NOVEL METHODS OF RECORDING FLOW CURVES IN PROTON IRRADIATED MATERIAL

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Albert D. Smith

School of Materials
Contents

CONTENTS .............................................................................................................................................. 1

LIST OF FIGURES .................................................................................................................................. 4

ABSTRACT .............................................................................................................................................. 9

DECLARATION ....................................................................................................................................... 10

COPYRIGHT .......................................................................................................................................... 10

ACKNOWLEDGEMENTS .......................................................................................................................... 11

1 INTRODUCTION ...................................................................................................................................... 12

1.1 THE PROJECT ................................................................................................................................... 12

1.2 MOTIVATIONS FOR INVESTIGATING THE EFFECTS OF PROTONS .............................................. 12

1.3 POLITICAL CLIMATE ..................................................................................................................... 13

1.4 NUCLEAR MATERIALS .................................................................................................................... 14

2 LITERATURE REVIEW .......................................................................................................................... 16

2.1 FLOW CURVES ............................................................................................................................... 16

2.2 IRRADIATION DAMAGE .................................................................................................................. 19

2.2.1 Particle Damage and Cascade .................................................................................................... 20

2.2.2 Particle Dependent Damage and Efficiency .............................................................................. 21

2.2.3 Defects ......................................................................................................................................... 24

2.2.4 Correlating Damage .................................................................................................................... 26

2.3 MECHANICAL PROPERTY CHANGES DUE TO IRRADIATION DAMAGE ........................................ 27

2.3.1 Yield Shift .................................................................................................................................... 28

2.3.2 Plasticity ....................................................................................................................................... 29

2.4 MEASUREMENT OF MECHANICAL PROPERTIES IN ION IRRADIATED MATERIALS .................. 33

2.4.1 Composite Behaviour .................................................................................................................. 33

2.4.2 Indentation Testing ....................................................................................................................... 35

2.4.3 Flow Curves .................................................................................................................................. 36

2.4.3.1 Compression ............................................................................................................................ 37
3.6.1 Automated Cross Polish ................................................................. 73
3.6.2 Overtilt ............................................................................................. 74
3.6.3 Specimen Fabrication........................................................................... 75
3.6.4 Orientation Mapping ........................................................................... 79
3.6.5 Loading Pin ......................................................................................... 80
3.6.6 Piezo-Actuated Mechanical Testing ....................................................... 83
3.6.7 X-ray Computed Tomography (XCT) .................................................... 87
3.6.8 Finite Element Analysis ........................................................................ 87

3.7 HIGH RESOLUTION DIGITAL IMAGE CORRELATION (HRDIC) .................. 88
3.7.1 Vapour assisted remodelling ................................................................. 88
3.7.2 Image acquisition .................................................................................. 90
3.7.3 Orientation Mapping ............................................................................ 91
3.7.4 Displacement Calculation ..................................................................... 92
3.7.5 Pattern Morphology and Sub Window Optimisation ......................... 93
3.7.6 Analysis ............................................................................................... 94

4 INTRODUCTION TO MANUSCRIPTS ...................................................... 96
4.1 MANUSCRIPT 1: A NEW METHODOLOGY FOR RECORDING UNIAXIAL STRESS-STRAIN CURVES OF THIN SURFACE LAYERS ................................................................................................. 97
4.2 MANUSCRIPT 2: ON THE APPLICATION OF XE+ PLASMA FIB FOR MICRO-FABRICATION OF SMALL-SCALE TENSILE SPECIMENS .......................................................................................................... 111
4.3 MANUSCRIPT 3: NOVEL METHODS OF RECORDING FLOW CURVES IN PROTON IRRADIATED MATERIAL ................................................................................................................................. 132
4.4 MANUSCRIPT 4: HIGH RESOLUTION PLASTIC STRAIN MAPPING OF 100 MDPA PROTON IRRADIATED POLYCRYSTALLINE AUSTENITIC STAINLESS STEEL .................................... 150

5 CONCLUSIONS .......................................................................................... 178

6 FUTURE WORK ......................................................................................... 180

REFERENCES .................................................................................................. 183
List of Figures

Figure 1: Yearly national nuclear R&D spending [10]................................................................. 13
Figure 2: Schematic of typical tensile test, where a, b, c and d denote the elastic, stable
plastic, onset of plastic instability and unstable plastic flow [26]............................................. 16
Figure 3: Flow curves of non-irradiated an irradiated mild steel. Irradiated material exhibits
an increased yield point and decreased ductility [4]...................................................................... 19
Figure 4: Depiction of the various stages of the collision cascade from the initial collision (a)
to the final defect morphology (k) [29]...................................................................................... 20
Figure 5: Displacement efficiency of different particles in nickel [35]................................. 22
Figure 6: SRIM calculation of 3 proton energies in steel, displacement efficiency decreases
with increasing particle energy ..................................................................................................... 22
Figure 7: Particle dependent damage morphology, average recoil energy and displacement
efficiency at 1 MeV [9]............................................................................................................. 23
Figure 8: Two dimensional representation the (001) plane of a primitive cubic lattice
containing a) vacancy and b) interstitial atom [38].................................................................... 24
Figure 9: Yield shift following irradiation at three different facilities, plotted in terms of: a)
fluence and b) dpa [52]............................................................................................................. 27
Figure 10: Dose dependent mechanical properties of bcc and fcc steels, with a schematic of
obstructed dislocations accounting for increasing yield stress [44]........................................ 30
Figure 11: True stress –true strain curves for stainless steel. With irradiated curves of 0.5,
1.1, 2.5, 3.6 and 10.7 dpa offset by 0.14, 0.18, 0.23, 0.28 and 0.385 respectively [71]............ 31
Figure 12: True stress strain curve for duplex stainless steel for as received and pre-strained
by 5% [72].................................................................................................................................... 31
Figure 13: a) strain hardening exponent of EC316LN displayed in Figure 11, with A533 &
Zric 4 from same ref. [76], plotted against log damage, with projected intersection
corresponding to Dc; b) deformation mode map of 316 variants, with intersection of PIS and
yield corresponding to Dc [76].................................................................................................... 32
Figure 14: Relationship between change in hardness and change in yield strength [84]...... 35
Figure 15: Schematic of effects to be considered when considering nano indentation of proton irradiated surface [88].

Figure 16: a) Example of annular milling, prepared normal to the surface [101]; b) Example of lathe milling prepared by multiple oblique cuts [100].

Figure 17: a) Example of pin loaded tensile specimen [82]; b) Example of shoulder loaded tension test [83].

Figure 18: Normalised flow stress for FCC crystals tested in compression and tension as a function of specimen diameter [119].

Figure 19: Diameter of region containing 50% of the beam as a function of current for Xe⁺ and Ga⁺ sources [149,150].

Figure 20: Crystal diffraction of x-rays [159].

Figure 21: Fraction of total diffracted intensity of CrKα in steel as a function of tilt angle.

Figure 22: Schematic of sin²ψ measurement of d-spacing response to uniaxial stress [163].

Figure 23: Orientation maps of (a) SA508-4N and (b) 316L displayed in IPF Z.

Figure 24: Tensile test of SA508-4N steel at decreasing strain rates.

Figure 25: Strain rate sensitivity in terms of a) hardening exponent and b) tensile strength.

Figure 26: Damage as a function of depth in steel at 1, 2 and 3 MeV calculated using SRIM code.

Figure 27: Specimen “jigsaw configuration on end station a) mounted specimens with specimen clamping shim in place; b) specimen arrangement mounted with a windowed hold down plate; c) schematic of stage configuration at DCF.

Figure 28: Pyrometer imaging of irradiation a) configuration with poor thermal contact due to an indium leak; b) configuration with good thermal contact, white arrows highlight the irradiated region.

Figure 29: Histogram of temperature during irradiation experiment for each batch, measured using pyrometer.

Figure 30: a) System of beam control and monitoring; i) pyrometer; ii) optical camera; iii) current measurement; iv) tantalum vane; v) thermocouple; vi) ceramic fixture to linear...
motion rod; vii) viewing port; viii) beam aperture; b) unfocussed beam fluorescing quartz insert; c) $X + Y$ rastered beam onto aperture veins; d) alignment onto shim in $Y$; e) alignment onto shim in $X$. Adapted from ref. [221].

Figure 31: Histograms of current on target stage during irradiation experiment.

Figure 32: Hardness (Hv 0.05) of samples as a function of damage in SA508-4N.

Figure 33: Calibration standards with stress measured in $\Psi$ and $\chi$ geometry, for a) Al, powdered and solid standards; b) Fe solid standard.

Figure 34: Stress measured in standard as a function of distance above focal point, the dotted line represents the 95% confidence and the solid line is the least squares fit.

Figure 35: Rectangular cross section tensile sample under uniaxial stress, psi scanning parallel to the loading direction and PSD at fixed diffraction half angle orientated for side inclination ($\chi$ mode).

Figure 36: Typical paint pattern on a tensile specimen.

Figure 37: Noise for different binning window size, decreasing size not only increases noise and scatter.

Figure 38: Strain in the irradiated region at 2%, parallel to ($\varepsilon_{xx}$) and transverse to ($\varepsilon_{yy}$) the applied load.

Figure 39: Finite element analysis of proton irradiated steel (a) unmodified specimen (b) modified specimen; both are displayed as $\varepsilon_{xx}$, the irradiated region is marked with brackets.

Figure 40: Recommended specimen setup for future irradiation experiments.

Figure 41: a) Curtaining after high current milling at 1.3$\mu$A; b) Schematic of 2° cross-polish to eliminate curtaining, adapted from [149].

Figure 42: Xe$^+$ PFIB beam profile at varying mill currents in SA-508-4N. Currents are as follows: i) 6.7 nA; ii) 15n nA; iii) 59 nA; iv) 0.18 $\mu$A; v) 0.47 $\mu$A; vi) 1.3 $\mu$A.

Figure 43: Half angle at the root of the trench as a function of beam current.

Figure 44: Preliminary approach, manual high current lateral milling in 304 austenitic steel [226].
Figure 45: Iteration 1, fully manual approach with the specimen shape milled before final polishing.

Figure 46: Iteration 2, automated cross-polish with manual tensile specimen shaping. Specimens are not overtilted so possess some taper ≈1.6°.

Figure 47: a) specimen mounting fixture; b) pre-tilted microscope stub, with tilt angles ranging from 1–4° in 1 degree increments (courtesy of Jack Donoghue [227]); c & d) automated cross polish of specimen mounted in pre-tilted holder.

Figure 48: Iteration 3, semi-automated cross-polish with manual tensile specimen shaping, specimens are prepared using a 2° pre tilt holder resulting in a slight taper of ~0.44°.

Figure 49: Key steps in the preparation route of iteration 3 from a 50µm thick half-moon disk using the specimen route from iteration 3. An initial cut is made to align the flat edge of the specimen with the back of the specimen mount. Platinum is deposited to protect the specimen faces during thinning by automated cross-polishing of both sides. Specimens are milled into shape. It must be noted that the foil thickness in this sample batch negated the need of a high current top-down mill.

Figure 50: Orientation mapping geometry of inverted sample using a 45° pretilt holder, in order to avoid shadowing.

Figure 51: (a) Failure of SiC loading pin during a test, at a load of 0.44 N (b) Fracture surface of the SiC loading pin, failure was purely brittle originating at the root of the loading pin; (c) higher magnification of the crack origin, a proto-crack can be observed parallel to the point of failure and is marked ‘a’, the region marked as ‘b’ highlights the start of the failure surface.

Figure 52: a) Diamond pin as prepared in the PFIB, basalt structure visible; b) Post polishing using Ga⁺ FIB with selective carbon etch; c) High magnification secondary electron image of polished loading pin transition to radius.

Figure 53: a) MTR-3 piezo-actuated loading rig; b) schematic highlighting key components.
Figure 54: (a-c) Progression of load-displacement throughout calibration, load is applied by movement of the stage rather than via the piezo actuator; (c) load cell recorded force plotted against displacement measured manually. ................................................................. 84

Figure 55: Pre-contact and contact of the loading pin mounted in the SEM. ......................... 85

Figure 56: Fiducial markers applied to surface allowing for calculation of strain. .................. 86

Figure 57: Typical example of strain map correlated using the raw specimen surface, map is calculated with a final window size of 48 x 48 pixels, with smoothing on. ......................... 86

Figure 58: Schematic representation of the assumptions in a 2D plane strain model………... 88

Figure 59: Setup for water vapour assisted remodelling, the process takes place at ~300°C and is an open system [192] ................................................................. 89

Figure 60: Styrene remodelling setup takes place at a lower temperature, as low as 120°C, and is a closed system [131]. ................................................................. 90

Figure 61: Indentation in 316L steel, in non-irradiated state, irradiated before and after vapour assisted remodelling ...................................................................... 90

Figure 62: Schematic of origin of disparity of strain between irradiated and non-irradiated regions for equivalent displacement ......................................................... 91

Figure 63: Schematic of integral correlation and corresponding strain maps calculated ...... 92

Figure 64: Gold speckle pattern on a) non-irradiated and b) irradiated regions; strain calculated in undeformed specimens using overlapping areas of mosaic overlap at different binning window sizes for c) non-irradiated and d) irradiated regions. ......................... 94

Figure 65: Example of peak location and FWHM measurement using MatLab. ................... 95

Figure 66: Carburised 316N ex-service AGR material, provided by EDF & AMEC Foster Wheeler. Serrated curve corresponds to the substrate and open circles corresponds to magnetite oxide layer ......................................................... 180

Figure 67: (a) The spatial resolution of strain maps can be increased in PFIB prepared specimens by application of a Pt speckle pattern by electron beam, where the optimal diameter was found to be ~150 nm, EBSD orientation maps taken prior to pattern application allows strain localisation to be related to microstructural features. ............... 181
Abstract
Observing the physical effects of neutrons is logistically complicated due to their poor displacement efficiency, which requires irradiation durations extending from months to years to attain a relevant level of damage. Specimen activation leads to the requirement of a cooling off period to perform post irradiation examination outside of specialised facilities. Protons can produce defects with a similar structure and a density comparable to years of irradiation in a reactor in a few hours or days. Furthermore, at low energies their positive charge is repelled by nuclei, which reduces the probability of specimen activation and allows for off-site examination. The high dose rates and limited residual activity makes protons attractive as a surrogate for the study of irradiation damage. However, the limited penetration of protons, in the order of a few tens of microns, complicates studies probing standard mechanical properties beyond hardness measurement. In terms of the uniaxial tensile test the difficulty lies in the global nature of data acquisition, where the hardened surface properties are convoluted with that of the non-irradiated volume. The percentage of non-irradiated material in a 1 mm thick specimen irradiated with 3 MeV protons is upwards of 95%, which would lead to results heavily biased towards the non-irradiated properties. Therefore, the solution is to either employ a novel technique to directly record the surface properties or extract the desired layer. This project explored both solutions to the problem: 1) Directly probing the irradiated layer using a combination laboratory based X-ray diffraction (sin²ψ) & digital image correlation (DIC) and 2) Small scale tensile specimens were prepared using Xe⁺ plasma focused ion beam (PFIB) to increase specimen scale and attain a smallest representative volume. Both techniques were initially applied to non-irradiated SA508-4N for the purposes of validation. The combination of XRD and DIC accurately described both elastic and plastic regimes, that were recorded using the standardised technique on bulk specimens. Specimens prepared using PFIB exhibited a bulk representative yield stress, however specimen dimension and scale diminished the plastic response. Finite element analysis was applied to distinguish between the two limiting factors. It was demonstrated that the specimen geometry had a pronounced effect on the reduction of tensile strength and the reduced scale is thought to restrict strain hardening. The techniques were applied to SA508-4N irradiated with 3 MeV protons to 10 mdpa at the University of Manchester’s Dalton Cumbrian Facility. Both techniques recorded a positive yield shift in the same order estimated using indentation testing, with a reduction in strain hardening and an invariant tensile strength, which is consistent with literature reported behaviour. High resolution digital image correlation was applied to 316L in the non-irradiated state and irradiated to 100 mpda. A host of analysis techniques provided insight into deformation mechanisms just beyond the critical dose for dislocation channelling (100 mdpa). The work highlighted the differences in strain localisation and strain hardening behaviour of the two states and provided the opportunity to construct a flow curve based on the principal of equivalent pre-strain.
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I dedicate this work to my family and partner.
1 Introduction

1.1 The Project

This project was jointly funded by the EPSRC and Rolls-Royce plc, with work carried out within the NNUMAN (New Nuclear Manufacturing) research group, which forms a part of the Dalton Nuclear Institute. The work focussed on exploring novel methods of recording flow curves in proton irradiated material. Research outcomes are split across 4 manuscripts. Manuscript 1 applies the combination of x-ray diffraction and digital image correlation to recording flow curves in non-irradiated material. Manuscript 2 is the development of a specimen preparation technique using emerging Xe+ plasma focussed ion beam technology and its application to non-irradiated material. Manuscript 3 applies both techniques explored in the first two papers to proton irradiated SA508-4N steel. The final manuscript uses a combination of vapour assisted gold remodelling, automated mapping software and digital image correlation to map strain over large areas in proton irradiated 316L stainless steel.

1.2 Motivations for Investigating the Effects of Protons

It is widely accepted that the drive towards a nuclear future will require the development and testing of new materials to complement future generations of nuclear reactors, as well as to support the extension of current reactor lifespans. A significant challenge for new nuclear reactor technology is adequate material selection for the harsh environments associated with standard operating conditions, along with potential accident conditions. Components of next generation reactors will be subjected to temperatures up to 650°C [1], cyclic loading and thermal transients, corrosive environments and radiation damage up to the order of hundreds of displacements per atom (dpa) [2]. The sustained bombardment of in service materials by neutrons results in severe degradation of properties due to the radiation induced microstructural changes and defect structure [3]. Accordingly, prediction of component lifetime requires direct investigation into irradiated microstructure and irradiation induced mechanical changes [4]. However, observing the physical effects of neutrons is often logistically complicated. The tight controls and hazards associated with handling active materials mean that experiments can only be performed at specialised facilities with stringent protocols in place [4,5]. Primarily, simulation of reactor environments can take months to years of irradiation. A cooling off period is required to perform off-site examination, adding further time to the analytical process [6]. This turnaround time can be prohibitive to experiments that require a variety of irradiating conditions and the cost or safety case associated with storing active materials for prolonged periods can be restraining.
An understanding of the effects of neutron damage can be achieved by investigating the results of an analogous irradiation regime. The use of an analogue, such as protons or heavy ions, circumvent some of the logistical issues associated with neutron investigations. Low energy proton irradiation can produce doses comparable to years of neutron exposure in just a few days [6]. Protons produce comparable damage, benefit from high efficiency at producing freely migrating defects and give a nearly uniform damage profile over the majority of the range affected by protons. Ion irradiation has minimal residual activity, making post irradiation study easier to perform [5,7], which, when coupled with a high damage rate, dramatically reduces lead time. Although ion irradiation is limited by inadequate simulation of multiple damage characteristics [5], tight control of irradiation parameters allows for accurate simulation of fundamental mechanisms [8] and physical effects. This is due to the damage path being less important in post irradiation studies than the final state of the material [9]. Tuning experimental parameters until an ‘in service’ condition is met [9] gives an adequate representation of neutron irradiation damage over the irradiated volume.

1.3 Political Climate

The need for accurate prediction and modelling of materials behaviour of in service nuclear components has become increasingly important against the backdrop of nuclear “new build”. The UK Government’s energy strategy has changed in recent years, intent on reducing the carbon emissions generated during the process of electrical power generation. Effectively, it plans to shift the energy portfolio of the UK towards low carbon energy production and ultimately reduce national dependence on fossil fuels. In order to meet the UK’s legal obligation on reducing greenhouse gas emissions to 80% below that of 1990 levels [10], it plans on utilising a mix of carbon capture and storage, renewable energy sources and nuclear power [11].

The projected nuclear energy contribution to total UK supply in order to meet this target ranges between 30-49% depending on the organisation that made the projection. Previously, UK public sector fission R&D funding decreased steadily between 1972 and 1994 from over £800 million to ~£1 million [10], funding slowly increased and in 2009 reached £4.5 million (Figure 1). Funding cuts, lab closures and the privatisation of the UK’s nuclear industry led to the current situation, namely: an aging reactor fleet, workforce and a knowledge/skills deficit. With longer term planning in serious

Figure 1: Yearly national nuclear R&D spending [10].
consideration, there is a drive to develop technologies for future reactor generations and increase the knowledge and skills base in the UK. By 2030 the UK nuclear industry plans to deliver 16 GW of new nuclear energy production comprised of 12 new reactors at: Sizewell (EDF Energy/Centrica), Wylfa (Horizon Nuclear Power), Hinkley Point (EDF Energy/Centrica), Moorside (NuGeneration Ltd) and Oldbury (Horizon Nuclear Power) [12,13]. As worldwide demands for low carbon energy increases, so too does global investment in nuclear energy [1]. Approximately 13% of the world’s energy is generated by nuclear reactors (Table 1) with growth being considered essential to promote economic stability and prosperity [14], since it will alleviate global demand for fossil fuels. Consequently, there is a planned £930 billion of global investment into building new reactors and £250 billion into decommissioning [13].

Table 1: Nuclear power reactors worldwide [15]

<table>
<thead>
<tr>
<th>Reactor type</th>
<th># Units (in operation)</th>
<th>Net MWt</th>
<th># Units (forthcoming)</th>
<th>Net MWt</th>
<th># Units (total)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressurised light-water reactors (PWR)</td>
<td>267</td>
<td>246555.1</td>
<td>89</td>
<td>93,014</td>
<td>356</td>
</tr>
<tr>
<td>Boiling light-water reactors (BWR)</td>
<td>84</td>
<td>78320.6</td>
<td>6</td>
<td>8656</td>
<td>90</td>
</tr>
<tr>
<td>Gas-cooled reactors, all models</td>
<td>17</td>
<td>8732.0</td>
<td>1</td>
<td>200</td>
<td>18</td>
</tr>
<tr>
<td>Heavy-water reactors, all models</td>
<td>51</td>
<td>25610.0</td>
<td>8</td>
<td>5112</td>
<td>59</td>
</tr>
<tr>
<td>Graphite-moderated reactors, all models</td>
<td>15</td>
<td>1019.0</td>
<td>0</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>Liquid-metal-cooled reactors, all models</td>
<td>1</td>
<td>560.0</td>
<td>4</td>
<td>1016</td>
<td>5</td>
</tr>
<tr>
<td>Totals</td>
<td>435</td>
<td>369996.7</td>
<td>108</td>
<td>107,896</td>
<td>543</td>
</tr>
</tbody>
</table>

1.4 Nuclear Materials

There are a wide range of alloys in use within a nuclear power plant (NPP), the vast majority of which are subject to incredibly demanding environments. In addition to high temperature and corrosive environments present in all thermal power plants, NPP components will also be subject to irradiation damage. To ensure safe operation and remain economically viable, materials must be capable of operating in these harsh conditions without failure or need for replacement during extended periods. As new fission reactor designs are intended to operate with increased efficiency and at higher temperatures and pressures, the demands on materials are projected to increase with each subsequent NPP generation.

