-uniform sampling of SO(3) space – 1° steps in e.g. Φ does not create uniform rotation steps, especially approaching $\Phi = 0^\circ$ and $\Phi = 180^\circ$
Orientation matrix	Easy to understand and split into components Computationally efficient – rotation of a 3D vector requires 27 scalar multiplication operations and 18 addition operations, equivalent to using Euler angles Easy regularisation of floating point errors – set determinant to 1	Redundancy in information – need to store nine variables, only three of which are independent Degree of misorientation not immediately obvious between any two orientation matrices Orientations related by crystal symmetry not obvious by inspection

Axis-angle pairs	Easily visualised Relatively efficient to store – 1 redundant term	Mathematical manipulation usually requires going through other representations, e.g. orientation matrix or quaternions
Rodrigues vector	Efficient to store – no information redundancy Easy to convert between Rodrigues vector and Euler angles [155]	Lack of redundancy means rounding errors cannot be identified and corrected, leading to accumulation of floating-point errors in successive rotations
Quaternion	Relatively efficient to store – 1 redundant term which allows regularisation to correct floating point errors Can efficiently interpolate between orientations using spherical linear interpolation (SLERP) or spherical spline interpolation (SQUAD) algorithms [156], [157] Easy to estimate mean orientation of a group of orientations – simply the arithmetic mean of the terms [158] Quaternions related by crystal symmetry operators can be easily identified by inspection Misorientation angle is simple to calculate ($\angle(p, q) = 2 \cos^{-1}(\sum p_i q_i)$) allowing similarity of orientations to be quickly judged. (Note: this calculates the misorientation angle only. Full quaternion multiplication is needed to calculate the misorientation axis as well.)	Computationally less efficient than using orientation matrices or Euler angles – rotation of a 3D vector requires 32 scalar multiplication operations and 24 addition operations

Table 4: Advantages and disadvantages of representing orientation with different methods.

4.3 Some mathematical properties of quaternions

In the present work, quaternions have been chosen as the main representation used to store and calculate orientations. This is for its relatively low memory use compared to orientation matrices, easy correction of floating point errors after successive operations compared to Rodrigues vectors, and easy relation of twin misorientation quaternions to the twinning shear plane normal and the angle between the $\langle c \rangle$ -axes of the twin and parent. Therefore it is important to know some of the

basic properties and operations of quaternions. Equations 16-20 are taken from Reference [156], which also provides a more detailed mathematical treatment of quaternion algebra.

4.3.1 Conjugate of a quaternion

The conjugate of a quaternion q is denoted q^* . It can be obtained by reversing the direction of the rotation axis. This is also equivalent to performing a negative rotation along the same axis.

$$q^* = [q_0; -q_1, -q_2, -q_3] = [-q_0; q_1, q_2, q_3]$$

Equation 16: The conjugate of a quaternion.

4.3.2 Quaternion multiplication

The multiplication of quaternions comes from the relationships between the basis quaternions i, j, k , shown in Equation 17.

$$q = q_0 + iq_1 + jq_2 + kq_3$$

$$i^2 = j^2 = k^2 = ijk = -1$$

Equation 17: Multiplication of the basis quaternions.

Multiplication of two quaternions, p and q , is performed as in Equation 18. The quaternion multiplication operator is denoted $\times_q$. This operation is non-commutative, i.e. $p \times_q q \neq q \times_q p$.

$$\begin{bmatrix} p_0 \\ p_1 \\ p_2 \\ p_3 \end{bmatrix} \times_q \begin{bmatrix} q_0 \\ q_1 \\ q_2 \\ q_3 \end{bmatrix} = \begin{bmatrix} p_0q_0 - p_1q_1 - p_2q_2 - p_3q_3 \\ p_0q_1 + p_1q_0 + p_2q_3 - p_3q_2 \\ p_0q_2 - p_1q_3 + p_2q_0 + p_3q_1 \\ p_0q_3 + p_1q_2 - p_2q_1 + p_3q_0 \end{bmatrix}$$

Equation 18: Quaternion multiplication method.

The same operation can be used to multiply a quaternion by a vector, where the vector is treated as a quaternion with a zero q_0 component. Note that the product of a quaternion and a vector is not necessarily a vector.

4.3.3 Rotation of a vector by a quaternion

The vector $\mathbf{v}$ can be rotated by a quaternion q to obtain $\mathbf{v}_{rot}$ for either a passive or active rotation (Equation 19). Active and passive rotations are equivalent rotations of opposite sign.

$\mathbf{v}_{rot} = q \times_q \mathbf{v} \times_q q^*$ for an active rotation (rotating the vector in the reference axes)

$\mathbf{v}_{rot} = q^* \times_q \mathbf{v} \times_q q$ for an passive rotation (rotating the reference axes around the vector)

Equation 19: Rotating a vector by a quaternion.

4.3.4 Misorientations and disorientation between two quaternions

The misorientation quaternion between two quaternions, p and q , can be calculated by multiplying p by q^* (Equation 20, see also Equation 16 for definition of q^*).

$$\Delta(p, q) = p \times_q q^*$$

Equation 20: Calculating misorientation between two quaternions.

If there are symmetries in the crystal orientations, the disorientation (minimum misorientation angle when crystal symmetries are taken into account) can be calculated by applying the relevant symmetry operators to either p or q , then looking up the minimum value of all the permutations of the misorientation. In the HCP crystal system, there are twelve symmetries for each orientation, so that the disorientation should be calculated from twelve possible misorientations.

The 24 cubic symmetry operators in quaternion representation are given in Reference [153]. The twelve hexagonal symmetry operators are given in Table 5. They are obtained by rotating the two quaternions $[\pm q_0; q_1, q_2, q_3]$ six times each, in 60° increments about the Cartesian $[0,0,1]$ axis. The rotation quaternion for this axis-angle pair is $[\frac{\sqrt{3}}{2}; 0,0,\frac{1}{2}]$. It does not matter whether an active or passive rotation is used. As rows (4)-(12) are positive and negative permutations of the terms in rows (1)-(3), it is easy to see by inspection whether two quaternions are related by symmetry, after only relatively few operations.

(1)	q_0	q_1	q_2	q_3
(2)	$\frac{q_3}{2} + \frac{\sqrt{3}}{2} q_0$	$\frac{q_2}{2} + \frac{\sqrt{3}}{2} q_1$	$-\frac{q_1}{2} + \frac{\sqrt{3}}{2} q_2$	$-\frac{q_0}{2} + \frac{\sqrt{3}}{2} q_3$
(3)	$-\frac{q_0}{2} - \frac{\sqrt{3}}{2} q_3$	$-\frac{q_1}{2} - \frac{\sqrt{3}}{2} q_2$	$-\frac{q_2}{2} + \frac{\sqrt{3}}{2} q_1$	$-\frac{q_3}{2} + \frac{\sqrt{3}}{2} q_0$
(4)	$-q_3$	$-q_2$	q_1	q_0
(5)	$\frac{q_0}{2} - \frac{\sqrt{3}}{2} q_3$	$\frac{q_1}{2} - \frac{\sqrt{3}}{2} q_2$	$\frac{q_2}{2} + \frac{\sqrt{3}}{2} q_1$	$\frac{q_3}{2} + \frac{\sqrt{3}}{2} q_0$
(6)	$-\frac{q_3}{2} + \frac{\sqrt{3}}{2} q_0$	$-\frac{q_2}{2} + \frac{\sqrt{3}}{2} q_1$	$\frac{q_1}{2} + \frac{\sqrt{3}}{2} q_2$	$\frac{q_0}{2} + \frac{\sqrt{3}}{2} q_3$
(7)	$-q_1$	q_0	$-q_3$	$-q_2$
(8)	$-\frac{q_2}{2} - \frac{\sqrt{3}}{2} q_1$	$\frac{q_3}{2} + \frac{\sqrt{3}}{2} q_0$	$\frac{q_0}{2} - \frac{\sqrt{3}}{2} q_3$	$-\frac{q_1}{2} + \frac{\sqrt{3}}{2} q_2$
(9)	$-\frac{q_1}{2} - \frac{\sqrt{3}}{2} q_2$	$\frac{q_0}{2} + \frac{\sqrt{3}}{2} q_3$	$-\frac{q_3}{2} + \frac{\sqrt{3}}{2} q_0$	$\frac{q_2}{2} - \frac{\sqrt{3}}{2} q_1$
(10)	$-q_2$	q_3	q_0	$-q_1$
(11)	$\frac{q_1}{2} - \frac{\sqrt{3}}{2} q_2$	$-\frac{q_0}{2} + \frac{\sqrt{3}}{2} q_3$	$\frac{q_3}{2} + \frac{\sqrt{3}}{2} q_0$	$-\frac{q_2}{2} - \frac{\sqrt{3}}{2} q_1$
(12)	$\frac{q_2}{2} - \frac{\sqrt{3}}{2} q_1$	$-\frac{q_3}{2} + \frac{\sqrt{3}}{2} q_0$	$-\frac{q_0}{2} - \frac{\sqrt{3}}{2} q_3$	$\frac{q_1}{2} + \frac{\sqrt{3}}{2} q_2$

Table 5: 12 hexagonal symmetry operators in quaternion representation.

4.4 Conversions between representations of orientation

Conversions between Euler angles, orientation matrices, and quaternions are defined in this section.

This is useful for interpreting EBSD data, which are often given as Euler angles to aid data storage efficiency, but are difficult to visualise when comparing orientations. The following sections outline a method of converting of Euler angles into quaternions, using the orientation matrix as an intermediate step.

4.4.1 Conversion from Euler angles to orientation matrix

The overall rotation matrix $\mathbf{G}$ for a passive transformation, using the Bunge convention [151], can be represented as a series of three Euler angle rotations multiplied from right to left:

$$\mathbf{G} = \begin{pmatrix} \cos\varphi_2 & \sin\varphi_2 & 0 \\ -\sin\varphi_2 & \cos\varphi_2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} 1 & 0 & 0 \\ 0 & \cos\Phi & \sin\Phi \\ 0 & -\sin\Phi & \cos\Phi \end{pmatrix} \begin{pmatrix} \cos\varphi_1 & \sin\varphi_1 & 0 \\ -\sin\varphi_1 & \cos\varphi_1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$\mathbf{G} = \begin{pmatrix} \cos\varphi_2 & \sin\varphi_2 & 0 \\ -\sin\varphi_2 & \cos\varphi_2 & 0 \\ 0 & 0 & 1 \end{pmatrix} \begin{pmatrix} \cos\varphi_1 & \sin\varphi_1 & 0 \\ -\cos\Phi\sin\varphi_1 & \cos\Phi\cos\varphi_1 & \sin\Phi \\ \sin\Phi\sin\varphi_1 & -\sin\Phi\cos\varphi_1 & \cos\Phi \end{pmatrix}$$

$$\mathbf{G} = \begin{pmatrix} \cos\varphi_1\cos\varphi_2 - \cos\Phi\sin\varphi_1\sin\varphi_2 & \cos\varphi_2\sin\varphi_1 + \cos\Phi\cos\varphi_1\sin\varphi_2 & \sin\Phi\sin\varphi_2 \\ -\cos\varphi_1\sin\varphi_2 - \cos\Phi\sin\varphi_1\cos\varphi_2 & -\sin\varphi_1\sin\varphi_2 + \cos\Phi\cos\varphi_1\cos\varphi_2 & \sin\Phi\cos\varphi_2 \\ \sin\Phi\sin\varphi_1 & -\sin\Phi\cos\varphi_1 & \cos\Phi \end{pmatrix}$$

Equation 21: The equivalent rotation matrix for an arbitrary rotation defined by three Euler angles in the Bunge X-Z-X convention. This is suitable for the Bruker EBSD system.

4.4.2 Conversion from quaternion to orientation matrix

This conversion algorithm was taken from Reference [159], and the maths has been verified independently by the author.

To convert a quaternion into an orientation matrix, the matrix $\mathbf{G}$ which will perform an equivalent operation to rotating vector $[x, y, z]$ by quaternion q must be found.

$[x', y', z']$ is the vector obtained from performing an active rotation q on initial vector $[x, y, z]$, where $\times_q$ denotes quaternion multiplication (Equation 22, see also Equation 19).

$$\begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = q \times_q \begin{bmatrix} x \\ y \\ z \end{bmatrix} \times_q q^*$$

Equation 22: Conversion from quaternion to orientation matrix – a vector $[x, y, z]$ is rotated by a quaternion.

To multiply a quaternion by a vector, treat the initial vector as a quaternion with a zero angular term q_0 . It is important to not directly substitute zero into the angular term of $[s, x, y, z]$, since a vector multiplied by a quaternion is not necessarily a vector.

$$\begin{bmatrix} 0 \\ x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} q_0 \\ q_1 \\ q_2 \\ q_3 \end{bmatrix} \times_q \begin{bmatrix} s \\ x \\ y \\ z \end{bmatrix} \times_q \begin{bmatrix} q_0 \\ -q_1 \\ -q_2 \\ -q_3 \end{bmatrix}$$

Equation 23: Conversion from quaternion to orientation matrix – the vector is treated as a quaternion.

We can find the operation matrices equivalent to quaternion multiplication from the left and the right of the vector:

$$\begin{bmatrix} s \\ x \\ y \\ z \end{bmatrix} \times_q \begin{bmatrix} q_0 \\ -q_1 \\ -q_2 \\ -q_3 \end{bmatrix} = \begin{bmatrix} q_0s + q_1x + q_2y + q_3z \\ -q_1s + q_0x - q_3y + q_2z \\ -q_2s + q_3x + q_0y - q_1z \\ -q_3s - q_2x + q_1y + q_0z \end{bmatrix} \quad \text{RHS equation}$$

$$\begin{bmatrix} q_0 \\ -q_1 \\ -q_2 \\ -q_3 \end{bmatrix} \times_q \begin{bmatrix} s \\ x \\ y \\ z \end{bmatrix} = \begin{bmatrix} q_0s - q_1x - q_2y - q_3z \\ q_1s + q_0x - q_3y + q_2z \\ q_2s + q_3x + q_0y - q_1z \\ q_3s - q_2x + q_1y + q_0z \end{bmatrix} \quad \text{LHS equation}$$

Equation 24: Conversion from quaternion to orientation matrix – the quaternion multiplication is written out explicitly for pre- and post-multiplication of [s,x,y,z]

The equivalent operations of a 4-by-4 matrix on vector [s; x, y, z] can now be written:

$$\begin{bmatrix} q_0s + q_1x + q_2y + q_3z \\ -q_1s + q_0x - q_3y + q_2z \\ -q_2s + q_3x + q_0y - q_1z \\ -q_3s - q_2x + q_1y + q_0z \end{bmatrix} = \begin{bmatrix} q_0 & q_1 & q_2 & q_3 \\ -q_1 & q_0 & -q_3 & q_2 \\ -q_2 & q_3 & q_0 & -q_1 \\ -q_3 & -q_2 & q_1 & q_0 \end{bmatrix} \begin{bmatrix} s \\ x \\ y \\ z \end{bmatrix} \quad \text{RHS equation}$$

$$RHS = \begin{bmatrix} q_0 & q_1 & q_2 & q_3 \\ -q_1 & q_0 & -q_3 & q_2 \\ -q_2 & q_3 & q_0 & -q_1 \\ -q_3 & -q_2 & q_1 & q_0 \end{bmatrix}$$

$$\begin{bmatrix} q_0s - q_1x - q_2y - q_3z \\ q_1s + q_0x - q_3y + q_2z \\ q_2s + q_3x + q_0y - q_1z \\ q_3s - q_2x + q_1y + q_0z \end{bmatrix} = \begin{bmatrix} q_0 & -q_1 & -q_2 & -q_3 \\ q_1 & q_0 & -q_3 & q_2 \\ q_2 & q_3 & q_0 & -q_1 \\ q_3 & -q_2 & q_1 & q_0 \end{bmatrix} \begin{bmatrix} s \\ x \\ y \\ z \end{bmatrix} \quad \text{LHS equation}$$

$$LHS = \begin{bmatrix} q_0 & -q_1 & -q_2 & -q_3 \\ q_1 & q_0 & -q_3 & q_2 \\ q_2 & q_3 & q_0 & -q_1 \\ q_3 & -q_2 & q_1 & q_0 \end{bmatrix}$$

Equation 25: Conversion from quaternion to orientation matrix – operator matrices from the RHS and LHS equations in Equation 24 are identified.

Now LHS can be matrix multiplied with RHS to obtain the 4 by 4 vector rotation matrix G_q :

$$G_q = LHS \times RHS = \begin{bmatrix} q_0 & -q_1 & -q_2 & -q_3 \\ q_1 & q_0 & -q_3 & q_2 \\ q_2 & q_3 & q_0 & -q_1 \\ q_3 & -q_2 & q_1 & q_0 \end{bmatrix} \begin{bmatrix} q_0 & q_1 & q_2 & q_3 \\ -q_1 & q_0 & -q_3 & q_2 \\ -q_2 & q_3 & q_0 & -q_1 \\ -q_3 & -q_2 & q_1 & q_0 \end{bmatrix}$$

$$= \begin{bmatrix} q_0^2 + q_1^2 + q_2^2 + q_3^2 & 0 & 0 & 0 \\ 0 & q_0^2 + q_1^2 - q_2^2 - q_3^2 & 2q_1q_2 - 2q_0q_3 & 2q_0q_2 + 2q_1q_3 \\ 0 & 2q_0q_3 + 2q_1q_2 & q_0^2 - q_1^2 + q_2^2 - q_3^2 & 2q_2q_3 - 2q_0q_1 \\ 0 & 2q_1q_3 - 2q_0q_2 & 2q_0q_1 + 2q_2q_3 & q_0^2 - q_1^2 - q_2^2 + q_3^2 \end{bmatrix}$$

Equation 26: Conversion from quaternion to orientation matrix – LHS and RHS operators are multiplied to obtain the combined rotation matrix G .

Rigid body rotations are represented by unit quaternions, therefore $q_0^2 + q_1^2 + q_2^2 + q_3^2 = 1$.

This enables simplification of the diagonal terms:

$$\begin{bmatrix} q_0 \\ -q_1 \\ -q_2 \\ -q_3 \end{bmatrix} \times_q \begin{bmatrix} s \\ x \\ y \\ z \end{bmatrix} \times_q \begin{bmatrix} q_0 \\ q_1 \\ q_2 \\ q_3 \end{bmatrix} \equiv \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 - 2(q_2^2 + q_3^2) & 2q_1q_2 - 2q_0q_3 & 2q_0q_2 + 2q_1q_3 \\ 0 & 2q_0q_3 + 2q_1q_2 & 1 - 2(q_1^2 + q_3^2) & 2q_2q_3 - 2q_0q_1 \\ 0 & 2q_1q_3 - 2q_0q_2 & 2q_0q_1 + 2q_2q_3 & 1 - 2(q_1^2 + q_2^2) \end{bmatrix} \begin{bmatrix} s \\ x \\ y \\ z \end{bmatrix}$$

$$G_q \begin{bmatrix} s \\ x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 - 2(q_2^2 + q_3^2) & 2q_1q_2 - 2q_0q_3 & 2q_0q_2 + 2q_1q_3 \\ 0 & 2q_0q_3 + 2q_1q_2 & 1 - 2(q_1^2 + q_3^2) & 2q_2q_3 - 2q_0q_1 \\ 0 & 2q_1q_3 - 2q_0q_2 & 2q_0q_1 + 2q_2q_3 & 1 - 2(q_1^2 + q_2^2) \end{bmatrix} \begin{bmatrix} s \\ x \\ y \\ z \end{bmatrix}$$

Equation 27: Conversion from quaternion to orientation matrix – the G_q matrix obtained in Equation 26 is related back to the initial quaternion rotation in Equation 22.

Equation 27 is a 4 by 4 matrix, and three-dimensional orientation matrices are 3 by 3 matrices. The

first row and column can be taken off by letting $s = 0$, as $[s, x, y, z]$ is not a quaternion but a vector

$[0, x, y, z]$, therefore the 4 by 4 reduces to a 3 by 3 matrix:

$$G \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 - 2(q_2^2 + q_3^2) & 2q_1q_2 - 2q_0q_3 & 2q_0q_2 + 2q_1q_3 \\ 2q_0q_3 + 2q_1q_2 & 1 - 2(q_1^2 + q_3^2) & 2q_2q_3 - 2q_0q_1 \\ 2q_1q_3 - 2q_0q_2 & 2q_0q_1 + 2q_2q_3 & 1 - 2(q_1^2 + q_2^2) \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix}$$

$$\mathbf{G} = \begin{bmatrix} G_{11} & G_{12} & G_{13} \\ G_{21} & G_{22} & G_{23} \\ G_{31} & G_{32} & G_{33} \end{bmatrix} = \begin{bmatrix} 1 - 2(q_2^2 + q_3^2) & 2q_1q_2 - 2q_0q_3 & 2q_0q_2 + 2q_1q_3 \\ 2q_0q_3 + 2q_1q_2 & 1 - 2(q_1^2 + q_3^2) & 2q_2q_3 - 2q_0q_1 \\ 2q_1q_3 - 2q_0q_2 & 2q_0q_1 + 2q_2q_3 & 1 - 2(q_1^2 + q_2^2) \end{bmatrix}$$

Equation 28: Conversion from quaternion to orientation matrix – the $\mathbf{G}_q$ matrix is simplified back into a 3 by 3 matrix $\mathbf{G}$.

4.4.3 Conversion from orientation matrix to quaternion

The equivalent quaternion to a $\mathbf{G}$ matrix can be found by adding the diagonal (trace) terms of the 3 by 3 $\mathbf{G}$ matrix in Equation 28 and solving for the components of q .

$$\text{Trace}(\mathbf{G}) = 3 - 4q_1^2 - 4q_2^2 - 4q_3^2$$

Equation 29: Conversion from orientation matrix to quaternion – solving for q_0 from the diagonal terms of $\mathbf{G}$.

Since $|q|^2 = 1$ for a unit quaternion,

$$\text{Trace}(\mathbf{G}) = 4q_0^2 - 1$$

$$q_0 = \pm \frac{\sqrt{1 + G_{11} + G_{22} + G_{33}}}{2}$$

Equation 30: Conversion from orientation matrix to quaternion – solving for q_0 from the diagonal terms of $\mathbf{G}$.

By subtracting opposite non-diagonal terms and dividing by q_0 , the rest of the quaternion can be calculated:

$$q_1 = \pm \frac{G_{23} - G_{32}}{4q_0}$$

$$q_2 = \pm \frac{G_{31} - G_{13}}{4q_0}$$

$$q_3 = \pm \frac{G_{12} - G_{21}}{4q_0}$$

Equation 31: Conversion from orientation matrix to quaternion – solving for q_1, q_2, q_3 from the off-diagonal terms of $\mathbf{G}$.

$\text{Trace}(\mathbf{G})$ is necessarily greater than -1 for a rotation matrix. However, if it is close to -1, calculating q_1, q_2 and q_3 from the off-diagonal terms would require dividing by a q_0 value close to zero, which could lead to build up of floating point errors. To minimise this error, the highest value

term of q should be calculated by adding or subtracting the diagonal terms of $\mathbf{G}$. Figure 30 shows the process of selecting a method of calculating the quaternions from the orientation matrix [159].

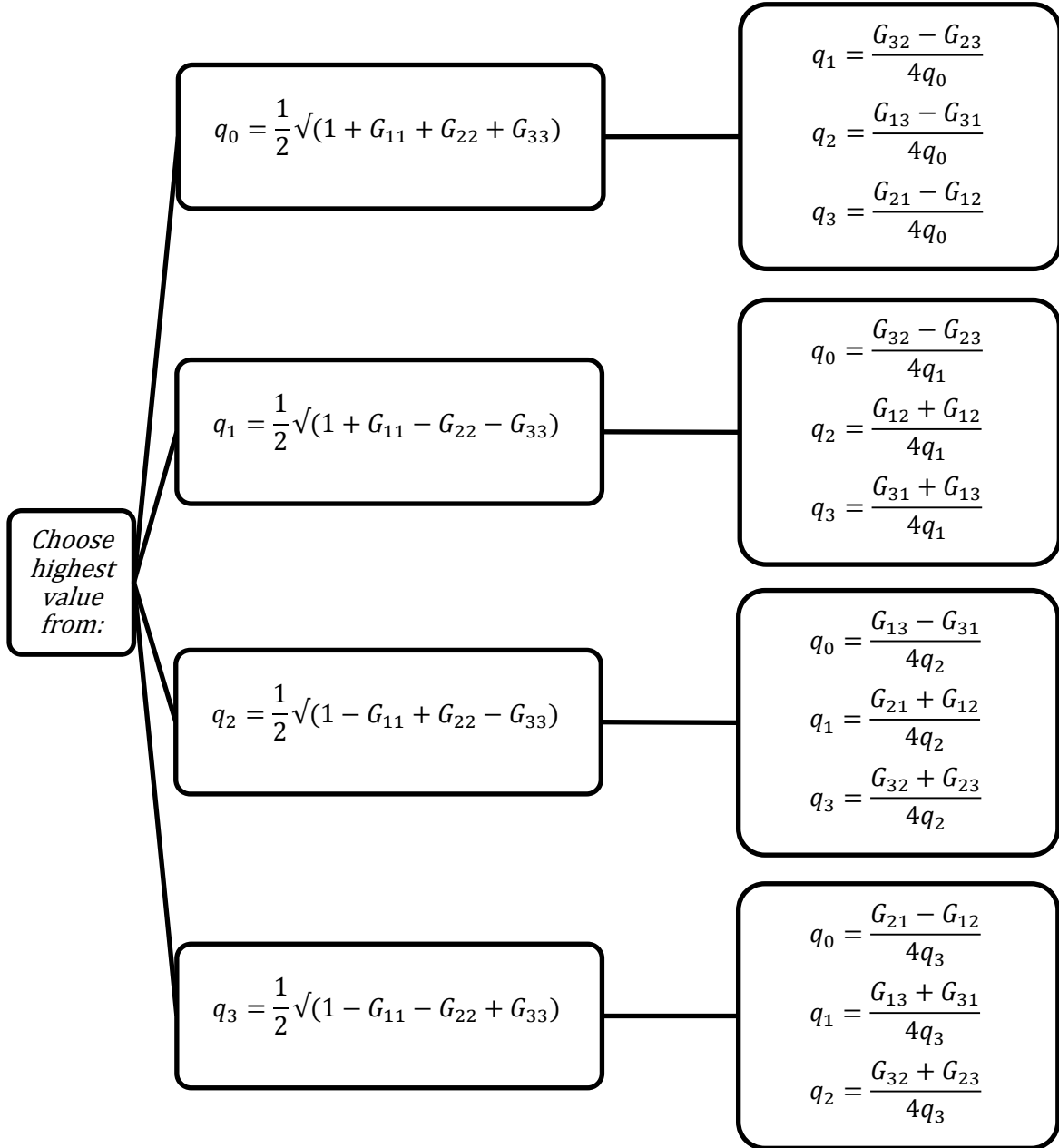


Figure 30 – Conversion from orientation matrix to quaternion – process of selecting highest combination of diagonal terms.

4.5 Grain boundary and special boundary identification

Raw EBSD data does not inherently distinguish between grains, but only produces a grid of orientation points. Grain and grain boundary identification must be performed in the postprocessing stage. In EBSD a grain boundary is observed as a step change in the orientation data between neighbouring points. Special boundaries are also of interest, e.g. twin boundaries or other special coincident site lattice (CSL) boundaries which are important in cubic crystal symmetries. This section outlines algorithms to identify grain boundaries and special orientation relations such as twin boundaries.

4.5.1 Grain boundary identification

The following steps should be taken to identify whether or not a grain boundary lies between two neighbouring EBSD data points:

1. Convert EBSD data, usually given in Euler angles, to quaternion orientations with respect to the sample axes. This process has been outlined in Section 4.4.
2. Calculate the disorientation quaternions between each point and its neighbours. This can be done as an array calculation on EBSD data by padding the data with zero values (grey in Figure 31). Two test arrays can then be created by shifting the points in the test arrays leftwards and upwards respectively. The quaternion disorientation (outlined in Section 4.3.4 and Equation 18) can then be calculated point by point in the array according to Figure 31, such that the disorientations between adjacent data points can be identified.
3. If the disorientation angle between two adjacent points exceeds a threshold angle, this is assigned as a boundary. The threshold angle is user defined and often between 5 and 10°.

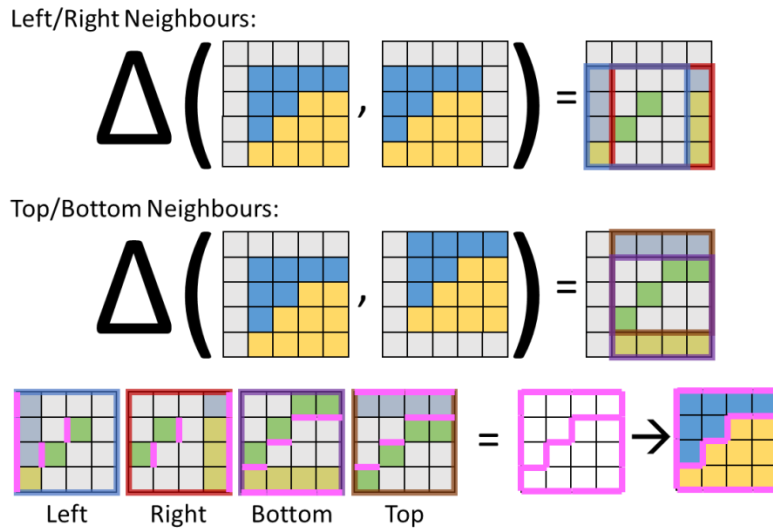


Figure 31: An array of EBSD points are padded with zero values and shifted in different directions to calculate neighbour disorientations.

