Texture Evolution and Variant Selection in Zr-2.5Nb During the $\alpha$-$\beta$ Phase Transformation

by

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Abstract

Zr-2.5Nb is used as the pressure tube material for Russian RBMK and 2nd and 3rd generation CANDU reactors. The physical properties of pressure tubes in service, including strength, dimensional stability, and delayed hydride cracking resistance, are largely dependent upon the crystallographic texture of the hcp α-phase, whose texture is predominantly developed during the extrusion stage of manufacturing. During extrusion and subsequent cooling, the formation of α may occur by transformation of the bcc β-phase to α according to the Burgers relationship and influenced by variant selection – that is, a preference for one or more of the twelve possible orientations of the hcp lattice relative to the bcc lattice. Variant selection has been observed in other Zr and Ti alloys, including the heat-affected zone in pressure tube welds and the bulk texture of heat-treated pressure tubes. Further, it has been proposed as a possible explanation for texture characteristics in pressure tubes that are not explained by the deformation mechanics of extrusion. However, the criteria for variant selection are unclear.

In this work, an understanding of the criteria for variant selection is developed through observations of the differing mechanisms at play during both directions of transformation, from α → β and β → α. Transformation via the Burgers relationship was confirmed; the existence of variant selection is also established. In thermal cycles
to the $\beta$-regime, this selection manifests as the selection of a new (0002) variant, as driven by anisotropic thermal stresses generated during heating. Upon cooling, the high-temperature $\beta$ texture is inherited by the $\alpha$ grains via the Burgers relationship; the magnitude of the texture maxima is driven by elastic transformation strains. Further thermal cycles to the $\beta$ regime demonstrate texture memory, with some development of cubic symmetry due to grain growth during the hold in the $\beta$-phase. No texture changes are observed if samples are not heated fully into the beta regime. Finally, a study of the biasing effects of both residual and external stresses is discussed. While the external stress did not appear to be capable of biasing variant selection during either heating or cooling, some texture changes were observed, likely due to deformation at high temperature.
Acknowledgments

This thesis would not have been possible without the support and guidance of my supervisors, Mark Daymond and Richard Holt. Your mentorship, broad knowledge background, and the opportunities you have given me have truly enriched both me and my experiences as a graduate student.

I would be remiss if I were not to thank the tireless beamline scientists at the numerous facilities I visited throughout my experiments: Sven Vogel and Helmut Reiche from HIPPO at the Los Alamos Neutron Science Centre; Jon Almer from 1-ID at the Advanced Photon Source; Michael Gharghouri from the Canadian Neutron Beam Centre at Chalk River Laboratories. Their unique ability to apply wisdom, humour, patience, and insight when needed (particularly in moments when my uncanny ability to be the Black Widow of Science was in full force) made my experiments a pleasure as well as an immeasurably valuable learning experience.

I’d like to thank both the members of the Nuclear Materials Group and the faculty members throughout the department for many helpful discussions. In particular, I would like to give thanks to Matthew Kerr and Eric Tulk, both of whom assisted me with some gruelling experiments. Charlie Cooney, too, was a wonderful resource; I count myself among the innumerable students who have been saved by his considerable practical knowledge and uncanny ability to spot trouble brewing.
Finally, I must give due credit to my family and friends. My family has been my most dedicated group of cheerleaders – thank you for the unwavering love and encouragement. To the many close friends who have offered me advice and encouragement: I will be forever grateful, and am happy that I am so constantly reminded of how lucky I am to know so many kind, generous, and intelligent people. Colleen Decker and Michele Romanow: You two have been my rocks for many years now in very complementary ways; I am so happy that you both came into my life, and I hope to someday return the favour. To Jacqueline Romanow, Jeff Jackson, and Steven Keating: perhaps you don’t realize it, but you’ve played a major role in keeping me sane over the past two years. I’d hoped that you’d keep me from teetering into the ‘weird grad student’ abyss, and you did the best that you could – but I didn’t anticipate that I’d also gain such close, extraordinary friends. Last but not least: Rebecca Toda and Greg Allen, my constant partners in crime and snacking – you pacified my frequent rants about the minutiae of life and research, encouraged me, and never failed to put a smile on my face each day. Thank you for your friendship.

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Statement of Contributions

Others contributed to the work presented in this thesis in two ways: modelling, and experiments.

The EPSC model that enabled the prediction and further study of phase transformation was developed by Dr. Mark Daymond.

Some initial thermal cycling experiments were conducted in 2005 and 2006 at the Los Alamos Neutron Science Centre by Dr. Feng Xu and Dr. Song Cai. The analysis and interpretation of the results were completed by me; I am grateful for the use of the data they collected.

Apart from this, all work presented in this thesis is my own.
Nomenclature

CANDU  CANada Deuterium Uranium (reactor)
BWR    Boiling Water Reactor
PWR    Pressurized Water Reactor
RBMK   Russian high power channel-type reactor
hcp    hexagonal close-packed
bcc    body-centered cubic
α      low temperature hcp phase of zirconium
β      high temperature bcc phase of zirconium
GSAS   General Structure Analysis Software
MAUD   Materials Analysis Using Diffraction
WIMV   Williams-Imhof-Matthies-Vinel algorithm
E-WIMV Extended Williams-Imhof-Matthies-Vinel algorithm
PF     Pole Figure
ODF    Orientation Distribution Function
mrd    Multiples of a Random Distribution
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Chapter 1

Introduction

This dissertation focuses on the study and evaluation of several proposed criteria for variant selection and texture evolution, working towards characterizing the texture changes that occur throughout the $\alpha - \beta - \alpha$ phase transformation in Zr-2.5Nb.

1.1 Motivation

Zirconium plays an important role in the nuclear industry due to its unique combination of physical properties, including high strength, good corrosion resistance, and low nuclear absorption cross-section. Zirconium alloys are used in a wide variety of structural components in reactors; Zr-2.5Nb, the material studied throughout this thesis, is currently used in pressure tubes in 2$^{nd}$ and 3$^{rd}$ generation CANDU reactors.

As the dominant $\alpha$-$hcp$ phase of zirconium alloys is inherently anisotropic, multiple pertinent macroscale characteristics (such as strength, elasticity, thermal expansion, plasticity, and creep behaviour) can be shown to be directly related to the orientation, or texture, of the $hcp$ crystals throughout. In service, many physical properties
of pressure tubes (including dimensional stability and delayed hydride cracking resistance) are similarly dependent on texture. Understanding texture is therefore a key facet of describing the properties and predicting the behaviour of these materials.

Zirconium alloys, among others, are often processed in either the two-phase or high-temperature β-bcc regime, with some heat treatments occurring in the full-β regime. As a result, understanding how texture is inherited through phase transformation and how deformation influences variant selection is of great interest.

The pressure tube provides a concrete example of the application of this research, as the evolution of the final texture of pressure tubes is not entirely understood. For example, two of the three texture components produced in Zr-2.5Nb pressure tubes by mechanical processing in the α + β phase field cannot be accounted for by any known deformation mechanisms of the α-phase per se. Rather, they appear to be related to variant selection during the transformation from β to α either during or after processing [1–3]. Various studies have been done on texture inheritance throughout phase transformation across a variety of alloys, but a consensus has not been reached on what is driving the evolution of the textures produced. Identifying and characterizing these mechanisms will lead to a greater understanding of how to predict and control texture development throughout the thermo-mechanical manufacturing steps of zirconium and similar materials.

1.2 Statement of Purpose

The purpose of the work is to develop a deeper understanding of the criteria for variant selection. A variety of experiments have been conducted with the aim of demonstrating the effect of a breadth of possible influences, including maximum temperature,
heating/cooling rates, temperature holds, residual internal stresses, and external biasing stresses. Further, it is important to characterize any directionally-specific mechanisms that occur during phase transformation – that is, whether different mechanisms act during heating than cooling.

The ultimate goal of this research program is to provide a thorough framework that will allow for the development and refinement of models of this class of materials. With this knowledge, existing processing methods and in-service behaviour can be better understood and improved.

1.3 Organization

This dissertation is divided into four main chapters. First, Chapter 2 will present a summary of the general concepts involved and a review of the body of literature pertaining to this research area. The experiments conducted and their associated apparatus will be discussed in Chapter 3, followed by an overview of the results of these experiments, given in Chapter 4. Chapter 5 provides a discussion of the results obtained, with reference to other results in literature and to models generated that have helped illuminate the driving forces for the phenomena witnessed. Finally, a summary of the main findings of the project is given, along with suggestions for future development in this experimental program.
Chapter 2

Literature Review

2.1 Zirconium

2.1.1 Zirconium in the Nuclear Industry

The environment of a nuclear reactor places unique demands on the characteristics and performance of materials used within, both in terms of structural behaviour and reactor kinetics; these requirements limit the use of conventional structural materials. Zirconium is therefore of great technical importance in the nuclear industry due to its unique combination of high mechanical strength and stability at elevated temperatures, good corrosion resistance, and low nuclear absorption cross-section. Zirconium is now used in all prominent power generator reactor designs (PWR, BWR, CANDU, RBMK) for a variety of reactor components, including fuel cladding/assemblies, calandria tubes, and pressure tubes.

A summary of common zirconium alloys, their compositions, and applications is given in Table 2.1.
Table 2.1: Overview of Zirconium alloys with application in the Nuclear Industry [4]

<table>
<thead>
<tr>
<th></th>
<th>Nb wt%</th>
<th>Mo wt%</th>
<th>Sn wt%</th>
<th>Fe wt%</th>
<th>Cr wt%</th>
<th>Ni wt%</th>
<th>O wt-ppm</th>
<th>Zr</th>
<th>Typical Application</th>
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<td>Zircaloy-2</td>
<td>–</td>
<td>–</td>
<td>1.2-1.7</td>
<td>0.07-</td>
<td>0.05-</td>
<td>0.03-</td>
<td>1000-1400</td>
<td>Balance</td>
<td>Fuel cladding/calandria and pressure tubes, in-reactor guides</td>
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<tr>
<td>Zircaloy-4</td>
<td>–</td>
<td>–</td>
<td>1.2-1.7</td>
<td>0.18-</td>
<td>0.07-</td>
<td>–</td>
<td>1000-1400</td>
<td>Balance</td>
<td>Fuel cladding/calandria and pressure tubes, in-reactor guides</td>
</tr>
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<td>Zr-2.5Nb</td>
<td>2.5</td>
<td>–</td>
<td>–</td>
<td>&lt;1300 ppm</td>
<td>–</td>
<td>–</td>
<td>950-1500</td>
<td>Balance</td>
<td>Pressure tubes</td>
</tr>
<tr>
<td>Zr-1Nb</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>300-500 wt-ppm</td>
<td>–</td>
<td>–</td>
<td>1000-1400</td>
<td>Balance</td>
<td>Fuel cladding</td>
</tr>
<tr>
<td>Zirlo</td>
<td>1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1000-1400</td>
<td>Balance</td>
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<tr>
<td>M5</td>
<td>1</td>
<td>0.8</td>
<td>3.5</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Balance</td>
<td>Possible Generation 4 Application</td>
</tr>
<tr>
<td>Excel</td>
<td>0.8</td>
<td>0.8</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>Balance</td>
<td>Possible Generation 4 Application</td>
</tr>
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</table>

There are two primary classes of zirconium alloys currently in use: α-zirconium alloys, and dual-phase α/β alloys. Zr-2.5Nb belongs to the latter class. Currently, niobium-containing alloys are used as fuel cladding (Zirlo, M5) and 2nd and 3rd Generation CANDU pressure tubes (Zr-2.5Nb); they also have a place in the higher-temperature Generation 4 reactors, where their strength at high temperature is required.

2.1.2 Metallurgical Characteristics

As shown in Table 2.1 above, the chemical composition of Zr-2.5Nb in commercial use is nominally 2.5-2.8wt% Nb, 950-1500ppm O, <1300ppm Fe, and balance Zr [5]. The niobium acts as a β-stabilizer, producing a zirconium alloy with vastly improved corrosion resistance and mechanical properties, as well as reduced hydrogen uptake in-service. The Fe is similarly mostly concentrated in the β phase and acts as a β stabilizer; it is also found in α-α grain boundaries [6]. The zirconium-niobium phase diagram is shown in (Fig. 2.1).
Zr-2.5Nb has an \(\alpha\)-hcp phase at low temperature, depicted in Fig. 2.2. As it is heated, it transforms into a \(\beta\)-bcc structure, fully transforming above approximately 925\(^\circ\)C (Note that this temperature is higher in the commercial alloy than that indicated in the phase diagram depicted in Fig. 2.1; the oxygen contained in the alloy is an \(\alpha\) stabilizer, and raises the phase transformation temperature to between 900-925\(^\circ\)C \cite{1}). In the area of the \(\alpha\)-\(\beta\) transus, the Zr-Nb binary phase diagram is a monotectoid, with the monotectoid reaction at approximately 600\(^\circ\)C and 20 wt\%Nb. Therefore, as an alloy in the 0.6wt\% to 20wt\% range cools from the high to low temperature, \(\alpha_{\text{Zr}}\) precipitates out at the phase transformation temperature, and the Nb content of \(\beta_{\text{Zr}}\) increases. (For pure Zr-2.5Nb, this occurs at approximately 860\(^\circ\)C \cite{7}, though the addition of oxygen raises this temperature as discussed above.). The diffusion of Nb is the rate-limiting factor throughout this process. At 600\(^\circ\)C, eutectic decomposition occurs under equilibrium conditions, and the remaining \(\beta_{\text{Zr}}\) transforms to hcp \(\alpha_{\text{Zr}}\) (0.5wt\%Nb) and bcc \(\beta_{\text{Nb}}\) (95wt\%Nb). This reaction occurs very slowly, however, and it is therefore common for Zr-2.5Nb to have a final room-temperature composition of approximately 90\% \(\alpha_{\text{Zr}}\) and 10\% metastable \(\beta_{\text{Zr}}\), with the Nb mostly concentrated in the \(\beta\) phase (<1wt\% in the \(\alpha\) phase and around 20wt\% in the \(\beta\) phase.)

Though approximately 10\% metastable \(\beta\) phase is retained in the final product, the vast majority of the material characteristics are determined by the microstructure and texture of the dominant \(\alpha\) phase, as well as the interactions between the \(\alpha\) and \(\beta\) phases.
Figure 2.1: Zirconium-Niobium Phase Diagram. Adapted from [8].
2.1.3 Crystallography

At low temperature, zirconium has an hexagonal close-packed structure; we describe the cell geometry using three coplanar \(< a >\) axes, at 120° from one another, and one \(< c >\) axis orthogonal to the \(< a >\) axes. These axes are shown in Fig. 2.2. Nominally, the unstressed lattice spacings for Zr at room temperature in the \(a\)- and \(c\)-axes are 3.23118 Å and 5.14634 Å, respectively, giving the crystal a \(c/a\) ratio of 1.59271 [9].

Correspondingly, the high-temperature beta phase has a body-centered cubic structure with three orthogonal \(< a >\) axes, as shown in Fig. 2.3. The unstressed lattice spacing in the \(\beta\) phase field for the \(a\)-axis is 3.62 Å at 850°C [9].