The largest single component in an NPP is the reactor pressure vessel (RPV), which houses the core components and as such is not possible to replace so has an operational lifespan equal to the plant life, up to 60 years [16]. Typically, this consists of a quenched and tempered low alloy steel (e.g. A533 or SA508 series), it is fabricated as separate sections and welded together. The materials are selected for their yield strength, toughness, weldability and resistance to thermal aging and neutron irradiation damage [17]. Whilst in terms of corrosion resistance it may be more suitable to use a stainless steel for this component, it is not economically viable due to it having a mass in the order of $10^5$ kg [17]. Hence, this component
is clad with a corrosion resistant stainless steel blanket welded to the vessel interior [18]. Within the field of nuclear materials, there is a concerted effort to develop clean welding techniques, which are intended to reduce the volume of microstructural heterogeneity in joined sections. With traditional welding techniques (e.g. MIG and MMA), significant volumes of material are required to be removed from the plate in order to perform multiple passes on thick sections. Whereas, newer techniques (e.g. laser and electron beam) require less material to be removed, having higher precision and cooling rates which leads to a narrower heat affected zone [19]. In addition to a heat affected zone, welds have been known to change local chemistry as a result of feed stock composition and coatings. A specific example is the copper coating applied to prevent the oxidation of filler material used in welds on early reactor designs. The local copper enrichment resulted in a loss of fracture toughness due to the formation and aging of copper rich precipitates [20].

In-core components are subjected to larger neutron doses than the RPV, so in addition to corrosion resistance are required to maintain a dimensional stability under these conditions. Since they are typically smaller components, more expensive alloys are viable for use. Due to their reduced size, maintaining dimensional stability under irradiation is of concern [16]. Irradiation assisted creep, swelling and growth of core materials has been observed in operational reactors [21]. Swelling is a particular issue in the zirconium-based cladding alloys, due to the possibility of fuel assembly deformation and contamination of coolant in the event of rupture. Zirconium alloys are selected for their low neutron cross section, which allows neutrons to travel relatively unimpeded and transfer energy to the coolant. In the majority of the UK civil fleet, no zirconium alloys are currently in use as cladding materials, with AGR fuel cladding composing of stainless steel [22]. Stainless steels are in widespread use as core components, for example: pipes, ducting, baffle bolts and valves [23]. Their good corrosion resistance at elevated temperatures, as a result of the high chromium content, makes them an excellent candidate for use in an NPP. However, they are also sensitive to intergranular stress corrosion cracking due to chromium depletion, which can be accelerated by irradiation damage [15]. Furthermore, it has been shown that stainless steel alloys lose their dimensional stability at high doses [24], so current alloys may be less suitable in future reactor designs.

More recently, the activation of materials is being taken into consideration, with it less desirable to use materials with isotopes that will produce isotopes with long half-lives. The use of “reduced-activation materials” will improve the logistics of disposal, possibly allowing recycling within ~100 years of decommissioning [25].
2 Literature Review

The following section is a summary of relevant literature relating to the mechanical testing of proton irradiated materials. It begins with an overview of the principals of mechanical testing, followed by the effects of irradiation damage in materials and the differences between ion and neutron irradiation. A discussion of current work will be presented highlighting the advantages and limitations of the methods, this will be followed by the principal of x-ray stress measurement and digital image correlation.

2.1 Flow Curves

Uniaxial tensile testing is a widely applied and heavily standardised technique. National and international standards, such as BSI (British Standard Institution), ASTM (American Standards for Testing of Materials) and ISO (International Organization for Standardisation) ensure that mechanical tests are relatable and repeatable. Conventional mechanical testing consists of a constant application of force along a single axis (uniaxial) by motorised displacement of specimen mounting grips. Force and displacement are normalised against gauge section geometry as stress/strain and plotted as a function of one another, forming a flow or stress-strain curve. Normalisation of instantaneous force and displacement to the original gauge section allows specimens of differing geometries to be related and are referred to as engineering stress and strain. Engineering stress ($\sigma$) is defined as the force (F) acting on a given area (A) of a body:

$$\sigma = \frac{F}{A_0}$$

Equation 1

Figure 2: Schematic of typical tensile test, where a, b, c and d denote the elastic, stable plastic, onset of plastic instability and unstable plastic flow [26].

Engineering strain ($\varepsilon$) is a measure of dimensional displacement relative ($\Delta l$) to the original dimension ($l_0$), defined as:
\[ \varepsilon = \frac{l_0 - l_1}{l_0} = \frac{\Delta l}{l_0} \]

Equation 2

A flow curve in a ductile material can be broken down into three key regions: elastic, stable-plastic and unstable-plastic. Figure 2 depicts this, the elastic range is the region whereby deformation is recoverable and a linear relationship is obeyed, where stress \((\sigma_x)\) and strain \((\varepsilon_x)\) are related by the modulus of elasticity \((E)\). It is expressed mathematically by Hooke’s law:

\[ \sigma_x = E\varepsilon_x \]

Equation 3

During elastic deformation, a longitudinal strain in \(x\) will result in a dimensional change, to conserve volume, extension is coupled with a transverse strain imposed on \(y\) and \(z\). The fraction of transverse strain and axial strain is the Poisson ratio \((\nu)\), with stress strain and elastic modulus represented as[27]:

\[ \varepsilon_y = \varepsilon_z = -\nu \varepsilon_x = -\frac{\nu \sigma_x}{E} \]

Equation 4

Yielding represents the end of the proportional limit and the initiation of unrecoverable deformation (plastic flow). In materials, where yielding is poorly defined, a common definition of proof stress is applied. A value for the proof stress is obtained by running a plot parallel to the elastic range offset by 0.2%, where the intersection with the flow curve represents the proof stress with the notation: \(\sigma_{0.2}\). Beyond the initial flow stress \((\sigma_0)\), deformation is permanent and experiences a hardening that manifests as a stress increase as a function of applied strain \((\sigma_{SH}(\varepsilon))\). The total flow stress is the product of the two contributions:

\[ \sigma_{Total}(\varepsilon) = \sigma_0 + \sigma_{SH}(\varepsilon) \]

Equation 5

During plastic deformation, the accelerated axial contraction and longitudinal extension leads to engineering stress and strain, defined by the nominal dimensions, misrepresenting the true state of the conditions. True stress \(\sigma_t\) and strain \(\varepsilon_t\) is determined by the instantaneous force acting on an instantaneous unit area, so accounts for the reduction in cross sectional area under the assumption of conserved volume as a tensile test progresses. True stress is described by:

\[ \sigma_t = \sigma(1 + \varepsilon) = \sigma \left( \frac{A_0}{A_t} \right) \]

Equation 6

And true strain is described by:
\[ \varepsilon_t = \ln(1 + \varepsilon) = \ln\left(\frac{l_f}{l_0}\right) \]

Equation 7

It must be stated that the true stress and strain calculated using this relationship is only valid up to the point of ultimate tensile strength (UTS), where strain hardening saturates and reduces to zero (Figure 2a&b). In an engineering stress-strain curve the UTS can simply be observed at the point that stress ceases increasing \( \left( \frac{d\sigma}{d\varepsilon} = 0 \right) \). This represents the transition between uniform plastic deformation and the onset of diffuse necking (non-uniform plastic deformation). Obtaining a true stress value for this transition can be achieved using Considère’s plastic instability criterion, where \( \sigma_{UTS} \) marks the point that the hardening rate is equal to the true stress, it is expressed as:

\[ \sigma_{UTS} = \frac{d\sigma_t}{d\varepsilon_t} = \sigma_t \]

Equation 8

At the point of macroscopic localisation (necking), the uniaxial condition ceases and the cross-sectional area reduces at a higher rate (Figure 2c&d). The stress and strain state becomes a more complex triaxial state and the assumptions of the true stress calculation break down. This behaviour is commonly referred to as strain softening, due to it consisting of a decrease in recorded stress as the test progresses. Generalised plastic flow up to the tensile strength is described in most metals using the Hollomon hardening model:

\[ \sigma_t = Ke_t^n \]

Equation 9

where \( \sigma_t \) is true stress, \( K \) is the strength coefficient and \( n \) is the strain hardening exponent. The strain hardening exponent is obtained by the gradient of the log-log plot in the plastic regime that obeys hardening, typically the range of the 0.2% offset from the proportional limit and the peak stress. The strength coefficient corresponds to the projected stress at 100% strain.

In three dimensions stress may be represented by the stress tensor, it is described by nine elements: three normal (\( \sigma_{11}, \sigma_{22}, \sigma_{33} \)) and six shear (\( \sigma_{12}, \sigma_{13}, \sigma_{23}, \sigma_{21}, \sigma_{31}, \sigma_{32} \)):

\[ \sigma_{ij} = \begin{bmatrix} \sigma_{11} & \sigma_{12} & \sigma_{13} \\ \sigma_{21} & \sigma_{22} & \sigma_{23} \\ \sigma_{31} & \sigma_{32} & \sigma_{33} \end{bmatrix} \]

Equation 10
\( \sigma_{ij} = \sigma_{ji} \) to disallow rotations, therefore, the tensor is symmetrical giving only six independent quantities. Due to the symmetric nature of the tensor, it is possible to find a reference frame in which all shear components are 0. This leaves only normal mutually orthogonal stresses (principal stresses):

\[
\begin{bmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & \sigma_{22} & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & \sigma_{33}
\end{bmatrix} \rightarrow \begin{bmatrix}
\sigma_{11}' & 0 & 0 \\
0 & \sigma_{22}' & 0 \\
0 & 0 & \sigma_{33}'
\end{bmatrix}
\]

Equation 11

The reference frame, can also be rotated to obtain a value of maximum shear stress \( (\tau_{\text{max}}) \), where all normal stresses \( (\sigma_{11}, \sigma_{22}, \sigma_{33}) \) are equal. Calculating the maximum in-plane (2D) shear stress is achieved using the following equation:

\[
\tau_{\text{max}} = \sqrt{\left(\frac{\sigma_{11} - \sigma_{22}}{2}\right)^2 + \left(\frac{\tau_{12}}{2}\right)^2}
\]

Equation 12

Similar to stress, three-dimensional strain is represented by the second rank symmetrical tensor \( \varepsilon_{ij} \), comprising of both normal and shear components.

\[
\varepsilon_{ij} = \begin{bmatrix}
\varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\
\varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\
\varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33}
\end{bmatrix}
\]

Equation 13

Obtaining principal strains \( (\varepsilon'_{11}, \varepsilon'_{22}, \varepsilon'_{33}) \) and maximum shear strains \( \gamma_{\text{max}} \) can be achieved using the same processes by substituting stress for strain in Equation 11 and Equation 12.

2.2 Irradiation Damage

Irradiation damage is the result of the interaction between a high-energy particle and a “target”, where in nuclear reactors this would be the vast majority of internal components, including structural materials. Understanding the effects of irradiation damage on structural, reactor pressure vessel (RPV), piping and ducting materials has significant importance with respect to plant safety and investment protection. Macromechanical effects such as embrittlement/hardening, ductility loss and decreased ductility [4]

Figure 3: Flow curves of non-irradiated an irradiated mild steel. Irradiated material exhibits an increased yield point and decreased ductility [4]
heterogeneous strain localisation are a result of defect microstructures (such as defect clusters and dislocation loops) and chemical response (e.g. radiation assisted segregation and transmutation) [4,28]. Figure 3 illustrates the stress/strain characteristics of neutron irradiated and non-irradiated mild steel [4], with the irradiated sample showing a significant increase in yield point and ductility loss.

2.2.1 Particle Damage and Cascade

Materials in an irradiating environment are continually bombarded by energetic particles (Figure 4a) introducing defects into their periodic array, the depth and morphology of which depends on target cross sections, particle type and energy. Energetic particle collisions with atoms in the lattice generate defects well outside thermodynamic equilibrium and originate from the energy transfer of the incident particle to the initially displaced atom (Primary knock-on atom, PKA). Provided the energy transferred (T) from initial ballistic impact to the PKA is above the threshold (E_d) required to displace the atom from its rest site (Figure 4b), it may trigger a cascade; this is typically in the range of ~10nm lasting in the order of 1 ps [25]. Due to the crystallographic structure of metals, there are inevitably orientations that align interstitial cavities. These aligned sites form channels that allow high energy recoils and particles to traverse relatively unobstructed; in a process referred to as channelling (Figure 4c) [29,30]. Channelled ions or displaced atoms do not retain all of their energy, although no nuclear interactions occur resulting in large energy transfers, its path is still obstructed by electrons. Transferring small increments of energy to the electron cloud leaves the atoms along its path in an ionised or excited state. This inevitably leads to localised charging by ionisation or release of photons (heat) in the case of excitation (Figure 4d), which would depend on the magnitude of energy transferred to the electrons.

If the energy carried by the PKA is below the required displacement energy, it will come to rest as an interstitial (Figure 4e), migrate to a defect sink or annihilate an existing vacancy [31]. Atoms displaced...
by the PKA are referred to as secondary knock on atoms (Figure 4f) and it so follows that they will displace tertiary atoms along their path, if they meet the condition $T \geq E_d$ (Figure 4g). Also a result of the crystallography is a phenomenon of replacement collision sequences (Figure 4h), which occurs with energy focussed along a close packed line, typically occurring at low kinetic energies [30]. Each displaced atom in turn displaces its neighbouring atom and occupies its site, with the process repeating along the line. The process of all displacements will continue until the transmitted energy of the $n^{th}$ recoiling atoms provides $T < E_d$. It must be said that displacement energy is not simply a result of the bond energy ($U$). In fact the bond energy is a fraction of $E_d$ [32]. There is a critical radius of volume ($r_v$) that a recoiling atom must exceed to avoid rapid recombination, where recoiling atoms $r_v <$ will result in a single replacement collision, giving no net defect production [30,32]. At the point that transferred energy is below the threshold energy required to displace atoms ($T < E_d$), energy is dissipated as lattice vibrations (heat), there is an associated thermal spike lasting approximately 0.1 ps. The defect structure associated with the thermal spike is a dense distribution of vacancies and interstitials due to displacement and thermal excitation (Figure 4i). As temperature falls, there is a period of relaxation, sometimes referred to as the cascade quench, where defects annihilate due to recombination and attain a more energetically favourable configuration. This step calls an end to the initial collision damage event and leaves a branching structure of stable Frenkel defects (vacancy-interstitial pairs) along the path of the primary, secondary and $n^{th}$ knock on atoms [33] (Figure 4k). The surviving Frenkel pairs are free to migrate and combine into larger defects, which will be described in section 2.2.3.

2.2.2 Particle Dependent Damage and Efficiency

The particle - matter interaction is heavily dependent on the identity and energy of the incident particle. This is due to the manner in which incident particles experience energy loss and ultimately transfer their energy to the affected matrix. Energy loss rate ($\frac{dE}{dx}$), expressed as electron volts per unit length, for incident particles is described by their collisions with electrons ($e$) and nuclei ($n$) along their trajectory [34]:

$$\frac{dE}{dx} = \frac{dE}{dx}\bigg|_n + \frac{dE}{dx}\bigg|_e$$

Equation 14

Electronic energy loss results in a low angle deflection and negligible energy loss and nuclear energy loss will result in appreciable energy loss and a larger angle deflection. The angle of attack, of course, is a dominant factor, where a glancing strike may not provide $T > E_d$ even if the particle’s energy is above the displacement energy. However, when considering a more
direct collision, energy loss differs between charged and uncharged particles (Figure 5). An incident particle either experiences interaction or is unhindered by the electrostatic field associated with an atom. Neutrons may travel relatively unimpeded through the lattice due to their charge neutrality and experiencing no repulsion until it meets a solid body (nucleus), where the repulsive force rapidly increases to infinity forcing the neutron to scatter or interact [32]. Conversely, a charged particle, such as a proton or heavy ion, will experience a force exerted upon it well in advance of physical contact, with force increasing with the inverse square distance to the similar charge. Additionally, charged ions will be more sensitive to electronic losses, however, this also depends on their energy and atomic mass (Z) (Figure 5) [34]. Therefore, the cross section (probability of interaction) is greatly increased for charged particles, since the relative size of the interaction volume is increased. In general, low energy - high mass particles will lose energy predominantly through electronic stopping, and for high energy – low mass particles nuclear stopping will dominate [34]. Counter intuitively, increasing the charged particle energy will decrease the efficiency of producing defects at a given depth (Figure 6). Since the efficiency of the Coulomb force to repel a particle diminishes with increasing energy. This has the effect of driving the particle a deeper into the material before an interaction occurs.

Figure 5: Displacement efficiency of different particles in nickel [35] Figure 6: SRIM calculation of 3 proton energies in steel, displacement efficiency decreases with increasing particle energy.

Ultimately, it can be said that particle type has a dominant effect on the damage morphology (Figure 7), where neutrons will penetrate deep into a material until it transfers a large amount of energy to a PKA, causing a dense cluster of defects. A heavy ion will experience limited penetration, so will transfer the majority of its energy close to the surface - resulting in the generation of high order knock-on atoms and a dense cluster of defects [9]. This would imply
that displacement damage for neutrons and heavy ions is similar (although the event is very different), in that heavy ion irradiation simulates more the PKA than the incident particle, which is initiated at the surface rather than deep within the material. Protons, however, may penetrate deeper into a material than heavy ions, since the coulomb potential is much lower, which reduces the relative cross section. They will lose their energy incrementally through a series of collisions, and due to their low mass, transfer enough energy to displace only low order knock on atoms, creating widely spaced lone Frenkel pairs [36].

The high dose rate of ions can be problematic when attempting to directly compare to neutron irradiated damage structures. Defects formed at a moderate dose rate at a given temperature will form a steady state reaction depending on the number of new defects and their mobility. Defects formed at a higher dose rate and the same temperature will possess the same mobility and annihilate at the same rate as the moderate dose rate example [32]. This will offset the steady state reaction and produce a net difference in final structure. Performing proton irradiation at dose rates $10^3$ times higher than neutrons would yield an comparable structure only if irradiation temperature is increased [32].

![Figure 7: Particle dependent damage morphology, average recoil energy and displacement efficiency at 1 MeV [9]](image)
2.2.3 Defects

Larger scale defect structures generally form by mobilisation of point defects, with the exception of transmutation and helium bubbles that form by fission following a high-energy ballistic impact [25]. Point defects fall into two categories: vacant atomic sites (vacancies, Figure 8 – (a)) and interstitial atoms (interstitials, Figure 8 – (b)). Vacancies are the result of removal of an atom from the crystal lattice, and interstitial atoms are the insertion of an atom at an interatomic site (i.e. \( \frac{1}{2} \frac{1}{2} 0 \)) in Figure 8 – (b)). The addition or removal of an atom from the crystal has a corresponding short-range strain field associated with it; vacancy and interstitial strain fields are positive and negative, respectively. The strain field is a result of the localised relaxation of the nearest neighbouring atoms. It should be said that the creation of a vacancy is not always coupled with an interstitial, as the displaced atom will migrate to wherever has the lowest associated accommodation energy. If a displacement occurs within the diffusion range of a crystal boundary or dislocation, this would be a more energetically favourable rest position than an interstitial site [37]. Vacancies are removed by migration to boundaries and dislocations, alongside the recombination with interstitials, provided the temperature is sufficient to facilitate diffusion. Diffusion will occur if the potential barrier between the origin and next site can be overcome, with frequency represented as [37]:

\[
v = v_0 e^{\left( \frac{S_m}{k} \right)} e^{\left( -\frac{E_m}{kT} \right)}
\]

Equation 15

where \( v \) is the migration frequency, \( v_0 \) is directional vibration frequency, \( S_m \) is the entropic increase \( k \) is the rate constant, \( T \) is the absolute temperature and \( E_m \) is the internal energy increase due to migration.

![Figure 8: Two dimensional representation the (001) plane of a primitive cubic lattice containing a) vacancy and b) interstitial atom [38](image)](image)
Dislocations are line defects and are often described as an additional half plane of atoms, they comprise of a mixture of components which are described by the relationship of the dislocation line and the magnitude and direction of slip (the Burgers vector). An edge component possesses a Burgers vector normal to the dislocation line and a screw component has a Burgers vector parallel to the dislocation line. Similar to the example of vacancies, provided above, there is also a strain field associated with the defect. However, in the case of a dislocation it has a positive and negative strain field projecting from the dislocation core which is compressive around the “additional” atomic half plane and tensile around the “missing” half plane.

The damage cascade results in a vacancy core surrounded by an interstitial shell. In austenitic steels, condensation of the core or shell onto a close packed plane will result in a stacking fault with dislocation loop boundary [33]. These small diameter interstitial loops, or Frank-loops are sessile and are required to unfault to gain mobility [39,40]. In ferritic steels, the formation of a stacking fault is impossible, due to the absence of a close packed plane. Similar to austenitic steels, they do form small interstitial loops [41,42], however, these loops are far smaller and highly mobile (glissile) [43,44]. In both steels, dislocation loops will grow as the matrix accumulates more damage. In-situ irradiation experiments carried out in ferritic steels have revealed an interaction between loops, which initiates a coalescence into larger loops [42,45]. In austenitic steels, faulted loops will grow by interstitial diffusion before unfaulting and forming glissile perfect dislocation loops [46]. The growth mechanism by coalescence of mobile loops has been described by Calverie and Cherkashin in terms of Ostwald ripening [47]. This is a process is driven by the thermodynamic stability of defects, where the energies of defect structures are low and high for larger and smaller respectively. It is more favourable for larger, more stable defects to grow rather than to retain smaller, less stable defect clusters. At high damages, dislocation loops can grow to a large enough radius that they interact with other large loops, entangling and recovering in the same way as network dislocations in deformed materials [46].

As shown in Equation 14, diffusion is a thermally activated process, hence in addition to the amount of damage, the defect microstructure is heavily influenced by irradiation temperature. At higher irradiation temperatures the mobility of point defects is increased, facilitating the formation larger diameter defects. In the low temperature regime (>300°C), defects are typically high density and possess narrow diameters that are resolvable as “black dots” [48]. In the intermediate regime (300°C ~ 500°C) defects are visible as Frank loops with diameters increasing as a function of temperature [46,48]. With increasing loop diameter, the number density of defects in the material will decrease as irradiation temperature increases. At high temperatures (>500°C), the loops have been shown to lose stability and the dislocation
structure will tend towards a network of dislocations [49]. In addition to dislocation loops, voids form due to the supersaturation of vacancies in the lattice where they form in a manner analogous to the precipitation of a second phase [6,44]. Voids share a similar temperature dependence as with dislocation loops, with density decreasing and diameter increasing as a function of increasing temperature [50], although void formation typically occurs at higher temperatures [46]. In addition to temperature, dose rate has an effect on defect morphology. When considering two materials irradiated at the same temperature and damage, but at different dose rates, the higher dose will produce larger number of defects generated in a given time increment, but thermal mobility will remain constant [32]. Hence, the trend of dose rate on defect structure will be inverse to that of temperature, with higher dose rates having a similar effect to irradiating at a lower temperature [6]. It has been suggested that the dose rate effect can be compensated for by increasing irradiation temperature [6,32].

In summary, irradiation damage induces a plethora of microstructural alterations in addition to voids and dislocation loops, amongst which are bubbles formed by transmutation and precipitation resulting from radiation-induced segregation and precipitation induced by thermal spikes [46]. Due to the temperature dependence of defect mobility, defect clusters typically increase in diameter and decrease in density as irradiation temperature is increased [46,48–50].