4.5.2 Special boundary identification

A grain boundary can be identified as a twin boundary by calculating the misorientation angles between the neighbour disorientation data and the ideal twin quaternion misorientation for a specific twin type using Equation 20. For twin boundaries in HCP systems, the neighbour disorientation is close to the misorientation of one of six symmetric twin variants in the HCP crystal system, such that the ‘mis-misorientation’ is below a small threshold angle $\Delta\theta$. The threshold angle can be determined according to the Brandon criterion, $\Delta\theta = 15\Sigma^{-1/2}$ [160], where Σ is the ratio of coincidence sites to lattice sites in CSL theory. It should be noted that twins in HCP are not $\Sigma 3$ CSL boundaries (as they are in cubic systems), but $\Sigma 24$ and $\Sigma 11$ for T1 and T2 zirconium twin types respectively [161]. This means a narrower misorientation deviation from the ideal twin misorientation is allowed by the Brandon criterion. If significant plastic slip has occurred, in either the twin or the parent, post-twinning, the Brandon criterion may have to be relaxed to accommodate for this too. This process should be repeated for each twin type present in the material.

4.5.3 Boundary line reconstruction and grain identification

Using the disorientation data, data points adjacent to grain boundaries can be identified, but reconstructing the boundary line from the boundary points is still not trivial. After the boundary line is reconstructed, points belonging to the same grain can be identified.

To define the boundary line for reconstruction, each point in the EBSD neighbour disorientation map can be assigned a boundary value according to which of its four edges (top, bottom, left, and right) are grain boundaries. This procedure is illustrated in Figure 32.

1. Assign an initial value of 0 to all points on the EBSD map.
2. Grain interiors have a boundary value of 0.
3. If the left edge is a boundary, add 1 to the value of that point.
4. If the right edge is a boundary, add 2 to the value of that point.
5. If the bottom edge is a boundary, add 4 to the value of that point.
6. If the top edge is a boundary, add 8 to the value of that point.

Using powers of two ensures that the boundary lines are unambiguously defined on the EBSD map and enables reconstruction of the separate grains. For reconstruction and identification of special boundaries as well as grain boundaries, further successive powers of two can be used (e.g. if the left edge is a twin boundary, add 16 to the value of that point).

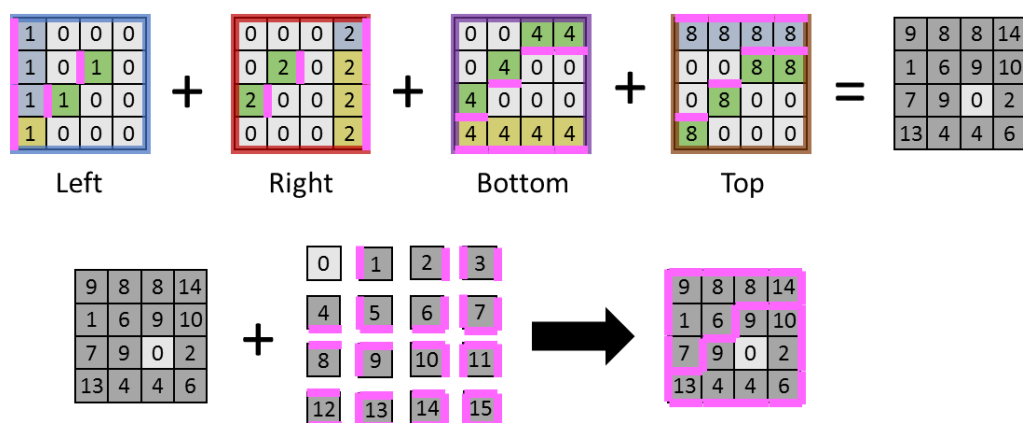


Figure 32: Assignment of boundary values to the disorientation map from an EBSD dataset.

The algorithm used for grain number identification ('grain ID') from a map of boundary values (Figure 32) are outlined below and shown as a schematic flowchart in Figure 33.

1. Identify grain boundary points and corresponding grain boundary values using the boundary detection algorithm in Section 4.5.3.
2. Assign all non-zero values, i.e. boundary points, in the resultant map to 'NaN' (not a number).
3. Assign a numerical 'grain ID' to each region of interconnected zero values, i.e. grain interiors.
4. Assign all NaN points a grain ID number according to its boundary value, which defines the boundary edge(s). For example, if a point has a boundary on its right edge (boundary value 2), the grain ID should be assigned from any of the top, bottom or left adjacent points.
5. If the boundary value is 15, it is an isolated point and a grain ID of zero should be assigned.

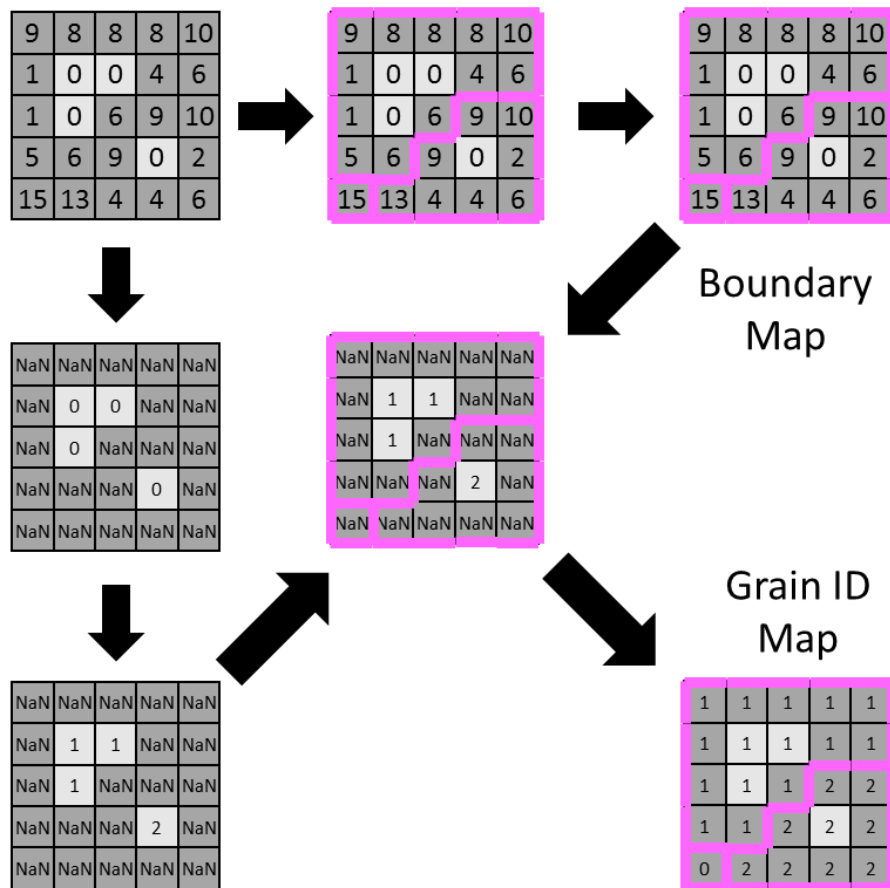


Figure 33: Grain identification from boundary map data.

A similar boundary definition to the algorithm in Figure 32 can also be used to separate out twin boundaries from other boundaries, and to differentiate between different types of twins. This creates a colour scale map when plotted which allows the user to quickly identify twin types. Because the points adjacent to the boundary line are simply filled in, instead of the boundary line being defined and reconstructed, there is no need to use powers of two in this case. An example of this is shown in Figure 34(b).

7. Assign an initial value of 0 to all points on the EBSD map.
8. If any edge of a point contains a grain boundary, replace the value of that point with 1.
9. If any edge of a point contains one type of twin boundary, replace its value with 2.
10. If any edge of a point contains another type of twin boundary, replace its value with 3.
11. This can be repeated with increasing values to unambiguously include all twin types.

This procedure does not define which edge of the EBSD point contains the boundary, but allows quick visualisation of the boundary points in a colour map. It cannot be used to reconstruct the original grain boundary line. As an example, Figure 34a) shows an example of a colour-coded edge map of twinned zirconium plate, and Figure 34b) the corresponding inverse pole figure (IPF) colour map along the plate transverse direction. The red and green boundaries are morphologically similar but are actually different twin types preferentially activated under different loading conditions. This analysis allows the two twin types to be distinguished from their different misorientations.

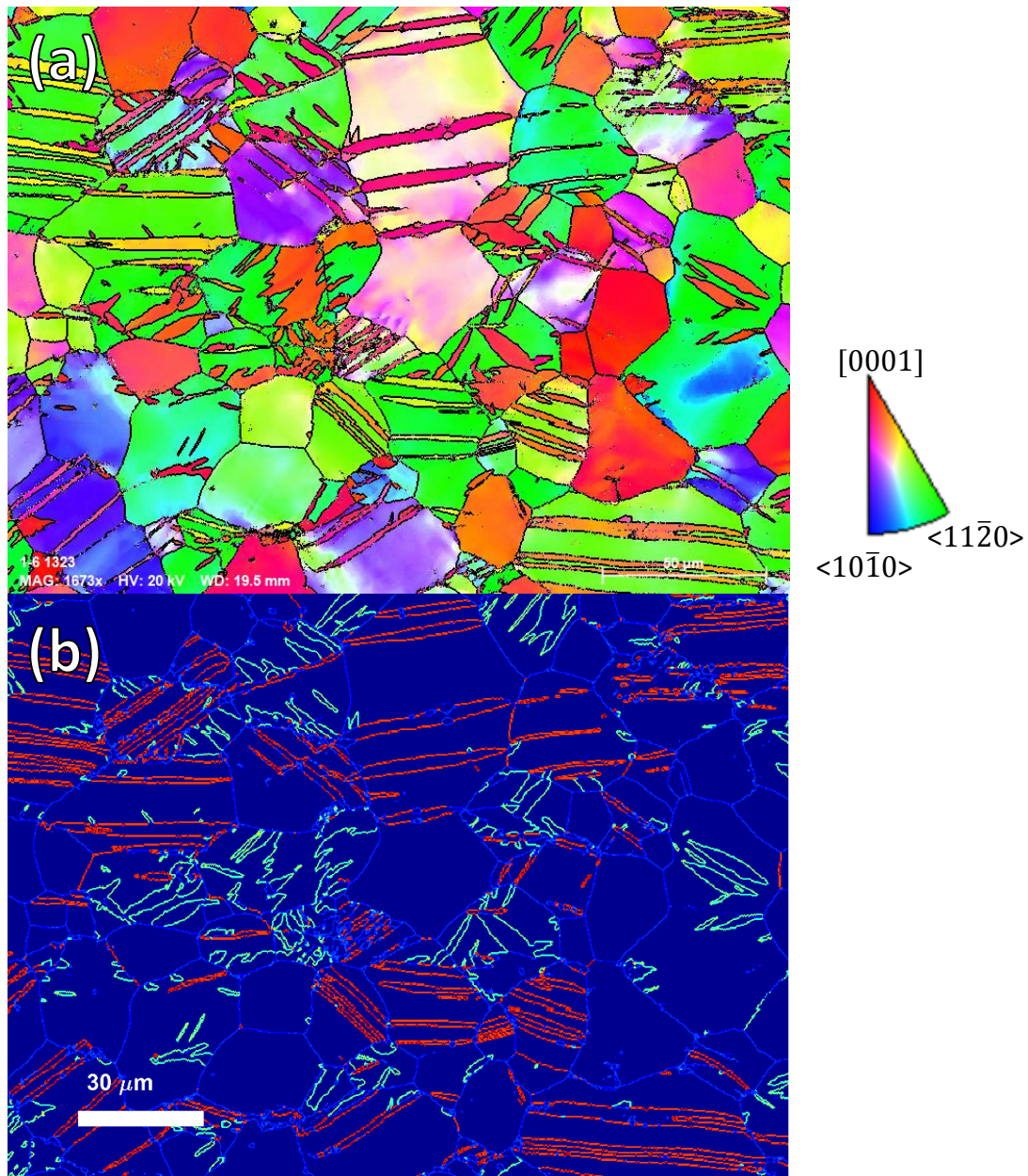


Figure 34: (a) EBSD map of deformed zirconium showing IPF colouring along TD. (b) Twin type edge map of the same sample. Red = T2 twin boundaries, green = T1 twin boundaries, and blue = normal grain boundary.

4.6 EBSD data clean up

Identification of twins requires careful identification of grain boundaries, and therefore requires points near the grain boundary to be assigned an orientation. Points near a grain boundary which are unindexed due to pattern degradation or overlap will need to be filled to reconstruct the grain boundary. Although this type of clean up is routine for EBSD data, it was written as an extra post-processing step as it is unavailable in the Bruker Esprit 2.0 [149] software.

This section outlines a routine that describes how to reconstruct a grain boundary from a poorly indexed grain boundary region within an EBSD map. The routine requires two major steps: (1) identification of the grain number (its 'identity'); (2) dilation of nearby grains into unindexed points, often due to pattern overlap, which are found as 'islands' in the grain boundary region.

The data is exported as a Channel Text File (CTF) which assigns Euler angles of $[0, 0, 0]$ to unindexed points, which may interfere with data analysis by creating artificial boundary points. If the unindexed point is at a grain boundary, the grain boundary line will appear to 'split' around the unindexed point(s), and if it is a twin boundary, the twin type will not be identified correctly.

Misindexed points are not dealt with separately here as they can be removed within the Esprit software, which assigns to them Euler angles of $[0, 0, 0]$ in the exported CTF file. They can therefore be treated in the same way as unindexed points.

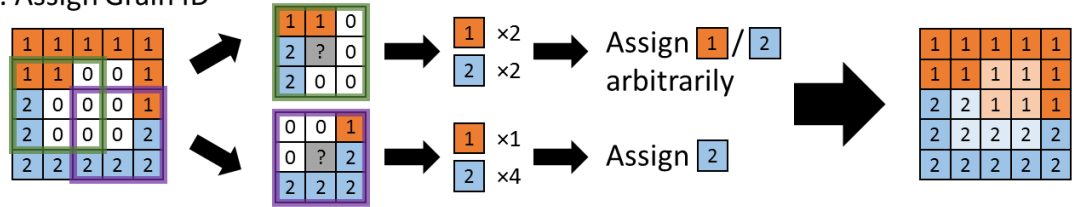
The algorithm used for data clean up of an EBSD map using the grain ID and quaternion orientation data is outlined below and shown as schematic flowcharts in Figure 35.

1. The Bruker Esprit software has a built in function to replace misindexed 'wild spike' data points with unindexed zero points. In the exported EBSD data, unindexed points have Euler angles of $[0, 0, 0]$, which are then converted into the quaternion $[0; 1, 0, 0]$.
2. Assign a grain ID of 0 to all points with a quaternion orientation of $[0; 1, 0, 0]$.
3. Identify the non-zero grain ID values of the points in the 3 by 3 neighbourhood around each zero point. Assign the modal non-zero grain ID value of its neighbourhood to each zero point. If there are two modes (e.g. if the unindexed point lies on a grain boundary) the choice is arbitrary.
4. Assign an orientation to the zero point by averaging orientations of the relevant neighbourhood points. The average of a unit rotation quaternion is approximately the arithmetic mean of its terms [158]. A trimmed mean can be used to avoid an erroneous

mean orientation in case of a ‘wild spike’ misindexed orientation in the neighbourhood points.

5. The grain IDs and orientations have been dilated into the zero points, which means that large clusters of zero points will not be completely consumed. The cleanup process can be repeated until the majority of zero points have been assigned orientations. However, care must be taken for poorly indexed data that the grain shapes are not distorted or artefacts are not created from large amounts of interpolation. For the work presented in this thesis, two iterations of the clean up process were used.

1. Assign Grain ID



2. Assign Orientations

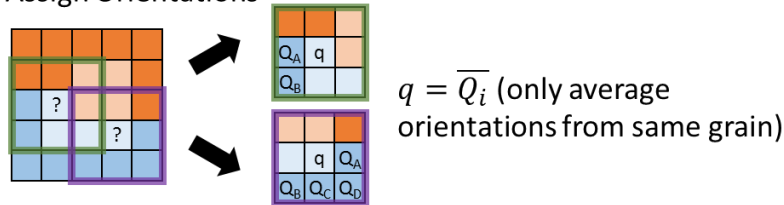


Figure 35: Data clean up in EBSD: assigning orientations to unindexed points by averaging neighbour orientations from the same grain.

4.7 Average orientations and orientation spreads

Each orientation in HCP symmetry can be equivalently represented by twelve different quaternions (see Table 5). It is useful to find a consistent quaternion representation in each grain, where the misorientation between any two points in the grain is equal to the disorientation. From this the average orientation, GROD, and GOS can be calculated. Figure 36 shows the average grain orientation calculation in pictorial form.

1. In grain G , identify its central point, furthest from the edge. Arbitrarily select one quaternion from this point (out of its possible symmetric equivalents) to represent its orientation. This is the reference quaternion Q_G^R for this grain.
2. For each of the other points in this grain ($Q_G^1 \dots Q_G^n$), calculate all of its possible misorientation angles from the reference quaternion ($mis_G^{i,1} \dots mis_G^{i,sym}$ for the i^{th} point in grain G). There are twelve possible misorientations in HCP symmetry.
3. Select the smallest value of $mis_G^{i,sym}$ to populate dis_G^i .
4. Verify that the disorientation angles between Q_G^R and Q_G^i are all less than a user-defined maximum threshold (e.g. 7-10° for lightly deformed metals). If the disorientation is higher than the threshold, discard this point as it is probably erroneous.
5. If the disorientation angles are all large (and therefore most or all of the points in a grain are discarded), the chosen reference Q_G^R may have been an incorrectly indexed point. In this case, a different reference point should be chosen and the process repeated, until a consistent set of quaternions are found for each grain.
6. Average orientation of a grain $\overline{Q_G}$ can then be calculated. It is useful to recall that the average of a set of unit quaternions is approximately the arithmetic mean for each term [158]. A trimmed mean may be used to remove any outliers in the average orientation.

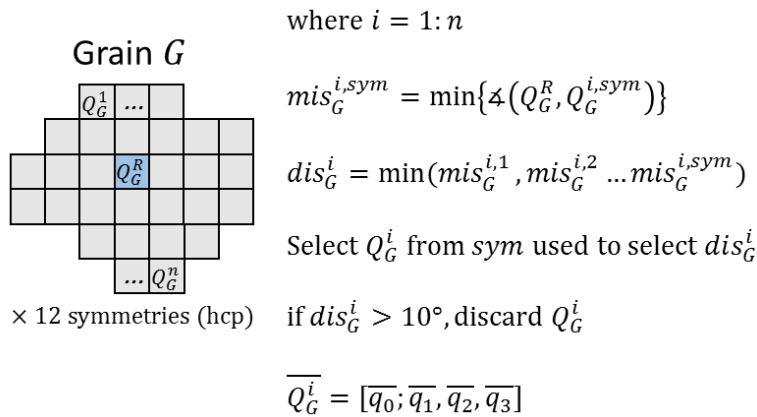


Figure 36: Average orientation calculation in grain G, using a disorientation threshold of 10°.

7. The GROD [162] is the disorientation angle between $\overline{Q_G}$ and Q_G^i (for the i^{th} point in grain G).

This can be plotted as a colour scale map to show regions of high and low deviation from the grain average orientation, corresponding to regions of high and low constrained slip, respectively. The GOS [76] is the GROD averaged over all points a given grain to provide an estimate of the average amount of constrained slip in the grain during polycrystal deformation. Example GROD and GOS maps are shown in Figure 37.

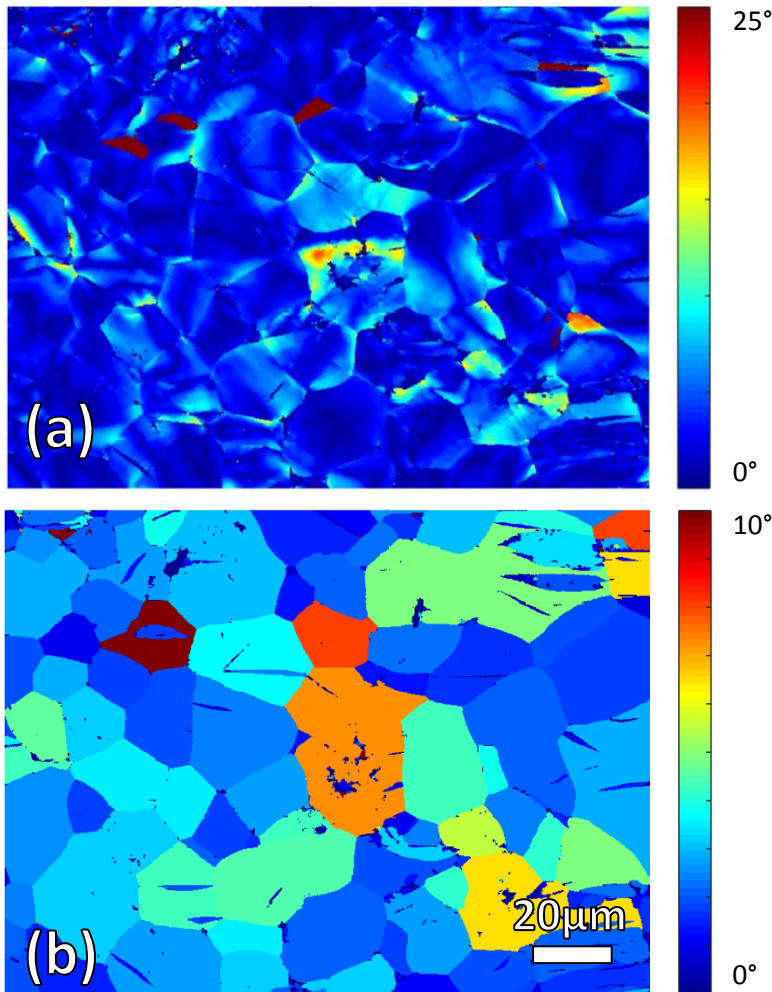


Figure 37: (a) Example GROD map of commercially pure Zr deformed to 10% strain. (b) Example GOS map of commercially pure Zr deformed to 10% strain.

4.8 Summary

EBSD is a powerful tool for mapping local crystallographic orientation maps, which can be used to probe a range of material properties. Care should be taken in orientation data handling in order to

extract correct information during postprocessing. This chapter has explored the different methods of representing rotations and orientations, and outlined procedures and algorithms on the following:

- How to convert between Euler angles, the most common representation of raw EBSD data, and other useful representations such as orientation matrices and quaternions.
- How to calculate misorientation between orientation quaternions, and thus define and identify grain boundaries or special boundaries from the misorientation data.
- How to clean up EBSD data and reconstruct grain boundaries, to minimise artefacts from poor indexing near grain boundaries which interfere with grain boundary identification.
- How to calculate the average orientation in a grain, and use the grain average orientation to map GROD and GOS distributions.

5. The formation of abnormally large grains in Zircaloy-4

5.1 Material and method

5.1.1 Material

The material used was Zircaloy-4 plate supplied by Rolls-Royce (schematic in Figure 38). The as-received grain size was $11\mu\text{m}$ measured by the circular intercept method (see Section 5.1.2.4) and had a typical Zr rolled and recrystallised texture with basal poles pointing $\pm 30^\circ$ away from the plate normal direction. Figure 39 shows a polarised light optical micrograph of the plate which was used to determine grain size.

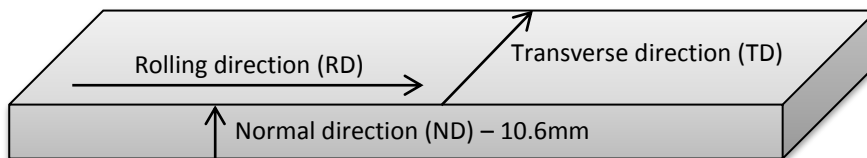


Figure 38: Schematic of Zircaloy-4 plate

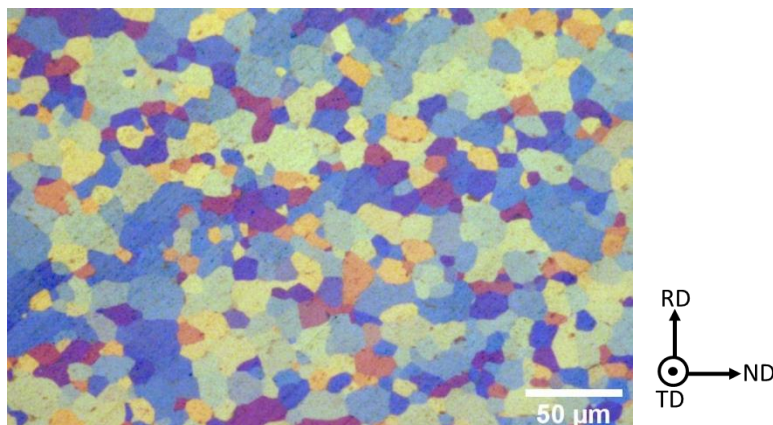


Figure 39: Cross-polarised optical micrograph of as-received Zircaloy-4 plate.

The formation of abnormally large grains in Zircaloy-4

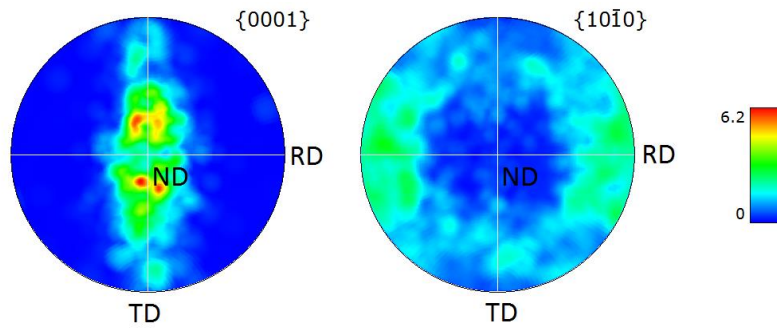


Figure 40: Basal and prismatic pole figures showing texture of as-received Zircaloy-4 plate, measured using EBSD of >1400 grains. Texture strengths shown by the pole figure colour scale are in multiples of random texture.

5.1.2 Method

The method used for grain growth studies is a strain-anneal, keeping the sample at all times within the alpha phase field. Two strain methods were used, uniaxial compression and three point bending.

5.1.2.1 Uniaxial compression

Approximately 3.5mm-sided cuboids of Zircaloy-4 plate were uniaxially compressed along either the ND or RD face normals in a 10kN Shimadzu AGS-X machine (Figure 41).

The samples were compressed at $1\mu\text{m/s}$ to a known stress, and the total strain was measured using digital image correlation (DIC). DIC is a full-field technique which enables measurement of strain homogeneity in the sample as well as the average strain. The sensitivity of the technique in strain is typically $\sim 1.5 \times 10^{-3}$ [163] and therefore often the majority of the strain measured on a metallic sample represents the total plastic strain applied to a sample.

The DIC face and the two faces to be in contact with the compression plates were ground to 2000 grit ($10\mu\text{m}$ SiC paper) after cutting, to ensure that they were parallel sided. The DIC face was sprayed with white paint and a speckle pattern was applied using black copier toner. PTFE spray lubricant was applied to the compression plates to minimise friction.

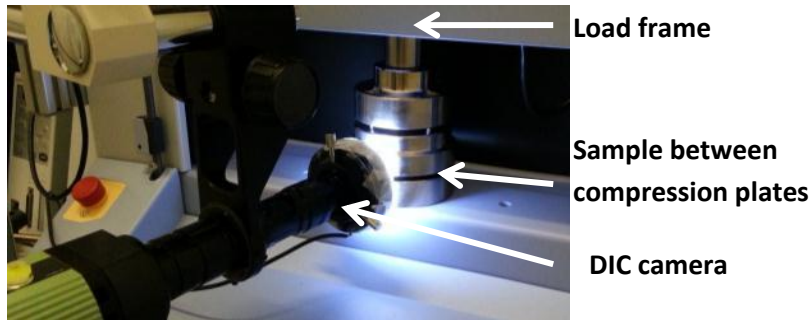


Figure 41: Uniaxial compression and DIC set up.

5.1.2.2 Three point bending

Three point bending was used to produce a well-defined strain distribution. Samples 29mm long, 2.8mm wide and 2.9mm high were bent to 2.5mm stroke displacement in a 2kN Gatan Mtest2000E mechanical test frame (Figure 42). The bend specimen was loaded along the plate normal direction and DIC imaging was performed on the face normal to the rolling direction.