Temperature and alloying elements affect the stress-free lattice spacings, elastic constants, and Young’s modulus [11].

Though this dissertation focuses on the study of zirconium, specifically from the Zr-2.5Nb alloy, it is worth noting that the results may apply equally to the study of
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2.1.4 Pressure Tubes

Pressure tubes are hollow cylinders of approximately 112mm OD/104mm ID; they are used as part of the fuel channels in the core of CANDU reactors where they contain the fuel bundles and primary D$_2$O coolant. In order to maximize the thermodynamic output of the reactor, the coolant (from which steam is generated) is pressurized to 10MPa (or a hoop stress of 130MPa on the pressure tube) in order to reach the operating temperature of about 250-310$^\circ$C. The difficulty and cost associated with replacing activated components of reactors during their serviceable life is large; as such, pressure tubes are intended to last for up to 30 years. It is clear that pressure tubes must therefore not only have good strength, but also exceptional creep and corrosion resistance.

The conventional manufacturing procedure for CANDU pressure tubes is shown in Fig. 2.4.

Following the formation of the billet, the material is preheated and then extruded.
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Figure 2.4: Steps of the standard pressure tube fabrication route.
at approximately 815°C, the \( \alpha + \beta \) phase regime, with an extrusion ratio of approximately 10-11:1. The microstructure is further influenced by a 25-30% cold draw. The final microstructure of the pressure tube is comprised primarily of platelet \( \alpha_{Zr} \) delineated by Nb-rich \( \beta_{Zr} \).

### 2.1.5 Microstructure

The microstructure of a standard pressure tube, shown in Fig. 2.5, consists of a network of elongated or plate-like alpha (dark) grains, with an aspect ratio of length /width /thickness = 25/5/1 and a thickness of 0.4 \( \mu \)m [12]. Note that the appearance of the relative phase fractions in Fig. 2.5 has been affected by etching, artificially making the beta phase (light) appear more prevalent.

![Figure 2.5: Zr-2.5Nb pressure tube microstructure, showing elongated alpha grains [12].](image)
Following the extrusion process outlined in Sec. 2.1.4, the final β phase composition is metastable \( bcc \, \beta_{Zr} \) with 20wt% Nb, as previously discussed. However, after the cold working and annealing (at 300-500°C) stages, the \( \beta_{Zr} \) partially transforms into equilibrium \( \alpha_{Zr} \) and \( bcc \, \beta_{Nb} \); the remainder consists of a mixture of metastable \( hcp \) ω-phase and Nb-enriched \( \beta_{Zr} \) [13–15].

2.2 Texture and Anisotropy

Texture refers to the preferred crystallographic orientation of crystals within a polycrystalline matrix. That is, if the orientations of individual crystals within a sample favour particular directions, a sample is said to have texture; if the crystals are randomly oriented, the sample has a random texture.

Several properties of alloys with a hexagonal crystal structure, such as zirconium and titanium, are highly dependent on the crystallographic texture. This arises from the significant anisotropy of properties at the crystallographic level, such as elasticity, thermal expansion, plasticity [16] and irradiation growth. For example, along the c-axis, the Young’s modulus is 125GPa, the maximum for the crystal; along the a-axis, it is 99 GPa; the minimum Young’s modulus is 89GPa [11]. A further example important to this dissertation is the anisotropy of thermal expansion: \( \alpha \)-Zr has thermal expansion coefficients of \( a = 5.3 \times 10^{-6} \, ^\circ C \) and \( c =10.1 \times 10^{-6} \, ^\circ C \) [17]. Further, the texture at each stage of fabrication can significantly influence the way in which subsequent steps are carried out, as well as the ease of these processes [18]. There is thus a significant interest in understanding the mechanisms of texture development through various thermo-mechanical processing steps, with the long term goal of refining these procedures and optimizing the texture of final products.
In a pressure tube, the texture of the tube is characterized by a strong preferred orientation of basal plane normals in the transverse (or hoop) direction of the tube (Fig. 2.6).

![Figure 2.6: Initial $\alpha$-(0002) texture of a pressure tube. Axial vertical, Radial in centre, Transverse horizontal.](image)

As the majority of forging is carried out in the fully-beta phase field, the billet itself has a random texture after quenching to room temperature. The pressure tube texture is developed primarily in the extrusion process, with minimal contribution from subsequent cold drawing [2]. As a result, for the standard pressure tube manufacturing conditions, the majority of opportunities for controlling the final physical properties of the tube lie during extrusion, though texture modifications have also been produced in "heat-treated" Zr-2.5Nb.

### 2.2.1 Texture Measurement

Texture measurements can be made using a variety of diffraction techniques; X-Ray, neutron, and electron diffraction are the dominant methods. X-ray diffraction
done with laboratory x-rays does not have the benefit of the energies required to penetrate distances beyond those on the order of microns. Though, historically, most bulk-texture measurements have been made with laboratory X-rays, this technique requires proper sectioning and sampling in order to ensure that the measured textures are representative of the bulk. Electron diffraction (e.g. electron back-scattering diffraction or EBSD) has an even smaller penetration depth than X-ray diffraction in general. Although the ability to produce texture maps is an advantage of this technique, measurements must be made with similar care.

The use of synchrotron x-ray diffraction, however, increases the possible penetration depth by several orders of magnitude. For example, for Zr-2.5Nb, experiments can be done in transmission with samples on the order of a few millimeters of thickness. Further, the brilliance of synchrotron x-rays improves counting statistics, thus paving the way for shorter data collection times which may be of aid in in situ studies. Neutron diffraction, however, remains as the method with the largest penetration capability. The benefits and drawbacks of these latter two techniques are discussed below.

Neutron Diffraction

Neutron diffraction represents a relatively old and well-established tool for the study of the atomic and magnetic structure of materials, often providing a complement to similar X-ray diffraction techniques. Several large research facilities, or neutron sources, exist worldwide; these sources tend to be of two forms: reactor sources (e.g. Canadian Neutron Beam Centre in Canada, Institut Laue-Langevin (ILL) in France) and accelerator or spallation sources (e.g. Los Alamos Neutron Science Centre
(LANSCE) and Spallation Neutron Source (SNS) in the USA, ISIS in the UK). These sources are widely used for studies of materials science and condensed matter physics. The neutron diffraction experiments outlined in this work were all carried out on the High Intensity Powder Preferred Orientation (HIPPO) instrument at LANSCE [19].

For engineering materials, neutron diffraction provides an advantage over X-ray diffraction in terms of grain sampling – a neutron beam has a much longer penetration depth than X-rays, and often, larger beam diameters are used. As a result, larger samples can be used, and the statistical representation of grain variation in a polycrystalline material is improved. However, count times required to adequately complete a diffraction measurement are often higher or have detector arrangements that are more restrictive. As a result, it is often more difficult to design a diffraction instrument that is capable of performing in situ or time-resolved studies.

Time-of-flight neutron diffraction is a technique that uses a polychromatic or ‘white’ incident beam that contains a continuous spectrum of wavelengths. The neutron beam itself is pulsed in order to provide for time discrimination; at LANSCE, for example, this is achieved by spallation of a tungsten target with protons from a linear accelerator. The output of this spallation is then moderated to produce a wavelength range suitable for study, and finally collimated into an incident beam. Upon interaction with the sample of study, the pulsed neutrons are then diffracted towards the detector array at a known, constant diffraction angle $2\theta$. The neutron time of flight from the moderator to the detector is given by Eq. 2.1:

$$V = \frac{h}{m_n \lambda} = \frac{L}{t}$$  \hspace{1cm} (2.1)

where the time-of-flight, $t$, is given by the total length, $L$, divided by the velocity of
the neutron, $V$; this velocity is a function of wavelength, $\lambda$, Planck’s constant, $h$, and the mass of the neutron, $m_n$.

Starting with Bragg’s law, Eq. 2.2:

$$n\lambda = 2d_{hkl} \sin(\theta)$$ (2.2)

(where $n$ is an integer, $d$ is the lattice spacing for a given $hkl$ set of planes, and theta is the angle made by the incident and scattering rays) and inserting Eq. 2.1 into Eq. 2.2, we can define this relationship for time-of-flight:

$$t_{hkl} = \frac{2d_{hkl} \sin(\theta)Lm_n}{h}$$ (2.3)

Time-of-flight is therefore proportional to neutron wavelength and the lattice spacing of the diffracting plane in the specimen; different grain orientations in the gauge volume diffract at different angles, related by the multiple wavelengths found in the polychromatic incident beam according to Bragg’s law. By measuring differences in the time of flight for neutrons with different velocities, a spectrum of diffraction peaks can be measured simultaneously rather than one-by-one. Summing over the angular range of the detector array, one can determine the underlying crystalline structure of the material and therefore make texture measurements [19]. A typical resulting TOF spectrum is shown below in Fig. 2.7, in this case representing a single-phase ($\alpha$-phase) zirconium spectrum.

Details about the diffractometer used, HIPPO at LANSCE, are given in Chap. 3.
Synchrotron X-Ray Diffraction

The development of third-generation high-energy synchrotron X-ray sources provided additional capabilities for materials science, biology, and condensed matter physics research [20]. There are currently several such facilities in the world; three of these feature ‘high energy’ (6-8 GeV) electron rings, providing a very high flux of high-energy X-rays: the Advanced Photon Source (APS) in the USA, European Synchrotron Radiation Facility (ESRF) in France, and SPring8 in Japan. These facilities, along with improvements in detector capabilities, allowed for improvements in transmission texture and strain measurements as well as microscale spatial resolution and time-resolution on the order of milliseconds, unrivalled by other techniques.

The X-ray diffraction experiments outlined in this dissertation were conducted at the 1-ID beamline at APS [21]. 1-ID makes use of an undulator/monochromator configuration which optimally produces X-rays at around 80 keV, but is capable of producing X-rays anywhere between 35 and 200 keV. As the probability of interaction
with matter (that is, cross-section) decreases with increased energy, the high energy characteristic of the beamline makes bulk measurements possible. X-ray penetration is also a function of atomic weight. Fig. 2.8 shows the transmission behavior of 80 keV X-rays as compared to 8 keV X-rays from a standard copper lab X-ray source; as indicated, 80keV operation is capable of producing 10% X-ray transmission through 2mm of zirconium.

Figure 2.8: Comparison of 10% X-ray transmission thickness of various elements: 80keV X-rays vs. a standard Cu lab X-ray source. Adapted from [21].

However, it is the brilliance (photons per second per unit solid angle per unit energy bandwidth) of these third-generation sources that enables the high spatial and time-resolution capabilities.

Further details about the beamline used, 1-ID at APS, are given in Chap. 3.

For texture studies such as those conducted here, spatial resolution is not maximized; for polycrystalline materials, it is important to obtain a good statistical average of the grains present. As a result, macrobeam focusing, with a lower limit of 20x20 to 50x50\( \mu \text{m}^2 \), was employed; this is achieved either with the use of slits (which both
reduces the beam area but also the beam flux), focusing optics (which maintains the flux level, but increases the angular divergence of the beam), or both. Microbeam optical focusing techniques can achieve spot sizes in the sub-micron range [21].

In powder diffraction – the technique representative of diffraction of polycrystalline materials – averaging due to different orientations of grains brings about smooth diffraction rings, as opposed to the discrete Laue spots seen in single-crystal diffraction. Each 2-D ring, as collected by a detector, makes a scattering angle $2\theta$ between the ring and the axis, and is representative of a particular reflection (or Debye-Scherrer cone), and thus a particular reciprocal lattice vector $G$. This relationship, outlined in Eq. 2.4, is in accordance with Bragg’s law (Eq. 2.2 above).

\[
G = q = 2k \sin(\theta) \tag{2.4}
\]

Physically, this arrangement is depicted in Fig. 2.9.

\[\text{Figure 2.9: Two-dimensional powder diffraction setup for high-energy X-ray diffraction [22].}\]

In studies where texture is expected, the sample is often rotated and imaged at several angles in order to improve statistics and better capture texture variation.
2.2.2 Texture Representation

Texture is traditionally represented graphically in three ways. The first, the pole figure (PF), is a stereographic projection of the frequency of a given crystallographic plane relative to sample coordinates. The second, the orientation distribution function (ODF), is a measure of the full 3-D crystallographic texture; the ODF represents the volume fractions of grains oriented along a certain direction \( g \), defined by three Euler angles. With a complete ODF, all pole figures can be defined. Finally, the inverse pole figure gives how the frequency of a given sample direction is distributed in the reference frame of the crystal. The magnitude of texture is represented by a texture coefficient in units of ‘multiples of random distribution’, or ‘mrd’.

As it is not possible to measure an ODF directly (except with EBSD measurements), texture measurement techniques rely upon collecting pole figures themselves which can be reconstituted into a full expression of the ODF. Two such techniques will be outlined below in Sec. 2.2.3.

In order to provide a simple quantitative method of visualizing the magnitude of texture in hcp materials, including quantifying relative texture changes, it is common to calculate the Kearns or ‘F factor’, thus defining texture in terms of \( F_T \), \( F_A \), \( F_R \), and \( Z = F_R/F_T \), where \( F_X \) is the resolved fraction of basal plane normals in a given orientation (\( T = \) transverse, \( A = \) axial, \( R = \) radial). These values can be calculated according to Eq. 2.5 below:

\[
F_X = \sum V(\theta) \cos^2 \theta
\]

Where \( V(\theta) \) is the volume fraction with basal plane normals at an angle \( \theta \) to the reference direction [23]. This value is useful because, in hcp crystals, most of the
physical characteristics are approximately isotropic in the basal plane. As a result, most of the information about the anisotropy of a polycrystal can be gleaned from basal pole figures (and, in turn, the calculated Kearns factors).

2.2.3 Data Analysis

A variety of analysis techniques can be used to extract pole figure or ODF data from the experimental results obtained. Two programs (with differing methods) were used in the experiments completed in this thesis: 1) General Structure Analysis Software (GSAS), which uses the Rietveld method and represents texture in ODF space using a spherical harmonics approach, and 2) Materials Analysis Using Diffraction (MAUD), which again employs the Rietveld method, but can refine texture through a variety of algorithms in direct space. The E-WIMV (Extended Williams, Imhoff, Matthies, and Vinel) texture computation algorithm within MAUD will be focused on here.

A more detailed comparison of the two analysis methods (harmonic vs. direct), with reference to the results obtained, is included in Appendix B.

The Rietveld Method

The Rietveld method is similar to a least-squares approach to function fitting; it is particularly good at dealing with peak overlaps, which can exist even in single-phase materials. It does so by loading a known crystal structure and using a pattern predicted from this structure as a basis to adjust the lattice parameter (or peak location) as it fits, and then fitting peak heights accordingly. The Rietveld method thus refines the instrumental, structural, and textural parameters for all spectra simultaneously, collected as groups of data obtained in terms of directions relative to the sample. In
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GSAS, this is carried out directly using a matrix diagonalization method.

