Characterization of the Mechanical Response to Residual Stress in Corroded Zirconium Alloys

by

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Abstract

Zirconium (Zr) alloys are used in the manufacture of safety critical components such as nuclear fuel tubes. These alloys are suited to structural applications within the aqueous, high pressure environment of a nuclear reactor core, because they are transparent to neutrons, have excellent corrosion resistance and good mechanical properties. However the zirconium fuel tubes have become the life limiting factor in achieving high burn-ups.

High compressive stresses build up in the oxide due to the large volumetric expansion (>50%) that occurs while the oxide forms. These residual stresses play a key role in stabilising the protective oxide. When stability is lost, cracks often form in the oxide, allowing water ingress, resulting in corrosion of the metal substrate. The tensile stresses existing in the metal substrate, close to the oxide interface are high enough for material creep to occur. This thesis focuses on investigating the mechanical response to residual stress in corroded zirconium alloys.

Novel methodologies used in this study include nanoindentation (NI) and focused ion beam (FIB) milling to determine residual stress. Digital image correlation (DIC), electron back scattering diffraction (EBSD) and energy dispersive X-ray spectroscopy (EDX) were used in the analysis of data.

Mapping NI hardness gradients across the oxide led to a comprehensive, systematic examination into the causes of scatter found in the NI data, with an interesting and surprising outcome. A feasibility study is included using a relatively new method of measuring strain by FIB milling and DIC analysis. It is thought to be the first time this method has been used on zirconium alloys. NI creep testing was used to evaluate time dependent deformation, resulting in high values of the stress exponent ($n$). An investigation found good correlation between $n$ values from indentation testing and those from load relaxation testing, suggesting a relaxation of deformation modes, possibly activated during the loading process. A comparative analysis was performed on the plastic deformation zone underneath a large Vickers indent and the highly deformed region of the load relaxation tested sample, to ascertain whether twinning mechanisms were dominant in the deformation process.
Declaration

This thesis is submitted to The Open University for the degree of Doctor of Philosophy. The work described in this thesis was carried out in the Materials Engineering Group (DDEM), in the Faculty of Mathematics, Computing and Technology between November 2007 and October 2011, under the supervision of Prof. M.E. Fitzpatrick and Dr. M.A. Rist. It is an original work of the author except where reference is made to the work of others. None of this work is submitted or is in the process of submission, in whole or part, for a degree at any other university.
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I make no apology for the length of this section and hope you will indulge me. For it is a case of, there but for the grace of one Almighty God, one unique institution and several very special human beings....go I.

The Open University gave me the chance to attain a BEng (Hons), and now, possibly a research degree. So it is without hesitation that I thank the founders and the current caretakers for these opportunities.

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Like most PhDs there have been good and bad parts. It was tough losing my mother, father, mother-in-law and aunt so close together in my 3rd year. But their memory has spurred me on, and I have written this thesis with them on my mind. I know that they would have been proud.

Lastly, but mostly, I thank my family. To my dear husband David, for his unfailing love and support, I give my extreme gratitude. During the eleven year period spanning my undergraduate degree and my PhD he has been my rock. It is his faith in me and his constant encouragement that has enabled me to finish. Thanks also to my sons Mike and Joe, for lending a hand, for all the cuppas, for their interest in my work, and their pride in their grumpy mum.
This thesis is dedicated to

David Alan Storer
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The hope I dreamed of was a dream,
Was but a dream; and now I wake,
Exceeding comfortless, and worn, and old,
For a dream’s sake.

Christina Rossetti 1830-1894
Chapter 1: Introduction

1.1. Background

There is an increasing global demand for sustainable energy. If this demand is to be met, many believe that renewable sources alone are not adequate. So, in the UK ambitious targets have been set as part of a nuclear renaissance, with existing reactors being decommissioned, and a plan in place for an extensive build programme of new pressurised water reactors (PWRs).

If nuclear power is to provide a sufficient and safe supply of energy, it is essential to maintain the structural integrity of safety critical, in-reactor assemblies, components and their materials. For components subjected to the high stress, the extreme temperatures and radiation field of a PWR, it is also important to consider how deformation will affect the materials of those components, over time.

Zirconium alloys are used in the build of safety critical components such as fuel tubes (see figure 1.1), spacer grids and pressure tubes. Since the 1950s, the alloys have been used for uranium fuel cladding. Zr alloys were chosen for the following advantages:

- Low thermal neutron cross section
- High resistance to corrosion, particularly in the aqueous in-reactor environment.
- A combination of adequate mechanical properties in terms of strength.

Figure 1.1: Bundles of fuel tubes [1].

(This is an alternative image. The original image used in the examined thesis could not be used in this access version due to lack of copyright clearance)
Zirconium’s resistance to corrosion relies on its affinity with oxygen, and the thin protective layer of oxide that, almost immediately, forms on the surface of the metal. However, due the complicated kinetics involved in the continuing oxidation process, eventually cracks and pores form in this protective layer, allowing water ingress and leading to corrosion of the metal tubes. Components within the core of a PWR reactor are exposed to high pressures (150 bar) and water/steam temperatures >300˚C [2]. The strain resulting from this constant exposure can take its toll, and lead to an eventual loss of structural integrity in the component or material. This in turn could lead to catastrophic failure within a nuclear power plant.

In the current situation, the uranium fuel has a life of several years, yet due to corrosion, the Zr alloy fuel tubes need to be replaced every 18 months to 2 years [3]. This results in low efficiency burn-up, regular shut downs of reactors to replace the tubes, fuel waste and high monetary costs.

Over the years both the mechanical properties and the corrosion resistance have been improved by the addition of different alloying elements. However, in order to improve the efficiency and safety of nuclear energy production, more research is needed to establish an enhanced understanding of the factors influencing and controlling the corrosion of zirconium alloys.

1.2. The Zirconium Project

This research study is part of the EPSRC funded Zirconium Project; Mechanistic Understanding of Zirconium Corrosion (MUZIC) (EPSRC grant number: EP/E036171/1); a collaborative partnership between academia and industry. The project leaders are Manchester University, working alongside academic partners, Oxford University and The Open University. Industry partners include Westinghouse, Rolls-Royce Marine, EDF, INSS, Nexia Solutions/NDA and Serco Assurance.

The overall aim of the MUZIC project is to develop a fully mechanistic understanding of the corrosion processes in zirconium alloys.
1.3. This research project

As zirconium oxide forms and grows inward from the surface of zirconium alloy metal, there is a volume expansion of more than 50% (Pilling Bedworth ratio; 1.56). This expansion leads to high compressive residual stresses in the oxide layers nearest to the metal interface, and tensile stresses in the metal below the interface. There is a school of thought that believes the high compressive stresses to be the controlling factor in the rate of oxidation [4-7].

This thesis presents an experimental study, involving a range of novel techniques, in an attempt to characterise the residual stresses. A wide range of characterisation and analysis methods were used to try and understand the response of several different Zr alloys, in particular, how the materials responded under load. The time dependent behaviour was also investigated.

Despite a resurgence of interest in the research of zirconium alloys there still remain some unresolved issues. The results of the experiments in this project were not always as expected, which led to further analysis to provide a better understanding of the findings. When completing the review of the literature, no other studies of this kind on zirconium were found. For this reason, it is hoped that this thesis will provide information to fill some of the gaps in research.

1.4. Thesis structure

This work follows a traditional format for an engineering thesis, however the review of literature is presented a little differently, in that it spans three separate chapters;

Chapter 2: Nanoindentation
Chapter 3: Residual stress
Chapter 4: Oxidation of zirconium alloys

This form of literature review was thought to be the most logical and least complicated, considering the varied elements involved in this research project.

Chapter 2 explains the background to hardness testing. Here, both theoretical and empirical past research is chronicled to show how instrumented indentation developed, to
enable the accurate measurement of mechanical properties in very small volumes of material. This chapter covers how a nanoindenter works and how the relevant mathematical equations are applied in the analysis of the elastic/plastic loading and unloading of the indenter. Limitations to the technique, such as ‘pile up’ and ‘sink in’, are also discussed.

Early in Chapter 3 the different types of residual stresses are defined along with descriptions of conventional measurement techniques, and how the stresses are quantified. Two literature reviews are presented; the first shows how others have used nanoindentation to determine residual stress. This literature represents experiments on cross sections of various materials. However, there was no evidence of the indentation technique being used to map hardness (or stress) variations from the outer to inner oxide, over the interface and then into the metal. Researchers using methods such as synchrotron X-ray diffraction [8] and Raman spectroscopy [9, 10] have managed to quantify and exhibit trends in residual stress across the oxides of Zr alloys, and this is important information in the quest to understand the oxidation kinetics of zirconium alloys. In comparison, nanoindentation has not, as yet, been used to quantify residual stress, however, if a proven mapping technique can be identified to determine residual stress, it will add another higher resolution, small scale, non-destructive methodology to the portfolio, and perhaps eliminate the high costs of neutron diffraction experiments.

The second literature review in chapter 3 covers focused ion beam (FIB) milling and digital image correlation (DIC) techniques to measure residual strain from surface patterns on the top of stress relieved pillars. This is a very recent, small scale, virtually non-destructive technique, and again there is no literature available on this methodology being used on zirconium alloys. Hence, the experimental research contained later in this thesis will possibly be the first on this material. Chapter 3 also contains the fundamental basics as to how the FIB and DIC techniques work.

Chapter 4 provides an overview of different zirconium alloys and their alloying elements, alongside a description of the phase changes in both metal and oxide. This chapter focuses on the oxidation kinetics such as transition stages and the eventual
'breakaway' oxidation. The structure of the oxide is defined, as is the topography of the metal/oxide interface. Also contained is a review on the different oxidation rate controlling factors cited in the literature.

Chapter 5 lists the materials used in this project, with the metallography procedures used to prepare the samples for testing. A study of the microstructure for each material is presented. A variety of experimental methods and associated software analysis packages have been facilitated during this research, and a précis of each are given in chapter 5. Besides those already mentioned (indentation and FIB/DIC), methodologies include:

- Field Emission Gun/Scanning Electron Microscopy (FEGSEM).
- Optical microscopy.
- Electron back scattering diffraction (EBSD).
- Energy-dispersive X-ray spectroscopy (EDX).
- Atomic force microscopy (AFM).
- Mechanical load relaxation testing.

Chapter 6 is an experimental chapter describing the way that nanoindentation was used to try to map hardness variations across the three specimens of Zr alloys with the thickest oxides. The derivation of indentation hardness (indenter load/contact area) correlates closely with the stress equation (force/area).

A method has been devised to determine the optimum loading conditions for the indenter and the material, Zircaloy 4. Moreover, the method can probably be applied to any of the Zr alloys.

Data from the indentation mapping tests was highly scattered. So an investigation evolved as to why the results displayed such a high percentage of scatter. This study led to an interesting conclusion that perhaps could only be attributed to the unique characteristics of zirconium.

Chapter 7 forms an experimental feasibility study into whether the FIB/DIC technique, already proven successful on TiN PVD, is suitable for performing on zirconium alloys and associated oxides. Many months of experiments were trialled to determine the optimum...
beam parameters before conclusions could be drawn. As far as is known, the exercise is the first attempt to use this technique on zirconium alloys.

Chapter 8 is devoted to a study of the deformation of different Zr alloys. In particular, nanoindentation was used to investigate the time dependent deformation; commonly known as nanoindentation creep. A comparative study of indentation loading rate sensitivity was carried out, which led to an examination of the high values of the stress exponent ‘n’ resulting from the tests.

Values of stress exponent ‘n’ resulting from a conventional load relaxation test correlated well with those found using indentation. Chapter 8 concludes with an EBSD assessment of both tested specimens to determine whether twinning deformation could be the cause of the high values of the stress exponent.

Observations and discussions are presented at the end of each experimental chapter, whilst the final conclusions are written in chapter 9. Also included are suggestions for future work.

Appendices A and B include tables and further results necessary to validate statements and outcomes written in the main text.
Chapter 2: Instrumented indentation testing

Chapter 2 offers a comprehensive literature review on the history and background of instrumented indentation testing. This chapter describes how a nanoindenter works and the process of analysing load/displacement data. Also given are the equations used in data analysis to extract the mechanical properties of a material.

2.0. Contact mechanics: Hardness testing

Hardness is a measure of a material’s resistance to plastic deformation or damage, for example indentation or scratches.

The theory and application of hardness testing comes from the field of contact mechanics. It can be described as a hard material (the indenter), with known mechanical properties (hardness and elastic modulus), making contact under load, and normal to the surface, of a softer material with unknown properties (the specimen). At the end of the test process a hardness impression (indent) remains in the specimen. Traditional micro hardness testers, still used today, such as Brinell, Rockwell, Vickers and Knoop, produce indents in the macro to micro scale range, and the hardness \( H \) is calculated using dimensions directly measured from the indentation imprint. At this scale, the indents are more suited to determining bulk hardness in large samples, such as metal forgings and castings. However, as technologies have advanced and components have reduced in size, a more accurate and less destructive method of hardness testing has developed; instrumented indentation testing (IIT). IIT is also known as depth sensing indentation or nanoindentation and it has evolved over the last three decades. In contrast to micro hardness testers, a nanoindenter will continuously monitor load and displacement into the surface as a function of time, for the complete loading and unloading process. The indents are of sub-micron dimensions, giving scientists the advantage of probing mechanical properties of a single material grain.
2.1. Contact in the Hertzian regime and beyond

2.1.1. Elastic contact

Hardness testing has its origins in the late 19\textsuperscript{th} century, when in 1881 Heinrich Hertz was the first to solve the problem of contact between two spherical elastic solids of different radii. By contacting a rigid spherical indenter of known radius, with a flat specimen with infinite radius of curvature, Hertz \cite{11} discovered that the radius of contact ($a_c$) is linked to the applied load ($P$), indenter radius ($R$) and the reduced elastic modulus ($E_r$) of both materials by the following equations:

\begin{equation}
    a_c = \sqrt[3]{\frac{3PR}{4E_r}}\tag{1}
\end{equation}

\begin{equation}
    h = \sqrt[3]{\frac{9P^2}{16RE_r^2}}\tag{2}
\end{equation}

\begin{equation}
    P_0 = \sqrt[3]{\frac{6PE_r^2}{\pi^2R^2}}\tag{3}
\end{equation}

where $h$ is the displacement of the indenter into the specimen and $P_0$ is the maximum pressure at the centre of contact. $E_r$ represents the reduced modulus; this is, in fact, the combined elastic modulus of the indenter material and the specimen material, explained in section 2.1.2. The parameters according to the Hertz model are shown in figure 2.1.
Whereas Hertz’s analysis assumes no friction or adhesion between the two spherical, elastic contacting bodies under equal pressure distribution, Boussinesq [12] extended the theory to include frictional contact between an elastic half space and a hard rigid axisymmetric indenter. During the 1930’s Love [13] added his analysis of the elastic deformation of a flat ended cylinder and conical indenter tips. Further significant contributions [14-16] included studies on the behaviour of hard spherical indenters and conical indenters. These experiments on a variety of metals identified a relationship between the residual indent shape and the shape of the indenter tip, subsequently exposing a connection between the shape of the total unloading curve, the recovered displacement and the elastic modulus, all relating to the contact area of the indent.

In 1965 Sneddon [17] published his renowned paper on the indentation of an elastic half space by indenters of arbitrary profiles. In terms of extracting mechanical properties by indentation, this work is considered the beginning of the accurate determination of elastic modulus. By indenting into an elastic half space with ridged punches of different geometries, Sneddon provided the link between the load ($P$), displacement ($h$) and
radius of the contact area ($a_c$). The following equations show this relationship for each of the tip geometries [18]:

Flat punch: \[ P = \frac{4Ga_ch}{1-\nu} \] (4)

where $G$ and $\nu$ are the shear modulus and Poisson's ratio of the material sample, respectively.

Conical: \[ P = \frac{4G\cot \phi}{\pi(1-\nu)}h^2 \] (5)

where $\phi$ is the semi-vertical angle of the conical tip.

Paraboloids of revolution: \[ P = \frac{8G}{3(1-\nu)}\left(2kh^2\right)^{1/2} \] (6)

where $2kh = a_c^2$ (7)

In substituting constants $\alpha$ and $n$ for each of these geometries, a single power law relation is adequate to determine the maximum load $P$ for each geometry:

\[ P = \alpha h^n \] (8)

where $\alpha$ is a constant that relates to either $\alpha_p$ for elastic-plastic loading or $\alpha_e$ for elastic unloading [19, 20] and $n$ is a constant depending on the indenter tip shape. For example, $n = 1$ for flat punch cylinders, $n = 2$ for cones, including Berkovich, and $n = 1.5$ for spheres and paraboloids of revolution. Elastic/plastic loading and elastic unloading are explained in more detail in section 2.2.1.

These early explorations in the field of elastic contact mechanics and hardness testing built the foundations for the theory and practice of today's depth sensing indentation method.
2.1.2. Determining stiffness using different indenter geometries

Leading on from Sneddon’s findings, experiments were performed in the 1970s using Vicker’s microhardness testers to extract load/displacement data [21-24]. Bulychev et al. [21] derived a correlation between their Vicker’s test results for elastic modulus (E) and a material’s stiffness (S).

\[ S = \frac{dP}{dh} = \frac{2}{\sqrt{\pi}} E_r \sqrt{A_c} \]  \hspace{1cm} (9)

\( A_c \) is the projected area of the elastic contact, that is, the projected elastic cross section area at depth \( h_c \). The parameter \( h_c \) is shown later in Figure 6. The reduced modulus (\( E_r \)), sometimes known as combined modulus, takes into account that elastic displacements occur in both the indenter and the material sample. Reduced modulus is defined as [22]:

\[ \frac{1}{E_r} = \left(1 - \nu_m^2\right) \frac{E_m}{E_i} + \left(1 - \nu_i^2\right) \frac{E_i}{E_m} \]  \hspace{1cm} (10)

where \( E_i \) and \( \nu_i \) are the indenter’s elastic modulus and Poisson’s ratio respectively.

\( E_m \) and \( \nu_m \) are the material’s elastic modulus and Poisson’s ratio respectively.

Further work by Bulychev et al. [25] confirmed that equation 9 also applied to spherical, cylindrical, flat punch and pyramidal indenters. Later Pharr, Oliver and Brotzen [26] showed that equation 9 applies to any indenter tip shape, if it can be shown to be a ‘body of revolution of a smooth function’. The geometry of a body of revolution is shown in figure 2.2 [26].
The body follows Sneddon’s arbitrary function \[ z = f(\rho) \] where the geometry described is revolved about the z-axis to produce a solid of revolution. In order to determine an accurate depth of indentation (h), the body must have a ‘smooth function’, meaning that it does not have any discontinuities [17, 26].

The evidence of Pharr et al. [26] was supplemented by King [27], who analysed indents made using flat ended punches with cylindrical, quadrilateral and triangular cross sections. In addition, King’s findings on the elastic effect of substrates on attached thin films, extended the stiffness equation, by adding a solution referring to other tip geometries including those that do not follow the example of bodies of revolution; Vickers, Knoop and Berkovich. Accordingly, a new equation for stiffness resulted [27]:

\[
S = 2\beta \sqrt{\frac{A}{\pi} E_{r}}
\]  

(11)
where $\beta$ is a constant, necessary for accurate measurement of material properties and is dependent on the geometry of the indenter tip thus [19]:

Spherical/conical, $\beta = 1.00$

Triangular/pyramidal: Berkovich/cube corner, $\beta = 1.034$

Quadrilateral/diamond: Vickers, Knoop, $\beta = 1.012$

2.2. *Instrumented indentation testing: Nanoindentation*

Nanoindentation is a high resolution, low load scale, depth sensing indentation method used to probe the mechanical response of materials. The technique is used on materials as diverse as glasses, ceramics, metals, polymers and biological matter.

To allow continuity of the literature review, a description and diagrams of how a nanoindenter works have been included at the end of this chapter in section 2.4.

2.2.1. *The load/displacement curve; modes of deformation*

The load/displacement data extracted from a nanoindentation test has been described as a “mechanical fingerprint” [28] from which a range of parameters and mechanical properties can be extracted.

In the early 1980s, research found that Young’s modulus could be determined by constantly monitoring the upper slope of the unloading curve (stiffness), as a function of penetration depth [29, 30]. This hypothesis is depicted in figure 2.3. During loading, the material specimen undergoes both elastic and plastic deformation. However, during the initial unloading, only elastic recovery occurs.
Figure 2.3 shows a typical load/displacement curve for a material exhibiting both elastic and plastic responses. At initial loading, the material deformation will be elastic, so if the load was withdrawn at this stage, there would be no residual indent in the surface due to full elastic recovery. However, if loading continues, the deformation process will change from elastic to elastic/plastic, producing a hardness impression in the material. At a preset peak load or peak depth, the load is removed and unloading begins. The physical elastic recovery of the indented material begins immediately the indenter starts the unloading process. The shape of the unloading curve varies according to how much elasticity a material exhibits.

Figures 2.4 and 2.5 show two extremes of elastic recovery; figure 2.4 depicts a typical load/displacement curve from indentation of a soft metal, exhibiting least elastic recovery, so the unloading curve is near vertical. In this case there would be a clear indent visible in the tested material.
Chapter 2: Instrumented indentation testing

Figure 2.4: A load/displacement curve showing no elastic recovery after indentation of a soft, perfectly plastic, metal.

Figure 2.5 depicts a load/displacement curve from indentation of a hard ceramic. The ceramic exhibits full elastic recovery, with the loading curve overlaying the unloading curve, so there would be no residual indent visible in this case.

Figure 2.5: A schematic representation of a load/displacement curve showing full elastic recovery after indentation of a hard, perfectly elastic, ceramic.
2.2.2. Stiffness analysis: ‘The Oliver and Pharr method’

During the late 1980s, Oliver, Hutchings and Pethica [31] discovered that from the stiffness equation (11), the contact area \( A_c \) can be calculated as a function of displacement into the surface, that is, the cross sectional area of the indenter tip as a function of the distance from its tip. This is known as the indenter tip function.

Ensuing research by Doerner and Nix [32] provided the first complete data analysis of a nanoindentation test. Using flat cylindrical punches, they were the first to relate the load/displacement data to the contact area of an indent. Their method of obtaining the unloading stiffness from the fit of the upper 30% linear segment of the unloading curve was later disputed by Oliver and Pharr’s empirical publication [20]. Oliver and Pharr argued that, in terms of extracting hardness and modulus values from unloading data, the flat punch method was not fully accurate. Following tests on a variety of materials, with a range of known hardness and moduli, the authors proposed ‘an improved method’ for analysing load/displacement data, which accounts for curvature of the initial section of unloading. The analysis concluded that none of their data was linear and that the unloading curves were in fact concave. The same data was found to be linear when re-plotted on logarithmic axes. The authors suggest that the unloading data follows a power law relation derived from equation (8); \( P = ah^n \)

\[
P = \alpha(h_m - h_f)^n
\]

(12)

Where \( \alpha \) and \( n \) are material constants established from a least squares fitting technique, and \( h_m \) and \( h_f \) represent maximum and final elastic displacement respectively. This particular analysis has become known as the Oliver and Pharr method, and is represented in figures 2.6 and 2.7.
Chapter 2: Instrumented indentation testing

Figure 2.6: A schematic representation of a section through an indent, showing parameters used in the Oliver & Pharr method of analysis.

Figure 2.7: A schematic representation of a load/displacement graph, showing parameters used in the Oliver & Pharr method of analysis.
2.3. The determination of material properties by nanoindentation

2.3.1. Hardness

The hardness of a material correlates directly with its tensile strength and wear resistance [33]. In terms of indentation, it is defined as:

\[ H = \frac{P}{A_c} \]  \hspace{1cm} (13)

where \( P \) is maximum load and \( A_c \) is the projected contact area. The contact area is calculated as a function of contact depth [20] thus:

\[ A_c = f(h_c) \]  \hspace{1cm} (14)

where \( f \) is an area function that depends on the geometry of the indenter tip.

For the Berkovich tip used in this study, the contact area is given by:

\[ A_c = 24.56(h_c^2) \]  \hspace{1cm} (15)

where

\[ h_c = h_{\text{max}} - 0.75P/S \]  \hspace{1cm} (16)

2.3.2. Elastic Modulus (Young’s modulus)

Elastic modulus is a measure of a material’s resistance to elastic deformation. Essentially, this means the ability of a material to resist changes in length when under tension or compression [33]. The equation for Young’s modulus (\( E \)) evolves from Hooke’s law which states that stress (\( \sigma \)) is proportional to strain (\( \varepsilon \)), accordingly:
\[
E = \frac{\sigma}{\varepsilon}
\]  

(17)

It is important to note that accurate values for stiffness and elastic modulus are dependent on an indent’s true contact depth \(h_c\) and its true area of contact \(A_c\). If there are discrepancies in either, it is likely to be due to ‘pile-up’ or ‘sink-in’.

### 2.3.3 Limitations of the nanoindentation technique: Pile-up and sink-in

In some materials it is more difficult to predict the contact depth \(h_c\). So when applying equation (16) the result will significantly either under-estimate or over-estimate the contact depth [34]. If the contact depth is greater than expected, it is normally shown that the contact area is smaller than expected, so when using equations (11) and (13), values of hardness and elastic modulus will be larger than average literature values. This is due to pile-up. Pile-up occurs when the volume of material under the indenter cannot be accommodated elastically, so that material builds up around the indenter tip, as shown in figure 2.8. Bolshakov and Pharr [35] found that significant pile-up can lead to an underestimation of the contact area of an indent by as much as 60%.

Pile-up is often exacerbated by work hardening [14, 35, 36]. It occasionally occurs when indenting soft films adhered to hard substrates. For this reason the ‘1-10% rule’ is applied. This rule states that when indenting for hardness, indent depths should be between 1% and 10% of the film thickness to avoid influence from the substrate and its properties [37-40].
Figure 2.8: A schematic of Berkovich indents, with and without pile-up, also showing an SEM image of pile-up around an indent.

On the other hand, if the contact depth is less than expected and the contact area is greater than expected, it is likely that the opposite, sink-in, has occurred. Consequently hardness and modulus values will be lower than normal. Sink-in tends to happen when indenting heavily annealed metals [14, 36] and is depicted schematically in figure 2.9.

Figure 2.9: Schematic of Berkovich indents, with sink-in.
2.3.4. Indenter tips

The evaluation of accurate material properties is dependent on choosing the correct tip for the application. Table 2.1 lists the most common tip geometries used in ITT testing [41].

<table>
<thead>
<tr>
<th>Tip name</th>
<th>Berkovich</th>
<th>Vickers</th>
<th>Cube corner</th>
<th>Conical</th>
<th>Spherical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometry</td>
<td>3 sided pyramid</td>
<td>4 sided pyramid</td>
<td>3 sided pyramid with perpendicular faces</td>
<td>Cone</td>
<td>Sphere</td>
</tr>
<tr>
<td></td>
<td>&gt;100nm thk. Polymers.</td>
<td>Films &amp; foils.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Scratch testing.</td>
<td>Scratch testing.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Wear testing.</td>
<td>Wear testing.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Approx radius of curvature</td>
<td>50-150nm</td>
<td>&gt;500nm</td>
<td>30-70nm</td>
<td>0.5-100 μm</td>
<td>&gt;100μm</td>
</tr>
<tr>
<td>Centreline to face angle, α (See figs below)</td>
<td>65.3°</td>
<td>68°</td>
<td>35.2644°</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Area (projected), A(h)</td>
<td>24.56h²</td>
<td>24.504h²</td>
<td>24.5981h²</td>
<td>π a²</td>
<td>π a²</td>
</tr>
<tr>
<td>Volume-depth relation, V(h)</td>
<td>8.1873h²</td>
<td>8.1681h²</td>
<td>0.8657h²</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Aspect ratio of tip</td>
<td>1:8</td>
<td>7.1</td>
<td>1:1</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

Table 2.1: Specifications of different indentation tips [41].
A Berkovich diamond tip is the most popular tip used, and is supplied and fitted to new nanoindenters as standard. It was chosen for this study because it is ideal for hardness testing on bulk metals, cross-sectioned bulk ceramic oxides, as well as for use on the surface of thin films >200nm in thickness. This is due to the fact that a three sided pyramidal shape can easily be ground to a sharper point than a four sided pyramidal tip (cube corner). The tip radius of a Berkovich tip is typically 100-150nm, although sharper tips (50nm radius) are available. Additional advantages of a Berkovich indenter include:

- this geometry induces plasticity at very low loads, thus allowing a valid measure of hardness
- it has a relatively large included angle (65.3°) which minimises frictional influences
- the mechanical properties of diamond are known; $E_i = 1141\text{GPa}$, $v_i = 0.07$.