2.2.4 Correlating Damage

With the variation of interaction between differing particles and matter, it so follows that the damage effect will be drastically different depending on particle type, energy and exposure time. Particle irradiation is measured above a given energy threshold (E > x MeV) as fluence (time integrated flux), n cm$^{-2}$ for neutrons and Q cm$^{-2}$ for charged particles [51]. The effect of different particles and energy ranges cannot be directly compared without a common unit of dose. For example, fast reactors, mixed spectrum reactors and accelerators, as illustrated in Figure 9a, give a yield shift that varies between facilities at similar fluences [52]. The root of this lies in the range of spectra emitted by different sources: where reactors provide a spectrum extending over a wide range, up to 10 orders of magnitude [52], accelerators give a comparatively tight spectrum and are essentially mono-energetic. As the previous sections summarise, damage is dependent on energy transfer and consequently, the spectrum of incident particles will have a dramatic effect on the spectrum of recoiling atoms. It so follows that damage should generally be compared by a particle’s effect, rather than fluence since it is the material’s response that is of most interest; enter the unit of displacements per atom (dpa). Figure 9 illustrates the same data sets from three drastically different neutron sources in terms of (a) fluence and (b) dpa. The mechanical effects compare directly in terms of dpa and are not based solely on fluence above an energy threshold [52]. While the unit can be used
to compare differing fluences, it becomes more complex when relating different particle type. The dpa calculation is a measure of instantaneous damage based on energy transfer, however, irradiating species, temperature and dose rate have a pronounced effect on defect microstructure. Gan and Was [6] showed a notable variation in loop diameter and density between protons and neutrons, with larger diameter and higher density of loops generated by the latter. This was despite applying the recommended temperature correction, furthermore the diameters and densities were not simply offset from one another, but also showed a variation in trends. Differing defect structures inevitably leads to a variation in measured properties, for example yield shift measured by indentation has been shown to vary up to 400 MPa between similar damages using neutrons and protons [5]. The variations in defect microstructures and mechanical properties demonstrate that quoting only instantaneous damage is insufficient. A more complete representation of an irradiated material’s condition will include particle type, a value of dose (in dpa) complimented by dose rate (dpa/s) and temperature.

Figure 9: Yield shift following irradiation at three different facilities, plotted in terms of: a) fluence and b) dpa [52]

2.3 Mechanical Property Changes Due to Irradiation Damage

Materials in an irradiating environment undergo significant degradation of their mechanical properties resulting in hardening and embrittlement. It must be said that there are a host of additional effects during the service cycle that contribute to the degradation in properties, including an increased DBT (ductile to brittle transition temperature), helium embrittlement, solute segregation and sensitisation to stress corrosion cracking. However, for the purpose of this investigation the following sections will focus on the stress-strain behaviour due to matrix damage.
2.3.1 Yield Shift

The associated strain field of irradiation-induced defects interact with dislocations obstructing their flow and inhibiting source operation. The analogy of a quenched or work hardened metal is often applied when describing the defect density, due to both structures retaining defects well outside thermal equilibrium. In general terms, plastic flow is facilitated by the unpinning and multiplication of dislocations, occurring beyond a critical applied stress. Critical unpinning stress ($\tau_c$) varies depending on the material’s shear modulus ($G$), dislocation Burger’s vector ($b$) and separation of pinning points ($l$) as described by the following equation [40]:

$$\tau_c = \frac{Gb}{l}$$

Equation 16

Mobile dislocations are affected by long-range strain fields generated by dislocation density increase (pile-ups) at grain boundaries (described by Hall-Petch [39]) and obstacles, and stresses generated by short-range interactions with obstacles. Yield strength ($\sigma_y$) increases due to long-range stresses generated by dislocation entanglements (dislocation-dislocation interactions) which can be described by the Taylor equation [27]:

$$\sigma_y = \sigma_0 + \alpha Gb(\rho_d)^{1/2}$$

Equation 17

where $\sigma_0$ is the initial yield strength, $\alpha$ is dimensional strength factor (constant between 0.3 and 0.6 for fcc and bcc materials), $\rho_d$ is dislocation density and $b$ is Burger’s vector.

The effect of short range stresses are described by the Taylor factor (M), defect strength ($\alpha$) number density ($N$) and size ($d$) in the Orowan model [53]:

$$\Delta\sigma_y = MaGb(Nd)^{1/2}$$

Equation 18

The general themes of Equation 16, 16 & 17 are that hardening increases as the distance between strengthening bodies decreases. Hence, higher defect densities increase yield point due to the additional stress required to break away from the obstacles. Different obstacles generated by irradiation damage possess different strengths and ranges. With contributions of obstacles summed to provide the total contribution to the increase in yield strength [37]. In terms of the aforementioned dislocation loops, smaller black dots and Frank loops are treated...
as intermediate strength short range obstacles, whereas, larger “perfect” loops and dislocation networks are long range weak obstacles [54]. Black dot loops, which have been shown to be small faulted loops have a higher defect strength than larger more easily identifiable Frank loops [46,55]. A strong barrier will require a dislocation to bow around an obstacle and the critical stress to break free is described by Equation 15. The stress required to bow a dislocation is dependent on the diameter and volume fraction of strengthening barriers. This indicates that faulted loop diameter is inversely proportional to defect strength (α). As has already been discussed, an increase in diameter is generally coupled with a decrease in number density and has been shown to reduce the relative contribution to yield stress. The presence of larger loops and dislocation networks harden a material due to interactions with mobile dislocations causing sessile jogs and kinks, leading to entanglements [56]. Flow stress contribution is dependent on dislocation density rather than diameter and number density. Dislocation networks and perfect loops are treated as weak obstacles and have been shown to make a lesser contribution to the yield stress [57]. Their contribution increases at higher irradiation temperatures, this is likely due to the unfauling of Frank loops reducing their number density and contributing to the perfect loop and dislocation network density [55].

2.3.2 Plasticity

By the assumptions stated, increasing dose will generally increase yield point, as illustrated in Figure 10. However, if mechanical behaviour were based solely on defect strength, load increase would lead to a positive strain hardening rate, where the increasing dislocation density would further strengthen the material as the test progresses [27]. This is not the general observation in stress – strain curves for irradiated materials, where yield increase is associated with an apparent reduction in strain hardening rate [58–61].

In the case of non-irradiated materials, diffuse necking occurs before the point that strain hardening becomes negative (strain softening). The formation of a neck is the result of strain localisation, with heterogeneous plastic flow inevitably leading to failure under continuous load [27]. It appears that for an irradiated material there is an internal mechanism giving a similar effect. A widely observed phenomena is formation of defect free channels which could account for the plastic instability preceding necking ultimately leading to decreased ductility [62,63]. Glissile dislocations are thought to clear a path through irradiation-induced damage, destroying the strengthening defects by cutting and annihilation of loops above a critical dose [58,63–66]. The interaction of mobile dislocations with dislocation loops has been simulated using dislocation dynamics modelling, in some cases leads to kinks (mobile) or jogs (pinned) in the passing dislocation or the reaction completely consumes loops [66,67]. While dislocation jogs will result in new barriers, the generation of kinks or complete annihilations
will provide a defect free path. These narrow channels have been shown to have widths ranging from tens to hundreds of nanometres, generally increasing in scale as a function of dose [62,64]. It is thought that the narrow path provides a low resistance route for dislocations to traverse and due to the narrow channels, the chance of dislocation entanglement is greatly reduced, effectively contributing to the decrease in work hardening rate [64]. Xiao et al. suggested that the decrease in hardening rate is controlled by the absorption of dislocation loops, lowering the overall density when dislocation channels are formed [68]. With increasing strain, that the activation of new channels will further decrease the dislocation loop density and macroscopically contribute to the reduction in strain hardening rate. It is not the case that no dislocation interference occurs within these channels, Cui et al. (2014) observed the blocking of an active slip system within a channel and activation of the next favourable slip system to accommodate strain [69]. Early observations by Tucker also show dislocation entanglements occurring regularly at points within these channels [63]. However, the scale and effect of them were assumed diminishingly small when compared to those in non-irradiated materials. Hence, the strain accommodated by dislocation channel deformation (DCD) is massively imbalanced compared to the surrounding matrix. Farrell et al state that the levels of strain within the channels are high as several hundred percent [64]. McMurtrey et al. confirmed this using digital image correlation to process SEM images of gold nanopatterned samples, and measure strain around channel-grain boundary intersections [70]. Within channels that do not terminate at grain boundaries, i.e. transmitted through or assimilated to facilitate grain boundary slip, strain was measured to range from 50 to 450% “total strain” in stark contrast to the 3.5% global strain [70]. This would correspond with up to 128 times higher strain rate when compared to the un-channelled matrix.

![Figure 10](image.png)

Figure 10: Dose dependent mechanical properties of bcc and fcc steels, with a schematic of obstructed dislocations accounting for increasing yield stress [44]
Byun & Farrell later observed that the strain-hardening rate of irradiated bcc, fcc and hcp materials was nearly identical to non-irradiated material when converted to true stress – true strain. In Figure 11 the non-irradiated curve is in good agreement with irradiated curves when transposed along the strain axis [71] and appears analogous to cold work, an example is illustrated in Figure 12. This similarity between irradiated and pre-strained behaviour was first observed by Ohr (1968) noting that the required shift increases with fluence [60]. The work introduces the concept of an effective pre-strain for irradiation damage and infers that strain hardening behaviour is dictated by the sum of effective strain ($\epsilon_o$) and true plastic strain ($\epsilon_p$) (termed generalised strain) and is quantitatively described by a modified Hollomon equation:

$$\sigma_t = K(\epsilon_o + \epsilon_p)^n$$

Equation 19

where $\sigma_t$, $K$ and $n$ are the true stress, strength coefficient and strain hardening exponent respectively.

![Figure 11: True stress –true strain curves for stainless steel. With irradiated curves of 0.5, 1.1, 2.5, 3.6 and 10.7 dpa offset by 0.14, 0.18, 0.23, 0.28 and 0.385 respectively [71].](image1)

![Figure 12: True stress strain curve for duplex stainless steel for as received and pre-strained by 5% [72].](image2)

The work of Ohr, and more recently Byun & Farrell, state that pre-straining behaviour reinforces the analogy that irradiation has a similar effect to plastic deformation and it is believed that the evolution of strain hardening rate with increasing stress is intrinsic to a material. Furthermore, in channels cleared of defects the dislocation entanglement
strengthening mechanism would be nearly identical to those that occur in non-irradiated material. Under this assumption, dislocation interactions remain the dominant mechanism in controlling strain hardening rate, irradiation has no effect on strain hardening behaviour, only the force required to mobilise dislocations [73,74]. This appears contradictory to the understanding that the defect free channels provide an easy path for dislocation movement. It has been suggested that below the critical dose for plastic instability at yield, the channelling mechanism can be exhausted with a return to positive strain hardening at a reduced rate [75]. The saturation of channels has been observed in irradiated and deformed Ni & Au by Okada et al. [58]. It was shown that at low doses the deformation mode reverted from channelling to the formation of dislocation cells at higher applied strains [58]. This may account for the theory of the effective pre straining on the macroscopic flow curve and dislocation channels observed by microscopy.

Figure 13: a) strain hardening exponent of EC316LN displayed in Figure 11, with A533 & Zirc 4 from same ref. [76], plotted against log damage, with projected intersection corresponding to D_c; b) deformation mode map of 316 variants, with intersection of PIS and yield corresponding to D_c [76].

Ashby-type property maps were presented by Byun and Farrell over a series of papers with yield stress, plastic instability stress (PIS) and fracture stress (FS) plotted in the stress dose plane [59,71,74,76]. Their work showed that at a critical dose (D_c) the positive yield shift is substantial enough to be raised beyond the materials intrinsic PIS, resulting in immediate instability at the onset of plasticity. At D_c, \( \sigma_y = PIS \) and according to Considere’s plastic instability criterion strain hardening is zero. Plotting dose dependent strain hardening exponent, the exponent not accounting for effective strain equivalence, against dpa allows for the prediction of the critical dose by extrapolation. D_c is situated at the intersection of the extrapolated gradient and abscissa. Figure 13a illustrates the dose dependent decay of strain hardening.
hardening exponent calculated using ArizOna Graph Click from the data displayed in Figure 11. Figure 13b is the corresponding deformation mode map from the same authors in a following study [76]. This approach correlates with the reported critical dose for the illustrated case of EC316LN (~30 dpa [76]). Furthermore, the critical dose was calculated using this approach for A533 and Zircalloy-4 and were compared against the values measured in ref. [76]. Critical doses were found to be in the correct order of ~0.07 dpa and ~0.05 dpa respectively.

2.4 Measurement of Mechanical Properties in Ion Irradiated Materials

While neutron irradiation results in a homogeneous alteration of mechanical properties, the localised effect of ion irradiation complicates measurements. This leads to the requirement of employing novel techniques for both direct and indirect measurement of mechanical properties. An example of direct measurement is to extract the irradiated region using a focussed ion beam (FIB) and measure stress & strain in the isolated specimen [77–83]. Indirect measurement, such as indentation testing, records a convolution of yield stress, UTS and strain hardening behaviour, with yield stress estimated from the empirical relationship between irradiation hardening and yield shift [84].

2.4.1 Composite Behaviour

The limited and nonlinear damage profile of ion irradiation makes standard mechanical tests difficult, since the non-irradiated material still contributes to flow characteristics. Increasing particle energy will flatten the region between the surface and peak damage region (Bragg peak) and increase depth. However, the variation in damage as a function of depth will inevitably result in a gradient in mechanical properties. For the purpose of this subsection, the term irradiated surface will be applied to the flat region of the damage profile, which will also be treated as perfectly flat and the Bragg peak will not be considered.

With that said, an ion irradiated sample can be considered as the most basic model of composites (the slab model), with the irradiated surface behaving as a stiff reinforcing plate and the non-irradiated volume as a more compliant matrix. If the sample surface is irradiated in its entirety, the axial strain across the whole sample (ε_c) can be treated as continuous during uniaxial loading:

$$\varepsilon_c = \varepsilon_I = \varepsilon_m$$

Equation 20

Subscripts _I and _m represent the irradiated and non-irradiated matrix volumes respectively.
Since $\varepsilon = \frac{\sigma}{E}$ (Where, $\sigma$ is stress and $E$ is elastic modulus) it must so follow that under the assumption of Equation 20 [85]:

$$\varepsilon_c = \varepsilon_i = \frac{\sigma_i}{E_i} = \varepsilon_m = \frac{\sigma_m}{E_m}$$

Equation 21

This allows elastic stress or modulus to be calculated based on their relative volume fractions ($V_1+V_m=1$) and the total stress and strain acting on the material. In a uniaxial tensile test, axial stress and stiffness are represented by [85,86]:

$$E_c = E_i V_i + E_m V_m$$

Equation 22

$$\sigma_c = \sigma_i V_i + \sigma_m V_m = E_i \varepsilon_c V_i + E_m \varepsilon_c V_m$$

Equation 23

Under the same assumptions of a uniform irradiated layer and equivalent global plastic strain, a modified Hollomon equation can be applied. Recall that plastic flow is described by:

$$\sigma_c = K \varepsilon^n$$

Where $K$ and $n$ are strength coefficient and strain hardening exponent. Thus, for the rule of mixtures can be expressed as:

$$\sigma_c = \sigma_i V_i + \sigma_m V_m = V_i K_i \varepsilon^n_c + V_m K_m \varepsilon^n_c$$

Equation 24

In terms of application to bulk mechanical testing of ion irradiated materials, the hardened region is far more complicated than a simple monolayer and, due to the relative thickness of the layer to the non-irradiated substrate, would be difficult to implement. This approach was applied in the field of small scale tensile testing by Reichardt et.al in a study of He$^+$ irradiated copper, to separate the behaviour of the low and high damage regions of the non-uniform dose profile [82]. The through thickness depth of the high damage region was in the order of 28%, which allowed the calculation of a large contribution to flow stress due to the damage being ~10x higher than the low damage region.

34
2.4.2 Indentation Testing

Indentation testing is a well-established method used to probe the flow properties in a specimen surface. It is performed by impressing a tip of known geometry, under a known load into a specimen surface and measuring the response, be it the size of the remaining indent or the load displacement curve. Early work by Tobor [87] related the hardness of a material directly to yield stress by way of a correlation factor. The correlation factor is calculated by the ratio of yield and Vickers hardness and was found to be approximately 3. This work was revisited by Busby et.al and applied to neutron irradiated materials, relating the increase in measured hardness ($\Delta H_v$) to the increase in proof stress due to irradiation hardening ($\Delta \sigma_y^{irr}$) [84]. A correlation factor was derived for Ferritic and Austenitic stainless steels, expressed as:

$$\Delta \sigma_y^{irr} = C\Delta H_v$$

Equation 25

Where, C is the correlation factor, 3.03 and 3.06 in austenitic and ferritic steels respectively.

The relationship was shown to break down for hardness increases above $\sim$100 kg mm$^{-2}$, where above a critical dose (3dpa) a greater hardness increase as a function of yield stress is shown Figure 14. This was attributed to the large decrease in work hardening rate experienced by materials with irradiation damage [60,61].

![Figure 14: Relationship between change in hardness and change in yield strength [84]](image-url)
This approach has been applied to ion irradiated materials, where its surface sensitivity makes the technique ideally suited to probing the properties of the ion irradiated surface [77,88,89]. Indentation testing of ion-irradiated material tends to employ a great deal of nano-indentation. The decreased interaction volume of a shallower indent can be applied to probe the properties of low penetrating species, such as heavy ions [90]. As with the majority of techniques using decreased probe sizes, the sensitivity to errors is increased and is coupled with scaling effects [91]. Studies have highlighted the advantages and pitfalls of indentation testing ion irradiated materials [88,92]. An important highlight is the interaction of the indenter plastic zone with the non-uniform dose profile, which is balanced against indenter size effect and sensitivity to surface implantation, summarised schematically in Figure 15.

2.4.3 Flow Curves
Generating flow curves by uniaxial loading is an extremely well-established technique, providing data on a material’s mechanical response to load that is relatively straightforward to analyse. It provides data on a material’s elastic and plastic response, whilst offering some insight into the underlying mechanisms of plasticity. By integrating the area under the curve, it is possible to calculate the mechanical energy consumed up to a value of strain, where testing a sample to failure will allow an estimation of toughness. The difficulty in applying the standardised approach to proton irradiated materials lies in the global nature of data acquisition. For example, in a specimen irradiated with 3 MeV protons, the irradiated layer in relation to a millimetre-thick specimen will only correspond to approximately 4% of the volume. Recent work by Rafique et. al applied standard mechanical testing of 3.5 MeV proton irradiated zirconium [93]. Despite the relatively high beam energy and thin specimens (0.5mm), this still only corresponded to approximately 13% of the volume being irradiated. They recorded an unexpected inverse relationship of hardening to dose, which was attributed to annealing of strengthening defects by the incident protons. While beam heating may have annealed the substrate, the convolution of non-irradiated and irradiated volumes most likely offset the measurement of any irradiation hardening in the proton stopping range. This study
particularly highlights the requirement of novel techniques to measure ion irradiated property changes.

Increasing the incident beam energy to the extent that a specimen experiences through thickness irradiation is one solution to the problem. The most extreme example of this is spallation targets irradiated with high energy protons, in the order of hundreds of MeV [94–98]. This circumvents the penetration depth problem, however, increasing the kinetic energy will reduce the displacement efficiency. Furthermore, increasing beam energy will overcome the coulomb barrier and in the order of 100s of MeV induce a spallation reaction [25] resulting in sample activation. Miller et. al. (1994) reports that a minimum of six months of cooling were required for Mo alloys irradiated with 590 MeV protons to ~0.6 dpa. The drawbacks of increasing incident energy serve to offset the advantages of employing protons as an analogous irradiation regime [92]. Hence, miniaturised testing has flourished in the field of ion irradiation, where mechanical tests can be carried out on specimens irradiated with lower energy protons and other low penetration species, thereby taking advantage of the increased dose rates, limited residual activity and experimental flexibility it affords. The following subsections discuss examples of the work carried out on miniaturised uniaxial mechanical testing of ion irradiated materials and highlight some of the limitations associated with testing at this scale.

2.4.3.1 Compression
The more common uniaxial micromechanical testing technique is compression using a technique developed by Uchic et.al in 2004 [99]. Micro-compression specimens come in a range of shapes and sizes but preparation can be broken down into two general categories, those normal to the surface (Figure 16a) and those oblique to it (Figure 16b)[100]. Specimens prepared normal to the surface have the advantage of being prepared with standard patterns, but suffer from taper. On the other hand, specimens prepared oblique mitigate the issue of taper (discussed in section 2.4.3.5) but take longer and require specialised scripts to automate [101]. Loading is typically achieved using a modified nano-indenter tip, with load and displacement recorded as standard [99,101,102]. It is also possible to use specially designed piezo actuated mechanical test device, such as that developed by Wheeler [103]. The technique was applied by Pouchon et.al to annealed neutron irradiated ferritic ODS alloys [104]. Although neutron irradiation produces even damage over the whole range of standard specimen sizes, the advantage to miniaturisation in this case is in the volume reduction. Reducing the amount of material to be tested reduces the overall activity of each specimen, therefore tests can be performed outside of specialised facilities without restrictions of shipping and storage [104,105]. Hosemann et.al carried out an initial study on the application of the technique to investigate proton & helium irradiated ferritic/martensitic steels [77].
Specimens were prepared transverse to the irradiated surface, which is now the established approach for testing ion irradiated material [78–81]. This method allows control of specimen length, where top down milling from the same direction would not only limit the specimen to the penetration depth of the ions, but also possess a property gradient. In this orientation, the only limiting factor due to dose profile is specimen diameter. By comparing results with the more established indentation technique, they demonstrated that the micropillar compression tests yielded similar results [77].

Figure 16: a) Example of annular milling, prepared normal to the surface [101]; b) Example of lathe milling prepared by multiple oblique cuts [100]

2.4.3.2 Tension

Small scale tensile testing is by no means new and has been applied to testing <100μm diameter single crystal whiskers since the late 1950s [106]. More recently, work was performed by Kiener et.al [107] on the tensile testing of FIB prepared specimens, using micro indenters installed within scanning electron microscopes (SEMs). Specimens were prepared as a “T” shaped sample with the base static and remaining attached to the material the specimens were prepared from. Load was applied to the tab by gripping with a modified dovetail tip, in an arrangement referred to as shoulder loading in larger scale tests [108]. This configuration is useful, in that it affords a level of access allowing the direct observation of deformation behaviour in “real time”. For example, Kiener & Minor applied the same loading configuration to sub-micron scale samples for in-situ TEM tensile testing, allowing for the observation of dislocations that could be correlated to the specimen’s stress-strain response.

Although small scale tensile testing has been applied to observation of fundamental behaviour [107,109] and thin films [110], there is precious little work applying the technique to ion irradiated material. Two recent studies have been carried out, both taking a slightly different approach to specimen loading. Reichardt et.al [82] employed a pin loading piezo actuated microtester, in the same arrangement described in ref. [111], to investigate the effect of He$^{+2}$
in single crystal copper (Figure 17a). They measured an upwards yield shift and a decrease in
ductility as a function of fluence. Furthermore, they observed a completely different failure
mode between the stopping peak and the flat portion of the dose profile. The opportunity to
observe fracture surface, in particular speaks for the potential in application to ion irradiated
materials, since it provides the opportunity observe the failure mode, which is not possible in
compression tests. Vo et.al [83] employed a pico-indenter and shoulder loaded with a modified
tungsten gripper, in a similar configuration to Kiener et.al [107], to investigate proton
irradiated single crystal stainless steel (Figure 17b). They recorded irradiation hardening and
despite the small scale, reported good correlation between their own results and the effect of
irradiation on large scale standard tests.

Figure 17: a) example of pin loaded tensile specimen [82]; b) example of shoulder loaded
tension test [83].