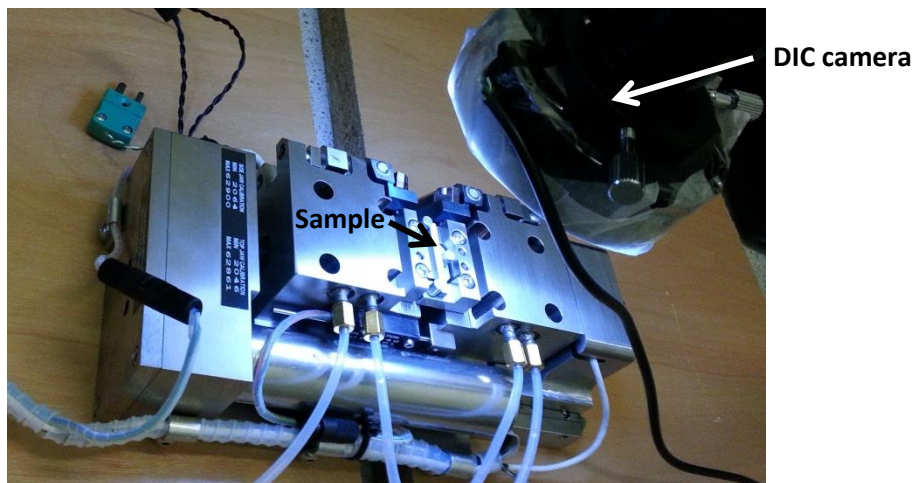


Figure 42: Three point bending and DIC set up.

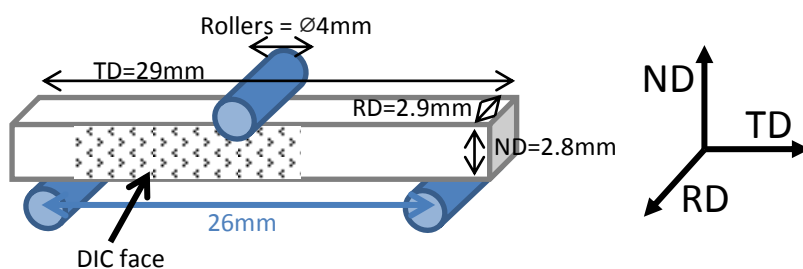


Figure 43: Schematic of three point bending set up.

5.1.2.3 Annealing heat treatment

The lower alpha-beta transus temperature in Zircaloy-4 is approximately 810-820°C [24], [164], therefore to achieve maximum grain growth most samples were held at 800°C. After straining, samples were cleaned and encapsulated in an argon atmosphere for heat treatment. To enable samples to reach an equilibrium state, they were held at temperature for 336 hours (14 days).

Thermocouples were wrapped around the quartz tube and the temperature was maintained within $\pm 5^\circ\text{C}$ of the target temperature. The furnace was preheated before samples were inserted, and samples were air cooled inside the quartz tubes after annealing. Ramping the sample up to temperature and cooling back down took around ten minutes each, leading to a heating and cooling rate of approximately 1°C/s .

For as-received samples annealed to produce blocky alpha grains, the samples were first annealed at 300°C for 3 hours before any other heat treatment in order to relieve any surface stresses from machining or grinding that could nucleate blocky alpha grains.

5.1.2.4 Grain size measurement

Average grain size is reported for samples with unimodal grain size distribution, where the blocky alpha transformation has either fully completed or not yet begun. The method used is a circular intercept method (adapted from ASTM Abrams three circle procedure [165]) implemented in MATLAB script. Using a circular intercept method instead of a linear intercept method minimises error from the ends of lines, especially with large grains where few intercepts are present in the field of view. Three circles of different radii are drawn onto the micrographs in black and the grain boundary intercepts are marked on in white (Figure 44). Grain size is calculated from dividing the total circumference lengths by the number of intercepts present, correcting for the pixel size of the micrograph. (Note that mean circular intercept length is not equivalent to the mean grain diameter; the mean circular intercept length is typically slightly smaller.)

For large grained samples it is common for the counting field to have fewer than 50 intercepts, as opposed to the 500 intercepts required in the standard ASTM procedure. This means that there is a large statistical uncertainty associated with the measurement particularly for large grained samples. This uncertainty is $<5\mu\text{m}$ for small grained samples (>90 intercepts) but up to $40\mu\text{m}$ for small grain samples (<50 intercepts). The error is the range obtained by repeating the grain size measurement at different positions on the same micrograph.

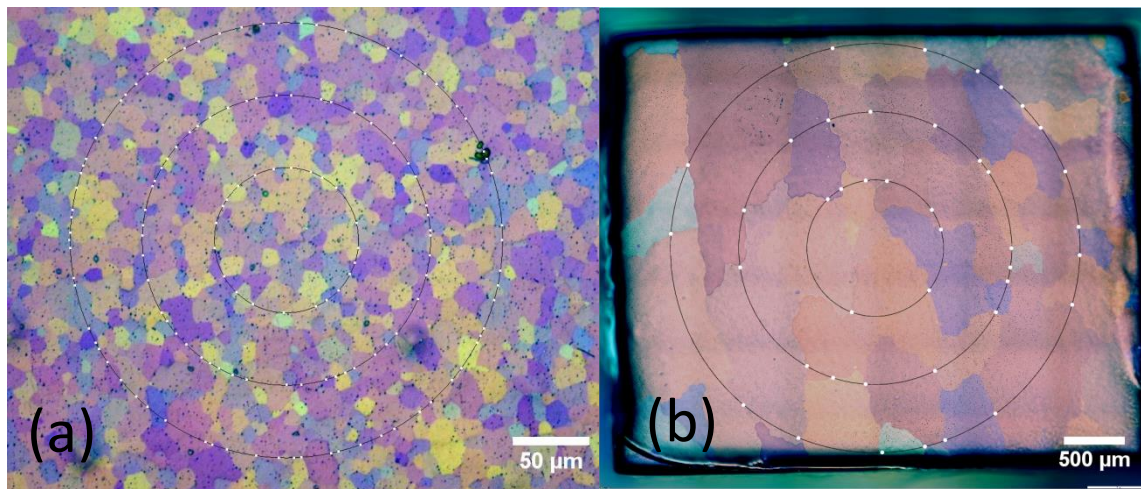


Figure 44: (a) Circular intercept counting for small grained sample. (b) Circular intercept counting for large grained sample. The white dots are put in by the user and mark the intercepts between the circles and grain boundaries.

5.1.2.5 Percentage transformed into blocky alpha measurements

In the grain growth rate tests (Section 5.2.1.2), blocky alpha was seen to nucleate in a ‘patch’ spreading out across the sample. To measure the area fraction of blocky alpha, optical micrographs of the entire sample were taken and printed onto A4 paper. The structure was drawn out on tracing paper out to show the boundaries between blocky alpha and the small-grained matrix. The traced boundaries were scanned, then thresholded and flood-filled on ImageJ to calculate the volume fraction of blocky alpha present. The process of tracing and flood-filling is shown in Figure 45.¹

¹ There is a small (likely $<2\%$) error associated with the black traced sample boundary being counted as blocky alpha.

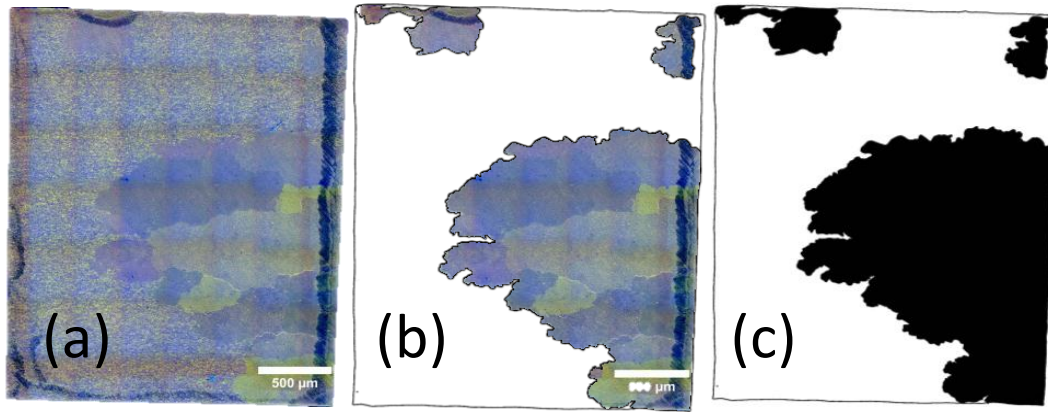


Figure 45: Processing of micrographs to calculate percentage transformed into blocky alpha. (a) Original micrograph showing blocky structure growing into small grains. (b) Traced boundaries between blocky grains and small grains, overlaid with blocky grains. (c) Flood-filled image used in volume fraction analysis.

5.2 Results

5.2.1 Uniaxial Compression study

5.2.1.1 Effect of strain on equilibrium grain size

The grain size in fully transformed microstructures was measured as a function of prior strain and strain direction. Results from 800°C heat treatments for 336 hours are shown in Figure 46.

Significant grain growth from the starting grain size of 12μm is seen in all samples heat treated for 336 hours at 800°C, even in fully recrystallised as-received samples pre-annealed for 3 hours at 300°C to relieve machining stresses (these data points are shown as green crosses in Figure 46). 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 grain size).

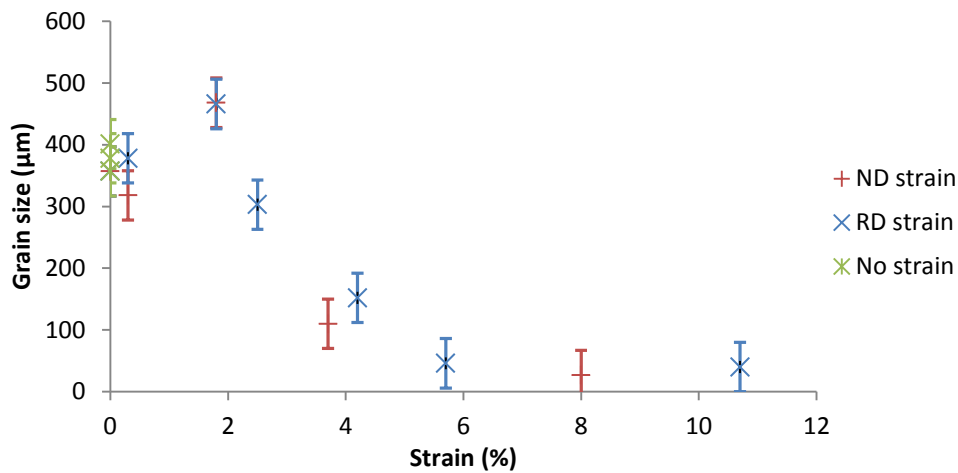


Figure 46: Effect of strain on equilibrium grain size (336 hours) for 800°C anneal.

5.2.1.2 Grain growth rate at 800°C

Grain growth rate was measured in terms of percentage of sample transformed into blocky alpha (outlined in Section 5.1.2.5), as samples tended to have 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 Figure 47. A series of samples were compressed to the same stress and heat treated for increasing lengths of time.

In the annealed 0.3% strained samples, there is an incubation period of 20-48 hours before which blocky alpha growth does not occur or is extremely limited. For 2% strained samples, this incubation period either disappears or is less than 20 hours. By 96 hours grain growth is nearly complete in all samples.

Figure 47(b) shows that the blocky alpha transformation is patchy. This could have arisen from small strain heterogeneities from uniaxial compression speeding up the growth of blocky alpha grains in higher strained regions. The DIC measured strain distribution maps (not shown) of the sample surface contain strain heterogeneities on the ~100 μm lengthscale. The micrographs in Figure 47(b) are not from the same surface plane, as samples were polished after annealing, but the strain heterogeneities should be similar and therefore patchy growth can be expected.

The formation of abnormally large grains in Zircaloy-4

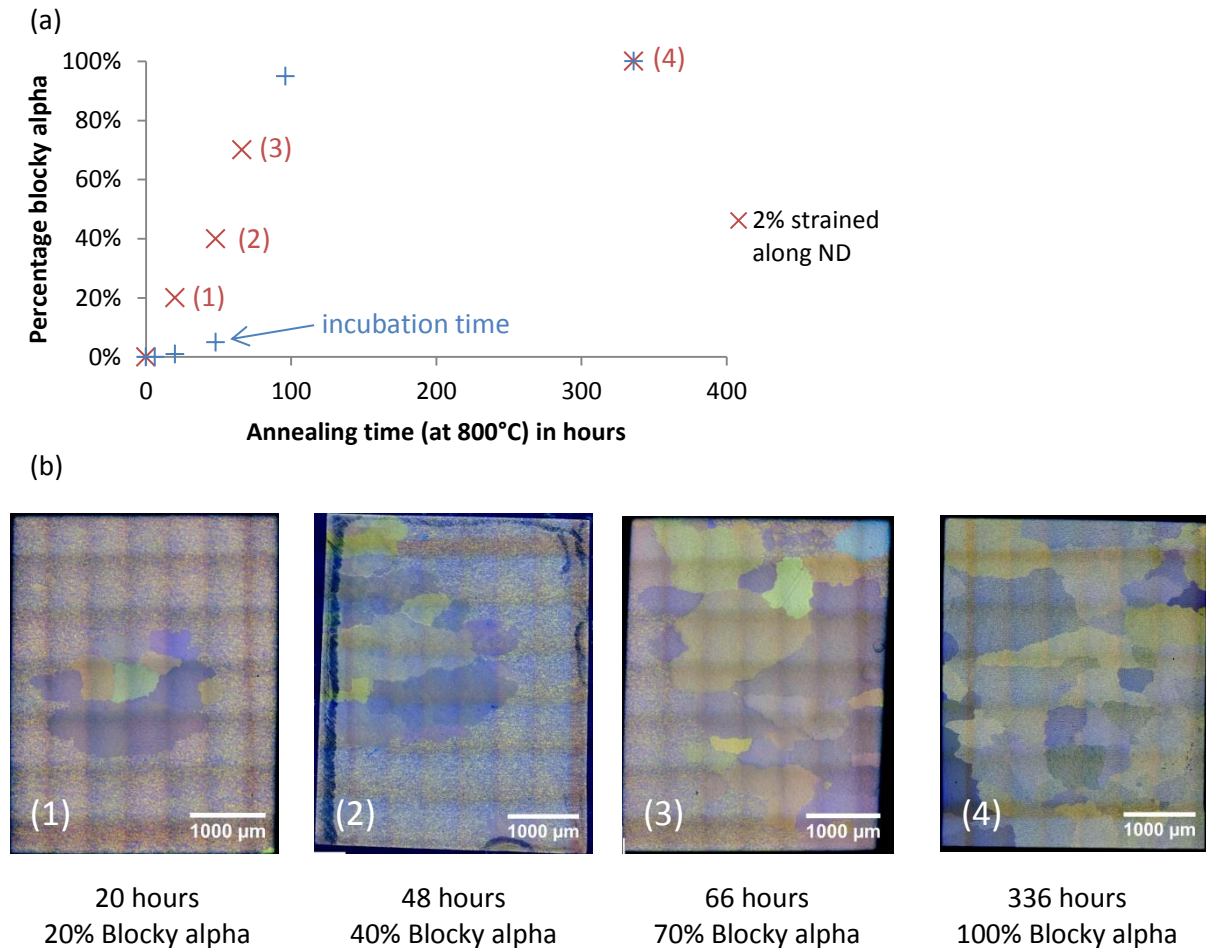


Figure 47: (a) Grain growth rate at 800°. Data for 0.3% strain at 66 hours, 2% strain at 6 hours, and 2% strain at 96 hours in preparation. (b) Micrographs of samples heat treated at 800°C to different times after 2% strain along ND, showing grain growth process. Numbers in brackets link micrographs with corresponding data points on the graph. Each data point is measured from a different sample.

5.2.1.3 Orientation and grain size measurements by EBSD

EBSD data was collected for two blocky alpha samples, one of which had been compressed to 2.3% strain along ND and the other 1.9% strain along RD. Comparing this with the original plate texture, the EBSD orientation maps are similar in all three IPF directions, one of which is shown in Figure 48. The heat treated texture is independent of strain path at low uniform strains.

Grain sizes measured by EBSD (average grain diameter) can be compared with the circular intercept method. The grain sizes for the samples in Figure 48 are shown in Table 6. In general, the mean intercept lengths are slightly smaller than the mean grain diameter, which is expected as the intercept length for any given grain must be smaller than or equal to the grain diameter.

Figure 48(c) is a case where the mean intercept length diverges strongly from the EBSD data. This is probably due to the heterogeneous grain size distribution and low number of grains in the sample, which decreases the accuracy of the circular intercept method. Most of the smaller grains are located towards the right edge of the sample, which does not intersect the circular fields. The ASTM procedure [165] also requires that the smallest circular field is three times larger than the average grain diameter, which cannot be the case for this sample due to the very large grain size and small sample size.

The EBSD maps in Figure 48(b) and (c) are also taken at very low magnification in the SEM, where the fields of view are around 5mm by 4mm. As a result there is a significant amount of image distortion, especially at the 70° tilt needed for EBSD. This introduces errors into the EBSD grain size measurement.

However, the average grain sizes are comparable with the circular intercept method from optical micrographs, as long as the grain size distribution is relatively uniform and a reasonable number of grains (>50) are sampled in the circular field.

The formation of abnormally large grains in Zircaloy-4

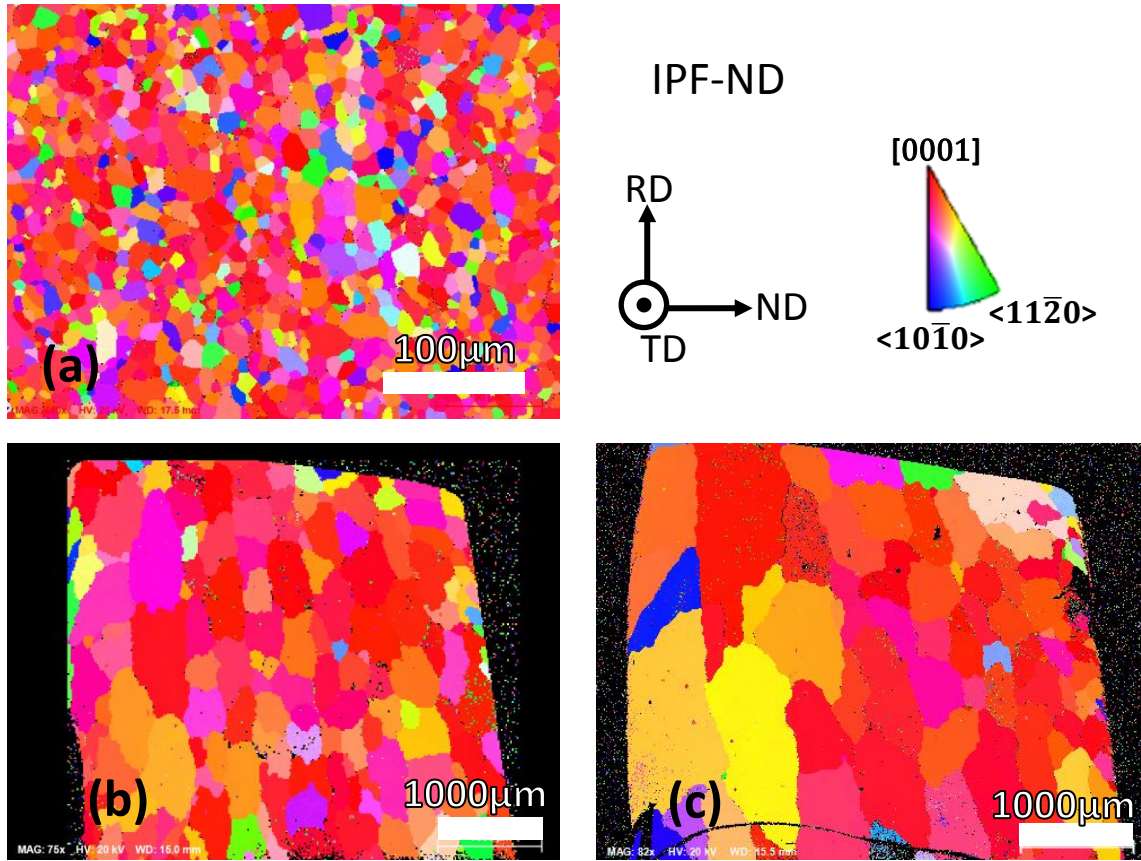


Figure 48: IPF orientation EBSD maps with respect to the original plate ND showing similar orientations in as received and heat treated material independent of strain path. (a) Orientation map of original plate. (b) Orientation map of plate strained to 2.3% in ND and then annealed. (c) Orientation map of plate strained to 1.9% in RD and then annealed. There is a small amount of misalignment in the compression plates in sample c) leading to grain size heterogeneity along the horizontal axis.

Sample	Mean grain diameter / μm (EBSD)	Mean circular intercept length / μm
(a)	12	11
(b)	330	310
(c)	375	470

Table 6: Grain size measured using EBSD and circular intercept method from an optical micrograph, for the three samples shown in Figure 48. Grain size measurements are comparable if the grain size is relatively uniform.

5.2.1.4 HR-EBSD of a blocky alpha grain and an as-deformed sample

The GND densities in as-deformed and blocky alpha grains were analysed using HR-EBSD. 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 $67.5\mu\text{m}$.

Figure 49(a)-(b) show EBSD data for Zircaloy-4 plate deformed to 0.3% strain along the original plate rolling direction (RD). The as-deformed sample 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.

Figure 49(c)-(f) show a similarly deformed sample, but annealed after deformation to produce blocky alpha. The EBSD data shows a blocky alpha grain surrounding an island grain. Island grains are a feature characteristic of abnormal grain growth in other material systems, such as Al-3.5Cu [85]. These island grains have a grain size of the same order of magnitude as the original grain size, and have been observed in all blocky alpha samples.

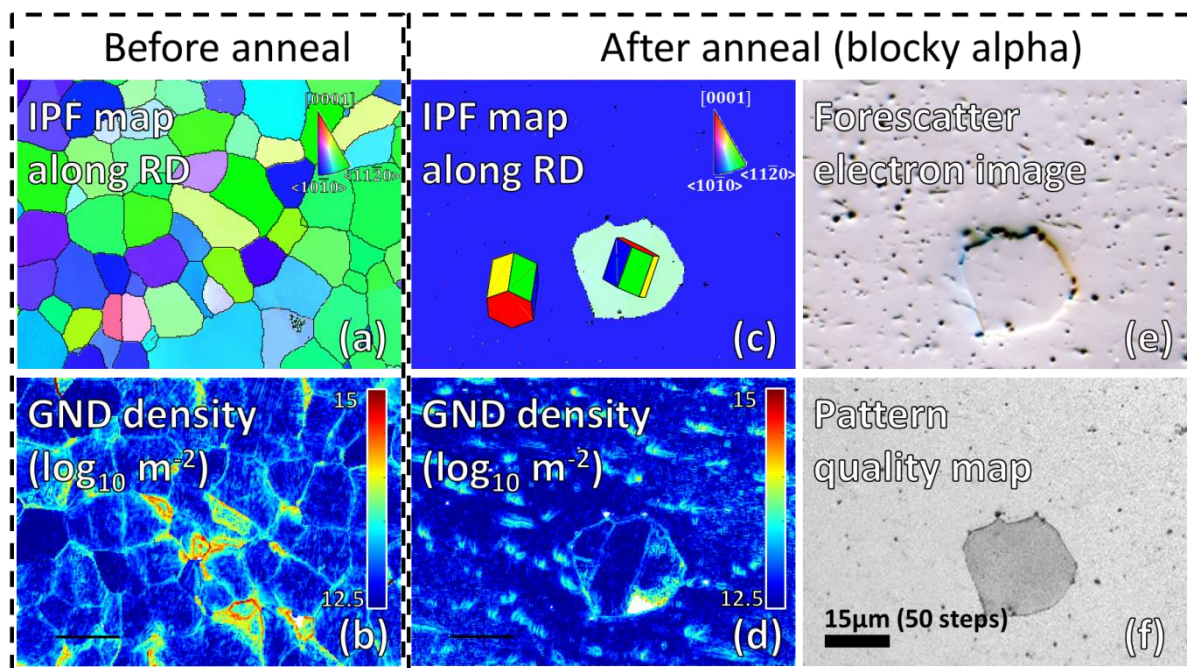


Figure 49: EBSD analysis of 0.3% strained Zircaloy-4 before (a-b) and after (c-f) blocky alpha heat treatment (800°C for 336 hours). All fields of view are the same size. (a) IPF map with respect to the original plate rolling direction (horizontal in figure), showing an average grain size of 11µm and classic rolled and recrystallised texture. (b) HR-EBSD derived GND map, revealing isolated grain boundaries with very high GND density; (c) IPF map of blocky alpha sample, showing one large grain surrounding one island grain. (d) HR-EBSD derived GND map, revealing areas high GND density isolated throughout the blocky grain and located towards the grain boundary within the isolated grain. (e) Forescatter image, revealing topography of the island grain and the presence of small surface pits (which correlate with areas of high GND density in (d)); (f) EBSD pattern quality map, showing regions of lower pattern quality associated with pitting.

GND density hotspots, spaced around 10-15µm apart, are present within the large blocky alpha grain in Figure 49(d). The spacing of the dislocation density hotspots is comparable to the grain size of 11µm in the as-deformed sample in Figure 49(a). Apart from one region which has not cross-

correlated well, the island grain has quite low GND density. The misorientation angle between the island grain and the blocky alpha grain is around 40°.

Some pitting has occurred in the blocky alpha sample from electropolishing (as seen in the foreshatter electron image), which is usually a result of preferential chemical attack on highly strained regions and SPPs. However, the higher dislocation density regions in the blocky grain extend beyond the pits and areas of reduced pattern quality from pitting.

5.2.2 Three point bending study

The effect of strain has been shown to influence grain growth and therefore a three point bend test was performed to impose a strain gradient on the sample. A finite element simulation using von Mises plasticity was performed by Dr Zhen Zhang from Imperial College London to indicate the macroscopic strain variation in the chosen sample geometry (Figure 51). This model was not intended to capture local microstructural changes during three point bending, but was used to predict an optimal bend geometry to achieve appropriate strain levels.

The sample was bent to 2.5mm displacement of the central roller, heat treated for 336 hours at 800°C, and subsequently metallographically polished. A typical load-displacement curve obtained from bending is shown in Figure 50 – note that frame compliance is not accounted for, so the displacement of the beam itself is less than 2.5mm. The geometry of the bending experiment is described in Figure 43.

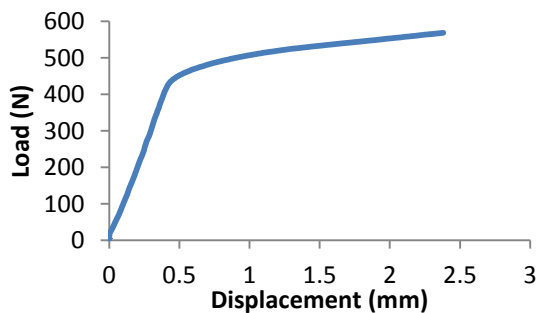


Figure 50: A typical load-displacement curve obtained from three point bending.

5.2.2.1 Strain measurement for three point bending

The effective plastic strain distribution was predicted with von Mises plasticity finite element analysis (Figure 51) and measured using digital image correlation. ϵ_{xx} plots from the finite element analysis (FEA) are shown in Figure 51. The DIC analysis was performed using commercial software Davis [166] by Te-Cheng Su from Imperial College London, and the results for ϵ_{xx} are shown in Figure 52.

Due to the high compliance of the test frame which artificially increased the measured displacement in the stress-strain data (Figure 50), the displacement input for the finite element analysis was not 2.5mm, but chosen so that the maximum tensile stresses in the FEA and DIC data would match.

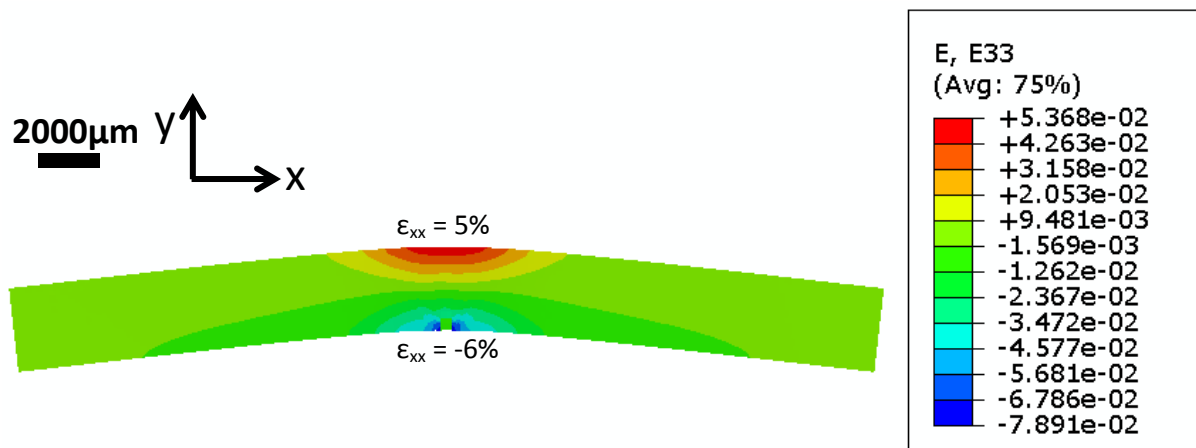


Figure 51: Von Mises plasticity simulation of three point bending. Colour scale shows ϵ_{xx} true strain. (Analysis courtesy of Dr Zhen Zhang, Imperial College London.)