### 2.3.5 Tip shape calibration

Over time, most indenter tips will develop a certain amount of tip rounding due to wear. Excessive tip rounding can affect the elasto-plastic deformation zone around the indent. Consequently, inaccuracies in the calculated H and E values may occur, resulting from an inexact contact area.

![Diagram of tip shapes](image)

*Figure 2.10: A schematic diagram showing the geometries of a perfectly sharp indenter tip and a rounded tip [42].*
In figure 2.10, dimension $d_{\text{diff}}$ is the difference in depth between the tip of a perfectly sharp tip and the imperfect, rounded indenter tip. To allow for this difference, particularly if shallower indentation depths are required (e.g. when indenting thin films), an extension is necessary, to amend the Oliver & Pharr area function for a perfectly sharp Berkovich tip:

$$A_c = 24.56(h_c^2)$$

(18)

For indentation depths $\leq 2\mu m$, the area function is equated thus:

$$A_c = 24.56(h_c^2) + Ch_c$$

(19)

If the Berkovich tip is nearly new and hardly worn, the constant $C$ has a value of 150 nm or less [41]. As a tip degrades over time, and tip rounding increases, it becomes necessary to test a reference sample, every time the test instrument is used [43]. A method of calibrating the tip shape, was devised by Oliver and Pharr [20] and is based on the fact that $H$ and $E$ values should not vary with depth of indentation. The reference sample in this case is polished fused silica. Fused silica is ideal for this experimental calibration for the following reasons [44]:

- It is homogenous, so the material properties should not vary with depth.
- It is elastically isotropic
- The $H$ and $E$ values are known (9 GPa and 73 GPa respectively)
- It is non-oxidising
- It is not prone to pile-up
- The sample is not likely to degrade over time.

2.3.6. Load Frame Compliance

To determine overall accuracy and repeatability when extracting $H$ and $E$ values, particularly at high loads, it is important to take into account the load frame stiffness. This is because the nanoindenter’s displacement sensor detects both the stiffness of the load frame and the stiffness of the material being measured. Consequently, qualitative
evaluation of the indentation process depends on the meticulous calibration of load frame compliance. To find the load frame stiffness, the material sample and the load frame are modelled as two springs in series, under load $P$. Figure 2.11 illustrates this model schematically [18].

\[ C_{TOTAL} = C_S + C_{LF} \]  

(M) The Mass of the indenter  
$C_{LF}$ A constant representing stiffness of the load frame (\(\sim1.13\text{m/MN}\))  
$C_M$ A constant representing stiffness of the material sample  
$C_{DS}$ A constant representing the capacitive displacement sensor  
$C_S$ A constant representing the stiffness of the support springs (\(\sim60\text{m/MN}\))(typically 50-100N/m)  

*Figure 2.11: Dynamic Contact Model [45].*
The total indenter compliance $C_{TOTAL}$ is related to the total stiffness by the following equation:

$$C_{TOTAL} = 1/S_{TOTAL}$$ \hfill (21)

The material sample compliance is related to the contact stiffness, $S$, by [46]:

$$C_M = 1/S.$$ \hfill (22)

To find the load frame stiffness ($C_{LF}$), a series of indents are made into a reference sample such as fused silica. Assuming hardness does not change with depth, then $C_{LF}$ can be extracted from a plot of $C_{TOTAL}$ as a function of $1/\sqrt{P_{MAX}}$.

### 2.4. How a nanoindenter works

Figure 2.12 shows a schematic of a standard nanoindenter system and its components. Figure 2.13 is a photograph of the MTS nanoindenter used in this research.
Figure 2.12: Schematic diagram of a nanoindenter system.

Figure 2.13: The MTS nanoindenter XP used in this experimental research.
The indenter tip approaches the surface of a material specimen, and the sensors calculate the stiffness of the spring assembly, from the load/displacement data. As the tip makes contact with the surface of the material sample, this stiffness can increase up to four-fold. At this point of contact the load is zero, and this zero point acts as a reference point for the start of the load/displacement curve. It is also the point from which the test time is measured, as shown in figures 2.14 and 2.15. Each segment of a typical load/displacement curve as shown in figure 2.14 can be cross referenced to the steps listed on the left in the flow diagram figure 2.15.

![Diagram](image)

*Figure 2.14: A typical load/displacement curve, showing test segments 1-5, as explained in flow diagram figure 2.15.*
Figure 2.15: Chronology of a typical nanoindentation test sequence.

0
(see figure 2.14)
Indenter approaches surface until contact is sensed (i.e. increase in stiffness)
Approach rate and detection limit are user specified.

1
Increasing load is applied as the indenter tip is pressed into contact with the sample material. This produces the loading curve.
Loading rate and loading limit are user specified.

2
Indenter tip continues ‘pressing’ until either preset maximum load or maximum displacement is reached.
The mechanism can be load controlled or displacement controlled. This is user specified.

3
The maximum load is held constant for a hold time period (s) if required, prior to unloading. This allows for any time dependent plastic effects in the material to subside.
The hold time period is user specified.

4
The indenter tip is withdrawn from the material sample. This produces the unloading curve. After 80-90% of unloading, another hold period can be set to allow for thermal expansion and contraction of the material.
The rate of unloading is similar to the prior loading rate set by the user.

5
The indenter tip is withdrawn completely, and a residual hardness impression (indent) is left in the material.
Following complete unloading, both graphical and tabular results are produced for user analysis.
During the loading part of the test sequence, data is gathered on both elastic and plastic deformation. The unloading part recovers only the elastic portion of the depth penetration. Taking the stiffness equation (9) and rearranging in terms of \( E_r \), gives:

\[
E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}}
\]  

(23)

The measured contact stiffness in this equation, as with that in equation (16), is:

\[
h_c = h_r - 0.75P/S
\]  

(24)

which represents the connection between load and displacement, at the point where the indenter is first retracted from the sample. At this point, the material response is purely elastic. We know from Oliver & Pharr’s power law relation, equation;

\[
P = \alpha(h_m - h_f)^n
\]  

(12)

that the result of the bracketed components gives the elastic displacement. This has already been illustrated in figures 2.6 and 2.7.

2.5. Chapter conclusions

Nanoindentation has proved to be a unique and important tool for probing the mechanical properties of materials, particularly over small volumes of materials at very low scales. This technology takes precedence over any other in accurately determining properties of thin films and coatings, due to its ability to penetrate materials at such shallow depths.
Chapter 3: Residual stress

Chapter 3 focuses on residual stresses, their implications and the means of quantifying those stresses at different spatial resolutions. Also covered are the negative and positive influences of residual stresses. The chapter ends with literature reviews on two small scale techniques used to determine residual stress: nanoindentation, and a method using focused ion beam (FIB) milling and digital image correlation (DIC). Both methods have been used in this project, and are covered in experimental chapters 6 and 7.

3.0. Introduction

Any stress, applied or residual, can seriously affect the structural integrity and the mechanical performance of a material, component or an assembly. Existing techniques to measure residual stress vary according to the scale of the stress. This chapter introduces techniques in the nanometre to micrometre range, a relatively new field in the determination of residual stress.

3.1 Definition and origins

Residual stresses are internal stresses that remain within a material after any external load on that material has been removed. These internal stresses are caused by local mismatches normally generated by one or more of the following physical origins [47]:

- Plastic flow e.g. following mechanical processing
- Thermal expansion e.g. following heat treatment
- Volume change e.g. as a result of oxidation

These ‘locked in’ stresses originate when a material is physically constrained in such a way that it cannot expand or contract. There are different types of residual stresses dependent on their spatial resolution.

3.2 Types of residual stress

3.2.1 Type I stresses

Type I stresses are also known as macrostresses. They may vary uninterrupted over several material grains, extending to length scales in the order of millimetres, or even
centimetres [47]. Shot peening, welding and plastic deformation by bending are examples of mechanical induction. Furthermore, Type I residual stresses can develop from extreme thermal influences during welding or heat treatment of materials.

### 3.2.2 Type II stresses

Type II stresses, also known as microstresses, are intergranular, so will vary only over the grain scale [47]. Mismatches often occur in polycrystalline materials due to thermal or mechanical processing, thereby causing different crystallographic orientations (anisotropy) of the grains. Alternatively, thermal or elastic misfits between different material phases can result.

### 3.2.3 Type III stresses

Type III stresses exist within a material grain. Like type II stresses, they are in the microstress range [47]. However the scale of type III stresses is much smaller, in fact, in the atomic range. They are commonly caused by dislocations, point defects or the intergranular embrittlement caused by the effect of impurities on grain boundary cohesions [47-49].

### 3.3 Measurement of residual stress

Residual stresses cannot be measured directly, or at a specific point. The mismatch stresses can have different origins, as well as different spatial resolutions. Residual stresses are self-equilibrating, so there are no known vectors or forces on which to base stress calculations. Consequently, they can be very difficult to quantify. This is also because they are part of a three dimensional framework. In effect, it is strain that is measured. Stress is evaluated from a related measure of strain displacement, by: difference in strain/original strain ($\Delta \varepsilon / \varepsilon$). There is more about converting strain to stress later in section 3.5.2.
3.3.1 Methods used to determine residual stress

There are two classes of method used to determine residual stress: destructive and non-destructive. Within these two methods, an engineer or material scientist has a choice of many techniques. The choice will depend on several factors, for example:

- The size of the material specimen
- Whether the specimen can be damaged; if it is required for future use
- Whether there exists a stress free reference specimen, for comparison
- Whether the specimen has any pre-existing stresses

3.3.1.1 Destructive Techniques

Destructive methods rely on the removal of a portion of material to relieve stress, so that strain displacements can be measured. Following material removal, it is possible to examine the deformation response in the stress-relieved portion. Strain is normally determined from either a change in dimensions between two or more points on the surface, or from the changes in profile of a cut surface. Comparisons can then be made between strain measurements of the strain-relieved material and the original stressed material.

The removal of material essentially damages the specimen. This damage can be extensive or relatively minor depending on the technique. The means of removing material include slicing, sectioning, milling, hole drilling and chemical etching. Examples of destructive and semi-destructive techniques include:

- Hole drilling
- Contour method
- Slitting method
- Curvature method
- Crack compliance method
- Indentation
- Focused ion beam (FIB) milling
Indentation has been included in this list because it is relevant to the research experiments described later in this thesis. However, indentation cannot be described technically as removal of material, it is more deformation of the material. Nevertheless, nanoindentation has recently been used alongside FIB milling to determine surface residual stress, based on analysis of penetration depths of the indent impressions [50].

3.3.1.2 Non-destructive techniques

Non-destructive techniques have the advantage of determining surface stresses, as well as sub-surface stress distributions, without damaging the specimen. The X-ray and spectroscopy techniques are particularly useful for measuring stress in the micro range. The methods listed below use X-ray, ultrasonic, laser or magnetic wave procedures to probe for residual stress:

- X-ray diffraction
- Neutron diffraction
- Ultrasonics
- Magnetic techniques
- Raman spectroscopy

Figure 3.1 shows the spatial resolutions and typical penetration depths for some of the destructive and non-destructive methods listed.
3.4 The implications of residual stress

3.4.1 Negative and positive influences of residual stress in engineering materials and components.

It seems impossible to prevent residual stresses developing in materials during manufacturing processes such as machining, forming, joining, surface treatments and heat treatments. Locked in residual stress values are always added to externally applied stress values, and both can affect a material similarly in terms of structural integrity. For example, in adding residual stress values to external stress values, premature yield of a material can occur, often influencing the in service performance and/or reducing the life of a component or structure. Another life limiting example is in the case of welds, when thermal gradient mismatches of residual stress are created around the weld joints following cooling and solidification, eventually causing strains resulting in warping or cracking of the welded materials. Tensile residual stresses are known to drive accelerated
crack growth within a material, whereas compressive residual stresses are often introduced to restrain crack propagation.

The intentional introduction of compressive residual stress to restrict crack growth is just one of the many ways that the ‘intelligent use of residual stress’ [47] can result in positive benefits to the in service use, and life of materials. Residual stresses are often generated purposefully within a material to strengthen it. For example in brittle materials such as toughened glass, where rapid cooling, following high temperature manufacture, creates compressive surface residual stress to counterbalance internal tensile stress. This compressive stress strengthens the glass surface against damage. Pre-stressed concrete is a brittle material where compressive residual stress is used to improve its low tensile strength. The insertion of steel rods, held in tension whilst the concrete is setting around them, pre-stresses the concrete in compression, balancing the rods’ tensile stress, therefore improving the structural integrity of blocks or beams often used in construction of roads and bridges.

3.4.2 Residual stress in thin films and oxides

Having touched on how residual stresses can affect the mechanical reliability of bulk materials, it is important to consider their influence on thin films attached to bulk material; as in the case of this research project, oxide layers on metal substrates. Here residual stresses are caused by an expansion mismatch that occurs when the volume of oxide exceeds the volume of the constraining metal substrate. This mismatch and dilation of the crystal lattice creates a residual stress gradient across the oxide scale which can slow down the oxidation process. This retardation is often complemented by the fact that the high residual stresses found in the oxide near the metal interface are known to stabilise transition phases, inhibiting oxide growth. However, despite these beneficial aspects of the residual stresses, eventually the high stresses will be relieved by cracking and spallation of the oxide layers, shortening the life of components such as zirconium fuel tubes in pressurised water reactors (PWR) [7, 51] . The oxidation of zirconium alloys is covered in detail in chapter 4 of this thesis.
3.5. *Quantifying residual stress*

3.5.1. Why it is necessary to measure residual stress?

Engineers and designers often need to evaluate the load bearing capacity of a material, a component or an assembly, to regularly review structural integrity. The magnitude of ‘locked in’ residual stresses will need to be added to any known external or internal stress values, in order to remain within safe yield limits.

3.5.2. Converting strain to stress

To re-iterate, using the techniques mentioned, it is not stress that is measured, but strain via displacements. However that strain needs to be converted to stress. According to Hooke’s Law, stress ($\sigma$) is directly proportional to strain ($\varepsilon$). The constant of proportionality in this case is Young’s elastic modulus ($E$), giving equation:

$$\sigma = E\varepsilon$$  \hspace{1cm} (25)

where stress is normal stress and strain is normal strain.

Firstly, to determine the normal strains, the equations are as follows:

$$\varepsilon_1 = \frac{\sigma_1}{E} - \frac{v}{E}(\sigma_2 + \sigma_3)$$  \hspace{1cm} (26)

$$\varepsilon_2 = \frac{\sigma_2}{E} - \frac{v}{E}(\sigma_1 + \sigma_3)$$  \hspace{1cm} (27)

$$\varepsilon_3 = \frac{\sigma_3}{E} - \frac{v}{E}(\sigma_1 + \sigma_2)$$  \hspace{1cm} (28)

where $v$ is Poisson’s ratio and $\varepsilon_1$, $\varepsilon_2$, $\varepsilon_3$, and $\sigma_1$, $\sigma_2$, $\sigma_3$ are the principal strains and principal stresses respectively. The principal strains develop in the same directions as the principal stresses. The principal stresses being the maximum stress (i.e. *major* principal stress, $\sigma_1$) or the minimum stress (i.e. minor principal stress, $\sigma_2$), and are most useful in terms of gauging structural integrity. By combining and rearranging equations 25, 26 and 27, the principal 3D stresses can be calculated thus:
\[
\sigma_1 = \frac{E}{(1 + \nu)(1 - 2\nu)} \left[ (1 - \nu)\varepsilon_1 + \nu \varepsilon_2 + \nu \varepsilon_3 \right]
\] (29)

\[
\sigma_2 = \frac{E}{(1 + \nu)(1 - 2\nu)} \left[ \nu \varepsilon_1 + (1 - \nu)\varepsilon_2 + \nu \varepsilon_3 \right]
\] (30)

\[
\sigma_3 = \frac{E}{(1 + \nu)(1 - 2\nu)} \left[ \nu \varepsilon_1 + \nu \varepsilon_2 + (1 - \nu)\varepsilon_3 \right]
\] (28)

In this project, we are dealing with biaxial plane stress in the zirconium alloys and their oxides, so in any strain or stress calculated, \(\sigma_3\) will always be equal to zero.

This concludes the background section on residual stress. Here follows literature reviews on residual stress determination by nanoindentation and by FIB milling. Experimental chapters 6 and 7 describe how these two methodologies have been used in this research project.

### 3.6 Determining residual stress using nanoindentation; literature review

To briefly summarise the basics of nanoindentation, already described in chapter 2, the technique involves pressing a hard diamond tip into a softer material, and from the resultant area of the residual impression, material properties such as hardness (H), stiffness (S) and elastic modulus (E) can be calculated. One advantage of nanoindentation is that very small volumes of material can be assessed using extremely low loads and very shallow displacements (minimum 0.1 nm).

Consequently there is very little damage to the tested material. Another advantage is that there is no need to remove a film or oxide from its substrate, prior to testing. This makes it possible to map an array of indents over both film and substrate. This project uses this methodology to investigate the high residual stresses that occur in the oxide scales of polycrystalline zirconium alloys. The metal substrate immediately underneath the oxide, at its interface, is also examined.
As previously mentioned, some residual stresses are beneficial in terms of stabilising a material or component. However in the case of oxide growth due to thermal expansion, an understanding of the origins and generation of residual stresses during the oxidation of polycrystalline materials is essential, to optimise the structural integrity of corrosive materials used in engineering applications.

Over a number of years, researchers have adopted the aforementioned techniques to investigate the high compressive residual stresses that develop in growing oxides [9, 52, 53]. Whereas these methods have proved popular and successful in determining and quantifying residual stress and strains, the use of indentation is not widely used. Researchers have, however, developed methodologies to determine the existence and the sign of such stresses using indentation.

Experimental studies using microindentation tests were carried out as early as 1932 [54] when the influence of strain on Vickers hardness was assessed. Tensile and compressive uniaxial bending stresses were applied to various metals (steel, brass, copper, aluminium etc.) [54]. Hardness tests were performed on the strained specimens, and changes in hardness values were reported with 5-10% reduction in specimens under tensile stress, whilst specimens under compressive stress showed up to 3% increase in hardness values. Simes et al. [55] found similar results using Vickers tests on mild steel plates under tensile biaxial stress.

Experiments using Rockwell hardness tests on high carbon steel bar under applied four point bending stresses [56] detected comparable results to [54] and [55]. Others, using nanoindentation, have also observed relatively insignificant changes in hardness, by testing aluminium and tungsten thin films under both tension and compression [32].

These early findings linking applied stress to hardness were later rationalised by Tsui et al. [57] when using nanoindentation, to test uniaxially stressed specimens of aluminium alloys. Their results replicated the others in that hardness values decreased more with tensile stress than they increased with compressive stress. However, by using optical examination at high magnification, the actual contact area of the indent was measured and it was discovered that it was not in fact the applied stress changing the hardness
values. The optical micrographs revealed that the applied stress influenced the pile up of material around the indent, which in turn, reduced the contact area, thereafter affecting the hardness value. In reality, the Oliver and Pharr method of measurement had overestimated the hardness value by as much as 15%. (Pile up is explained in chapter 2, section 2.3.3).

In an attempt to understand the pile up of material, using nanoindentation testing on metal samples under applied stress, Bolshakov et al. [58] used finite element modelling to simulate the tests and the pile up around an indent. This investigation confirmed that, in aluminium alloys, pile up is accentuated in materials under applied compressive stress, and decreases in material under tensile stress. These results contradict those in the earlier research [54, 56]. Bolshakov et al. emphasise that any inaccuracies of hardness values due to pile up, in their study, have only been confirmed on aluminium alloy 8009, and so cannot be generalised; with regard to pile up, other materials may behave differently.

Methods for estimating residual stress by indentation have been suggested over the past six decades. As early as 1950, [59] researchers used a spherical indenter to indent a surface with residual stresses, whilst monitoring the electrical resistance of the contact point between the material surface and the indenter. Under increasing indenter load, an unexpected fall in resistance occurred when the zone under the indent reached plasticity. Residual stress was then calculated by a correlation between the load at this point and the estimated surface stresses.

An alternative method uses indentation fracture mechanics. By performing indentation at a load high enough to induce radial cracks around an indent, researchers have monitored the propagation of these cracks, to see how they are influenced by residual stress within brittle materials [60-62].

Nanoindentation by spherical tips has been carried out, with a view that the tip geometry is more sensitive to residual stress than sharp indenters. Taljat and Pharr [63] used finite element modelling of the indentation process on a variety of elastic/ideal plastic materials under applied biaxial compressive and tensile residual stress. Their results revealed
significant influence of stress on the load/displacement (P/h) data. This influence was particularly evident at a specific point in the material's deformation process; the onset of yielding. The material began to yield at the following points in the elastic-plastic transition regime:

1. At low indent displacements the material yields at the point of full elastic deformation.
2. At high indent displacements the material yields at the point of full plastic deformation.

This suggests that during the elastic/plastic transition, the tensile and compressive residual stresses already existing in the material affect the deviatoric stress beneath the indenter tip. This in turn directly influences the way that the material yields.

Swadener et al. [64] built on the above observations and developed two new methods for quantifying residual stress using spherical indenters for load and depth sensing indentation. The first method involved tensile and compressive biaxial stresses applied to highly polished discs of various aluminium alloys of known yield strength. Using indentation and recording the depth at which yielding occurs, by Hertzian contact mechanics, it was possible to observe how the indentation contact pressure responded to the applied stresses.

The second method entails analysing the dependence of the mean indentation pressure (P_M) on the contact radius of the indent. By comparing the load/displacement (P/h) data from samples with stress to those without, Swadener et al. demonstrated that the P/h graphs were offset from each other by a distance relative to the level of applied stress in the material. Figure 3.2 shows these results were promising, suggesting proportional measurements of residual stress within 10-20%. However, the application of this method may not be suitable for thin films or layered materials, as influences from the substrate may occur to adversely alter the measurements. [64, 65]
Figure 3.2: Mean pressure ($p_m$) as a function of the normalised contact radius for spherical indentation of aluminium 2024-T3. Measurements were made in the elastic-plastic transition. The influence of biaxial residual stress shows as vertical offsets of the curves. [64, 65]

Prior to these studies, earlier researchers had also investigated residual stress using nanoindentation data from load/displacement curves. The first of these was probably LaFontaine et al. [66], who in 1991 used P/h data to examine the role of residual stress on values of hardness and elastic modulus. They experimented using both Vickers and Berkovich indenters, on thin aluminium films (0.3, 0.53 and 1.17 μm) pre-stressed by heat treatment. Stress relaxation was then measured, at room temperature, by X-ray diffraction, resulting in a value of 380MPa for the 0.3 μm thick film. These X-ray results show that the biaxial tension relaxed by approximately 50% in a period of about 100 hours, suggesting that the tensile residual stress relaxes with time. Furthermore, following nanoindentation testing (Berkovich), results showed that hardness values increased by 200% in the same 0.3 μm film.

When extracted hardness values were compared between the three film thicknesses, the difference in hardness between a stress free sample (not heat treated) and the sample
100 hours after heat treatment, the main difference was in the two thinner films. This is shown in figures 3.3 and 3.4, demonstrating a connection between the nanoindentation hardness and the X-ray measured residual stress.

![Figure 3.3: Stress relaxation results for a 0.3 \( \mu \)m thick aluminium film [66].](image)

Continuing their experiments on the 0.53 \( \mu \)m film, LaFontaine et al. found that hardness values from Vickers micro testing were higher than those resulting from nanoindentation.

![Figure 3.4: Stress relaxation results for a 0.53 \( \mu \)m thick aluminium film [66].](image)
The authors suggest that the larger, flatter Vickers tip has a less hemispherical plastic zone under the indent, therefore is less affected by the underlying substrate. Comparisons between stressed and stress free materials are shown in figure 3.5.

![Graph showing hardness vs indentation depth for a Vickers indented 0.53 µm thick aluminium film](image)

*Figure 3.5: Hardness vs indentation depth for a Vickers indented 0.53 µm thick aluminium film [66].*

Based on these results, Tabor’s (17) original equation to relate indentation hardness ($H$) to applied uniaxial yield stress ($Y_{APP}$) was used:

$$H = cY_{APP} \quad (29)$$

where $c$ is a proportionality constant dependent on the indenter geometry.

To compare the yield stress of stress free films ($Y_{FREE}$) against those with residual stress ($Y_{APP}$) and to extract the residual stress ($\sigma_R$), the following equation is given:

$$Y_{APP} = Y_{FREE} + b\sigma_R \quad (33)$$

where $b$ is another proportionality constant.
Finally, the relationship between indentation hardness and residual stress is given as:

\[ \sigma_R = \Delta H / C \]  

(34)

where \( \Delta H \) is the measured change in indentation hardness of the stressed material.

\[ C = cb \]  

(36)

where \( C \) is a constraint factor related to the mean indentation pressure \( (P_M) \) underneath an indent, and can be distinguished by [16, 67]:

\[ H = P_M = C\sigma_R \]  

(37)

The mean indentation pressure is defined by the indenter load \( (P) \):

\[ P / a_c \]  

(38)

where \( a_c \) is the indenter contact area and is directly proportional to the yield stress when a material is under compression [19].

Each of the researchers quoted in this review and others mentioned in experimental chapter 6 [68-71], have added significant models in the quest to quantify residual stress by indentation, however, to date, there have been no publications to demonstrate success in actually measuring residual stress directly using nanoindentation.

*Prior to the next literature review, for continuity and clarity, a section has been inserted next on the background and workings of the FIB and DIC techniques.*
3.7. Residual stress measurement using the focused ion beam (FIB) and digital image correlation (DIC) techniques

Material scientists have developed a process to measure residual stress using FIB milling in combination with SEM imaging and imaging analysis software. However, this is a fairly new technique that continues to be developed and extended to incorporate new materials.

Until recently, FIB milling has been used mainly for preparation of thin foil specimens for observation using transmission electron microscopy (TEM) and atom probe [72, 73]. Recent FIB applications include 3D analysis of the tomographic microstructure of materials [74] and the effects of FIB milling on the mechanical behaviour of milled micropillars [75, 76]. The growing interest in micro-machining ‘pillars’, has led to the development of a novel technique to measure residual stress in a single material, before and after strain relief. This removes the need for a separate stress free sample.

3.7.1. FIB Instruments; beam columns

FIB instruments and systems have been manufactured for use in the scientific field for the past three decades. The first publication was in 1979 by Seinger et al. who designed the first ‘focused scanning probe’ [77, 78]. Early use focused on the preparation and imaging of microelectronic components within the semiconductor manufacturing industry. Originally FIB systems were designed with a single beam of ions (SBFIB). The most commonly used ion source is gallium (Ga), and this is the source used in the experiments for this research project. The ion beam is essentially used for two processes:

1. Milling material at nano and micro scales.
2. Scanning for imaging.

However, FIB images are not as well defined as those produced on a scanning electron microscope (SEM). So, dual beam systems (DBFIB) were introduced, which comprised both an ion beam and an electron beam. The electron beam is used solely for imaging at high resolutions, and can be beneficial in terms of viewing a specimen at different stages of the FIB milling process. Figure 3.6 illustrates schematically the components of a DBFIB and figure 3.7 shows a photograph of the dual beam FIB system as used in this project.
Figure 3.6: A schematic diagram of the dual beam FIB system.

Figure 3.7: The dual beam FIB system as used on this project [79].

(This is an alternative image. The original image used in the examined thesis could not be used in this access version due to lack of copyright clearance)
3.7.2. The dual beam FIB system

Liquid gallium used in FIB systems is stored in a reservoir at the rear of the ion beam column. From the reservoir, the Ga liquid flows through, and to the tip, of a sharp tungsten (W) needle. Here a high extrusion force (>10^8 V/cm) pulls the liquid into a cone shape (radius 5-10nm) and an ionization process takes place to form the Ga ions. These ions are then accelerated down the FIB column, accurately positioned to aim at a preset point on the specimen surface. Typical accelerating voltages are 5-50 keV [80].

The ion beam column uses a high strength electrostatic lens to focus the larger, heavier positive particles onto the sample surface, whereas the smaller, lightweight negative particles from the electron beam are focused using a lower strength electromagnetic lens [81].

Both the ion beam and the electron beam emit charged particles that interact with the surface of a material sample, under vacuum chamber conditions. The ions are positively charged, whilst the electrons are negatively charged. The SEM is basically used for imaging, whereas the FIB is used to mill or etch material; it can also deposit material.