Harmonic Method

GSAS, the original LANSCE Rietveld program for determining crystal structure, uses a spherical harmonics method in order to solve for pole figures and ODFs. This approach relies on the assumption that both the pole figures and ODF are mathematically well-behaved, and can therefore be fitted by a series expansion with, in this case, spherical harmonic functions. The computation is performed in Fourier space.

To produce pole figure values, the \((hkl)\) pole figures, \(p(\alpha, \beta)\) are expanded in a series of spherical harmonic functions [16]:

\[
p(\alpha, \beta) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{n=-l}^{l} Q_{lm} P_{l}^{m}(\cos\alpha) e^{im\beta} \tag{2.6}
\]

where \(Q_{lm}\) are the coefficients to solve for, \(P_{l}^{m}(\cos\alpha) e^{im\beta}\) is a spherical harmonic function, and \(l\) and \(m\) govern the shape of the function. In this particular formulation, \(l\) represents the ‘order’ of the spherical harmonic function. The orthogonality of the functions can be exploited to solve coefficients \(Q_{lm}\) from the data, \(p\), by integration [16]:

\[
Q_{lm} = \int_{0}^{\pi} \int_{0}^{2\pi} p(\alpha, \beta)(\cos\alpha) e^{-im\beta} \sin\alpha d\beta d\alpha \tag{2.7}
\]

The ODF can similarly be expanded in a series of spherical harmonic functions:

\[
f(\Psi, \Theta, \phi) = \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \sum_{n=-l}^{l} W_{lmn} Z_{lmn}(\cos\Theta) e^{im\Psi} e^{im\phi} \tag{2.8}
\]

where \(W_{lmn}\) are the coefficients of the series in this case.
It should be noted that, while these functions represent an infinite series, in practice they must be truncated at some finite value (or finite order, $l$) according to the quantity and quality of data available.

These equations can be used to produce an equation that will allow us to transform between the PF coefficients, $Q_{lm}$, and the ODF coefficients, $W_{lmn}$:

$$Q_{lm} = \sum_{n=-l}^{l} W_{lmn} P_l^n (\cos \xi) e^{-in\eta}$$  \hspace{1cm} (2.9)

Once the complete set of $W_{lmn}$ is known, we can use these to recalculate pole figures, even those that were not initially measured.

A common pitfall of any refinement is the potential for overfitting data; in harmonic refinement, this is most frequently produced by refining the data to too high of an order, $l$. It is important to choose a high enough order to be certain that all unique features are being adequately captured by unique peaks, but not go beyond the limits imposed by the quantity and resolution of data collected. A simple rule of thumb is to select an order equal to:

$$Order = \frac{360}{b}$$  \hspace{1cm} (2.10)

where $b$ is equal to the angular resolution of the detector [24].

Even without overfitting, a large drawback of the harmonic method is the existence of ‘ghosting’, or the creation of inaccurate or false texture components like negative texture; these ‘ghosts’ are brought about by the fact that ODF coefficients with an odd order, $l$, are not represented in the pole figure coefficients (for further explanation, see [16]). Ghosting can lead to both an underestimation of true texture maxima
or undesirable artifacts – both positive and negative. These artifacts can be of a magnitude on the order of 10% of the maximum peak height or even more for strongly textured samples. Though, for a strongly-textured sample, these features may simply fall within the range of noise, more subtly textured samples (or, indeed, more subtle texture features within a strong texture) could easily be obscured.

Direct Method

Direct texture computation methods were developed as an attempt to deal with the problem of ‘ghosting’ produced by the shape and mathematical procedure of the harmonic method. In this formulation, both the PF and ODF are represented by discrete values, usually achieved by producing a regularly-spaced grid of cells and subdividing these domains, and then solving an ODF for each [16].

There are many different direct algorithms used; E-WIMV, a modification of the WIMV method, was used for the analysis completed within this dissertation.

The WIMV class of algorithms, generally speaking, makes its final estimate of the ODF (with pole figure data input) based on an iterative process. Traditionally, WIMV uses a regular $5^\circ \times 5^\circ$ grid. ‘Projection paths’ are established between the ODF and PF, and the value in each PF cell ($p_h$) is the average of the weighted values in the ODF cells ($f$):

$$p_h(y) = \frac{1}{N} \sum_{i=1}^{N} f(y \leftarrow g_i) \quad (2.11)$$

To compute the solution, first an initial estimate of the ODF is made. Then, PFs that would result from that ODF are calculated, and these recalculated pole figures are compared with experimental data. The initial ODF estimate is updated based on
any differences found. This process is iterated through until a satisfactory agreement between the experimental data and recalculated pole figures is reached. The algorithm tends to converge rapidly, often on the order of 10 to 12 iterations [16].

E-WIMV is intended to be an improvement on the WIMV algorithm. It provides better integration into the Rietveld method and texture computation in a variety of ways. For example, it uses a 2-D ‘tube cell’ projection between the ODF and PF (WIMV uses a ‘projection line’); this is more time-consuming, but improves the smoothness of the ODF. Further, the ODF cell path for each measurement is computed explicitly for the true measurement angles – that is, it is not confined to a specific 5°x5° grid [24].

Though these methods were developed in order to minimize ghosting effects, these still can exist in a different form. As the computation routine involves the inversion of a large (but sparse) matrix, there is often insufficient data to provide a unique solution. Further, this solution is not possible without setting additional conditions which can, in turn, influence the resulting solutions [16].

2.3 Phase Transformation and Variant Selection

Zirconium is an allotropic element, exhibiting a low-temperature \( hcp \) \( \alpha \)-phase and a high-temperature \( bcc \) \( \beta \)-phase as outlined in Sec. 2.1.2 above.

The transformation between the \( \alpha \)-phase and the \( \beta \)-phase in zirconium can occur via two mechanisms: by growth of the existing pro-monotectoid \( \beta \) phase, thereby inheriting its texture, or by transformation of the \( hcp-\alpha \) to \( bcc-\beta \) according to the Burgers relationship and influenced by variant selection.

In the latter case, in both zirconium and titanium, Burgers transformation occurs
according to the Burgers relationship, with, for example, the planes \{110\}_\beta // \{0002\}_\alpha and directions \langle111\rangle // \langle1 \bar{1} 20\rangle remaining parallel in orientation throughout transformation [25]. The relationship between \{110\} and (0002) corresponds to closest packed planes, while the relationship between \langle111\rangle and \langle11 \bar{2} 0\rangle corresponds to nearest neighbour directions [26]. The relationship has been observed for single crystals [27] and is correct within measurement accuracy for polycrystals, e.g. [28]. During heating (\alpha \rightarrow \beta), there are six equivalent orientation variants of transformation; during cooling (\beta \rightarrow \alpha) there are twelve equivalent orientation variants. There are therefore 72 equally-possible variants of transformation throughout a full \alpha \rightarrow \beta \rightarrow \alpha transformation. The crystallographic relationship for the transformation is shown schematically in Fig. 2.10 (adapted from [2]). During this transformation there is also a significant transformation strain. For the transformation from \beta \rightarrow \alpha under unconstrained conditions, this amounts to 10\% contraction along a \langle100\rangle direction, and a 2\% contraction and 10\% expansion respectively along two perpendicular \langle110\rangle directions.

Assuming that each of the 72 variants is statistically equally likely, one would expect that, given a particular non-random starting texture, repeated thermal cycling from \alpha \rightarrow \beta \rightarrow \alpha would lead to a randomization of the texture. However, this effect has not been seen in literature; instead, a preference for a particular crystallographic orientation, be it either distinct from or retaining the prior texture, has been observed. This behaviour is referred to as variant selection.

Hutchinson et al. [29] reviewed a number of mechanisms for variant selection during cool down, with the particular aim to explain texture memory: (1) stresses generated by the phase transformation strain during heat up biasing the subsequent
Figure 2.10: Schematic showing crystallographic relationship between $\alpha$- and $\beta$-phases through the Burgers relationship, as well as the strain changes associated with the $\beta$ to $\alpha$ transformation. The strains associated with the $\alpha$ to $\beta$ transformation will simply be the reverse of the ones shown. [25]
transformation; (2) remnant thin films of the low temperature phase at the boundaries of the high temperature phase act as nuclei during cool down; (3) grain boundaries are formed in the high temperature phase with optimal characteristics for nucleation of certain orientations of low temperature phase. Each of these hypotheses will be discussed throughout the body of the thesis with respect to the results obtained.

2.4 Recrystallization

Recrystallization refers to the process whereby the stored energy from deformation in pre-existing deformed grains drives the migration of high-angle grain boundaries (those with more than a 10-15° misorientation), thus replacing those grains via the nucleation and growth of new, undeformed grains [30].

Recrystallization that occurs after deformation (i.e. during cooling from high-temperature or during a subsequent heat treatment) is referred to as static. Recrystallization that occurs during deformation is termed dynamic. The latter, however, is poorly understood; this discussion will focus on those known aspects of static and dynamic recrystallization that are related to recrystallization textures.

2.4.1 Recrystallization Textures

The evolution of recrystallization textures is dominated by two theories: 1) Oriented nucleation, wherein certain nuclei are preferentially activated, thus determining the final recrystallization texture, and 2) Oriented growth, wherein those grains with the best orientation relationship to the deformed matrix grow fastest and form the recrystallization texture [31].
In mechanism 1), first proposed by Dillamore [32], high-misorientation bands formed during deformation act as nucleation sites. For mechanism 2), proposed by Barrett [33] and Beck [34], it was observed that grains misoriented at a particular angle grew at an accelerated rate, thus dominating the final recrystallization texture.

Models have been created which aim to reproduce the complex relationship between the deformed and recrystallization textures. For example, Lee et al. [30] proposed a model which assumes the driving force for recrystallization is related to the stored energy due to dislocations, with arrangement dependent on the deformation texture. In this formulation, the deformation texture determines the absolute maximum principal stress direction; this direction becomes the minimum elastic modulus direction of the recrystallized texture.

In cold-worked Zr-2.5Nb, it has been observed that annealing below the $\alpha$ to $\beta$ transformation temperature for a long time (i.e., below 625°C for 100 hours) can cause the $\alpha$ phase to recrystallize [35]. However, recrystallization was not observed for shorter annealing treatments throughout the $\alpha$ and $\alpha+\beta$ regimes [36].

Recrystallization-related texture change has been observed during short heat treatments in other Zr alloys and Ti alloys, however; for example, it has been observed that recrystallization caused previously split maxima in the $\{11\bar{2}0\}$ plane to merge and become a single strong RD maximum [37]. This effect, a reorientation of the $<a>$ axes, has been attributed to grain growth and recrystallization, and corresponds to a 30° rotation about the $<c>$ axis [38].
2.4.2 Review of Results of Experiments Conducted on Zirconium and Titanium Alloys

A ‘texture memory’ effect has been observed by many authors; that is, when the material is transformed from $\alpha$-phase to $\beta$-phase and back to $\alpha$-phase again, the original $\alpha$-phase orientations are maintained either perfectly, or to some extent. A memory effect indicates that variant selection must be occurring, as if no variant selection occurred, the texture would be expected to be significantly randomized by the phase transformation. This effect was seen by Cheadle and Ells [35] in $\beta$-treated Zr-2.5Nb, where the $\alpha$ texture had cubic symmetry after a single cycle into the $\beta$-phase field, but subsequent cycles had little further effect. A similar memory effect throughout phase transformation was reported by Jourdan et al. [27] in single crystals. The preservation of rolling textures has been observed to various extents in polycrystalline zirconium and titanium [28,39]; however, the reported results are not consistent. For example, in two alloys of zirconium (Zircaloy-2 and Zircaloy-4) under different heating and cooling conditions, where recrystallization was observed on heating, Romero et al. [37] report no variant selection during heating, but significant selection on cooling. This lead to some randomization of the room temperature $\alpha$-phase texture during the first thermal cycle, and some degree of strengthening of the alpha-phase texture on subsequent cycles. Gey et al. [40], reported a strengthening of the room temperature $\alpha$-phase texture on the first cycle. Wenk et al. [28], however, report near perfect texture memory in Zircaloy-4 on the first cycle, though this is likely due to the fact that they did not reach a temperature sufficient to fully transform the room temperature alpha grains to the beta phase.

Two of the three $\alpha$ texture components produced in Zr-2.5Nb pressure tubes by
mechanical processing in the $\alpha + \beta$ phase field cannot be accounted for by any known deformation mechanisms of the $\alpha$-phase \textit{per se} and appear to be related to variant selection during the transformation from $\alpha$ to $\beta$ during or after processing [1-3].

It is the aim of this thesis to investigate how the mechanisms involved in phase transformation operate and influence texture in Zr-2.5Nb. It is hoped that, with this knowledge, we will be able to move towards a) explaining existing pressure tube textures, and b) accurately modelling and predicting textures of this and similar materials throughout a variety of thermomechanical processing stages.
Chapter 3

Experiments

3.1 Experimental Method and Motivation

Since the measurement of the $\beta$-phase texture at 900°C+ is experimentally challenging, the majority of studies of such effects have focused on measurements of the $\alpha$-phase. Interpreting changes in texture only at ambient conditions requires coupled assumptions to be made about the selection occurring during heating as well as during cooling. Studies of the high temperature phase using SEM techniques [41] are somewhat ambiguous due to the presence of a free surface, which undoubtedly affects any variant selection that is influenced by the stress state. However, recently, diffraction using penetrating radiation (neutrons or synchrotron x-rays) has been demonstrated as a powerful technique for the measurement of bulk textures under non-ambient conditions e.g. [28, 37]. In this dissertation, experimental measurements of texture through the $\beta$ phase transformation, carried out on a Zr-2.5Nb alloy, are reported, as well as the results of preliminary studies of similar heating cycles under a biasing external stress.
A complete list of all experiments conducted and referenced within this dissertation is given in Appendix A.

3.2 Material

All experiments described throughout this dissertation were carried out on samples of a Zr-2.5Nb alloy. As described further in Sec. 2.1.4, samples were taken from material either immediately after the hot extrusion stage or the cold-worked stage, though the majority of samples fall into the former category. Details of the microstructures associated with these processing steps are given in Sec. 2.1.5. Both pieces of tube came from the same ingot, and so all samples have a nominal composition (by weight) of 2.6-2.7%Nb, 1250-1290 ppm O, 960-1030 ppm Fe, <3 ppm H, and balance Zr and impurities.

Sample dimensions, which vary depending on the type of diffraction being conducted, will be discussed below in each section.

3.3 Neutron Diffraction

3.3.1 Experimental Work

Neutron diffraction measurements were made at HIPPO, a time-of-flight diffractometer at the LANSCE pulsed neutron source [19]; HIPPO employs fixed detectors to count moderated, polychromatic neutrons. HIPPO was designed with the aim of providing the ability to perform a variety of in situ experiments, including time-resolved texture measurements at high temperatures and stresses. To enable this, a detector
array was designed that would both allow for unique sample environments and reduce required count times, allowing for a wider variety of time-resolved studies. The detector panels feature 1360 $^3$He tubes spread over 50 panels (tilted to give constant resolution across the surfaces by compensating for the change in $2\theta$ due to the finite angular range covered by each panel and, therefore, the resulting change in sample-to-detector flight path). These panels are then divided into five ‘banks’, at 10$^\circ$, 20$^\circ$, 40$^\circ$, 90$^\circ$, and 150$^\circ$ normal to the beam direction, as depicted in Fig. 3.1. For the purpose of texture measurements, only the 40$^\circ$, 90$^\circ$, and 150$^\circ$ panels are used due to the low resolution of the low-angle detectors; the remaining detector panels have a resolution in the range of 12-15$^\circ$ [19].