2.4.3.3 Additional Techniques

It is also possible to derive flow curves using other small-scale approaches, which have been
readily applied to irradiated materials. These techniques apply loading conditions which are
not uniaxial, for example cantilevers [112] and spherical tip indentation [113]. However, with
the focus of the project addressing uniaxial testing, they will not be further discussed.

2.4.3.4 Size effect

Since the development of small scale mechanical testing it has been noted that the reduction
of scale has an effect on the mechanical response [114]. The early work on whiskers outlined
some assumptions on the origin of scaling effects [106,115,116] which were based on the
reduced scale containing shorter diameters between defects required to operate Frank-Read
sources. This was linked to the observation that strength increased inversely proportional to
whisker diameter, where at the lowest length scale crystals approached their theoretical
strength [106]. Subsequent work has related specimen diameter to yield strength by a power
law relationship that follows a similar form as the Hall-Petch effect [117,118]:

\[ \sigma_d = K_d \left( \frac{1}{d} \right)^m \]

where \( \sigma_d \) is the yield strength, \( d \) is the specimen diameter, and \( K_d \) and \( m \) are
constants.
\[ \sigma_Y = \sigma_0 + Ad^m \]  
Equation 26

and

\[ \tau_{res}/G = A\left(\frac{d}{b}\right)^m \]  
Equation 27

where \( \sigma_0 \) is the bulk yield stress, \( \tau_{res} \) is resolved shears stress, \( G \) is shear modulus, \( d \) is pillar diameter, \( b \) is Burger’s vector magnitude, and \( A \) and \( m \) are empirical fitting parameters.

Greer and Hosson reviewed the size effect and illustrated the behaviour of various crystal structures. They highlighted that FCC metals share a common scaling relationship with a power law exponent of \(~-0.6\) (Figure 18), whereas BCC crystal exhibit a less unified response [119]. There remains no consensus on the exact origin of this strengthening behaviour and a number of models have been proposed. Greer et.al proposed a mechanism of dislocation starvation, whereby dislocations more readily annihilate as the scale is reduced and the surface area to volume ratio is increased [102,120]. This would require a new dislocation to be produced for plastic deformation to occur, which requires more stress to activate than to move an existing dislocation. From a similar vein is the model of source truncation, where rather than complete annihilation the result is a truncated dislocation. The proposed formation is the bowing of a Frank-Reid source in a limited diameter specimen resulting in two shorter sources pinned between the original point and the specimen surface. Since the distance is shorter and the Orowan stress required to activate a source is inversely proportional to its length, the stress required to generate subsequent dislocations is much larger [121]. The rapid creation and annihilation of dislocations also has an effect on the flow behaviour during plastic deformation. Bursts of dislocation activity are quickly followed by annihilation which inhibits the accumulation of dislocation and therefore strain hardening does not occur in the traditional sense [122], which manifests as a serrated or stochastic flow. Ng and Ngan performed a study coating Al micropillars with a tungsten coating, which supports this understanding. The coating effectively constrained the pillars and inhibited the escape of dislocations, hence, the samples exhibited a suppression of flow curve serrations and enabled normal strain hardening to occur [123]. Kiener et.al [124] investigated size effects in proton irradiated Cu single crystals with diameters ranging from 80nm – 1500nm. They found that below a threshold diameter (~350nm), irradiation had no effect on yield stress, with hardening only occurring due to the same scaling effect as non-irradiated [124]. This was attributed to the sample being smaller in diameter than the mean distance between irradiation induced defects. Due to the
insufficient number density of strengthening defects in a small volume specimen, the flow stress is controlled by the “standard” mechanisms at this scale.

Figure 18: Normalised flow stress for FCC crystals tested in compression and tension as a function of specimen diameter [119].

The bulk of studies investigating size effect is related to single crystal work, as the absence of grain boundaries allows the separation of size effects related to scale (extrinsic) from those that are material or microstructure dependent (intrinsic) [119]. In polycrystalline samples and at length scales appropriate to the current work, the extrinsic scaling effects are diminished. Due to the intrinsic property changes, the scaling effect is more a result of the number of grains in a test volume rather than scale [125]. This has resulted in work being carried out at a number of length scales and exhibiting a similar response, which are typically plotted as a function of diameter or thickness normalised against grain size. Early work investigating thin foils related proof stress and work hardening exponent to specimen thickness. It was demonstrated that below a critical diameter the properties exhibit a deviation from bulk behaviour [125–128]. This behaviour has been reported in subsequent studies, where at low ratios of diameter (D) or thickness (t) to grain size (d) there is large difference in properties which converges with bulk at a critical value [129,130]. The effect of D/d or t/d on measured properties is thought to be due to the ratio grains intersecting the free surface to those fully constrained in the bulk [131]. In a low t/d case, there are less barriers for dislocation annihilation in free surface grains than a fully constrained grain. This was substantiated with TEM, where a heterogeneous dislocation structure was noted between the specimen surface and core [126,132]. Dislocation cells were found to possess a larger diameter in the surface region than in the core, therefore the dislocation density is lower and so too is their contribution to flow stress.
2.4.3.5 Issues with FIB manufacture

Focused ion beams afford a level of precision that enables the fabrication of site specific specimens from the nano to the micro-scale. However, some concerns are associated with this preparation route. The milling process uses an accelerated beam of heavy ions to sputter material, which inevitably produces an irradiated layer through the same collision processes previously outlined. Damage has been studied using a combination of TEM and SRIM. At 30kV an amorphized region in the surface was shown to be ~20nm thick in Si [133] and 7nm in copper [134], which decreases as a function of beam energy. The effect of FIB induced hardening in single-crystal molybdenum alloy was investigated by Bei et.al using nano indentation. Measured hardness increased as a function of beam energy, which was recorded in the 30kV case as double the hardness of the electropolished, with no change in modulus [135]. At 5kV the hardening was more modest (~500MPa), which highlights the requirement for a low energy cleaning following bulk milling [136]. Stoller et.al performed a study of LiF FIB fabricated and grown micropillars. They measured a yield stress in the FIB prepared specimens of ~600MPa and the as grown ~400MPa, which corresponds to an increase of yield in the order of ~30% [137]. Considering a damaged layer in the order of ~30nm in a 5μm diameter pillar and using a rule of mixtures to calculate the damaged layer’s contribution to flow stress [82], this would correspond to an FIB induced hardening of ~8.7 GPa. The opposite behaviour has been recorded in pillars at diameters typically dominated by size effects, where additional defects were observed to reduce flow stress when compared to grown pillars [138].

Property modification is not solely due to displacement damage, Ga⁺ implantation has been demonstrated to have an influence at depths outside the stopping range predicted by TRIM in a range of materials. It has been estimated that atomic fractions of Ga at the sample surface could be as high as 50% [139]. Such a high atom fraction can lead to phase transformations in the surface regions of some alloys. Aluminium is known to be particularly sensitive and undergoes grain boundary embrittlement due to Ga diffusion [140]. Austenitic steels have been observed experiencing γ-α phase changes due to Ga implantation [141]. The γ-α phase change was observed by Babu et.al at depths in excess of 10 times the predicted stopping range for some crystallographic orientations [142]. Chemistry is not assumed to be the only source of the γ-α phase change, internal strain is also thought to be a contributor, especially in metastable alloys [141,142].

Redeposition of sputtered material leads to a side-wall tapering between the top and bottom of a cut. This can be problematic when employing the more common annular milling approach, in which the beam is normal to the specimen surface. Different tapering has been reported between studies in the range of 2°-7° [122,143,144], which depends on sample length, beam current and material [145]. The tapering of specimens is so ubiquitous in FIB
preparation that a 2°-4° taper is considered slight [146] and tapering <1° is considered taper free [146]. However, it must be stated that this depends on specimen length, where any taper becomes more of an issue with increasing length. Tapering has an effect on the measured mechanical properties, due to the inevitable triaxial stress state. With a deviation from uniaxial loading, strain localisation can occur at the narrow point of the sample [143,146] and initiate specimen compliance in the elastic range, although compliance can be corrected mathematically [147]. Taper can be mitigated using an alternate milling routine to complete preparation, the sample is overtilted to offset the taper and milled at low current. The process is repeated after incremental rotation of the specimen (5°-10°) until all sides have been “straightened”, this process was developed by Uchic and Dimiduk and is termed lathe milling [101]. This technique is however, limited to use in specimens larger than 2μm in diameter [101,147].

The manufacture of meso-scale specimens typically requires high currents, which not only enhance tapering but also introduce striations or curtains; a particular issue in polycrystalline samples [139,145]. Differential milling rates of some grain orientations and second phase particles will introduce topography which is amplified as milling progresses. There are two solutions to removing the curtain effect, the first is the standard low current low energy cleaning and the second is a cross polishing process [148]. Cross polishing typically takes place at high currents, and an offset-tilt (X°) relative to the top-down approach ±α (-X° ≤ α ≤ X°) between consecutive cuts and supresses the curtaining artefacts [148,149]. The advantage to this approach is owed to the relatively high current and automation, resulting in a far less time-consuming process than the inclusion of a conventional low current/energy cleaning step.

2.4.3.6 Alternative Microfabrication Methods
The majority of specimens in the field of small scale mechanical testing are prepared using Ga⁺ focussed ion beam milling. Due to the nature of the liquid metal ion source (LMIS), beam spot size rapidly increases above a current of 5nA [150]. This leads to an ill-defined beam which possesses a spherical aberration above 20 nA that causes large beam tails [149,150]. Consequently, the diminished mill rates mean that specimens prepared for mechanical testing in a practicably achievable timeframe are limited to a diameter of ~10 μm [100]. However, achieving the smallest representative volume requires manufacture of larger specimens, hence it is not practical to prepare them using conventional FIB. To address this, various processes have been proposed and tested, in general terms a technique better suited to the removal of bulk material is applied which is followed by a cleaning step using conventional FIB to remove the damaged layer. Micro-electrodischarge machining (micro-EDM) is one such technique and is capable of fabricating large shapes in short time frames from CAD models. Uchic &
Dimiduk demonstrated that it is possible to attain a rough shape 20 μm diameter pillar in 15 minutes using micro-EDM and proposed that cleaning the recast with FIB takes relatively little time [101]. This was more recently applied by Shin et.al to investigate specimen size effects and manufactured 18 μm diameter pillars with 54 μm height [129]. Another promising CAD based preparation route is the use of femtosecond laser, which due to the extremely high frequency pulsing results in ablation and limited heat input. Feng et.al demonstrated in Ni base superalloy that the technique results in no remelt or heat affected zone, with only a 2 μm thick plastic deformed region [151], so this approach would also require little in the way of finishing with FIB.

![Figure 19: Diameter of region containing 50% of the beam as a function of current for Xe⁺ and Ga⁺ sources [149,150].](image)

A common manufacturing technique in microelectronics is the use of a stencil mask and broad ion beam, this has also been applied to manufacture larger scale specimens in some preliminary studies. Shade et. al manufactured tensile specimens with gauge cross section of 21 μm x 38 μm and combined tension tests with 3-D electron backscatter diffraction (EBSD) [152]. Although not explicitly stated, the measured proof stress in these specimens was in the order of the bulk proof stress of the high purity nickel investigated ~150 MPa [153]. The same methodology was applied by Wheeler et al. to manufacture tensile specimens from a copper foil with a gauge cross section of 30 μm x 10 μm, where the large scale foil specimens displayed a yield stress consistent with that of the literature reported bulk [111]. These studies both required subsequent FIB cleaning to remove the stencil mask applied to shape the specimens. The common attribute of the summarised alternate techniques is the advantage of rapid production of multiple specimens, so would be well suited for performing batteries of tests.
The current work utilises the Xe\(^+\) plasma-FIB to manufacture larger small-scale specimens, which does not suffer from the same mill rate restrictions as a conventional FIB. It has been shown that the large “virtual” source affords retention of beam control at high currents due to a columnated beam and as such is not affected by the spherical aberration experienced by LMIS (Figure 19) [150]. However, this does come at the expense of poorer beam control at currents below 5nA, where the beam diameter is ~60\% larger than Ga\(^+\) FIBs in this range [150]. It has been demonstrated in Si that Xe\(^+\) ions do not penetrate to the same extent as Ga\(^+\) ions and are more efficient at sputtering due to their high mass [133,154]. Furthermore, due to the use of an inert ion, Xe\(^+\) prepared surfaces do not suffer from the same surface chemistry modification as those prepared with more reactive species [154,155]. Prior work has applied the PFIB to the investigation of MEMS failure, taking advantage of the high dose rates to increase scale [156]. Recently, the PFIB has been applied to 3D volume characterisation of materials, where the high current allows the rapid serial sectioning of larger sample sets [149,157].

2.5 X-Rays
The current work applies x-ray diffraction stress measurement to record applied stress during a tensile test. Laboratory x-rays have a penetration depth in the order of a few tens of microns and are ideally suited to measuring property changes in proton irradiated materials.

2.5.1 Production of Laboratory X-rays
X-Rays are produced following the rapid deceleration of an electrically charged particle, typically an electron in laboratory systems. The x-ray tube consists of an evacuated tube containing a cathode and anode. By applying a potential difference of tens of kilovolts, electrons are accelerated from the cathode towards the anode. The interaction of electrons and the target results in the generation of x-rays in all directions, and phonons within the crystal lattice, causing both fluorescence and a temperature increase. Sharp and distinct peaks manifest once a critical acceleration voltage is met and are a result of cascading electrons filling unoccupied states [158]. The wavelength of the emitted x-rays corresponds to the magnitude of the transition between quantised states. Each element has a discrete energy difference between their quantum states, so the wavelengths of emitted x-rays are characteristic of the target (anode).

2.5.2 Diffraction
Diffraction of a propagating wave will occur if its wavelength (\(\lambda\)) is comparable to the spacing (d) in a periodic structure. The condition is that a parallel monochromatic incident beam will make positive or negative amplitude contributions to the reflected beam. The constructive and destructive interference of the diffracted beam will dictate the “strength” of the diffracted
beam due to the phase relationship of the beam. In phase will enhance the signal and out of phase will weaken the signal.

X-rays have a wavelength in the order of interatomic distances, so satisfy the diffracting condition. A group of in-phase parallel waves enter a crystal and are scattered by different adjacent and parallel atomic planes. In order for the exiting beam to remain in phase, the additional distance travelled by waves penetrating deeper into the crystal must be an integer number of wavelengths.

Figure 20 depicts this schematically. The condition that wave fronts XX’ and YY’ will experience constructive interference is that the additional distances ML and LN must be equal to some integer value of the wavelength (n \( \lambda \)) [159,160]. By trigonometry it stands that ML + LN = \( d' \sin \theta \), and for continuity of beams:

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

Equation 28

Figure 20: Crystal diffraction of x-rays [159]

Where n is the order of reflection (n=1, 2, 3….). This is the fundamental basis of crystal diffraction theory.

Equation 28 indicates that for a monochromatic source of x-rays impinging on a single crystal, diffraction would only occur at an angle that satisfies the \( n\lambda/2d = \sin\theta \) condition. Probability of diffraction is increased by illuminating a group of crystals at random orientations. That way, by chance, some crystals will satisfy the Bragg condition and contribute to the diffracted beam. This is referred to as the “powder method” and extends to polycrystalline samples. Powders and texture free polycrystalline aggregates consist of thousands of randomly orientated crystallites. Those that satisfy the Bragg condition for a specific plane will diffract
at a fixed angle. However, the rotation around the incident beam vector is not fixed, leading to the formation of a Debye-Scherrer cone from the various contributions.

It should be noted that x-ray diffraction is not limited to using a monochromatic beam; there are methods that utilise the heterochromatic spectrum. An example of using the continuous spectrum is the single crystal Laue method, where the range of energies increases the probability of satisfying the diffraction condition rather than a random orientation of crystallites.

2.5.3 Attenuation
Due to the interaction between x-rays and the atomic lattice, most metallic materials attenuate beam intensity to near zero a short distance from the surface. This means that in laboratory systems, the diffraction information is collected from only the near surface region. The diffracted beam intensity fraction \( G_x \) attenuates exponentially (Figure 21) with depth and, for back reflection, is described by [159]:

\[
G_x = 1 - e^{-\mu x \left(\frac{1}{\sin \beta}\right)}
\]

Equation 29

Where \( \beta = 2\vartheta - 90^\circ \), \( \mu \) is the linear absorption coefficient and \( x \) is the penetration depth.

And for differing values of \( \psi \) (described in 2.5.4) [160]:

\[
x = \frac{l n \left(\frac{1}{1 - G_x}\right)}{\mu \left(\frac{1}{\sin(\theta + \psi)} + \frac{1}{\sin(\theta - \psi)}\right)}
\]

Equation 30

[Figure 21: Fraction of total diffracted intensity of CrK\( \alpha \) in steel as a function of tilt angle.]
2.5.4 Determination of Stress by Laboratory Diffraction

Diffraction stress-measurement techniques are used as a non-destructive method of measuring internal stresses, which may be applied or residual. The technique relates a lattice plane’s elastic response to stress using the appropriate elastic constants. Therefore, the fundamental assumption calculating stress from lattice strain is a linear response to stress over the sampling volume. Lattice strain ($\varepsilon_{lat}$) is measured by selecting one (or more) diffracting plane(s) and measuring peak shifts, corresponding to a distortion of interplanar spacing:

$$\varepsilon_{lat} = \frac{d_1 - d_0}{d_0}$$

Equation 31

Where $d_0$ and $d_1$ are the unstrained lattice spacing and the strained lattice spacing respectively, calculated by Equation 28.

Calculating the stress in a given direction requires measurement of the lattice strain normal to the applied stress, as this is the maximum strain imposed (as: $\varepsilon_{11} = -\frac{\nu\sigma_{11}}{E}$). In laboratory diffraction experiments direct measurement of the $\varepsilon_{11}$ and $\varepsilon_{22}$ is unattainable due to the planes being perpendicular to the sample surface, this leads to a condition where diffraction in reflection is impossible. The limited penetration of laboratory x-rays means that surface strains are biaxial and in an ideal condition $\sigma_{11}$, $\sigma_{22}$ are non zero, and $\sigma_3$ and its associated shears are zero [161]. Measurement of a single stress along a given direction is achieved by taking multiple lattice measurements at various inclinations. Diffraction half angle is fixed in this configuration, so maintains measurement of a single hkl plane. Tilt angle ($\beta$) allows measurement of different orientations of crystallites with respect to the sample surface. The relationship between the diffracted plane normal and sample surface is termed $\psi$, the magnitude of the change in d-spacing will increase as the angle between $\psi$ and the in-plane stress approaches 90°. Lattice strain in a given direction as a function of tilt angle is represented by [162]:

$$\varepsilon_{hkl}^{\phi\psi} = \frac{d_{hkl}^{\phi\psi} - d_{0}^{hkl}}{d_{0}^{hkl}}$$

Equation 32

The relationship between stress ($\sigma_{\phi}$) and strain ($\varepsilon_{\phi\psi}$) along an inclined line in a given direction for an isotropic solid is [159–161,163,164]:

$$\varepsilon_{\phi\psi} = \left(1 + \frac{\nu}{E}\right)\sigma_{\phi} \sin^2 \psi - \left(\frac{\nu}{E}\right) \left(\sigma_{11} + \sigma_{22}\right)$$
Combination of Equation 32 and Equation 33 allows $d_{hkl}^{\psi\psi}$ to be solved as [165]:

$$d_{\psi\psi}^{hkl} = \left[ \left( \frac{1 + v}{E} \right)_{(hkl)} \sigma_{\phi} d_0 \sin^2 \psi \right] - \left[ \left( \frac{v}{E} \right)_{(hkl)} d_0 (\sigma_{11} + \sigma_{22}) + d_0 \right]$$

Equation 34

The assumed $\varepsilon_3$ zero strain condition indicates that $d_{\psi=0}$ can be taken as a value of $d_0$ with a negligible error. In practice, there is no requirement to solve $d_{\phi\psi}^{hkl}$, due to it being measured directly by diffraction. The inclined lattice spacing ($d_{\phi\psi}^{hkl}$) varies linearly as a function of the angle of tilt ($\sin^2 \psi$), its gradient is used to calculate the average stress acting in the measured direction:

$$\sigma_{\phi} = \left( \frac{E}{1 + v} \right)_{(hkl)} \frac{\delta d_{\phi\psi}^{hkl}}{\delta \sin^2 \psi} \frac{1}{d_0}$$

Equation 35

Due to the intrinsic sampling nature of the method, there are some requirements for measuring stress to a high degree of accuracy. The material under investigation must be polycrystalline and texture free to maximise the probability that grains will satisfy the Bragg condition at varying tilt angles. There is a sensitivity to errors in the presence of shear stress, the technique cannot differentiate between normal and shear strains. Texture and the presence of shear strains will introduce error due to a breakdown in the linear relationship of $d_{\phi\psi}^{hkl}$ and $\sin^2 \psi$, where texture introduces oscillations and $\psi$-splitting are a result of non-zero shear components [160,163–166].

![Figure 22](image)

Figure 22: Schematic of $\sin^2 \psi$ measurement of d-spacing response to uniaxial stress [163]

2.5.5 Diffraction Elastic Constants (DEC)

Measuring stress using single peak x-ray analysis requires the $\{hkl\}$ plane specific elastic properties of the peak of interest. The elastic properties for diffraction represent the ratio of
the Poisson coefficient ($\nu$) and Young’s modulus ($E$) of a single atomic plane. Specifically, DEC is broken down into $S_1$ and $(1/2) S_2$. In (quasi-) isotropic specimens $S_1$ is related to $d_{\text{min}}$ and is equal to $- \frac{\nu_{hkl}}{E_{hkl}}$ and $(1/2) S_2$ is related to $m^*$ (Equation 36) being equal to $(1 + \nu_{hkl}) / E_{hkl}$ [164]. In principle, the bulk mechanical elastic properties may be used to calculate stress using x-ray measurements. However, this will only provide accurate results if the material is mechanically isotropic [167]. With the dependence of an x-ray measured stress value on DECs, major proportional systematic error can arise from an inadequate constant selection, which can be as high as 40% [159,165] when using bulk or calculated constants. In the case of extreme mechanical anisotropy, the error between mechanical and hkl elastic properties has been reported as high as 80% (for Incoloy 903) [168].

The most common method for experimental derivation of DEC reports the use of a 4-point bending apparatus to apply a load to the specimen. With knowledge of the bulk elastic properties, it is relatively simple to apply a resistance strain gauge to the surface of the sample and calculate the applied stress within the elastic range. Relating the uniaxial applied stresses ($\sigma_{\text{app}}$) to the lattice strain ($\varepsilon_{\psi}=\Delta d/d_0$) measured at different $\Psi$ angles within the elastic range allows the calculation of $S_1$ and $1/2 S_2$ by way of the uniaxial $\sin^2\Psi$ equation [168–171].

For each stress increment:

$$m^* = \frac{\delta \varepsilon_{\psi}}{\delta \sin^2\psi}$$

Equation 36

This gives $\frac{1}{2} S_2$ at a single stress increment. Differentiating the gradient of $m^*$ with respect to applied load gives $\frac{1}{2} S_2$ for the diffracting plane [164].

$$\frac{1}{2} S_2 = \frac{\delta m^*}{\delta \sigma_{\text{app}}}$$

Equation 37

and:

$$S_1 = \frac{\delta I_{\varepsilon(\psi=0)}}{\delta \sigma_{\text{app}}}$$

Equation 38
where \( I \) is the intercept of \( m' \) at \( \psi=0 \) [164,172]. Calculation of \( S_1 \) depends heavily on a high degree of linearity in the acquisition of \( m' \).