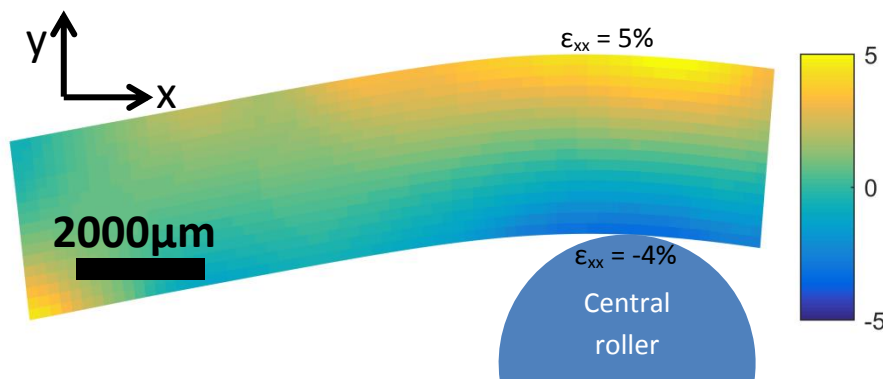


Figure 52: ϵ_{xx} near the middle of bend sample measured using commercial DIC software Davis, with central roller off centre. (Analysis courtesy of Te-Cheng Su, Imperial College London.)

Figure 51 and Figure 52 both show tensile and compressive regions as expected in ϵ_{xx} . The maximum ϵ_{xx} in the plastic compressive region is between -4 and -6%, and the maximum ϵ_{xx} in the plastic tensile region is 5%. Figure 53 shows that the strain distributions in the centre of the bend sample are similar in the FEA and DIC measurements, and the positions of the neutral axes fall within 0.2mm of each other.

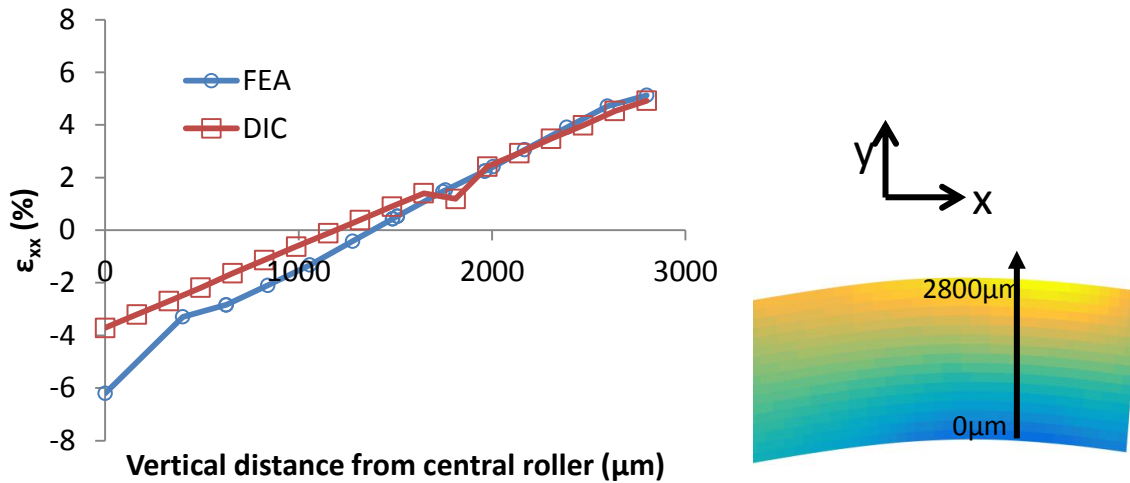


Figure 53: Comparison of ϵ_{xx} engineering strain calculated with FEA and measured with DIC, as a function of the y-distance from central roller.

5.2.2.2 Characterisation of as-bent sample

An as-bent sample was characterised using a variety of EBSD-based techniques to identify microstructural features or areas with high stored energy, which could potentially provide driving force for blocky alpha nucleation. Slip and twinning are the main deformation modes in zirconium alloys. Twinning behaviour is characterised in the current section, and constrained slip behaviour is characterised in Section 5.2.2.4.

5.2.2.2.1 Bulk texture in as-bent sample

The texture in the as-bent sample was measured by EBSD in the highly strained plastic tensile and compressive regions and compared with texture in the as-received microstructure. Over 9000 grains were sampled in each region of the as-bent sample, and 1300 grains were sampled in the as-received microstructure. This conforms to the guidelines for bulk texture measurement given by Humphreys in [146], which suggest that at least 500-1500 grains are required for reliable texture measurement.

Inverse pole figures have been used as opposed to the more conventional pole figure representations to minimise spottiness in the plots due to the small number of grains in the annealed sample (shown later in Figure 61), where the texture measurements comprise of tens of grains only.

The inverse pole figures in Figure 54, Figure 62 and Figure 63 are exported directly from the EBSD vendor Bruker Esprit 2.0 [149] software. There is a problem with the texture strength estimation algorithm in this software, as the edges of these reduced inverse pole figures plotted on the standard stereographic triangle have lower values. If the standard stereographic triangle is unfolded to form the full inverse pole figure projection, the results near the triangle edges are unphysical. These artefacts in the texture strength estimation algorithm do not affect the conclusions drawn in this chapter.

Inverse pole figures for each region are plotted in Figure 54. The texture sharpens considerably after deformation (from 21000 times random in the as-received sample to over 80000 times random in the bent sample) due to lattice reorientation from slip during bending. Prismatic directions pointing along RD switch from first order prismatic ($\langle 11\bar{2}0 \rangle$) in the as-received sample to second order prismatic ($\langle 10\bar{1}0 \rangle$) directions after bending. Texture peaks in the plastic compressive and tensile regions are very similar in both orientation and strength.

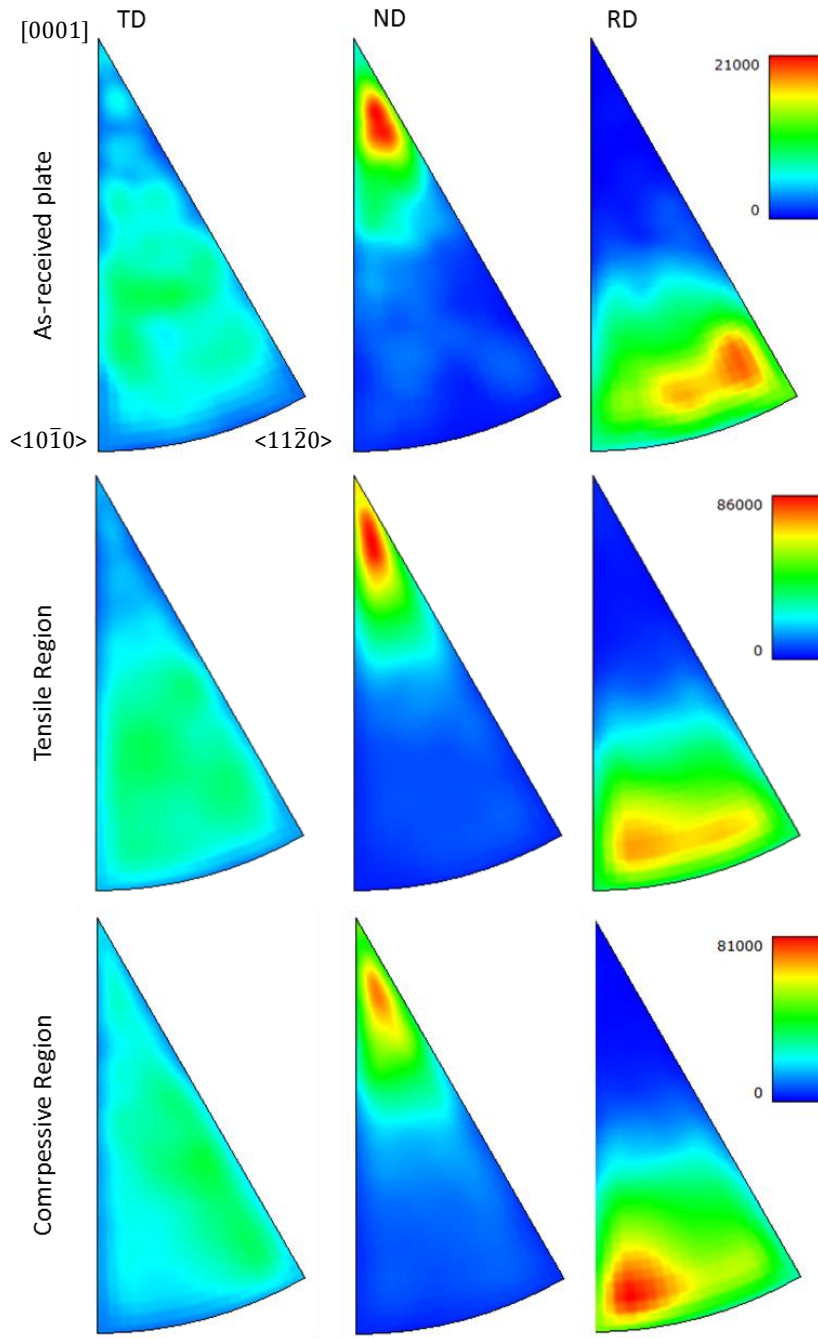


Figure 54: Inverse pole figures showing texture in the as-received plate, and the plastic tensile and compressive regions of the as-bent samples. Texture strengths (colour scale) are in multiples of random texture.

5.2.2.2.2 Twinning frequency in as-bent sample

Twinning frequency was measured from the same EBSD maps in the as-bent sample which were used to produce inverse pole figures in Figure 54. Twin boundaries were identified using in-house developed post-processing software described in Chapter 4 and twin interiors were flood-filled to

identify twin fraction as a function of vertical distance along the bend sample. Only $\{10\bar{1}2\} \langle 10\bar{1}1 \rangle$ (T1) twins were observed, and these are highlighted in green in Figure 55. The step size used was $1\mu\text{m}$ so only twins larger than this could be identified; the twin fractions are therefore indicative values only showing the relative distribution of twins.

The twin fraction generally decreases with distance from the edge where the stress concentration is highest, although in the 100-200 μm closest to the sample edges there is a decrease in twin fraction, probably due to the strain being localised to a very small region around the ‘hinge’ of the bend specimen.

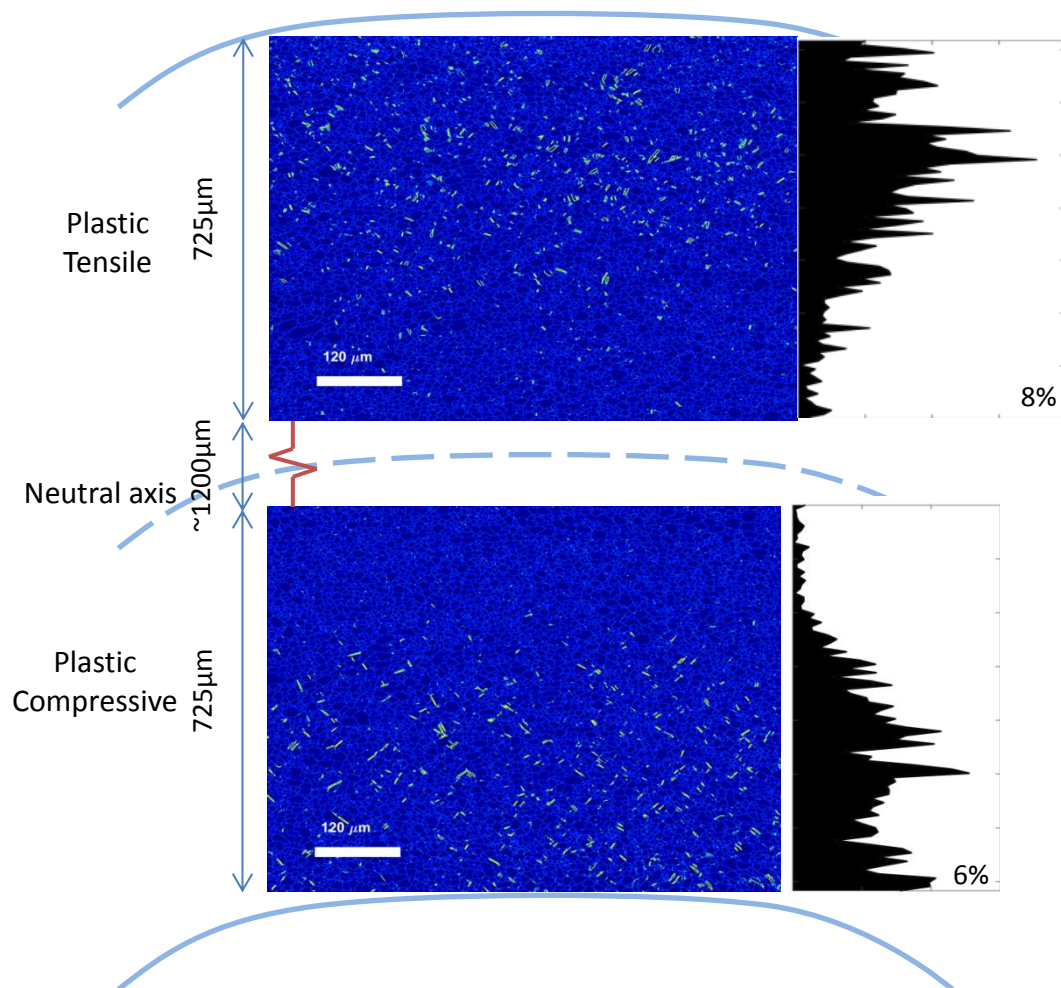


Figure 55: Grain boundary maps in the plastic tensile and compressive regions of the bend specimen, with non-special boundaries highlighted in blue and T1 twins highlighted in green. Step size used for EBSD mapping was $1\mu\text{m}$.

5.2.2.2.3 Twinning textures in as-bent sample

Higher spatial resolution EBSD maps were taken to identify twin variants present in the as-bent microstructure, shown in Figure 56 (plastic tensile region) and Figure 57 (plastic compressive region). The IPF colouring is shown with respect to the horizontal direction, which is the plate transverse direction (TD).

Although all twins are of the same type, different variants are preferentially activated in the plastic tensile and compressive regions. The difference occurs because the T1 twinning shear accommodates only extension strain along the basal direction of the HCP unit cell, and the primary loading direction is reversed for the different fibres of the bending sample. Twin microstructures for the plastic tensile and compressive region are shown in Figure 56 and Figure 57 respectively.

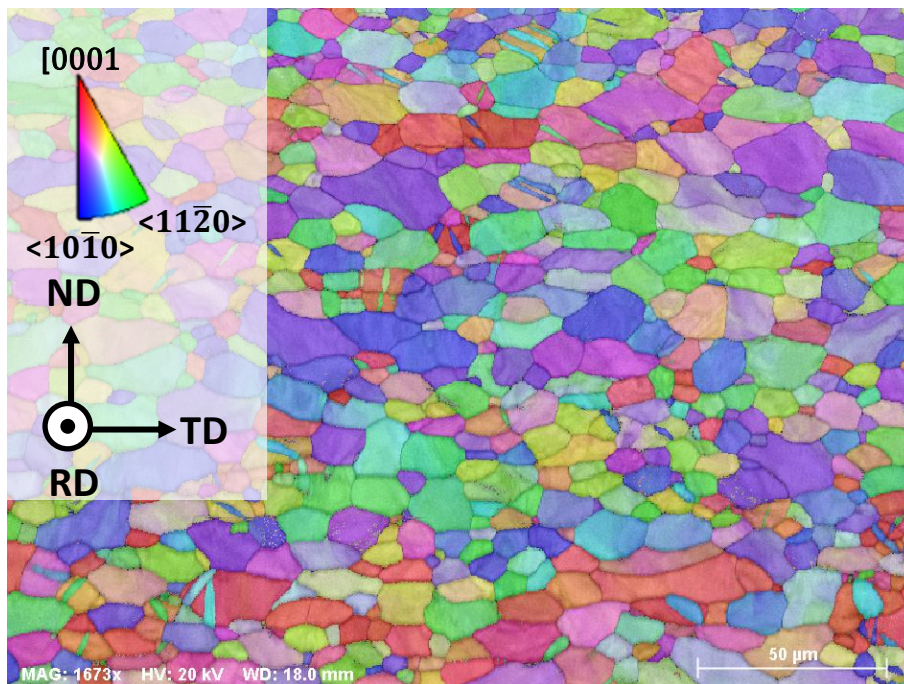


Figure 56: High spatial resolution EBSD map of plastic tensile region in bend sample. Pattern quality overlaid with IPF colouring along TD, the primary loading axis of the bend sample. Twins are aligned along prismatic directions (blue and green) and parent grains along basal directions (red).

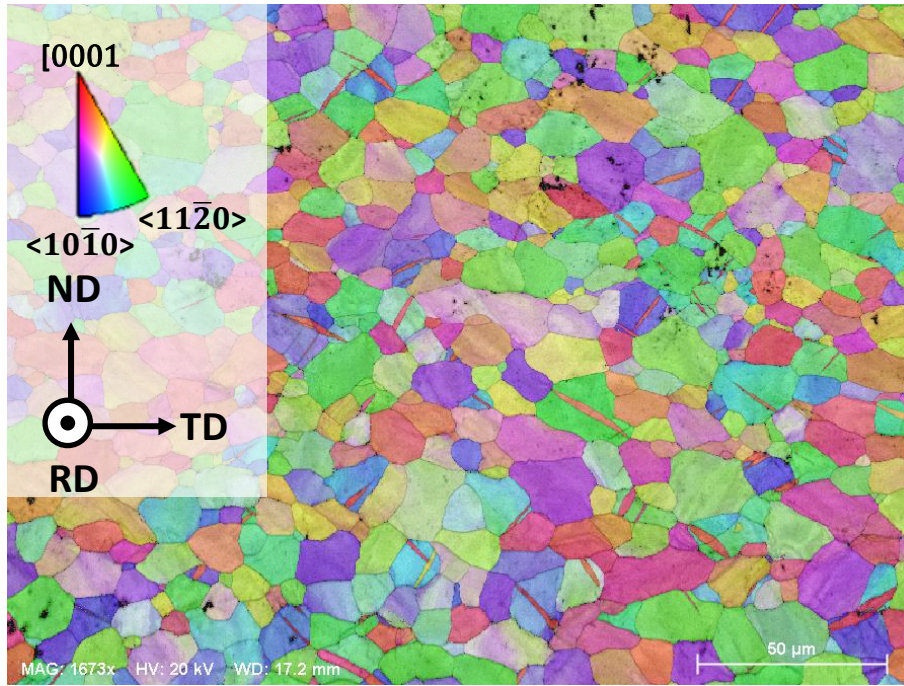


Figure 57: High spatial resolution EBSD map of plastic compressive region in bend sample. Pattern quality overlaid with IPF colouring along TD, the primary loading axis of the bend sample. Twins are aligned along basal directions (red) and parent grains along prismatic directions (blue and green).

In Figure 56, this region of the sample is loaded in primarily in tension along the horizontal direction. Grains which twin tend to have their [0001] basal direction pointing along the loading axis (i.e. they are red). They are hard grains which are poorly oriented for $\langle a \rangle$ prismatic slip, so the twins accommodate strain parallel to the loading axis, as a substitute for deformation slip.

In Figure 57, this region of the sample is loaded in primarily in compression along the horizontal direction. Grains which twin tend to have their [0001] basal direction nearly perpendicular to the loading axis (i.e. they are near green or blue). Twins allow strain in the directions perpendicular to the loading axis to accommodate Poisson contraction and allow compatibility strain between grains.

The twins have a different texture to the initial untwinned microstructure, as for T1 twinning there is an 85° degree rotation between the twin and parent basal directions. In addition, different subsets of orientations are favourable for twinning under each loading condition, so the parent grains have a different texture to the rest of the untwinned material.

5.2.2.2.4 HR-EBSD of a twin in an as-bent sample

Figure 58 shows GND densities obtained from HR-EBSD mapping of a twin in the plastic tensile region of the sample, approximately halfway between the tensile edge of the sample and the neutral axis. This region was chosen to avoid large amounts of slip and therefore isolate the effect of twinning. There is a GND hotspot ahead of the top of the twin tip. This is in agreement with the literature, where large local residual strains are associated with twin tips in commercially pure Ti [167] and Zircaloy-2 [4], and dislocations are formed in and around fine Zr twins that are not recovered during annealing to 500°C [168]. There are also other regions of high GND density both inside and outside the twinned grain.

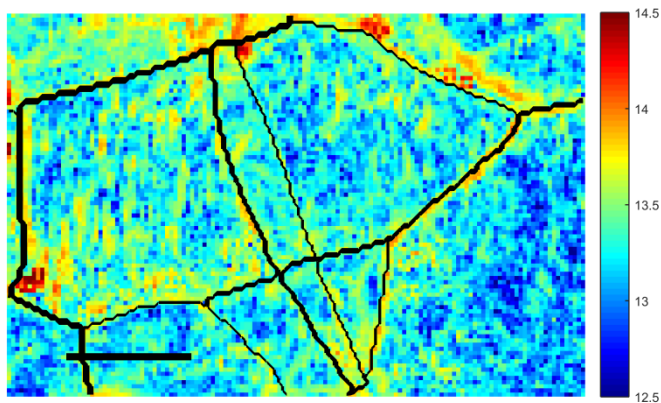


Figure 58: GND density map showing hotspot in neighbouring grain ahead of the twin tip. Scale bar is 3 μm and step size is 0.1 μm . Colour scale is in units of $\log_{10}(\text{dislocations}/\text{m}^2)$.

5.2.2.3 Characterisation of annealed sample

5.2.2.3.1 Optical microscopy of annealed sample

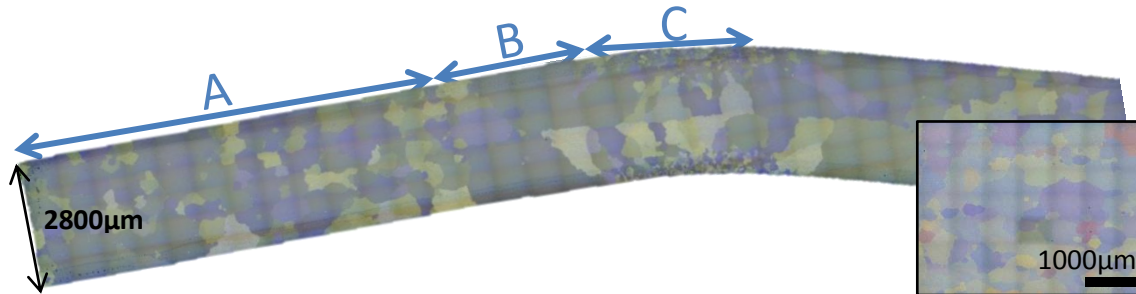


Figure 59: Optical micrograph of three point bend specimen annealed at 800°C. Right insert: Microstructure of as-received Zircaloy-4 annealed at 800°C for 336 hours, showing 350µm grain size.

Figure 59 shows the microstructure after three point bending and annealing for 336 hours at 800°C.

The microstructure can be divided into three distinct regions, labelled A, B and C in Figure 59.

In region A, the grain size is around 400µm, similar to heat treated unstrained material. The strain from three point bending in this region is minimal. The neutral axis is not visible from the grain morphology.

In region B, blocky alpha grains meet at the neutral axis but do not cross it, and the average grain size is very large, nearly 1000µm.

In region C, blocky alpha grains also meet at and do not cross the neutral axis, and the grain size varies strongly with position, with the smallest grain size areas corresponding to the highly strained areas in bending. The large grains towards the centre of the sample stop at the neutral axis, and the major axes of the large grains point perpendicular to the neutral axis.

Further investigation of the neutral axis effect (Figure 60) reveals that grain size is not strongly affected by the sense of the strain (compressive or tensile), which is also seen when uniaxially compressing different texture components of the plate (RD and ND points in Figure 46 lie along a similar curve). However, EBSD analysis shown in Figure 61 reveals significant change in crystal

orientation either side of the neutral axis. Orientations of the large grains either side of the neutral axis have been overlaid onto the EBSD map in Figure 61.

5.2.2.3.2 Grain size distribution of annealed sample as a function of strain

The grain size distribution in the central region of the annealed sample was measured from EBSD data using a linear intercept method. Five lines were drawn onto an EBSD grain map of the bend specimen and the intercept lengths recorded (Figure 60). There are significant optical distortions present at very low magnification and high tilt angle in the SEM during EBSD data acquisition, skewing the shape of the EBSD map. Therefore, instead of measuring the line length using the scale bar, the total length of each line was normalised to the known sample height of 2800 μm . The grain size distribution as a function of vertical distance from the central roller is plotted with the normal strain ϵ_{xx} calculated from DIC.

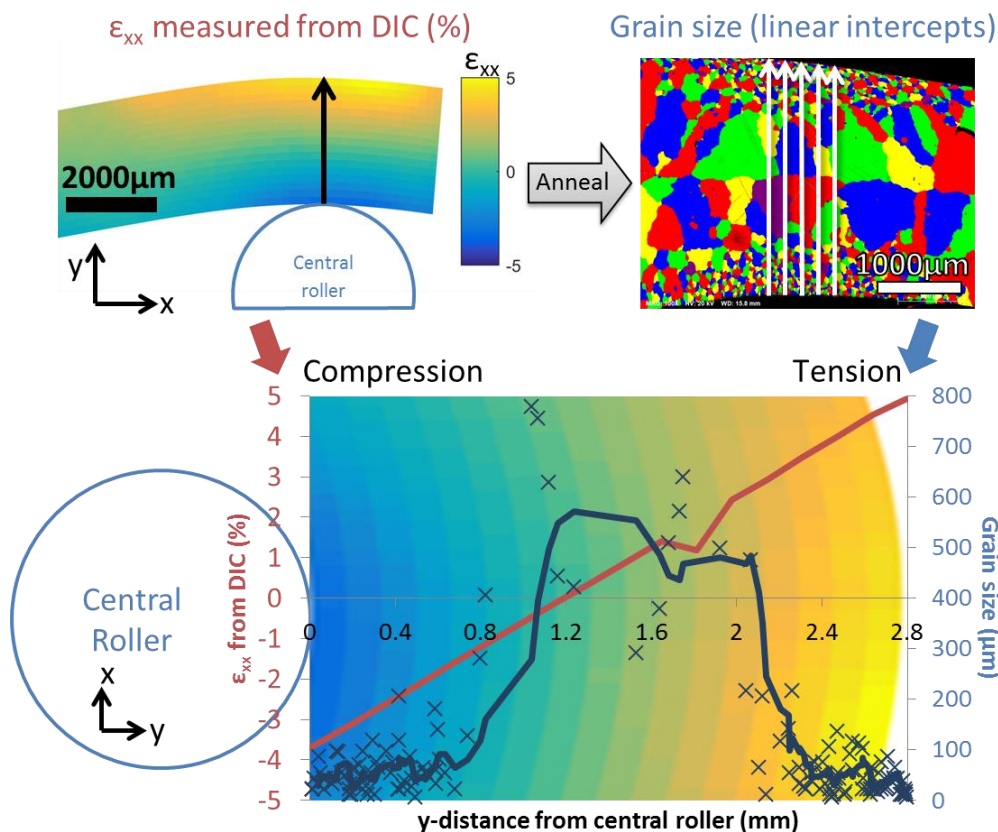


Figure 60: Prior strain dependence of blocky alpha grain size in three point bend specimens annealed at 800°C for 336 hours.

The grain size is relatively symmetric in tension and compression, especially when the scatter intrinsic to the linear intercept grain size measurement method is taken into account, as the intercept line does not always cross at the maximum grain length.

Where the prior strain ϵ_{xx} is greater than $\pm 2\text{-}3\%$, the intercept lengths are around $100\mu\text{m}$ and are relatively independent of prior strain. Below this strain level, new grains stop nucleating and the final grain size is large. Figure 61(a) shows that many of the largest grains span the entire region between the end of the small-grained region and the neutral axis, where it meets another similarly large grain.

5.2.2.3.3 EBSD of annealed sample

The textures in the bend specimen can be divided into four regions: small-grained and large-grained areas in the plastic compressive and plastic tensile regions respectively. There are relatively few grains in the sample due to the large grain sizes; therefore the inverse pole figure textures are very sharp in Figure 62 and Figure 63. The strength of the texture peaks (measured in multiples of random texture) is a function of both the texture strength and the number of grains sampled. No meaningful conclusions can be drawn from the texture peak strengths as only tens of grains have been sampled, fewer than the 500-1500 grains required for a representative macro-texture measurement according to Humphreys et al. [146].

To ease interpretation of the inverse pole figures, the preferred orientations in RD, TD and ND of the different regions are summarised as cartoon schematics in Figure 64.