The electron beam does not damage the specimen surface, it only scans the specimen surface in order to produce an image. The ion beam also continually scans the specimen surface, so that an optical signal is detected, enabling viewing of the surface. However, whenever the beam is switched to FIB mode, the gallium ions continue to bombard the specimen surface, and in physical terms, the surface is skimmed, even though the beam is not programmed to mill. Even when the beam current is set to less than 100 pA, there is some loss of surface integrity, due to sputtering of ions [80]. This makes it difficult to keep any surface pattern unchanged.

3.7.3. FIB Milling

The heavy gallium ions are slow moving but easily gather momentum and become very energetic, bouncing off the surface to be milled. By accurately positioning the ion beam set at a suitable diameter, accelerating voltage and current, the energy from the ions can be transferred to the sample surface, resulting in a precise and controlled milling or sectioning. Figure 3.8 depicts this process.
3.7.4. Layer deposition by FIB

The ion beam can be used in conjunction with a gas assisted gun, which deposits metal films or layers onto a specimen surface, by chemical vapour deposition. These films usually act as a conducting, insulating or protective layer. For example, tungsten may be used to protect a surface, or often a film of platinum or gold is deposited, prior to milling, on surfaces of poor conductive materials prone to charging. Alternatively, ‘straps’ of metal are accurately positioned to allow conductivity between specific areas on a sample.

3.7.5. Limitations to FIB milling; charging/drifting

Whilst most gallium ions from the beam will remove surface material, a few will lose momentum and just stop, remaining ‘trapped’ in the material, as shown in figure 3.8. As a consequence, the specimen surface builds up positive charge which repels the positive ions still being emitted from the beam. This repulsion causes the beam to deflect and drift away from its programmed position to start milling elsewhere [81].
There are one or two processes to counteract charging. Firstly, inside the vacuum chamber there is an optional flood gun, which emits low energy electrons that can be directed onto the specimen surface as shown in figure 3.8. These negative electrons cancel out any charging effects, by neutralising the positive charge accumulation [81]. Secondly, it is good practice to adopt a trial and error approach initially, to determine the ideal parameters of accelerating voltage and beam current for each specific material, because all materials will behave differently under FIB milling conditions.

Experimentalists have found that, in some materials, a very low beam current will help dissipate charging effects [80, 82]. Here follows a brief literature review on the use of FIB milling to measure residual stress.

### 3.8. Measuring residual stress using FIB milling and DIC; literature review

The main advantage of FIB milling is its ability to remove material, in situ, at micron and sub-micron scales. Apart from its original use in the semiconductor industry, nowadays FIB mills are most commonly used to expose cross sections, particularly for samples used to examine microstructure by TEM. The removal of material by FIB can be focused on a particular area with extreme precision [81]. However, the milling time is dependent on the characteristics of the material itself, and on the quantity of material to be removed. For example, ceramics will mill more slowly than metals. To reduce milling time, and reduce the quantity of waste material, the surface is often sequentially cut away in steps as shown in figure 3.9. This is known as a staircase mill.
3.8.1. Stress relief in thin films

Kang et al. [83] claimed to be the first to introduce a FIB method to relieve stress in both amorphous films and crystalline thin films. The FIB milling system was used alongside high resolution 2D strain mapping software (VIC-2D) to measure surface strain relieved displacements both before and after milling. Slots (10µm long) were milled into the surface of diamond like carbon (DLC) which had been deposited as a 0.44 µm thick layer onto a substrate of soda lime glass.

Figure 3.10 (a) shows two ‘marker’ rectangles on the surface imaged by SEM prior to milling [83]. This is to record the surface features or patterning. Figure 3.10 (b) displays the SEM image taken after slot milling. By using the imaging software to compare the before and after surface patterns, displacements between surface features can be measured on both sides of the slot. These measurements give the strain, which can then be converted to stress. Moon et al. [84] determined values of compressive residual stress within 5% of stress values measured, on the same film, by the widely established buckle technique.
Later, Sebate et al. [85] introduced a different approach. Their work on MEMS structures involved a scaled down version of the popular hole drilling method. This macro scale method uses strain gauges to measure displacements around a hole following strain relaxation resulting from traditional hole drilling. By using FIB to mill the hole there is no need for strain gauges as strain displacements are measured by DIC. DIC analyses out of line, distinctive surface features or pre-deposited markers, on a high resolution digital image taken before the strain relief, and compares them to the same surface features after milling. By analysing two or more out of line surface features or markers around the hole, strain displacements in three orientations can be calculated.

To calculate residual stress from the strain displacements, accurate values of elastic modulus and Poisson’s ratio are essential as:

\[
\sigma = S(1 + \nu)E
\]  

Sabate et al. extracted residual stress values within ~7% of stress values on the same film using the bulge test method [85, 86].
3.8.2. The ring core method

FIB milling methods of measuring residual stress by strain relief have led to a modified revival of an early technique first tried in the early 1950s by Milbarndt [87] and Gunnert [88]. The technique involves cutting an annular trench (ring) around a point on a specimen surface, to which a strain gauge rosette is attached, as shown in figure 3.11. The ring is milled in increments, relieving the stress in the core, and the average strains are calibrated using the strain gauge grids [89]. The resolution of this technique is determined by the size of the strain gauge rosette. At this macro scale, depending on the application, the technique could be considered destructive.

![Macro scale ring core milling with strain gauges attached](image)

Figure 3.11: Macro scale ring core milling with strain gauges attached [90].

In its early days, the milling of the ring core was carried out by traditional milling tools and techniques, such as fly cutting [88], small end milling [91, 92] and hollow cylindrical cutting [93]. More recently, material has been removed by modern cutting processes, such as air abrasion, electro-discharge (EDM) and spark erosion techniques [89, 94]. However, the EDM methods have their disadvantages as the cutting is done in liquids and the strain rosette must be protected. Also, even under controlled conditions, these methods can sometimes cause localised temperature changes that may affect the accuracy of strain measurements by gauges [89].
The advent of focused ion beam systems has revived this method, making it possible to mill an annular ring at nano or micro scale, consequently reducing surface damage. The use of DIC software to match before and after surface patterns has eliminated the need for strain gauges. Figure 3.12 shows a cross sectioned ring mill schematically.

![Cross section](image)

**Figure 3.12: A schematic representation of a typical ring mill (not to scale).**

The FIB/DIC ring core method has developed very recently. In fact, over the last three years, Korsunsky et al. [95] have investigated inherent, compressive residual stress using the FIB ring core method on TiN PVD (physical vapor deposited) coating (3.8 µm thick). Using DIC analysis, a residual stress value of −6.04 GPa was measured. This value agreed with an independent measurement of −5.84 GPa, determined by micro X-ray diffraction. The same researchers went on to apply their method to a more compliant Au MS (micro spark) PVD coating (1.5 µm thick) with inherent tensile residual stress. Similarly well matched results resulted; +261.2 MPa (FIB/DIC) and +280 MPa (XRD).
Korsunsky et al. were the first to conclude that if complete strain relief \((\Delta \tilde{\varepsilon})\) of the core is attained, in plane, equi-biaxial residual stress can be calculated by [96]:

\[
\tilde{\sigma} = -\frac{E \Delta \tilde{\varepsilon}}{(1 - \nu)} \tag{40}
\]

For non equi-biaxial residual stress, the stress is written in terms of principle strain reliefs:

\[
\tilde{\sigma}_1 = -\frac{E}{(1 - \nu^2)} \left[ \Delta \tilde{\varepsilon}_1 + \nu \Delta \tilde{\varepsilon}_2 \right] \tag{41}
\]

\[
\tilde{\sigma}_2 = -\frac{E}{(1 - \nu^2)} \left[ \Delta \tilde{\varepsilon}_2 + \nu \Delta \tilde{\varepsilon}_1 \right] \tag{42}
\]

where strain indices 1 and 2 refer to the principal stress and strain directions at the sample surface.

**3.9. 2D DIC**

As mentioned, DIC analysis relies on two high resolution images of surface patterns:

1. Prior to milling with FIB - before strain relief
2. After milling with FIB - after strain relief

A natural surface pattern can include scratches, grains, second phase particles or even simply debris on the surface. If however, the surface is devoid of features, surface embellishment can be applied artificially prior to first imaging. A pattern can be added by etching or grinding of the specimen surface, or by the FIB gas assisted gun, sputtering random patches of metallic film, such as platinum [97].

A full description of DIC analysis is given in experimental chapter 7.
Chapter 4: Zirconium alloys in the nuclear fuel industry

Chapter 4 forms a review of Zr alloys and their oxidation. The chapter covers aspects such as material properties, crystal structure and phase changes in both metal and oxide. Alloying elements for the most commonly used metals in nuclear reactors are listed, along with examples of their applications. The oxidation process is explained, especially in terms of the transition stages and the eventual ‘breakaway’ oxidation. Illustrated here is the ‘peak’ and ‘trough’ topography of the metal/oxide interface and the uncracked ‘veins’ that appear in the oxide, above the ‘peaks’. The structural growth of the oxide is described, together with some of the factors considered to influence the oxidation rate, particularly the high compressive residual stresses.

4.1. Zirconium alloys; material properties

A combination of distinctive properties make zirconium (Zr) alloys very suitable materials for use in nuclear fuel cladding and other structural components in water cooled, pressurised water reactors (PWR) [3]:

- A very low neutron absorption cross section.
- A high resistance to corrosion, particularly in high temperature aqueous environments (e.g. mechanical and chemical stability in PWRs).
- Good high temperature mechanical strength (e.g. high resistance to deformation when uranium fuel thermally expands).
- Good heat transfer.
- Adequate mechanical properties (e.g. ductility and strength).

4.1.1. Crystal structure

Zirconium is a crystalline material made up of ordered and symmetrical arrays of atoms. The stable low temperature alpha (α) phase (up to ~850°C) has a hexagonal close packed (hcp) structure. At temperatures exceeding (850°C), the crystal structure transforms into the more open body centred cubic (bcc) array. This high temperature induced phase is the stable beta (β) phase. There is an interim omega (ω) phase which may form when Zr
is in alpha phase at room temperature, but only if the material is under pressure >2GPa [98]. Figure 4.1 shows the three phases.

![Figure 4.1: An experimentally determined temperature/pressure phase diagram for zirconium [98].](image)

### 4.1.2. Alloying elements

Alloying elements are added to pure zirconium primarily to improve corrosion resistance and enhance mechanical properties such as ductility, toughness and resistance to creep [99]. However, when zirconium alloys are used in the steam and water environment of a nuclear reactor, the alloying elements also help dilute harmful effects of impurities such as oxygen, nitrogen and carbon [100].

There are distinct differences between the alloying elements, in their rate of solubility over the α-Zr to β-Zr phase transformation. For instance, an oxygen atom will dissolve interstitially, so that oxygen atoms occupy spaces between existing atoms in the zirconium lattice structure as shown in figure 4.2. If the content of oxygen is monitored and regulated, it can increase the yield strength of the parent material. The increased strength
results when the substantially smaller oxygen atoms elastically deform the existing Zr lattice, thus restraining the movement of dislocations [101].

Figure 4.2: Schematic sketch of three interstitial atoms in solid solution in a simple cubic lattice [101].

The addition of tin (Sn) is stabilising to the α-Zr phase and helps in attaining solution hardening. In contrast to oxygen, tin dissolves substitutionally in the matrix. A substitutional solid solution contains solute atoms (Sn) with a radius closer in size to the solvent (Zr) atoms. The atomic radius should not differ by more than 15% [102]. As shown in figure 4.3, the solute atoms (Sn) do not occupy spaces between existing solvent (Zr) atoms, but actually replace the solvent atoms. As a result, the lattice distorts and in turn restricts dislocation motion.

Figure 4.3: Substitutional solid solutions viewed schematically [101].
Small amounts of alloying elements such as iron (Fe), nickel (Ni) and chromium (Cr) are added to the commercial zirconium alloys to increase corrosion resistance. The solubility of Fe, Ni and Cr in alpha phase zirconium (<810°C) is relatively low (<100ppm), although they are totally soluble in the beta phase (>980°C) [103]. In fact these three elements help to stabilise the beta phase at low temperatures. On the other hand, due to their low solubility in α-Zr, Fe, Ni and Cr are precipitated as second phase particles (SPPs). It is the size and distribution of these SPPs that contribute the main influencing factors on the mechanical and corrosion properties of Zircaloy 2 and Zircaloy 4 [98]. The addition of Fe, Ni and Cr to zirconium has also resulted in Zr alloys with good creep resistance under irradiation [100]. The addition of niobium (Nb), to alloys without tin, has produced high strength and creep resistant zirconium alloys with a lower tendency towards hydrogen absorption. The commercially named zirconium alloys used for nuclear reactor applications are listed in table 4.1 along with their chemical compositions. It can be seen from the table that Zircaloy 4 has no nickel and slightly higher iron content than Zircaloy 2. These variations in composition are intended to minimise hydrogen pick-up, which in high volumes, can lead to the precipitation of hydrides, resulting in gross embrittlement of the Zircalloys during reactor operation [104].
### Table 4.1: Chemical compositions for zirconium alloys and their nuclear applications [100].

<table>
<thead>
<tr>
<th>Alloy element</th>
<th>Zircaloy-2</th>
<th>Zircaloy-4</th>
<th>ZIRLO®</th>
<th>Zr-2.5 Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn (wt.%)</td>
<td>1.2–1.7</td>
<td>1.2–1.7</td>
<td>0.7–1.5</td>
<td>–</td>
</tr>
<tr>
<td>Fe (wt.%)</td>
<td>0.07–0.2</td>
<td>0.18–0.24</td>
<td>0.07–0.28</td>
<td>&lt;650 ppm</td>
</tr>
<tr>
<td>Cr (wt.%)</td>
<td>0.05–0.15</td>
<td>0.07–0.13</td>
<td>0.07–0.28</td>
<td>&lt;100 ppm</td>
</tr>
<tr>
<td>Ni (wt.%)</td>
<td>0.03–0.08</td>
<td>&lt;40 ppm</td>
<td>0.07–0.28</td>
<td>&lt;35 ppm</td>
</tr>
<tr>
<td>O (ppm)</td>
<td>900–1300</td>
<td>900–1400</td>
<td>–</td>
<td>900–1300</td>
</tr>
<tr>
<td>N (ppm)</td>
<td>&lt;80</td>
<td>&lt;65</td>
<td>–</td>
<td>&lt;65</td>
</tr>
<tr>
<td>Nb (wt.%)</td>
<td>–</td>
<td>–</td>
<td>0.5–2.0</td>
<td>2.4–2.8</td>
</tr>
<tr>
<td>Cu (wt.%)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mo (wt.%)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>H (ppm)</td>
<td>&lt;25</td>
<td>&lt;25</td>
<td>–</td>
<td>&lt;5</td>
</tr>
<tr>
<td>C (ppm)</td>
<td>&lt;270</td>
<td>150–400</td>
<td>&lt;220</td>
<td>&lt;125</td>
</tr>
<tr>
<td>Cl (ppm)</td>
<td>&lt;20</td>
<td>–</td>
<td>–</td>
<td>&lt;0.5</td>
</tr>
<tr>
<td>P (ppm)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>&lt;10</td>
</tr>
<tr>
<td></td>
<td>Fuel tube and plug material for BWR, PHWR</td>
<td>Fuel tube and plug material for PWR and PHWR</td>
<td>Fuel tubes. Structural and flow mixing grids. Instrumentation tubes. Guide thimble. PWR</td>
<td>Pressure tube material for PHWR</td>
</tr>
</tbody>
</table>

#### 4.2. Oxidation

Zirconium alloys are known for their high resistance to corrosion; however, they are prone to an almost instant oxidation due their chemical affinity with oxygen. Even at room
temperature a thin protective film layer forms on the alloy surface. This film is sometimes called ‘the air formed oxide film’ and is typically 2-5 nm thick [105, 106]. In high temperature aqueous environments, over time, Zr alloys form a thicker oxide layer that adheres firmly to the bulk metal. The chemical reaction is [3]:

\[ \text{Zr} + 2\text{H}_2\text{O} \rightarrow \text{ZrO}_2 + 2 \text{H}_2 \]

The oxidation kinetics from this point onwards are complex.

4.2.1. Oxidation kinetics

During the early stages of the corrosion process oxide growth is uniform. However, under pressures greater than 5 MPa, and when Zr metal is situated in temperatures above 450°C a localised oxide growth occurs [98] on the surface of the metal. As this oxide thickens and gains weight, three distinct stages take place:

1. Pre-transition stage
2. Post transition stage
3. Breakaway

4.2.2. Pre-transition oxide

In the early stages, at temperatures below 500°C, as the localised compact, protective layer develops, it adheres firmly to the metal substrate. This layer remains cohesive, even after cooling to room temperature. The material grains within this protective oxide layer are small and equiaxed (5-10nm) [107] and have differing orientations compared to the single orientation of the grains of the zirconium metal on which they form [108].

The crystallographic phase structure at this pre-transition stage is tetragonal. At this stage, the rate of oxidation is limited by the diffusion of oxygen ions inwardly through any existing oxide layers, predominately through grain boundaries [109]. The diffusion process is thermally activated; the higher the temperature, the higher the diffusion rate [110].

At temperatures greater than 200°C the thin protective oxide film grows steadily inward. The newly formed oxide nearest the metal interface remains dense and holds a high fraction of tetragonal phase (up to 60%) [111]. This tetragonal phase stays stable until the oxide layer reaches a certain thickness. It is commonly reported that this stabilisation is
due to the high compressive stresses (~88 MPa to ~2 Gpa [111]) that evolve from the volumetric increase during oxidation. The Pilling Bedworth ratio for zirconium is 1.56 [112]. However, others suggest that the stabilising mechanism might be the small grain size of the oxide [113, 114] or vacancies (point defects) in the lattice structure [115, 116]. Whatever the stabilising mechanism, many researchers implicate this dense oxide as the main factor controlling the rate of oxidation.

Pre-transition ZrO$_2$ growth behaviour is parabolic and decreases over time until a thickness of approximately 2µm is reached. At this point a transition occurs and the tetragonal phase changes to monoclinic. Martensitic phase changes lead to a monoclinic oxide forming on top of the tetragonal oxide, and visually, the colour changes from black to grey, as captured in the figure 4.4 image [108].

![Figure 4.4: ZIRLO SRA tube, displaying pre and post transition oxides.](image)

### 4.2.3. Post-transition oxide

Following the first transition, the oxide growth behaviour becomes quasi-linear, progressing cyclically through several repetitive transitions [117]. Corrosion in zirconium alloys is characterized by this repetitive process of growth then transition, and is represented schematically in figure 4.5.
These repetitive transitions seem to occur at every 2µm layer thickness. Due to a volume expansion of 5-7%, along with strain relief, at each transition layer, horizontal cracks and voids appear, parallel with the oxide/metal interface (transition cracks).

Figure 4.6 shows a typical cross section of oxide. It can also be seen that non-cracked ‘veins’ appear perpendicular to the periodic undulations of the interface. The presence of these ‘veins’ that seem to manifest above convex undulations in the metal/oxide interface has been reported [118, 119]. However, little is known as to how the topography originates and evolves. Hutchinson and Lehtinen [120] offer the theory that the spacing of the non-cracked ‘veins’ is related to density and dispersion of second phase particles (SPPs). In response, Cox [121] argues that previous researchers [122, 123] found the ‘veining’ to be caused by the rejection of tin alloying elements at the interface. Despite these contradictions, it remains an interesting topic, worth exploring in the quest to understand the corrosion mechanisms of Zr alloys.
Hutchinson and Lehtinen [120] offer a rationalization for the undulating topography of the oxide/metal interface of Zircaloy 2 alloy. They propose a mechanism where the troughs are stabilized by ‘enhanced tensile stress’ in the metal, in front of the advancing oxide growth. It is suggested that oxide growth is retarded at the peak undulations by high compressive stresses in the oxide, which are also considered responsible for the formation of tetragonal oxide in the un-cracked veins. A schematic representation of Hutchinson and Lehtinen’s theory is shown in figure 4.7. The authors clearly indicate that there exists a reverse state of stress at interface peaks than at troughs.
4.2.4. Breakaway oxidation

The transition cracks along with the evolving porosity provide a path for the corrosive elements to reach the protective oxide layer at the interface. In an aqueous environment, as the oxide thickens, the rate of growth decreases. Eventually, when the oxide reaches a certain thickness, the rate of growth suddenly accelerates and rapidly increases with true linear growth behaviour. This point is termed ‘breakaway’, and results in spallation of the outer oxide and an almost total loss of protection [52, 124]. This loss of protective properties is significantly detrimental to nuclear reactor fuel tubes. Following the onset of breakaway, the oxide colour changes from grey to white [108].

Over the years there have been several strands of thinking on which mechanism might lead to breakaway in Zr alloys, but even today, despite all existing justifications, there has been no real consensus on the subject.

Figure 4.7: A schematic representation showing the three stages of the mechanism proposed by Hutchinson and Lehtinen [120].
4.3. Oxidation rate

The structure, size and density of zirconium grains play an important role in controlling the oxidation rate. In the early stages, the rate is very slow. This is because the oxygen diffusion is through sub-micron scale grain boundaries.

Despite extensive publications, with varying opinions, there remains some discord between researchers surrounding which mechanism controls the rate of oxidation. One point of view is that the oxidation rate is defined by the diffusion of oxygen through grain boundaries in the protective layer at the metal interface [111, 124, 125]. Oxide scale forms on zirconium metal by the inward diffusion of oxygen ions (O$^{2-}$) via anion vacancies. As the scale thickens, the ions migrate preferentially through the crystallite boundaries (these are described in section 4.5.2), taking the path of least resistance through cracks and voids from the oxide/air interface to the oxide/metal interface. In turn, oxygen vacancies at the metal/oxide interface diffuse outwards in the opposite direction to the O$^{2-}$ ions. In addition, electrons (Zr$^{4+}$ cations) carrying electrical charge, also diffuse outwards towards the air interface, and charge neutrality is achieved [33] according to the following chemical reaction: Zr O$_2$ → O$^{2-}$ + Zr$^{4+}$. An electrical potential builds up across the oxide and by measuring the drop in potential at the oxide/air interface and relating it to the drop at the oxide metal interface, Cox [124] concluded that it is in fact the electron diffusion process which controls the oxidation rate.

Others [126, 127] have suggested that Zircaloy 4 oxidises at different rates according to the crystallographic orientation of the grains at the surface. For example, at the interface, when the orientation of the oxide lattice matches the orientation of the zirconium metal, the diffusion rate is enhanced [128].

Grain size and grain morphology have also been implicated as rate controlling factors. Park et al. [129], using synchrotron X-ray diffraction, observed that grain size increases as the oxidation rate decreases. This observation was later verified by Yilmazbayhan et al. [107] in their study using transmission electron microscopy (TEM).

Some researchers indicate that second phase particle (SPP) distribution and volume fraction could be the dominant rate controlling factors [130, 131]. The rate limiting steps...
suggested are the oxygen diffusion rate or the electron conductivity rate [132, 133]. Rudling and Wikmark [131] found unoxidised SPPs in the oxide ~1µm from the metal interface. The optimum size of SPPs for a given volume fraction are linked to the limiting rate [132].

Despite these persuasive and evidential claims, there is a well-established contingent that believes the major rate controlling elements are the high compressive stresses at the metal/oxide interface, and their relief by cracking [4-7].

4.4. Residual stress gradients in Zr oxides

Across the whole thickness of the oxide, a gradient of compressive residual stress develops during the oxide growth process. The highest compressive stresses are found at the metal/oxide interface. Values as high as −2 GPa have been found at the metal/oxide interface of Zircaloy4 in pure water, using Raman spectroscopy [10]. Values decreased to ~200 MPa towards the air/oxide interface, where the porous layers no longer show evidence of stress. Godlewski et al. [10] found these values correlated well with the presence of tetragonal ZrO$_2$. Their compressive stress values reached their lowest at the point where tetragonal ZrO$_2$ transformed to monoclinic.

Stress gradients across ZIRLO oxide 85 µm thick have been found using Raman, as part of the Zr project [9]. At the metal/oxide interface values of −1 GPa were estimated, decreasing to ~ −600 MPa in layers near this interface. At 22.5 µm away the stress decreased rapidly to ~ −50 MPa. The metal below the interface is balanced by tensile residual stresses. Raman readings of ~50 MPa were recorded near the oxide interface, reducing to 3.2 MPa at 22.5 µm into the metal [9].

Experimental chapter 6 describes attempts to expose the stress gradient by indentation mapping.
4.5. Structural growth of zirconium oxide

4.5.1. Sub oxide

In the metal substrate immediately below the oxide interface, a layer of regularly shaped ‘blocky’ grains has been observed [107]. Figure 4.8 shows an example of blocky grains in Zircaloy 4. The width of these grains is 100-150 nm. Yilmazbayan et al. [107] found that the grain size differed between alloys: Zircaloy 4 was the largest. They also found that the width of this blocky grain region matched that of the oxygen rich region existing in the metal, directly below the interface.

The sub oxide layer varies between 80 and 100 nm thickness, and has a different oxygen content percentage than both metal and oxide [107]: Bulk oxide ≈ 60 at% oxygen, sub oxide ≈ 44-52 at% oxygen.

Similar oxygen contents have been found in pre-transition oxide; Zircaloy 4 recrystallised annealed (RXA) sheet as 1.2-1.5 TEM foils using electron energy loss spectroscopy (EELS) [134].

![Figure 4.8: A TEM image of the ‘Blocky’ grains forming sub-oxide [134].](image)
4.5.2. Early oxidation grain structure

The initial air formed ‘smear’ layer is made up of tiny equiaxed grains (~2nm diameter) of irregularly shaped crystallites [108]. These crystallites have many different orientations, and it is difficult to determine whether they are cubic or tetragonal oxide [135]. At temperatures above 200˚C some of the orientations grow preferentially as columnar grains. Their direction of growth is determined by the path of least stress resistance [108]. The growth orientations have been found to vary between different alloys [107].

At the metal interface, where this new oxide is forming, high tetragonal phase fractions have been evidenced by X-ray diffraction methods [136, 137], and linked to the high compressive residual stress, although there seems some controversy regarding whether the high compressive stresses influence the presence of this tetragonal ZrO$_2$, [4-7] amongst others.

4.5.3. Evolving grain structure

The tetragonal columnar crystals remain compact, and thus protective and beneficial to corrosion resistance [138]. They grow to lengths of around 2 µm before transition occurs [108]. The high compressive stresses that were stabilising the tetragonal phase, can no longer be sustained and horizontal cracks appear. From this first transition point, the oxide grows cyclically, so strata materialise of columnar grains interspersed with the earlier formed equiaxed grains. This is portrayed below in figure 4.9.
Chapter 4: Zirconium alloys

Figure 4.9: Oxide strata of Zircaloy 4, shown schematically and as a bright field image [134].

This layered strata is common to Zircaloy 4, ZIRLO [136] and Zircaloy 2 [139]. Yilmazbayhan et al. [107] published TEM micrographs showing evidence that the columnar grains were not associated with the cracking, only the equiaxed layer, every 2 µm, once again confirming transition at this interval. New protective oxide is continually forming at the metal interface, but as each transition occurs, and the oxide moves into the metal, the outer layers near the air/oxide interface become increasingly porous, allowing ingress of corrosive elements.
Chapter 5: Materials and experimental methods

Chapter 5 lists the materials used in the research experiments. Details of the metallurgical preparation are given and a microstructure study is included. There is comprehensive background information reported for most of the different methodologies used. However, extensive descriptions of the FIB and nanoindentation techniques have already been covered in Chapter 3.

5.1. Materials

The materials studied in this project are zirconium alloys and their associated oxides, with occasional tests on reference samples of fused silica and aluminium, for comparison or explanatory purposes. Table 5.1 gives details of the materials used and the experimental methods that were used on each.