![Figure 3.1: Illustration of the HIPPO diffractometer and its detector panel array [19].](image)

Samples of approximately 1cm$^3$ from both the hot-worked and cold-worked stages were measured (see Sec. 2.1.4). The beam was collimated to a 10mm diameter; the
samples were positioned approximately 9m from the moderator. Sample heating was performed with an ILL-type furnace with vanadium (instead of the standard niobium) heating elements and shields [38]. All tests were carried out under high vacuum (approximately $10^{-6}$ Torr) to prevent the oxidation of both the vanadium shields and the samples at high temperature. HIPPO’s large detector coverage allows for the measurement of a complete orientation distribution function (ODF) with only rotation about the vertical axis; the validity of these measurements was confirmed through comparison to conventional goniometer measurements of the initial texture under ambient conditions [19] and to measurements of texture at the Chalk River Laboratory (CRL) reactor source (see Appendix B).

A variety of experiments were conducted, as outlined in Appendix A, with various experimental parameters varied (e.g. maximum temperature reached, rate of heating, hold times at each temperature). Throughout each test, samples were heated to a particular temperature (or series of temperatures) at which texture measurements were made. For example, for sample ‘CW Tube’ from the HIPPO 2007 experiments, the sample was heated to 625°C (at this temperature, the relative fractions of $\alpha$-phase and $\beta$-phase are the same as at room temperature) and the texture measured; samples were then heated to a maximum temperature, 975°C at a rate of 20°C/minute, the texture was measured, and then the sample was cooled back down to 625°C at the same rate. This cycle was repeated. Fig. 3.2 displays the heating/cooling cycle for this sample. Sample temperatures were measured with thermocouples attached to the samples. At each temperature, samples were rotated about the vertical axis to four orientations: $0^\circ$, $45^\circ$, $67.5^\circ$ and $90^\circ$; data acquisition periods of about 20 minutes were sufficient to produce texture measurements of both the alpha and beta phases.
Figure 3.2: Heating cycle for sample ‘CW Tube’ (see Appendix A), where each point corresponds to the beginning of a measurement. Note that the measurement time is extended for the first set of 250°C readings due to a delay caused by the beam temporarily going off.
3.3.2 Data Analysis

Data collected at the $150^\circ$, $90^\circ$, and $40^\circ$ detector banks (shown in Fig. 3.1) was binned into 98 histograms, and incomplete pole figures were extracted from this data; these were refined simultaneously using a spherical harmonics approximation in GSAS [42] in order to produce an ODF. For the alpha and beta phases, 16th order and 8th order spherical harmonics functions, respectively, were sufficient to describe the ODF – increased harmonic orders did not significantly decrease the $\chi^2$ value of the fit.

The results obtained were in good agreement with those achieved using MAUD and an E-WIMV approach [43], as shown in Appendix B. Pole figures were calculated using the computed ODF and plotted with Beartex [44].

3.4 X-Ray Diffraction

3.4.1 Experimental Work

X-ray texture measurements were performed at the I-ID beamline at the Advanced Photon Source (APS) at Argonne National Laboratories [21]. The beam was tuned to 87 keV with a beam size of 300x300 $\mu$m and a sample-to-detector distance of 1330 mm. Diffraction patterns were collected on a GE 2D detector with a resolution of 2048x2048 pixels (where one pixel is 200$\mu$m). Each ‘pattern’ was measured as a summation of ten 0.2-second exposures in order to avoid detector saturation, while still obtaining good statistics for low intensity peaks.

Samples were prepared from hot-worked material in both cylindrical and cylindrical dogbone (for compression and tension tests, respectively), with a resulting gauge
diameter of 3mm and a gauge aspect ratio of approximately 3:1. Appendix C contains schematics which show both the samples themselves and their relationship to the tube axes. Drawings of the sample grips for the dogbone tension samples are also given.

A series of loading-at-temperature experiments were performed using a hydraulic loading apparatus and an infrared ‘clamshell’ line heater, shown in Fig. 3.3. To prevent oxidization, a small holding chamber made of quartz tubing was continuously flushed with argon gas in order to displace the oxygen present. Samples were heated from room temperature to 250°C, 625°C, 815°C (the extrusion temperature of CANDU pressure tubes), then 975°C (full beta phase) at a heating rate of approximately 100°C/minute; sample temperatures were measured using a thermocouple spot-welded to the sample. Diffraction patterns, taken at five angles about the z-axis (or vertical axis) of the sample, i.e. at 0°, 8°, 16°, 24°, and 32°, were measured, resulting in a hold of approximately 30 seconds at each temperature. Samples were then cooled and measured at each temperature above in turn. Using this heating schedule, samples were loaded with a constant force of 50 ± 8 N (equivalent to a stress of 1.8 MPa). This load was the maximum load that could be applied throughout the entire thermal cycle without causing the samples to fail. The load was applied in either tension (axial and transverse orientations) or compression (axial, transverse, and radial orientations) in three ways: 1) Stress throughout the entire thermal cycle, 2) Stress on heat up only, and 3) Stress on cool down only. Fig. 3.4 shows a sample heating/loading curve for sample comp_transverse2 (see Appendix A), where a compressive load was applied throughout the full cycle to 975°C.
3.4.2 Data Analysis

The resulting spectra were background-corrected and then divided (or ‘caked’) into 36 10-degree sections (e.g. [45]), each of which was averaged to produce a diffraction spectrum. The 36 spectra at all five rotation angles at a given temperature were refined simultaneously in MAUD using the Rietveld method, with texture incorporated via the E-WIMV algorithm [43]. Each data set received the same texture refinement method; the ODF was refined to 5° with 15 iterations in both phases, and anisotropic strain was introduced in the alpha phase to account for precession and strain effects. Pole figures were plotted with Beartex [44]. Some comparisons between the use of neutron and synchrotron diffraction for measurement of texture can be found in [46] as well as Appendix B.
Figure 3.4: Heating and loading cycle for sample ‘Comp_transverse2’ (see Appendix A), where each point corresponds to the beginning of a measurement.
3.4.3 Sources of Error

Potential sources of error throughout experimentation include the fact that samples subjected to stress throughout the entire thermal cycle were held under stress during the 975°C measurement; this resulted in significantly more strain than other measurements (i.e. those experiments with stress applied during only one direction of the thermal cycle), and therefore could have affected the subsequent texture development. The existence of any effect cannot be confirmed by this data set.

Secondly, during final pole figure preparation in Beartex, many samples had to have their ODFs rotated in order to account for sample misalignment. During this process, it was noted that some samples’ final textures required slightly different rotations than the initial textures. The magnitude of these rotations was, at most, on the order of 10-15° and not in the direction of applied stress, but could be evidence of sample movement during testing.

Finally, the use of transmission X-ray measurements potentially introduces a grain sampling issue. Because the samples are limited in their dimension in order to allow for transmission measurements to be made, smaller samples must be used; in addition, as discussed in Sec. 2.2.1, a much smaller sampling area (on the order of 300x300µ, in the case of these experiments) is used than in neutron diffraction. In terms of the measurement methods used, poor grain sampling is indicated by a ‘spotty’ diffraction pattern, shown in Fig. 3.5(b); each grain measured will produce a ‘spot’ about the expected path of Debye-Scherrer rings. As the analysis of these diffraction patterns requires integrating these spot intensities over an angular section of the full ring, if a particular section contains very few ‘spots’, then only a small number of grains are being measured and therefore used to calculate the average intensity over the region.
As a result, depending on the grain size in the diffracted sample volume (which can be exacerbated by grain growth at high temperature), this can limit the statistical quality of the data produced, perhaps diminishing its ability to accurately represent the bulk texture.

Fig. 3.5 shows a comparison between a smooth Debye-Scherrer pattern (Fig. 3.5(a)) and one with decreased grain sampling (Fig. 3.5(b)).

Each diffraction pattern was inspected in order to determine if any significant sampling issues were present. In general, all low-temperature \((\alpha + \beta\)-phase) patterns were quite smooth, whereas the high-temperature \(\beta\)-phase patterns (and some final low-temperature \(\alpha\)-phase patterns) exhibited more spottiness due to grain growth, though none were deemed to have poor enough counting statistics to be excluded. Given a fixed beam and sample size, improved sampling can be obtained by rastering the beam over the sample in order to increase the volume being measured. This was not possible given the experimental setup used for these experiments, however.

Following cooling from the \(\beta\) phase, the final pattern (Fig. 3.5(c)) does not produce the same degree of ‘spottiness’ or grain sampling issues, despite the grain growth of the beta phase. As shown below in Fig. 3.6, we can see the trace of the grain boundaries of the prior large beta grains. Because cooling is occurring at relatively slow rates (i.e. samples were not quenched), the newly-forming alpha grains grow out of and between these grain boundaries rather than transforming directly to the alpha phase. This produces many alpha grains growing from each beta grain, resulting in the parallel plate structure seen.
Figure 3.5: Debye-Scherrer patterns for a) a room-temperature measurement prior to heating to the beta phase, b) a measurement at 975°C showing ‘spotty’ rings, and c) a measurement at room-temperature following a cycle to the beta phase.
Figure 3.6: Microstructure image of hot-worked material following two thermal cycles to the beta regime.
Chapter 4

Results

The results presented herein have been divided into two main sections, the first of which comprises a large series of Neutron Diffraction experiments conducted on samples that underwent a variety of heat treatment cycles. The results of these experiments motivated a study of the effects of thermal cycling under stress, conducted with X-ray diffraction. The discussion of these experiments makes up the second part of the results section.

4.1 Thermal Cycling – Unstressed

4.1.1 Neutron Diffraction

Hot-Extruded Tube

Measurements of texture made at 625°C are, as expected, equivalent to those measured at room temperature. Fig. 4.1(a) shows the starting alpha phase texture for a hot-extruded sample; note the strong transverse texture component in the (0002)
CHAPTER 4. RESULTS

direction. Fig. 4.1(b) and Fig. 4.1(c) show the texture of the sample after 1 and 2 cycles to the full-beta phase (975°C), respectively, with a hold at high temperature of approximately 5800 seconds (96.85 minutes) each. There is a significant change in texture through the first cycle with, for example, the strongest (0002) texture component moving from the transverse direction to the axial. After the second thermal cycle, some cubic symmetry is seen in the α-phase texture although many features of the texture are preserved through the transformation.

Figure Fig. 4.2 displays the β-phase textures corresponding to the Figure Fig. 4.1 α-phase textures. The initial texture is relatively weak. The initial β-phase texture (Fig. 4.2(a)) is not in a Burgers relationship with the initial α-phase texture (Fig. 4.1(a)). However, after one thermal cycle, the high-temperature temperature β-phase texture (Fig. 4.3) appears to be inherited from the α-phase, with the textures of the low temperature α- and β-phases connected by the Burgers relationship. There is then some shifting and strengthening of the major components on subsequent cycling, with a strong cubic symmetry apparent.

The Zr-2.5Nb alloy, however, did not appear to undergo recrystallization of the α-phase via nucleation and growth of new crystals. This is a departure from the behaviour observed in other zirconium alloys such as Zircaloy-2 (e.g. see [37]), where recrystallization is observed as a 30° rotation about the c-axis during heating. Similar to that seen in [35], the strong initial transverse texture from hot extrusion is retained up to at least 875°C, as seen in Fig. 4.4.
Figure 4.1: Low temperature (625°C) alpha phase texture for the (10\{\text{10}\}), (11\{\text{20}\}) and (0002) pole figures for hot worked material. a) initial [max 16.4mrd] b) after 1 thermal cycle [max 28.8 mrd] c) after 2 thermal cycles [max 12.1 mrd]. Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.2: Low temperature (625°C) beta phase texture for the (100), (110) and (111) pole figures for hot worked material. a) initial [max 4.3 mrd] b) after 1 thermal cycle [max 6.9 mrd] c) after 2 thermal cycles [max 8.4 mrd]. Axial vertical, Radial in centre, Transverse horizontal.
**Figure 4.3:** High temperature (975°C) beta phase texture for the (100), (110) and (111) pole figures for hot worked material on the first heating [max 12.5 mrd]. Axial vertical, Radial in centre, Transverse horizontal.

**Figure 4.4:** High temperature (875°C) alpha phase texture for the (10\bar{1}0), (11\bar{2}0) and (0002) pole figures for hot worked material on the first heating [max 13.65 mrd]. Axial vertical, Radial in centre, Transverse horizontal.
Measurements on Cold-Worked Tube

As an initial point of comparison of the effect of deformation on texture throughout phase transformation, experiments were performed on pressure tube material that had received subsequent cold work after hot-extrusion. Measurements conducted on the cold-worked material, shown in Fig. 4.5, produced a broader, less-strong texture; the initial texture of this material Fig. 5.3(a) shows many qualitative similarities to that of the hot extruded tube. However, after one thermal cycle, with a hold at 975°C of 22.52 minutes, while we see that the drastic texture reorientation of the (0002) poles to the axial direction is repeated, a significant portion of the intensity remains in the original orientation (that is, the transverse direction), shown in Fig. 4.5(b) and compared quantitatively by Kearns factors (Eq. 2.5) to the results of the hot-worked tube in Table 4.1. The high-temperature beta phase texture during the first heating is shown in Fig. 4.6.

A second observation relates texture features found after two thermal cycles of hot-worked material to similar features observed in the cold-worked data after only one thermal cycle. In the pole figures for hot-worked material, cubic symmetry is developed; this texture, particularly along the transverse-radial plane, is mirrored in the cold-worked sample after only one thermal cycle (Fig. 4.5(b)). Further, the final (0002) texture for the hot-worked sample sees an increase in intensity about the original transverse direction, similar to that observed in the cold-worked sample.

Incomplete Transformation Experiments

In order to investigate and isolate the effects of full vs. incomplete cycling into the β-phase, experiments that did not go entirely into the β-phase regime (i.e. had a
CHAPTER 4. RESULTS

Figure 4.5: Low temperature \(625^\circ C\) alpha phase texture for the (10\bar{1}0), (11\bar{2}0) and (0002) pole figures for cold worked material. a) initial \([\text{max } 8.7\text{ mrd}]\) b) after 1 thermal cycle \([\text{max } 14.1 \text{ mrd}]\). Axial vertical, Radial in centre, Transverse horizontal.

Figure 4.6: High temperature \(975^\circ C\) beta phase texture for the (100), (110) and (111) pole figures for cold worked material on the first heating \([\text{max } 12.5 \text{ mrd}]\). Axial vertical, Radial in centre, Transverse horizontal.
Table 4.1: Calculated (0002) Kearns factors throughout two thermal cycles: Comparison between cold-worked tube, hot-worked tube, and hot-worked (slow heat) tube.