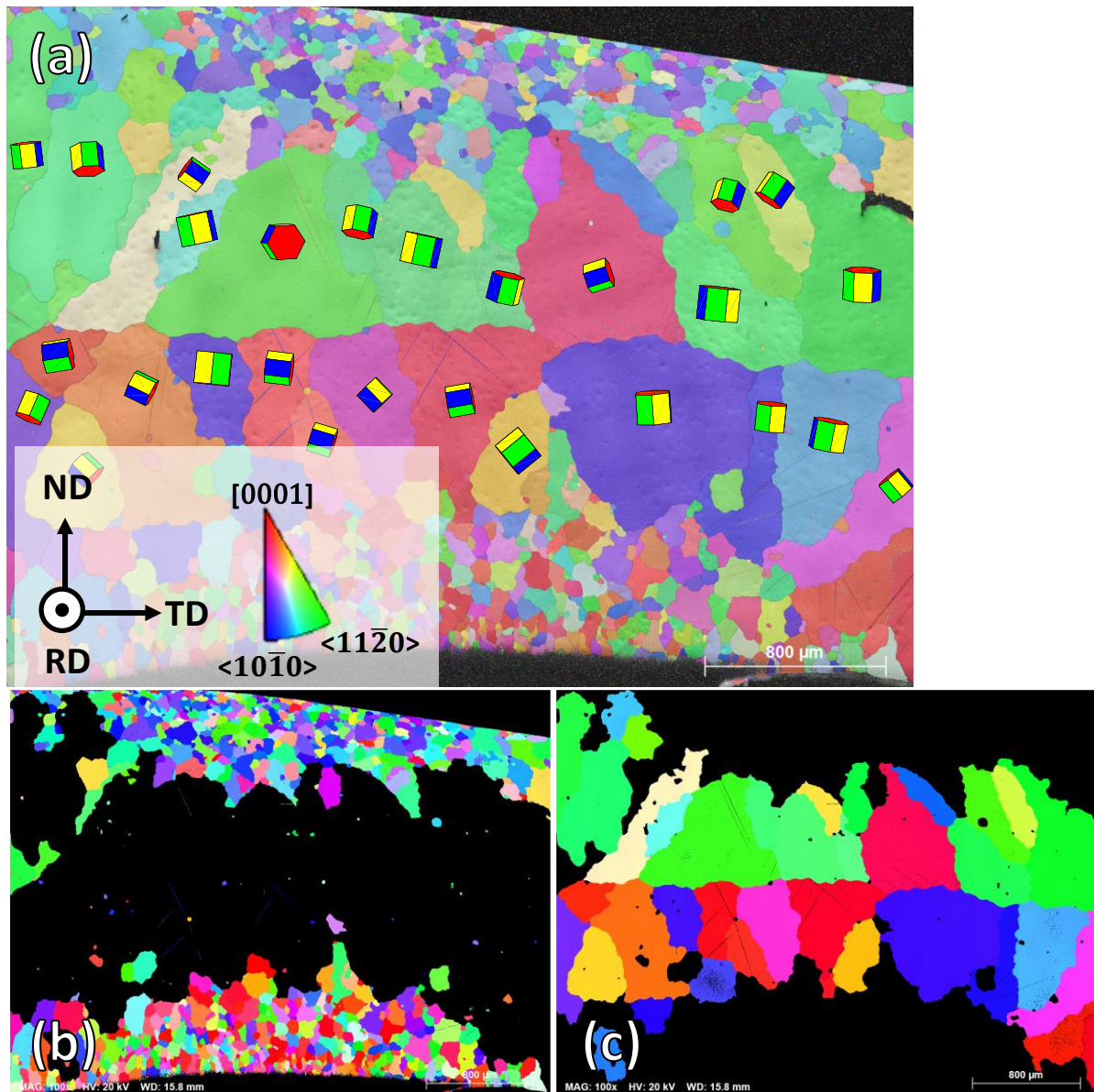


Figure 61: (a) EBSD map of the three point bend region annealed at 800°C for 336 hours with IPF colouring along TD showing region C in Figure 59 with orientations and image quality overlaid. (b) Small grained regions segmented from the EBSD map. (c) Large grained regions segmented from the EBSD map.

5.2.2.3.3.1 ND texture component

All regions have a basal texture component in ND, although the basal texture for the small grains in the plastic compressive region is comparatively less strong than the other regions.

5.2.2.3.3.2 RD texture component

The textures of the plastic compressive region are shown in Figure 62. Along RD, there is a switch between first order and second order prismatic planes in the large and small grained region. In the plastic compressive region, RD aligns with the $\langle 11\bar{2}0 \rangle$ directions in the small grained region and the

$\langle 10\bar{1}0 \rangle$ directions in the large grained region. This effect is reversed in the plastic tensile region shown in Figure 63. RD aligns with the $\langle 10\bar{1}0 \rangle$ directions in the small grained region and the $\{11\bar{2}0\}$ directions in the large grained region.

5.2.2.3.3 TD texture component

Along TD, there is a near-90° c-axis rotation between the plastic tensile and compressive regions. In the plastic tensile region, the plastic tensile region align along TD. In the plastic compressive region, the basal direction preferentially aligns along TD, though the textures here are less sharp.

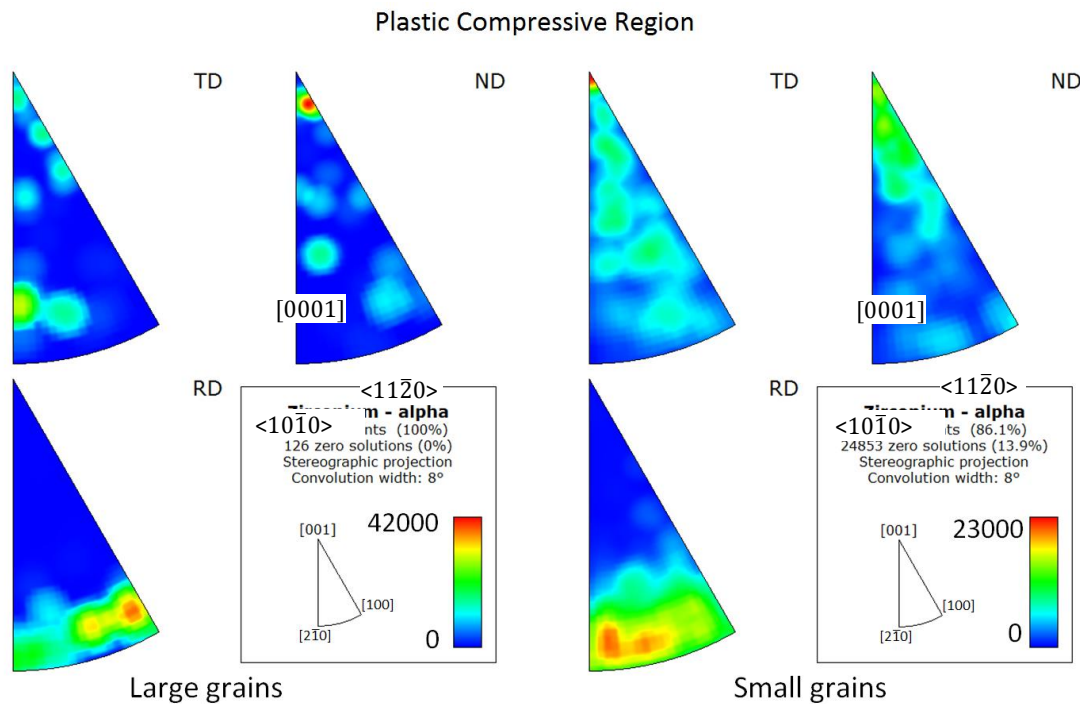


Figure 62: Inverse pole figures of large (left) and small (right) grains below the neutral axis (plastic compressive region). Texture strengths (colour scale) are in multiples of random texture.

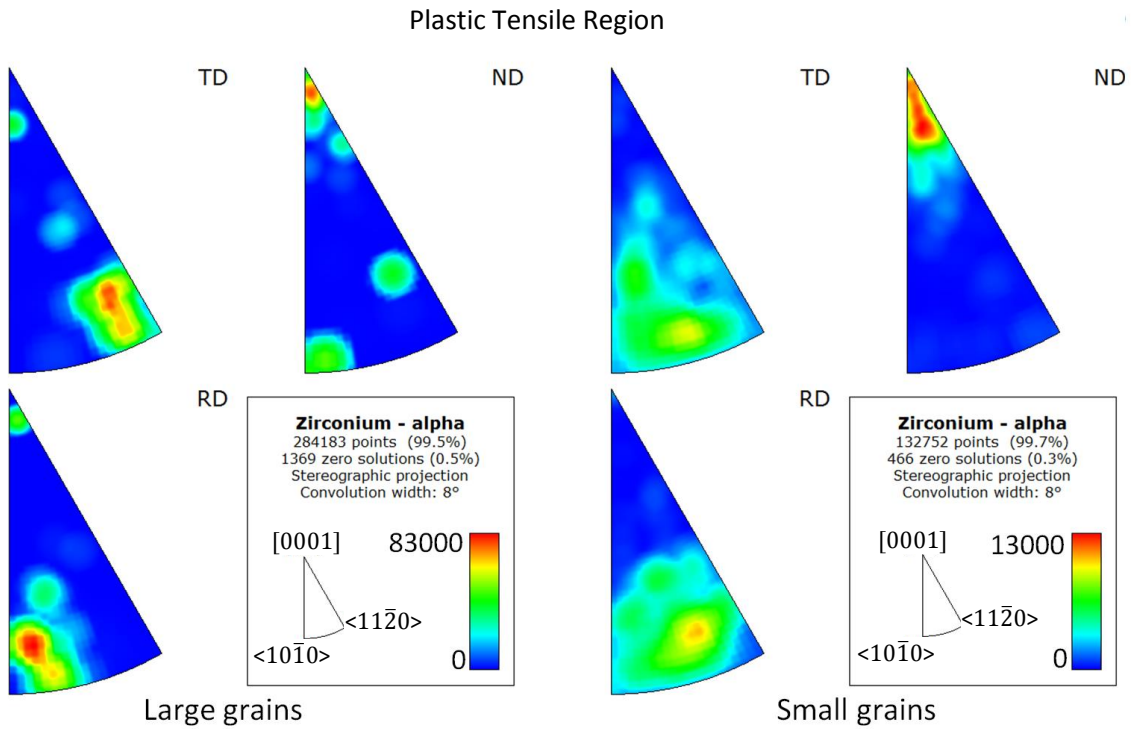


Figure 63: Inverse pole figures of large (left) and small (right) grains above the neutral axis (plastic tensile region). Texture strengths (colour scale) are in multiples of random texture.

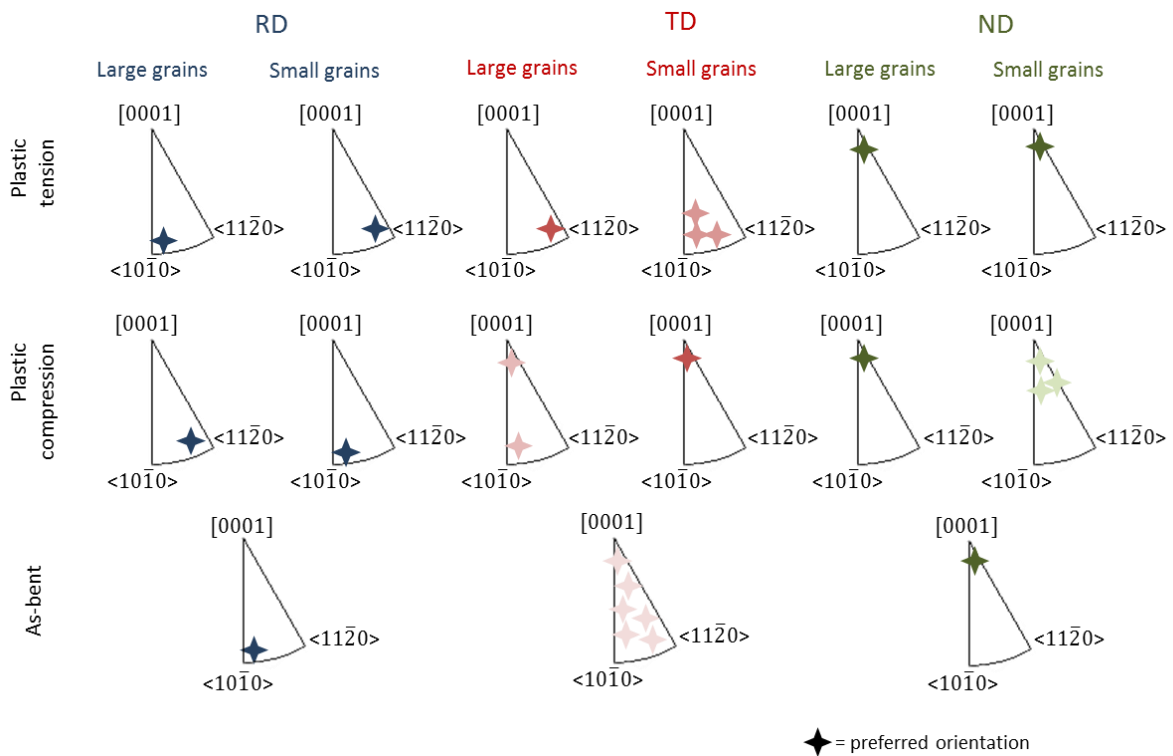


Figure 64: Cartoon schematic of the preferred IPF orientations in different regions of the bend sample, after and before annealing. Cartoon is drawn according to data from Figure 54, Figure 62, and Figure 63.

The textures of the parents and twins in the as-bent sample (Figure 56 and Figure 57) can be compared to the large-grained areas of the annealed microstructure (Figure 64). Table 7 shows the alignment of crystallographic directions for each set of grains with respect to the three macroscopic axes. The blocky alpha orientations in the plastic compressive region of are largely inherited from the parents and twins in this region of the as-bent sample. The blocky alpha orientations in the plastic tensile region are similar to the as-bent texture but have sharpened such that the $\langle 11\bar{2}0 \rangle$ directions ($\{10\bar{1}0\}$ planes) point along TD, and the $\langle 10\bar{1}0 \rangle$ directions ($\{11\bar{2}0\}$ planes) point along RD. This is a typical deformation texture in Zr rolled sheet [169]. Two ‘rogue’ grains have orientations shown in parentheses in Table 7.

	Compressive (TD)	Compressive (ND)	Compressive (RD)	Tensile (TD)	Tensile (ND)	Tensile (RD)
Parents	$\langle 10\bar{1}0 \rangle$ $\langle 11\bar{2}0 \rangle$	$[0001]$	$\langle 11\bar{2}0 \rangle$ $\langle 10\bar{1}0 \rangle$	$[0001]$	$\langle 10\bar{1}0 \rangle$ $\langle 11\bar{2}0 \rangle$	$\langle 11\bar{2}0 \rangle$ $\langle 10\bar{1}0 \rangle$
Twins	$[0001]$	$\langle 10\bar{1}0 \rangle$ $\langle 11\bar{2}0 \rangle$	$\langle 11\bar{2}0 \rangle$ $\langle 10\bar{1}0 \rangle$	$\langle 11\bar{2}0 \rangle$ $\langle 10\bar{1}0 \rangle$	$\langle 10\bar{1}0 \rangle$ $\langle 11\bar{2}0 \rangle$	$[0001]$
As bent	fibre	$[0001]$	$\langle 11\bar{2}0 \rangle$ $\langle 10\bar{1}0 \rangle$	fibre	$[0001]$	$\langle 11\bar{2}0 \rangle$ $\langle 10\bar{1}0 \rangle$
Blocky (large grains)	$\langle 10\bar{1}0 \rangle$ $[0001]$	$[0001]$ $\langle 11\bar{2}0 \rangle$	$\langle 11\bar{2}0 \rangle$ $\langle 10\bar{1}0 \rangle$	$\langle 11\bar{2}0 \rangle$ $([0001])$ $(\langle 11\bar{2}0 \rangle)$	$[0001]$ $(\langle 11\bar{2}0 \rangle)$ $(\langle 10\bar{1}0 \rangle)$	$\langle 10\bar{1}0 \rangle$ $(\langle 10\bar{1}0 \rangle)$ $([0001])$

Table 7: Orientations of the parent and twin grains in the as-bent microstructure, compared with the blocky orientations. Directions are colour-coded according to the IPF colour scale in Figure 57. Orientations which appear in parentheses () are ‘rogue orientations’ which are only adopted by a single grain in the field of view.

These two ‘rogue’ blocky alpha grains in the plastic tensile region are related to the overall texture peak by twin relations. Figure 65 shows the locations and orientations of these two grains and compares these to the orientation of the texture peak position in the large grained plastic tensile region. One grain is a T1 twin and the other is a C1 twin. C1 twins were not observed in EBSD of the as-bent samples when characterised with a step size of $0.3\mu\text{m}$.

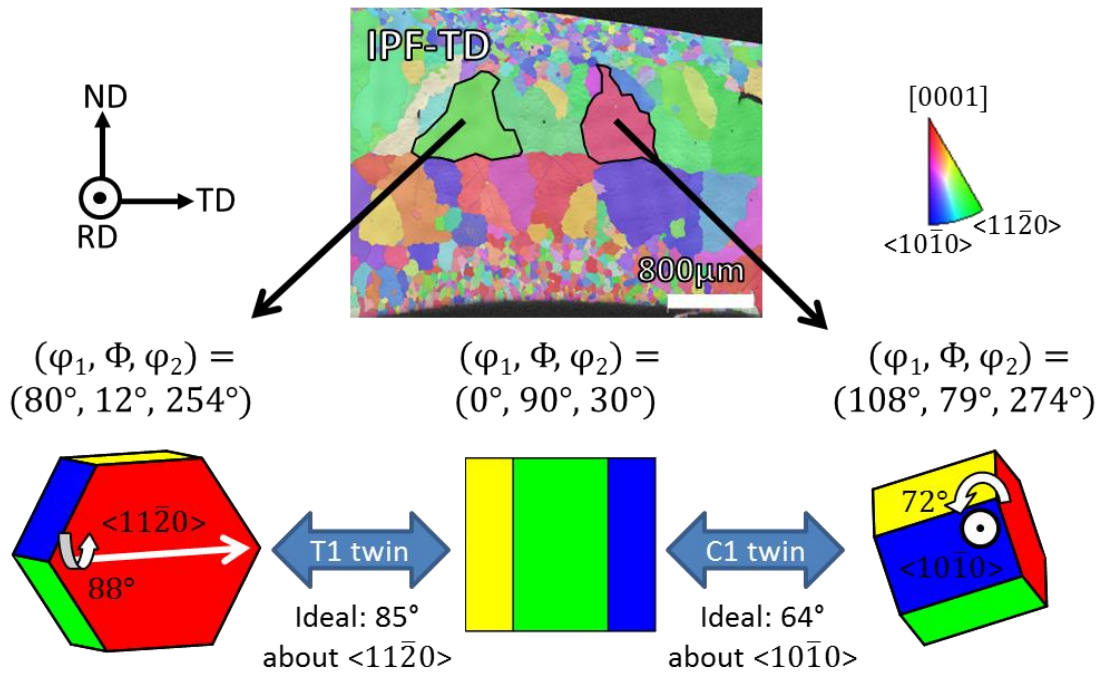


Figure 65: Orientations of the two ‘rogue’ grains in the plastic tensile region, compared to the orientation of the texture peak in the same region. The axis-angle misorientation relations in HCP indices are shown on the unit cells. Comparison with the ideal twin relations shows that the green grain has a T1 twin relation and the red grain has a C1 twin relation to the texture peak orientation.

5.2.2.4 Constrained slip in as-bent sample

Preferential growth of twins and parents can describe the blocky texture in the plastic compressive region, but the texture in the plastic tensile region is a deformation texture which has sharpened compared to the as-bent sample. Therefore the amount of constrained slip in this region has been estimated using GOS plots, to study the relationship between blocky alpha nuclei orientations and the amount of constrained slip in the as-bent grains.

Intragranular orientation gradients arise from the presence of GNDs caused by constrained slip in polycrystals. Grains with large orientation gradients on average have slipped more than grains with smaller orientation gradients.

The GROD for each point on an EBSD map can be determined by calculating the misorientation between the data point and the average orientation of the grain it belongs to. The GOS for each grain in an EBSD map is the average GROD for all the points in each grain. It is an indicative measure of how much constrained slip each grain has gone through.

Most of the grains in the plastic tensile region of the annealed bend sample (Figure 61) can be segmented from the texture peaks in the inverse pole figure, which correspond to grains misoriented less than 30° away from the $(\varphi_1, \Phi, \varphi_2) = (0^\circ, 90^\circ, 30^\circ)$ orientation. The segmented EBSD map of the annealed sample is shown in Figure 66.

An EBSD map was taken from an as-bent sample in the plastic tensile region. GOS was calculated and the distribution plotted as a probability histogram for (1) the entire map and (2) the subset of orientations which contribute to the final blocky alpha texture. They show similar peaks and distribution shapes. The subset of orientations which ultimately contributes to the blocky alpha texture does not have especially low or high GOS.

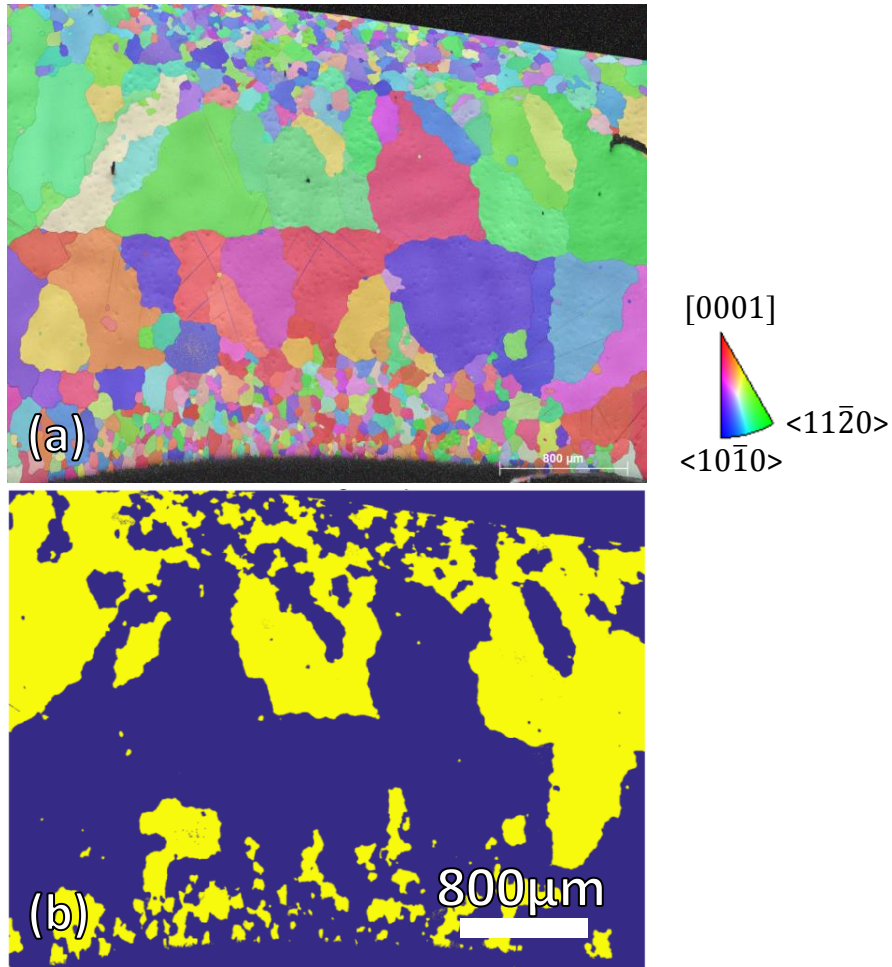


Figure 66: (a) IPF colour map along plate TD (horizontal in map) of three point bend sample annealed at 800°C for 336 hours to produced blocky alpha grains. (b) Thresholded grain map of the same data showing grains less than 30° away from the $(\varphi_1, \Phi, \varphi_2) = (0^\circ, 90^\circ, 30^\circ)$ orientation (yellow in figure).

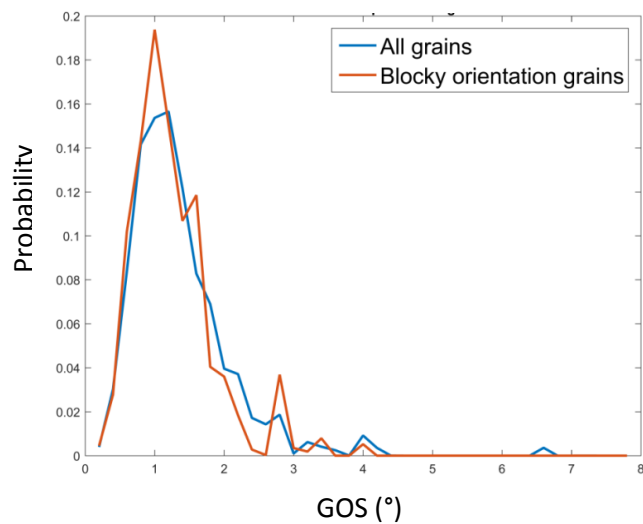


Figure 67: GOS distributions calculated from EBSD, of an as-bent sample in the plastic tensile region (also shown in Figure 56).

5.2.3 Temperature dependence of blocky grain growth

As blocky alpha is an industrial problem for fuel rod cladding in pressurised water reactors, there is an incentive to suppress its formation by adjusting processing routes to avoid certain strain and temperature combinations. Therefore, the temperature dependence of blocky alpha grain growth was studied using three point bending.

A sample was bent according to Section 5.1.2.2, and then annealed for 366 hours at 750°C. Figure 68 shows a cross-polarised optical micrograph of the resultant microstructure. The grain size distribution is comparable to that of the 800°C similarly annealed sample in Figure 59, apart from the regions of low strain close to the neutral axis, where the grain size has remained small. There is a qualitative texture difference in the compressive and tensile regions of the micrograph, which can be seen from the polarised light colours in Figure 68, which show contrast according to the $\langle c \rangle$ -axis direction of the grains. The presence of the neutral axis is apparent, but here it is seen as a region of limited grain growth.

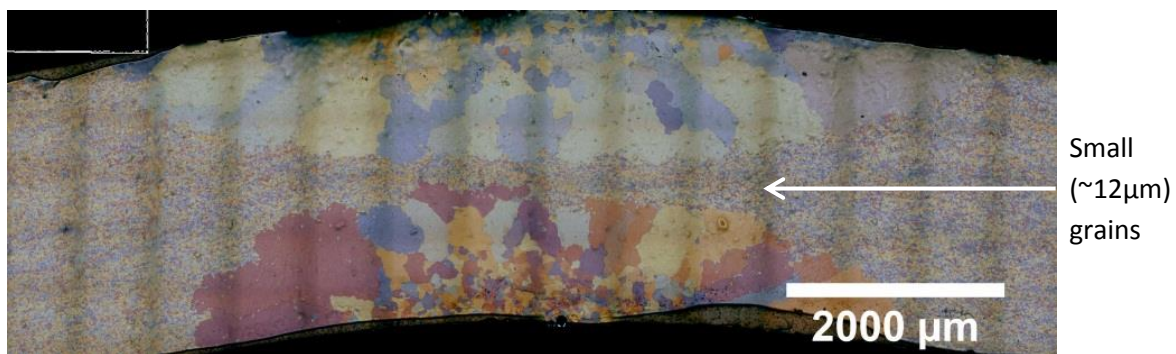


Figure 68: Optical micrograph showing central region of three point bend specimen annealed at 750°C for 336 hours.

EBSD data of this sample shows that in addition to the texture differences (which are also comparable to the textures of 800°C annealed material shown in Figure 64), there are significant numbers of unconsumed island grains surrounded by large-grained material. The presence of more island grains than in the 800°C annealed material suggests that the area of limited grain growth is due to the slower growth kinetics at 750°C and Figure 68 does not show the equilibrium grain structure. The texture of the untransformed grains around the neutral axis is shown in Figure 69.

These grains remain around 12 μm in size and have the same texture as the original as-received material (Figure 40), indicating that they have not recrystallised.

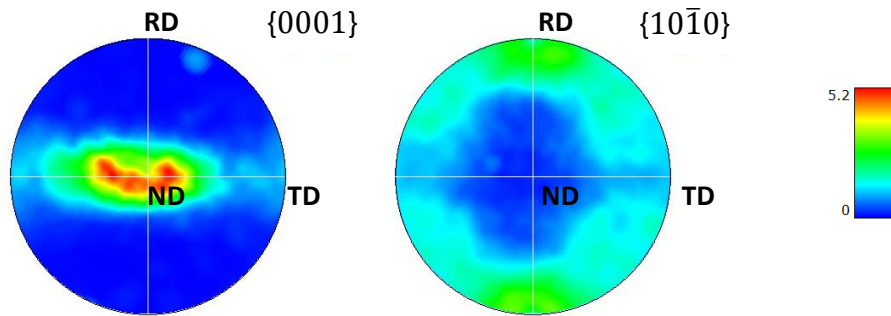


Figure 69: Basal and prismatic pole figures showing texture of small grains around the neutral axis in the three point bend specimen annealed at 750°C for 336 hours.