<table>
<thead>
<tr>
<th>Material</th>
<th>Description</th>
<th>Autoclave Temp.</th>
<th>Time in autoclave</th>
<th>Experimental methods used</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zircaloy 4</td>
<td>Cold rolled plate</td>
<td>N/A</td>
<td>N/A</td>
<td>Nanoindentation, FIB milling, AFM, SEM, Optical microscopy</td>
</tr>
<tr>
<td>Zircaloy 4</td>
<td>Hot rolled plate</td>
<td>N/A</td>
<td>N/A</td>
<td>Nanoindentation, FIB milling, EBSD</td>
</tr>
<tr>
<td>Zircaloy 4</td>
<td>Tube LOCA (loss of coolant accident)</td>
<td>980°C</td>
<td>4200 s</td>
<td>Nanoindentation, FIB milling, EDX, SEM, Optical microscopy</td>
</tr>
<tr>
<td>Zircaloy 2</td>
<td>Tube Beta quenched</td>
<td>415°C</td>
<td>570 days</td>
<td>Nanoindentation, SEM</td>
</tr>
<tr>
<td>ZIRLO</td>
<td>Plate RXA</td>
<td>415°C</td>
<td>660 days</td>
<td>Nanoindentation, SEM</td>
</tr>
<tr>
<td>ZIRLO</td>
<td>Tube SRA</td>
<td>415°C</td>
<td>134 days</td>
<td>Nanoindentation, SEM</td>
</tr>
<tr>
<td>Pure zirconia</td>
<td>Rod</td>
<td>N/A</td>
<td>N/A</td>
<td>Nanoindentation</td>
</tr>
<tr>
<td>Pure aluminium oxide</td>
<td>Rod (AL203)</td>
<td>800°C, 1100°C, 1400°C (sintering temps; see section 5.4.7)</td>
<td>N/A</td>
<td>Nanoindentation</td>
</tr>
</tbody>
</table>

Table 5.1: Material specimens investigated and experimental methods used.
5.2. Sample preparation

5.2.1. Cutting and cross-sectioning of Zirconium alloy specimens

The Zr alloy coupons were all wet cut using electrical discharge machining (EDM). This eliminates any dust particles that are prone to combustion. Brass wire of 0.25 mm diameter was used for cutting, with a precision tolerance of +/- 1 µm.

The cutting process was performed carefully, at low speeds in an attempt to minimize mechanical deformation. Any residual deformation was removed by subsequent grinding and polishing steps.

5.2.2. Mounting of specimens

Specimens were hot mounted using MetPrep Conducto-Mount conductive mounting compound granules. Once the granules are fused by heat and pressure, the resin hardens to provide good edge retention and conductivity.

5.2.3. Surface grinding

To remove surface damage caused by cutting, the following grinding procedures were applied. For all specimens silicon carbide grinding papers were used and constantly lubricated with water. Gentle hand grinding was applied to specimens prior to the early microstructure study. To ensure an evenly abraded surface, the specimens were periodically rotated by 90 degrees.

Automated rotational grinding, at 160-170 rpm, was performed on all other specimens prior to experimental testing.

For both grinding methods, abrasive grinding papers of 500, 2500 and 4000 grit were used sequentially, with sample surfaces washed and dried between each paper change.

5.2.4. Surface polishing

To remove surface damage from grinding, the following polishing procedures were applied.

Gentle hand polishing was used on specimens for the early microstructure study. To ensure an evenly polished surface, the specimens were periodically rotated by 90°.
Automated rotational polishing at 250 rpm was performed on all other specimens prior to experimental testing.

The polishing sequence and method for all specimen surfaces was the same, except for those samples to be investigated by electron back scattering diffraction (EBSD). Details are given in section 5.3.2. Moisten MD NAP polishing cloths were used; one each, for grit sizes 6, 3 and 1 µm self-lubricating diamond suspensions. Scant applications of diamond suspensions were applied alternately with applications of red lubricant suspension (water and oil based), whilst the cloths rotated at 250 rpm. Sample surfaces were washed and dried between each polishing sequence.

Final polishing was performed using a mixture of 50% colloidal silica suspension (OPS) mixed with 50% distilled water, applied at regular intervals to ensure the cloth is well lubricated. This OPS procedure continued until a mirror finish was achieved.

**5.2.5. Surface etching**

On the alloys that were etched for initial microstructure study (see table 5.1), the following etchant was applied to grease and smear free sample surfaces:

- 10 ml *Nitric acid*
- 3 ml *Hydrofluoric acid*
- 12 ml *distilled water*

Cotton wool swabs soaked in etchant were applied to each sample surface using gentle sweeping motions. After 10 seconds, the surface was thoroughly cleaned and dried before being observed using an optical microscope. This process was repeated until a full grain structure was observed.

Only metal surfaces were etched for microstructure evaluation. Attempts were made to etch the oxide surfaces, but these were not successful.
5.2.6. Anodising for microstructure study

To improve contrast between grains and intermetallic compounds, the samples for microstructure characterization were anodized using the following anodic oxidation recipe:

- 120 ml ethanol
- 70 ml distilled water
- 40 ml lactic acid
- 20 ml glycerine
- 10 ml phosphoric acid (concentrated)
- 4 g citric acid

The electrolytic anodisation was performed at the maximum current and voltage of 30-40 V. The specimens were held in solution for 15 s until the surface turned a yellow bronze colour.

5.3. Sample preparation specific to experimental methods

5.3.1. Mounting of samples for nanoindentation

Hot mounted resin has proved to be more stable under indentation than cold mounted epoxy. So the specimens for indentation testing were mounted in Conducto-Mount resin as section 5.2.2.

Following surface preparation of the specimens, the resin stubs were glued on top of aluminium stubs of the same diameter. The metal stubs provide extra stability when the specimen is under load of indentation. Finally, secure clamping of the overall stub, into the nanoindenter stage, is via tightened grub screws.

5.3.2. Sample preparation for electron back scattering diffraction (EBSD)

The EBSD technique, data acquisition and Kikuchi patterns will be explained in detail in section 5.5.3 of this chapter.
Excellent sample preparation is the key to obtaining good Kikuchi patterns, so samples for EBSD experiments were given an extra sequence of polishing using 0.25 µm diamond suspension, prior to the OPS stage. This was to reduce surface damage to a minimum before etching.

Zirconium alloys are well known for their non-conformity when it comes to conventional metallography [140, 141]. Vander Voort wrote, "perhaps the most difficult refractory metal and alloys to prepare for EBSD have been zirconium and its alloys. Numerous approaches have been tried, using all sorts of procedures, with poor results" [141]. So by preparing these Zr alloy samples using the following etchant and a newly defined four-step application process, it was very satisfying to achieve EBSD indexing of around 90%. The etchant recipe used on surfaces subject to EBSD is as follows;

*distilled water*

*nitric acid*

*hydrofluoric acid*

*mixed together in this order, in a ratio of 9:9:1*

The following four-step method of application was developed and used to etch the surface of Zircaloy 4 hot rolled plate. The resultant surface finish led to good Kikuchi patterns.

Following grinding and polishing as per sections 5.2. (including the extra stage polishing as above) the sample surface was swabbed with cotton wool soaked in etchant, for three 30 s increments. The specimen was washed and dried between each etching, prior to imaging using an optical microscope to record the extent of surface damage.

Finally after a total of 90 s swabbing, a ‘puddle’ of etchant was dropped onto the sample surface to cover the area. The ‘puddle’ was left in-situ for 45 s; long enough to remove all signs of surface damage. Figure 5.1 shows the sample surfaces at different stages of etchant application.
5.3.3. Electro-polishing of samples for nanoindentation

Samples of Zircaloy 4 hot and cold rolled plates used in experimental chapter 6 were electropolished according to the following procedure. An electrolyte solution of 960 ml methanol/2-butoxyethanol mixed together with 60 ml of perchloric acid was used in the reservoir of a Struers Lectropol 5 electropolishing machine. With the sample immersed in the electrolyte liquid, scanning was performed until the best plateau (when the voltage and current reach steady state) was achieved. Initial electropolishing was carried out at 45 V for 60 s. This removed approximately 30 μm of material surface. So to achieve a final surface removal depth of just over 100 μm, the process was continued for a final 3
minutes at 45 V. The same parameters were used for samples of both hot and cold rolled plates, and good surface finishes resulted.

5.4. Microstructure studies

A Reichert-Jung MeF3 inverted metallurgical microscope, fitted with a Q-image digital camera, was used for all microstructure evaluation in this project. Objective lenses 20 x and 100 x magnification were chosen for the micrographs displayed in this thesis.

5.4.1 Zircaloy 4 cold rolled plate (material supplied by Rolls Royce Marine).

Optical microscopy was performed on Zircaloy 4 in the three principal planes: rolling, transverse and normal. Cross sections were imaged in the rolling direction (ND) and the transverse direction (TD). The normal direction (ND) was imaged on the surface.

The micrographs in figure 5.2 show Zry 4 single phase α alloy. Table 4.1 in chapter 4 section 4.1.2 shows the chemical composition for this alloy. Despite the low solubility of elements in Zr alloys, some precipitation at grain boundaries can be seen in the RD and TD cross sections.

Generally the microstructure shows uniform and equiaxed grains, although the grains in micrographs (e) and (f) appear to be slightly elongated. This is possibly due to the fact that this is the rolled surface (ND). The grains seem to be a uniform diameter of between 20 and 30 microns. Some inter-granular particles are visible; black on micrographs (b) and (d), and white on micrograph (f). These are thought to be second phase particles.
Figure 5.2: Microstructure of Zircaloy 4 cold rolled plate in RD cross section (a) and (b), TD cross section (c) and (d), and ND surface (e) and (f).

5.4.2. Zircaloy 4 hot rolled plate (material supplied by INVAP, Argentina).

Optical micrographs for Zircaloy 4 hot rolled plate in three principal processing directions are shown in figure 5.3. The micrographs were performed under polarised light. The single phase α structure of Zircaloy 4 hot rolled plate is similar to the cold rolled plate, with grains of consistent shape and size (20-30 µm diameter). However, there seems no evidence of precipitation along grain boundaries.
The smear lines visible in images (b) and (d) were unlikely to have been an artefact of surface preparation, because the samples were regularly rotated during grinding and polishing. It is not yet understood whether the lines are linked with the processing history of the material [142].

Figure 5.3: Microstructure of Zircaloy 4 hot rolled plate in RD cross section (a) and (b), TD cross section (c) and (d), and ND surface (e) and (f).

Micrographs courtesy of Dr Olivier Zanelatto [142].

5.4.3. Zircaloy 4 tube, 980°C (LOCA) (material supplied by Dr Bob Comstock, Westinghouse Electric Corp. Pittsburgh, USA).

A specimen of Zircaloy 4 tube was exposed to 980°C steam for 2400 s until an oxide layer of approximately 60 micron thickness had formed. The specimen was then quenched in water. This whole process is to simulate conditions of a reactor loss of coolant accident (LOCA).
Figure 5.4 shows grain structure in the alpha regions, below the oxide interface. A report by The Nuclear Energy Agency (NEA) [143] describes the grains in this region as columnar. However in the NEA experiment, the Zr cladding was exposed to temperatures of around 1200˚ C. It is not known why the grains shown in the LOCA sample (figure 5.4) appear more equiaxed and of varying size and shape. These alpha grains seem randomly orientated with a typical diameter range of 15-30 µm, although some are much larger.

![Figure 5.4: An SEM image of cross sectioned Zry4 LOCA tube specimen, showing alpha grain structure in metal, just below the oxide interface. For details of the crack see section 6.2.2.](image)

**5.4.3.1. Evolution of microstructure layers in LOCA Zr alloys.**

In 1965, experiments were performed at Oak Ridge National Laboratory to investigate extreme embrittlement of Zircaloy 4 cladding, when the alloy was exposed to a range of high temperatures of steam [144]. These experimental findings were followed up by Fujishiro et al. [145], who published evidence, following in-reactors tests that the
embrittlement was caused by extreme microstructural changes within the cladding cross section.

Figure 5.5 shows the typical five layered microstructure of a tube specimen found under LOCA conditions. This layered structure is formed at temperatures in excess of 800˚ C, when the alpha phase (hcp structure) changes to beta phase (bcc structure).

As oxide grows on the surface, high oxygen solubility causes oxygen to dissolve into the underlying metal substrate. So, just below the oxide interface a layer of oxygen stabilised α-Zr forms. When saturation point of the α-Zr is reached, beta stabilising alloying elements such as iron and chromium are rejected from the alpha phase and forced into the beta phase [143]. In Zircaloy 4 the diffusion coefficients of iron and chromium are high enough to allow fast diffusion within the metal, at a distance from the oxide interface [143], resulting in a distinct border between the alpha and beta regions, as shown in figure 5.5.

In figures 5.5 and 5.6, between the two alpha layers, a wide region of acicular grains can be seen forming a basketweave pattern (Widmanstatten structure). This structure evolves after quenching by the coolant, following a phase retransformation of β-Zr back to α-Zr. This region is referred to as the prior-β phase, with platelets of 50-100 µm long and 20-25 µm wide.

Due to high solubility of hydrogen in the prior-β region, hydride precipitates are often found at the lath boundaries. These hydrides can lead to embrittlement and loss of ductility of the cladding material. This in turn reduces the structural integrity of the material, with the possibility of catastrophic results to in-reactor components.
Figure 5.5: An optical microscope image of cross sectioned Zry 4 LOCA tube, showing alpha phases under oxides and central prior beta phase.

Figure 5.6: An optical microscope image of cross sectioned Zry 4 LOCA tube, showing evidence of Widmanstatten 'basketweave' structure in the prior-β phase.

The Zircaloy 4 LOCA specimen was used in this research project for investigations using nanoindentation testing and EDX spectroscopy.
5.4.4. Zircaloy 2 tube, beta-quenched, 415°C, 570 days in autoclave

(virgin material supplied by Westinghouse and autoclaved at EDF Energy, France)

Figures 5.7(a) and (b) show the basketweave grain structure typical of β-quenched metals. Bundles of alpha platelets consist of laths a few microns thick and 30-60 µm in length. There is evidence of fine second phase precipitates around plate boundaries in micrograph 5.7(b).

![Figure 5.7: Widmanstatten (basketweave) microstructure of β-quenched Zircaloy 2 tube cross-section.](image)

5.4.5. ZIRLO plate, RXA, 415°C, 660 days in autoclave (autoclaved and supplied by Westinghouse)

It proved difficult to etch this autoclaved ZIRLO, as it was prone to over etching very easily. However, the distribution of the second phase precipitates visible in figures 5.8 (a) and (b) may indicate some grain structure and size according to grain growth estimates for the autoclave temperature and holding time.

![Figure 5.8 (a) and (b): Micrographs of ZIRLO plate, 415°C, 660 days in autoclave.](image)
5.4.6. ZIRLO strain relieved annealed (SRA) tube, 415°C, 134 days in autoclave (virgin material supplied by Westinghouse and autoclaved at EDF, France)

Figure 5.9 shows a close up view of the outside surface of ZIRLO SRA tube. Patchy oxides (black; pre-transition and grey; post transition) are clearly visible.

![Figure 5.9: Patchy oxide scale on outside surface of ZIRLO SRA, 415°C 134 days.](image)

5.4.7. Pure aluminium oxide (material supplied by Queen Mary’s University)

Three samples of pure alumina were prepared using a spark plasma sintering technique. For compaction, alumina powder in graphite moulds was subjected to pressures of between 50 and 200 MPa prior to heating. A high frequency induction heat sintering (HFIHS) technique, similar to hot pressing, was used to consolidate the powder. This technique has been used to successfully achieve densities near to those measured in the literature [146].

As listed in table 1.1, samples were sintered to three different temperatures; 800, 1100 and 1400 °C. Evidence has been shown that density will not increase at temperatures above 1400 °C [146].

A large alternating current driven through a coil, is used to supply the heat source for the HFIHS technique leading to sintering at a rapid rate; temperatures of 2000 °C can be reached in less than a minute (Dr K.B. Chong, personal communication by email, 21st September 2011). This can result in small amounts of carbon diffusing from the moulds.
into the alumina specimen. The carbon is seen as black specks. Thermal annealing is then necessary to remove the carbon and thus retain the purity of the alumina. Details of thermal annealing and indentation testing of the alumina samples are included in the experimental chapter 6.

5.4.8. Zirconia

Attempts were made to etch the Zr oxides using both chemical and mechanical etching methods. This proved unsuccessful.

5.5. Microscopy based techniques

5.5.1 Field Emission Gun/Scanning Electron Microscope (FEGSEM)

A Zeiss Supra 55VP FEGSEM was used to image the material specimens for this research. The high magnification and enhanced depth of field provided by SEM was beneficial in acquiring images of very small nanoindents, also for characterizing the topography of the Zr oxides.

The SEM software offers a similar x,y co-ordinate stage system to that of the nanoindenter instrument. The following method, shown in figure 5.10, was devised to expedite finding the location of indents to view under SEM.
5.5.2. SEM

Although the first concepts of SEM started in the 1930s, it was not until the early 1950s that the first 2D images were produced at a resolution of 50 nm, using scanning electrons instead of light (as in an optical microscope) [147]. SEMs today produce high resolution surface images at magnifications up to 50,000 times, at a resolution of 2 nm at 30 kV. Figure 5.11 illustrates a schematic layout of a typical FEGSEM system.
A fine tungsten tip within the field gun emits a beam of electrons of less than 10 nm diameter. A magnetic field grid inside the gun provides the very strong electric field ($10^9 \text{ Vm}^{-1}$) needed to extract electrons from the tungsten tip [149]. The grid then channels the electron beam vertically downwards, under vacuum, to an anode that accelerates the beam. The electrons pass through magnetic lenses and apertures that focus the beam onto a specimen's surface. The beam at this stage is approximately 2 nm in diameter. Scanning coils raster the beam across the specimen's surface, and the electrons are then reflected back to detectors, in the form of X-rays, backscattered electrons or secondary electrons. The detectors collect the electrons, and convert them into output signals that
eventually translate as an image displayed on a computer screen. Most images of nanoindents and oxide scales shown in this thesis were captured using FEGSEM.

5.5.3. Electron back scattering diffraction (EBSD)

The Zeiss Supra 55VP FEGSEM at The Open University is equipped with an HKL/Oxford Instruments' EBSD system [150]. ‘Flamenco’ acquisition software was used to obtain the grain maps. The ‘Channel 5’ suite of software programs was used to analyse the data maps from Flamenco; ‘Tango’ for the grain orientation maps and ‘Mambo’ for the pole figures.

EBSD is used mainly for the analysis of microstructure in crystalline materials. Success of the technique relies on an exceptionally good surface finish, void of any surface defects or damage. This is because the diffraction pattern signal is obtained from the first few nanometres depth of a sample’s surface.

The first observations of EBSD patterns were recorded on film by S. Nishikawa and S. Kikuchi in 1928 [151]. Later in 1954 Alam et al. [152] published their fundamental paper on the variety of diffraction angles measured using electron back scattering on crystals. Alam et al. named the EBS patterns as the ‘Kikuchi’ patterns we know today. It took another twenty years before a camera was installed into an SEM chamber to record the patterns [153, 154].

5.5.3.1. The EBSD technique

Figure 5.12 shows the components of a typical EBSD system. A polished sample is fixed onto a stage within the vacuum chamber of the SEM. The stage is tilted at 60-70 degrees to the horizontal. This high tilt ensures a high fraction of electron scatter from the sample surface, as well as optimum contrast of the diffraction patterns. The electron beam is aimed at the area of interest on the sample surface, resulting in a scattering of electrons radiating from a point just below the sample surface. Some of the diffraction angles will satisfy Bragg’s equation:

\[ n \lambda = 2d \sin \theta \]  

(43)
Where $n$ is an integer, $\lambda$ is the wavelength of the electrons, $d$ is the spacing of diffraction planes and $\theta$ is the angle of incidence.

The scattered electrons that satisfy Bragg’s equation diffract into the formation of two cones to each diffraction plane, as shown in detail in figure 5.13. These cones of electrons create an image on a phosphor screen attached to a CCD video camera. At the points where the cones intersect with the plane of the phosphor screen, they appear as thin bands. The width of the bands depends on the $d$ spacing of the diffraction planes. These are the Kikuchi bands that form typical EBSD patterns, as shown in figure 5.14.

*Figure 5.12: Schematic showing components of an EBSD system [150].*
5.5.3.2. EBSD data acquisition; Flamenco software

Prior to the acquisition process, a ‘point analysis’ [150] is carried out. This is achieved by positioning the electron beam onto several random individual grains in the area of interest on the sample surface. This exercise provides a cross section of grain orientations or diffraction planes, in order to achieve the highest indexing (%) and therefore collect the best Kikuchi patterns. The actual acquisition process takes a few hours, but the software can be left running, unmonitored, if required.
The electron beam is programmed to scan using pre-set steps or increments at regular intervals, across a specified area. The step size is chosen in relation to the average grain size. This ensures as many grains as possible are investigated. At each step, crystal orientation is calculated from the position of the Kikuchi bands. A typical map is shown in figure 5.15.

![Figure 5.15: A typical grain map, as output by Flamenco software.](image)

5.5.3.3. EBSD: Post processing of data

The following modules from the Channel 5 post processing software was used to analyse data acquired from EBSD:

**Tango** [150]

Grain boundary maps showing interfaces between individual grains were produced to investigate deformation under an indent. This is covered in experimental chapter 8. Misorientation maps were produced to show angle differences between adjacent grains and to look for evidence of grain twinning.

**Mambo** [150]

Pole figures showing distribution of the orientation of the material grains were created for texture analysis.
5.5.4. Energy-dispersive X-ray spectroscopy (EDX)

Energy dispersive X-ray spectroscopy is another feature of the SEM used in this research. The EDX technique was implemented to obtain information on the chemical composition of a volume of Zircaloy 4 alloy.

5.5.4.1. The EDX technique

As the electron beam from the FEGSEM scans across the sample, the surface releases electrons that have been ejected due to the excitation of surface atoms. These electrons are often emitted from the very inner shells of an atom, leaving vacancies in the electronic structure. Vacancies are filled by electrons from the outer shells. There is an energy difference between the inner and outer electrons, so, at this point X-rays are emitted to balance the energy levels. The X-ray detector in the SEM chamber measures the number of X-rays emitted against their energy levels. The EDX database holds many chemical elements and the difference in energy between their two atomic states. So, by measuring the wavelength of the emitted X-rays, at any point on the sample's surface, a diffraction spectra of chemical elements can be recorded [33, 148]. Figure 5.16 is a schematic representation of a typical EDX system.

![Figure 5.16: A schematic view of an EDX system of components.](image)
5.5.5. Dual beam focused ion beam (FIB/SEM)

The dual beam electron microscope used for imaging and FIB milling for this research was the FEI Quanta 200 3D FEG system. A full description of the FIB techniques used in this research has been given in chapter 3, section 3.7 of this thesis.

5.5.6. Atomic force microscopy (AFM)

An AFM is connected to the XP Nanoindenter, and for this research, it was used to examine the effects of pile up around nanoindents. Information on the phenomena of pile-up has been given in chapter 2, section 2.3.3.

Atomic force microscopy has proved to be a valuable and versatile investigative tool [156-158]. Initial AFM principles were developed from scanning tunnelling microscopy in the mid-1980s by Binnig and Rehrer [159]. As the name suggests, AFM has the advantage of viewing and imaging the topography of sample surfaces at the atomic scale. Hence the technique is often used alongside nanoindentation.

In obtaining good quality images, the AFM technique is reliant on a system of components within a circuit, as depicted schematically in figure 5.17. A sharp probe tip (<10 nm diameter) is fixed to one end of a cantilever, whilst a piezoelectric scanner is fixed to the other end. The probe tip scans the specimen surface using one of three interaction modes; contact, tapping or non-contact [160]. The tip scans the sample surface using a raster motion, which is constantly monitored by a diode laser beam pointed at the top of the cantilever. When the tip is closest to the surface (<10 nm) repulsive forces (Coulombic) cause the beam to deflect [161]. When the tip is further away from the surface (>10 nm), attractive forces (Van der Waals) also cause beam deflection. The cantilever can display both vertical bending and torsional deflections, depending on how much friction occurs as the tip scans over surface asperities. The amplitudes of these deflections are measured by a photo-detector.
Topography of the surface is recorded by a ‘feedback’ circuit which applies the most appropriate voltages for the tip to maintain contact with the surface in the z axis. In turn, ‘voltage ramps’, in a parallel circuit, apply appropriate voltages to the piezoelectric scanner to provide x and y motion of the tip. ‘Feedback’ and ‘voltage ramps’ components are connected in an ‘in series’ circuit via the operating system PC and the photo-detector.

This constant monitoring of probe tip deflection alongside surface/tip integration enables creation of a 3D image of the sample surface [160]. The software also outputs line profiles of cross sections of the sample surface, for example, through a nanoindent. These line profiles can often give an enhanced representation of surface topography. The resolution is in the micrometre range. Examples of a 3D image and the corresponding line profiles are shown in figure 5.18.
5.6. Mechanical testing techniques

5.6.1. Nanoindentation

The nanoindentation technique has already been described extensively in Chapter 2, section 2.2 of this thesis. Nanoindentation has been implemented, in this research, as a tool to:

- Extract mechanical properties of Zr alloys and oxides.
- Map nanoindentation hardness variance over Zr metal and oxide.
- Investigate the time dependent deformation behaviour of Zr alloys and oxides.

5.6.2. Load relaxation testing

Load relaxation testing is an efficient form of mechanical testing often used to investigate the effects of strain rate on the deformation behaviour of the tested material. A test specimen, under constant constraint, is strained in uniaxial tension, whilst load and strain data are recorded. The term ‘relaxation’ refers to the decrease in load over time.

Test specimens are normally ‘dogbone’ shaped with wider ends to allow for gripping. It is assumed that deformation will be localized in the central region of the narrower gauge cross section.

A schematic layout showing components of a typical tensile testing machine is shown in figure 5.19. The test specimen is clamped at each end. One clamp is attached to a
vertically moveable beam (the crosshead) and the other lower clamp is attached to a fixed beam. Both beams are held within a stable test frame. The test specimen is constrained, without lateral movement, throughout the test; this avoids any bending or side loading of the specimen. Strain gauges and an extensometer are fitted to the test specimen, in the area where most strain is expected to occur.

A load cell assigns a voltage applicable to the pre-determined force. The cross head speed is set to allow for the test specimen to be loaded in a controlled manner, at a constant strain rate. The whole relaxation test procedure is computer controlled.

Figure 5.19: A schematic showing the main components of a load relaxation test, as described in the text.

5.6.2.1. How load relaxation is determined

The load is pre-set with a specific plastic strain extent in mind. In the tests performed in this project, the load was set for the material to deform until just beyond its yield point.
When the pre-determined plastic strain is reached, crosshead movement is stopped and load relaxation (displacement strain) in the test material is monitored for a period of time. The stress relaxation rate is the slope of the output graph at any point.

5.6.2.2. Analysis of load relaxation data

The load frame of the test machine behaves elastically, whilst the test specimen behaves both elastically and plastically. The stress of the specimen is calculated from the set load and the cross sectional area of the specimen. The specimen and the load frame are treated as springs in series, and the strain rate of the specimen ($\dot{\varepsilon}_S$) can be calculated from [163]:

$$\dot{\varepsilon}_S = \dot{\varepsilon}_E + \dot{\varepsilon}$$

(44)

where $\dot{\varepsilon}_E$ is elastic strain rate, and $\dot{\varepsilon}$ is plastic strain rate.

As previously mentioned, at a pre-determined plasticity point, the crosshead is stopped, so in effect the actuator strain is equal to zero. By recording the load relaxation from this point onwards, it can be shown that the plastic strain rate in the test specimen is related to the rate of change in stress ($\dot{\sigma}$) according to the following equation [163].

$$\dot{\varepsilon} = -\dot{\sigma} \left( \frac{1}{E} + \frac{1}{E_{LF}} \right)$$

(45)

where $E$ is the elastic modulus of the specimen material and $E_{LF}$ is the elastic modulus of the load frame.

The results of a load relaxation test on Zircaloy 4 plate can be viewed later in experimental chapter 8. The next three chapters focus on experiments carried out using the above materials and methodologies.
Chapter 6: Determining residual stress using nanoindentation

Chapter 6 reports experimental results of point to point hardness mapping across Zr oxides using nanoindentation. Scatter in the data is investigated, and the resulting implications for using this methodology to determine residual stress are discussed.

6.1 Initial set-up; defining the conditions for nanoindentation of zirconium alloys.

In order to determine exactly how zirconium alloys respond under nanoindentation load, a series of high and low load indentations were performed on Zircaloy 4 cold rolled plate. This exercise was also an attempt to discover the optimum load parameters, prior to experimental testing.

The Zircaloy 4 plate was supplied very early on in the project, and the microstructure study had been completed (see chapter 5, section 5.4). It was the ideal material to trial in this exercise, because the coupons had been cut and prepared to expose surfaces in the three principal material directions; rolling (RD), transverse (TD) and normal (ND). Both polished and etched specimens were indented by loading normal to all three surface directions; six samples in all, as listed in table 6.1. This material had not been exposed to autoclave conditions, so the only oxide formation is likely to be the air formed ‘smear’ layer (~2-5 nm thick) described in chapter 4, section 4.2.