The errors accumulated by improper elastic constant selection, composition and variation of material properties from processing history may heavily distort results [168]. Elimination of the bias can be achieved by experimental derivation of DECs for a material that has the same composition, grain size, heat treatment and processing history [170,172].

A clear concern in terms of this study is whether or not irradiation damage influences the diffraction elastic constants. Studies have been carried out on the residual stresses generated by ion implantation damage in semiconductors [173–176], which in all cases used standard “pristine” constants. This is a valid approach when considering the documented linear response to applied stress in the plastic range [177], the elastic response is clearly not influenced by an increasing defect density. In terms of bulk modulus, there are a range of studies reporting no change due to irradiation damage [46,82,89,90,112,178]. However, the assumption of unchanged elastic properties may break down in the event of irradiation induced structure changes at high levels of damage, such as amorphisation or phase changes [15,142].

2.5.6 Correct Selection of Reflection

Measurement of stress in the plastic regime by interplanar strain is a counter intuitive concept when considering slip plane activation. Within the elastic range, in the same sense as a macroscopic stress-strain curve, the relationship between applied stress and diffraction elastic strain is proportional. At a sufficient applied stress, the softest grain family will yield, which is marked by the proportional limit on the macroscopic stress strain curve, leading to relief through slip on those planes. Load is transferred onto harder grain families causing a deviation in linearity in the undeformed planes and once stress is sufficient for harder grain families to yield, there is a further redistribution. Furthermore, in a polycrystal, the soft and hard grain families will yield at different stresses depending on their Schmid factors, adding complexity to the stress state [179]. The magnitude of the deviation from linearity in grain families under applied stress depends heavily on the elastic anisotropy of the material, where high anisotropy results in larger deviations [180]. Hence, lattice strain will vary greatly depending on the selected hkl reflections.

Plotting lattice strains at increasing applied macroscopic stress allows assessment of the suitability of measuring stress for the given planes. The underpinning requirement for accurate representation of residual or applied macroscopic stress is a linear interplanar strain response to stress. Deviation from linearity indicates a rate change in the accumulation of lattice strain, originating from the generation of intergranular strains [181,182]. Consequently, reflections of planes with large intergranular strains will exhibit the most extreme nonlinearity and lead
to an erroneous representation of macroscopic stress during plastic deformation [183]. Planes with small intergranular strains have been shown to retain a roughly linear response to applied stress during plastic deformation. Due to the roughly linear behaviour of these planes during plastic deformation, the hkl strains can be related to the macroscopic stress state. Calibrating the planes against applied stress using the methodology outlined in the preceding section allows the suitable planes to be utilised as an “internal load cell”. There is no method currently understood to select the correct plane from first principals, therefore it is selected empirically. In FCC and BCC materials the diffracting planes are typically 311 and 211 respectively, although this can vary depending on microstructure and direction of measurement [184].

2.6 Digital Image Correlation

Digital image correlation (DIC) is a computational, image based, full-field surface displacement mapping technique [185,186]. Displacement mapping is achieved by comparison of sequential images in varying states of strain against an unstrained reference image. This is a particularly powerful tool in the field of strain analysis, offering a high volume of detailed unambiguous data per-experiment [187]. In metallurgy, DIC is applied to measuring strain heterogeneity in deformed sample surfaces [185,186,188–190]. Scale is subject to requirement and can range from macro, as a tool for defect detection for nuclear structural components [191], to submicron, for the investigation of active slip planes in deformed metals [192–195]. A distinct pattern is generally an applied coating or surface treatment [186], typically a “speckle pattern” [185,189,190,196–199], however, in some cases an undecorated surface may be sufficient [186,188,189]. The patterned surface provides features for the chosen computer algorithm to track, where a displacement vector is plotted between origin and new position. This is realised by breaking pre- and post-deformation full-field images into sub regions, which are required to capture sufficient distinct features that no two subsets can be confused, and comparing the relative pixel intensities of the sub regions [186]. There are a variety of correlation algorithms to track feature displacement, all of which are generally designed to average subset pixel displacement ($u$) to the centre of sub regions (anchoring point) for each strain increment [186,188,200]. Vectors are plotted for each sub region, generating a displacement map and can be differentiated to calculate any component of the strain tensor. In a 2-D single camera configuration, only planar strain data may be extracted:

$$
\varepsilon_{xx} = \frac{\delta u_x}{\delta x}, \varepsilon_{yy} = \frac{\delta u_y}{\delta y}, \varepsilon_{xy} = \frac{\left(\frac{\delta u_y}{\delta x} + \frac{\delta u_x}{\delta y}\right)}{2}
$$

Equation 39
Feature quality defines maximum allowable spatial resolution, where poor patterns introduce noise [185,186,189]. While images can be magnified to near atomic resolution (through electron microscopy), a poor pattern inhibits correlation of images at any magnification. Poor patterns are constituted by feature ambiguity; for example, a periodic array of uniform features is indistinct, making sub region confusion inevitable. Large features and sparse distribution can introduce errors, reducing sub region image quality by not providing sufficient features. However, if oversized features are evenly distributed, the sub region can simply be enlarged, reducing noise at the cost of spatial resolution [185]. It so follows that for the same reasons, decreasing sub region size will introduce errors. “Magnifying” the region of interest with decreased sub region size will increase relative feature scale and their spacing. Increasing sub region size may misrepresent underlying small scale strains, showing only an average strain [197]. The experimental parameters do vary depending on the information required; for example, in service monitoring of structural component deformation does not require information on strain in specific slip systems. The optimal feature size is defined as approximately 3 x 3 pixels, this is a useful rule of thumb since it is independent of magnification and can be applied to any scale experiment provided the feature density is sufficient [186].

Feature quality is not only dictated by the physical pattern, feature – signal conversion process is extremely important. Inconsistencies in the manner that the computer program interprets features can propagate error. Consequently, the process can be sensitised to a variety of systematic errors from hardware, ambient conditions and software. For example, spherical and chromatic lens aberrations leads to miscalculation of displacement due to the alteration of feature shape and intensity, with displacement errors increasing in magnitude at the periphery of the image [201]. Out of plane motion & rotation also has significant consequences, in that erroneous strains will manifest due to a perceived tension or compression, depending on the direction of motion [202,203].

Table 2: Average measured DIC errors and their sources, (from [189])

<table>
<thead>
<tr>
<th>Error source</th>
<th>Mean error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Out-of-plane displacement</td>
<td>Displacement (mm) $\times 2 \times 10^{-3}$ (mm$^{-1}$)</td>
</tr>
<tr>
<td>Lighting</td>
<td>$[2.2 \sim 4] \times 10^{-3}$</td>
</tr>
<tr>
<td>Speckle pattern</td>
<td>$[0.5 \sim 3.7] \times 10^{-3}$</td>
</tr>
<tr>
<td>Subset size</td>
<td>$[0.9 \sim 2.1] \times 10^{-3}$</td>
</tr>
<tr>
<td>In-plane translation</td>
<td>$[0.4 \sim 1.7] \times 10^{-3}$</td>
</tr>
<tr>
<td>In-plane rotation</td>
<td>$[0.4 \sim 1.5] \times 10^{-3}$</td>
</tr>
<tr>
<td>Grid pitch</td>
<td>$[0.9 \sim 1.4] \times 10^{-3}$</td>
</tr>
<tr>
<td>Environment</td>
<td>$[2 \sim 8] \times 10^{-4}$</td>
</tr>
<tr>
<td>Perfect displacement</td>
<td>$[0.5 \sim 2.4] \times 10^{-3}$</td>
</tr>
</tbody>
</table>
One significant source of error can be the interpolation function selected, where interpolation is essential to measure non-integer pixel displacements [186,190,197]. Interpolation smooths data by increasing the amount of pixels measured, effectively enlarging the dataset [186]. Schreier et. al. (2000) observed that manifested relative strain bias can be as high as ~40% when interpolated using a linear method [204]. The errors were found to be reduced when using higher order interpolators [204–207], however, this can come at the cost of increased sensitivity to signal noise [205]. Signal noise is unavoidable using CCD cameras as they are subject the same random fluctuations as any solid state device above 0K [186].

3 Experimental Methods

3.1 Materials

The material investigated in Manuscripts 1-3 was a developmental forging of SA508-Gr4 supplied by Rolls-Royce plc, its composition is displayed in Table 3. It was initially heated at 60°C/hr and austinitised at 860°C for 10 hours and water quenched to <200°C over a 2 hour period. The forging then received tempering treatment by heating at a rate of 60°C/hr to a temperature of 640°C for 15 hours and air cooled over a 20 hour period. Figure 23a displays the microstructure displayed in IPF Z, it composes of a mixture of tempered martensite and bainite with a prior austenite grain size of ~34 μm. This was calculated by reconstruction with the Matlab analysis package MTeX using a 7° cut off.

Table 3: Composition of SA508-4N forging [208]

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>S</th>
<th>V</th>
<th>Al</th>
<th>Sn</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>0.2</td>
<td>0.09</td>
<td>0.34</td>
<td>1.76</td>
<td>3.85</td>
<td>0.545</td>
<td>0.03</td>
<td>0.002</td>
<td>0.048</td>
<td>0.002</td>
<td>0.004</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

This alloy is a candidate reactor pressure vessel material and has a microstructure that is typically a mix of tempered martensite and bainite [209,210]. By comparison to the commonly used SA508-Gr3, grade-4 has a higher Ni and Cr content, which is intended to improve fracture toughness by microstructural refinement [209]. Improving the mechanical properties of RPV steel allows for the reduction of material and improves in service endurance. Although exposed to lower fluxes than other reactor components, the RPV is the single largest component in a nuclear reactor and houses a great deal of components. As such, this component is not viable to be replaced [4]. Consequently, RPV materials are required to retain toughness and be relatively resistant to irradiation damage and temper embrittlement throughout the plant’s operational lifespan.
Manuscript 4 investigates irradiation induced strain localisation in irradiated 316L austenitic stainless steel. A 50 mm forged plate of 316L was supplied by Roll-Royce plc, its composition is listed in Table 4. In the as received state, the forging contained some inclusions which were dissolved by a solution annealing treatment 66 hrs at 1100°C. The final microstructure, displayed in Figure 23b, was texture free and consisted of equiaxed austenite grains with a diameter of $32 \pm 17 \mu m$ and a high proportion of annealing twins; $\sim 40\%$ of grain boundaries possessed a $60^\circ$ rotation around the $<111>$. There was also a small ($<1\%$) volume fraction of delta ferrite stringers.

Table 4: Composition of 316L forging [211]

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>S</th>
<th>P</th>
<th>O</th>
<th>Si</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt%</td>
<td>0.028</td>
<td>0.36</td>
<td>1.77</td>
<td>17.32</td>
<td>10.20</td>
<td>2.1</td>
<td>&lt;0.001</td>
<td>0.035</td>
<td>0.012</td>
<td>0.36</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

This alloy possesses a high corrosion resistance which makes it well suited for a range of roles in the reactor. The composition of 316L consists of a lower carbon content than alloys in the same series, which increases toughness and corrosion resistance. The constitution of 316L is predominantly austenite, with a small volume fraction of ferrite stringers. Other iterations of austenitic stainless steels see wider use in all generations of reactor. For example, the advanced gas cooled reactor uses a 20-Ni 25Cr steel as fuel cladding [212] and 316L-N will be used as part of the vacuum shell in the international thermonuclear experimental reactor [213]. In addition to the corrosion resistance, it has been demonstrated that austenitic stainless steels are more resistant to displacement damage than other structural metals, evident in their reduced hardening rate [214]. They maintain plastic stability at doses as high as 30 dpa [71]. Consequently, the alloys are well suited to fulfils roles in fusion reactors where doses are expected to be far higher than are experienced in fission. However, austenitic stainless steel is known to swell at a rate of 1%/dpa in high temperature environments, which limits the scope of application [215].

Figure 23: Orientation maps of (a) SA508-4N and (b) 316L displayed in IPF Z
3.2 Specimen Preparation

SA508-4N and 316L specimens were extracted from their respective forgings using a bandsaw and cut to blanks using electrical discharge machining (EDM). Removal of the recast layer was performed by mechanical grinding on a water-cooled platter, using coarse silicon carbide (#320 grit) grinding paper. Subsequent grinding steps through to #4000 grit paper were carried out in preparation for polishing. Progress of each step was monitored by optical microscope ensuring elimination of scratches before progression to the next step. Mechanical diamond polishing was performed, using an abrasive of 6μm, 3μm, 1μm and 0.25μm. Specimens were also polished with a colloidal silica solution on a rotating synthetic cloth to remove fine scratches left by the diamond paste. Flat dog-bone samples tested using in-situ x-ray diffraction comprised of a further step of electropolishing in a cooled 8% perchloric acid and acetic acid solution, typically for 1 minute at 60V, which removed ~40μm to relieve surface stresses. Surface quality in both mechanically prepared and electropolished was verified using a Zeiss Axio (Scope.A1) optical microscope.

3.3 Conventional Mechanical Testing

Conventional mechanical tests are recorded using an extensometer and load cell during a progressive and continuous displacement. An extensometer or strain gauge records displacement assuming a continuous interface between itself and the specimen. Standard metallic extensometers rely on the strain/resistance relationship of electrical conductors described by the equation [216]:

\[
\frac{dR}{R_0} = \varepsilon (1 + 2\nu) + \frac{dQ}{Q}
\]

Equation 40

where \(R\) is electrical resistance and \(Q\) is resistivity (1/R).

Application of a constant voltage or current to the circuit results in an imbalance proportional the change in resistance. The signal is amplified and processed, giving a value of strain. A load cell is comprised of a metal beam of prescribed modulus and dimension, monitored by a bank of resistance strain gauges. Application of a load induces a deflection of the monitored beam, where the deflection magnitude is recorded by resistance strain gauges. Bending stress, and therefore force, can be calculated due to the beam being loaded within the limits of proportionality. This is the origin of load cell rating within predefined limits. Plastic deformation of the beam will lead to a break down in the calibrated behaviour, hence a misrepresentation of the recorded force.
3.3.1 Experimental Parameters

Standard mechanical tests were carried out on an Instron 5569 in order to benchmark the developed novel methods. Cylindrical specimens were machined with a 7mm x 50mm gauge section to maintain the minimum 5:1 length to radius ratio recommended by ISO 6892-1 [217]. Force and gauge section extension were measured using a 25kN load cell and two extensometers respectively. The double extensometer arrangement was intended to accurately capture uniform deformation with a 25mm MTS fixed length gauge and contain the neck following plastic instability with a longer 50mm MTS fixed length gauge. In practice, more commonly than not, localisation would initiate in the contact region between the blades and specimen. Two loading regimes were carried out: continuous and quasistatic. Continuous tensile tests were strain rate controlled, at rates of $10^{-3}$ s$^{-1}$, $10^{-4}$ s$^{-1}$ and $10^{-6}$ s$^{-1}$ with three repeats carried out for $10^{-3}$ s$^{-1}$ & $10^{-4}$ s$^{-1}$ and a single test for $10^{-6}$ s$^{-1}$. Quasistatic tests were carried out using crosshead control to emulate the loading regime during in-situ tension experiments using a microtester. A lack of strain channel in the microtester rendered strain control by feedback loop impossible during in-situ testing. Therefore, the bulk test took place at a displacement rate of 0.3 mm min$^{-1}$ with a crosshead control resulting in a varying strain-rate at any stage beyond yield. This corresponded to a nominal strain rate of $\sim 6 \times 10^{-3}$ s$^{-1}$ during the loading phase of the quasistatic tests, which was selected to be consistent with the in-situ tension tests carried out in Manuscript. The static segments of the bulk loading regime consisted of freezing the crosshead for 10 minutes to mimic the in-situ loading regime, when plotted against time resembles a staircase and is referred to as such in manuscript 1.

![Figure 24: Tensile test of SA508-4N steel at decreasing strain rates.](image-url)
Due to the quasistatic nature of each of the techniques, a series of mechanical tests were carried out at differing strain rates. Figure 24 illustrates the results of the tests. The lower strain rate tests experienced a sharper downturn beyond UTS, due to the formation of a neck at the interface of the strain gauge blade, therefore only data up to the UTS was considered. All strain rates exhibited a similar response in terms of yield and UTS calculated using the Considéré plastic instability criterion. The largest variation between strain rates was the strain hardening exponent. Since deformation is a thermally activated process, it is expected that at lower strain rates more opportunities for dislocation annihilation occur at a given increment of strain. This would result in a lower density of accumulated dislocations and will manifest as a reduction in strain hardening as the test progresses in lower rate tests. The range of strain rates were tested in order to attempt to compare the two loading regimes and obtain an equivalent strain rate for continuous loading. It was found that the hold points had a negligible effect on strain hardening; ~0.12 at a nominal strain rate of ~6 x 10^{-3} s^{-1} which was comparable to the continuous strain rate of 10^{-4} s^{-1} with a hardening parameter of ~0.12.

3.4 Proton Irradiation

All proton irradiation experiments were carried out at The University of Manchester’s Dalton Cumbria Facility (UK) on the Dalton Accelerator For Nuclear Experiments (DAFNE) beamline. DAFNE is a 5 MV tandem pelletron manufactured by National Electrostatics Corporation (NEC) and is a high current version of the NEC 15SDH-2 Pelletron [218]. This work was carried out in preparation for Manuscript 3: Novel Methods of Recording Flow Curves in Proton Irradiated Materials and Manuscript 4: High Resolution Plastic Strain Mapping of 100 mdpa Proton Irradiated Polycrystalline Austenitic Stainless Steel.

3.4.1 SRIM

In preparation for the irradiation experiment, a SRIM (stopping range of ions in matter) calculation was made to calculate a near flat damage profile that extends beyond the range of x-ray penetration. Three proton beam energies were simulated using a quick Kinchin-Pease
calculation, which negates replacement collisions, all crystallography and effects such as channelling and focusing. This parameter was chosen over the “Full Cascade” calculation for continuity with calculations performed by the wider radiation damage community, as recommended in ref. [219]. It is generally accepted that the Kinchin-Pease calculation is more representative of the the more “realistic” but computationally expensive NRT model [220]. The alternative calculation has been demonstrated to overestimate the number of displacements and vacancies created, when compared to the quick Kinchin-Pease calculation and NRT model [219].

The selected energies were: 1, 2 and 3 MeV in a single 40 µm layer for a composition matching SA508-4N (Figure 26) with damage simulated using 9.9 x10^4 H+ ions. Of the simulated energies, 3 MeV was deemed the only suitable energy for stress measurement using Cr Kα x-rays. This was based on the 99% attenuation of Cr Kα radiation diffracted from a depth of 35 µm. The units of “displacements per Angstrom-ion” (SRIM output) were converted to dpa using the following equation [221]:

\[
D = disp_{A-ion} \frac{Qm \cdot 10^8}{AepN_A}
\]

Equation 41

where, D is dose (dpa), Q is the accumulated charge, m is the average target mass number, A is the area irradiated (cm²), e is the fundamental charge of a proton (C), \( \rho \) is density (g cm⁻³) and \( N_A \) is Avogadro’s constant.

![Figure 26: Damage as a function of depth in steel at 1, 2 and 3 MeV calculated using SRIM code.](image)
3.4.2 Experimental Setup

Specimens irradiated with protons were prepared by EDM from SA508-4N and 316L forgings. They were all polished to a mirror finish using the method outlined in section 3.2. The specimens were irradiated in batches, with each batch comprising of 4 coupons, 3 dog bone tensile samples and a blank. Coupons were of the dimension 25 mm x 3 mm x 1 mm and the blank was a 75 mm x 3 mm x 1 mm bar, although the role of blank was later fulfilled by a sacrificial unpolished coupon. The dog bone tensile samples were 50 mm in length, grips were 10 mm x 5 mm with a radius of 2.5 mm leading into the gauge section of 25 mm x 2 mm; the whole specimen was 1 mm thick. All specimens were designed to slot into one another in a “jigsaw” configuration, the tensile samples length was the same as the width of the mounting stage which allowed for easy manual alignment (Figure 27a). The specimens were attached to the stage using a windowed steel hold down plate (Figure 27b), which was subsequently covered with a tantalum window to avoid activation due to beam spill.

The specimen stage is displayed in Figure 27c and comprised of a water cooled block with heaters and indium-tin eutectic baths to facilitate heat transfer. Temperature was monitored in the stage using thermocouples and due to the thermal degradation of the epoxy resin used to fix the cooling loop in place, the stage temperature was not allowed to rise above 170°C. This lead to the requirement of a ceramic heater which was sandwiched between 2 steel shims containing the indium-tin eutectic baths. The indium-tin eutectic melts at ~120°C and when in its liquid state provides good thermal contact with the specimens, delivering temperature regulation throughout the experiment. Figure 28 a&b shows examples of poor and good thermal contact. The poor contact was a result of a liquid eutectic leakage due to a slight height difference of the samples stemming from the hand polishing preparation for irradiation. It is notable that there is a striking temperature difference between coupons and tensile specimens, which is due to the improved thermal contact between specimen tabs and the steel shim. On
the other hand, the coupons have a higher temperature due to the relatively small contact area to conduct into the shim. This issue of differing thicknesses was mitigated by inserting rolled aluminium foil as braces between the specimen surface and the steel windowed hold down plate. Although a crude solution, this effectively solved the problem as is evident in Figure 28b.

![Figure 28: Pyrometer imaging of irradiation a) configuration with poor thermal contact due to an indium leak; b) configuration with good thermal contact, white arrows highlight the irradiated region.](image)

Temperature was monitored throughout the experiment using a pyrometer camera, which was pre-calibrated before irradiation. This was achieved by heating the specimen to the desired temperature and using the temperature recorded by thermocouples, which were spot welded to the coupons, to calibrate surface emissivity against temperature. The emissivity calculation is valid under the assumption that the specimens do not fluoresce under the beam in the range of sensitivity for the pyrometer CCD. Each of the specimen batches were irradiated at slightly different temperatures in the range of 320 – 360°C for SA508-4N and 316L respectively. For the SA508-4N, the 320°C corresponds to a little over the service temperature of an RPV steel of ~300°C [44]. Likewise, the 316L ducting of pressurised water reactors can operate in the region of 300°C [222]. However, as discussed in earlier chapters the damage rate of protons is far greater than experienced in a reactor. Irradiating using protons close to the operational temperature, is likely to reflect damage that would be observed in lower temperature neutron irradiations [32]. These lower temperatures were intended to be compared against the low temperature work carried out in refs. [59,71,74,76] on similar materials, to provide a measure of accuracy by calibrating against peer-reviewed research. Proton irradiation was intended to be carried out at the same temperatures, the variation was due to the reliance on thermal energy generated by the beam-sample interaction to retain a liquid state of the indium-tin eutectic bath, rather than using the stage heater which was found to generate too high a temperature.
Solidification of the liquid backing was found to have a similar effect as a leakage in terms of temperature regulation. Consequently, due to the difference in thermal conductivity between the two alloys, the average temperature for 316L (~16 W m$^{-1}$ K$^{-1}$) was higher than that of the SA508-4N (~41 W m$^{-1}$ K$^{-1}$ [223]). Histograms of the temperature for each alloy and batch are shown in Figure 29.