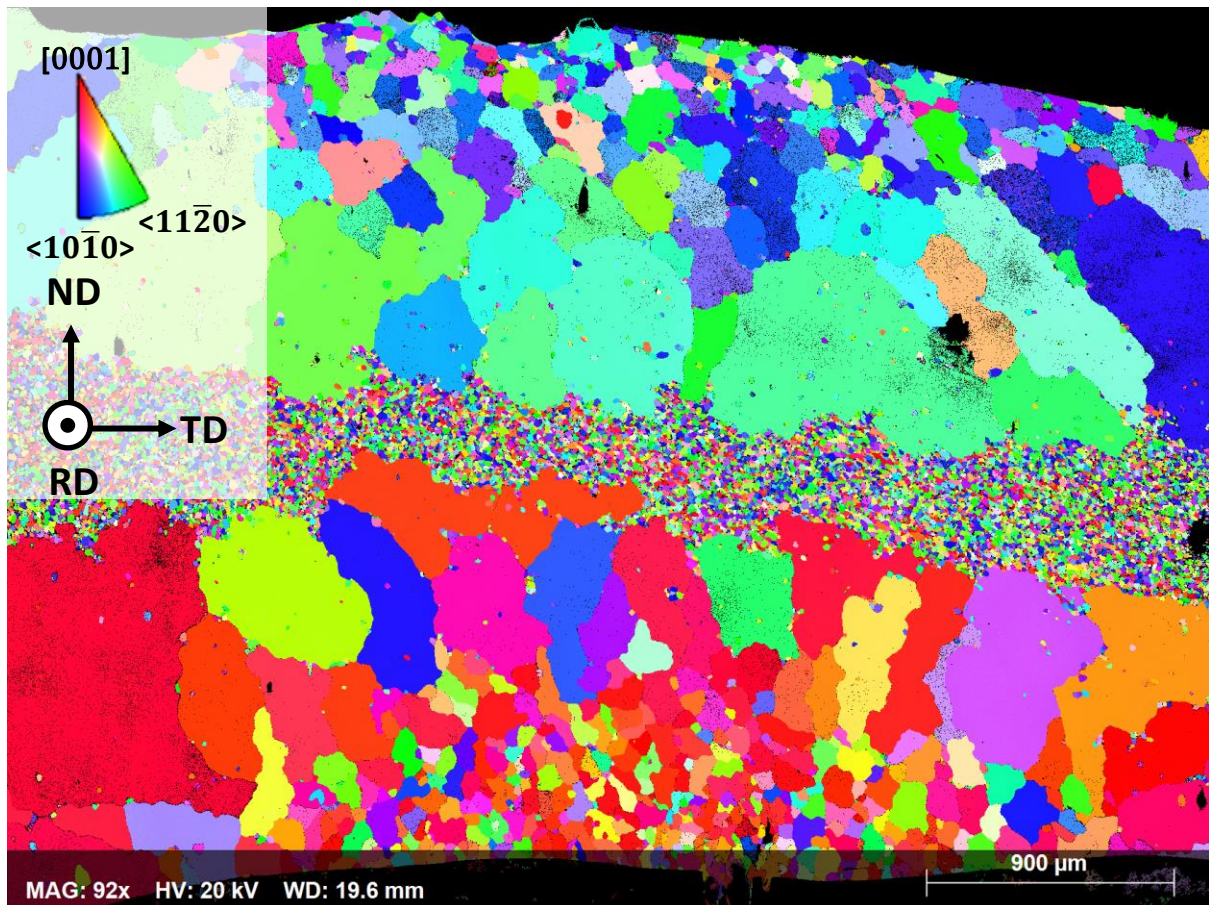


Figure 70: EBSD map with IPF colouring along TD showing centre of bend specimen heat treated at 750°C for 336 hours.

A similarly bent specimen was annealed at 750°C for 720h (30 days). The resulting microstructure is shown in Figure 71. The grains are all large and have a blocky morphology, which confirms that the

The formation of abnormally large grains in Zircaloy-4

remaining small grains present in Figure 68 were indeed due to growth kinetics. The grains towards the centre of the specimen still meet near the neutral axis, but this effect is much less marked than in the 800°C specimen annealed for 336 hours shown in Figure 59, where the outline of the neutral axis is sharp and extends across a longer region of the sample. The grains have also coarsened considerably compared to Figure 59.

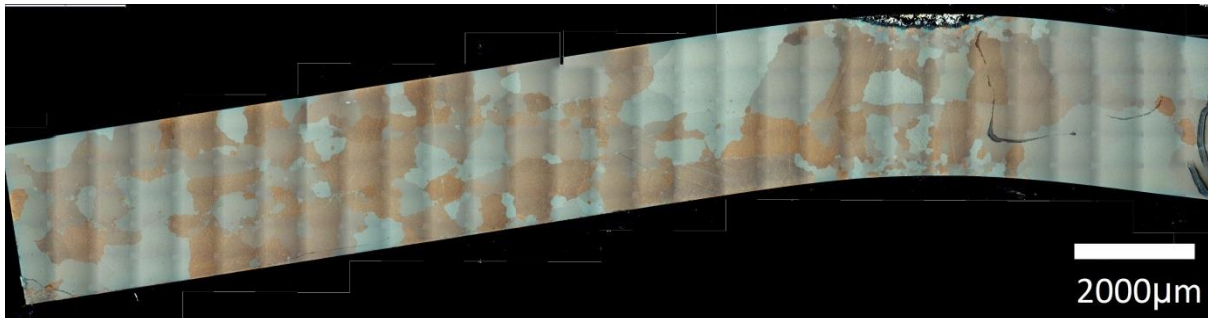


Figure 71: Optical micrograph showing three point bend specimen annealed at 750°C for 720 hours (720 hours).

When the temperature is further lowered to 700°C for the same 720 hours heat treatment time (Figure 72), most of the grains remain small and grain growth is limited to the relatively highly strained regions, where the grain size grows to 100-300µm from an initial grain size of 12µm.

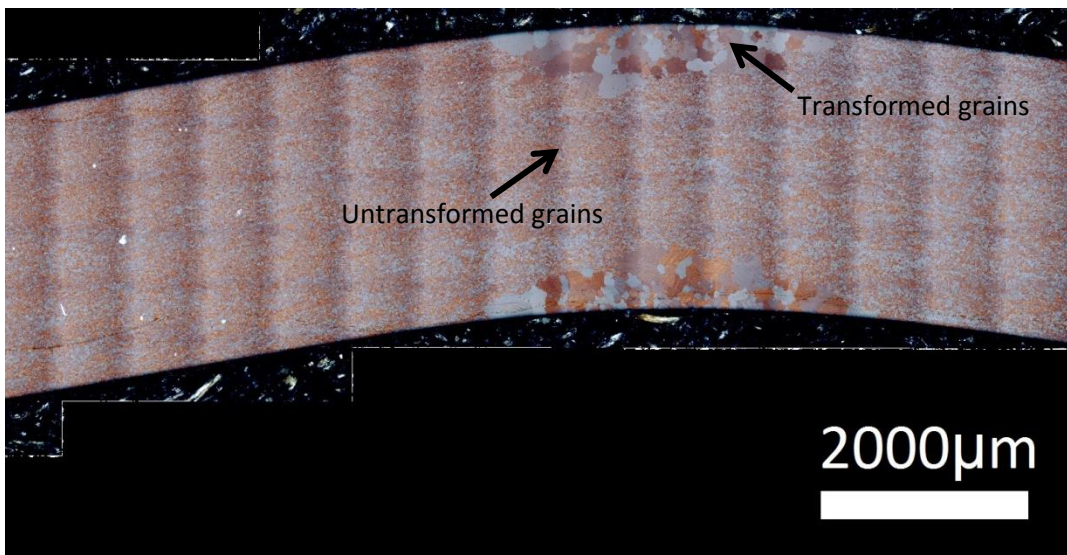


Figure 72: Optical micrograph showing three point bend specimen annealed at 700°C for 720 hours.

5.2.4 Grain growth study of commercially pure zirconium

The effect of the iron and chromium-rich SPPs in Zircaloy-4 was explored by heat treating commercially pure zirconium, which has a similar grain morphology and initial grain size of 30µm but does not contain these precipitates. Table 8 compares the compositions of the two alloys.

	Hf	Fe	Cr	Sn	O	C	N	H	Zr
CP-Zr	1.1%	total 0.16%		0%	0.16%	0.02%	0.008%	0.001%	Balance
Zry-4	<0.02%	0.12-0.18%	0.05-0.15%	1.2-1.7%	<0.05%	0.027%	0.008%	0.0025%	Balance

Table 8: Compositions of commercially pure zirconium (CP-Zr) [170] and Zircaloy-4 (Zry-4) [171].

The starting material was a commercially pure zirconium sample [170] with a starting grain size of around 30µm with a typical unidirectionally rolled and recrystallised Zr plate texture very similar to the Zircaloy-4 plate used in the rest in this chapter (pole figures for the CP-Zr and Zircaloy-4 plates are shown in Figure 78 and Figure 40 respectively). A sample was electropolished to etch the grain boundaries and the surface relief was used to identify the original boundaries. It was then heat treated for 336 hours in an encapsulated back-filled argon atmosphere, so that no thermal grooving of either new or old boundaries would occur.

Figure 73 shows a polarised light micrograph of the as-annealed microstructure. New grain boundaries are visible from colour contrast, and the old boundaries are visible from brightness contrast due to grain boundary etching during electropolishing. The new boundaries do not fall along the old boundaries.

Figure 74: EBSD map (IPF-TD) showing the grains and grain boundaries in the annealed material.

shows an EBSD map of the annealed grains. Some of the grains have grown to over 100µm, significantly larger than the starting grain size of around 30µm, but most of them stay a similar size, producing a bimodal grain size distribution. The morphology is neither typically blocky nor completely polygonal.

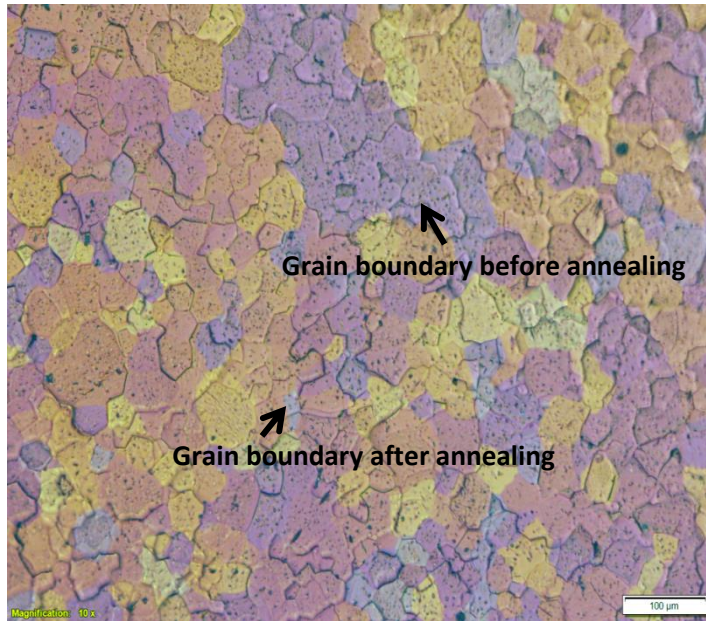


Figure 73: Polarised light micrograph of annealed commercially pure Zr microstructure showing grain boundaries before and after annealing for 336 hours (336 hours) at 800°C.

The textures (not shown) are largely similar to the starting material. There are many very small flecks of different indexed orientation which look like noisy misindexed data points; however, observation of the EBSD patterns shows that these points produce good and significantly different EBSD patterns to the rest of the grain. These are likely a different phase (e.g. hydrides or oxides). Figure 75 shows that both hydrogen and oxygen are highly soluble in Zr at 800°C [172][173], so that any surface hydrides or oxides should not pin grain boundary motion and affect the grain growth behaviour due to a second phase, although there might be solute drag from dissolved hydrogen and oxygen which could inhibit grain growth.

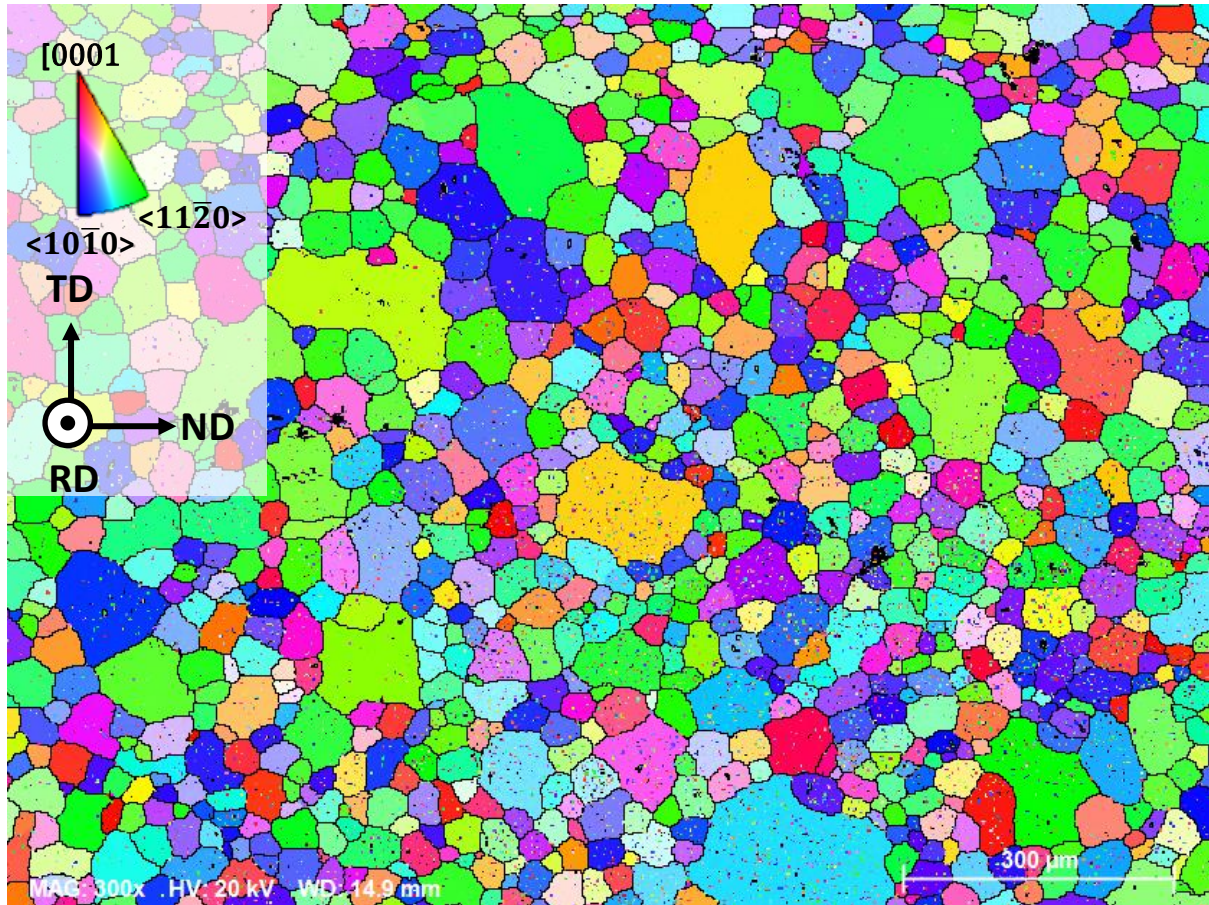


Figure 74: EBSD map (IPF-TD) showing the grains and grain boundaries in the annealed material.

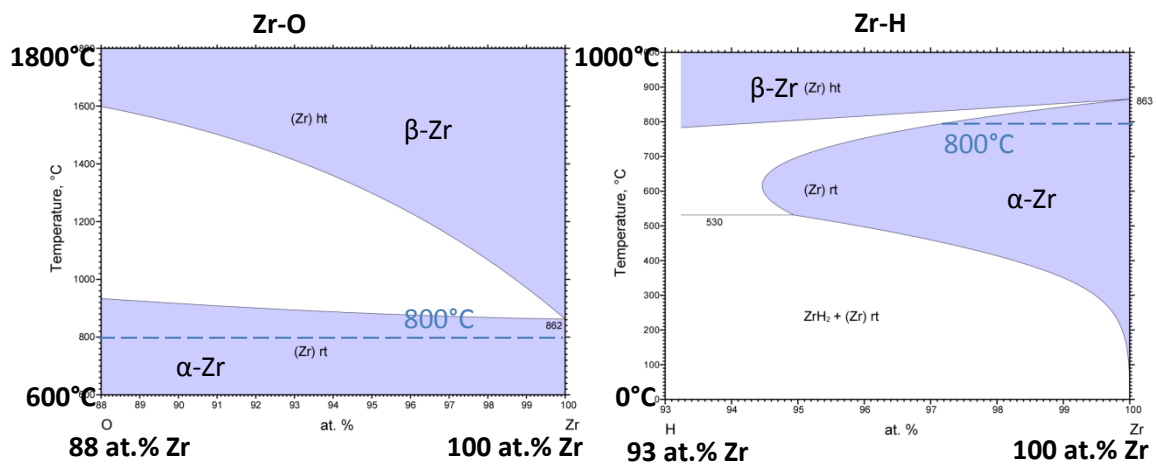


Figure 75: Zr-O [173] and Zr-H [172] phase diagrams showing hydrogen and oxygen solubility at 800°C.

5.3 Discussion and potential further work

5.3.1 Critical strain for grain growth

Grain growth in Zircaloy-4 is present when samples are held at high temperatures for long times within the alpha phase field. This can occur both within as received samples, even with stress relaxation and defect removal anneals (3 hours at 300°C) prior to long term annealing, and samples deformed at higher strain levels. The reduction in grain size beyond the peak 2% strain indicates that there is a critical strain for maximum blocky alpha grain growth. Note that even with no macroscopic plastic strains, there could be significant intergranular thermal strains, as the thermal expansivity of HCP Zr is anisotropic, and maximum strains of 0.4% can result when Zr is heated to 800°C by $\Delta T = 780K$ [60]. Significant thermal strains could therefore build up at grain boundaries where neighbouring grain orientations have near perpendicular $\langle c \rangle$ axes, such as in a T1 twinned grain [15].

As further work, the residual strain at grain boundaries due to thermal expansion mismatch could be measured using HR-EBSD analysis on an as-received sample annealed at 800°C for a short time (around 6 hours), before blocky alpha begins to nucleate. In this way, the local strains caused by different thermal expansion coefficients along the $\langle a \rangle$ and $\langle c \rangle$ crystal axes could be quantified by measuring residual stresses near grain boundaries, and their effect on blocky alpha nucleation in undeformed samples can be explored.

The bend sample annealed at 800°C for 336 hours (Figure 59) has a blocky microstructure throughout the entire sample, even far away from the bent region near the outer rollers where the strain is negligible. This indicates that the critical strain is lower than the thermal strains induced when heating to 800°C.

The bend sample annealed at 750°C for 336 hours (Figure 68) shows an absence of grain growth near the neutral axis and in less strained regions, which at first seems to indicate the presence of a critical strain when annealing at 750°C. However, when the same 750°C heat treatment is prolonged

to 720 hours (Figure 71), the microstructure is blocky in all regions of the sample. This indicates that the kinetics of grain growth is slower at 750°C than 800°C but not inhibited.

The bend sample annealed at 700°C for 720 hours (Figure 72) shows small grains in the entire sample apart from the highly strained central regions, where a limited region of recrystallised grains has formed. A longer heat treatment was not performed. This could be studied as further work.

It is therefore inconclusive whether there exists a critical strain for blocky alpha grain growth, or if blocky alpha formation is controlled only by kinetics and dependent on annealing time. Limiting annealing times to shorter than 720 hours and temperatures to below 700°C should be sufficient to suppress blocky alpha formation in lightly deformed ($\epsilon < 4\%$) Zircaloy-4. The long term microstructural stability of Zircaloy-4 under typical reactor conditions (>3 years at 350°C) currently requires significant extrapolation.

5.3.2 Incubation time and kinetics of grain growth

The incubation time for grain growth in samples strained along ND and annealed at 800°C is less than 20 hours for 2% strain and around 48 hours for 0.3% strain. This matches observations in the literature [11] of the incubation time decreasing with increasing strain. It is also consistent with the normal grain growth behaviour of the 2% strained samples after the blocky alpha transformation is complete, which results in the 2% strained samples having a larger final grain size than the 0.3% strained samples (Figure 46).

Further work to quantify the incubation period could be done using *in-situ* SEM observation of grain growth during heating, using three point bend samples deformed to different strains. Three point bending should be used so that the first blocky alpha nucleation event can then be constrained to the highly-strained parts of the central region in the sample. As the SEM environment is a hard vacuum, thermal grooving on mirror-polished samples could be used as a way of etching boundaries and tracking boundary motion.

The long incubation period for blocky alpha formation has been attributed to the coarsening and dissolution of SPPs in zirconium alloys [11], [12]. No positive conclusions can be drawn about the role of SPPs in blocky alpha formation from the commercially pure Zr heat treatment study (Section 5.2.4), but they appear to play a part in blocky alpha formation, as blocky alpha formation is suppressed without them, although a bimodal grain structure has developed in the CP-Zr. This can be seen by comparing Figure 73 (CP-Zr grain structure) with Figure 47(b) (typical blocky alpha structures).

5.3.3 Driving force for grain growth

A combination of stored strain energy and thermal energy provide the driving force for the nucleation step of blocky alpha formation. The source of strain energy can either be thermal strain from a T1 twin where the $\langle c \rangle$ axes are 85° misoriented, and 'rogue grain pairs' with nearly perpendicular $\langle c \rangle$ axes, or alternatively applied strain during uniaxial compression or bending. Grains with high stored strain ahead of the grain boundary form blocky alpha nuclei via SIBM, and progressively consume neighbouring grains to form a blocky alpha structure.

Once nucleation has occurred, the reduction of grain boundary area and energy is the driving force for blocky alpha growth, corresponding to an abnormal grain growth phenomenon. This is supported by the observation that blocky alpha grain growth occurs in the absence of a macroscopic strain field, as shown by the data points marked by green crosses in Figure 46. These samples were not deformed prior to annealing and were pre-annealed at 300°C to relax residual stresses and high dislocation density regions from machining, but still exhibit blocky alpha grain growth, resulting in a final grain size similar to that of samples deformed just past the yield point to 0.3% strain. In these cases, SIBM operates at local stress concentrations from anisotropic thermal expansion only to nucleate blocky alpha growth, but does not provide the driving force for grain growth once the blocky alpha grain has nucleated. Local stress concentrations from thermal expansion mismatch cannot recrystallise the material in the as-received case as there is no strain energy ahead of the

transformation front to lower the energy of the system. The material studied here is relatively strongly textured (Figure 40 shows pole figures of the as-received material) and therefore 'rogue grain pairs' with near perpendicular $\langle c \rangle$ axes are likely to be sparsely distributed and will not contribute significantly to the total strain energy in the material. This has not been quantified in the present work, but were the rogue grain pairs to contribute significantly to stored strain energy in the system (and be well distributed throughout the microstructure) it could change the likely mechanism for blocky alpha formation from abnormal grain growth to nucleation-site limited primary recrystallisation.

The original grain boundary networks are initially preserved (in the absence of coarsening) and this can be seen from the waviness of the grain boundaries leading to the characteristic blocky structure. This process is outlined in the schematic in Figure 76. In normal grain growth of single-phase materials, the grain boundaries are straight sections pinned at triple junctions so that the boundary surface energy is minimised [85].

In the three point bend specimen where the blocky alpha transformation is interrupted (annealed at 750°C for 336 hours), the neutral axis has small grains similar to the as-bent grain size, with a texture (Figure 69) similar to that of the as-received plate (Figure 40). The fact that the neither texture nor grain size have changed in the central small-grained region around the neutral axis indicates that these grains probably have not recrystallised. This might suggest an abnormal recrystallisation (equivalent to primary recrystallisation) mechanism [65] for blocky alpha formation. However, the stored strain energy in this region near the neutral axis is low, and there is insufficient driving force for recrystallisation to occur in the first place. The driving force for the blocky alpha transformation is therefore most likely reduction of grain boundary area, corresponding to an abnormal grain growth mechanism [63].

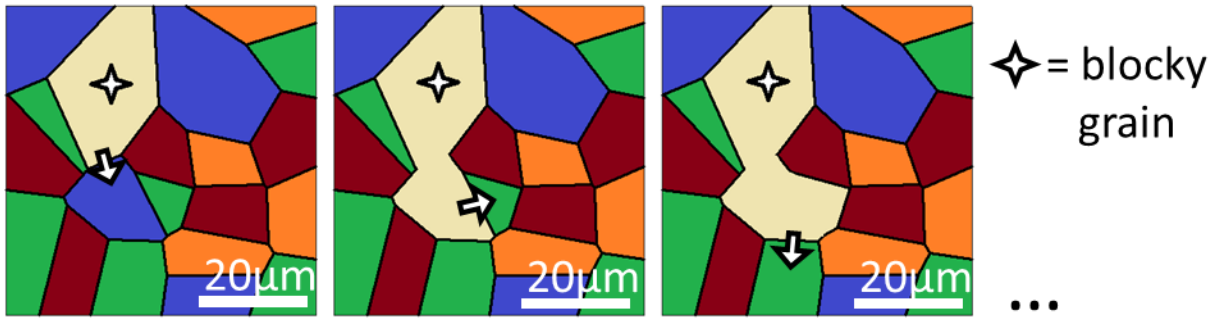


Figure 76: Schematic of proposed grain growth mechanism for blocky alpha.

5.3.4 Blocky alpha transformation front

The spacing of GND density hotspots in the pre- and post-anneal samples in Figure 49 is similar, although the absolute GND density is much lower post-annealing as most (but not all) of the GNDs are removed by the blocky alpha transformation. It seems likely that the GND density hotspots in the blocky alpha sample (Figure 49(d)) could be decorating the original grain boundaries or triple junctions. This suggests a whole grain consumption mechanism, where the blocky alpha transformation front leaves dislocation debris behind as it migrates into new grains.

The presence of dislocation debris on what is presumably the original grain boundaries or triple junctions is in contradiction to some literature, which say that recrystallisation leaves perfect crystal behind it, and grain growth only happens in recrystallised, near-perfect crystal, although the mechanism by which the recrystallisation process removes defects is not known [66]. If this is true, neither abnormal recrystallisation nor abnormal grain growth mechanisms should leave dislocation debris left behind the blocky alpha transformation front. However, the GND patterning seen here is significantly above the noise floor of the HR-EBSD technique. Dislocation densities of 10^{14}m^{-2} are observed compared to the noise floor of $<10^{13}\text{m}^{-2}$ [135] for the EBSD acquisition settings used here (full resolution patterns of 1600 by 1200 pixels, and step size of $0.3\mu\text{m}$).

Pitting in the blocky alpha sample can degrade pattern quality (Figure 49(e)-(f)) and increase uncertainty in the GND density measurement, and indeed the positions of GND density hotspots do correlate with pitting and reduced pattern quality. However, the higher dislocation density regions in

the blocky grain extend much further beyond the pits and areas of reduced pattern quality from pitting. As pitting does not in itself stress the material, the longer-range GND density hotspots cannot purely be an artefact of reduced pattern quality from pitting. Pitting during electropolishing in this case is a sign of preferential chemical attack on high stored energy sites.

5.3.5 Blocky alpha growth direction

Figure 77 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. It can be seen from the difference between the maps that the growth direction of the blocky alpha transformation front is from the edges of the recrystallised region inwards towards the neutral axis. The major axes of the blocky alpha grains in the 'completed transformation' microstructure all point perpendicular to the neutral axis, suggesting that the growth is towards the neutral axis. This growth from the lightly strained region inwards towards the neutral axis is highlighted in the incompletely transformed microstructures (for samples heat treated at lower temperatures).

In the fibres that are strained to above 2-3% in magnitude, the linear intercept grain size is less than 100µm and remains relatively constant with strain level and the texture of these grains are different to the large blocky alpha grains (Figure 64). This indicates that grains recrystallise readily above a threshold strain of 2-3%. However, below this threshold strain, nucleation is limited and the outer 'layer' of blocky alpha grains grow inward towards the neutral axis, creating elongated grains in the presence of a strain gradient (i.e. towards the neutral axis). Since the large blocky alpha grains nucleate along a similar fibre of the bend specimen, the blocky alpha transformation fronts meet at the centre of the specimen around the neutral axis. When the thermal energy is limited, i.e. through a lower temperature heat treatment for the same length of time, the blocky grains do not reach the neutral axis and this indicates that the rate of progress of this transformation front is temperature sensitive.

Figure 64 shows that the textures of the recrystallised grains are different to the blocky alpha grains, suggesting that a different mechanism is operating in the highly-strained finer-grained regions compared to the lower-strained blocky alpha regions.