<table>
<thead>
<tr>
<th>Step</th>
<th>Step</th>
<th>$F_T$</th>
<th>$F_A$</th>
<th>$F_R$</th>
<th>$F_T/F_A$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cold-worked</td>
<td>Initial</td>
<td>0.4811</td>
<td>0.1677</td>
<td>0.3511</td>
<td>2.8688</td>
</tr>
<tr>
<td></td>
<td>First cycle</td>
<td>0.3093</td>
<td>0.4519</td>
<td>0.2388</td>
<td>0.6844</td>
</tr>
<tr>
<td></td>
<td>Second cycle</td>
<td>0.3282</td>
<td>0.4078</td>
<td>0.2639</td>
<td>0.8048</td>
</tr>
<tr>
<td>Hot-worked (S7)</td>
<td>Initial</td>
<td>0.5952</td>
<td>0.0619</td>
<td>0.3429</td>
<td>9.6155</td>
</tr>
<tr>
<td></td>
<td>First cycle</td>
<td>0.2206</td>
<td>0.5815</td>
<td>0.1979</td>
<td>0.3794</td>
</tr>
<tr>
<td></td>
<td>Second cycle</td>
<td>0.3487</td>
<td>0.3436</td>
<td>0.3077</td>
<td>1.0148</td>
</tr>
<tr>
<td>Slow heat (S1)</td>
<td>Initial</td>
<td>0.4726</td>
<td>0.1096</td>
<td>0.4179</td>
<td>4.3120</td>
</tr>
<tr>
<td></td>
<td>First cycle</td>
<td>0.1682</td>
<td>0.6892</td>
<td>0.1426</td>
<td>0.2441</td>
</tr>
</tbody>
</table>

maximum temperature of 815°C) were conducted. As mentioned previously, and further shown in Fig. 4.7, it was observed that samples maintained a strong $\alpha$-phase fiber at this temperature. The resulting textures (compare Fig. 4.7(a), initial texture, to Fig. 4.7(d), final texture) do not display the large texture changes observed upon full thermal cycling (e.g. from Fig. 4.1(a) to Fig. 4.1(b)). Further, the long hold of 110 minutes at 815°C did not cause any noticeable texture evolution (compare Fig. 4.7(b) to Fig. 4.7(c)).

4.1.2 Effect of Additional Cold Work

Samples of hot-worked material were deformed 9.4%, 9%, and 10% in the axial, transverse, and radial directions, respectively, prior to undergoing the same thermal cycle treatment as the undeformed hot-worked material.

The initial texture of these samples, Fig. 4.8(a), varied only slightly from that seen in Fig. 4.1(a). Following a heating into the full beta regime, the resulting alpha texture (Fig. 4.8(b)) displayed the same reorientation to the axial orientation as samples without the additional deformation (Fig. 4.1(b)).
Figure 4.7: Alpha phase textures for the (10\overline{1}0), (11\overline{2}0) and (0002) pole figures for hot worked material. a) initial 250°C b) first 815°C measurement c) last 815°C measurement d) final 250°C. Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.8: Alpha phase textures for the (0001), (10\overline{1}0) and (11\overline{2}0) pole figures for hot worked material with additional cold work (10\% strain) along the radial direction. a) initial 250\(^\circ\)C texture b) texture at 625\(^\circ\)C after undergoing one thermal cycle to 975\(^\circ\)C, and c) texture at 625\(^\circ\)C after undergoing two thermal cycles to 975\(^\circ\)C. Axial vertical, Radial in centre, Transverse horizontal. Each division = 1.2mrd.
4.1.3 Effect of Thermal Cycling Variables

The thermal cycling experiments on the hot- and cold-worked samples had different heating and cooling rates and different hold times at high temperature; it is therefore of interest to characterize both of these effects.

Effect of Rate of Heating and Cooling

As a contrast to those experiments done on hot-worked material introduced earlier, Fig. 4.9 shows the alpha textures during heating of a sample that underwent a relatively slow heating and cooling cycle (a heating ramp of $10^\circ$C/min, with measurements every $50^\circ$C between 625$^\circ$C and 975$^\circ$C; each temperature required a hold of approximately 110-120 minutes to collect data), and a hold at 975$^\circ$C of 119 minutes.

Fig. 4.10(a) and Fig. 4.10(b) show the initial 250$^\circ$C alpha texture and final alpha texture after one thermal cycle, respectively. Comparing the final texture (Fig. 4.10(b)) to that of a sample that underwent a faster thermal cycle (Fig. 4.10(c), where the sample was heated at approximately 20$^\circ$C/min with no measurement holds throughout the ramp), it appears that a more complete reorientation to the axial orientation has occurred. This observation is reinforced by the Kearns factors calculated for this sample, included in Table 4.1.
Figure 4.9: $\alpha$-phase texture evolution throughout a slow heat at 10°C/minute to 975°C. a) 675°C, b) 725°C, c) 775°C, d) 825°C, and e) 875°C.
Figure 4.10: Alpha phase textures for the (10\(\bar{1}\)0), (11\(\bar{2}\)0) and (0002) pole figures for hot worked material. a) initial 250°C b) final 250°C after undergoing a slow thermal cycle, and c) final 250°C texture for a more rapid thermal cycle for comparison. Axial vertical, Radial in centre, Transverse horizontal. Each division = 1.4mrd.
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Texture Evolution at High Temperature

Fig. 4.11 shows the initial high-temperature (975°C) beta texture (Fig. 4.11(a)), and finally the texture after being held for 96.85 minutes (Fig. 4.11(b)). The significant texture development shown, featuring a sharpening of the existing texture and an evolution towards cubic symmetry, is related to grain growth.

This evolution is further displayed throughout multiple thermal cycles – for example, compare Fig. 4.11(b), with only a little cubic symmetry, to Fig. 4.11(d), after one thermal cycle (and another long hold), to Fig. 4.11(f), after a second thermal cycle and hold. It is clear that the cubic symmetry has continued to develop and stabilize.

Two additional samples with holds of different lengths were conducted at temperatures below the β-phase transition point – one for approximately 4.5 hours at 825°C (Fig. 4.12) and another, for approximately 10 hours, at 875°C (Fig. 4.13). The figures below show the alpha-phase textures at the start and end of the respective holds. Only the latter sample, the 10-hour hold at 875°C, displayed any significant texture changes.
Figure 4.11: Development of high temperature (975°C) beta phase texture for the (110) pole figures for hot worked material. a) start and b) end of first high temperature dwell; c) start and d) end of second high temperature dwell; e) start and f) end of third high temperature dwell. Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.12: Development of high temperature (825°C) alpha phase texture for the for hot worked material. a) start of high-temperature dwell at 825°C, and b) end of a high temperature dwell at 825°C for approximately 4.5 hours.
Figure 4.13: Development of high temperature (875°C) alpha phase texture for the hot worked material. a) initial low-temperature texture, b) start of high-temperature dwell at 875°C, and c) end of a high temperature dwell at 875°C for approximately 10 hours.
4.1.4 X-Ray Diffraction

Unstressed Thermal Cycling

One sample was subjected to the same thermal cycling schedule as described in the ND experiments above in order to confirm agreement between the measurements conducted with different techniques; Fig. 4.14(a) and Fig. 4.14(c) show the low-temperature (625°C) α-phase and high-temperature (975°C) β-phase textures for the first cycle; Fig. 4.14(e) shows the final (0002) texture after one thermal cycle. The resulting textures are in good agreement with those obtained via neutron diffraction (compare to Fig. 4.14(b), Fig. 4.14(d), and Fig. 4.14(f)).

4.2 Stress at Temperature

This section will report the results of the low-temperature (625°C) α- and β-phase and high-temperature (975°C) β-phase textures before and after the application of a) 1.8MPa constant stress both on heating and cooling, b) 1.8MPa stress on heating only, and c) 1.8MPa stress on cooling only. Stresses were applied along the transverse and axial directions in both compression and tension, and compression applied along the radial direction. Tests were done in both tension and compression in an attempt to provide a snapshot of two stress ‘extremes’.

For all stress conditions, it should first be noted that there is very good agreement among initial texture measurements (Figures a) of Fig. 4.15–Fig. 4.28); any variability is likely due to a combination of texture variation throughout the tube and issues relating to poor grain sampling inherent to synchrotron diffraction, as discussed in Sec. 2.2.1 and Sec. 3.4.3.
Figure 4.14: X-ray diffraction (left column) and neutron diffraction (right column) textures for: a,b) Low temperature (625°C) (0002) alpha phase texture, c,d) high-temperature (975°C) beta phase texture e,f) Final (625°C) (0002) alpha phase texture after one thermal cycle. Axial vertical, Radial in centre, Transverse horizontal.
4.2.1 Transverse Stress

Figures 4.15-4.20 show the result of the application of a stress in the transverse direction throughout different stages of the thermal cycle; the top row of each figure (Figures a), b)) represent the initial and final low-temperature (0002)\textsubscript{\alpha} textures, respectively; the bottom row of each figure (Figures c), d), e)) represent the initial low-temperature, high-temperature, and final low-temperature \{110\}_\beta phase textures. For stresses along the transverse direction, in both compression (Fig. 4.15-Fig. 4.17) and tension (Fig. 4.18-Fig. 4.20), it can be seen that there is no significant qualitative difference in the initial and final (0002) textures for figures a) and b) within each set, i.e. if a stress is applied during different stages of the thermal cycle heating, there appears to be no or a negligible effect. In fact, these textures appear to be the same as those obtained after a thermal cycle without stress Fig. 4.14(e).
Figure 4.15: Textures throughout thermal cycling for a compressive stress applied along the transverse direction during the full thermal cycle. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.16: Textures throughout thermal cycling for a compressive stress applied along the transverse direction during heating to 975°C. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.17: Textures throughout thermal cycling for a compressive stress applied along the transverse direction during cooling from 975°C. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.18: Textures throughout thermal cycling for a tensile stress applied along the transverse direction during the full thermal cycle. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.19: Textures throughout thermal cycling for a tensile stress applied along the transverse direction during heating to 975°C. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.20: Textures throughout thermal cycling for a tensile stress applied along the transverse direction during cooling from 975°C. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
4.2.2 Axial Stress

Figures 4.21-4.26 show the result of the application of a stress in the axial direction throughout different stages of the thermal cycle; the top row of each figure (Figures a), b)) represent the initial and final low-temperature (0002)\(_a\) textures, respectively; the bottom row of each figure (Figures c), d), e)) represent the initial low-temperature, high-temperature, and final low-temperature \{110\}_\beta phase textures. For stresses along the axial direction, it is once again observed that no new variants are developed as a result of an applied external stress on heat up or cool down. However, it can be seen that, instead of the texture clustering mainly about the axial direction, the texture has appeared to ‘drift’ slightly towards the radial direction – a movement of 10-20\(^\circ\) depending on the data set (e.g. see Fig. 4.24(b) or Fig. 4.26(b)), the final alpha phase texture). Upon examination of the high-temperature and final beta-phase texture corresponding to the final alpha-phase texture (Figures d) and e), respectively), in some cases, we see this ‘drift’ has already begun to occur at high temperature (e.g. Fig. 4.23(d)); in other cases, it is not present yet at high temperature, but does appear in the final beta-phase texture (e.g. Fig. 4.22(e)). In the former case, similar to what has been observed in other experiments, the alpha phase texture is inherited directly from the heated beta phase on cool-down, and so the texture features are present in both.
Figure 4.21: Textures throughout thermal cycling for a compressive stress applied along the axial direction during the full thermal cycle. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.22: Textures throughout thermal cycling for a compressive stress applied along the axial direction during heating to 975°C. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.23: Textures throughout thermal cycling for a compressive stress applied along the axial direction during cooling from 975°C. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.24: Textures throughout thermal cycling for a tensile stress applied along the axial direction during the full thermal cycle. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.25: Textures throughout thermal cycling for a tensile stress applied along the axial direction during heating to 975°C. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.26: Textures throughout thermal cycling for a tensile stress applied along the axial direction during cooling from 975°C. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
4.2.3 Radial Stress

For compressive stress along the radial direction, similar results to the axial stress tests were obtained; though there was no obvious movement of the axial poles, there was still no evidence of the selection of new variants. Results are shown in Fig. 4.27 – Fig. 4.29.

Figure 4.27: Textures throughout thermal cycling for a compressive stress applied along the radial direction during the full thermal cycle. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
CHAPTER 4. RESULTS

Figure 4.28: Textures throughout thermal cycling for a compressive stress applied along the radial direction during heating to 975°C. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Figure 4.29: Textures throughout thermal cycling for a compressive stress applied along the radial direction during cooling from 975°C. a) Initial alpha texture (625°C), b) alpha texture after one thermal cycle (625°C), c) initial beta texture (625°C), d) high-temperature beta texture (975°C), and e) final beta texture after one thermal cycle (625°C). Axial vertical, Radial in centre, Transverse horizontal.
Chapter 5

Discussion

In this section, the results of the experimental work will be interpreted and discussed in order to evaluate which mechanisms – including variant selection – are inducing the texture changes seen. First, the effect of the thermal cycling variables and the use of different diffraction and analysis techniques will be evaluated. The overall observations of the unstressed thermal cycling data (both with complete and incomplete transformation to the beta regime) will be discussed with reference to the phase transformation mechanisms at play, and then compared to the results of modelling work completed by others [36]. Finally, the results of thermal cycling under stress will be discussed.

5.1 Thermal Cycling

In order to establish a basis for variant selection, it is first necessary to understand the mechanisms by which phase transformation is occurring – that is, to establish the origins and path of nucleation and growth of each phase.
5.1.1 Effect of Varying Thermal Cycling Variables

As some of the experiments discussed within the body of this dissertation were carried out under different experimental conditions, it is important to assess the degree to which these variations may affect our ability to compare the results. The most commonly varying elements were the rate of heating and the hold time at high temperature.

The hold time at high temperature (individual or cumulative over multiple cycles, in the full beta regime), demonstrated an effect on the texture evolution over time, as shown in Fig. 4.11. This evolution is also reflected in the low temperature textures of both the $\alpha$ and $\beta$ phases in Fig. 4.2 and Fig. 4.3. With measurements made at 50-75°C above the $\alpha + \beta$ to $\beta$ transus, the samples would have completely transformed to the $\beta$ phase, as confirmed by inspection of the diffraction patterns at high-temperature where there are no visible $\alpha$ peaks. This evolution is likely associated with grain growth, the only microstructural process likely to be occurring under these conditions.

The existence of grain growth is suggested by the increasing ‘spottiness’ of the pole figures with time at temperature in Fig. 4.11, indicative of a decrease in the number of grains being sampled (see Sec. 3.4.3). It is therefore possible that this texture evolution is due to preferential growth of favourably oriented grains. One possible explanation is that some crystal orientations could have a higher amount of stored energy in the form of dislocations created as a result of the constraints associated with phase transformation, and these are preferentially consumed by grains of lower stored energy. As a further note, some authors have noted a relationship between texture and grain growth; for example, in a Ti-6Al-4V study, Ivasishin et al. observed that
the kinetics of grain growth were strongly affected by texture, where more strongly-textured rolled samples displayed retarded grain growth [47]. Though initial texture variation among our hot-worked samples was low or nonexistent, if it is possible that there may be some texture components which encourage grain growth, this observation might go some way towards explaining the differences seen between cold-worked and hot-worked samples in terms of the development of cubic symmetry (see Sec. 5.1.2 and Sec. 5.1.2 below).