The area of irradiation on the specimens was controlled by tantalum apertures situated between the raster control magnets and the specimen. Figure 30a illustrates the system of beam control and monitoring in the beamline immediately prior to the stage. The beam was focussed and positioned using marked quartz slides that fluoresce under the proton beam. All beam alignments were carried out at low current to avoid excessive accumulation of damage during this step. A procedure was developed whereby the aperture veins were opened to allow the cropped beam to fall on the slides framing the specimens (Figure 30c). The aperture veins were closed in one dimension to the marked region on the slide and the position noted (Figure 30d). This was followed by re-opening the vein to the starting position and repeating the process on the remaining dimension (Figure 30e). The veins were moved to the calibrated locations, which positioned the beam onto the correct area of the specimens allowing for a 25 x 5 mm$^2$ region to be irradiated. Once correctly positioned, the proton beam was adjusted in focus and raster so that 60% of current was measured on the stage and 40% of the current was measured on the aperture veins. This eliminated the gaussian beam tails and ensured that the irradiated region had “hard edges”, hence the damage was consistent over the irradiated area. Histograms for current measured on the stage are displayed in Figure 31 for each batch of specimens. The current was relatively low (<15μA) throughout all irradiation experiments, due to the accelerator hall x-ray dose rate limits (10 μSv h$^{-1}$) imposed at DCF. As a consequence of the 3 MeV protons, collisions with the stripper gas and beam miss-steering could result in a Bremsstrahlung significant enough to initiate automatic shutdown of the beam. The solution was to regulate the beam within a current range that would minimise the risk of this occurring.
Figure 29: Histogram of temperature during irradiation experiment for each batch, measured using pyrometer.
Figure 30: a) System of beam control and monitoring; i) pyrometer; ii) optical camera; iii) current measurement; iv) tantalum vane; v) thermocouple; vi) ceramic fixture to linear motion rod; vii) viewing port; viii) beam aperture; b) unfocussed beam fluorescing quartz insert; c) X + Y rastered beam onto aperture veins; d) alignment onto shim in Y; e) alignment onto shim in X. Adapted from ref. [221].

Figure 31: Histograms of current on target stage during irradiation experiment.
3.4.3 Indentation testing

Micro-hardness indentation profiling was carried out to locate the irradiated region, it was performed using a Struers Durascan automated Vickers indenter. A series of indents were made at a spacing of 300μm under a load of 0.5 N and was applied for 10 seconds resulting in an approximate indentation depth of 4μm. The shallow indent was intended to avoid penetrating through the irradiated layer or indeed sample the stopping peak. Assuming the plastic zone will have penetrated to 5 times that depth, it would result in a sampling range of 24 μm in total, which corresponds to approximately 60% the penetration depth of the peak damage. Figure 32 shows the hardness increase measured as a function of damage shown on a logarithmic scale for the SA508-4N steel, with the 10 mdpa specimen investigated in Manuscript 3. Manuscript 4 investigated the 100 mdpa irradiated 316L, which exhibited significantly less hardening at that damage of 19 ± 10 Hv.

3.5 Combination of $\sin^2 \psi$ and DIC

Manuscript 1 and 3 applies the combination of x-ray diffraction and digital image correlation to measure in-situ stress and strain in the near surface region. Manuscript 1 applies the technique to non-irradiated SA508-4N and Manuscript 3 applies the technique to the same alloy irradiated to 15 mdpa. The following sub-sections describe the procedures, preliminary work carried out and specimen design for the irradiated specimens.

3.5.1 $\sin^2 \psi$ & Side Inclination Method

A Kammrath Weiss 5kN tension-compression microtester was utilised during this work with the loading axis situated approximately 15mm below the top of the specimen grips. This resulted in obstruction of the diffraction cone at high tilt angles in the most common $\psi$-
configuration which was corrected for by rotation of the goniometer by 90°. Measuring the residual stress in calibration standards, in both ψ and χ-mode (side inclination), allowed for assessment of error between measurements taken in each orientation. Ten measurements were taken in each orientation of stress free powder and shot peened Al standards, a further ten measurements were taken in each orientation on a Fe shot peened standard. Lattice strain in the {222}(Al) and {211}(Fe) planes were measured using a Proto iXRD with a focused CrKα radiation beam through a 2mm round aperture. The tilt arc ranged from -27° to +27°, with measurements taken at 11 points along the arc, each comprising of 20 two-second exposures. Peak positions were determined by the control software using a Gaussian fit; residual stresses and errors were also automatically calculated by the program. The variations between both ψ and χ-mode were no more than 13 MPa for the minimum and maximum values. Furthermore, the largest variation in average measurements was 9 ± 6 MPa in the powdered Al standard and the average deviation between 10 measurements in the Fe solid standard was 5 ± 6 MPa. The results of the standards measured in ψ and χ are displayed in Figure 33 and the relatively small variation between the two measurement techniques indicates the two approaches are comparable and the results collected in the χ-configuration are valid with no correction necessary.

Figure 33: Calibration standards with stress measured in Ψ and χ geometry, for a) Al, powdered and solid standards; b) Fe solid standard.

3.5.2 Defocus

It is well known that during uniaxial testing, a specimen experiences an axial contraction under tension. A height offset experiment was carried out to assess the effect of defocussing of the x-ray beam as the contraction moves the specimen surface away from the focal point. $\sin^2 \Psi$ stress measurements were carried out on a shot peened Fe standard in χ-mode with an increasing distance from the focal point, increasing in 20 μm increments. Peak measurements
were taken over a -27° to +27° range under the same conditions as those outlined in section 3.5.1. The results are displayed in Figure 34 with the measured stress as a function of defocus. The measured stress trends upwards, resulting in a net decrease in measured stress as a function of defocus of 30 MPa over the entire range. A fit of the results gives a gradient of 78 ± 14 MPa mm\(^{-1}\) with an R\(^2\) value of 0.62, where the relatively poor R\(^2\) is due to the oscillatory response in the upwards trending stress. Due to the change in stress as a function of displacement, the beam was refocussed after each 1mm displacement during in-situ XRD and DIC experiments. In the range of uniform deformation, a 1mm displacement over a 27mm long 1mm thick specimen will result in an axial contraction of ~20 μm assuming a Poisson’s ratio of 0.3. Hence all measurements are taken in the range where the defocussing effect on measured stress is minimal.

Figure 34: Stress measured in standard as a function of distance above focal point, the dotted line represents the 95% confidence and the solid line is the least squares fit.

3.5.3 Diffraction Elastic Constants

Diffraction elastic constants (DEC) were measured in accordance to the ASTM E1426 -98 standard [171], in tension rather than a 3-point bending using the same configuration as Marion & Cohen [172]. A microtester was used, rather than a 4-point bending rig, to eliminate the possibility of miscalculation of applied load, which can be a major source of error. Single peak {211} lattice strain measurements were performed on a Proto iXRD in χ-geometry to avoid shadowing by sample grips. An initial calibration was performed on a stress-free steel powder standard to ensure correct measurement of stress. Microtester mounted specimens were arranged as illustrated in Figure 35 under a Cr K\(_{a}\) beam using a 2 mm round aperture. The diffractometer took measurements at 11 ψ-angles between ±25° which was the maximum
achievable angular range without shadowing, with 10 exposures lasting 1 second each. Peak position was determined using a Gaussian curve fit by the diffractometer control software. Samples were carefully mounted in the microtester using slip gauges to ensure that samples were aligned straight and parallel to the axis of loading. Load was increased to 70%σ_y and unloaded to 0%σ_y in three cycles to ensure no presence of hysteresis, with deviation from linearity indicating inadequate mounting. The absence of shear strains was verified by loading to 70%σ_y and performing a sin^2Ψ scan under constant load, while ensuring no Ψ-splitting existed in the d vs. sin^2Ψ plot. Splitting would have indicated that the sample was not loaded parallel to the loading axis, or the loading axis was non-parallel to the Ψ-plane. Samples were loaded with increasing increments of ~5, 20, 40, 50, 60 and 70% σ_y at a strain rate of 5 μm s^−1, with x-ray measurements recorded at each increment under constant load. The load regime was reversed with measurements taken at constant load through decreasing increments, with two more cycles repeated after the load reached 0 N. The experiment was repeated over 5 specimens, with the average 1/2S_2\left(\frac{1+\nu}{E}\right) diffraction elastic constants calculated as 5.94 x 10^−6 MPa^−1.

Figure 35: Rectangular cross section tensile sample under uniaxial stress, psi scanning parallel to the loading direction and PSD at fixed diffraction half angle orientated for side inclination (χ mode)

3.5.4 Digital Image Correlation

Digital image correlation provides a non-contact method of recording strain in the surface of a specimen. To improve accuracy of the measurements a speckle pattern was applied using spray paint. It should be noted that diffraction peaks resulting from the paint were sufficiently far away from the {211} ferrite peak and therefore did not interfere with the stress analysis. The specimens were initially painted with a white anti-reflective (AR) coating to avoid saturation of the image, following curing of the white coat a black speckle pattern was applied. It was found that spraying directly onto the specimens resulted in coarse blotches of paint,
therefore paint was applied to the interior of a makeshift spray box allowing only the dust to settle on the sample. This gave a sufficiently fine pattern with ~55 \( \mu \text{m} \) diameter features. A typical example is displayed in Figure 36. Painted samples were allowed to cure naturally for 24 hours prior to testing.

![Figure 36: Typical paint pattern on a tensile specimen](image)

The displacement calculation was carried out using the commercially available LaVision DaVis 8.1.5 to correlate optical images collected at hold points throughout the test. All images were acquired at 2048 x 2048 pixels\(^2\) resolution at each hold point. An image taken at the start of the test in an undeformed state formed the reference image for subsequent calculations. The displacement calculation was carried out as an integral sum of differential vector fields, whereby each differentially calculated vector field is summed so that each vector is the product of the preceding vectors. This procedure was chosen to avoid any miscalculation of vectors at large displacements, which can occur in a single step calculation to the original reference image. The optimal sub window settings were found to be a single pass at 500 x 500 pixels\(^2\),
followed by a 5 passes of decreasing window size to a final sub window of 32 x 32 pixels² with 0% overlap. Strain was then calculated by differentiation of the displacement vectors using Equation 39 in section 2.6. To select the optimal sub window size a noise measurement was carried out and is shown in Figure 37, where 2 images of a sample experiencing no deformation were correlated using different window sizes. The calculated maps were exported as maximum shear strain in the form of a spreadsheet, where each pixel in the strain map is a cell, allowing the calculation of average strain and standard deviation. Evident in Figure 37 is the increase in measured noise and scatter as the sub window is decreased. This is due to the relative feature size increasing as the window decreases, which causes uncertainty in the position calculated by the correlation [185].

All strain calculations were in the X-Y plane due to the single camera setup, rendering out of plane measurements impossible. There is an error due to out of plane displacement and, as previously discussed, the tensile test is coupled with an out of plane contraction as it progresses. This is due to the relative movement of features as the object is moved in the Z plane, which generates a false compression or tension. It is defined as [202]:

$$\varepsilon_{xx} = \varepsilon_{yy} = -\frac{\Delta Z}{Z_{eff}}$$

Equation 42

where $\varepsilon_{xx}$ and $\varepsilon_{yy}$ are the erroneous strains generated; $\Delta Z$ is the translation in the Z-plane and $Z_{eff}$ is the effective distance between lens and specimen surface.

Therefore, increasing $Z_{eff}$ will reduce the erroneous strain generated by out of plane movement [202], where in the experimental setup of the current work, the $Z_{eff}$ is in the order of 1 m. This would lead to an erroneous compressive strain of $10^{-3}$% for every millimetre of out of plane movement, which is in the order of systematic noise and therefore is not considered to be of consequence.

3.5.5 Measurement of Stress and Strain

Flow curves were generated by performing stress and strain measurements as close to parallel to each other as was feasible. The experiment was much a continuation of the DEC measurements and used the same acquisition settings and strain rate described in section 3.5.3. Rather than unloading at 70% $\sigma_y$, the sample was incrementally displaced to deform the specimen plastically and stress measurements were taken at hold points under constant load. The surface was imaged for strain measurement at each hold using a LaVision MX 4M camera equipped with a Nikon Nikkor 105mm lens which was mounted on a tripod above the goniometer facing vertically down onto the tensile sample. In order to maintain consistent
brightness and contrast between tests, specimens were illuminated using a ring light directed at the sample surface and positioned around the camera lens. At each hold point, the specimen surface was imaged before and following each stress measurement by slewing the goniometer to the maximum of 25° to avoid obstruction. The images were later processed using the parameters outlined in section 3.5.4. Although the full field was available for strain measurement, strain was taken as an average from the region measured by the x-ray beam to ensure a representative measurement.

3.5.6 Irradiated Specimen Design

Manuscript 3 applied the combination of XRD and DIC to measure the stress strain curve in proton irradiated specimens. This highlighted a problem with the standard specimen geometry, which was 27 mm x 2 mm gauge length with a 4 mm irradiated strip bisecting the centre. It was noticed that the flow curves in this region were giving an erroneous response both in terms of stress and strain. As the two regions deformed at different rates, a strain localisation formed at the interface between irradiated and non-irradiated regions. The strain localisation initiated a complex strain state leading to the irradiated region being put in a state of biaxial tension (Figure 38). This was confirmed using finite element analysis (FEA), where the localisation at the interface caused a triaxial strain state during the test (Figure 39a). In order to address this issue, the specimen was redesigned to obtain a uniaxial stress-strain state in the irradiated region of the specimen.

Figure 38: Strain in the irradiated region at 2%, parallel to ($\varepsilon_{xx}$) and transverse to ($\varepsilon_{yy}$) the applied load.

Candidate designs were tested using Abaqus CAE, with specimens modelled as a bi-layer composite. The irradiated region was partitioned as a 40 μm deep 4 mm long layer with varying widths which depended on the design. Elastic and plastic properties were obtained experimentally for the non-irradiated partition, the irradiated properties were generated using an assumption equivalent pre-strain outlined by Ohr [60], with a transposition sufficient to
provide a 100 MPa yield shift. Using a transposed curve not only captured the yield shift but also the reduction in strain hardening comparable to this level of damage. All samples were meshed with an adaptive hexahedral mesh, which decreased from 1 mm to 20 μm in the irradiated region, the larger mesh was employed in the regions of least interest, such as specimen grips, to reduce computational load. A dynamic boundary condition was applied to the faces of the dog-bone tabs to simulate the application of load through the microtester grips. The boundary condition was constrained in all rotation axes and all but the directional x-axis, where a displacement of 0.5 mm was applied from each side. FEA was performed on multiple iterations of designs before the final design was settled on, which is shown in Figure 39b. It reduced the cross-sectional area to 1 mm with the start of the 0.5 mm radius for each side of the sample at the start of the irradiated region. This was found to be the best compromise of maintaining as much irradiated area as possible whilst maximising aspect ratio. It must be stated, that due to the specimen modification being carried out following irradiation, the double-dog bone design was not optimal. The specimen was designed around the irradiated region, which ranged from 3 – 4 mm in length. This meant that the parallel portion of the irradiated dog bone was at best a ratio of 3:1 and at its least optimal 2:1. Although the modified samples are a vast improvement on the continuous dog-bone design, this geometry is not the optimal 5:1 gauge section ratio recommended for uniaxial tensile testing in ASTM E8M-09[224]. The recommended design, would consist of a 5 mm x 1 mm x 1 mm parallel with a radius of 0.5 mm. This requires a larger irradiated area, which would increase the required beam time for irradiation. However, the specimen design would reduce possible errors in measurement and risk of damage during modification. The irradiated area was located by microhardness indentations (outlined in section 3.4.3) along each side of the irradiated region within 100 μm of the specimen edge separated by 200 μm on both edges. Once the area had been located, larger indents were made using a load of 0.98 N to mark the boundary. The specimens were then prepared using EDM to form the modified shape and remove the indentations, ensuring no stress concentration from the indents occurred during testing. Each step of locating the irradiated area and EDM specimen modification put the irradiated area at risk of damage. Therefore, any future replication of this work should follow the recommended dimensions and a proposed specimen arrangement for the irradiation experiment, which is displayed in Figure 40.
Figure 39: Finite element analysis of proton irradiated steel (a) unmodified specimen (b) modified specimen; both are displayed as $\varepsilon_{xx}$, the irradiated region is marked with brackets.

Figure 40: Recommended specimen setup for future irradiation experiments

3.6 Small Scale Mechanical Testing

Manuscripts 2 and 3 addresses attempts to scale up the work carried out by others using Ga⁺ FIB for non-irradiated and irradiated material. Increasing the scale of microfabricated materials was realised by application of the Xe⁺ plasma focussed ion beam (PFIB). In contrast to the Ga⁺ FIB, PFIBs enjoy a larger virtual source which mitigates the effects of the spherical aberration, which in standard FIBs results in a poorly focussed beam at high currents [149,150]. Consequently, the PFIB benefits from a greatly increased mill rate and sputtering efficiency per ion, therefore is capable of manufacturing larger scale specimens. This study employed an FEI Helios FEG-SEM equipped with a Xe⁺ plasma ion beam column, which is capable of achieving currents up to 1.3 µA. However, more recent iterations of the equipment are capable of attaining usable currents as high as 3 µA [225]. The following subsections outline the methods, process and procedure development.

3.6.1 Automated Cross Polish

The higher current of the PFIB leads to a significant increase in curtaining, which is due to preferential milling of different microstructural features which builds up over time to form
large channels in the milling direction (Figure 41a) [139]. A method of reducing curtaining is to perform a cross polish, which involves tilting to an angle that intersects existing curtains and removes them [148]. An automated approach limits user error and was applied to the later sample preparation iterations. Automation was facilitated by use of the automated serial sectioning tool in the FEI Auto Slice and View 4 software. The automated cross-polish performs a series of slices, similar to that of the cleaning cross section, where a stage tilt inclines the specimen by 2° relative to the start point for each line progression, thereby avoiding reinforcement of pre-existing curtains (Figure 41b). Tracking of fiducial markers allowed the routine to track specimen position and ensure all slices were parallel. Fiducial markers were milled using the cleaning cross section tool, it was found that this gave the hardest edges and therefore the best contrast for the routine to track.

![Figure 41: a) Curtaining after high current milling at 1.3µA; b) Schematic of 2° cross-polish to eliminate curtaining, adapted from [149].](image)

3.6.2 Overtilt

Overtilt is required due to the high operating currents used to manufacture specimens. PFIBs suffers from the same limitation observed in Ga⁺ FIB with respect to generating the “classic” v-shaped trench, generated by redeposition of sputtered material [145]. High current, coupled with Xe⁺ ions providing more efficient sputtering [133,154] sensitises the technique to the tapering effect. An example of trench profile as a function of milling current is illustrated in Figure 42, it must be stated that this is exaggerated with respect to specimen preparation, since the beam does not penetrate through the entire thickness as it does in the specimen cuts, therefore, sputtered material has difficulty escaping the trench. It is clear that as current is increased (moving left to right), the channel increases in width, extent of curtaining and angle of interior face. The plotted angle (Figure 43) reveals a roughly logarithmic increase with the exception of 1.3 µA, where there is a sharp uptake in angle. This is more than likely due to the reported current, which is related to the current allowed through a perfect aperture. Figure
vi shows a clear beam asymmetry due to aperture wear, which can be observed in the effect of the asymmetric beam tails on the protective platinum layer. This manner of aperture wear, due to the high operating currents, is of particular concern when milling tensile specimen shape. Verification of aperture quality was achieved by milling a test trench immediately prior to milling the specimens.

Figure 42: Xe⁺ PFIB beam profile at varying mill currents in SA-508-4N. Currents are as follows: i) 6.7 nA; ii) 15nA; iii) 59 nA; iv) 0.18 µA; v) 0.47 µA; vi) 1.3 µA

Figure 43: Half angle at the root of the trench as a function of beam current.

3.6.3 Specimen Fabrication
Development of the specimen fabrication route took place over several iterations. For ease of understanding, this section is broken down into four stages: Preliminary and Iterations 1-3.
The preliminary preparation route was carried out prior to this study during the commissioning of an in situ microtesting system at The University of Manchester [226] on 304 austenitic stainless steel. This consisted of a high current mill perpendicular to the gauge length with no polishing step, resulting in a large amount of curtaining that would lead to stress concentrations during testing (Figure 44).

Figure 44: Preliminary approach, manual high current lateral milling in 304 austenitic steel [226].

The following described designed iterations were undertaken as part of the current project and applied to SA508-4N steel, as the technique was intended to complement the work carried out using XRD and DIC. This project was chosen to assist in the development of a sample fabrication technique for the microtesting specimens as the small lath size in the material was believed to provide a bulk representative sampling of grains. All specimens were prepared from a foil thinned by mechanical grinding and polishing, to a thickness of 60-80 µm. A disk was extracted using a standard TEM specimen punch and the foil mounted between two glass slides with wax and ground into a half moon. Transferring the specimen to a mounting fixture, to be directly attached to the microtester, ensured that all alignments related to the loading axis of the test rig. All PFIB milling was carried out at 30 kV, beam currents and milling tools are stated with each described stage of preparation.

For the first iteration, a thinned lamellar, for the specimen shapes to be subsequently milled from, was prepared using the box mill tool, which involves rastering of the ion beam dynamically in all directions in a reduced area. A high current milling step was performed using the box mill tool at 1.3 µA to thin the mounted foil to ~40 µm. A further polishing step at 0.18 µA removed the deep curtaining left by the preceding high current step, achieving a final lamellar thickness of ~30 µm. “T-bone” specimens were milled at 0.47 µA using the box mill tool to trace the outline of the specimens, followed by removal of the superfluous material, the specimens followed the same general form as that suggested in ref. [101]. The material between each tensile specimen was removed to facilitate easier access during the gauge section polishing, performed using a ‘cleaning cross section tool’ at 59 nA. In contrast to the box mill
tool, the cleaning cross section scans successive lines within a reduced area and has the effect of performing multiple successive slices.

Milling the specimen shape before polishing instigated some issues that became evident during cleaning of the gauge section. Primarily, milling across edges in specimen shape resulted in curtains transmitted over the gauge surface which greatly increased the preparation time, as successive mills were required to remove curtaining from the previous steps. This was compounded by the incident angle of the beam relative to the gauge length (45°), where obstruction of the beam by the specimen grip prompted shadowing of the ion beam and gave rise to different mill rates of the shadowed and illuminated regions. A further downside of this technique was how after each box mill a stage adjustment had to be applied manually, and would be difficult to automate leading to a very labour-intensive process. A typical example of specimen prepared using this approach is displayed in Figure 45.

Figure 45: Iteration 1, fully manual approach with the specimen shape milled before final polishing.

It was therefore decided for the second iteration to attempt to polish the lamella before milling the specimen shape. Simple attempting to remove the curtains using progressively lower currents is not effective due to the size of areas involved, and the respective mill times required. It was therefore decided to incorporate an automated cross-polish step following the initial high current thinning. The specimens were cut at 0.18 μA once a satisfactory surface finish had been achieved. Figure 46 illustrates the gauge section finish achieved using this approach. Unfortunately, due to the microscope stage possessing a single tilt axis, which was used by the automated cross polish routine, sample overtilt was impossible. Therefore, specimens prepared using this method possessed a slight taper which was later measured using XCT as ~1.6°.
Figure 46: Iteration 2, automated cross-polish with manual tensile specimen shaping, specimens are not overtitled so possess some taper ~1.6°.

Figure 47: a) specimen mounting fixture; b) pre-tilted microscope stub, with tilt angles ranging from 1-4° in 1 degree increments (courtesy of Jack Donoghue [227]); c & d) automated cross polish of specimen mounted in pre-tilted holder.