Ten indents were performed at each load, on each specimen. Each indent was positioned at least 2.5 times its diameter away from other indents or edges. The indentation method used was CRL (constant rate of loading), so the load was preset, as opposed to the depth defining constant stiffness measurement (CSM). The loading time was 15 s for all tests.
<table>
<thead>
<tr>
<th>Zircaloy 4 cold rolled plate</th>
<th>High loads (Newtons)</th>
<th>Low loads (Newtons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rolling direction; polished</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rolling direction; etched</td>
<td>10 N</td>
<td>0.75 N</td>
</tr>
<tr>
<td>Transverse direction; polished</td>
<td>7.5 N</td>
<td>0.5 N</td>
</tr>
<tr>
<td>Transverse direction; etched</td>
<td>5.0 N</td>
<td>0.25 N</td>
</tr>
<tr>
<td>Normal direction; polished</td>
<td>2.5 N</td>
<td>0.1 N</td>
</tr>
<tr>
<td>Normal direction; etched</td>
<td>1 N</td>
<td>0.05 N</td>
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<tr>
<td></td>
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<td>0.01 N</td>
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<td></td>
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<td>0.005 N</td>
</tr>
</tbody>
</table>

*Table 6.1: Zircaloy 4 specimens, along with the ranges of high and loads applied.*

6.1.1. Data analysis

Hardness (H) and elastic modulus (E) values were extracted for each indent according to the Oliver and Pharr method already described in chapter 2, section 2.3.1. Mean values of hardness and modulus were determined for each set of ten indents. To find the optimum load range, all mean values were plotted as a function of load.

Due to the wide variation in loads, an average error bar was determined for hardness and elastic modulus results. The average error bar was calculated by taking the average standard deviation (x2) for each data set extracted for each load.

6.1.2. Results

Figure 6.1 shows all high and low load mean hardness values, as a function of load, for both polished and etched samples over all three crystallographic directions. Literature values for hardness vary between 2 and 3 GPa, whilst Young’s modulus for this material is around 100 GPa. Figure 6.2 shows mean elastic modulus values (high and low load results) as a function of load, for both polished and etched samples over all three principal directions.

On both graphs, lines between data points were added for clarity when comparing the different samples.
6.1.3. Observations and discussion

In figure 6.1 significant scatter of hardness data is evident at loads up to 0.1 N. However, hardness values tend to stabilize at loads between 0.1 N and 1 N. The elastic modulus values in figure 6.2 display a similar levelling out of results between loads of 0.1 N and 0.5 N.
According to results shown in figures 6.1 and 6.2, it was determined that loads between 0.1 N and 0.5 N are the most ideal to ensure accurate, stable results, when nanoindentation testing for hardness and elastic modulus on zirconium alloys.

6.2. Mapping indent arrays across oxide/metal interface

6.2.0 Introduction

It is important that fuel cladding maintains stable mechanical properties during normal in-reactor service. The structural integrity of the cladding material must be upheld, particularly in a loss of coolant accident. So, as already indicated, there is a need to understand the oxidation of Zr alloys, particularly with regard to residual stresses in the oxide (compressive) and in the metal under the oxide interface (tensile). In an attempt to map stress variation patterns, arrays of nanoindents were placed over the cross sectioned oxides and into the metal substrates.

Three particular specimens were chosen:

- Zircaloy 4 tube, exposed to 980°C steam (LOCA).
- Zircaloy 2, autoclaved at 415°C for 570 days.
- ZIRLO, autoclaved at 415°C for 660 days.

The three samples were chosen for their thickness of oxide scales (>50 µm), thus enabling an adequate resolution for an array of nanoindents with sufficient spacings.

The depth defined continuous stiffness measurement (CSM) indentation method was used for this exercise. The advantage of using CSM for the indent arrays is that each of the indent displacements is identical, therefore the indent diameter should also be of a consistent size, thus allowing accurate mapping of indents across a proposed surface area. Whereas, if the CRL method was used, depending on how the material deformed under load at each specific point, the displacements will vary, so indent diameters will also vary. This would make it more difficult to keep the indent array within the confines of the restricted surface area of the oxide.
Other researchers have managed to distinguish a trend in biaxial residual stress using nanoindentation on aluminium alloys [164] and Raman spectroscopy on zirconium alloys [9]. Nevertheless, there seems no evidence of trends being exposed in zirconium alloys using nanoindentation techniques.

### 6.2.1. Mapping indent arrays; Zircaloy 4, tube, (LOCA)

As explained in chapter 5, section 5.4.3, this LOCA tube material has a highly saturated oxygenated region in the metal under the oxide interface. This specimen has been subjected to high temperature steam (980-1000°C), leading to significant embrittlement, resulting in a loss of structural integrity, particularly in the central region of metal exhibiting Widmanstatten structure [143].

There has been limited research into the topography of ‘peak’ and ‘trough’ undulations that evolve along the metal interface as the oxide grows inward (chapter 4 section 4.2.3). There is no consensus on the cause of the undulations [120, 121]. However, there is some agreement [120, 165] that the tensile stresses in the metal ahead of a ‘trough’ are influential in enhancing the oxidation rate, whereas the compressive stresses in the oxide are claimed to retard oxide growth, resulting in the ‘peaks’. These observations go some way to build a picture of the mechanisms of corrosion in Zr alloys but, it is clear that further study is essential to gain a full understanding. This thesis attempts to characterize the residual stresses found over the interface region, by mechanical testing.

### 6.2.2 Experimental details; LOCA specimen

To investigate point to point hardness variations below the metal interface and into the embrittled alpha metal substrate, nanoindents were placed in two long single arrays A and B, as displayed in figure 6.3. The two arrays were positioned under a ‘trough’ in the interface undulation. There is evidence of cracking along the interface (figures 6.3 and 6.4) but not in the region of the two arrays. There are periodic cracks, perpendicular to the interface in the metal, possibly caused by embrittlement due to quenching. These cracks show no pattern as to where they occur, however, they do seem to appear relatively equidistant from each other, as seen in figure 6.4.
The LOCA sample is a cross sectioned tube, and arrays A and B were indented on the tube's inner circumference of oxide. The indents in the oxide started approximately 5 µm from the metal interface, and finished in the metal substrate about 110 µm below the interface. The CSM method was used for nanoindentation, with a depth of 75 nm set for all indents. Each array consists of 70 indents, with a spacing of 1.5 µm between each indent.

![Image of two single row indent arrays A & B, in Zircaloy 4 LOCA sample.](image)

**Figure 6.3:** SEM image of two single row indent arrays A & B, in Zircaloy 4 LOCA sample.

![Image of perpendicular cracks and interface cracks as described in the text.](image)

**Figure 6.4:** SEM image of perpendicular cracks and interface cracks as described in the text.

Hardness values were extracted for each indent and plotted as a function of distance from the oxide/metal interface. The results for each array are shown in figures 6.5 and 6.6. Error bars have not been shown on the graphs. This is due to the fact that the MTS XP
nanoindenter load resolution is 50 nN [166], and with the average test load between 1.5 and 2 mN, at this high accuracy, to plot an error bar at each individual data point, would mean that the error bar would be smaller than can be shown effectively on the graph.

Figure 6.5: Zircaloy 4 LOCA sample, array A hardness variation.

Figure 6.6: Zircaloy 4 LOCA sample, array B hardness variation.
6.2.3. Observations and discussion

Overall, the hardness values show a steady decline, however, in the metal, at about 80 µm from the interface, in both arrays, a sharp drop in hardness is evident. Although there is some discrepancy in the total drop in hardness, in array A the value drops from 13 to 2 GPa, whereas in array B the value drops from 13 to 6 GPa. In both cases there seems some stability in hardness (12-14 GPa) in the region between 40 and 80 µm from the interface.

Following indentation, energy dispersive X-ray spectroscopy (EDX) was used to quantify oxygen variation over the same area. Row B was chosen for analysis, as it is positioned furthest from the nearby crack perpendicular to the interface. No procedure was found to define error or accuracy using the EDX quantification software. Hardness and oxygen results are displayed in figure 6.7.

![Figure 6.7: Zircaloy 4 LOCA sample, array B, hardness vs oxygen variations.](image-url)
The SEM image in figure 6.8 shows clearly the region of high oxygen concentration and embrittlement in the metal underneath the oxide. The interface between this alpha phase and the prior beta phase is situated between 70 and 80 microns from the oxide interface. This is the point where the hardness values dipped dramatically in earlier results for both arrays A and B. As the hardness trend recovers to continue at the same gradient, the drop in hardness may be due to the surface inconsistencies in the region, which in turn may be have been worsened by uneven or preferential polishing, resultant from metallographic surface preparation of the specimen.

![SEM image of Zircaloy 4 LOCA sample, showing α-phase.](image)

**Figure 6.8:** An optical microscope image of Zircaloy 4 LOCA sample, showing α-phase.

### 6.3. Indentation array over a peak and a trough undulation; LOCA sample

#### 6.3.1. Experimental details

This study was continued by repeating the above tests, but this time over a peak and a trough in the interface topography, to compare hardness results in terms of stress variation, but also to determine any differences in material properties over the two undulations.

A single array (array C) of nanoindentation hardness tests was set over a trough and an identical array over a peak (array D) as imaged in figures 6.9 (a) and (b). Fifty indents
were set in each array at 100 nm deep using the CSM method. The spacing between each indent was 2.5 µm.

**Figures 6.9 (a) and (b):** SEM images of two single row indent arrays ‘C’ over a ‘trough’ and ‘D’ over a ‘peak’ at the oxide/metal interface of the Zircaloy 4 LOCA sample

(a) A higher magnification view of indents in oxide, and metal immediately below the interface  
(b) a view of both full length arrays.

The hardness results were calculated using the Oliver and Pharr method. Indents that were located on voids or cracks (array C; indents 12 and 14; array D; indents 11 and 12) were excluded from the graph due to inconsistent or missing hardness values. Following analysis, data from the two arrays was overlaid for comparison, and graphical results are displayed in figure 6.10. As previously explained in section 6.2.2, error bars have been
omitted due the high resolution of the nanoindenter and the low peak loads resulting from the testing (2.25-2.75 mN as confirmed in figure 6.11).

Figure 6.10: Zircaloy 4 LOCA sample; Overlay of hardness results for arrays C & D, (indents falling on cracks extracted from graph, as listed in the text).

6.3.2. Observations and discussion

The hardness overlay in figure 6.10 displays similar results to those of arrays A and B (figures 6.5 and 6.6); high hardness values in the metal under the interface, steadily decreasing as indents move into the metal. However in comparison, Figure 6.10 displays extra results for hardness measurements; over the entire outer to inner oxide thickness, and into the metal. High hardness values, matching those recorded in the oxide, are evident in the metal up to a point about 20 µm from the interface. Higher scatter is evident in the oxide and metal immediately below the interface, stabilizing as the indents move into the metal substrate.
It was hoped that the graph overlay might expose evidence of a reversed stress state between interface peak and trough. Unfortunately too much scatter existed and no pattern was observed. The overlay of indentation hardness results shows no differences between indentations over a peak compared to those over a trough.

6.4. Scatter in data

The trend in hardness values in the LOCA sample would suggest that a similar trend may be evidenced when overlaying several load/displacement curves, with peak loads higher at the oxide/metal interface, and reducing towards the more porous outer oxide. However, the P/h graphs from the above tests on array C exposed significant scatter in peak load; ~20% and no trend in the data. The results are shown in figure 6.11. It should be noted that for the tests in array C the nanoindenter was programmed to indent to a peak displacement (rather than peak load) thus allowing measurement of the scatter in peak load.

![Figure 6.11: Zircaloy 4 LOCA sample, scatter of peak load results in oxide (array C).](image-url)
In order to explore the cause of the scatter, a different Zr alloy was indented for comparison. A sample of ZIRLO, autoclaved at 415°C for 660 days was chosen, because the oxide thickness was slightly thicker than that of the LOCA sample. The thicker oxide of ZIRLO, unlike the LOCA sample, displayed clear cracked and non-cracked veins evolving from the peaks in the interface undulations, thus allowing for precise positioning of indents over these areas. An added incentive was that residual stress variations had already been measured in the ZIRLO material, using Raman spectroscopy.

Several diagonal indent arrays across the oxide were analysed, and the percentage of scatter in the data was consistent. Further examples are included in appendix A. Several columnar arrays were also positioned down through the oxide on the non-cracked veins. Similar scatter resulted, and no trend was found in either the resultant hardness graphs, or the peak hold graphs. Examples can be viewed in appendix A.

6.4.1. Experimental details: ZIRLO 415°, 660 days autoclaved

In an attempt to find a trend in hardness or peak load, a large rectangular array was indented. As in previous experiments on the LOCA sample, the CSM method was used. This time the pre-set depth was 500 nm, to ensure stable and consistent values over such a large rectangular array, also allowing for any excessive tip rounding of greater than the normal Berkovich tip diameter (~150 nm).

Diagonal single arrays of indents were chosen for analysis to allow for the maximum variation of indents across the oxide. Data from the single diagonal array, highlighted in red on figure 6.12 was analysed for this chapter. Similar quantitative results for the other two arrays, highlighted in blue, are evidenced in appendix A.
Figure 6.12: An optical microscope image of the large rectangular array of indents positioned over oxide and metal on the ZIRLO sample. The three individual diagonal arrays highlighted were chosen for analysis.

6.4.2. Results

Hardness results are shown in figure 6.13 and the load/displacement graphs in figure 6.14. These results are for each indent in the diagonal array A15 to H11. The scatter in this data is not understood, but a broad investigation is carried out in section 6.5, with the findings reported later in this chapter.

Figure 6.13: ZIRLO 415° 660 days, hardness results over diagonal array A15 to H11.
As an alternative investigation of the hardness variation in the ZIRLO specimen, a contour map of the larger area over the whole rectangular array is shown in figure 6.15.

Figure 6.15: Contour map over ZIRLO large rectangular array indents A1 to N40, with 'islands' of metal referred to in the text (indicated by arrows).
6.4.3. Observations and discussion

Figure 6.13 displays scatter in the hardness values of between 10 and 15 GPa. If there is a residual stress variation across the oxide thickness, we would expect to see a trend where hardness values are apparently lower at the ‘outer’ air/oxide interface and increase towards the ‘inner’ metal/oxide interface.

Similarly in figure 6.14 no trend in peak load is evident from outer to inner oxide. There is scatter of around 33% in peak load results for all three diagonal arrays.

The contour map (figure 6.15) confirms no hardness pattern exists over the area of the three diagonal arrays, nor further into the large rectangular array. However, the three small blue areas arrowed are positioned in a non-cracked vein, above a peak in the interface undulations. These islands have hardness values closer to those of metal than oxide. Perhaps these are examples of the ‘entrapped islands of unoxidised metal’ studied by Hutchinson and Lehtinen [120].

Further studies were carried out to try and determine why there is such scatter in the results.

6.5. Possible causes of scatter

6.5.1. Surface work hardening

Initially it was important to eliminate surface work hardening, due to plasticity resulting from grinding and polishing processes, as a cause of scatter of data following nanoindentation. Zircaloy 4 hot rolled and cold rolled plates were tested using nanoindentation. One sample of each was ground and polished according to the process as described in chapter 5 section 5.2. Another sample of each was electropolished according to the parameters described in chapter 5, section 5.3. The electropolished samples are not subject to any mechanical rubbing or pressure, so work hardening should be avoided.
6.5.1.2. Experimental details; work hardening

Ten indents, loaded to 0.5 N, were made in each of the four specimens. A peak hold period of 30 s was set for each test to allow for time dependent effects to subside. The indent arrays were positioned well away from edges, on smooth surfaces.

6.5.1.3 Results; work hardening

Figure 6.16 (a): Cold rolled Zircaloy 4 plate (RD) traditionally polished.

Figure 6.16 (b): Cold rolled Zircaloy 4 plate (RD) electro-polished.
As seen in figures 6.16 (a) to (d), the amount of scatter from the test results on traditionally polished and electropolished samples is comparable, at between 6% and 12%. This indicates that work hardening is not likely to be the cause of the data scatter.
6.5.2. Pile-up

As nanoindentation hardness is determined from load/area, accurate results depend on accurate indent areas. Experiments earlier in this research had led to an investigation to determine whether pile-up was causing imprecise calculations of area in Zircaloy 4 plate.

6.5.2.1. Experimental set up; pile-up

Manual measurements were taken from SEM images for a selection of indents. Each manual measurement was then compared to the same indent area, as calculated by the Testworks 4 software, using the Oliver and Pharr method. Image J software was used to manually draw around the surface area of each indent in the SEM image. A table of comparison results was created, and this can be found in appendix A.

Figure 6.17 (a) shows an image taken using atomic force microscopy (AFM). The AFM imaged three separate cross sections of an indent. The cross sections are each represented by red, green and blue lines (figure 6.17 (b)).

Figures 6.17 (a) and (b): (a) AFM image; view on top of an indent in Zircaloy 4 plate (b) cross sectioned profile of the same indent.
6.5.2.2. Observations and discussion; pile-up

Following the results of manual measurements of indent area compared to Testworks 4 calculated area by O & P method, the outcome showed little or no difference in the areas, indicating that pile-up is not significant in this material.

Pile-up is also not evident from the AFM images. The gradient of the red line cross section matches on both sides of the indents, which most likely indicates a surface gradient in this plane, and not pile-up.

In addition, these findings correlate well with Bolshakov and Pharrs’ empirical studies [35] showing that pile-up is not significant in materials that only moderately work harden, and where the ratio of indentation final displacement/maximum displacement is < 0.7.

Taking the $h_{\text{final}} / h_{\text{max}}$ ratio for ten separate indents in ZIRLO oxide, and averaging, gave a mean ratio of 0.73.

Evidence has been shown here that pile-up is insignificant in this material and will not affect the indent area to any consistent or detrimental degree. Therefore, pile-up is not the cause of scatter in the indentation results.

6.5.3. Porosity

It has not been possible to establish a trend in load/displacement results when analyzing an array of indents diagonally across the oxide. As we have seen, figure 6.14 highlights the significant scatter that occurs on both loading curves, and final displacements, in ZIRLO oxide.

The oxidation process of Zr alloys has already been described in Chapter 4. The oxidation kinetics lead to the outer layers of the oxide forming pores, whilst cracks occur all the way through thicker oxides. The SEM image in figure 6.18 shows the porous nature of the outer oxide layers of an unpolished cross section of ZIRLO oxide. Figure 6.19 is an SEM image of ZIRLO oxide surface porosity.
6.5.3.1. Indentation of pure zirconia

A homogenous material is required for accurate indentation with minimal scatter in hardness results [29]. So for comparison purposes, dense, white, zirconia was indented. The pure zirconia rods have a density of 5720 kg/m$^3$ and were supplied by The Technical Glass Company.

6.5.3.2. Experimental details

A cross section of zirconia rod was cut, mounted, ground and polished according to the procedures in Chapter 5. A series of ten nanoindentation tests were performed using the CSM method, set to a depth of 200 nm.
6.5.3.2. Results

The load/displacement test results on pure zirconia are shown in figure 6.20.

![Figure 6.20: Load/displacement results from testing pure (white) zirconia.](image)

6.5.3.3. Observations and discussion

It can be seen that the scatter in peak load is negligible, at less than 10%, compared to scatter resulting from testing the ZIRLO and LOCA oxides (up to 35%). There is considerably less scatter in the actual loading curves in comparison to those ringed in figure 6.14.

The results from instrumented indentation of very dense (6000 kg/m$^3$ [167]) pure zirconia show that there is evidence of inherent scatter not affected by porosity.

6.5.4. Indentation of alumina oxides at three different porosities

To obtain further evidence, the porosity experiments were extended to include three samples of sintered aluminium oxide. The three samples were laboratory prepared by
sintering at three different temperatures, and as density increases with temperature, this resulted in specimens with three different degrees of porosity as listed in table 6.2

### 6.5.4.1. Experimental details

<table>
<thead>
<tr>
<th>Alumina specimen; sintering temperature (°C)</th>
<th>Density (kg/m³)</th>
<th>Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>1319</td>
<td>Most porous</td>
</tr>
<tr>
<td>1200</td>
<td>1874</td>
<td></td>
</tr>
<tr>
<td>1400</td>
<td>2165</td>
<td>Least porous</td>
</tr>
</tbody>
</table>

*Table 6.2: Details of the three alumina samples.*

As explained in chapter 5 section 5.4.7, black specks of carbon were visible after sintering, so prior to surface preparation, the alumina was placed in a furnace at 600°C for 1.5 hours, and left to cool in the furnace. This exercise served to evaporate any carbon existing in the oxides, emptying the pores, to obtain ultimate porosity.

The three cross sectioned alumina stubs were then mounted, ground and polished as previous samples. Five indents were performed on each specimen. To ensure structural integrity, under indentation, of such porous samples, the set load method (XP) was used. A reasonably low load of 100 mN was set, as this load is well below the recommended maximum load as set under the cracking threshold ($P_{\text{max}} \leq 200$ nm [168]).

### 6.5.4.2. Results

As these tests on alumina were completed at lower loads, and therefore lower displacements than the ZIRLO and LOCA specimens (CSM method), it was not considered an accurate comparison. So, the results were compared to indentation tests, completed earlier in the research on Zircaloy 2 oxide, using the same test parameters. The results for both alumina and Zircaloy 2 are displayed in figures 6.21 and 6.22 below. The amount of scatter in the displacement results for alumina specimens is between 18% and 20%. The amount of displacement scatter in Zircaloy 2 oxide is about 16%.
Figure 6.21: Load/displacement scatter in results for three different porosities of alumina.

Figure 6.22: Zircaloy 2, 415°, 570 days autoclaved, P/h curves at 100 mN load in oxide.
6.5.4.3. Discussion; pure zirconia, alumina and Zircaloy 2 oxide.

**Pure zirconia**

The pure zirconia sample is a dense, homogenous material devoid of residual stress, yet the test results in figure 6.20 depict approximately 9% scatter, showing that there is inherent scatter not affected by porosity.

**Pure alumina**

The three scatter results following indentation testing of pure alumina at three different porosities (figure 6.21) are as expected. The most porous sample exhibits the most scatter in displacement data and the least porous shows least scatter.

When the percentage of displacement scatter is compared to that in the Zircaloy 2 displacements (figure 6.22), the results are very close (within 2 or 3%). This suggests that porosity is not an influence on amount of scatter in the alumina data.

**Zircaloy 2 oxide**

In comparison to the alumina results, the lesser 16% scatter of test results on Zircaloy 2 oxide is probably due to the much higher density of zirconia (6000 kg/m$^3$).

Overall, the results indicate that porosity is not responsible for the scatter in the indentation results.

6.6. Indentation response: $E/\sigma_Y$ ratio

Residual stress has been found to influence the indentation response using conical [58], sharp [70, 169], and spherical [64, 170] indenters. Parameters such as contact areas ($A_c/A$) [170, 171], displacements ($h_{\text{max}}/h_{\text{final}}$) [63, 64], and peak load variation ($\Delta P$) [71, 172, 173] have been cited as having an influence on the indentation response. Both elastic and plastic responses have been examined, primarily by observing the load/displacement curves. Responses are revealed in the curvature of the loading curves, as well as the magnitude of change between different loading curves.

Applied equi-biaxial stress exposed a stress induced shift in peak load of 10% in API x65 steel [169] for both compressive stresses (~415/~414 MPa) and tensile stresses.
(428/427 MPa). However no shift was seen in pure shear stress (~239/231 MPa) when compared to a stress free reference sample.

To ensure true geometric, accurate indents, a homogenous, isotropic material is necessary [174]. Chen and Chen’s graph [174] shown in figure 6.23 modelled the indentation response to different values of residual stress, on materials assumed to be homogenous and isotropic. Their model follows semi-empirical studies by Suresh and Giannokopolous [71], showing that loading curves positioned above the stress free curve represent compressive stress, and those below are representative of tensile stress. The loading curves presented earlier in this experimental chapter in figures 6.11 and 6.14 do not show this trend nor do they show any systematic offsets in graphical results.

Figure 6.23: Fig 4 from Chen et al. paper [174] showing variations in P/h curves for different residual stresses.

In 2001, Dao et al. [70] used computational modelling to find that the plastic properties of a material extracted using nanoindentation are very sensitive to even small variations in the P/h curves following their instrumented indentation tests on aluminium alloys. Early in 2011, Japanese researchers [172] used inverse analysis of micro-indentation on austenitic stainless steel, alongside FE modelling, to conclude that applied equi-biaxial residual stress mainly affects plastic deformation in the zone under an indent.
Nevertheless, the loading curve contains both elastic and plastic parameters, and it is important to consider the relative amounts of elastic and plastic deformation. The measure of the amount of elastic deformation that a material can accommodate prior to yielding plastically is recorded by the ratio of elastic modulus to yield stress \([170]\) (referred to from now on as the \(E/\sigma_Y\) ratio). In a perfectly elastic material \(E/\sigma_Y < 100\) and towards a perfectly plastic material \(E/\sigma_Y > 100\) [170], as depicted schematically in figure 6.24.

![Figure 6.24: A schematic representation of the \(E/\sigma_Y\) ratio limits](image)

6.6.1. The \(E/\sigma_Y\) ratio of zirconium oxide

The elastic modulus of zirconium oxide is 186 GPa and the compressive yield strength is 3 GPa [175], giving an \(E/\sigma_Y\) ratio of 62.

6.6.2. Nanoindentation of zirconium oxides; indentation response to residual stress

As there was so much scatter in peak load data of Zr oxides in these experiments, it seemed rational to investigate the indentation response to residual stress in the current material. The influence of residual stress on the indentation peak load of materials with varying \(E/\sigma_Y\) ratios is modelled in figure 6.25.
Figure 6.25: A model showing the influence of residual stress on the indentation peak load in materials with different E/σ_Y ratios [164].

6.6.3. Observations and discussion

It can be seen that the peak load (P) has a linear relationship with the σ_r/σ_Y ratio, increasing with compressive stress and decreasing with tensile stress. The slope of the linear curves is dependent on the E/σ_Y ratio; there is a larger dependence of peak load on residual stress in the material with the lower E/σ_Y ratio of 50. This is because, in materials with an E/σ_Y ratio >100 (see figure 6.24), the deformation under the indent is dominated by plasticity with little or no elastic deformation [171], therefore showing very little influence on hardness, which is related to peak load by the equation H= P/A.

Next to the highest peak load point on the blue, green and brown curves, is displayed the relative, compressive residual stresses that would be applied at these points. The percentage variation in peak load is also shown. Taking the blue graph, which has an E/σ_Y ratio closest to that of Zr oxide, we see that a high compressive residual stress of 1.1 GPa
is required to cause a relatively small change in the peak load (~15%). Proportionally, this is much lower than the percentage scatter in peak load shown in test results from the ZIRLO and Zircaloy 4 LOCA samples (figures 6.11 and 6.14).

There is a larger dependence of peak load, and therefore hardness, on materials with low E/σ_Y ratios. The peak load has a linear relationship with, and varies with yield, so very large residual stress is needed to make a small percentage change in peak load/hardness results.

In the same autoclaved ZIRLO material as tested in this chapter, compressive residual stresses as high as 1.2 GPa have been measured in the oxide, at the metal/oxide interface, using synchrotron X-ray diffraction [8].

6.7. Modelling; to determine indentation response to residual stress

6.7.1. Finite element model

Due to the amount of scatter in the load/displacement comparisons, it was impossible to see from experimental results, exactly how, or if, residual stress would influence any variation in offset of the loading curves, as seen in figure 6.23. So, to see the loading and unloading response of zirconium oxides under high stress, a finite element (FE) model was designed to simulate the process of nanoindentation using a Berkovich indenter tip.

6.7.2. Details of 2D model of the indentation process

DEFORM-2D finite element software was used to simulate a two part model showing deformation of an axisymmetric material by indentation using a rigid indenter.

Material

The Von Mises criterion was applied to investigate elastic/plastic deformation of zirconium oxide. The compressive yield stress of Ceramtec 848 zirconia is 3 GPa [175]. The elastic modulus was given as 186 GPa [175] and a Poisson’s ratio of 0.33 [175].

The model size is 1.5 µm by 1 µm. To obtain an accurate simulation, a finer mesh was applied in the area where most deformation takes place: the region of contact between indenter and material. The total number of elasto-plastic quadrilateral elements in the material model is 2097.
**Indenter**

The model for the rigid indenter was based on the same area to depth function as a diamond Berkovich tip: a cone of 70.3°.