A hold conducted in the $\alpha + \beta$ regime at 825°C for approximately 4.5 hours, Fig. 4.12, did not display any texture changes. The overall appearance of the pole figures is the same, and the magnitude of the texture maxima are nearly identical. However, a hold at 875°C for 10 hours appears to have produced some weakening of the texture; the texture maximum in Fig. 4.13(a) is larger than that in Fig. 4.13(b). As there were no significant changes in the volume fraction of the alpha and beta phases between these two measurements, it is quite possible that this effect is instead related to grain coarsening. A similar effect was observed by Choubey et al., where a sample of Zr-2.5Nb $\beta$-quenched billet held at 850°C for 300 minutes displayed alpha grain coarsening relative to a sample that had only undergone a 15 minute hold at 780°C [12]. The 4.5 hour hold at 825°C, similar to the ‘long hold’ sample of [12], would have experienced this grain coarsening, too, but clearly not to the degree where it would have affected the texture of the sample.

As to the thermal ramp rates, it has been shown that decreasing the rate of heating by half and adding several lengthy holds during the heating and cooling periods (resulting in a total 250°C-975°C heating time of approximately 1300 minutes, as compared to approximately 38 for the original hot-worked sample) has had a small
CHAPTER 5. DISCUSSION

effect on the final texture (see Sec. 4.1.3). In Fig. 4.10, we see that nearly all of the (0002) poles have reoriented from the transverse to the axial direction. This is reinforced by the Kearns factors for Sample 1 reported in Table 4.1. The calculated Kearns factors show that the initial transverse texture is slightly weaker than that of the hot-worked sample (S7) that underwent a faster thermal cycle; this is likely due to sample-to-sample variation. Following a cycle into the full-beta regime, we see that the final texture has an even stronger axial concentration than the hot-worked sample. This change, from a weaker transverse texture to a relatively stronger axial texture, represents a more dramatic overall change than that experienced by S7.

One might anticipate that changing these heating and cooling rates might influence the various growth and transformation mechanisms at play during both heating and cooling. It is important to determine which stage of the thermal cycle (either heating, cooling, or the hold at high temperature) is responsible for the changes observed in addition to establishing the mechanism itself.

During cooling for both S1 and S7, the rate was ultimately controlled by the natural rate of cooling in high vacuum. The only difference between the two was the hold required to make each measurement, every 50°C, for S1. This difference, however, is likely negligible; these rates were still very slow compared to a quench, for example, and both would have provided adequate time for the diffusion of Nb, likely the rate-limiting factor. Further, any stresses generated during heating would have been relaxed during the hold in the beta phase, so it is unlikely that any inherited characteristics from the heating process would have had a subsequent effect during cooling.
It is similarly unlikely that the texture changes would have been developed during the hold in the beta regime; as observed in Fig. 4.11, such a hold, at least for the lengths studied here, only results in the development of cubic symmetry. As a result, it is most likely that the texture change was developed during heating. On heating, all rates used were still quite slow. Once again, assuming that there was ample time for diffusion to occur, the effect of diffusion differences between the tests would be negligible. Table 5.1, containing estimates of the average diffusion distances associated with different stages of the thermal cycling across samples S1, S7, and the unloaded APS sample, reinforces this hypothesis.

The relationship between bulk and grain boundary diffusion throughout phase transformation is complex. However, comparing grain and bulk diffusion values at 625°C, we see that bulk diffusion is dwarfed by the diffusion that can occur along grain boundaries. This is confirmed elsewhere in literature [48, 49].

For S1 and S7, the thermal ramps occur over very short periods of time compared to the holds at temperature. It is therefore unlikely that much diffusion would have occurred during the ramps relative to that of the dwells. Comparing diffusion lengths for the holds at 975°C vs. 925°C, we see that the diffusion length at 925°C is much smaller, but still significant. This length decreases with temperature, becoming negligible at 625°C. Even summing the diffusion likely to have been achieved after each
hold in S1, we see that the overall diffusion length is still likely to be within an order of magnitude of that occurring with S7. $\alpha$-Zr consists of elongated grains that are initially 0.4 $\mu$m thick [12], and the prior $\beta$ grain boundary in Fig. 3.6 shows a beta grain with a diameter of approximately 250 $\mu$m. Comparing these length scales to those calculated for diffusion, we can see that the diffusion lengths achieved in all three experiments (S1, S7, and APS) exceed both the alpha and beta grain sizes. As a result, it is unlikely that there would be a wholesale difference between the three samples (and therefore any of the experiments presented in this thesis) in terms of the effects of diffusion, and therefore the basic mechanisms of phase transformation.

However, the additional time during heating might have allowed for greater movement of dislocations. As discussed later in Sec. 5.1.2, it is hypothesized that the stress state, as generated by the increased dislocation density in cold-worked pressure tubes, could be acting to inhibit reorientation to the axial orientation. It is possible that the slow heat could be having the opposite effect by allowing recovery of the dislocations, and therefore reducing the magnitude of internal stress present. There would therefore be less inhibition of the reorientation to the axial direction.

### 5.1.2 Unstressed Thermal Cycling

#### General Observations

It is evident that transformation is occurring via the Burgers relationship and influenced by variant selection as opposed to growth of prior grains; for example, compare the textures of the initial and final (0002) alpha and \{110\} beta phase textures (Fig. 4.1(a) and Fig. 4.2(a), respectively) to the intermediate high-temperature \{110\} beta phase in Fig. 4.3. If transformation had occurred via growth from prior beta
grains, the initial and high-temperature beta pole figures would resemble one another. This is not the case, though it is theoretically achievable with very slow heating rates. If the high-temperature phase is not formed by wholesale growth of the existing retained low-temperature $\beta$ phase, this growth must instead occur either due to nucleation from the $\alpha$ phase, or by preferential growth of certain existing $\beta$-orientations. Growth from the $\alpha$ phase is unlikely unless nucleation occurs at the $\alpha - \beta$ grain boundaries; the Nb content of the $\alpha$-phase is very low (< 1%), and thus there is minimal driving force for nucleation of $\beta$ (with 20% Nb) within the $\alpha$ grain itself. The latter explanation, the preferential growth of selected $\beta$ orientations, has been suggested as a mechanism in literature for Ti-6Al-4V ([38, 50]), though in these studies, measurement of the initial $\beta$-phase texture was not possible due to poor statistics, and the initial $\beta$-phase texture was instead inferred by considering the low-temperature $\alpha$ texture and potential Burgers relationships. Though the balance between the growth of existing textures and potential nucleation of grains from the $\alpha$-phase is expected to be highly dependent on thermal ramp rates, we see that even at the relatively slow heating rates used in the neutron diffraction experiments, wholesale growth of the majority of existing $\beta$ grains is not occurring.

In order to study the relationship between the parent and daughter textures throughout the heating steps, a model of the variants involved in transformation was generated. First, as seen in Fig. 5.1(a) and Fig. 5.1(b), idealized textures of the initial alpha and high-temperature beta phases, respectively, were generated. The (0002) and \{10\overline{1}0\} are shown as examples of the alpha texture, and \{110\} and \{100\} as examples of the beta texture. Following this, and starting with the textures shown in Fig. 5.1(a), the locations of the poles associated with all six variants that could
possibly occur during transformation from alpha to beta were calculated and plotted; (Fig. 5.1(c)) shows an example of one. The same procedure was repeated for the transformation from beta to alpha, starting with Fig. 5.1(b), where there are 12 possible variants. An example of one such variant is plotted in Fig. 5.1(d). Fig. 5.1(e) and Fig. 5.1(f) show the sum of all possible variant locations during transformation from alpha to beta and beta to alpha, respectively.

Examining these figures, it can be shown that the locations of all dominant texture features during transformation are represented by maxima in Fig. 5.1(e) or Fig. 5.1(f), depending on the case. That is, compare the texture of Fig. 4.3 to Fig. 5.1(e), and the texture of Fig. 4.1(b) to Fig. 5.1(f). It is clear that textures associated with transformation are inherited through the Burgers relationship.

Examining the development of the alpha-phase texture throughout heating, Fig. 4.9, there do not seem to be any large texture differences between the incremental 50°C temperature measurements up to 825°C. The alpha-phase texture of Fig. 4.4, at 875°C, does show some difference from its predecessors, both in terms of the appearance of some texture features (e.g. features along the transverse-radial axis of the (0002) look quite different) as well as a decrease in the overall magnitude of the texture (e.g. the \{10\10\} axial texture has decreased significantly). As the volume fraction of the alpha phase at 875°C is only approximately 25% of the composition (as compared to well over 40% at 825°C), it is possible that some share of these differences may be due to difficulty in fitting the spectrum of the now-weaker phase. If these texture changes are not related to this, however, Fig. 4.4 could be providing some information about transformation and selection.

The calculated Kearns factors during heating are given in Table 5.2; as seen, the
Figure 5.1: Predicted textures associated with certain transformation variants. a) Idealized alpha phase initial texture; b) idealized beta phase high-temperature texture; c) texture of an example single variant associated with transformation from alpha to beta; d) texture of an example single variant associated with transformation from beta to alpha; e) texture plot of all six variants associated with transformation from alpha to beta, starting with a); f) texture plot of all twelve variants associated with transformation from beta to alpha, starting with b).
transverse texture stays nearly constant up to 825°C; at 875°C, there is only a very small decrease. The overall shape of the transverse texture similarly remains the same.

Table 5.2: Calculated (0002) Kearns factors throughout a slow heat.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$F_T$</th>
<th>$F_A$</th>
<th>$F_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>675</td>
<td>0.5135</td>
<td>0.0549</td>
<td>0.4316</td>
</tr>
<tr>
<td>725</td>
<td>0.5162</td>
<td>0.0596</td>
<td>0.4242</td>
</tr>
<tr>
<td>775</td>
<td>0.5185</td>
<td>0.0552</td>
<td>0.4263</td>
</tr>
<tr>
<td>825</td>
<td>0.5128</td>
<td>0.0669</td>
<td>0.4204</td>
</tr>
<tr>
<td>875</td>
<td>0.4931</td>
<td>0.1969</td>
<td>0.3100</td>
</tr>
</tbody>
</table>

However, comparing the \{1010\} pole figures of Fig. 4.9(d) (825°C) and Fig. 4.4 (875°C), we see a dramatic decrease in the strength of the axial texture. This is reinforced by Kearns factors calculated for the \{1010\} figures, shown in Table 5.3, where this decrease appears to be occurring gradually throughout heating. If transformation were occurring randomly, i.e. without a preference for the transformation of grains of a particular orientation, one would expect to see an overall equal weakening of all texture components. However, the fact that the axial \{1010\} texture appears to be weakening prior to other components suggests that certain grain orientations may preferentially transform before others.

Table 5.3: Calculated \{1010\} Kearns factors approaching the beta regime.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$F_T$</th>
<th>$F_A$</th>
<th>$F_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>675</td>
<td>0.1958</td>
<td>0.6085</td>
<td>0.1956</td>
</tr>
<tr>
<td>725</td>
<td>0.1970</td>
<td>0.6013</td>
<td>0.2017</td>
</tr>
<tr>
<td>775</td>
<td>0.1989</td>
<td>0.5989</td>
<td>0.2021</td>
</tr>
<tr>
<td>825</td>
<td>0.2171</td>
<td>0.5645</td>
<td>0.2183</td>
</tr>
<tr>
<td>875</td>
<td>0.2835</td>
<td>0.4278</td>
<td>0.2886</td>
</tr>
</tbody>
</table>
On cool-down the Burgers relationship can be seen again when comparing the strong \{110\} axial component Fig. 4.3 with the final strong axial (0002) component Fig. 4.1(b). It is therefore clear that during the $\alpha \rightarrow \beta \rightarrow \alpha$ phase transformation in Zr-2.5Nb some selection is occurring. The Burgers relationship is followed, but not all variants are selected equally. There is variant selection on both heating, as evidenced by the strong \{110\} axial component, Fig. 4.3, and cooling, evidenced by the very strong axial (0002) component, Fig. 4.1(b). This behaviour has been observed elsewhere, e.g. in the heat-affected zone in a pressure tube weld [51]. There is also a texture ‘memory effect’ as evidenced by the stability of the cubic symmetry of the textures on subsequent cycling. Both of these effects have been inferred by previous workers from room temperature textures, though the driving forces, or criteria, had not been confirmed.

The phenomenology of this ‘texture memory’ effect upon the second cycle could be explained in part by the mechanisms for selection on cool-down, reviewed by Hutchinson et al. and described in Sec. 2.3. The second mechanism relates to the retention of thin films of the $\alpha$ phase at high-temperature acting as nuclei for the transformation upon cool-down; this is unlikely, as samples were heated well past the point where full transformation to the $\beta$ phase would occur, certainly supported by the observation of the drastic texture change on the first cycle.

The third mechanism reviewed by Hutchinson et al. (see Sec. 2.3) is that of Stanford and Bate [52] who suggest a mechanism for texture memory and variant selection during cooling of Ti-6Al-4V that is based on the crystallography relationships across $\beta$-phase grain boundaries. If these boundaries are unchanged during a heating / cooling cycle, we can expect strong texture memory effects, while if they move (due to
e.g. grain growth) we can expect changes in the observed texture through a thermal cycle. It follows that any texture memory effect will be highly dependent on how the initial texture has been produced. Our starting material had α and β phase textures associated with hot extrusion in the 2-phase regime; as noted, these textures are not in Burgers relation to one another (compare Fig. 4.1(a) to Fig. 4.2(a)). Thermal cycling into the β-phase regime (with no stress applied) led to drastic changes in the texture on cooling. However the α and β phase textures produced by cooling without applied load are, excepting grain growth, reproduced on a 2nd thermal cycle (Fig. 4.1(c)), hence demonstrating a ‘texture memory’.