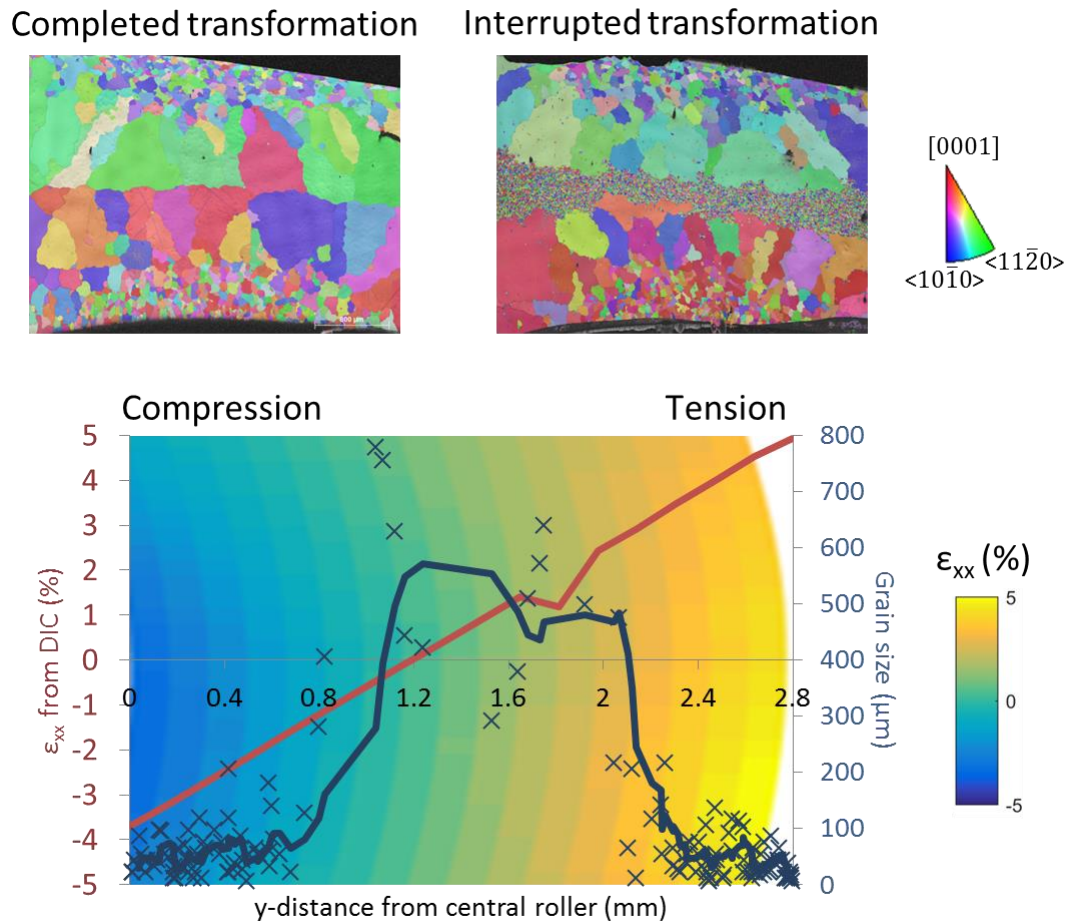


Figure 77: Summary of nucleation sites and growth direction of blocky alpha grains in three point bend specimen, redrawn from parts of Figure 61, Figure 60, and Figure 70.

The grain size obtained for a given ϵ_{xx} in bending is similar to but slightly different from Figure 46, which shows the blocky alpha grain size as a function of strain in uniaxial compression. In uniaxial compression, the blocky alpha grains are largest around 2% strain, and then decreases sharply between 2.5 and 4% strain. The small difference in the threshold strain (where recrystallisation nuclei start to form readily) may be due to the presence of a strain gradient, which changes the recrystallisation nucleation site frequency from a uniform distribution to a non-uniform one.

5.3.6 Coarsening after completing transformation

In the proposed mechanism, once the critical strain is reached, fewer competing nucleation sites (lower strain) should lead to a larger final grain size. This is broadly true in Figure 46, where large strains lead to a lower final grain size. However, it is at first unclear why the 2% strained sample has a larger final grain size than the 0.3% strained sample, even though critical strain for blocky alpha formation is reached for both samples (Figure 46 and Figure 47). A proposed explanation for this is that since the kinetics of blocky alpha growth increases with the level of prior strain, the blocky alpha transformation finishes more quickly in the 2% strained samples. This gives grains in the 2% strained an opportunity to coarsen via normal grain growth and increase further in size. Normal grain growth is possible after the blocky alpha transformation, as any SPPs which initially inhibited normal grain growth would have dissolved by this point (100 hours at 800°C) [174].

As further work, the coarsening effect could be explored by annealing 2% strained samples at 800°C using holding times between 66 hours and 336 hours (Figure 47), so as to catch the end of blocky alpha formation before coarsening begins. The grain size and morphology should be similar to the microstructure in Figure 44(b), which shows undeformed Zircaloy-4 heat treated at 800°C for 336 hours.

In the bend specimen heat treated at 750°C for 336 hours, the vertical distance between the neutral axis and the highly strained region contains a few grains. However, after 720 hours the vertical distance between the neutral axis and the highly strained region is dominated by a single grain, and the neutral axis effect is much less pronounced. This implies that the smaller blocky grains were consumed by larger blocky grains, and also that blocky grain boundaries can migrate into other grain boundaries.

5.3.7 Nucleation of blocky alpha in uniaxial compression

Figure 48 shows similar textures in ND and RD compressed material. Although RD compressed material is in an orientation favourable for twin formation, at 2% strain and a 12µm grain size there

are likely very few T1 twins in the RD sample and none in the ND sample. Since the texture is broadly inherited from the parent plate, it can be concluded that arbitrary grains in the sample nucleate, such that the heat treated texture is inherited directly from the parent material with no preference for a particular orientation (unlike abnormal growth of Goss oriented grains in Fe-Si steels [175]).

5.3.8 Nucleation of blocky alpha in three point bending

There is a significant texture switch between the plastic tensile and plastic compressive regions of the blocky alpha three point bend specimen. This texture switch may be caused by a combination of deformation slip or twinning. Twinning is tension/compression asymmetric and significantly reorients the crystal lattice. Although only one twin type ($\{10\bar{1}2\} \langle 10\bar{1}1 \rangle$) is present in the entire as-bent sample (Figure 56 and Figure 57), twinning is activated in different subsets of grain orientations in the tensile and compressive regions of the bend specimen. Slip is largely insensitive to the sense of the strain as dislocations can move in either direction along a slip plane, and slip does not significantly reorient the crystal lattice as twins do. Therefore, it is unlikely that slip alone contributes to the different textures.

5.3.8.1 Role of slip

Figure 67 shows that GOS distributions in the subset of grains in the as-bent sample that contribute to the annealed three point bend texture do not have particularly low GOS values, and therefore do not, on average, have neighbours with higher stored energy (and thus encourage consumption of their neighbours by SIBM). However, only a tiny fraction of this subset will actually nucleate a blocky grain; indeed the EBSD data field of view (shown in Figure 56) used for this analysis is only 240 μm by 180 μm . The grain size in the highly strained 'small grained' plastic tensile region is still around 150 μm (Figure 61), and if the EBSD data is a 2D section of three or four blocky grains at most, it is conceivable that there might not even be one potential nucleant grain present in this data.

Due to the sparseness of nucleation sites, the GOS distribution tails are much more important than the distribution peaks. In the present data (Figure 67), the number of grains sampled is not large

enough to provide meaningful conclusions, and it cannot be concluded whether or not highly slipped regions play a part in nucleant selection. Three-dimensional synchrotron techniques (such as far field high energy diffraction microscopy [176]) to measure grain orientations and grain average strain would allow far more grains to be sampled and avoid the limitations associated with using 2D sections.

5.3.8.2 Role of twinning

High GND density has been observed ahead of a twin tip in Figure 58, taken from the plastic tensile region of an as-bent sample. However, GND density hotspots are not found only at the twin tip, but also in other regions of the parent grain and in neighbouring grains. This suggests that several competing nucleation sites could contribute to nucleation of blocky alpha. Any of the GND density hotspots around the twinned grain have higher stored energy and should equally lead to blocky alpha nucleation.

5.3.8.3 Orientations of blocky alpha grains

In the plastic compressive region of the three point bend specimens, twin and parent orientations dominate the final texture. The role of twinning is especially clear in Figure 62, where the TD inverse pole figure in the large-grained plastic compressive region has two smaller peaks separated by about 85°. This misorientation is close to a $\{10\bar{1}2\} <10\bar{1}1>$ T1 twin misorientation angle of 85°. Given the initial as-bent texture (Figure 57), the $[0001]$ peak probably nucleated from a twin and the $<10\bar{1}0>$ peak nucleated from a parent grain.

In the plastic tensile region, though the twinned fraction is similar to and even slightly larger than the plastic compressive region (Figure 55), neither twins nor parents selectively nucleate blocky alpha grains. Instead, the texture is inherited from the as-deformed material, with the exception of two 'rogue' grains with C1 and T1 twinned orientations. C1 twins are primarily observed at liquid nitrogen temperatures in Zr [177], and were not observed in the as-bent material when mapped

with an EBSD step size of $0.3\mu\text{m}$ over a $240\mu\text{m}\times 180\mu\text{m}$ field of view. The origin of the C1 twin relation with respect to the rest of the blocky alpha texture is unclear.

The deformation texture present in the as-bent material is sharpened in the plastic tensile region on annealing, indicating selective nucleation of highly deformed grains. This is in contradiction to some of the literature which indicates that grains with low GOS should grow preferentially via SIBM into neighbouring grains with high GOS [80].

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 final texture. As future work, uniaxial compression could be used to selectively activate or suppress twinning and test the role of twinning in the absence of a strain gradient. It would be interesting to see the texture differences on annealing between Zircaloy-4 plate compressed to around 4% in ND (little or no twinning) and RD (profuse T1 twinning) respectively.

5.4 Summary

Abnormally large grains, also called blocky alpha in Zircaloy-4, form as a result of annealing after low (<4%) strains, which can be from either mechanical deformation or 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.

There may be a critical strain for nucleation of blocky alpha which is less than 0.4% strain when annealing at 800°C . At very low strains (less than 0.3%) there is a ~50 hour incubation time before blocky alpha nucleates; this decreases to less than 20 hours at 2% strain.

The nucleation of blocky alpha is believed to be whole grain consumption 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 applied strain before annealing, or from anisotropic thermal expansion, which can cause up to 0.4% intergranular strain when annealing at 800°C.

The driving force for blocky alpha growth is most likely the reduction of grain boundary area, which corresponds to an abnormal grain growth mechanism. This explains the absence of a macroscopic critical strain required for blocky alpha growth at 800°C, as strain is only required on a local grain level for nucleation. In three point bend specimens annealed at 800°C, there is a switch from ~100µm recrystallised grains to extremely large blocky alpha grains as the strain magnitude decreases past 2-3%, where primary recrystallisation nuclei stop forming readily. As a result, grains at the edge of the highly strained regions grow inward towards the neutral axis. This effect is roughly symmetric in tension and compression, so that the blocky alpha grains meet in the middle of the specimen and do not cross the neutral axis.

The nucleant selection mechanism which gives rise to the final texture is strongly dependent on the direction of strain. Twinned grains dominate the blocky alpha texture in the plastic compressive region of annealed three point bend specimens, whereas deformed grain orientations dominate the blocky alpha texture in the plastic tensile region.

6. Deformation twinning in commercially pure zirconium as a function of texture and strain rate

6.1 Motivation

Zirconium alloys are used in nuclear reactors as fuel rod cladding due to zirconium's high strength and low neutron absorption cross section. Knowledge about the rate dependence of competing deformation modes is important especially during forming of the cladding tubes and during reactor accident conditions. $\langle a \rangle$ prismatic slip has the lowest critical resolved shear stress slip system in alpha zirconium, but cannot accommodate deformation along the unit cell $\langle c \rangle$ axis. Twinning along pyramidal planes can provide an alternative to $\langle c + a \rangle$ pyramidal slip, which has a high critical resolved shear stress in zirconium. Therefore, the competition between deformation slip and twinning modes as a function of texture and strain rate is critical in understanding deformation behaviour.

6.2 Method and materials

The starting material used was commercially pure zirconium (97.0% purity), from Advent Research Materials Ltd. which was nominally supplied in a clock-rolled condition. However, the texture measured by EBSD in Figure 78 shows a typical unidirectionally rolled and recrystallised texture, indicating that the texture had been dominated by the final rolling pass. Therefore, plate directions will be referred to as the rolling/normal/transverse directions (RD/ND/TD) instead of in-plane/through-thickness directions (IP/TT). Pole figures and an EBSD IPF colour map shows the texture of the material measured from ~6000 grains (Figure 78).

Mechanical testing was performed by Dr Euan Wielewski. Four cylindrical samples were machined from the as-received plate, two with the cylinder axis aligned along the TD direction ('TD samples') and two along ND directions ('ND samples'). Samples along each direction were compressed to 10% engineering strain in either a split Hopkinson bar at a high strain rate of 10^3s^{-1} ('HR samples') or in a conventional crosshead device for mechanical testing at a quasi-static strain rate of 10^{-3}s^{-1} ('QS samples').

The deformed samples were cross-sectioned to reveal the rectangular mid-plane, and after grinding to 4000 grit ($5\mu\text{m}$ particle size) SiC paper finish, electropolished for 120 seconds at 25V and -40°C in a electrolyte solution of 50ml perchloric acid and 450ml methanol. EBSD data of the deformed samples were collected on either a Zeiss Auriga field emission gun SEM or a FEI Quanta field emission gun SEM. In both cases, data was collected using a Bruker eFlashHR EBSD camera with a step size of $0.3\mu\text{m}$ over a $240\mu\text{m}\times 180\mu\text{m}$ area.

The fields of view were chosen to be approximately in the centres of the sample to minimise observation of edge friction artefacts during compression. The statistical variability of twinning data collected by EBSD has been measured in textured zirconium by Morrow et al. [178]. It was found that using a different sectioned plane (with respect to the plate texture) does not significantly skew twin statistics, whereas microstructural variability can present a bigger problem. To circumvent this issue, larger EBSD maps (which are not shown here) were also collected for all samples to verify that there were no significant variations in texture or twinning frequency along the compression axes and sample radii.

The orientation data was post-processed using in-house written software in MATLAB to produce grain boundary maps with twin types identified. This process has been outlined in Chapter 4. In all maps the indexing rate exceeded 95%, and two iterations of data clean up were used for the grain boundary maps so that twin boundaries could be properly identified. The data clean up algorithm

dilates the EBSD map into unindexed points, assigning these points the average neighbour orientation.

Twin boundaries were identified using the quaternion representation of the four common twin misorientations [15], which can be characterised by a rotation about the shear plane normal axis. The axis-angle misorientations for the different twin types in zirconium are tabulated in Table 1 in Chapter 2.1.

The data clean up and twin boundary identification algorithms are outlined in Chapter 4. From the edge map, the twin numbers, lengths and widths were measured by hand. Area fractions were calculated from colour segmentation of grain and twin boundary maps (e.g. Figure 34) with twins flood filled.

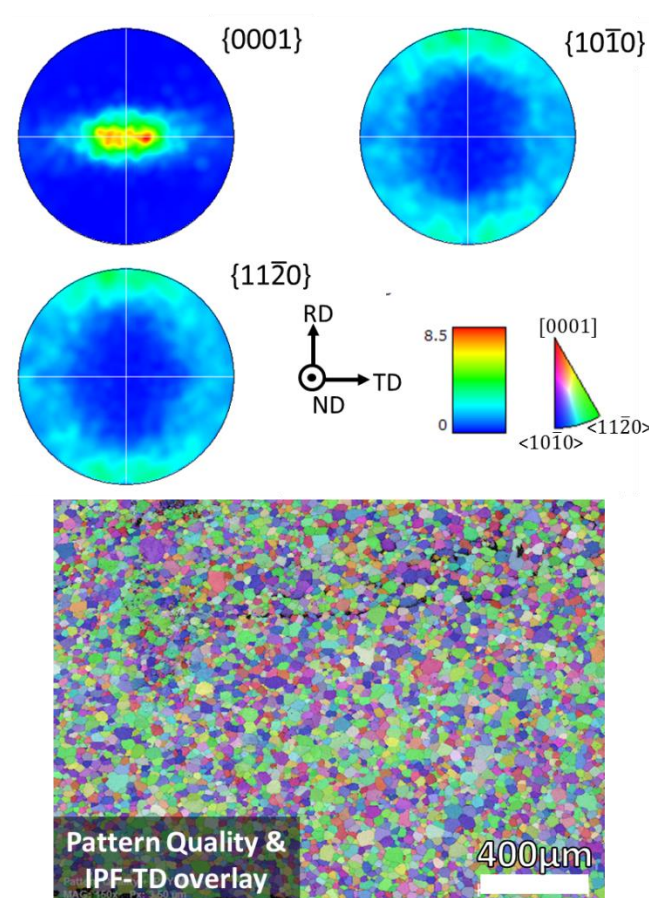


Figure 78: Texture and grain morphology of starting material, with pole figure colour scale in multiples of random texture. The average grain size measured by EBSD is 25 μm .

6.3 Results

6.3.1 Mechanical data

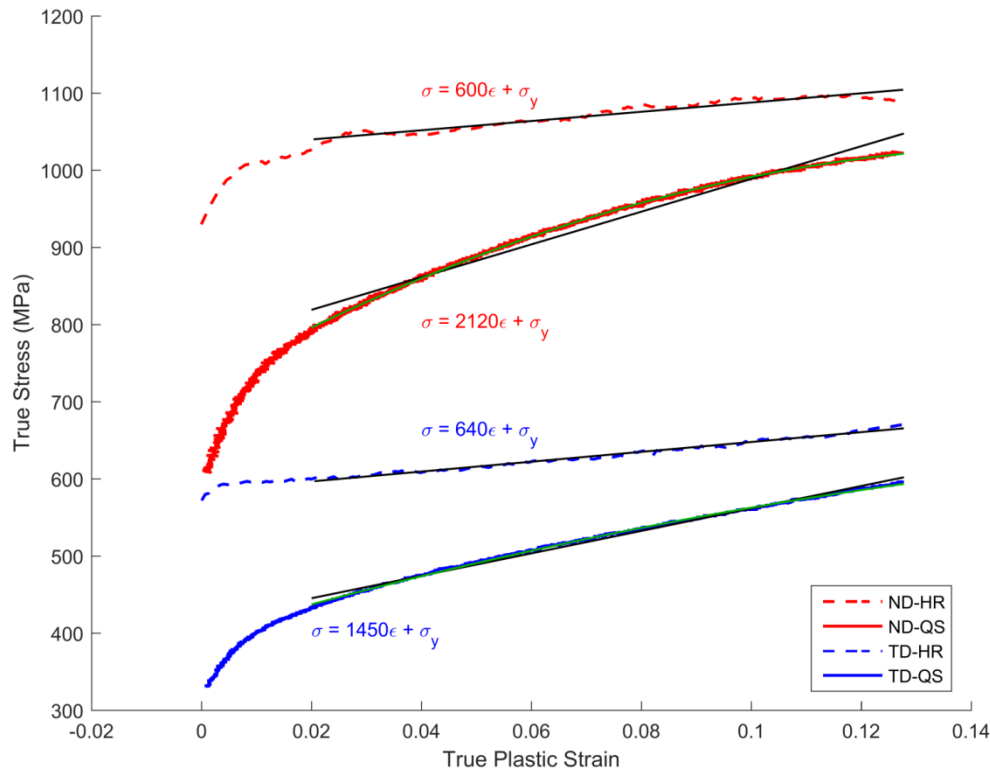


Figure 79: Mechanical data for the compressed samples. Black lines are for a linear best fit and green lines are a parabolic best fit (parabolic best fit for QS samples only).

The mechanical data is shown in Figure 79 as true stress plotted against true plastic strain, with linear fit work hardening rates shown. True stress and strain measure the instantaneous stress and strain during deformation, taking into account the change in cross-sectional area as the deformation progresses. The HR samples show linear work hardening behaviour and the QS samples show parabolic work hardening behaviour. This is seen by comparing the black and green best fit lines in the QS plots; the green (parabolic fit) follows the test data much more closely than the black (linear fit) line.

The (linear fit) work hardening rate for the QS samples is much greater than for the HR samples, but the compression direction (TD versus ND) does not have a large effect on the work hardening rate.

6.3.2 EBSD data

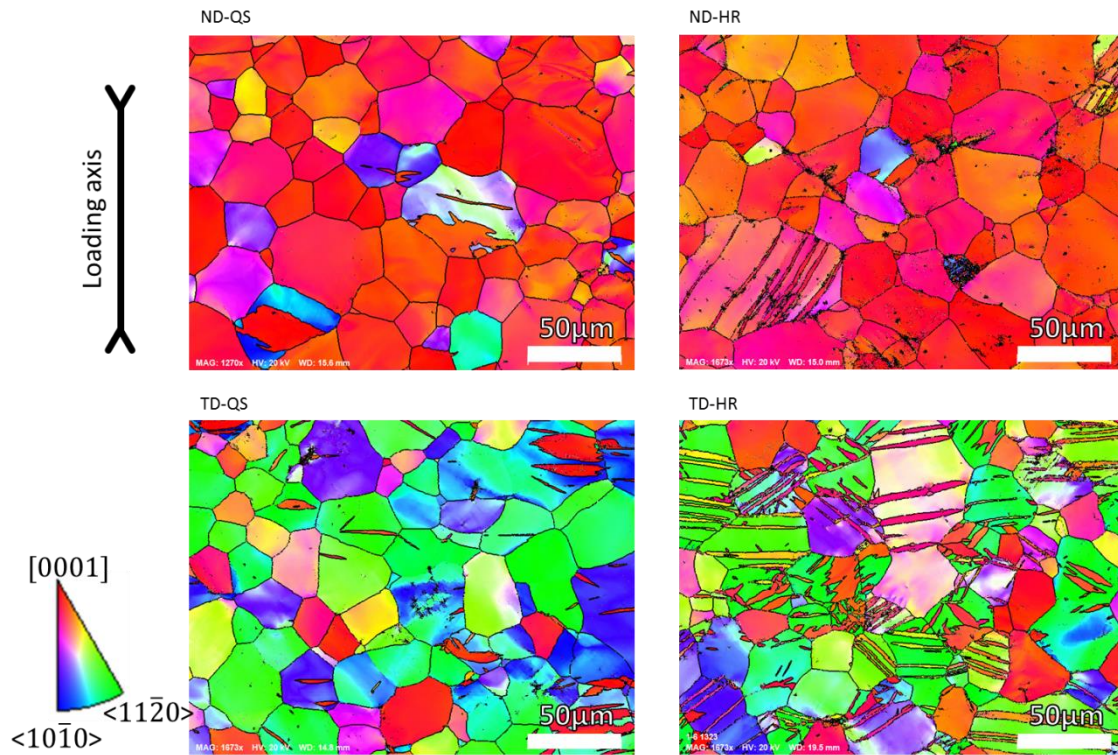


Figure 80: IPF colour maps with respect to the loading axis (vertical in the maps). Grain boundaries (neighbour misorientation $>5^\circ$) are highlighted in black.

IPF colour maps of the samples are shown in Figure 80. The loading axis is vertical in the map and the IPF directions are with respect to the loading axis.

The textures of the samples are different between the two loading directions. Twins, lenticular shaped grains growing across parent grains, are visible in all maps. Ignoring twins (since these orientations are not present in the as-received material), the average orientations of the grains in in ND and TD samples can be regarded approximately as $\langle c \rangle$ axis and $\langle a \rangle$ axis compression of the hexagonal unit cell respectively. At this strain level (10% engineering strain or 12.5% true strain), the grains are not expected to have reoriented significantly via slip.

In ND-QS, the majority of grains have basal directions $[0001]$ pointing along the loading axis. There are a few twins in this sample, and all of them are in grains with basal poles pointing away from the

loading axis, which are exceptions to the principal texture orientations in this sample. Grains where the basal pole is very well aligned with the loading axis (i.e. red in Figure 80) generally do not contain twins.

In ND-HR, the majority of grains have basal poles $[0001]$ pointing along the loading axis. The twin density in this sample is slightly higher than in ND-QS. Twinning occurs predominantly but not exclusively in grains where the basal pole is oriented away from the loading axis.

In TD-QS, the majority of grains have prismatic poles $\langle 11\bar{2}0 \rangle$ and $\langle 10\bar{1}0 \rangle$ pointing along the loading axis. The twin density in this sample is higher than both ND-QS and ND-HR.

In TD-HR, the majority of grains have prismatic poles $\langle 11\bar{2}0 \rangle$ and $\langle 10\bar{1}0 \rangle$ pointing along the loading axis. There is a very high twin density in this sample, with multiple twin variants or types activated in each grain. Most of the twins are orange or red, i.e. close to the basal orientation. As twin growth occurs, an increasing fraction of basal poles are rotated towards the loading axis, contributing to increased work hardening.

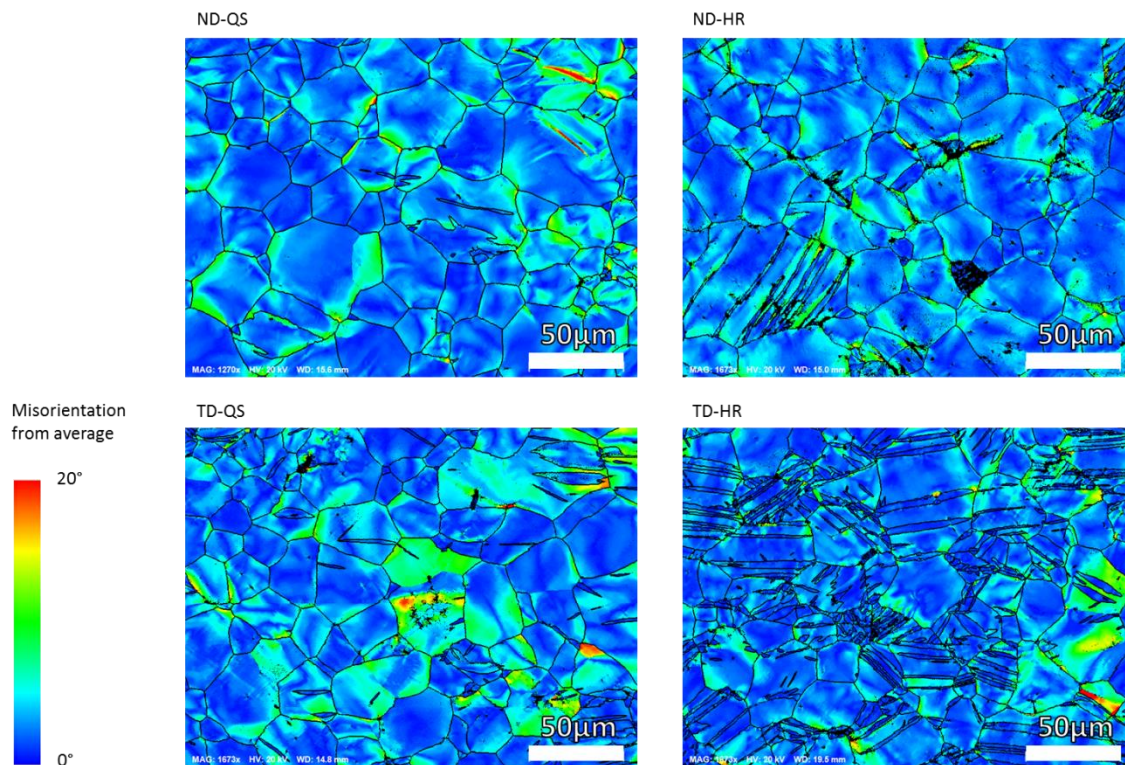


Figure 81: GROD maps showing constrained slip in grains. Grain boundaries (neighbour misorientation $>5^\circ$) are highlighted in black.

GROD measures the misorientation of each point as an angular deviation from the grain averaged orientation. It indicates the degree of constrained plastic slip due to dislocation motion, and therefore increases with increasing levels of plastic deformation [179]–[181]. Long range orientation gradients in a grain show regions of constrained single slip, and the short range orientation gradients present as flecks in the maps show the formation of dislocation cell structures from multiple active slip systems. In all samples, GROD is always highest near grain boundaries and triple junctions.

In the ND-QS GROD map, most of the orientation gradients are long range and continuous, with misorientation increasing towards the grain boundaries and triple junctions, corresponding to single slip in a constrained polycrystal. There are a few instances of ‘flecks’ showing higher misorientation nearer the grain centres, corresponding to multiple slip systems activated. Fragmentation of grain orientations and formation of low angle boundaries is visible in some grains, marked by localised areas of high misorientation.

In the ND-HR GROD map, these long range continuous orientation gradients are also present but less common. There are more 'flecks' of higher misorientation in the HR samples, which also appear near grain centres. The average GROD near the grain centres is higher for this sample than for ND-QS. The large twinned grain in the bottom right of the ND-HR map shows wavy twins with relatively low GROD and parents with high GROD.

The TD-QS GROD map looks very similar to ND-QS. Most of the orientation gradients are long range and continuous, with misorientation increasing towards the grain boundaries and triple junctions. There are a few instances of 'flecks' showing higher misorientation nearer the grain centres, but in general the grain centres in TD-QS have lower misorientation than ND-QS.

TD-HR has significantly lower GROD than the other maps. There are some regions of long-range orientation gradients near triple boundaries but these occupy a much smaller area. There is also profuse twinning in this sample, and twins have lower GROD than their parent segments. The areas ahead of twin tips are associated with regions of higher GROD. This is not as obvious in the other three maps.