### 6.7.3. Simulation details

The finite element mesh is shown in figure 6.26.

![Finite element mesh](image)

*Figure 6.26: Finite element mesh. Model courtesy of Dr M.A. Rist, Materials Engineering Group, The Open University.*

The simulation assumed constant contact between the rigid indenter and the material, so no coefficient of friction between the two was applied.

In order to predict the behaviour of zirconium oxide under indentation, model simulations were performed by pushing the indenter 75 nm into the material, then withdrawing. This indentation process was repeated on the material modelled as:

- a stress free reference specimen
- a specimen under compressive residual stress
- a specimen under tensile residual stress.

In order to examine the reproducibility of the loading/unloading curves from experimental nanoindentation tests done on the Zircaloy 4 LOCA specimen (examples shown in figures 6.27 and 6.28), different magnitudes of residual stress were applied to the model.
Figure 6.27: Experimental example 1; P/h curves from indentation tests in the oxide of the Zircaloy 4 LOCA specimen.

Figure 6.28: Experimental example 2; P/h curves from indentation tests in the oxide of the Zircaloy 4 LOCA specimen.
6.7.4. Results

Figure 6.29 shows the effect of 1 GPa applied residual stress on indentation at 75 nm deep.

Figure 6.29: Simulated load/displacement curves, with applied residual stresses (yield stress; 3 GPa).

Whilst figure 6.29 simulates the shape of the loading curve quite well, further simulations were performed to provide a comparison between real and modelled unloading curves. Results are shown in figure 6.30.

Figure 6.30: Simulated load/displacement curves, with applied residual stresses (yield stress; 6 GPa).
6.7.5. Observations and discussion

The results shown in figure 6.29 show evidence of a 7% peak load shift when a large residual stress (1 GPa) is applied to the model. This is a small percentage change for such a high magnitude residual stress. Previously, when indenting oxides of both LOCA and ZIRLO specimens, experimental results reflect an overall scatter in peak load of 20% and 33% respectively (figures 6.11 and 6.14).

Compressive residual stresses of up to –2 GPa have been measured in zirconium oxides using Raman spectroscopy [9, 10]. At these high magnitudes of stress, any peak load variation or trend will be lost in the scatter on zirconium oxides.

The yield stress inserted in the first simulation (3 GPa) is of the magnitude stated in the literature [175]. However, when the second simulation was performed, to match the same peak loads and consequent displacements as the experimental results (figures 6.27 and 6.28), the model required a yield stress of 6 GPa to be inserted. If this magnitude of yield stress is more likely in zirconium oxides, it would reduce the $E/\sigma_Y$ ratio to 31.

So, from these experimental results, we can deduce that the high residual stress within the oxide causes only a small change in nanoindentation response, and one that is less than the inherent scatter. In order to reproduce the nanoindentation response using FE modelling, a material with a high value of yield stress is required.
Chapter 7: Determining residual stress using focused ion beam (FIB) and digital image correlation (DIC)

Chapter 7 forms a feasibility study to assess whether zirconium alloys are suitable materials on which to use the FIB milling/DIC technique already described in chapter 3, section 3. Results are shown of FIB milled strain relieved pillars. One of the pillar surface patterns is analysed for strain differentiation, using DIC. Following several unsuccessful milling attempts due to drifting, there is a chemical analysis using EDX to try and determine if the alloy samples are absorbing gallium ions during the milling process.

7.0 Introduction

A description of the ring core technique involving the removal of material using a focused ion beam, and the subsequent measurement of induced strains in the ‘relaxed’ pillar, has been covered in chapter 3 section 8.

The ring core method was first established in the 1950s [87], when it involved the use of traditional milling methods alongside strain gauges to measure strains. Modern methods of FIB milling with analysis using DIC, is a relatively new sector of research. In fact, no literature was found during this research project to indicate that the methodology has been used on zirconium alloys. So, to progress towards the aim of characterizing residual stress, and to determine the feasibility of applying this method to Zr alloys, several experiments were carried out.

Zirconium, metal and oxide, are known for their poor electrical conductivity, whilst the very principle of FIB milling entails the bombardment of a material by charged particles. So, to minimize charging effects, each Zr sample was glued to metal mounts using conductive adhesive. For extra conductivity and stability, conductive tape was applied as additional fixing of the sample to mount.

As stated previously, the natural surface of the material often lacks the surface textures necessary to allow adequate DIC data acquisition. So, it is often necessary to apply an artificial, high contrast surface decoration, to facilitate pattern displacement measurements after relaxation of the pillar. Prior to ring milling, it was important to
determine the best form of surface patterning for the zirconium alloys, hence, three different patterning techniques were trialed. The main objective of these trial experiments was to retain the same surface pattern on the pillar after milling as before milling.

### 7.1 Surface patterning using nanoindentation

#### 7.1.1 Experimental details

To improve the conductivity of the Zircaloy 4, 980°C, LOCA specimen, a platinum coating 30 nm thick was deposited using a beam current of 50 pA. An array of nanoindents, each 250 nm deep, was then positioned on the surface of the platinum. This array can be seen most clearly in figure 7.1(a). The white circles show the original position where the beam was set to mill.

To obtain sufficient strain relaxation of the pillar, it is important to mill the annular trench to around the same depth as the inner diameter of the pillar [95, 96, 176]. Ring core diameters as set to FIB were as follows:

- Inside diameter = 10 µm
- Outside diameter = 12 µm
- Depth = 12 µm

On this occasion, due to excessive milling time, the ring was milled in a single increment. The gallium beam parameters were set to mill at an accelerating voltage of 30 kV and a beam current of 300 pA.

Figure 7.1 (b) shows the image after milling of the pillar.

![Figure 7.1 (a) and (b): SEM images of nanoindent patterning, before and after FIB milling.](image)
7.1.2. Observations and discussion

It can be seen in figure 7.1 (b) that drifting has occurred. This has distorted the surface pattern of the four indents on the pillar surface. The four indents are difficult to see after milling, probably due to the re-deposition of material from the milled ring. The surface texture has also changed, again partly due to material deposition, but also possibly as a consequence of continued rastering of the Ga beam across the surface, whilst in imaging mode, as previously described in chapter 3 section 3.7.

It is imperative to obtain ‘before’ and ‘after’ images, with a high spatial resolution, if digital image correlation (DIC) is to be used for analysis. The two images should exhibit no changes in patterning between ‘before’ and ‘after’. However, following further attempts using lower beam currents, and milled rings with smaller diameters, the resolution and patterning remained poor. For this reason, it was decided to abandon the use of nanoindentation for patterning.

7.2. Surface patterning using gold coating

7.2.1. Experimental details

In an attempt to reduce the charging and drifting problems, a 20 nm thick gold coating was deposited on the sample surface, using a plasma current of 2kV.

When viewed on the SEM, it became apparent that the gold coating itself gave a mottled effect to the surface. So, to enhance this patterning for imaging, and later DIC analysis, the surface was scanned using the gallium beam, according to the following parameters:

Beam current: 30 pA
Accelerating voltage: 30 kV

The gallium beam was scanned and rescanned across a surface area of 30 x 30 µm for about four minutes, resulting in a pattern similar to that shown in figure 7.2.
Chapter 7: Determining residual stress using FIB/DIC

Figure 7.2: SEM image of the gold coated surface of Zircaloy 4 LOCA sample after scanning to enhance patterning.

This patterning was considered more suitable for DIC analysis than the previous nanoindent pattern due to the higher resolution of ‘speckles’. Several milling experiments were carried out on specimens with this surface pattern. Experimental details and a description of the DIC methodology are given later in this chapter.

7.3. Surface patterning using FIB milled indents

7.3.1. Experimental details

Following the unsuccessful attempts using nanoindents to form a pattern, the Ga beam was used to mill out a similar array of indents. Each indent was milled to a size 100 x 100 x 200 nm deep using 30 kV accelerating voltage and 30 pA beam current. At these dimensions it was possible to obtain a better depth/diameter ratio than with the previous nanoindents. The indents were positioned closer together, and the increased depth of the indents suggested that the pattern may be less affected by material deposition caused by the milling process.

An image of the FIB milled indents on a square of platinum coating is shown in figure 7.3.
Figure 7.3: SEM image of FIB milled indents on a platinum square deposited on the surface of recrystallized ZIRLO.

Several milling experiments were carried out on specimens with a surface pattern formed from FIB milled indents, although not all on platinum coating. Further experimental details are given later in this chapter.

7.4. Determining the best conditions for FIB milling annular rings

7.4.1. Experimental details

Optimum milling results depend on obtaining the correct balance of FIB parameters. Each material will behave differently under milling conditions. So, a trial and error approach was taken to determine the best parameters for ring core experiments on Zr alloys.

An accelerating voltage of 30 kV was found to sputter the material too vigorously, thus causing increased material re-deposition after milling, which in turn obscured the original pattern to some extent. The best accelerating voltage was found to be 20 kV.

Milling was attempted under low beam currents, as this was recommended in the literature to cause less charging [95, 96, 176]. Previous researchers suggested milling at small incremental depths, and realigning the central pillar position after each increment.
Chapter 7: Determining residual stress using FIB/DIC

[50, 95, 96]. Pursuing the empirical findings of others [95] who have succeeded in using the ring core, FIB milling technique on TiN PVD coating on a WC/Co substrate, it was attempted to follow suit. It was not possible to find examples in the literature of others using this technique on zirconium alloys.

Results of a selection of millings, completed during this early experimental period, with associated parameters and comments, are shown in figures 7.4 (a) to (e). The majority of the millings here were performed on the same specimen of Zircaloy 4 exposed to 980°C steam (LOCA sample), although there was one mill on Zircaloy 4 rolled plate (see figure 7.4 (e)). The material surfaces were gold coated, with mottled patterning, according to the process described earlier in section 7.2.1. The priority at this stage was to retain a good match between before and after patterns, so different widths of annular trench were tried (figure 7.4 (a)) in an attempt to reduce material deposition on the surface.

![Figure 7.4 (a): The first of a selection of five experimental millings.](image)

(a) LOCA sample; metal

Parameters:
- Wider annular trench
- Acc. voltage 20 kV
- Beam current **23 pA**
- O/D 6 μm  I/D 4.5 μm
- Depth 1 x 2 μm increment
- Circular mill process (see figure 7.5)

Comments:
- A single shallow increment, but the pattern has already been obscured by material re-deposition, despite the wider trench
Figure 7.4 (b)

(b) LOCA sample; metal

Parameters:
Accelerating voltage 20 kV
Beam current 4 pA
O/D 5 μm I/D 4.5 μm
Depth 2 x 0.5 μm increment
Circular mill process
Repositioned after first increment

Comments:
Two incremental mills at a lower beam current than image (a). Pattern has remained reasonable but significant drifting meant the before and after patterns were not comparable due to distortion.

Figure 7.4 (c)

(c) LOCA sample (metal)

Parameters:
Accelerating voltage 20 kV
Beam current 23 pA
O/D 6 μm I/D 5.5 μm
Depth 20 increments of 50 nm = 1 μm
‘Serpentine’ mill process (see figure 7.5)
No repositioning between increments.

Comments:
The best result so far, although still not milled to full depth. 20 incremental mills at the higher beam current. Larger inside diameter has reduced material re-deposition. This time used ‘serpentine’ mill instead of circular. Pattern has remained reasonable (ringed in red)
Figure 7.4 (d)

(d) LOCA sample; metal

Parameters:
- Accelerating voltage 20kV
- Beam current 23pA
- O/D 6μm I/D 5.5μm
- Full depth 110 increments of 50nm = 5.5μm
- 'Serpentine' mill process.
- No repositioning between increments.

Comments:
- The first ring to be milled to full depth.
- 110 incremental mills at the higher beam current.
- Larger inside diameter has reduced material re-deposition.
- Pattern has remained reasonable (ringed).

Figure 7.4 (e)

(e) LOCA sample; metal (high stress) and Zircaloy 4 rolled plate; metal (low stress)

Parameters (both mills):
- Acc. voltage 20 kV Beam 4 pA
- O/D 4 μm I/D 3.5 μm
- Depth 5 x 50 nm increments = 0.25 μm
- Serpentine mill process
- Repositioned after each increment

Comments:
- This was an exercise to see if the drifting may be caused by high residual stresses in the material.
- A mill in the highly stressed LOCA sample is compared to a mill with same parameters, in the low stressed Zry 4 plate. Both drifted.

Figures 7.4 (a)-(e): A selection of mills, with parameters, completed to define the optimum conditions for FIB milling Zirconium alloys.
7.4.2. Observations and discussion

It is clear from the images above that a beam current of 23 pA seems most suitable for milling zirconium alloys. At the lower beam current (4 pA) significant drifting occurred (figures 7.4 (b) and (e)).

This finding seems contradictory in itself, as a lower beam current gives a beam of a smaller diameter, therefore fewer gallium ions are hitting the surface, so one could assume there would be less charge, resulting in less drifting.

It can be seen from the images and parameters above that at 23 pA beam current, changing to a serpentine mill process improved the final result. Figure 7.5 below shows a schematic that depicts the paths of circular milling and serpentine milling processes.

![Circular mill raster](image1)
![Serpentine mill raster](image2)

*Figure 7.5: A schematic representation of the two raster patterns used for FIB milling*

These early trial experiments also show that for this Zr material, re-positioning of the mill position after each incremental cut is not advisable. More drift was evident on those mills where the positions were re-aligned after each incremental cut, as evidenced in figures 7.4 (b) and (e).

Following these results, it was concluded that a larger diameter mill means that material re-deposition remains at the periphery of the pillar, thus leaving a relatively good before and after pattern match in the central region of the pillar surface. At this stage, it was assumed that the mottled pattern effect from the gold coating would be suitable for DIC analysis.

In conclusion, the optimum conditions for the FIB milling of Zr alloy material is considered to be as follows:
Accelerating voltage: 20 kV
Beam current: 23 pA
Outer diameter of annular trench: 6 µm
Inner diameter of annular trench: 5.5 µm
Depth of annular trench: 5.5 µm (milled in 220 increments of 25 nm)

7.5. FIB milling; initial experimental setup

7.5.1. Experimental limitations

Once the ideal parameters had been set, several milling experiments took place regularly. A fair number were unsuccessful, with some mills drifting more than others. There was a period when the milled rings were finishing as offset to each other, as evidenced in the low stress image in figure 7.4 (e). This turned out to be a problem with the FIB mounting stage, and was finally resolved.

A neutralizing flood gun was used on two separate occasions (24/11/09 and 12/01/10 by Dr K.B. Chong, Materials Group, DDEM, The Open University) in an attempt to reduce charging, according to the process described in chapter 3, section 3.7.5 of this thesis. However, the flood gun apparently made little difference to the amount of charging and consequent drifting in the Zr material and it is not understood why, therefore this technique was not used again in this research.

7.5.2. Making the beams co-incident

Having used the ion beam to scan an area of gold coating, to result in a suitably mottled pattern as described earlier in this chapter (section 7.2.1), it is necessary to stop any further scanning by the ion beam when in imaging mode, so that the pattern remains unchanged. So, the stage is tilted back to zero degrees and the surface is then viewed solely in SEM mode. When the patterned area has been focused using SEM, a suitable high resolution (3584 x 3094 pixels) ‘before’ image is captured.

The flow chart in figure 7.6 describes the sequential process of making the electron beam coincident with the ion beam, to enable the mottled gold pattern to remain intact.
Following the last stage in the flow chart, the stage is tilted back to 0˚, and the electron beam is switched on. Using SEM, the milled pillar can be refocused at the same magnification as that in the ‘before’ image, so that an ‘after’ image is taken at the same high resolution.

**Figure 7.6: A flow chart showing the sequence to align electron and ion beams coincident.**
7.6. FIB milling to determine residual stress; gold coated patterning

7.6.1. Experimental details

Using the above process, a ring core was milled on the highly stressed Zircaloy 4 LOCA specimen, in the metal, about 12 µm under the interface. The outside diameter was 6 µm. The annular trench was milled to a depth of 5.5 µm, in 220 incremental depths of 25 nm, to match the inside diameter. The milling parameters were:

Accelerating voltage: 20 kV
Beam current: 23 pA
Serpentine mill raster

The high resolution ‘before’ and ‘after’ images are shown in figures 7.7 (a) and (b). Some drifting is evident, but a section of patterning (ringed) remained consistent. So DIC analysis was carried out using the resulting patterns from this experiment.

![Image 7](image7.png)

Figure 7.7: Before (a) and after (b) SEM images of patterning on the LOCA specimen.

7.6.2. The analysis of gold patterning using digital image correlation

Using the patterning inside the ringed areas shown in images (a) and (b) above, DIC acquisition was applied to the same areas. Figure 7.8 shows the position of the pillar in relation to the metal/oxide interface, and the x and y axes used in the DIC analysis.
7.6.3. Experimental details; DIC

The working principle of the technique depends on the tracking of ‘speckles’ within the surface pattern, and the eventual measurement of displacements of these ‘speckles’. The correlation is between patterns on the surface imaged before and after ring milling.

Prior to analysis, the two images were aligned and corrected for rotations. The success of accurate displacement measurement relies on adequate contrast and intensity of pixels within the pattern.

For the analysis, the interrogation areas (i.e. those ringed in the figures) were masked off from the remainder of the image. These analysis areas were then divided into smaller sub-regions (about 64 x 64 pixels) and each sub-region was individually correlated. Each sub-region has a unique pattern, and each pixel within that pattern has different intensities. The correlation function tracks a particular pattern of pixel intensities, computationally cross correlating it with neighbouring sub-regions, whilst continually referring back to the reference image. Finally, the optimum correlation was calculated by computational algorithms, and the distance between the ‘before’ and ‘after’ sub-regions is...
regarded as the displacement vector. By repeating the process over several sub-regions, a full field displacement map was achieved for each experiment, as shown in figures 7.9 (a) and (b). The displacement strains were then numerically differentiated, simultaneously, in both axial directions, by DIC software.

7.6.4. Results

Figure 7.9 (a)
7.6.5. Observations and discussion

The maps above show that the strain in the acquisition area does not seem to be uniform. So another strain analysis was performed on a smaller, more consistent area on the surface of the same pillar, within the rectangular borders highlighted in figures 7.10 (a) and (b).

As equi-biaxial stress is being measured in this case, the stress results from the DIC analysis are close, but not equal; 347 MPa on the x-axis and –368 MPa on the y-axis. However, due to the reduced area of interrogation, and the inconsistency within the pixel patterns on the DIC maps, the accuracy of these stress measurements cannot be relied upon.

In fact, the map should show uniform colour across the whole of the pillar surface. However, the map representing analysis of the y-axis (figure 7.9 (b)) clearly shows two areas of relatively high stress, within the tensile spectrum. These two areas are related directly to the direction and areas of drift seen in the SEM image figure 7.7 (b). This could be a result of the correlation being affected by the rounding of the edge of the pillar in those regions.
Another reason might be an effect that has been recorded in other strain relieving methodologies, in materials where the yield stress is comparable to the magnitude of the residual stress being measured. In studies of hole drilling [177], ring core milling [178] and the slitting method [179], the measurement of residual stress has been subject to inaccuracies, due to stress concentrations resulting from the cutting process. The stress concentrations tend to occur at the cut edge of the material, impacting on the high residual stresses, resulting in local yielding. This in turn increases the dimensions of the strain displacements, thus leading to over estimation of residual stress measurements. This is because the interaction of the stress concentrations with the residual stresses cause the material to deviate from linear behaviour, so influencing the linear interpretation of strain measurements, that is, vectors in DIC analysis and linear equations in other forms of analysis [180].

![Figure 7.10 (a)](image)
Figures 7.10 (a) and (b): DIC maps and strain results from more concentrated areas of analysis (a) stress on x-axis (b) stress on y-axis.

The patterning technique using gold coating followed by DIC analysis was attempted on three different milled pillars. The results recorded in this chapter were the most successful. The DIC results of the other two attempts can be viewed in appendix B.

It was concluded that the gold patterning technique does not result in a high enough intensity of pixels, and is too prone to damage by material re-deposition. Therefore, when used on zirconium alloys, it is not a suitable patterning technique for accurate digital image correlation analysis.

The FIB milled indents patterning technique was trialed next.

7.7. FIB milling to determine residual stress; FIB indent patterning

Existing research [95] has resulted in successful ring core milling for residual stress evaluation, using FIB milled indents for patterning. An example of their image is reproduced in figure 7.11.
Figure 7.11: SEM image of a ring core mill (TiN PVD coating on a WC/Co substrate) using FIB indents for patterning [95]. A thin layer of platinum (50 nm) was applied prior to indentation.

Using this patterning technique it is essential that the indents are close enough together, and covering the whole pillar surface, to allow for an adequate intensity of pixels for DIC analysis.

### 7.7.1. Experimental details

Previous milling experiments have been on cross sectioned specimens, and in locations of high residual stresses. The priority at this stage was, initially, to obtain a good, clean mill with sharp edges to the pillar, and crisp indents, in an effort to obtain improved DIC results. So the following experiment involves milling the rolling direction surface, of low stress, Zircaloy 4 rolled plate.

Two annular trenches were milled into the metal, on the same specimen, one resulting in a strain relieved pillar without indents on the surface, and the other with an indent array milled into the surface.

In an attempt to reduce charging/drifting effects, a thin layer of the top surface was milled away, thus removing any air formed oxide that may have grown on the surface over time; figure 7.12 shows the square area milled away in the metal ~25 µm from the oxide interface. The square, 12 x 12 x 1.5 µm deep, was FIB milled using the following settings: accelerating voltage 20 kV; beam current 0.76 nA; serpentine mill. Using the same beam
conditions, and physical dimensions, a similar square was milled, followed by an array of indents, as shown in figure 7.13 (a).

Prior to milling the ring, due to the excessive time required to ‘draw’ the grid for positioning indents over the whole area, a smaller array of indents was used for initial trials of this technique. Previous experience of drifting was another consideration in performing this initial trial mill.

Figure 7.13 shows the array of 100 FIB milled indents. The dimensions of each square indent is 100 x 100 x 150 nm deep, with a centre to centre pitch of 260 nm. The ion beam conditions for the patterning were:

- Accelerating voltage: 30 kV
- Beam current: 30 pA

The milling parameters for both annular trenches were the same as those used previously, 6 µm outer diameter, 5.5 µm inner diameter, and 5.5 µm total depth, milled in 220 incremental depth stages of 25 nm. The beam conditions matched those used in the previous experiments:

- Accelerating voltage: 20 kV
- Beam current: 23 pA

Serpentine mill

### 7.7.2. Results

A high resolution image of the first mill (without indents) is shown in figure 7.12.
Figure 7.12: SEM ‘after’ image of the milled pillar (Zry4 plate) without indents.

Presented in figure 7.13 (a) and (b), are the ‘before’ and ‘after’ images of the indented mill.
Figures 7.13 (a) and (b): Zircaloy 4 plate with indents (a) SEM ‘before’ image (b) SEM ‘after’ image, showing the initially pre-set mill position.

7.7.3. Observations and discussion

The first pillar (figure 7.12) was milled in the same material, to the same dimensions, and with identical beam conditions as the second pillar (figure 7.13). The only difference is that the second pillar had an array of indents milled by the FIB. Both mills show evidence of very slight drifting, and this is likely to have taken place during the mill process. However, a different type of drifting has taken place on the indented pillar. Figure 7.13 (b) shows a white cross hatched ring in the exact position where the FIB milled ring should have come out. The remainder of the indent array shows that the individual indents are still intact, with only those at the very edge showing any signs of distortion. However, the ring itself has been milled in a totally different position. This effect is sometimes caused by beam deflection. Some materials are more prone to taking on gallium ions than others. During ion bombardment of the surface, some ions lose momentum and remain within the material, building up positive charge on the specimen surface. This charge repels the positive charge from the Ga ions, and the beam deflects to start milling in a totally different position than was pre-set [81].
As no record has been found, in this literature search, of scientists using this FIB/DIC methodology on zirconium alloys, it seemed that further study might prove interesting. So the investigations were taken further with a short experiment to evaluate whether zirconium takes on gallium.

7.8. The effect of gallium on zirconium alloys

7.8.1. Experimental details

Gallium is used in solid state diffusion bonding [181] particularly with aluminium alloys [182], however the bonding process must take place rapidly or the gallium will attack the aluminium base metal, causing embrittlement at grain boundaries. When gallium is rubbed on aluminium at room temperature, within minutes, the aluminium will bend easily. This is due to the gallium diffusing into the grain boundaries of the aluminium material, causing weakening. To see if gallium has the same effect on zirconium, two Zr alloys were rubbed with gallium; Zircaloy 4 hot rolled plate and ZIRLO plate. First, the Zr surfaces were cleaned and hand sanded using emery paper. This is to remove any grease, and oxidised layer. The gallium was rubbed onto the surface of both alloys, for a few seconds. After waiting a few minutes, attempts were made to bend the Zr specimens. It was not possible to bend either specimen by hand.

In order to expedite solubility of the gallium into the Zr grain boundaries, the two specimens were placed in a furnace for five days at a constant temperature of 400℃. After removal from the furnace, the specimens were left to cool naturally at room temperature.

As no photograph was taken of the samples before they were placed in the furnace, for clarity, a drawing showing the original shapes of the samples is shown in figure 7.15 (a).

7.8.2. Results

Bearing in mind that the melting point of Zr is 1850℃, the results shown in the photograph below in figure 7.15 (b), were unexpected.

After cooling, the ZIRLO plate resembled a pile of ash, whereas in the Zircaloy 4 result, a pile of what looked like, individual particles were observed. The reason for this
discrepancy in appearance is not known at this stage. Further exploration might provide definitive answers.

Figure 7.14 (a): A drawing of the two specimens of Zr alloys, prior to their time in the furnace (not to scale).

Figure 7.14 (b): The effect of gallium on two specimens of Zr alloys, photographed on removal from the furnace. The specimens are viewed from above.
As in the case of aluminium, one might assume that the Zircaloy 4 metal has absorbed the gallium more readily through its grain boundaries. As a result, it was possible to capture a few individual particles (on a sticky pad) to view under SEM. A selection of images are shown in figures 7.15 (a) to (d).
Figures 7.15 (a) to (d): (a) Zircaloy 4 ‘grains’ after gallium intake experiment, (b) to (d) A selection of SEM images, showing Zircaloy 4 and embedded gallium. Full EDX analysis results are shown in Appendix B.
7.8.3. Observations and discussion

It is clear from the SEM images that there is some interaction between gallium and Zircaloy 4. However, it is difficult to determine which material grains we are viewing in figures 7.15 (b) to (d), without extra analysis. So, a comprehensive energy-dispersive X-ray spectroscopy (EDX) analysis was performed on these same material fragments. The round grains (arrowed in image (b)) were found to be gallium the rest of the matter is zirconium. The full EDX results along with the analysis points are available to view in appendix B.

It was not possible to find a Zr-Ga binary phase diagram that showed phase changes at temperatures as low as the 400°C used in this experiment. However, there are two factors that should be considered;

1. The melting point of Zirconium is around 1852 °C and in comparison, the melting point of gallium is only 29.78 °C [183].
2. There is a large difference in atomic size between zirconium and gallium [183].

Taking these two facts into account, the possibility of liquid metal embrittlement via grain boundaries cannot be ruled out as the cause of the experimental results shown in figure 7.14 (b) and figure 7.15 (a)-(d).

The SEM images indicate that zirconium does indeed take on gallium. To understand the extent of gallium solubility, it was advisable to compare the results here, with another material thought to be less affected by gallium.

Pure titanium foil was chosen, mainly due to its large grain size so fewer grain boundaries, making it less likely to take on gallium ions during the milling process. The lack of added elements means there are no extraneous effects from the properties of other elements, sub grains or secondary phases (Dr. A. Shirzadi, personal correspondence by email, 8th September 2011).
7.9. FIB milling of pure titanium

7.9.1. Experimental details

The dimensions of the pillar, the indent array and the ion beam conditions for the pure titanium experiment were exactly the same as those used earlier on Zircaloy 4 plate (section 7.7.1). Prior to milling the annular trench, a shallow square was milled in the titanium surface, as in the previous experiment, with the aim of removing any oxidized layer.

As for the previous sequence of experiments on Zircaloy 4, a pillar was milled without indents on the surface, followed by another milled pillar with an array of indents. In this experiment the emphasis was not to obtain a good high resolution ‘before’ and ‘after’ image, but to see how the pure titanium behaved under gallium ion bombardment. The SEM image in figure 7.16 shows the first mill, in titanium, of the pillar without indents.