**Cold Work**

In comparing the hot-worked and cold-worked samples, we observe the same general phenomenon: a strong selection event taking place that leads to the reorientation of the (0002) poles to the axial direction, Fig. 4.5. Upon examination of the β-phase high temperature texture Fig. 4.6, we see that this texture is similarly not inherited by large scale grain growth from the low temperature β-phase texture, and must instead derive from the transformation of α-phase grains. However, as shown in Fig. 4.5 and by Kearns factors in Table 4.1, some of the original transverse orientation is maintained. When comparing the high-temperature β-phase \{110\} textures for the hot-worked and cold-worked material (Fig. 4.3 and Fig. 4.6, respectively), it can be seen that this ‘incomplete’ reorientation in the cold-worked material is evident in the \{110\} texture. As the only difference between the hot- and cold-worked material is the additional 25-30% cold draw, we would anticipate that microstructural or texture differences during this stage would be the driving factor for this difference in evolution. Comparing
Fig. 4.1(a) to Fig. 5.3(a), there is little difference in the starting textures. However, we would expect the cold drawing process to produce a much stronger dislocation density, and therefore a higher internal stress state, than that of the hot-worked material; this additional internal stress could be affecting transformation. Again, it is possible that either a) grains with certain crystal orientations may have higher stored energy as a result of these dislocations, and as transformation proceeds, these grains may be preferentially consumed by grains of lower stored energy, or b) the internal stress is inhibiting certain variants from occurring. A third possible explanation is that the retained transverse texture feature is not a function of selection, but rather, associated with grain growth in the beta phase; if we compare the final cold-worked texture (Fig. 4.5(b)) to that of the hot-worked sample after two cycles (Fig. 4.1(c)), we see that, after two cycles, some of the transverse texture has similarly re-emerged. As discussed in Sec. 5.1.1, it is possible that either texture or microstructural differences could be controlling the beta grain growth rate, thus causing cubic symmetry to develop at different stages within the thermal cycling.

The data sets presented show how essential it is to study the intermediate stages of the thermal cycle, in particular the high-temperature $\beta$ texture, as it is very difficult to draw conclusions about the mechanisms at play from room temperature studies alone. Throughout the thermal cycling of the hot-worked sample, we see both a) texture memory, and b) a well-defined relationship between the $\alpha$ and $\beta$ phase textures. Without a view of these high-temperature texture measurements, enabled by the type of in situ studies described here, it would be impossible to deconvolute these processes and determine the origin of their relationship. It has also been observed that variant selection is highly dependent on how the initial texture has been produced;
in the Zr-2.5Nb samples used here, the $\alpha/\beta$-phase textures are associated with hot extrusion in the two-phase regime (i.e. around 815°C). A first thermal cycle into the $\beta$ phase brought about a drastic texture reorientation; however, the textures are reproduced (excepting some changes due to high-temperature grain growth) upon a second thermal cycle, i.e. a ‘texture memory’ is observed. The importance of the starting texture explains some of the discrepancy of observations in literature.

It is clear that some form of variant selection is associated with the extrusion process used in manufacturing pressure tubes from Zr-2.5Nb [1–3]. Prior to extrusion, the primary $\alpha$ and $\beta$ both have rather random textures associated with the forging process and $\beta$ heat treatment. The $\alpha$-phase of the resulting billet can have a Widmanstätten-like morphology resulting from $\beta$ to $\alpha$ transformation after forging. The extrusion process is normally carried out at 815°C, at which temperature the proportions of $\alpha$ and $\beta$ are approximately 60:40. During this process, the two-phase material could be experiencing a variety of deformation mechanisms ($\alpha$- or $\beta$-slip, phase-boundary sliding, grain boundary sliding) and recrystallization. Following extrusion, the texture comprises a predominantly transverse basal plane normal component with a strong $\{10\overline{1}0\}$ axial fiber (Fig. 4.1(a)), which persists through the cold-drawing stage (Fig. 5.3(a)). This component does not correspond to any known deformation system in the $\alpha$-phase and the crystals in this orientation are effectively dislocation-free [3]. It is also seen that the c-axes of the crystals associated with this texture are parallel to the long dimension of the grains in the radial/transverse plane [3,53], possibly due to preferred growth of $\alpha$ grains induced by the combined stress/strain of extrusion and Burgers transformation. Another observation is that, similar to the preferred variant seen in Fig. 4.1(b), crystals that develop a Widmanstätten-like structure on
cooling after extrusion exhibit very strong selection of the variant with $c$ in the axial direction of the tube [3]. Additionally, it has been observed that the final $\alpha$ and $\beta$ textures (i.e. Fig. 4.1(a) and Fig. 4.2(a)) are not linked by the Burgers relationship to one another. This result is strange given the texture development observed during unstressed thermal cycling, where the final low-temperature $\alpha$-phase texture (Fig. 4.1(b) was inherited from the high-temperature $\beta$-phase texture (Fig. 4.3). This suggests that mechanical processing is playing an important role in variant selection, and further that the stresses induced may be influencing selection. The preliminary results obtained from thermal cycling experiments under an external biasing stress are a step towards understanding this phenomenon.

5.1.3 Modelling

Another piece of evidence that suggests that the texture effects seen during the first thermal cycle are due to variant selection (particularly, the reorientation to the axial direction) relates to modelling work conducted on the data sets discussed above [36].

In this modelling study [36], the formation of texture on heat up and cool down was examined with the use of an EPSC model, wherein the model is discretized into individual orientations of ‘grains’ and weighted so that the ODF is represented by the grain population generated. Each of these ‘grains’ then can be transformed into a particular variant during a simulated phase transformation, producing a new population of grains; if criteria for selection are not imposed, the expected texture due to a random Burgers relationship can be calculated from this. Alternatively, a variety of selection criteria that define whether particular variants are ‘allowed’ or not can be incorporated. The effects of the thermal anisotropy of the $\alpha$-phase of
zirconium (and the stresses generated by it during heating) as well as the elastic strains generated by phase transformation were probed. A particular variant was allowed only if said variant was ‘favoured’ by the stress state, i.e. whether or not it would oppose or assist the stress-free transformation strains shown in Fig. 2.10. In terms of a thermally induced stress criterion, the variants were allowed if the strain generated exceeded that of the transformation strains. This method relies on the use of stresses in a relative sense, and therefore the relative ease in which certain variants are selected. As a result, the model only gives a qualitative, rather than quantitative, sense of the mechanisms involved and resulting variant selection criteria values.

It was proposed that the thermal stresses on heating could generate an internal bias for the selection of variants. Fig. 5.2 compares the measured high-temperature beta phase (Fig. 5.2(a)) to a series of predicted high-temperature beta textures with varying degrees of selection criteria allowed during the transformation upon heating; each model generated started with the measured low-temperature alpha phase, i.e. Fig. 4.1(a). In Fig. 5.2(b), heat up without selection criteria, while we see some correlation between the measured and predicted textures, there are many additional features. However, with the addition of some thermal anisotropy-based selection criteria, Fig. 5.2(c), we immediately see some improvement in the agreement between the two. With a large amount of selection allowed based on these criteria (Fig. 5.2(d)), we see that the model provides an excellent qualitative prediction of the textures obtained at high temperature, although the intensity is underpredicted. This is conclusive evidence that thermal stresses are influencing variant selection, and that strong selection is occurring on heat up.

Fig. 5.3 shows the predicted final alpha texture after one thermal cycle, starting
with the measured high-temperature beta texture (Fig. 5.2(a)). On cool down, even without variant selection imposed, we see roughly the correct texture, but with a much lower predicted intensity than seen experimentally (Fig. 5.3(b)). As the beta phase is thermally isotropic, and any strains generated during heating will likely be relaxed via diffusional processes during the hold at high temperature, thermal anisotropy-related stresses on cooling will not be significant. A criterion based on elastic stresses related to the crystal structure change (shown in Fig. 2.10) must therefore dominate. However, adding this effect as a selection criterion was still not able to perfectly predict the intensity of the maxima, but it marked an improvement over the model without selection (Fig. 5.3). On cool down, there must, therefore, be some selection in order to produce the observed texture, but apparently this selection process is not as important as that which operates upon heating.

Similarly, models were created to study the texture inheritance of the cold-worked material, shown below in Fig. 5.4. As discussed in the results section, when comparing the measured high-temperature beta phase \{110\} textures of the hot- and cold-worked samples, we see some retained transverse texture (Fig. 5.4(a)). Starting with the low-temperature alpha-phase texture (Fig. 5.3(a)) and using the same selection criteria as with the hot-worked material models, Fig. 5.4(b) (no selection criteria) and Fig. 5.4(c) (strong selection based on thermal strain) were generated. Again, without the selection criteria (Fig. 5.4(b)), we see in the \{110\} figure that the model does not select the axial variant; this is improved somewhat by the inclusion of a strong selection criterion, though it does not produce nearly as good an agreement as that found with the hot-worked material (there are several incorrectly predicted features,
**Figure 5.2:** Prediction of high temperature (975°C) beta phase texture for the (100), (110) and (111) pole figures for hot-worked material, using the alpha texture from Fig. 4.1(a) as the starting point. (a) Measured high-temperature beta texture; (b) no variant selection (max 2.6 mrd, (111)); (c) weak variant selection (max 2.2 mrd, (111)); (d) strong variant selection (max 4.4 mrd, (110)). The axial direction is vertical, the transverse direction is horizontal and the radial direction is about the centre.
Figure 5.3: Prediction of low temperature (625°C) alpha phase texture for the (1010), (11\bar{2}0), and (0002) pole figures for hot worked material, using beta texture from Fig. 4.3 as the starting point; a) measured alpha texture after one thermal cycle; b) no variant selection [max 9.2 mrd]; c) variant selection based on phase transformation stress, as described in reference [43] [max 14.6 mrd]. Axial vertical, Radial in centre, Transverse horizontal.
e.g. many aspects of the \{111\} figure). Therefore, the cold-work is influencing the selection process in some way, (a phenomenon that has also been observed in titanium, e.g. [54]), though not to a large degree. As discussed in Sec. 5.1.2, any effect seen is likely due to the stronger dislocation density present.

### 5.1.4 Recrystallization

A notable characteristic of the Zr-2.5Nb alloy in [35] was that, at least for short hold times, the $\alpha$-phase does not appear to undergo recrystallization by the nucleation and growth of new crystals during heatup. This recrystallization would be evidenced by a 30° rotation about the c-axis during heating [38]), and has been observed in other Zr alloys, e.g., Zircaloy-2 [37]. We see the same behaviour as reported in [35] here: Fig. 4.4 shows the typical strong (0002) axial fibre from hot extrusion, despite the fact that the material has now been heated to 875°C. This phenomenon is likely related to the lack of high-angle grain boundaries (whose migration is required for recrystallization) in Zr-2.5Nb due to the presence of the continuous $\beta$-network in the original microstructure. This lack of recrystallization is clearly reflected in the $\beta$-phase texture formed on initial heating, Fig. 4.3, where the $\{110\}_\beta$ maps to $\{10\bar{1}0\}_\alpha$ as well as (0002)$_\alpha$ through the Burgers relationship.

Romero et al. observed that, on heat up, their Zircaloy-2 alloy did not undergo any significant variant selection, but observed that it did recrystallize, signified by a 30° rotation about the $< c >$-axis, or ‘merging’ of previously split maxima in the $\{11\bar{2}0\}$ pole figures (see Fig. 2 of [37]). On cool down, they did observe selection. It is likely that the existence of recrystallization on heat up is responsible for the different selection characteristics seen between their results and those presented here. As the
Figure 5.4: Prediction of high temperature (975°C) beta phase texture for the (100), (110) and (111) pole figures for cold-worked material, using the alpha texture from Fig. 5.3(a) as the starting point. a) measured high-temperature beta texture; b) no variant selection [max 1.7 mrd]; c) strong variant selection [max 3.2 mrd], using the same selection criteria as imposed to generate Fig. 5.2(d). Axial vertical, Radial in centre, Transverse horizontal.
anisotropic $\alpha$ grains heat and transform to the $\beta$ phase, the same thermal strains are generated; however, in the case of Zircaloy-2, this drives recrystallization, and the associated recovery process relaxes these strains. As such, the strong driving force for the selection of a new variant – identified as being due to these thermal stresses on heating – does not exist, and instead no selection is observed.

A second result from [37] is that, while they did not observe selection during the transformation, i.e. from $\alpha$ to $\beta$, they did observe some selection on cooling back to $\alpha$. This result does not contradict what we have observed; throughout the modelling described above, we have identified that some selection does occur in this direction, too, though it is of much smaller magnitude than that observed on heating. Again, as the high-temperature $\beta$-bcc phase is isotropic, thermal expansion does not contribute to the stress state of the material; this selection must therefore be related to the internal stress misfit generated by the elastic strains associated with transformation. Like the results we obtained with Zr-2.5Nb during cooling, the authors of [37] observed a selection during cooling that contributed to the magnitude of the maxima rather than their position.

5.1.5 Incomplete Transformation

As shown in Sec. 4.1.1, experiments carried out that did not go entirely into the $\beta$-phase regime (e.g. had a maximum temperature of 815°C), did not display the large texture changes observed upon thermal cycling into the $\beta$-phase (e.g. from Fig. 4.1(a) to Fig. 4.1(b)), producing instead a strong memory effect. It is likely that this contributed to, for example, the strong memory effect seen by Wenk et al. ([28]; see the diffraction pattern in Figure 1 from [28]) where the maximum temperature
was not sufficient to fully enter the $\beta$-phase regime. Similar results are reported in Zircaloy-2 by Romero et al. [37]. These sets of observations lead to the conclusion that, in cases where the remnant $\alpha$-phase is present at high temperature, it acts to control the low temperature texture, at least at low cooling rates where there is enough time for diffusion to occur, allowing the remnants to grow as the material cools. This effectively represents the second mechanism reviewed by Hutchinson et al. ([29]), wherein thin $\alpha$ films at the boundaries of the high temperature phase act as nuclei during cool down. At faster rates, where the diffusion of Nb is not possible, the remnant alpha will not have time to grow and dominate the final microstructure – leaving instead a final alpha grain structure in Burgers relationship to the high-temperature beta phase.

These observations are also well-described by the third mechanism reviewed by Hutchinson et al. and proposed by Stanford and Bate [52] in studies of Ti-6Al-4V, as described above. This mechanism is based on changes in crystallography, i.e. relationships across $\beta$-phase boundaries. If boundaries do not change throughout a thermal cycle, as might be expected if samples are not taken fully to the beta phase, there will be no accompanying texture changes. A strong memory effect would instead occur.

## 5.1.6 Stress at Temperature

Thermal cycling experiments were conducted in order to determine if an external biasing stress could serve to act in the same way as the thermal (internal) stresses on heat up – that is, to see if they could force a particular type of selection.

These experiments were conducted using a different type of furnace that had the
ability to employ higher thermal ramp rates (rates on the order of 100°C/minute were used, as compared to 10° or 20°C/minute). As discussed in Table 5.1 and Sec. 5.1.1, this different ramp rate is unlikely to have contributed to any mechanistic changes in transformation. Further, the experiments used a different type of scattering – X-ray rather than neutron – where fewer grains are measured. This brought about grain sampling challenges (see Sec. 3.4.3). The resulting data was analyzed using a different technique (the ‘direct’ approach in MAUD with the E-WIMV texture algorithm instead of the spherical harmonics approach in GSAS). Despite these differences, the results obtained for unstressed thermal cycling experiments at APS were comparable to those conducted at HIPPO (see Fig. 4.14 and Sec. 4.1.4 for further commentary).