Iteration 3, followed a similar semi-automated procedure as iteration 2. A protective layer of platinum was deposited on the leading edge of the specimen prior to the automated cross-polish. This limited the effect of curtain transmission originating from the initial cut to align the specimen. The key improvement was the use of a pre-tilted holder to which the specimen mount (Figure 47 a) could be directly attached. It comprised of 4 pre-tilt angles at 1-4° increasing in 1-degree increments (Figure 47 b) allowing both a cross polish and over tilt simultaneously. Specimens were prepared by cleaning-cross section in the 2° holder, where this was the taper estimated in the previous batch by observing the parallax from the top edge. The use of a lower current (59 nA) to shape the specimens significantly improved the quality of the gauge section (Figure 48). A schematic of preparation steps is illustrated in Figure 49.
Figure 48: Iteration 3, semi-automated cross-polish with manual tensile specimen shaping, specimens are prepared using a 2° pre tilt holder resulting in a slight taper of -0.44°.

Figure 49: Key steps in the preparation route of iteration 3 from a 50µm thick half-moon disk using the specimen route from iteration 3. An initial cut is made to align the flat edge of the specimen with the back of the specimen mount. Platinum is deposited to protect the specimen faces during thinning by automated cross-polishing of both sides. Specimens are milled into shape. It must be noted that the foil thickness in this sample batch negated the need of a high current top-down mill.

3.6.4 Orientation Mapping
Orientation mapping was carried out in the same FEI Helios FEG-SEM as the specimen preparation using the Oxford Instruments Nordlys Max³ EBSD detector at an operating at 20kV and a 0.1µm step size at ~50Hz. Kikuchi patterns were indexed using AZtec HKL with an image binning of 8x8. Figure 50 illustrated the geometry employed for orientation mapping, where it was found that due to the tensile specimens being recessed after thinning, the diffracted beam was obstructed on exiting. The specimen was mounted inverted in a 45° pre-tilt holder with a stage tilt of 25°, although this could have been easily solved by machining a lateral mount into the same pre-tilt holder. EBSD was primarily employed to relate strain
localisations to microstructural features, however also allowed for lath size measurements in each specimen.

![Orientation mapping geometry](image)

Figure 50: Orientation mapping geometry of inverted sample using a 45° pretilt holder, in order to avoid shadowing.

3.6.5 Loading Pin

In situ tensile testing of small scale specimens in an SEM generally involves two methods of load application: shoulder loading [83,107,110,228] or pin loading [82,111]. A shoulder loading arrangement involves a micro gripper applying load to the shoulders of the specimen tab. This has the advantage of a large scale relative to the specimen, so has little chance of failing under load. The loading configuration has also been used for larger scale tests, where, in the event of limited material shoulder loading allows the specimen tabs to be retained for characterisation [229]. In terms of the present work, the disadvantage is the large specimen grips required are not compatible with the sample manufacture methodology, due to the close proximity of specimens (~ 30 µm maximum). It has also been stated that shoulder loading specimens can cause some high aspect ratio geometries to rotate under load [111], however, for the near 1:1 aspect ratio of specimens in the current work this would not be expected to be an issue.

Pin loading involves the application of load through contact with the interior of a loop milled into the specimen tab. The advantage is that specimens can be fabricated in close proximity, the single point loading allows some specimen self-alignment. Contact alignment between the specimen surface and loading pin is also advantageous using this configuration, since it involves half the contact surfaces as that of the shoulder mount. A disadvantage to this method is the specimen tabs are required to be much larger than those loaded on the shoulders. This is due to two key issues relating to stress distribution, first the large compressive stress acting on the loop interior behind the loading pin, which has been shown to be as high a double that of the tensile stress acting on the gauge section [111]. Second, the loading pin must also be
large to withstand the force acting upon it when applying the load, both effects increase the required size of specimen tabs.

Figure 51: (a) Failure of SiC loading pin during a test, at a load of 0.44 N (b) Fracture surface of the SiC loading pin, failure was purely brittle originating at the root of the loading pin; (c) higher magnification of the crack origin, a proto-crack can be observed parallel to the point of failure and is marked ‘a’, the region marked as ‘b’ highlights the start of the failure surface.

Due to its compatibility with the current work a pin loading configuration was employed. While other research utilising the same configuration and equipment utilised a Si loading pin [82,111], the large scale and high strength of the specimens in this study required a higher strength material. Initially, the loading pin was fabricated from SiC and worked well for the initial two batches, however, after multiple tests the pin failed at 0.44 N of load (Figure 51a). Prior experiments had taken the load as high as 0.56 N using the same pin, leading to the assumption that failure was due to the development of a small fatigue crack. Inspection of the fracture surface (Figure 51b) reveals a purely brittle failure originating from the root of the loading pin, which was identified as the high stress region in ref. [111]. The inlay (Figure 51c) highlights the origin of the crack, which appears to be the interface of terracing in the basalt structure that is typical when milling this material. It appears that the lever action at the base of the pin initiated fissures at the terracing and since the critical crack length for fast fracture is so short in SiC (~1 μm [230]), resulted in catastrophic failure.
Clearly, a stiff and hard material with higher fracture toughness would be beneficial for pin fabrication. Unfortunately, due to project time constraints a diamond pin was employed, which possesses a lower fracture toughness than SiC [231]. However, identification of the critical failure point of the previous pin made it possible to design around the lower fracture toughness. Diamond exhibits the same terraced structure as SiC when milled in the Xe⁺ PFIB. Therefore, preparation employed a two-step route, where high current milling was carried out in the PFIB, followed by a polishing step in the Ga⁺ FIB. The initial shaping of the diamond pin was carried out at 30 kV and a current of 1.3 µA, a rough pin shape was cut followed by a radius at the base of the pin to avoid the stress concentration identified in ref. [111]. Figure 52a highlights the rough surface generated by milling in the PFIB. Polishing was performed in a Quanta 3D FEG-SEM equipped with a Ga⁺ ion beam column. All milling was carried out at 30kV using a selective carbon etch with H₂O, which is known to improve the sputtering yield and surface finish when milling diamond [232]. An initial mill of 5 nA using the dynamic rectangle tool with 3º overtilt, followed by a polishing step at 1 nA with a 1º overtilt using the same tool. The rectangle tool was employed rather than a cleaning cross section because it allowed real time monitoring of progress. Figure 52b illustrates the surface following cleaning; the terracing is significantly reduced and retains only a few curtains. A point of concern was the small channel at the base of the pin marking the transition into the radius. This was due to the “shoulders” at the base of the pin instigating differing mill rates across the surface. Figure
Following satisfactory surface finish, the loading pin was seated against a specimen in the microtester rig to verify good surface contact. It is noteworthy that the diamond pin has survived multiple tests with no failures, reaching loads as high as 0.73 N.

### 3.6.6 Piezo-Actuated Mechanical Testing

All in-situ small scale mechanical testing was carried out on an MTR-3 (micro-test rig) by Microtesting Solutions mounted in a Zeiss Sigma FEG-SEM. The use of a piezo actuator provides the level of precision in the sub-nanometer scale [233] that is required for this manner of testing. A photograph of the MTR-3 is shown in Figure 53a along with a schematic diagram in Figure 53b. Specimens attached to the specimen mount are fixed directly to the piezo-electric positioning stage, which has a 10nm resolution with 8mm of travel in x, y and z. The loading pin is fixed to the piezo actuator, which possesses a <1nm resolution with a maximum of 150μm of travel [234]. Stress was recorded using a 4.4N load cell, although the rig is capable of mounting other load cells, the highest capacity was selected to avoid damage. Displacement was recorded by imaging fiducial markers on the gauge section which were converted to strain by the Labview control software.

![Figure 53: a) MTR-3 piezo-actuated loading rig; b) schematic highlighting key components](image)

The quasistatic test required a hold point for imaging throughout the test, where the Labview based virtual interface allows the predetermined holds to be selected at specific displacements. Approximate displacement (δ) is calculated using the unloaded piezo voltage motion (free piezo voltage) and load cell compliance, expressed as [235]:

$$\delta \approx (C_d V) - (C_{LC} P)$$

where $C_d$, $V$, $C_{LC}$ and $P$ are displacement coefficient, applied voltage, load cell coefficient and load respectively.

Calibration to obtain a displacement coefficient allowed a more accurate approximation of displacement, ensuring that hold points were as accurate as possible. This was achieved by
positioning the loading pin against the specimen block and moving the block in the x-direction so to put the loading pin into compression. The loading pin was impelled to multiple displacements, imaged, and the displacement measured using the microscope control software (Figure 54a-c). By recording the loading for each displacement using the MTR-3 load cell, a relationship is derived between displacement and load. The results are plotted in Figure 54c, where the linear regression of the displacement and load equates to the displacement coefficient of the device [235].

![Figure 54: (a-c) Progression of load-displacement throughout calibration, load is applied by movement of the stage rather than via the piezo actuator; (c) load cell recorded force plotted against displacement measured manually.](image)

Positioning the specimens onto the loading pin is a non-trivial process, in part due to the poor depth perception in the microscope, and the opportunities to damage specimens are abundant. The procedure followed in the current work was developed through experience to minimise risk to the specimens. Before mounting the microtester in the microscope, the specimen was manually positioned to less than 1 mm above the loading pin. Once the MTR-3 was mounted on the microscope stage and connected to the control computer, the piezo actuator was polarised with 150V, causing the loading pin to extend by ~150 μm. The specimen was then manoeuvred in the x-direction such that the specimen tab and loading pin were within the
same image frame. Relative distance was approximated by focussing on the loading pin and the specimen tab surface and subtracting the respective working distances. With the specimen away from the loading pin, the microscope was focussed on the top of the loading pin and the specimen translated in z, until the loading pin and specimen face are in focus. This ensured the top faces were at the same z-position, the specimen was then raised by ~100 μm to ensure no contact was made during positioning and translated in x to align the loop centre with the loading pin. By translating the specimen downwards with the pin in focus, the specimen was again moved in z until both faces were in focus, with slight adjustments made in x and y to ensure the pin remained central to the loop. With both faces flush, the specimen was at a point too high on the pin to perform the test as it would have provided the maximum torque at the base of the pin and invited failure. The poor conductivity of the loading pin provided an easy method of ensuring the pin was properly seated at the pin bottom. Out of contact with the specimen the poor conductivity of the diamond possesses a surface charge, which is subsequently discharged upon contact with the specimen, the resultant change in contrast was a good indicator of specimen seating (Figure 55). The specimen was then moved +1 μm in z and the load cell reset, which allowed the specimen to be moved into the contact position in x, it was also coupled with a contrast change, which was verified against the load cell.

Figure 55: Pre-contact and contact of the loading pin mounted in the SEM.

Uniaxial tensile load was applied by the steady reduction of voltage to the piezo actuator causing a contraction of the loading pin. The test was therefore performed using voltage control, which would correspond to displacement control in a conventional mechanical test as the two are interchangeable. All experiments took place at a displacement rate of ~100 nm s⁻¹, corresponding to a nominal strain rate of 7x10⁻⁴ s⁻¹. Load was measured by the loadcell and recorded using the Labview control software. Hold points at 200nm displacements allowed imaging for strain calculation. Secondary electron images were taken at each hold point at 8 kV in high current mode. Scans took approximately 4 seconds to complete, with a dwell time of 50 ns and line averaging x 4 to reduce noise from the rapid acquisition. During the tests
strain was calculated by tracking the feducials rather than using the predicted displacement calculated from the voltage drop across the piezo. The direct measurement of strain discounts any system compliance, however there remains a slight specimen compliance during the initial loading. Strain was measured using the control software which tracks the displacement of fiducial markers applied in Pt (Figure 56). Additional strain measurements were made using the DaVis 8 software package in Manuscript 2 to support the FEA of XCT. In both cases that it was employed, the surface finish was sufficient to obtain a strain map. Due to the lack of an ideal distinct pattern, the strain maps contained a high degree of noise compared to that of a patterned surface. For this reason, the strain maps were only used to assess the relative distribution of strain rather than the absolute values. Strain maps were calculated using the FFT correlation function, with the regions outside the gauge length masked out. The calculation comprised of 5 passes, the initial pass was 1k x 1k pixels$^2$ followed by 4 passes of decreasing sub window size, down to 48 x 48 pixels$^2$. A typical example of a strain map is shown in Figure 57, in terms of maximum shear strain. The out of plane error, discussed in section 3.5.4, when imaging with an SEM are increased due to the shorter work distances ($Z_{eff}$) involved. With a work distance of ~15mm, an erroneous $\varepsilon_{xx}$ and $\varepsilon_{yy}$ strain of -6.65x10^-3 % will be generated for each micron of out of plane deformation.

![Figure 56](image)

**Figure 56:** Fiducial markers applied to surface allowing for calculation of strain.

![Figure 57](image)

**Figure 57:** Typical example of strain map correlated using the raw specimen surface, map is calculated with a final window size of 48 x 48 pixels, with smoothing on.
3.6.7 X-ray Computed Tomography (XCT)

XCT was carried out to assess the taper of specimens prepared using no overtilt and with overtilt for Manuscript 2. X-ray computed tomography (XCT) was performed using a Zeiss Versa XRM-520. A power of 10.2 W was a result of an accelerating voltage of 100 kV and a current of 91 µA. The 3D structure was made up of 1601 projections for each specimen. Each projection comprised of a 40 s exposure, using a low energy filter at the source (LE3). The source and detector were positioned 14.04mm and 37.02mm from the specimen respectively, with a magnification of 20x and a camera binning of 2x. This configuration provided a resolution with a voxel size was 0.3693µm. Images were processed and reconstructed using Zeiss Scout and Scan. Analysis and visualisation was performed using Avizo 9.0.0 software. The constructed projections were subsequently meshed with an adaptive tetragonal mesh using the Synopsis Scan IP software package and an average element size ranging from 1.6 µm -1.8 µm.

3.6.8 Finite Element Analysis

Manuscript 2 investigated the effect of specimen taper using finite element analysis and was performed using Dassault Systemes SIMULIA Abaqus/CAE 6.14-2. Two types of models were tested, the first were multiple 2D plane strain models and the second was tetragonal meshed reconstructed XCT models. The 2D models were based on the assumption that there is variation of the stress state through thickness, which is displayed schematically in Figure 58. A series of plane strain models were constructed in Abaqus CAE with a common length but varying ratios between thickness at either end: 1:1, 1:1.01, 1:1.1, 1:1.2 and 1:1.3. The model constructed had 50% the ratios reported and were doubled by a symmetric boundary condition applied to the bottom edge. 2D plane strain models were also tetragonally meshed and had a mean element size of 1.5 µm. In addition to the symmetric boundary condition, a static boundary condition was applied to one edge and the other edge a dynamic boundary condition to apply a 25 µm displacement in the x-direction. This had the effect of application of a uniaxial load from one side of the specimen, in a similar manner to that of the experimental tests performed using the MTR-3. The meshed XCT was tested in a similar manner, where all elements at the base of the model were pinned and all elements on the inside of the loops back face were displaced in the x-direction with a dynamic boundary condition. Therefore, the dynamic boundary condition replicated the loading pin and the static boundary condition replicated the specimen fixture. Mechanical properties were obtained experimentally and applied as elastic and plastic parameters, an estimated Poisson’s ratio of 0.3 was also applied. Data was extracted from all elements in the gauge section as stress and strain in the x-direction. The data for each element was averaged and plotted as a stress strain curve, with tensile strength and strain hardening parameter extracted using the standard method.
Figure 58: Schematic representation of the assumptions in a 2D plane strain model.

3.7 High Resolution Digital Image Correlation (HRDIC)

Manuscript 4 utilised styrene vapour assisted gold remodelling to apply nano-scale markers to a specimen surface for High Resolution Digital Image Correlation (HRDIC). HRDIC is generally applied to DIC studies performed in an SEM, with the spatial strain resolution heavily dependent on pattern scale, distribution and contrast [236]. There are a variety of pattern application methods including evaporated colloidal silica particles [237], electron beam Pt (E-beam Pt) decoration [238,239] and gold colloids [70,239], with a range of particle sizes densities and contrasts. Typically, colloid based patterns consist of small, widely spaced particles with good contrast and E-beam Pt is coarse and dense with lower contrast. Both of these processes benefit from being low temperature, so are well suited for studying irradiation damage. However, the reduced spatial resolution can obscure some finer features such as diffuse slip, which would appear as homogeneous strain. Vapour assisted remodelling has been shown to give consistently fine, dense, high contrast patterns which maximises resolution [192–194,240–242], however it is a comparatively high temperature process. The gold remodelling technique was applied to non-irradiated and 100 mdpa proton irradiated 316L austenitic stainless steel, to probe the effect of irradiation on deformation mechanisms and attempt to relate plastic strain localisation to mechanical behaviour.

3.7.1 Vapour assisted remodelling

To track the local deformation on a scale sufficient to measure slip bands requires fine set of markers on the surface for the correlation algorithm to track. At this scale, the imaging is carried out in an SEM to resolve localised strains resulting from slip. Therefore, fine high atomic weight particles are the markers of choice due to the good contrast between marker and substrate when imaging backscattered electrons. A system of gold remodelling was developed by Luo et. al [243] who applied it to glass slides using a iodobenzene, which was subsequently further developed for the purpose of HRDIC by Gioacchino and Fonseca [192]. Remodelling is a process whereby a thin sputtered film “dewets” from the surface forming agglomerates to reduce surface energy through a process of Ostwald ripening. The majority of HRDIC studies that used this particular pattern application method utilised water vapour as
the solvent to remodel the sputtered gold film (Figure 59) [192–194, 240–242]. The remodelling temperatures ranged from 250 to 320°C. This method uses a temperature in a similar order to the irradiation temperature in the current study. Therefore, this approach was considered unsuitable for pattern application to irradiated material, as it likely to result in damage being annealed out. Figure 60 shows a recently developed closed system which uses styrene as the remodelling solvent. It consists of a closed glass vessel with a gas inlet, gas outlet and integrated hotplate. The incoming argon gas is sent through a styrene reservoir and forms an argon-styrene vapour mixture, which flows into the remodelling chamber [195]. This approach was developed because the closed loop styrene system protects against surface oxidation. However, in terms of the present work, the advantage is in the reduced temperature required for remodelling, as low as 120°C, at the expense of time.

In this work, a thin gold film was applied to the sample surface using an Edwards S150B sputter coater, sputtering for 3 minutes at a deposition rate of 5-8 nm min\(^{-1}\) [193]. The polished tensile sample was remodelled for a period of 168 hours at 120°C. Indentation testing was carried out to assess the effect of prolonged temperature on the irradiation hardening. A Vickers indent profile was made along one edge prior to remodelling using a Struers Durascan automated indenter, allowing location of the irradiated region. The indentations were 300 μm apart and used 0.5N of load for a period of 10 seconds. This resulted in a mean indentation depth of ~4.5 μm. The relatively light load was selected for the reasons outlined in section 3.4.3. A second profile was made following remodelling using the same parameters, a slightly lower hardness was recorded between the pre- and post-remodelling irradiated regions of ~3 Hv (Figure 61). This value was well within the standard deviation of ~9 Hv. A further set of indentations were applied to the surface to mark the boundary of irradiated and non-irradiated regions, using a load of 1 N for 10 seconds. The areas to be imaged were marked out with 0.5 N indentations as reference points to aid orientation in the microscope.

![Figure 59: Setup for water vapour assisted remodelling, the process takes place at ~300°C and is an open system][192].
Figure 60: Styrene remodelling setup takes place at a lower temperature, as low as 120°C, and is a closed system [131].

![Styrene remodelling setup](image)

Figure 61: Indentation in 316L steel, in non-irradiated state, irradiated before and after vapour assisted remodelling.

![Indentation in 316L steel](image)

3.7.2 Image acquisition

All images were acquired using an FEI Magellan FEG-SEM with an insertable Circular Backscatter detector (CBS). Imaging in backscatter provided good compositional contrast between the gold markers and steel substrate. The images were acquired at an accelerating voltage of 5 kV and a current of 0.8 nA, with a 2 kV stage bias and a dwell time of 10 μs, as these conditions minimise the interaction volume and maximise spatial resolution. The low accelerating voltage required a work distance of 4.6 mm to obtain a strong enough signal. A large area was covered using an automated mapping routine (FEI Maps), allowing a 15x15 montage to be taken. Each image was acquired with a horizontal field width of 19 µm at 2048 x 1768 pixels². A 40% overlap of each image ensured gave a montage horizontal field with of
178 µm at 19069 x 16676 pixels² (9nm pixel⁻¹). Each frame was taken with a stabilisation pause of 5 seconds between each image to reduce vibration and maintain a high spatial resolution. Focus was maintained over the entire mapping region by an interpolated focus function included in the mapping package. The microscope is focussed at the top and bottom extremities of the map and the software adjusts as each image was acquired. Images were taken before the first loading stage and after each subsequent loading stage.

Figure 62: Schematic of origin of disparity of strain between irradiated and non-irradiated regions for equivalent displacement

Tensile load was applied with a Kammrath-Weiss 5 kN tension-compression microtester at room temperature and at a displacement rate of 5 µm s⁻¹, corresponding to a nominal strain rate of 2x10⁻⁴ s⁻¹. The load regime was ex situ, in that the specimen was deformed plastically, then unloaded and removed from the microtester for mapping. This process was repeated 4 times, with a map taken for each of the non-irradiated and irradiated regions. Although the displacement increments were the same due to the single sample arrangement, the average total strain was different in each region for the same increment. Average ε_{xx} in the non-irradiated region was 1%, 1.7%, 2.4% and 3.1% and the irradiated was 0.7%, 1.3%, 1.9% and 2.5%. This disparity between the two regions is due to the irradiation hardening decreasing the accumulation of plastic strain for an equivalent displacement (Figure 62).

3.7.3 Orientation Mapping

Following acquisition of the final image map, the gold pattern was removed by manual polishing using a dilute colloidal silica solution. Orientation mapping was carried out in a CamScan FEG-SEM equipped with an Oxford Instruments Nordlys Nano EBSD detector and with diffraction patterns indexed using Aztec HKL. Mapping was performed at 20kV with a step size of 0.4 µm with 8x8 binning at a rate of 40 Hz. Indexing rates were high in both non-irradiated and irradiated regions, with 0.4% and 0.5% non-indexed solutions respectively.
EBSD data was processed and analysed using HKL Channel 5. Orientation maps were displayed in the IPF colour scheme relative to the loading plane. Schmid factors for \{111\}\langle\overline{1}10\rangle type slip was mapped with the x-direction as the loading axis. The average Schmid factor was calculated by exporting the maps as a text file and calculating average and standard deviation for both regions using a spreadsheet.

3.7.4 Displacement Calculation

All displacement calculations were carried out using the commercially available DaVis 8.1 and maps were processed as stitched mosaics rather than individual tiles. Maps obtained in the deformed state were shift corrected relative to a distinct feature, such as a grain boundary triple point, in the preceding map. Although the pattern can provide sufficient distinct features to shift correct, the distinct larger scale feature was selected to allow easy manual verification of the shift correction. The cross-correlation calculation was performed as integral, which calculates all vectors relative to the undeformed reference image (S0) (Figure 63). This function was selected rather than the integral sum of differential vector fields described in section 3.5.4 due to the increased resolution. The high resolution sensitises the calculated maps to noise, which can be propagated by summing together successively calculated strain maps.

![Figure 63](image)

Figure 63: Schematic of integral correlation and corresponding strain maps calculated.