![Figure 7.16: SEM image of the 1st mill (without indent pattern) in pure titanium.](image)

The SEM image in figure 7.17 shows the second mill, in titanium, to the same parameters, this time on the pillar with indents.
7.9.2. Observations and discussion

As seen previously on Zircaloy 4 plate, the pillar without indent array, milled in pure titanium, shows little sign of drifting. However, once the surface has indents milled using the gallium ion beam, the drift is more significant. The red rings show where the annular ring should have been milled. As there is more drift than on the Zr mill, and the drift here seems to match the offset of the yellow and red rings, it does not indicate that the beam has deflected to the same extent as the Zircaloy 4 deflection. But does this mean that the pure titanium foil has not taken on gallium ions? To investigate, a comparative analysis was carried out on the two specimens, using EDX, to quantify the gallium uptake.

7.10. Investigation by energy-dispersive X-ray spectroscopy (EDX)

A comprehensive EDX data acquisition and analysis, was performed on the surfaces of the four milled pillars:

- Zircaloy 4 hot rolled plate, no indents
- Zircaloy 4 hot rolled plate, with indents
- Pure titanium foil, no indents
- Pure titanium foil, with indents
7.10.1. Experimental details

EDAX Genesis live mapping system was used for these EDX experiments. The mapping resolution was 256 x 200 with a dwell time of 200 µs at each point. Each data acquisition was left for a period of 50-70 seconds. Accelerating voltage for the SEM was set to 15 kV, and the magnification was around x 45000.

The EDX analysis on Zircaloy 4 with indents, was carried out on a different milled pillar than that imaged in figure 7.13. The pillar chosen for this data acquisition, showed increased deflection of beam, so it was thought that it might show a higher solubility of gallium.

7.10.2. Results

Table 7.1 gives the overall results of the EDX measurements, on different areas of the pillars’ surfaces. The full size images, complete data spectra and results for both Zr and Ti, can be viewed in appendix B.
### Table 7.1: Table of EDX acquired data on element content (wt%) for Zr, Ti and Ga.

<table>
<thead>
<tr>
<th>Material</th>
<th>Base metal content (wt%)</th>
<th>Ga content (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Zircaloy 4 pillar without indents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centre of pillar surface</td>
<td>97.19</td>
<td>2.81</td>
</tr>
<tr>
<td>Bottom right quadrant of pillar surface</td>
<td>96.72</td>
<td>3.28</td>
</tr>
<tr>
<td><strong>2. Zircaloy 4 pillar with indents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-indentated area</td>
<td>96.94</td>
<td>3.06</td>
</tr>
<tr>
<td>Indented area</td>
<td>95.63</td>
<td>4.37</td>
</tr>
<tr>
<td><strong>3. Pure titanium pillar without indents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Centre of pillar surface</td>
<td>95.35</td>
<td>4.65</td>
</tr>
<tr>
<td>Bottom right quadrant of pillar surface</td>
<td>93.88</td>
<td>6.12</td>
</tr>
<tr>
<td><strong>4. Pure titanium pillar with indents</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Non-indentated area</td>
<td>92.10</td>
<td>7.90</td>
</tr>
<tr>
<td>Indented area</td>
<td>96.61</td>
<td>3.39</td>
</tr>
</tbody>
</table>
7.10.3. Observations and discussion

As shown in the results table, there is an increase in wt % gallium, between all point acquisitions taken at the central, non-indentated regions and those taken in the bottom left quadrant of the pillar surface (experiments 1-3 on table 7.1). However, in the pure titanium indented pillar (experiment 4 on table 7.1), it was not possible to take data acquisition at the centre without indents, and these results oppose those of experiments 1-3. The high value of 7.9 wt% gallium in experiment 4 was probably due to the high incidence of gallium in the interrogated area. This is evidenced in the EDX map in figure 7.18, where green represents gallium, and red represents the bulk material, in this case titanium. The map shows that in reading the data for this EDX analysis, there was not a suitable acquisition area available that was free of gallium and outside the area of indents.

![Figure 7.18: An EDX map showing solubility areas of pure titanium (red) and gallium (green) as ref.4 on table 7.1.](image)

Differentiation in results on the titanium acquisitions is larger than those on zirconium. This is the opposite of what was expected, but no attempt was made to investigate this further.

The EDX results on the Zircaloy 4 sample do show a small increase in gallium count, at around 1%. It is not known whether this is enough of an increase to cause deflection of the ion beam.
Results from the EDX analysis comparing zirconium and titanium in terms of gallium uptake during FIB milling are not conclusive. This research did not set out to investigate the uptake of gallium in zirconium alloys, and the experiments were completed whilst writing this thesis was in progress, so time was limited. Nevertheless, it was an interesting exercise, and it is thought that this is the first time gallium penetration of zirconium alloys has been investigated using these techniques. It is hoped that these findings may provide a framework for further explorations in this field.

7.11. Chapter conclusions

This part of the research was aimed at FIB milling a strain relieved pillar in a zirconium alloy, so that strain differentiation could be measured using displacement of pattern changes between the pre-milled (stressed) material surface, and the post milled (stress relieved) surface. It was hoped that digital image correlation would be successful in analyzing the patterns changes.

Several annular trenches were milled to obtain optimum pillar sizes and beam conditions. Three different patterning techniques were trialed; nanoindent arrays, FIB mottled gold coating and FIB indent arrays.

The main limitation in the milling experiments was zirconium’s inclination to charging and drifting. The drifting prevented a totally level pillar surface, reducing the ‘whole area’ pattern, leading to discrepancies in the before and after images. As a consequence, there was not a good enough correlation for successful digital image analysis by DIC.

The main conclusion to be drawn from this chapter is that zirconium is an unsuitable material for FIB milling to such accurate precision.
Chapter 8: A study of the deformation of zirconium alloys

This chapter includes a systematic study of four different Zr alloys, in terms of the way that they deform under load. The experiments contained in this chapter focus on the time dependent behaviour of the materials. Aspects covered include; indentation creep, high strain exponents \( (n) \) determined by nanoindentation, strain exponents by mechanical relaxation testing, EBSD analysis of texture, and deformation twinning underneath a high load Vickers indent.

8.0 Introduction

Metals and components in high temperature environments, such as light water reactors, and those under a high stress regime, can sometimes exhibit continuous increases in strain, even when the applied stress is below the value of yield stress of the material. This is known as time-dependent deformation or creep.

In chapter 6 we saw that nanoindentation loading curves showed only a small percentage offset in response to a high magnitude residual stress. To see if indentation creep tests responded to changes in residual stress, an experimental study into the deformation of four different materials was conducted.

8.1 Creep

Conventional creep tests involve subjecting a specimen to uniaxial load, monitored over long periods of time, at a constant temperature greater than \( 0.4 \ T_m \), where \( T_m \) is the absolute melting temperature, in Kelvin, of the specimen material. Under these conditions, the change in length (creep strain) of the specimen is measured over fixed time intervals.

8.1.1. Conventional uniaxial creep testing

In a conventional creep test, on the initial application of load, an instantaneous elastic deformation takes place. This is indicated in figure 8.1.
Primary creep, Stage I, is a period of decreasing creep rate. During this period deformation takes place and the resistance to creep increases until stage II. Secondary creep, Stage II, is a period of almost constant creep rate, referred to as steady state creep. Stage III indicates when there is a change in cross sectional area of the specimen (necking), eventually leading to fracture.

Creep can occur via different mechanisms, for example, dislocation glide (climb or glide-plus-climb) and diffusion (lattice diffusion or grain boundary diffusion), dependent on the material structure, stress, and temperature conditions. The mechanisms of creep depend on stress and temperature. There are basically two types of secondary creep mechanisms that occur in metals [185]:

1. Dislocation creep
2. Diffusion creep

Dislocation creep involves the motion of dislocations (crystallographic defects) in a material under high stress. At low temperatures, movement of dislocations occurs through 'glide' along slip planes. Dislocations will 'glide' to adjacent slip planes to avoid obstacles in their path. These obstacles might include material defects such as precipitates, grain
boundaries or other dislocations. At high temperatures, vacancies in the crystal lattice can diffuse into locations of dislocations. These dislocations are then energised and can ‘climb’ over obstacles and move to a different slip plane [185].

**Diffusion creep** relies on their being free neighbouring sites in a material’s crystal lattice for atom diffusion to occur. There are two types of diffusion creep:

1. Nabarro-Herring creep
2. Coble creep

*Nabarro-Herring creep* is strongly temperature dependent and dominates at high temperatures [186, 187]. In materials under stress, this creep process occurs by atomic vacancies or defects diffusing through the crystal lattice. This form of creep is also known as bulk diffusion.

*Coble creep* occurs at lower temperatures and lower activation energies than Nabarro-Herring creep. In a material under stress, atoms diffuse within the boundary of a material grain, causing the grain to elongate along the stress axis. The rate of Coble creep is higher in materials with a small grain size, and lower in materials with larger grains, as there are fewer grain boundaries [188].

In conventional time and temperature based creep tests, power-law creep behaviour, during steady state creep, is described by the following equation [34]:

\[ \dot{\varepsilon} = C\sigma^n \exp\left(\frac{-Q}{RT}\right) \]  \hspace{1cm} (46)

Where \( \dot{\varepsilon} \) is the difference in strain/difference in time (known as strain rate or creep rate). 
\( C \) is a constant dependent on the structure of the material, \( Q \) is the activation energy in terms of the rate controlling process, \( T \) is the absolute temperature in Kelvin, and \( R \) is the universal gas constant. \( n \) is the exponent of stress (\( \sigma \)). The activation energy (\( Q \)) is responsible for the movement of dislocations, and results from the thermal motion of atoms, in addition to applied stress [189].

**8.1.2. Indentation creep tests**

In a typical constant rate of loading (CRL) instrumented indentation test, it is recommended to set a dwell period at maximum load before unloading [190] [191]. The
maximum load is held steady for an advised dwell time of 10 to 60 seconds to allow any creep to dissipate. In some materials, the indenter will continue to displace (creep) into the surface, even though there is no increase in load. Depending on the material, at the beginning of the dwell period, the creep rate can reach values of several nanometres per second, whereas by the end of a 10-20 s dwell period, the value can be as low as 1 nm/s [191]. Keeping the dwell time short has the added advantage of eradicating thermal drift effects during testing [192].

The constant monitoring of instrumented indentation tests during the loading/unloading process makes it very easy to collect information during extended peak load dwell periods, to evaluate creep in a material. During the whole test process the displacement and time are being constantly monitored and the resultant data can be used to plot displacement/time graphs.

As we know, creep is time-dependent plastic deformation, under stress. In conventional creep tests the stress is defined as uniaxial force/cross-sectional area (F/A), whereas in indentation creep tests, the equivalent of the stress, \( \sigma \), in equation 8.1 is indentation hardness; \( H = P_{\text{max}}/A_C \). So, the equation for measuring steady state strain rate by indentation is adapted from equation (46) accordingly [34]:

\[
\dot{\varepsilon}_i = C_i \, H^n \, \exp \left( \frac{-Q}{RT} \right)
\]

(47)

In materials that exhibit time dependent behaviour when under indenter load, creep occurs in the plastic deformation zone immediately under the indenter tip, even at room temperature. Early researchers defined the general deformation field under an indent as almost hemispherical [193, 194], with the area immediately under the indenter tip representing a hydrostatic cavity expanding under pressure [195] as depicted schematically in figure 8.2.
Stress in the material below the indenter is at its highest magnitude nearest to the tip [190]. This indenting stress is linked to a power law relationship representing uniaxial stress/strain behaviour as defined in equations 8.1 and 8.2. Stress exponents range from $n = 1$ (for a Newtonian viscous solid) and $n = \infty$ (for a rigid, perfectly plastic solid) [196]. Most metals have a stress exponent value between 1 and 10 [197-199]. However, there have been experiments yielding very high stress exponents with values between 30 and 100 [200-202].

**8.1.2.2. Indentation creep strain rate**

The diameter of the deformation zone under the indenter has a linear relationship to the displacement of the indentation [203]. According to Bower et al. [196], even though the deformation zone under an indent will expand during indentation loading, the related stress in the material under the indenter does not vary to any extent. However, the indent contact area will change over time. The rate at which the deformation zone boundary expands into the material is thought to be a controlling factor in the indentation creep process [197].

Nanoindentation testing carried out in this research involved using a Berkovich pyramidal indenter tip, for which the strain rate equation is [198]:

![Figure 8.2: A schematic representation of the deformation field, including the hydrostatic cavity immediately below the indenter tip [192].](image-url)
The change in indentation depth ($\Delta h$) during the dwell period is plotted over the change in time ($\Delta t$) during the dwell period. By taking the log of indentation strain rate as a function of the log of indentation hardness ($P/A_c$), a straight line graph is produced, and the slope of this graph defines the stress exponent, $n$.

### 8.2. An experimental study into the deformation of zirconium alloys

#### 8.2.1 Materials

Four alloys were used in this study:

- Zircaloy 4 hot rolled plate (RD)
- Zircaloy 4 980˚C steam (LOCA), tube
- ZIRLO, RXA, 415˚ C 660 days autoclaved, plate
- ZIRLO, SRA, 360˚ C 134 days autoclaved, tube

All specimens were indented at room temperature, in an isolated room with an ambient temperature of 21˚ C. All specimens had been prepared according to grinding and polishing conditions outlined in chapter 5, section 5.2. No oxides were indented.

#### 8.2.2. Indentation creep; experimental details

Each of the four materials was exposed to three different indentation loads; 10, 0.5 and 0.1 N. The latter two loads have already been defined as the optimum loads for obtaining the most accurate values of hardness and elastic modulus, using the analysis method described in chapter 6, section 6.1. During the indentation testing, each material was set a dwell time at peak load. Three different durations of dwell time were set; 30 s, 60 s and 300 s. Ten tests were done at each load and for each dwell period. The data from the median of those ten tests was used for analysis.

#### 8.2.2.1. Indentation creep; experimental analysis

For each of the four alloys, creep strain ($\Delta h/h_{\text{max}}$) was calculated from every data point over the peak load dwell period, for each of the three loads. The creep strain was then

\[
\dot{\varepsilon} = \frac{1}{h} \frac{\Delta h}{\Delta t}
\]
plotted over all changes in time data for the same dwell periods. Some results for the 30 s hold period are displayed in figures 8.3. These tests had a loading time of 15 s.

8.2.2.2. Indentation creep; experimental results

Figure 8.4(a) displays a set of conventional creep curves ($\Delta$ displacement/$\Delta$ time) for the Zircaloy 4 cold rolled plate (rolling direction). These are results from early experiments in this project and have been included as further evidence of the indentation creep findings to be discussed in the next section. The loads and peak load dwell holds are stated on the figure. The loading time was 15 s. Figure 8.4(b) shows the nominal creep strain ($\Delta h/h_{\text{max}}$) as a function of peak load dwell time (30 s).
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**Figure 8.4(a):** A set of creep curves from nanoindentation creep tests on Zircaloy 4 cold rolled plate metal.

**Figure 8.4(b):** A set of creep curves showing creep strain/hold time for the 30s dwell period for the three different loads (taken from same data set as shown in figure 8.4(a)).
8.2.2.3. Indentation creep tests; observations and discussion

For each test, during the peak load dwell time, the load remained constant, yet displacement of the indent increased. The deformation zone of material under the indent was continually expanding and enveloping more of the unstrained material, even though there was no load being applied.

During the peak load dwell period, the contact area of the indent is increasing, so, as the overall contact pressure on the material reduces, the rate of indent displacement decreases proportionally. The increase in indent contact area can lead to a reduction in measured hardness values, in accordance with the equation for indentation hardness:
\[ H = \frac{\text{load}}{\text{area}} = \frac{P}{A} \] [34].

What’s interesting in the figure 8.4(b) results is that all the creep curves overlay each other, irrespective of load. A similar phenomenon is seen in three of the graphs shown in figure 8.3. However, scatter is observed in the curves of the LOCA sample, possibly due to the high embrittlement in this sample.

The fact that the creep curves overlay is indicating that the creep strain rate is the same for each of the different loads. As we know in an indentation creep test, the load is held constant over a peak load dwell period, so in theory and according to the conventional steady state creep process, the cross sectional area should also remain constant, so stress (F/A) will remain constant. However, in these test results, because the indenter continues to displace, the contact area of the indent is increasing. Hence, the stress (F/A) is decreasing and therefore not constant. This suggests that what we are seeing here is not creep in the conventional sense and so may not be a result of creep deformation, but this is not yet clear.

8.2.3. Defining stress exponent ‘n’ by nanoindentation

8.2.3.1. Deformation mechanisms

As shown earlier in equation 8.1, \( n \) is the stress exponent (or creep exponent) in the equation for steady state creep. Different values of \( n \) have been linked to the various deformation mechanisms of plasticity that in turn, contribute to indentation creep.
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For example, for \( n \) values of around 1, diffusional creep may dominate, especially in materials with a grain size < 0.4 µm. For \( n \) values >3, particularly in materials under high stress, it is likely that movements of dislocations in the crystal lattice are dominating the creep process [204, 205]. By accounts of others in the literature, it seems that plasticity by dislocation glide, at temperatures ranging from room temperature to the materials melting point, is the dominating mechanism for controlling creep. Whether creep is controlled by dislocation glide or glide plus climb will depend on physical obstructions to the process, such as grain boundaries or interfaces [204-206].

8.2.3.2. Defining stress exponents using nanoindentation

Figure 8.5 shows the components of a single, typical indentation test load ramp/hold sequence performed at room temperature on Zircaloy 4 plate. The data was obtained for loading of the indenter to a pre-defined peak load (10N), and for the whole duration of the dwell time at peak load (30 s). The loading time was 15 s. When determining the indentation strain rate (\( \dot{\varepsilon} \)) the following is assumed:

\[
\dot{\varepsilon} = \frac{\dot{h}}{h}, \quad \sigma = \frac{P}{Ah^2}
\]

Where \( \dot{h} = \Delta h/\Delta t \) and \( h \) is the displacement of the indent. \( \sigma \) is indentation hardness, \( P \) is indentation load, and \( A \) is the contact area of the indent as defined in equation 2.15 in chapter 2. It is assumed that hardness is proportional to stress and uniaxial strain rate is proportional to indentation strain rate [16].

8.2.3.3. Analysis of data to define stress exponents

Microsoft Office Excel was used to analyse the data and all indentation creep tests were analysed using the following methodology. To allow for any early extraneous affects like drift to subside, the first few data points from the indentation test were not analysed.

The stress exponent \( n \) is the slope of the graph defined as:

\[
n = \frac{\Delta (\log \dot{\varepsilon})}{\Delta (\log \sigma)}
\]

Strain rate and stress differentials from each alternate data point were extracted. The total data set analysed included differentials from the start of the 15 s loading ramp up to the last data point of the 30 s peak hold, just before the indenter unloaded.
8.2.3.4. The strain rate/stress graph

Figure 8.5 shows the components of a typical log strain rate/log H graph. The stress exponent is determined from the gradient of the peak hold section.

![Log strain rate vs log hardness graph](image)

*Figure 8.5: A graph showing the components of log strain rate/ log hardness. (Zircaloy 4 plate).*

8.2.4. Stress exponent values for the different zirconium alloys

Data from indentation tests on all four materials were analysed to determine the stress exponents. The analysis process used was the same as that described in section 8.2.2.1. These tests were also part of an investigation into loading rate sensitivity (discussed later in section 8.3), so different loading times were applied, as defined on the graphs in figures 8.6 to 8.9, displayed over the next two pages.
8.2.4.1. Stress exponents; results

Figure 8.6: Stress exponent values for 10 N load indentation tests on Zircaloy 4 plate at four different loading times.

Figure 8.7: Stress exponent values for 10 N load indentation tests on Zircaloy 4 980°C LOCA sample, at four different loading times.
Figure 8.8: Stress exponent values for 10 N load indentation tests on ZIRLO SRA, 134 days autoclaved, at four different loading times.

Figure 8.9: Stress exponent values for 10 N load indentation tests on ZIRLO RXA 660 days autoclaved, at four different loading times.
8.2.4.2. Observations and discussion; stress exponents

In all of the four materials, there seems no influence from loading times on the value of the stress exponents.

The 'n' exponent represents the relationship between creep (strain) rate and stress. The results shown in the section above prove that there is a very high stress dependence of the strain rate, and it is important to understand why. The high values of 'n' could be due to some unusual form of dislocation creep, or even deformation twinning, although twinning could be due to cracking under an indent [207].

The indentation strain rate directly monitors the increase in volume of the expanding hydrostatic cavity under the indent [208]. In theory, this means that strain rate should be linked in the same way, to both deformation by load relaxation as it is to deformation by compression [209]. So, to investigate the high values of 'n' in the Zr material, two further experiments were carried out. In brief, experiment 1 involved placing a large Vickers indent into Zircaloy 4 hot rolled plate, then cross sectioning through the centre of the indent to expose the deformed zone under the indent for EBSD analysis. Experiment 2 involved performing a load relaxation test on a dogbone shaped sample of the same plate. Coupons of material from the most deformed regions and the least deformed regions were then cut out and cross sectioned to expose the deformation zones for analysis using EBSD. Further details of these experiments are given in the next two sections.

8.2.5. Load relaxation test; Zircaloy 4 hot rolled plate

Load relaxation is an efficient form of mechanical, uniaxial testing, often used to investigate the effect of strain rate, and sometimes temperature, on the deformation of a material. The methodology of load relaxation testing has been covered fully in chapter 5, section 5.5.

8.2.5.1. Experimental details; load relaxation

A dogbone shaped sample of Zircaloy 4 hot rolled plate was cut for this experiment, according to the dimensions shown in figure 8.10. Testing focused on the central region of the gauge section, as deformation will be localised to this smaller cross sectional area.
Also shown in the figure above are two coupons cut out of the dogbone specimen after relaxation testing. Coupon ‘a’ is representative of the most highly deformed area, following the relaxation test. Coupon ‘b’ represents the least deformed area. The coupons were cut for an assessment using EBSD. The results are shown later in this chapter, section 8.6.

The relaxation test was performed according to the description in chapter 5 section 5.6.2. The test frame used for this experiment was an INSTRON 3367, with a 30 kN load cell capacity. The acquisition software was Instron Bluehill 2. The experiment was carried out at ambient room temperature and the test frame was isolated from vibration.

The wider ends of the dogbone specimen were used to clamp the sample onto the load frame, the clamped specimen was then aligned axially to minimise bending. Tensile loading of 24.48 kN was applied in extension control, at a constant strain rate. One end of the specimen was held firm by the fixed lower part of the frame, whilst the top cross head moved upwards at a rate of 2.5 mm per minute. Load/time data was continuously
recorded to beyond the material’s elastic limit; 200 MPa to a final loading point of ~380 MPa. At this point, the loading was stopped, so that any strain in the sample was kept constant, whilst the load decreased (relaxed) over time.

Mean data of the decrease in load/time was recorded during the relaxation period by strain gauges fitted to both faces of the dogbone specimen, in the central gauge section, with an extensometer.

This whole test was completed within a single cycle of loading and relaxation. Data was acquired every 0.2 s consistently throughout the whole test period, to enable later analysis for accurate values of stress exponent $n$.

8.2.5.2. Data analysis; stress relaxation

MS Office Excel software was used to analyse the data from the load relaxation test. Mean strain values were taken from the strain gauges to be plotted as a function of time. Strain rate data was taken from the whole period of tensile stress ‘relaxation’, from the moment that the top cross head stopped. Average tensile stress values were calculated from subsets of data points within the overall dataset. The average tensile stress value for each data subset was calculated by adding the value at the beginning of the subset to the value at the end of the subset, then dividing the result by two. This resulted in twelve average tensile stress values representing the whole relaxation period (716 s).

Using the same span of data subsets the strain rate was calculated by plotting the difference in strain over the difference in time over all data points in each subset, resulting in a value of strain rate corresponding to each of the twelve mean tensile stress values. The two columns of data were then plotted as log strain rate/log stress, to evaluate the stress exponent. Error bars were calculated on ±5% of the absolute values of log strain rate for each point. The resultant graph is shown in figure 8.11.

8.2.5.3. Results; stress relaxation

The graph in figure 8.11 defines the gradient of the straight line as $m = 36.8$. Hence, the value of the stress exponent for Zircaloy 4 rolled plate, as defined by load relaxation testing is $n = 36.8$. 
8.2.5.4. Observations and discussion; stress relaxation

The load relaxation test result of $n = 36.8$ correlates very well with the $n$ exponents resulting from nanoindentation creep tests, as displayed earlier in figure 8.6. This suggests that the same deformation mechanisms are working in both the tensile test and the indentation tests. What we are seeing here is not creep in the conventional sense, that is, deformation under constant applied loading, and usually at high temperatures. The results indicate that the deformation may be related to some kind of relaxation of the mechanism activated during the loading process.

Stress exponents have been found to exhibit a strong dependence on indentation loading time. Ma et al. [210] found that when indenting polycrystalline nickel thin films, they consistently found loading rate sensitivity in their material, and suggest that “there is a difference in deformation mechanism during creep”. So, to see whether the four Zr alloys listed in section 8.2.1, exhibit loading rate sensitivity, and to investigate if this may lead to an insight into the deformation mode being experienced, a further set of nanoindentation creep tests were performed.


8.3. Loading rate sensitivity

8.3.1. Experimental details; loading rate sensitivity

On each of the four alloys ten indentations were performed at 10 N load, with a 300 s peak load dwell period. These tests were repeated for four different loading times, that is, the time it takes the indenter to reach peak load. The loading times were; 5 s, 15 s, 30 s and 60 s. The median of each set of ten test results was used for analysis.

8.3.2. Experimental analysis; loading rate sensitivity

Firstly, to determine stress exponent, $n$, from each loading time data set, the same analytical process was used as described earlier in section 8.2.3. (log strain rate/ log stress). Figure 8.12 displays the graph of the four stress exponents, one for each loading time, plotted as a function of all four loading times.

For comparison figure 8.13 shows the results that Ma et al. [210] obtained from nanoindentation creep tests on nickel films.

8.3.3. Experimental results; loading rate sensitivity

![Figure 8.12: Variation of stress exponents/loading times for four Zr alloys.](image)

Figure 8.12: Variation of stress exponents/loading times for four Zr alloys.
8.3.4. Observations and discussion; loading rate sensitivity (LRS)

The results of Ma et al. as shown in figure 8.13 indicate significant sensitivity of their stress exponents to their loading times. In contrast none of the four Zr alloys tested in this study demonstrated sensitivity to loading times. The fact that Nickel is an f.c.c. metal, so will have more slip systems than zirconium, could be a possible explanation.

This discord in results throws up questions in need of further investigation. Ma et al. imply that, as the stress exponents in their material change according to the loading conditions, there is some intrinsic creep mechanism at work. The present results from both nanoindentation creep tests and the load relaxation test on Zircaloy 4 also indicate an unusual creep mechanism is involved, but the findings shown in figure 8.12 suggest that it is unlikely to be influenced by loading conditions.

Further investigations into creep mechanism continue with an examination of deformation by twinning.
8.4. Material deformation by twinning

Deformation by twinning is known to occur in h.c.p. materials at room temperature [207, 211, 212]. Huang et al. [207] suggest that deformation twinning may have been operative in the deformation of Zircaloy 4 following results from their relaxation tests carried out at a selection of temperatures including room temperature. Song and Gray [213] carried out a comparative study between twinning and slip deformation modes on pure zirconium at different temperatures. They found twinning to be the main mode controlling material deformation at very low temperatures (73 K), whereas they implicate slip as the dominating mechanism in environments above room temperature. In addition to twinning observations, changes in texture have been recorded in h.c.p. metals [212].

Twinning and texture are briefly explained in the next two sections. Following on are details of two experiments performed to assess twinning deformation and texture changes in the same Zircaloy 4 plate used to assess the high values of stress exponent.

8.4.1. Twinning

Twinning is where part of a crystal lattice is ‘flipped’ to form a mirror image of its other half. The plane of symmetry between the two halves is called the twinning plane. Mechanical twins are produced by shear forces that cause displacements of the atoms in a crystal lattice, and normally appear in metals with either b.c.c. or h.c.p. crystal structures. Annealing twins are a result of annealing heat treatments following deformation [33]. Figure 8.14 is a simple schematic representation of a crystal lattice before and after twinning.