It should be noted that initial sample-to-sample variation of the α-phase textures was low (Figures a) of Fig. 4.15–Fig. 4.28) and the overall quality of grain sampling was adequate with synchrotron X-rays. However, at high temperature, diffraction patterns developed some ‘spottiness’, indicative of poorer grain sampling. For example, throughout the tests where stress was applied in the transverse direction, no significant differences were observed between the final alpha phase textures. There was, however, a large degree of variability in both the initial low temperature and high-temperature beta phase textures, the former of which was likely related to the low volume fraction of β-grains present. These differences were not seen in the overall location of texture maxima, but rather the general appearance and magnitude of the maxima, shown in Fig. 5.5. Because observing the high-temperature beta phase texture is important for understanding the path of texture evolution, improvements would need to be made – for example by rastering the beam over the sample throughout the measurement – in order to improve confidence in such measurements for
future work. As noted in Sec. 3.4.3, these grain sampling issues do not exist in the final, low-temperature texture as the final alpha grain structure is much finer than the high-temperature beta grain structure.

![Figure 5.5](image)

**Figure 5.5:** High temperature ($975^\circ$C) beta phase texture for the (100), (110) and (111) pole figures for different stress-at-temperature tests. a) Compression on heat-up (and subsequently cool down), b) Compression on heat-up only, c) Compression on cool down only (no stress) d) tension on heat-up (and cool down), e) tension on heat-up only, f) tension on cool down only. Axial vertical, Radial in centre, Transverse horizontal.

None of the tests exhibited strong evidence of variant selection having been affected by the application of an external stress. This is reinforced by inspection of the
high-temperature beta phase. In the case of both the transverse tensile and compres-
sive stresses, upon heating, the high temperature $\beta$-phase textures are qualitatively
the same (compare the reorientation of the transverse texture to axial texture in the
$(0002)\parallel\{110\}$ direction, e.g., compare Fig. 4.3 to Fig. 4.15(d)). Further, there is
little difference between the final $(0002)$ textures where stress is applied throughout
the full thermal cycle and those where it is only applied on heat up (Fig. 4.15(b) and
Fig. 4.16(b), respectively.). This suggests that the application of stress on heat up
does not discourage the selection of the variant that would otherwise occur in the
absence of stress, i.e. the selection is still due to the internal thermal stresses.

The technique of flushing the sample chamber with argon gas in order to displace
the oxygen was not entirely successful as a replacement for high vacuum – samples dis-
played some oxidation following their heating cycle to the beta phase. This increased
O content could have led to some a-phase Zr being retained at higher temperatures
than expected (and therefore providing a potential nucleation site upon cooling if still
present at 975C), but a) this is likely only near to the surface of the sample, and b)
was not evident in the observed diffraction pattern. Such an effect has not appeared
to affect the overall transformation of the samples – the same strong reorientation to
the axial direction persists.

One sample, shown in Fig. 4.17, displayed slightly different behaviour. With
a compressive stress bias solely on cool down, we see that some of the transverse
$(0002)$ texture is retained (Fig. 4.17(b)). Additionally, in both stress during the full
thermal cycle and stress only on cool down, we see a similar texture in the $\{10\overline{1}0\}$
and $\{11\overline{2}0\}$ figures, though the former is significantly less strong. It is interesting
that different effects are seen following a stress during the full thermal cycle and just
during cooling. One hypothesis for this is that the ability to more easily affect texture on cool-down could be related to the strength of the ‘natural’ variant selection at play. In the models discussed above (Sec. 5.1.3), it was found that selection was very strong on heat-up, but much weaker on cool-down. It is possible that this difference in the relative strength of internal stress-driven variant selection paves the way for an ability to differently impact variant selection during heating and cooling with external stress. However, this hypothesis does not explain why similar results might not be obtained for tests with stress applied during the full thermal cycle as with stress applied only on cool-down. This texture retention in the transverse direction is similar to that observed with the cold-worked tube after one cycle (Fig. 4.5(b)), though the deformation histories that the respective samples underwent were different enough that one would not be able to draw any conclusions from this. It is possible that this effect is only seen where stress is applied in the transverse direction because of its relation to the existing texture: on heating, these stresses are applied parallel to the majority of (0002) normals; on cooling, given the observed reorientation to the axial direction, the stresses are perpendicular to the (0002) normals.

In other tests, particularly those conducted on select axial and radial samples in both tension and compression, a different phenomenon was detected. In unstressed tests, where the final alpha phase appeared to be inherited from the high-temperature beta phase via the Burgers relationship, the high-temperature beta phase simply transformed into alpha, leaving any remaining final low-temperature beta phase with a texture identical to what existed at high temperature. However, with the application of stress, it can be seen that the final low temperature beta texture deviates from the high-temperature beta-phase texture in the form of a shift of, e.g., the \{110\} texture.
CHAPTER 5. DISCUSSION

from the axial direction to slightly towards the radial direction (though the final beta texture is still correlated to that of the final alpha phase according to the Burgers relationship). In other cases, the new texture feature is already partially or fully present at high temperature. This suggests that the stress must be acting to change the beta phase texture at high temperature, prior to the beginning of transformation back to alpha.

These new texture features are unlikely to be the result of the selection of a new variant and have no relation to the original low-temperature $\beta$-phase textures (Figures c) of Fig. 4.15–Fig. 4.28). The movement from the axial to radial direction appears to be a gradual shift and does not represent a particular texture; that is, there are no likely variant candidates from the initial texture in this location (see the (0002) plot in Fig. 5.1(f)). For the former two observations (where there are new features but they are mirrored in the final alpha and beta phase textures), the resulting textures are likely produced by deformation in the high-temperature beta phase (and hence by slip or induced grain rotation), a possibility that will require further study.

The movement to the particular locations of the new texture maxima could possibly be related to dynamic recrystallization in the $\beta$-phase. The Zr-2.5Nb alloy used has not exhibited recrystallization leading to texture maxima movement even during holds at high temperature, but there is the possibility that the addition of stress during these high temperatures might have provided an adequate driving force for recrystallization. Further study of this hypothesis will be required.

While it has been shown that an internal stress misfit, produced by the anisotropy of thermal stresses on heating (or to a lesser degree, the elastic transformation strain on cooling), was capable of affecting selection on heating, it is not clear why the
external stress applied during these cycles was unable to provide a similar bias, unless local relaxation at high-temperature counteracted the far-field stresses being applied.
Chapter 6

Conclusions and Future Work

6.1 Conclusions

A number of in situ experiments were carried out in order to study and characterize the texture changes occurring during the $\alpha \rightarrow \beta \rightarrow \alpha$ transformation. It was observed that:

- The texture of the $\beta$-phase is inherited from $\alpha$-phase on the initial heating. $\alpha \rightarrow \beta$ variant selection occurs, driven by the interaction between thermal stresses produced in the $\alpha$ phase and the phase transformation strain. High levels of internal stress produced by cold work do influence this selection process, but not to a great extent.

- There is a preferred $\beta \rightarrow \alpha$ variant selection during cooling. Compared to random variant development, this selection does not significantly influence the location of the texture maxima (as observed during heating) but does affect the magnitude of the maxima observed. A selection criteria based on transformation
strain coupling to the elastic moduli of the \( \alpha \)-phase provides improved agreement between model and experimental texture.

- There are dramatic changes to the \( \alpha \)-phase texture during the first thermal cycle. The \( \alpha \)-phase texture on subsequent (2nd and 3rd) heatings can still be described as being driven by thermal stresses.

- There is an evolution and strengthening of the major components of the \( \beta \)-phase texture at elevated temperature. This strengthening is due to grain growth / recrystallization, and leads to the development of strong cubic symmetry. This evolution has been observed to occur only during holds in the full \( \beta \)-phase.

- The cubic symmetry of the high temperature \( \beta \)-phase is inherited by the low temperature \( \alpha \)-phase during the second cooling, i.e. changes in the high temperature \( \beta \)-phase texture are clearly reflected in the \( \alpha \)-phase texture upon cooling.

- Within the range of ramp rates studied, there appears to be a small effect of the heating rate (during a thermal cycle to the beta phase) on the final texture.

- At the ramp rates studied, a near perfect memory effect is seen if the maximum temperature does not result in 100\% transformation to the \( \beta \)-phase, at least for hold times up to a few hours.

- For long hold times in the range studied, at temperatures below the \( \alpha + \beta/\beta \) transus, a weakening of texture is observed, likely associated with alpha phase grain coarsening.

- The application of an external biasing stress throughout transformation does not appear to induce the selection of new variants, at least at the stress magnitudes
tested.

- Stress applied in the full-beta regime appears to influence texture.

6.2 Future Work

Looking beyond the experimental results discussed above, there are some future experiments that should be considered; these experiments will enable further understanding of the phenomenology of and criteria for variant selection and texture evolution through phase transformation.

6.2.1 Additional Unstressed Thermal Cycling Experiments

As observed, vastly different results were obtained among samples that either did or did not recrystallize upon heatup (compare the results in Chap. 4 to those of Romero et al. [37]). Additionally, when comparing the selection that takes place between the first and second thermal cycles of Zr-2.5Nb tube material, we observe different effects; this suggests that starting texture plays a role in the eventual selection processes that take place. To this end, it would be valuable to complete thermal cycling experiments on a variety of different alloys (both zirconium and titanium), as well as samples that have a variety of different starting textures. In addition, it would be worthwhile to study a cold-worked sample at a slower thermal ramp rate in order to determine if longer heating times are serving to influence the dislocation structure – and therefore the final texture. Finally, even in the absence of a beamline, it would be valuable to carry out a series of experiments that would quench partially-transformed specimens. These specimens could produce some valuable information about the mechanisms at
play, e.g. the role of grain growth.

6.2.2 Additional Stress-at-Temperature Experiments

Further tests can be carried out in order to study texture evolution under stress at elevated temperatures, isolated from phase change effects. These studies will be enabled by the use of a new instrument at HIPPO at LANSCE that will allow for neutron diffraction measurements under temperature and stress. For example, studying deformation in the beta regime by making measurements before and after a large stress is applied could go some way towards explaining some of the new texture features observed in several samples presented here.
References


REFERENCES


REFERENCES


Appendix A

Complete List of Samples and Experiments

A.1 Complete list of Samples and Experiments

Table A.1 below features an exhaustive list of all of the samples (and associated experiments) referenced in the body of this dissertation.
Table A.1: Complete list of Samples and Experiments

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<th>Run Numbers</th>
<th>Description</th>
<th>Environment</th>
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### Table A.1: Complete list of Samples and Experiments

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<td>Description</td>
<td>Environment</td>
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Appendix B

Comparison Between Analysis Techniques

This section will give a brief comparison of the results obtained using the spherical harmonics method of GSAS and the direct method of MAUD, with commentary on some of the general procedure and results obtained using both methods.

A general outline of the two methods and their mathematical basis is given in Sec. 2.2.3.

B.1 Comparison between Spherical Harmonics and E-WIMV Approaches

As shown below in Fig. B.1, we see that roughly the same results are obtained using GSAS (Fig. B.1(a)) and MAUD/E-WIMV (Fig. B.1(b)). The texture maxima are located in the same places and very similar overall maximum values (measured as mrd)
were obtained, but there are some discrepancies with respect to the relative magnitudes of the maxima themselves. For example, in the (0002) figure of Fig. B.1(b), we see that the transverse texture is far less concentrated and uniform than that seen in Fig. B.1(a).

Compared to pole figures measured at Chalk River, Fig. B.1(d), we see that this measurement more closely resembles that obtained with GSAS and the harmonic method. As this pole figure is computed based on direct measurements of the pole figures themselves rather than computed following the refinement of an ODF, the Chalk River figures can be assumed to be a reasonable standard.

It was noted that, in the fits resulting from the E-WIMV refinement, MAUD did not appear to do a particularly good job with fitting the (0002) peaks. This may be due in part to the fact that the technique involves taking a known crystal structure with known peak positions and adjusting various parameters (crystallographic, background, etc.) until the peak positions and overall peak shapes are a good match. As seen in Fig. B.2, MAUD has done a better job at capturing the intensity of the \{10\overline{1}0\} peaks than the (0002) peaks (for this particular bank of data). Typically, for an untextured sample, the \{10\overline{1}0\} peak is larger than the (0002) peak (see Fig. 2.7). This is frequently not the case in Fig. B.2, likely a function of the strong texture of the sample. It is possible that this strong texture is therefore making it more difficult for MAUD to fit the data based on its crystal model, and may go some way towards explaining the discrepancies between the GSAS and MAUD (0002) pole figures.

It is possible that improvements can be made to these fits by, for example, introducing more complex background functions or better refining the asymmetry of the peaks.
Figure B.1:  a,b) Comparison of results of the texture refinements of a common data set, as collected on the HIPPO instrument at LANSCE: a) GSAS, using a spherical harmonics approach and b) MAUD, using the direct E-WIMV algorithm.; c,d) Pole figures produced by direct measurement of a similar sample, measured on the E3 beamline at NRU at Chalk River.
Figure B.2: Peak fits obtained by MAUD for hot-worked material for one bank of data from HIPPO.

One of the primary arguments for using the E-WIMV algorithm over GSAS relates to the ‘ghosting’ effects seen in spherical harmonics fits, which produce imaginary textures (either negative or positive). However, WIMV algorithms also introduce their own ghosting effects. In Fig. B.3 below, the same pole figures as shown in Fig. B.1(a) and Fig. B.1(b) are reproduced, only the intensities of the maxima are limited to 1 m.r.d. in an attempt to highlight the background noise. (Note that these data sets have been processed so that negative values have been rejected.) At this level of intensity, we can see some noise, but that produced by MAUD and E-WIMV is far more uniform and less ‘blotchy’ than that of the results of GSAS and the spherical harmonics method. Given the strength of the texture, this noise is not particularly significant to the overall evaluation of the texture changes.
Figure B.3: Comparison of the noise generated during a texture refinement of the same data set by a) GSAS and a spherical harmonics approach, and b) MAUD and the direct E-WIMV algorithm.
Appendix C

Sample Design and Drawings

C.1 Sample Design and Drawings

The figures included in this section contain schematics showing the dimensions of the samples used throughout the experiments in this thesis. Fig. C.1 and Fig. C.2 show cylindrical samples created for axial and transverse compression experiments at APS, as described in Sec. 3.4.1. Radial compression samples were identical. Fig. C.3 and Fig. C.4 show the cylindrical dogbone samples used in tension tests at APS, as described in Sec. 3.4.1; these samples were placed in grips (Fig. C.5 and Fig. C.6) during the tension tests. All dimensions are in inches.
Figure C.1: Schematic showing axially-oriented cylindrical samples used in the neutron diffraction experiments outlined in Sec. 3.3.1.
Figure C.2: Schematic showing transverse-oriented cylindrical samples used in the neutron diffraction experiments outlined in Sec. 3.3.1.
Figure C.3: Schematic showing axially-oriented ‘cylindrical dog-bone’ tension samples used in the APS experiments outlined in Sec. 3.4.1.
Figure C.4: Schematic showing transverse-oriented ‘cylindrical dogbone’ tension samples used in the APS experiments outlined in Sec. 3.4.1.
Figure C.5: Schematic showing the top sample grip used in the APS tension experiments outlined in Sec. 3.4.1.
Figure C.6: Schematic showing the bottom sample grip used in the APS tension experiments outlined in Sec. 3.4.1. The holes running through the length of the grip are the input tubes for the argon gas.