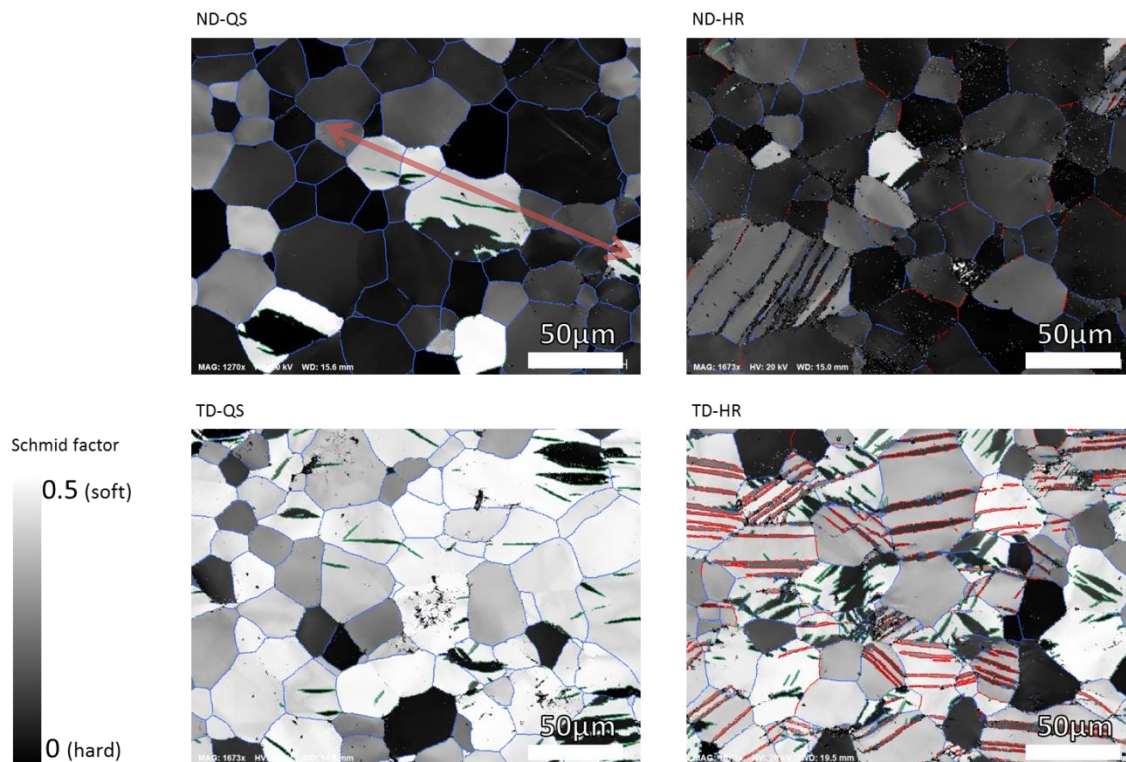


Figure 82: Schmid factor maps with respect to $\langle a \rangle$ prismatic slip system. Light coloured grains are favourably oriented for $\langle a \rangle$ prismatic slip and dark coloured grains are unfavourably oriented. Most of the T1 twin boundaries are highlighted in green and T2 twin boundaries are highlighted in red. Non-special boundaries (neighbour misorientation $>5^\circ$) are highlighted in blue.

Figure 82 shows the Schmid factors for $\langle a \rangle$ prismatic slip along the loading axis (vertical), which is the dominant slip system in zirconium. 0.5 (white) indicates a soft orientation well aligned for $\langle a \rangle$ prismatic slip, and 0 (black) indicates a hard orientation poorly aligned for $\langle a \rangle$ prismatic slip.

Boundaries with misorientation angle close to the T1 twin misorientation angle are marked in green, and boundaries close to T2 are marked in red. This allows differentiation between T1 and T2 twins, though some grain boundary segments have been incorrectly identified as T2 twin boundaries (such as the red grain boundary segments in ND-HR).

In ND-QS, the grains are generally poorly aligned for $\langle a \rangle$ prismatic slip. There is a band of softer grains in ND-QS marked by the red arrow in Figure 82. Several of these grains contain T1 twins (green boundaries).

In ND-HR, both T1 twins and T2 twins (red boundaries) are present. Both types of twin nucleate in the softer grains relative to the texture of the sample.

In TD-QS, only T1 twins are present. Most of the grains are very soft with a few hard grains. The harder grains do not contain twins.

In TD-HR, both T1 and T2 twins are present. The parent grains for T1 twins tend to be very soft, whereas the parent grains for T2 twins tend to be less soft. The very hard grains in the TD-HR map do not generally contain twins.

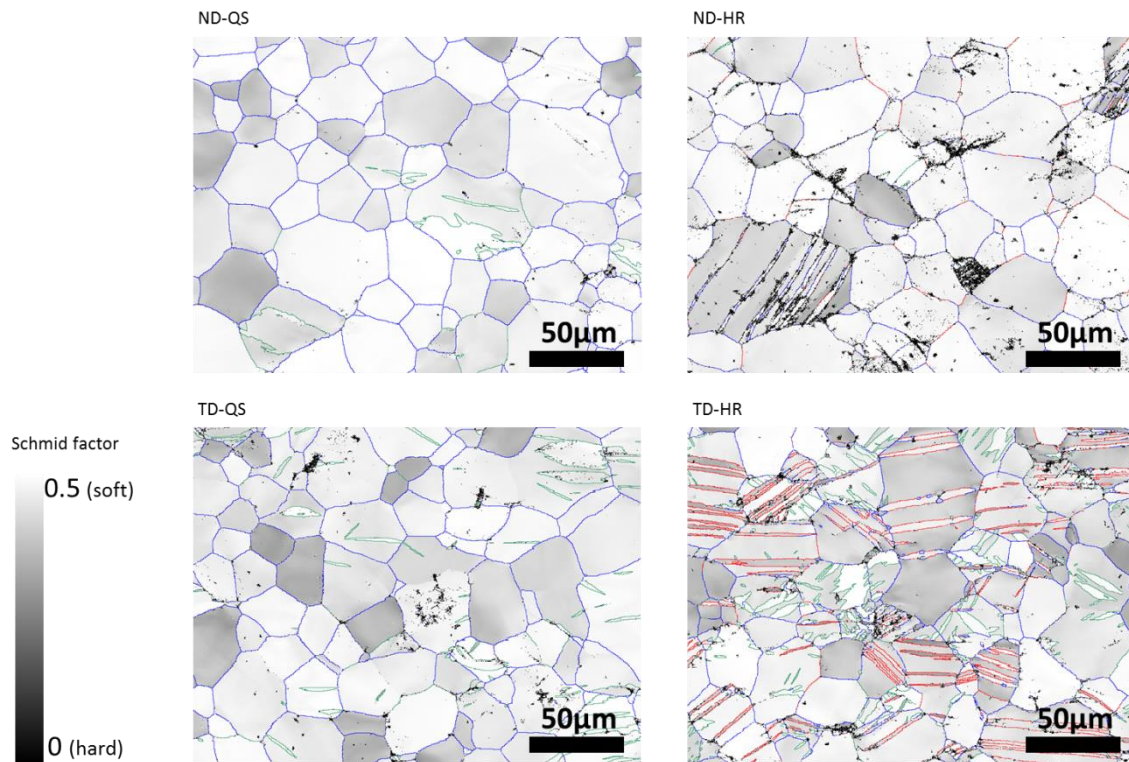


Figure 83 Schmid factor maps with respect to $\langle c + a \rangle$ pyramidal slip system. Light coloured grains are favourably oriented for $\langle c + a \rangle$ pyramidal slip and dark coloured grains are unfavourably oriented. Most of the T1 twin boundaries are highlighted in green and T2 twin boundaries are highlighted in red. Non-special boundaries (neighbour misorientation $> 5^\circ$) are highlighted in blue.

Figure 83 shows that most grains in all samples are very well oriented for $\langle c + a \rangle$ pyramidal slip. However, the critical resolved shear stress for $\langle c + a \rangle$ pyramidal slip is up to 3.5 times that for $\langle a \rangle$ prismatic slip, so only considering the Schmid factor, or the geometric alignment of a grain with respect to the loading axis does not provide a fair comparison. However, $\langle c + a \rangle$ pyramidal slip

could explain why there is evidence of constrained polycrystal slip in the GROD maps of ND-QS and ND-HR in Figure 81 even though these grains are poorly oriented for $\langle a \rangle$ prismatic slip. Since activating $\langle c + a \rangle$ pyramidal slip requires a much higher stress, this explains the mechanical data for ND samples in Figure 79, which show significantly higher flow stresses for ND samples than TD samples.

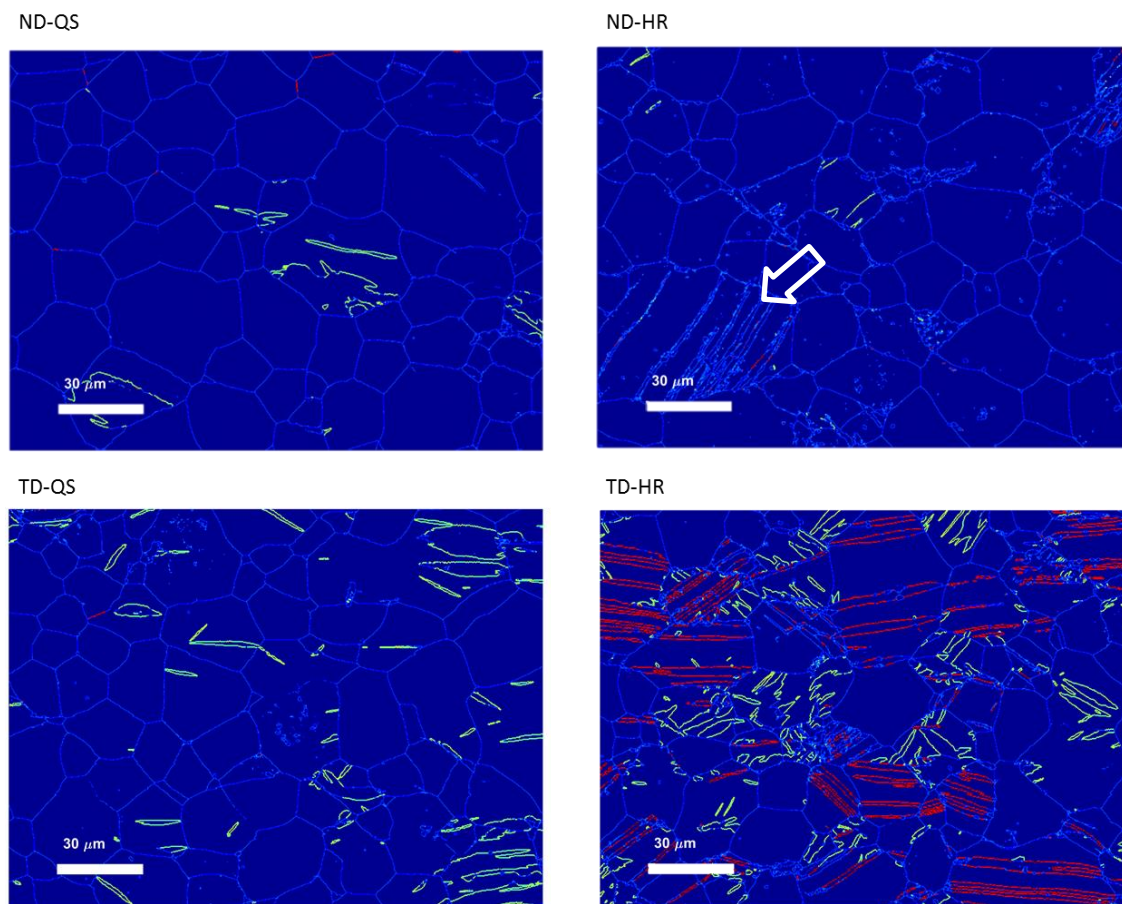


Figure 84: Grain boundary maps with T1 twin boundaries highlighted in green, T2 twin boundaries highlighted in red, and non-special grain boundaries (neighbour misorientation $>5^\circ$) highlighted in blue. The maximum allowed misorientation deviation from the ideal twin relation is 4.5° .

Figure 84 shows grain boundary maps of the samples. Non-special grain boundaries are blue, and T1 and T2 boundaries are shown in green and red respectively, according to the twin axis-angle misorientations. These maps allow twin boundaries to have a maximum of 4.5° misorientation

deviation from the ideal twin relation. 4.5° was chosen according to the Brandon criterion [160] and the CSL boundary type for T1 and T2 twins, which are $\Sigma 24$ and $\Sigma 11$ respectively [161].

Although most of the twin boundaries have been correctly identified, some twins in ND-HR have not been identified. This is most noticeable in the large grain with wavy twins (bottom right of map indicated by the white arrow). The waviness indicates that the twins and/or parent grains have slipped significantly away from the twin misorientation after twin growth. This means that in these samples, the Brandon criterion should be relaxed to account for slip after twinning.

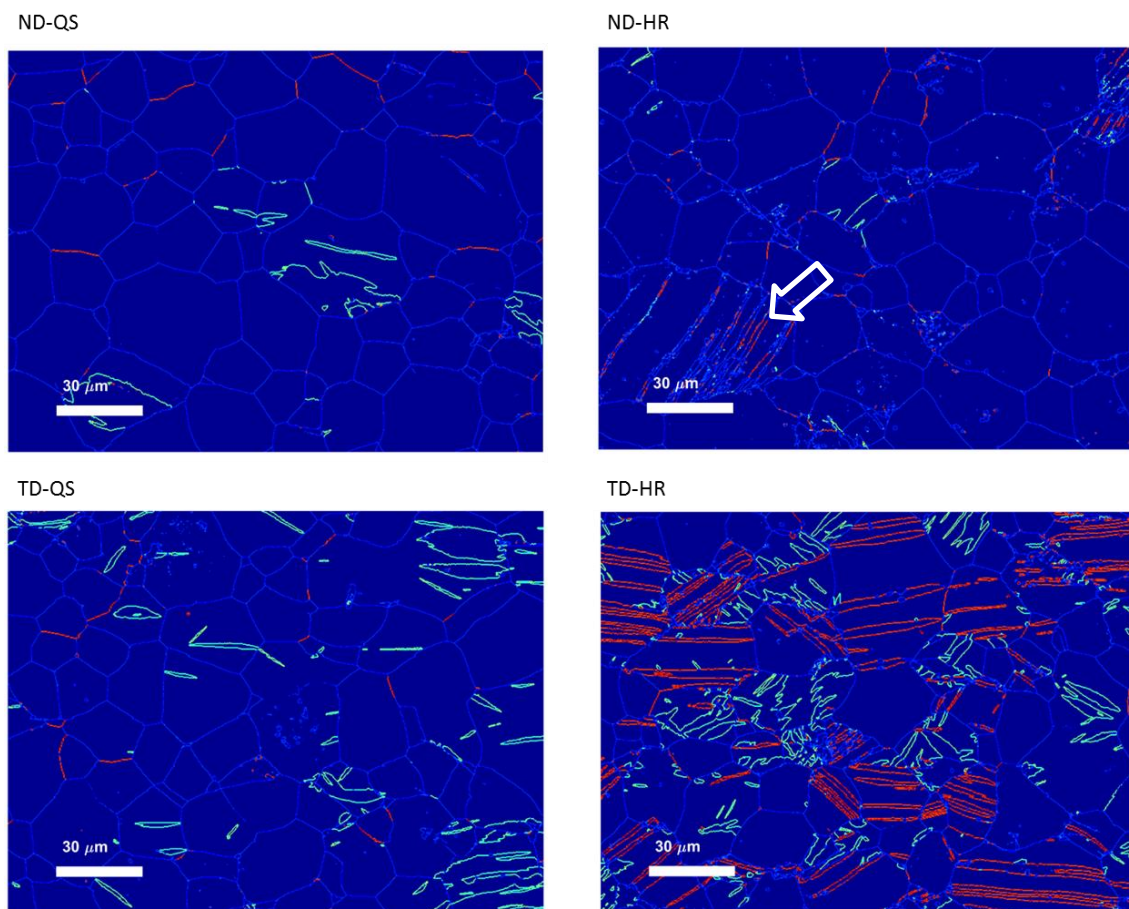


Figure 85: Grain boundary maps with T1 twin boundaries highlighted in green, T2 twin boundaries highlighted in red, and non-special grain boundaries (neighbour misorientation $>5^\circ$) highlighted in blue. The maximum allowed misorientation deviation from the ideal twin relation is 12° .

Figure 85 shows grain boundary maps of the samples. Non-special grain boundaries are blue, and T1 and T2 boundaries are shown in green and red respectively. Here, the Brandon criterion has been relaxed to 12° to allow for grains which slip significantly after twinning.

A few grain boundary segments have been misidentified as T2 twin boundaries. This is due to the large misorientation deviation of 12° allowed in these maps and does not denote anything special about the grain boundaries.

The ND-QS sample has a few twins, all of which are type T1. Some of these twins have lost their characteristic lenticular shape, and a few have consumed close to half of the parent grain. Whole grain consumption by twins in Zr has previously been suggested in the literature to explain texture change during deformation [182]; the presence of large non-lenticular twins seems to support this hypothesis.

The ND-HR sample has both T1 and T2 twins. The wavy twins in the large grain shown by the white arrow in ND-HR can be identified as type T2 following relaxation of the Brandon criterion; however, the twin boundary points are still not completely identified. This is in part due to significant slipping away from the twin misorientation after twinning, but also partly due to some double twinning and unindexed EBSD points still present at the twin boundaries. The twin density in ND-HR is slightly higher than ND-QS.

The TD-QS sample only has T1 twins, and there is a higher twin density in TD-QS samples than ND-QS or ND-HR samples. Many twins are short and fat, and terminate at grain interiors instead of being blocked at the next grain boundary.

The TD-HR sample has both T1 and T2 twins, and the twin density is the highest in all the samples. The T1 twins have a lower aspect ratio than T2 twins (quantified in Table 9), which tend to elongate along the twin plane until blocked on both ends by grain boundaries, instead of thickening normal to the twinning plane. In contrast, many T1 twins terminate at grain interiors. In the TD-HR map, there tends to be only one or occasionally two variants of T2 twin per parent, whereas there can be up to five variants of T1 twin per parent.

6.3.3 Twin statistics

	ND-QS		ND-HR		TD-QS		TD-HR	
	T1	T2	T1	T2	T1	T2	T1	T2
EBSD step size	0.3 μ m							
Total grains (inc. twins)	136		233		231		920	
Grain size (exc. border)	21 μ m		13 μ m		14 μ m		7 μ m	
Twin area fraction	4%	0%	2%	1%	6%	0%	9%	12%
Strain from twinning	0.4%	0%	0.2%	0.4%	0.7%	0%	1%	5%
Num. twins	13	0	5	14	67	0	150	121
Num. parents	7	0	3	4	32	0	37	41
Mean twins/ parent	1.9		1.7	3.5	2.1		4.1	3.0
Max variants/ parent	2		1	1	2		5	2
Mean twin length/ μ m	17 μ m		10 μ m	36 μ m	11 μ m		8 μ m	19 μ m
Mean twin width	6 μ m		3 μ m	2 μ m	2 μ m		3 μ m	2 μ m
Mean twin ellipse area	76 μ m ²		26 μ m ²	62 μ m ²	18 μ m ²		17 μ m ²	22 μ m ²

Table 9: Some twin statistics quantifying twin sizes, volumes, and variants activated.

6.3.3.1 Grain refinement

The average grain diameter measured by EBSD in the undeformed sample is 25 μ m (Figure 78), using a threshold misorientation angle of 7°. All samples show grain refinement due to twins splitting grains, and especially so for TD-HR which has a final average grain size of 7 μ m in Table 9.

ND-QS has a very low twin density and therefore the grain size should not change much. The decrease in grain size from 25 μ m to 21 μ m could be due to grain orientation fragmentation from accumulated slip and the formation of geometrically necessary boundaries [181], or it may be due to local variations from the low number of grains sampled.

6.3.3.2 Twin density and variants

In ND-QS, both the number density of twinning and the twin area fraction are very low. The (T1) twins are largest out of all the samples and are relatively short and fat.

In ND-HR, the number density of twinning and volume fraction of twinning are also very low. T2 twins tend to be long and thin, whereas T1 twins are short and fat. T2 twins on average are also larger than T1 twins.

In TD-QS, the number density of twins is much higher than in ND-QS or ND-HR, but since the twins are much smaller in area, the twin area fraction of TD-QS is similar to that of ND-HR.

In TD-HR, the number density of twinning and the twin area fraction are both high. T2 twins are long and thin, whereas T1 twins are short and fat. T2 twins on average are also larger than T1 twins. Up to five variants of T1 twin can be activated in a grain, but for T2 twinning, only one or at most two variants are activated.

6.3.3.3 Strain carried by twinning shear

The plastic strain from twinning has been calculated from $\varepsilon_{\text{twin}} = \sqrt{\frac{1}{2}} s V_t$, where s is the magnitude of twinning shear for each twin type (0.167 for T1, 0.63 for T2), and V_t is the volume fraction of twins [55] [15]. The plastic strain accommodated through twinning as opposed to slip has been estimated by approximating twin area fraction to be the same as volume fraction.

Since all samples have been compressed to 10% engineering strain, most of the deformation has been carried by slip in ND-QS, ND-HR and TD-QS, where twinning shear contributes to less than 1% strain. In TD-HR, which has twinned much more than any other sample, twinning shear contributes to 6% strain, i.e. twinning carries slightly over half the total deformation.

6.4 Discussion

6.4.1 Comparing mechanical response with EBSD data

The ND yield strengths in the mechanical data (Figure 79) are much higher than the TD yield strengths. This is confirmed in the Schmid factor maps (Figure 82), where ND grain orientations are in general much harder than TD.

Twinning-dominated deformation leads to a linear work hardening curve, and slip-dominated deformation leads to a parabolic work hardening curve [55]. Although the stress-strain curves for both QS samples fit better to parabolic than linear fits, ND-QS is significantly non-linear whereas the TD-QS response is much closer to linear. This is in agreement with the TD-QS sample containing many more T1 twins than ND-QS, suggesting that ND-QS is mostly slipping, whereas in TD-QS twins can carry part of the deformation. Even so, Table 9 shows that most of the strain in ND-QS and TD-QS is carried by slip, and the shear strain contribution from T1 twinning is actually quite small (>1% strain in both cases).

The mechanical data for ND-HR (Figure 79) may be surprising. The approximately linear work hardening curve suggests a twin dominated deformation mode, even though the total twin area fraction is only 3%, so that only 0.6% out of the 10% total strain is accommodated by twinning (Table 9). However, there is considerable measurement error in the stress-strain response seen as fluctuations and ‘waviness’ of the stress-strain curve, which could conceivably be masking a parabolic stress-strain response.

For both TD and ND samples, the (linear fit) work hardening rate is lower with HR deformation than QS deformation. Literature on similar material reports the rate of strain hardening (up to 25%) to increase with strain rate [52], but inspection of only the 0-10% strain region for both textures and strain rates shows good agreement in work hardening rates [52]. The work hardening rate increases at higher strain levels in HR deformation due to the increased level of twinning, which strengthens

the material by grain refinement. This leads to concavity in the HR stress-strain curve at strains between 10% and 25% [52].

6.4.2 Competition between twinning and slip

The fact that the twin density in the soft TD samples is higher than in the hard ND samples is somewhat surprising, since the ND samples cannot slip as easily as TD, and one might expect twinning to substitute slip as a deformation mode. Instead, T1 twinning competes with $\langle a \rangle$ prismatic slip at both strain rates, although T1 twins only occur in the softer grains of the ND samples. T2 twinning is only present in the HR samples.

The large twinned grain in the bottom right of the ND-HR map shows wavy twins with relatively low GROD and parents with high GROD. From Figure 84 we know that these grains have slipped away from the ideal twin misorientation. The GROD map shows that the parents, not the twins, have slipped most. This is in agreement with the $\langle a \rangle$ prismatic Schmid factor map, as the twins are a harder orientation than the parents.

Although most of the red T2 twin boundary points for TD-HR can be identified with a misorientation deviation of 4.5° (Figure 84), there are still a noticeable number of unidentified twin boundary points at a misorientation deviation of 4.5° which are correctly identified when this is relaxed to 12° , as the red T2 boundaries look more 'solid' in Figure 85 than Figure 84. This is not the case with the T1 twins, which are all correctly identified at 4.5° misorientation deviation and remain unchanged at 12° . This suggests that T2 twins nucleate and grow early in the deformation and then slip slightly away from the twin orientation, whereas T1 twins do not slip further, either because the twins are a hard orientation (Figure 82) or because they form later in the deformation process.

The lower GROD in TD-HR (Figure 81) may be due to grain fragmentation from twinning, as the GROD is calculated from each twin or parent segment, instead of the original reconstructed grain. Alternatively, low GROD may be due to the fact that twinning, instead of slip, carries most of the

deformation in this sample. GROD is not directly affected by twinning as a new orientation is created by the twin, but does increase with (constrained) slip.

6.5 Summary

Twinning frequency and type in zirconium depends on both texture and strain rate. At low strain rates, the deformation is always slip-dominated with twinning shear carrying less than 10% of the total strain. Most regions undergo single slip as shown by continuous long range intragranular gradients in the GAM maps, with limited activation of multiple slip systems shown as flecks in the GAM maps. At high strain rates, twinning carries more of the deformation. The texture which is more favourable for $\langle a \rangle$ prismatic slip also deforms more by T1 twinning. T1 twinning competes with $\langle a \rangle$ prismatic slip at both quasi-static and high strain rates, whereas T2 twinning is seen only at high strain rates. The growth mechanisms for T1 and T2 twinning are different – T1 twins preferentially thicken normal to the twinning plane and T2 twins elongate in the twinning shear direction.

7. Conclusion

In this thesis, the microstructural behaviour of zirconium relevant to its applications in the nuclear industry has been explored. It has been found that both grain growth and deformation behaviour can be very heterogeneous and careful processing is required to control the microstructure, which affects performance of the material in nuclear reactors. EBSD is the main characterisation technique used in this thesis as it allows a large range of microstructural properties to be studied. Information about material texture, grain size, intragranular misorientations, twinning, and GND density distributions have been used in this thesis.

The formation of blocky alpha phase with abnormally large grains in Zircaloy-4 was explored. It was found that blocky alpha forms on annealing at 800°C after low (<4%) strains. Blocky alpha nucleates via SIBM and grows by whole-grain consumption. Therefore, dislocation debris is left behind at the prior grain boundaries as the blocky alpha grain sweeps through the material. As with other abnormal grain growth mechanisms, the driving force for blocky alpha growth is the reduction of grain boundary surface area.

In samples annealed to form blocky alpha after three point bending, the presence of a strain gradient leads to a texture switch between the plastic tensile and compression regions of the three point bend sample. The texture switch has been linked to twins preferentially nucleating blocky alpha grains in the plastic compressive region and thus dominating the final texture, whereas in the plastic tensile region the deformation texture is largely preserved, apart from occasional 'rogue' grains which have a twinned orientation.

From an industrial standpoint, it is valuable to suppress the formation of such large grains. The formation of blocky alpha in lightly (<4%) strained Zircaloy-4 can be suppressed by annealing at temperatures below 700°C and limiting the holding time to less than 720 hours.

HR-EBSD mapping of GND density has been used to characterise Zircaloy-4 microstructures for this chapter. It was found that GND density hotspots appear near triple junctions and grain boundaries in the deformed material, which are not removed by the blocky alpha transformation. It was therefore necessary to check that these GND density hotspots near grain boundaries are real and not simply artefacts of the measurement technique. Therefore, the extent of pattern overlap near grain boundaries was measured for Zircaloy-4.

It was found that for the step size, material, and microscope settings used, pattern overlap does not severely reduce accuracy of residual strain and rotation measurements by HR-EBSD and does not create significant artefacts in EBSD maps. The extent of pattern overlap near grain boundaries varies with material, microscope, and EBSD scan settings, but can be quantified easily by simple pattern mixing calibration tests.

Twinning was found to play a significant role in nucleating blocky alpha, and is known to be an important deformation mechanism in hexagonal zirconium alloys as it allows deformation parallel to the $\langle c \rangle$ axis of the crystal unit cell. Therefore, the twinning behaviour in commercially pure zirconium deformed to 10% compressive strain was characterised. In order to characterise twinning behaviour given the limitations of the commercially available software, postprocessing software was developed in MATLAB to handle EBSD orientations, clean data, and identify grains, so that twin boundaries and intragranular misorientations could be identified. The algorithms associated with these operations have been written out explicitly using the quaternion representation of orientation.

The variation of twinning behaviour with strain rate and texture in commercially pure zirconium was studied. It was found that $\{11\bar{2}1\}$ (T2) twinning is activated at high (10^3) strain rates but suppressed at quasi-static (10^{-3}) strain rates, whereas $\{10\bar{1}2\}$ (T1) twinning operates at both quasi-static and high strain rates. Both the total twin area fractions and number frequencies are higher during high strain rate loading, and more of the deformation is carried via twinning instead of slip. In TD loaded samples, the majority of grains are favourably oriented for $\langle a \rangle$ prismatic slip; in ND loaded samples,

Conclusion

the majority of grains are poorly oriented for $\langle a \rangle$ prismatic slip. Regardless of texture, T1 twinning only activates in individual grains which are favourably oriented for $\langle a \rangle$ prismatic slip during loading, whereas T2 twinning activates in grains less favourably oriented for $\langle a \rangle$ prismatic slip. The morphology of T2 and T1 twins are different – T1 twins are thicker and some lose their lenticular shape, T2 twins are thinner and longer. This may be related to the much higher twinning shear associated with thickening of the T2 twin.

This thesis has explored the formation mechanism of blocky alpha grains in Zircaloy-4, and the twinning behaviour of commercially pure zirconium, which will inform efforts to control microstructure and performance during manufacture of safety-critical zirconium parts in nuclear reactors. In addition, the effect of pattern overlap at grain boundaries on HR-EBSD measurements has been quantified, and software enabling EBSD data postprocessing for identification of special boundaries and misorientations has been written, which enables confident characterisation of a range of microstructures.

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