![Figure 8.14: A simple example of twinning in a crystal lattice.](image)
At room temperature, in metals with very high stress concentrations, deformation twinning can occur [212]. In zirconium alloys, twinning can result from loadings in either tension [207] or compression [207, 211].

8.5.1.4. Texture

In metals and alloys subjected to considerable mechanical deformation (e.g. forming processes), the material grains tend to follow a preferred orientation (texture). The axial ratio c/a for zirconium is 1.593 [214]. This is below the normal crystal axial ratio of 1.633. The lower ratio in Zr means less lattice resistance, under deformation, in prism planes than for basal and pyramidal planes. Hence, in zirconium, slip occurs more easily on prism planes [215]. The different slip planes are shown schematically in figure 8.15.

![Figure 8.15; Different slip planes [142].](image)

In an h.c.p. crystal, slip deformation is considerably easier along the a axis than on the c axis. Axes a, b and c are shown in figure 8.16 Under this slip deformation, zirconium will develop a preferred crystallographic orientation (texture) [214].
8.5. **EBSD**

To investigate twinning as a possible deformation mechanism in the zirconium material, results from two experiments were assessed using EBSD. Details of the EBSD apparatus and technique are described in chapter 5, section 5.5.3. Both experiments were carried out on Zircaloy 4 hot rolled plate.

The first experiment involved looking at the deformation underneath a large Vickers hardness indent. For comparative analysis, a non-deformed area away from the indent was also examined using the same criteria. The second experiment involved comparing the deformation from coupons ‘a’ and ‘b’, as cut from the ‘dogbone’ sample used in the relaxation test as described earlier in section 8.2 of this chapter.

### 8.5.1. Experiment 1; deformation under large Vickers indent

A large Vickers indent was placed into the surface (rolling direction) of Zircaloy 4 hot rolled plate. The indent was then sectioned just offset from the centre using the EDM cutting technique (chapter 5, section 5.2). In order to obtain good EBSD indexing, the cross sectioned surface was then ground, polished and etched, according to the process described in chapter 5, section 5.2. An SEM image of the prepared cross sectioned indent is shown in figure 8.17.

The region immediately below the indent tip, and another area away from the indent were then examined using EBSD.
8.5.1.1. Experiment 1; EBSD data acquisition.

Immediately prior to data acquisition, random spot checks were carried out to obtain adequate Kikuchi patterns. An example of a resultant pattern is shown in figure 8.18. The actual data acquisition was performed using the Flamenco software [150]. Pre-set incremental steps of 0.5 µm were recorded over a matrix of 600 x 600 µm in the region immediately below the tip of the Vickers indent. The process has already been explained in more detail in chapter 5, section 5.5.3. This data acquisition process was then repeated in a non-deformed region about 2 mm away, on the x-axis from, the centre line of the Vickers indent. Indexing of around 75% was achieved in each test.
The SEM parameters for both EBSD tests were as follows:

Accelerating voltage: 20kV
Current mode: high (approx. 2.28 nA)
Aperture: 60 microns
Magnification: x600
Working distance 15 mm

8.5.1.2. Experiment 1 results; EBSD maps

The data produced by the Flamenco software were analysed using the Tango software module [150]. Figure 8.19 shows a CSL boundary map for the area immediately below the tip of the Vickers indent (shown schematically). The region of the highest deformation is arrowed. Grains showing twinning boundaries are ringed. The twins are recognised by their lenticular shape. Figure 8.20 shows a CSL boundary map for the non-deformed area away from the indent.

Figure 8.19: EBSD map of the area underneath the large Vickers indent (twins shown ringed). The area immediately under the tip of the indent is arrowed.
8.5.1.3. Experiment 1 results; twinning planes

Unfortunately, the Tango software will not produce actual twinning maps for h.c.p. materials, only cubic (Personal correspondence, Oxford Instruments by telephone 03/06/11). Therefore, it was necessary to produce misorientation maps, and then measure angle differences across the twinning plane to expose the indices. A selection of examples taken from the deformed area under the large Vickers indent is shown in figures 8.21 to 8.23.
Fig 8.21: EBSD map 1 showing an example of twinning in \{10\overline{1}2\} plane.

Fig 8.22: EBSD map 2 showing an example of twinning in \{1012\} plane.
Fig 8.23: EBSD map showing an example of twinning in \{11\overline{2}3\} plane.

The twins identified in the above maps correlate with the findings of others for the main twinning modes found in zirconium [212, 214, 216, 217].

8.5.1.5. Experiment 1: Texture; pole figures

In order to evaluate texture in the two regions around the Vickers indent, the Tango program was used to produce the inverse pole figures depicted below in figures 8.24 and 8.25.

Figure 8.24: EBSD pole figure for the deformed area underneath the large Vickers indent.
8.5.1.6. Experiment 1: Observations and discussion

As expected the deformed area immediately below the indent does show evidence of twinning, whereas in the non-deformed region away from the indent, no grain twinning can be seen. The twinning planes identified were predominantly in the \{1012\} direction. This follows the findings of others [212, 214].

When examining the inverse pole figures showing texture of both deformed and non-deformed regions, there is no significant general change in texture. Preuss et al. [212] observed significant texture changes at room temperature, even at very small percentages of deformation (<5%). However, when the pole figures from the experiments in this research are compared, apart from a loss of one of the ‘eyes’ (poles), there are no changes in the texture.

8.6. Experiment 2; deformation by load relaxation

8.6.1. Experiment 2; experimental details

Two coupons were cut from the dogbone shaped specimen:

1. From the central, most deformed region (coupon ‘a’ shown in figure 8.10)
2. From the least deformed region in the wide section of dogbone (coupon ‘b’ in figure 8.10).

Each coupon was then cut again in the plane shown in figure 8.10. The two coupons were then mounted in conductive resin, with the cut faces exposed for analysis by EBSD.
order to obtain good EBSD indexing, the cross sectioned surfaces were then ground, polished and etched, according to the process described in chapter 5, section 5.2.

8.6.1.1. Experiment 2; EBSD data acquisition

Both coupons ‘a’ and ‘b’ were examined using the same EBSD acquisition process as carried out in experiment 1. The central region of each coupon was examined. Flamenco software was again used for the data acquisition. However, this time, indexing values achieved were 87% for coupon ‘a’ and 94% for coupon ‘b’. SEM parameters were the same as those used in experiment 1, as listed in section 8.5.1.1.

8.6.1.2. Experiment 2 results; EBSD maps

Once again Tango software was used to produce the grain maps. Figure 8.26 shows a CSL boundary map of the most deformed central region of coupon ‘a’, that is the middle of the narrow section of the dogbone specimen. Figure 8.27 shows a map of the least deformed end section (coupon ‘b’) cut from the wider end of the dogbone.

![Figure 8.26: EBSD map of the most deformed area (coupon ‘a’), mid-section of the 'relaxed' dogbone specimen (twins shown ringed).](image)
Figure 8.27: EBSD map of the least deformed area (coupon 'b'), end-section of the 'relaxed' dogbone specimen.

8.6.1.3. Experiment 2 results; texture pole figures

Figures 8.28 and 8.29 show inverse pole figures for coupons ‘a’ and ‘b’ respectively

Figure 8.28: EBSD pole figure of the most deformed area (coupon ‘a’), mid-section of the 'relaxed' dogbone specimen.
8.6.1.4. Experiment 2; observations and discussion

Once again the results are as expected with twins exposed in the most deformed specimen and no twins evident in the non-deformed specimen.

Texture between the two coupons has not changed significantly, contrary to the findings of [212].

8.7. Chapter conclusions

According to twins highlighted in the EBSD maps (figures 8.19 and 8.26) the overall volume of twinning is low, hence there is no change in the texture. This is evidence that twinning is unlikely to be the deformation mechanism causing the high values of stress exponent.
Chapter 9: Conclusions, observations and further work

Chapter 9 forms a summary of the conclusions and observations from each experimental chapter. Suggestions for future work are included at the end of this chapter.

9.0. Overview

This research project set out to characterise residual stresses in zirconium alloys and their associated oxides. Several experimental methods were used to carry out the study. There was very little found in the literature to suggest these techniques had been used to any degree on zirconium.

Early results from nanoindentation experiments in this study were not as expected, which led to further explorations in different directions from those planned at the outset. As a consequence, not all the objectives were met, nevertheless it is hoped that the findings of this work will provide insights to fill some of the gaps in the field of research. The project has led to many questions in need of further investigation.

9.1. Conclusions from Chapter 6: Determination of residual stress using nanoindentation

- A method was developed for obtaining the optimum loads to apply when testing Zircaloy 4 alloy using nanoindentation to extract mechanical properties like hardness and elastic modulus. The methodology could be transferrable to other Zr alloys and even other materials. Evidence of this method being published in the literature has not been found, so this proposed method is therefore considered a contribution to the discipline of instrumented indentation.

- To determine residual stress variations in Zr alloys and associated oxides, point to point hardness mapping was attempted by placing single arrays of indents across the oxide thickness, over the metal interface and into the metal. In the ZIRLO material, this proved difficult due to significant scatter in the results. However, a decreasing hardness trend was evidenced when indenting the Zircaloy 4 LOCA
specimen. A chemical analysis using EDX was carried out to determine if there was the same trend in oxygen (%wt). The oxygen trend showed good correlation with the hardness trend. However, as the LOCA specimen is highly embrittled, it cannot be confirmed that it was stress being evaluated.

- To investigate undulations in the interface topography of the LOCA sample, single arrays of indents were placed in the oxide and in the metal, above and below a ‘peak’ and a ‘trough’. Hardness values were extracted for each and comparisons were made. A similar decreasing hardness trend to the one found earlier (see previous bullet point), was observed in the metal, in both arrays. However, no differences were seen between the two graphs. It was hoped that the overlay might expose evidence of a reversed stress state between ‘peaks’ and ‘troughs’, but no evidence was attained.

- Scatter in the mapping data was investigated. Three possible causes of the scatter were eliminated; surface work hardening, pile-up and porosity. The current study was not able to ascertain the actual cause of scatter.

- Inherent data scatter was found, using indentation, even in the pure ceramics Alumina and Zirconia.

- Due to the considerable scatter in the data, it was not possible to map hardness variations over the oxides of zirconium alloy, using nanoindentation.

- The significant data scatter led to further investigations into the indentation response to the high residual stresses known to exist in Zr oxides. A model demonstrated the influence of residual stress on the indentation peak load in materials with different Young’s modulus/yield stress (E/σ_Y) ratios. It showed that in materials with an E/σ_Y ratio close that of Zr oxide, an extremely high compressive residual stress is required to cause a relatively small change in the peak load.

- A 2D finite element model of the indentation process was created. Different magnitudes of residual stress were applied to assess how the stress would influence the indentation loading response. The results showed evidence of a 7%
peak load shift in the loading curve, when a large residual stress of 1 GPa is applied to the model. This is a small percentage change for such a high magnitude residual stress. Therefore, with compressive residual stress values of up to 2 GPa having been found in the Zr oxides, close to the interface, any trends in hardness that may have existed in our materials would be hidden in the scatter of test results. This is one of the more significant findings to emerge from this research project, and it seems that no similar investigations have been performed on Zr alloys.

- In the technique of mapping indent arrays over oxides, there is one limitation that needs to be acknowledged. The thickness of oxide cross sections varied between 2-3 µm and 80 µm, so due to the resolution, placing indent arrays proved awkward. The optical lens fitted in the MTS nanoindenter used in this research had a magnification of 50x, and so was not good enough to place individual indents in very specific locations (e.g. to avoid cracks in the oxide). This fact, alongside the recommended spacings between indents made it difficult to achieve a sufficient quantity of indents across the oxide thickness, even when diagonal arrays were used.

9.2. Conclusions from Chapter 7: Determination of residual stress using FIB/DIC

- The ring core FIB milling technique was trialled on zirconium alloys, followed by an analysis of surface displacement strains by DIC. This technique is relatively new, and it was not possible to find any published information on the FIB/DIC residual stress measurement method having been used on Zr alloys. So, any findings resulting from this feasibility study are considered an important contribution to the worthy yet limited body of literature.

- In order to carry out this study, it was necessary to mill a large quantity of pillars to ascertain the most suitable FIB and SEM parameters. This extensive background experimental work helped to determine the optimum beam conditions when milling
Zr alloys, as well as the most suitable dimensions for the pillars. This in itself contributes information to this new and exciting field of research.

- A systematic evaluation of different surface patterning techniques suitable for DIC analysis was performed. Some measurements of residual stress were obtained using a gold sputtered surface pattern. However when observing the DIC maps, it was obvious that the strain on the surface of the pillar was not uniform. The stress measurements could only be acquired from part of the pillar surface due to rounding of the edges, caused by drifting. For completely accurate results it is necessary for the whole of the pillar surface to be analysed and for the strain to be uniform across the whole surface of the stress relieved pillar.

- Substantial drifting occurred when milling cross-sectioned specimens of Zr oxide in the highly stressed regions close to the metal interface, so further FIB experiments on the oxide were curtailed.

- When a pattern of indents was milled on the surface of unstressed Zircaloy 4 metal, beam deflection as well as drifting occurred. So, an EDX chemical analysis was carried out to investigate whether gallium (from the ion beam) had been absorbed by the alloy surface, causing the beam to deflect and mill in a completely different area. Gallium was seen to be embedded in the Zr material in SEM images. However results from the EDX analysis reported only 1 at% increase in gallium counts in the area of the indents, when compared to a non-indented area unlikely to have absorbed gallium. Therefore, these findings were inconclusive, however further work is suggested in the next section.

- A limitation of this study was the poor conductivity inherent in Zr oxides. In the experiments performed on the Zircaloy 4 LOCA sample, this poor conductivity possibly extends into the metal under the interface, where this work has evidenced a high percentage of oxygen. As the majority of the ring core mills were in this metal region, the high oxygen content is thought to have influenced the drifting of the ion beam in these experiments.
9.3. *Conclusions from Chapter 8: Deformation of zirconium alloys*

- A comprehensive study into the deformation of four zirconium alloys was executed. To extract creep parameters, nanoindentation creep tests were performed with three different loads and with four different durations of hold times at peak load. Interesting results from the tests emerged; the conventional creep curves overlaid each other almost exactly, irrespective of applied indenter load or the length of hold times, thus indicating that the creep strain rate is the same for each of the different loads. This phenomenon appeared when viewing results from both stressed and stress free materials.

- High values of stress exponent ($n$) were extracted from room temperature nanoindentation tests, and analysed according to the widely used power law method where the log of strain rate is plotted over the log of nominal stress, or in this case indentation hardness. Others have found high values of stress exponents in different materials, however, despite many theories, there was nothing found in this literature search to prove empirically why or how the high values transpire. With this in mind, a further study into the cause of the high exponents was implemented.

- Following in the footsteps of other researchers [210] who found significant links between the high $n$ exponents and indentation loading rates in nickel films, this section of this research includes an examination into the possibility of loading rate sensitivity in zirconium alloy materials. In comparing the stress exponent values from all four alloys, none of the alloys demonstrated sensitivity to different indentation loading times.

- The same researchers who found the significant sensitivity to NI loading times also suggest that this is linked to an unusual type of mechanism at work in the deformation of their material. The findings from this research also suggest an unusual mode of deformation, but there is no evidence of loading rate sensitivity in the zirconium alloys tested. Clearly, considerably more experiments would be
required, however these initial findings may provide a framework on which to build a case for disproving the hypothesis of Ma et al. [210].

- As a comparative study to determine the stress exponent by a method other than indentation, a conventional, mechanical load relaxation test was carried out, at room temperature, on a dogbone shaped specimen of Zircaloy 4 rolled plate. The specimen was placed under tensile loading to a point just past the material’s yield strength. Following removal of the load, ‘relaxation’ data was recorded and analysed. The data was analysed and the stress exponent value extracted was found to correlate well with those found, in the same material, using nanoindentation. This implies that the same deformation mechanism is working in both the tensile test and the compressive indentation tests. This is not creep in the conventional sense i.e. deformation under constant applied loading, and usually at high temperatures. The results here indicate that the deformation may be related to some kind of relaxation of the mechanism activated during the loading process.

- According to Zhu et al. [205], “generally speaking the stress exponent is usually related to the deformation mechanism”. So, to investigate this further, a high load Vickers indent was placed in Zircaloy 4 plate, the indent was then cut through so that the deformation zone under the indent could be evaluated using EBSD. Two regions were examined a highly deformed region from directly under the indenter tip, and a non-deformed region some distance away. Some evidence of twinning was found in the deformed region, particularly in the 1012 direction, as is common in Zr alloys. However, the volume of twinning was not large enough to be determined as the predominant deformation mechanism. No evidence of twinning was found in the non-deformed sample.

- A similar exercise to that above was carried out on sections taken from deformed and non-deformed regions of the same dogbone specimen used in the load relaxation test. An EBSD analysis was performed and evidence of a small volume of twinning was found in the deformed sample. Again, no evidence of twinning was found in the non-deformed sample. Taken together the findings of the last two
experiments confirm that twinning did not play a significant role in causing the high values of stress exponents.

- To evaluate texture changes, inverse pole figures were created for both experiments; under the large Vickers indent and the load relaxation specimens. Pole figures for both the deformed regions and the non-deformed regions were produced from the data, using EBSD analysis software. When compared, there was no change in the texture between the deformed and non-deformed regions on any of the four samples. This result opposes that of others [212] who have observed significant changes in texture of Zr alloys at room temperature, even at very small percentages of deformation.

The contributions, implications and limitations of this research have been included within the conclusions above, for each experimental chapter, however there were two processes developed during this work and recorded in chapter 5 that are worth mentioning:

- A process was devised to expedite finding the location of indents when viewing with SEM. The scale resolutions between the optical on a nanoindenter and those on an SEM vary enormously, so it is often difficult to find nano sized indents on a millimetre sized sample. Hence, this process is considered a useful and time saving contribution to microscopy studies.

- A 4-stage process was developed to successfully etch zirconium alloys so that EBSD indexing of up to 95% was achieved. Good Kikuchi patterns and high mapping indexes are known to be difficult when assessing zirconium by EBSD. Therefore this etching process is considered to be a significant contribution to the practical metallography of zirconium.
9.4 Suggestions for future work

This work has made noteworthy contributions to the fields of:

1. Instrumented indentation.
2. The determination of residual stress in zirconium alloys using nanoindentation
3. The determination of residual stress in zirconium alloys using FIB/DIC.
4. The deformation of Zr alloys.

However, it is recommended that further research be undertaken in the same four areas accordingly:

1. Instrumented indentation
   - Section 6.1: The method developed to determine the optimum loads for extracting mechanical properties in Zircaloy 4 could be expanded to include other Zr alloys. Furthermore, other materials could be tested. It may be possible to incorporate other forms of hardness testing, such as Vickers, using this method.

2. The determination of residual stress in zirconium alloys using nanoindentation
   - Section 6.3: When comparing indent arrays over a ‘peak’ and a ‘trough’ in the interface undulations, no differences were found between the hardness graphs. As only one comparison was made in this research, further indentation tests following the same procedure are advised, to try and expose evidence of a reversed stress state [120].
   - If the resolution of the optical lens within a test instrument can be improved, it may be possible to perform additional testing in the non-cracked veins above the ‘peaks’ in the interface.

3. The determination of residual stress in zirconium alloys using FIB/DIC
   - Section 7.8: Others [218] have found concentrations of up to 20 at% gallium (after bombardment) several nanometres under the surface in samples of copper using Auger electron spectroscopy. In this research project, an EBSD assessment of gallium intake in Zircaloy 4 only showed a concentration of around 1 at% gallium. It is suggested that a further study is undertaken to determine whether 1 at% gallium
Conclusions

concentrate is enough to cause beam deflection when milling zirconium. Additional experiments using Auger electron spectroscopy may prove interesting.

- Further work is suggested to gain insight into the uptake of gallium by zirconium alloys and to develop an understanding of the grain embrittlement process. The experiment carried out on two alloys in this work, could be extended to other materials; performing a systemic, comparative study using a variation of furnace temperatures, according to the materials’ melting points might provide interesting results. Future work may make some contribution to the growing field of milling by gallium ion beams as well as perhaps providing new information in the processing of metallic powders and/or the absorption of impurities or alloying elements in metals.

4. The deformation of Zr alloys.

- Section 8.3: It is clear from the nanoindentation experiment described in this section, that the four zirconium alloys tested did not show any sensitivity to indentation loading rate. It may be interesting to further investigate the variation between the different Zr cladding types, perhaps by performing some similar tests on pure zirconium to compare results.

- Section 8.4: Reports have shown that very narrow twins can be missed by EBSD [219], so that the extent of twinning can be underestimated. In addition, the limitation of the Tango software in not producing specific twinning maps for h.c.p. materials meant that, in this study, it was necessary to determine twins from EBSD misorientation maps, by measuring angle differences across twinning planes. This may not be a reliable method to accurately quantify the volume of twinning, so a complimentary investigative study using TEM is proposed.

- Chapter 8 generally: This chapter covers a variety of testing and analysis techniques to investigate the deformation of Zr alloys. Results from the comparative study between nanoindentation and the load relaxation test suggest some form of relaxation mechanism is at work during the time dependent deformation of these alloys. Further experiments using both testing techniques are
required before a better understanding can be developed. A TEM study on the specimens used for the load relaxation test and the specimen indented with the large Vickers indent, may reveal how the grains are deforming under both tension and compression. Whatever findings result from this future work, it is hoped that a deformation mechanism can be confirmed, as this will help in the quest to understand the life limiting creep deformation known to occur in zirconium fuel cladding situated in the high temperature, high stress environment of pressurised water reactors.
References

1. Nuclear Regulatory Commission (NRCgov), Reactor Fuel Assembly Unit figure is licensed under CC BY-NC-ND 2.0.


5. Godlewski, J. How the Tetragonal Zirconia is Stabilized in the Oxide Scale that is Formed on a Zirconium Alloy Corroded at 400°C in Steam. in Proc. 10th Int. Symp. on Zr in the Nuclear Industry (2nd Ed. ed.),ASTM-STP-1245, American Society for Testing and Materials, . 1994. Philadelphia, USA.


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National Laboratory (ORNL); Shared Research Equipment Collaborative Research Center.


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Appendix A (chapter 6): Further examples of scatter in data from nanoindentation

Scatter

Graphs have been included in this appendix to show evidence of the consistency in the scatter of data over several arrays in different Zr alloys.

- Figures A1 and A2 display the scatter in peak load for the other two diagonal indentation arrays on ZIRLO, highlighted in blue on figure 6.12 in chapter 6.
- Figure A3 shows the scatter in hardness results from indentation across Zircaloy 2 oxide and into the metal interface.
- Figure A4 shows the scatter of peak load results extracted from several columns of indents from the outer oxide to the metal interface. No clear trend is seen in the results.

Figure A1: ZIRLO, load/displacement graphs for diagonal array A8 to H4, as highlighted in blue on figure 6.12, chapter 6.
Figure A2: ZIRLO, load/displacement graphs for diagonal array A21 to H17, as highlighted in blue on figure 6.12, chapter 6.

Figure A3: Zircaloy 2 beta quenched tube; an example of the scatter in hardness results after indenting across the oxide and into the metal.
Figure A4: ZIRLO RXA plate, oxide; scatter of peak load results taken from columns of data within a large rectangular array across the oxide.

**Pile up**

When investigating pile up in our materials, an exercise was performed to compare the indent contact areas of several indents made using a range of high and low loads. As referenced in chapter 6, section 6.5.2.1., table A1 below shows results of nanoindentation tests performed on Zircaloy 4 rolled plate. Both polished and etched samples were analysed, and in the three principal processing directions; rolling, transverse and normal. The last two columns in each table compare the area of one specific indent by using two methods of calculation;

1. The Oliver and Pharr method, calculated by Testworks 4 software.
2. Image J area calculation measured from outlines drawn manually around SEM image of the same indent.

Overall, there is good correlation between the results, showing further evidence to that shown in chapter 6; that pile up in this material is negligible, and not likely to influence results for hardness or elastic modulus.
## ZRY4 ROLLED PLATE: ROLLING DIRECTION, ETCHED

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<th>Disp. at max load, h, (nm)</th>
<th>Stiffness, S, N/m</th>
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<th>Disp. at max load, h, nm</th>
<th>Stiffness, S, N/m</th>
<th>Area (NI) nm²</th>
<th>Area (SEM) nm²</th>
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### ZRY4 ROLLED PLATE: NORMAL DIRECTION, ETCHED

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<th>Modulus, E (Gpa)</th>
<th>Hardness, H (Gpa)</th>
<th>Disp. at max load, h, nm</th>
<th>Stiffness, S, N/m</th>
<th>Area (NI) nm²</th>
<th>Area (SEM) nm²</th>
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<td>22 x 10⁶</td>
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**Table A1:** For comparison of indent areas calculated by Testworks (NI) software and those areas imaged on SEM then calculated by Image J software from outlines manually drawn around imaged indents in Zircaloy 4 plate.
Appendix B (chapter 7): Further examples of FIB and DIC experimental results

B.1. FIB/DIC

The first and third attempts at DIC analysis on FIB ring core mills on the highly stressed Zry 4 LOCA specimen are shown in figures B1 and B2 below. The second attempt which shows the best results, is included in chapter 7, section 7.6. These two analyses proved unsuccessful due to the poor quality of surface patterning remaining after the pillar was milled. The deterioration in the pattern in the ‘after’ image is due to material re-deposition resulting from the milling process.

Figure B1: A first attempt with DIC analysis of a pillar surface with gold sputtered pattern, on the Zircaloy 4 LOCA specimen.
Figure B.2: Another attempt on the Zry 4 LOCA specimen, using DIC to analyse surface patterns for strain displacements.

B.2. EDX analysis on the absorption of gallium ions by zirconium

Following the experiment described in section chapter 7, section 7.8, an EDX analysis was done on the Zircaloy 4 hot rolled plate material fragments following a period in the furnace. The results are shown in the figures B3 to B9 below. The magenta coloured crosshairs mark the position where analysis acquisition point is in each case.
### Appendix B (chapter 7): FIB, DIC and EDX

#### Figure B3

<table>
<thead>
<tr>
<th>Element</th>
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<th>At%</th>
</tr>
</thead>
<tbody>
<tr>
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<td>53.63</td>
</tr>
<tr>
<td>Ga</td>
<td>03.54</td>
<td>02.55</td>
</tr>
<tr>
<td>Zr</td>
<td>79.41</td>
<td>43.81</td>
</tr>
</tbody>
</table>

---

**Figure B3**

*Image showing an EDX spectrum with peaks for O, Ga, and Zr.*

---

*Image showing a SEM micrograph with a micrograph for Zr oxide.*

---

*Image showing a SEM micrograph with a micrograph for Zr oxide.*

---

*Image showing a SEM micrograph with a micrograph for Zr oxide.*

---

*Image showing a SEM micrograph with a micrograph for Zr oxide.*

---

*Image showing a SEM micrograph with a micrograph for Zr oxide.*

---

*Image showing a SEM micrograph with a micrograph for Zr oxide.*
<table>
<thead>
<tr>
<th>Element</th>
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</thead>
<tbody>
<tr>
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<tr>
<td>Ga L</td>
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<tr>
<td>Zr L</td>
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<td>25.61</td>
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Figure B4
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<th>Zr\textsubscript{L}</th>
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<td></td>
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**Figure B5**
### Element Analysis

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<tr>
<td>Ga</td>
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<td>68.78</td>
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<td>Sn</td>
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*Figure B6*
### Appendix B (chapter 7): FIB, DIC and EDX

#### Table B7

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<td>Sn L</td>
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<td>00.81</td>
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#### Figure B7

[Graph showing elemental distribution]
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Figure B8
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<td>GaL</td>
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</tr>
<tr>
<td>SnL</td>
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Figure B9
B.3. EDX comparative analysis on the absorption of gallium in indented regions compared to non-indented regions on Zircaloy 4 plate and pure titanium foil.

Figures B10 to B16 show all the EDX results from experiments 1-4 as reported in table 7.1 in chapter 7, section 7.10.2.

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<tr>
<td>ZrL</td>
<td>97.19</td>
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</table>

Figure B10: Zircaloy 4 plate, without indents
Figure B11: Zircaloy 4 plate non-indentated area
Figure B12: Zircaloy 4 plate, indented area
Figure B13: Pure titanium, non-indented area
Figure B14: Pure titanium, non-indented area
<table>
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<tr>
<td>GaK</td>
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Figure B15: Pure titanium, non-indented area
Figure B16: Pure titanium, non-indented area