Vectors were calculated by fast Fourier transform by the software in a series of multiple sub window passes. The initial calculation was performed with a single pass at an interrogation window size of 1024 x 1024 pixels\(^2\). Subsequent calculations were performed at decreasing interrogation window sizes down to an interrogation window size of 8 x 8 pixels\(^2\) for the actual calculation. At the final interrogation window sizes, 5 passes were performed to increase the accuracy of the calculation. No overlap was required due to the distinct features of the pattern and this helps to limit the propagation of noise. The final spatial resolution in each map was 74 x 74 nm\(^2\).
3.7.5 Pattern Morphology and Sub Window Optimisation

Systematic noise measurements were carried out to measure the error and obtain the correct sub window size to achieve comparable results from the slightly different speckle patterns. The differing polishing rates of the irradiation hardened surface and the non-irradiated leaves a slightly different surface finish which has been demonstrated to affect pattern morphology [192,193]. Gold particles in the non-irradiated region were better defined and slightly coarser (~14 nm) (Figure 64a), which indicates that the higher number of fine scratches in the softer material left by the colloidal silica served to seed the surface and aid remodelling. The irradiated region appeared to consist of finer particles (11 nm) (Figure 64b), which appear to be interconnected and less well defined. Patterns in both regions displayed a trimodal morphology, with the fine particles forming the majority of the background and a smaller distribution of slightly larger well-defined particles. The largest particles in both cases were ill defined and surrounded by a distinct depletion region. Although the origin of the coarse regions is not fully understood, it may have been due to condensation of the solvent on the surface during remodelling.

In a similar approach to the noise measurements made in section 3.5.4, images experiencing no deformation were correlated using a range of sub-window sizes. The 40% overlap of individual frames forming the mosaic were correlated from a total of 5 repeats for non-irradiated and irradiated regions. This resulted in the noise measurement relating purely to the system noise and the pattern, it is important to state that this approach does not address the noise due to removal from the microscope or differing brightness contrast settings. A series of window sizes were processed, ranging from 4 x 4 pixels\(^2\) to 48 x 48 pixels\(^2\), providing a spatial resolution in the range of 37 x 37 nm\(^2\) to 444 x 444 nm\(^2\). The results for the average maximum shear strain of the 5 repeats for non-irradiated and irradiated regions are displayed in Figure 64c&d. A similar trend noted in the optical DIC can be observed, where decreasing window size is coupled with an increased noise and scatter. This is again due to the relative feature size within each window, which is substantiated by the finer pattern in the irradiated region suffering from less noise and scatter overall [185]. A final sub window size of 8 x 8 pixels was selected to provide the best balance of spatial resolution and noise, which was measured as $5.6 \times 10^{-3} \pm 4.6 \times 10^{-3} \%$ in the non-irradiated and $3.9 \times 10^{-3} \pm 2.5 \times 10^{-3} \%$ in the irradiated regions. There is a slight variation in noise between the two patterns, however, this was well within standard deviation so was considered negligible. The absolute value of error was far lower than what is typically reported in the literature, which is typically in the order of ~0.5% [192,193]. The large difference is most likely due to the lack of removal from the microscope. When correlating overlapped regions, the microscope is imaging in identical conditions, therefore noise measurement is only due to pattern and thermal noise. Removal from the
microscope would be coupled with focus variation, stigmatism and contrast/brightness, which further contribute to noise.

Figure 64: Gold speckle pattern on a) non-irradiated and b) irradiated regions; strain calculated in undeformed specimens using overlapping areas of mosaic overlap at different binning window sizes for c) non-irradiated and d) irradiated regions.

3.7.6 Analysis

The manuscript employed three approaches to analyse the strain maps: frequency plots, fast fourier transforms and slip band profiling. Frequency plots were carried out by exporting strain maps as a spreadsheet, so that each pixel formed a cell and was processed using a python script written by Dr. David Lunt [193]. The frequency plots were binned in 0.5 intervals beginning at 0.25, with maximum shear strain normalised against average strain in the loading direction. This allowed direct comparison of distributions between regions deformed to slightly different strains for a given increment. Fast Fourier transforms were carried out on the processed maps exported in grayscale. The transforms were performed using Image-J [244], with profiling of the FFTs performed using a polar transform plugin in the package. Slip band profiling was carried out using the DaVis software package, allowing for measurement of spacing and intensity. Profiles were taken normal to the dominant slip band, with 12 profiles taken for each
strain increment in the non-irradiated and irradiated regions. They were placed within the centre of each of the measured grains to avoid any neighbourhood effects from grain boundaries. Due to the development of slip in close proximity to existing slip bands, the distance between peaks along the profile became less reliable as they merged together. This lead to a peak broadening approach, with FWHM measured as a function of loading direction strain. Peak location and broadening was measured using the MatLab Signal Processing Toolbox. Peak centres were defined using their local maxima, with the boundaries defined by prominence; which was set to 1x10^{-6} to increase sensitivity to double peaks. The FWHM was then measured directly, a typical example is displayed in Figure 65. This process was repeated for each profile location and strain map.

![Figure 65: Example of peak location and FWHM measurement using MatLab.](image-url)
4 Introduction to Manuscripts

The manuscripts presented in this thesis are to explore novel methods of recording flow curves in proton irradiated material in a volume that represents bulk behaviour. Manuscripts 1-3 address this directly using x-ray stress measurement, digital image correlation, Xe⁺ plasma FIB and finite element analysis. The 4th manuscript investigates the effect of irradiation on deformation mechanisms in 316L austenitic steel using vapour assisted gold remodelling and high resolution digital image correlation. All named author contributions are stated in the title page for each manuscript.

Manuscript 1 covers the application of a combination of x-ray stress measurement and digital image correlation to generate in-situ flow curves for non-irradiated SA508-4N. The surface flow curves were benchmarked against standard uniaxial tensile test. The reduced sampling volume resulted in scatter between individual tensile tests for the near surface region. This scatter was mitigated by averaging the results of a series of repeated tests. The fit generated using the average data collected from the surface region was shown to be in good agreement with the bulk standard flow curve.

Manuscript 2 details the development of a small-scale tensile specimen preparation method using an Xe⁺ PFIB, with the motivation of attaining the smallest representative volume. Mesoscale polycrystalline specimens were fabricated and tested in tension using a piezo actuated tensile testing rig. The tests displayed no size dependent hardening, however they did exhibit a limited plastic stability and tensile strength. XCT was carried out on some examples of the PFIB prepared specimens, which highlighted some gauge length taper. Finite element analysis was performed on plane strain and meshed XCT models to highlight anomalies introduced by geometry, which by elimination provided insight into size dependent anomalies.

Manuscript 3 reports the application of methods outlined in the preceding manuscripts to the same material irradiated to 15 mdpa. Both techniques measured a positive yield shift in the order that was estimated using indentation testing. However, the PFIB prepared specimens recorded a increased hardening than compared to the combination of XRD and DIC. This is thought to be due to the technique dependent sampling volumes, where XRD records data on average at a shallower depth than is recorded in the micro tensile specimens.

Manuscript 4 features the use of “low” temperature styrene vapour assisted gold remodelling to generate a gold marker pattern for high resolution digital image correlation of 100mdpa proton irradiated 316L stainless steel. Using a range of quantitative analysis approaches to process surface strain maps, it was possible to characterise strain heterogeneity due to irradiation damage. Strain profile peak broadening was also applied to assess slip band spacing
due to the overlapping of peaks in close proximity as the test progressed. Application of Fast Fourier Transforms (FFT) and strain profiling highlighted the irradiation induced strain localisation, recording a suppression of diffuse slip and an increase in planar slip.

4.1 Manuscript 1: A new methodology for recording uniaxial stress-strain curves of thin surface layers

Albert D. Smith, John Warren, Gary Harrison, Matthew S. Blackmur, Stuart Morse, Keith Wilford, Philip J. Withers, Michael Preuss

Named author contributions were as follows:

Albert D. Smith: Lead author, specimen preparation, experimental design, carried out tension experiments, performed all analysis.

John Warren & Gary Harrison: provided advice and insight during experimental design.

Stuart Morse: assisted with standard bulk tensile testing.

Matthew Blackmur: provided guidance on writing a MatLab script to extract $\sin^2 \psi$ data.

Keith Wilford, Philip. J Withers & Michael Preuss: Supervisors of Albert Smith

The manuscript was internally reviewed by Prof. Michael Preuss
A new methodology for recording uniaxial stress-strain curves of thin surface layers

Albert D. Smith¹, John Warren¹, Gary Harrison¹, Matthew S. Blackmur², Stuart Morse¹, Keith Wilford³, Philip J. Withers¹, Michael Preuss¹

The University of Manchester¹, National Nuclear Laboratory², Rolls-Royce plc³

Keywords: Diffraction Stress Measurement, In-situ Mechanical Testing, Digital Image Correlation, Surface Flow Curves, SA508 Grade 4-N steel

Abstract

This study applies a combination of laboratory based x-ray diffraction stress measurement and optical digital image correlation to construct flow curves of the near surface region. By comparison of flow curves collected from the surface to those collected using the standard method was possible to validate the proposed technique. It has been demonstrated that the combination of in-situ XRD stress measurement and DIC is capable of accurately describing the elastic and plastic response measured using standard testing. The validated methodology enables recording of flow curves in altered surface layers, such as shot peening, machining and low energy protons by the combination of two well established and easily accessible techniques.

Introduction

Surface treatments, films and oxide layers alter the performance of in-service components, be it positively or negatively. Predetermining the mechanical properties of such altered surfaces is required to enable accurate predictions of component performance and lifetime. Most commonly, mechanical properties of a material are recorded in terms of their strain response during the application of a uniaxial stress resulting in a stress-strain curve. The advantage of recording such stress-strain curves is that important engineering properties can be extracted such as yield stress, ultimate strength, work hardening behaviour and strain to failure. However, application of standardised methods to the measurement of surface properties provides an interesting set of challenges. Due to the global nature of data acquisition and the limited thickness of surface treatments, surface properties cannot be probed directly using conventional techniques. Any data collected is a convoluted response of the treated surface and substrate, which are heavily biased to substrate properties. Direct measurement of coatings using a decreased probe size is one solution to the issue of specimen scaling and removal of constraint. The most common example of this is indentation testing, which is readily used to record the properties of thin films. Indentation provides information on reduced modulus
strength and for brittle materials, the fracture toughness [246]. In the fields of cold-forming and irradiation damage, the linear relationship of hardness and the onset of plasticity can be applied to estimate the relative yield point within the surface layer [84,92,247–249]. Despite providing useful information on mechanical properties, the data collected is not uniaxial and is heavily dependent on surface finish and indenter geometry [250].

An increasingly prominent solution is to prepare micro-scale compression [77,78,92,124,143,251] and microcantilever [112] specimens using a Focussed Ion Beam (FIB) to be tested using an indenter tip. The more recent development of piezo-actuated mechanical testing equipment [252] allows the tensile testing of FIB prepared specimens extracted from a surface [82]. A key advantage of FIB fabrication is that it enables site specific samples to be prepared on a scale in the order of a few microns. These techniques are therefore well suited to obtaining detailed data on single crystals. However, it remains unclear how such data can be extrapolated to obtain the bulk response of materials. Furthermore, it has been demonstrated that reducing specimen scale has a dramatic effect on a materials mechanical response in terms of hardening [137] and plastic stability [129,132]. By the inherent nature of top-down FIB preparation the reduction of scale and removal of constraint is unavoidable.

Work by Foecke et al. explored the application of laboratory XRD stress determination (sin2ψ) and optical-video strain measurement for the incremental recording of biaxial stresses in the near surface region [253]. Both techniques are limited to surface measurements, with optical-video strain measurement recording the very outer surface and laboratory x-rays penetrating only a few tens of microns. The inherent surface sensitivity of both techniques makes them ideally suited for recording flow curves of a modified surface.

Residual stress determination by x-ray diffraction (XRD) using single peak analysis is a well-established non-destructive methodology. The underpinning requirement for accurate representation of macroscopic stress is a linear relationship between interplanar strain and stress beyond the initiation of plasticity. While there is a plethora of in-situ loading experiments using diffraction demonstrating that there are planes that behave in this way [170,181–183,254–256], the suitable plane must first be identified since there is no set rule that allows the appropriate plane to be calculated from first principals. Relating this linear response via the appropriate elastic constants makes it possible to calculate stress using lattice strain in both the elastic and plastic regime. The advantages of utilising laboratory-based methods are two-fold, in that there is wide availability of laboratory x-ray sources and the penetration depth of radiation is in the order of a few tens of microns, which is typically the range of surface treatments. This range combined with a wide aperture allows for an increased
sampling cross section of limited depth, giving a representative measure of a surface treatment’s response.

Surface strain can be determined either by the use of strain gauges or by imaging the gauge area during mechanical loading and using a full-field surface displacement mapping technique such as digital image correlation (DIC) [185–187]. Displacement mapping is achieved by comparison of the features of sequential images in varying states against an initial reference. DIC has a wide range of applications requiring the non-contact measurement of strain; in metallurgy it is used to measure the relative localisation of strain in deformed sample surfaces [186,192,257]. Scale is subject to requirement and can range from macro, as a tool for defect detection in nuclear structural components [185], to nano-scale resolution, for the investigation of active slip planes in deformed metals [192]. A distinct pattern, typically described as a “speckle pattern” [185,189,190,204] is required, which generally takes the form of an applied coating or surface treatment. However, in some cases the natural surface may be sufficient [188,189]. The patterned surface provides features for the chosen computer algorithm to track, where a displacement vector is plotted between the origin and the new position. Differentiation of displacement vectors will provide any component of the in-plane strain tensor.

The aim of the present work is to combine these well-established and widely available surface measurement techniques during in-situ quasistatic tensile loading experiments. Recording stress by $\sin^2\psi$-based XRD and strain by imaging based DIC analysis will allow the determination of flow curves representative of the near surface region (Figure 1). This paper attempts to validate the technique by its application to an unmodified surface, allowing for verification against bulk flow curves recorded using standard uniaxial tensile testing methodology.

**Experimental Methods**

The material investigated during this study was a SA508-4N steel, provided by Rolls-Royce plc, that has been forged, quenched & tempered. Dog bone tensile samples (27mm x 3mm x 1mm parallel) were machined for tensile testing using electrical discharge machining (EDM). The samples were ground to remove the recast layer and subsequently further prepared through grinding and electropolishing the flat faces. The material had an average grain size of ~5μm and was free of any noticeable crystallographic texture, which ensured ideal diffraction conditions throughout the range of $\psi$ -inclinations. The tensile samples were mounted into a Kammrath Weiss 5kN tension-compression microtester using slip gauges to ensure parallel alignment to the loading axis. Three load cycles to 70% of yield stress ($\sigma_y$) were initially performed to ensure the absence of hysteresis and eliminate any possible poor contact between
the specimen and the grips. Subsequently, the applied stress was incrementally increased using a displacement rate of 5 μm s⁻¹, which corresponds to an approximate strain rate of 1.9x10⁻⁴ s⁻¹, between hold points. During each hold period XRD-based stress and DIC-based strain measurements were carried out to provide stress and strain data that could be used to construct flow curves.

The x-ray diffraction analysis was carried out on a Proto iXRD using the Cr Kα radiation with a 2mm aperture and measuring the {211} reflection. Side inclination measurements were taken at 11 ψ-tilt angles between ±25° with 10 exposures, each lasting 1 second at every tilt angle. Although the material was practically texture free, a ±2° goniometer undulation was applied during each measurement to improve counting statistics. Peak position & shape was determined using a Gaussian curve fit.

Lattice strain was measured by tilting towards the loading axis at a range of ψ-tilts allowing for uniaxial stress (σₓ) to be calculated at each hold point using Equation 1.

$$\sigma_x = \left( \frac{E}{1 + \nu} \right) \frac{\delta d_{hkl}^{\psi}}{\delta \sin^2 \psi} \frac{1}{d_{\psi=0}}$$

Equation 1

where $d_{hkl}^{\psi}$ is the inclined lattice spacing rotated around an axis normal to the loading direction, $d_{\psi=0}$ is the stress-free lattice spacing at $\psi = 0^\circ$ and $\left( \frac{E}{1 + \nu} \right)_{hkl}$ are the effective elastic constants of the diffracting plane (1/2 S2).

Approximate values for material specific DECs are available from databases or may be calculated from single crystal properties. While this might be suitable for studies of relative stress variation, measurement of direct stress requires a higher level of precision. Given that microstructure can have a dramatic effect on constants [258,259], they were calibrated prior to testing. DECs were derived according to the ASTM E1426-98 standard [171], in tension rather than a 3-point bending using the same configuration as Marion & Cohen [172]. Provided a material has the same linear response to applied stress during plastic deformation, the DECs calculated in the elastic regime will remain valid during plastic deformation. Figure 2 illustrates the gradient of $\sin^2 \psi$ vs d spacing plotted against applied engineering stress. Beyond the deflection at yield, the gradient remains consistent in both regimes. The calibrated DECs were calculated to be $5.94 \times 10^{-6}$ MPa⁻¹.

In order to record images of the gauge region during mechanical loading a LaVision MX 4M camera equipped with a Nikon Nikkor 105mm lens was mounted on a tripod above the goniometer facing vertically down onto the tensile sample. To avoid saturation of images, a
white Anti-Reflective (AR) coating was initially applied to the sample surface. Subsequently, black speckles were applied to the surface by dusting spray paint over the AR coating. Painted samples were allowed to cure naturally for 24 hours prior to testing. It should be noted that possible diffraction peaks resulting from the paint were sufficiently far away from the (211) ferrite peak and therefore did not interfere with the stress analysis.

The optical images were analysed using the commercially available LaVision DaVis 8.1.5 software package to determine the total strain. A more detailed description on DIC-based strain analysis can be found in [186]. In brief, the strain analysis was performed using an integral sum of differential fields relative to the undeformed condition, which adds the differentially calculated vector fields from successive images. All areas outside the area measured by XRD were masked and the full-field displacement map differentiated to calculate a single value of strain parallel to the applied load ($\varepsilon_{xx}$):

$$\varepsilon_{xx} = \frac{\delta u_x}{\delta x}$$

Equation 2

where $u$ and $x$ are average subset pixel displacement and the given direction.

Stress and strain measurements were taken in succession within the gauge area equidistant from the mounting grips. Preceding and following each XRD $\sin^2\psi$ measurement the goniometer was moved to its maximum tilt and optical images were captured for DIC strain calculation. Images from before and after X-Ray measurement were processed in order to obtain an average strain value to compensate for systematic errors.

Standard mechanical tensile tests were performed for the purpose of validation on cylindrically machined samples on an Instron 5569 at a strain rate of $3 \times 10^{-4} \text{s}^{-1}$; samples were prepared and testing was carried out according to ASTM E8 [260]. Applied force was recorded using a 25kN load cell and strain was recorded using two MTS fixed length strain gauges, 25mm and 50mm. In addition to a set of continuous tension tests, to emulate the quasistatic experiment an additional test applied in a staircase configuration with the crosshead frozen for 10-minute intervals at hold points throughout the test.

Results

In this study, the proposed combination of the XRD & DIC techniques to measure stress and strain in parallel has been evaluated and validated against flow curves recorded using the standard methodology. All results for the recorded mechanical properties are summarised in Table 1. The assumption that the two techniques will yield equivalent results is valid provided:
the displacement applied is uniform throughout the thickness of the specimen and (2) the material contains no property gradient between the surface & bulk. Theoretically, in specimens with an unmodified and well-prepared surface, fulfilment of both requirements is assured.

Figures 3(a-d) illustrates the flow curves recorded in the surfaces of four specimens (open circles) strained to 10% $\varepsilon_t$ (true strain). Here, standard deviation in XRD stress measurements relates to deviation from the least squares regression of the $\sin^2 \psi$ plot. The serrated flow curve (solid line) in each plot is a quasistatic test performed using the standard technique. Elastic and plastic fits are displayed as dashed lines in each plot. There is some clear scatter in the behaviour of individual specimens, with surface 1 situated at the minima of relaxation during hold points in the bulk flow curve. However, this is not consistent amongst the other specimens with sample 2 and 4 providing results more consistent with a continuous flow curve. Sample 3 is a clear outlier, displaying an upwards transposition with respect to the standard curve. This scatter is evident in the tabulated mechanical properties. Surface Young’s moduli (E) for all specimens lay within $\pm 36$ GPa, displayed in Figure 4 a-d which is within 14% of the bulk measured value, with calculated surface values consistently lower than that measured in bulk using the standard methodology. This is thought to be due to the gripping fixture used in the microtester, which due to slight misalignments produces a scatter of lower moduli across individual samples using this configuration. Conversely, bulk measurements were taken using a cylindrical specimen geometry and the application of uniaxial joints, which provides better alignment than the gripped counterpart.

Table 1: Mechanical properties & appropriate $R^2$ values measured in the bulk and surface

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$\sigma_{0.2}$ (MPa)</th>
<th>$\sigma_1$ (MPa)</th>
<th>E (GPa)</th>
<th>E ($R^2$)</th>
<th>n ($R^2$)</th>
<th>UTS (MPa)</th>
<th>K (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk Cont.</td>
<td>656±9</td>
<td>688±8</td>
<td>210 ± 2</td>
<td>0.99</td>
<td>0.120</td>
<td>0.995</td>
<td>878±4</td>
</tr>
<tr>
<td>Surface 1</td>
<td>592±30</td>
<td>645±29</td>
<td>197 ± 63</td>
<td>0.99</td>
<td>0.121</td>
<td>0.915</td>
<td>833</td>
</tr>
<tr>
<td>Surface 2</td>
<td>637±37</td>
<td>685±29</td>
<td>179 ± 55</td>
<td>0.99</td>
<td>0.130</td>
<td>0.938</td>
<td>900</td>
</tr>
<tr>
<td>Surface 3</td>
<td>675±43</td>
<td>732±54</td>
<td>174 ± 11</td>
<td>0.96</td>
<td>0.116</td>
<td>0.966</td>
<td>940</td>
</tr>
<tr>
<td>Surface 4</td>
<td>692±38</td>
<td>712±36</td>
<td>187 ± 11</td>
<td>0.99</td>
<td>0.086</td>
<td>0.941</td>
<td>830</td>
</tr>
<tr>
<td>Surface Ave</td>
<td>649±74</td>
<td>693±77</td>
<td>184 ±85</td>
<td>***</td>
<td>0.113</td>
<td>***</td>
<td>875±53</td>
</tr>
</tbody>
</table>

The industry standard for defining yield point is to offset the proportional limit by 0.2% $\varepsilon_t$ to obtain a value of proof stress ($\sigma_{0.2}$). Proof stress for the curves shown in Figures 3(a-d) deviate from the bulk proof stress by a maximum of -64 MPa, with a mean surface proof stress 7 MPa
below. This variation is not only a result of the apparent transposition in curves 1 and 3, the
effect is intensified, by the region of non-linearity in the interplanar response to applied stress
(Figure 2). This region corresponds to a period of diminished strain hardening in the bulk
material immediately following to yield, although it is not clear they are related. Consequently,
yielding was also characterised at an offset at 1% following stabilisation of plastic flow.
Applying a 1% offset reduces the individual deviation from bulk to +43 MPa and average to
+5.5 MPa. While sample 3 remains the largest outlier with a large upwards transposition,
sample 4 exhibits a slightly above average stress at this point due to an inhomogeneity,
generated by the electropolishing process, which ultimately led to its premature failure. The
log–log curves in Figure 4(a-d) illustrate the plastic flow, which is described by the Hollomon
equation:

\[ \sigma_t = K \varepsilon_t^n \]

Equation 3

where \( \sigma_t \) is true stress, \( \varepsilon_t \) is true strain, \( K \) is the strength coefficient and \( n \) is the strain
hardening exponent.

The strain hardening exponent is calculated by the slope of the log-log plot, in the plastic range
from 1%-10% for all flow curves (Figure 5). A bulk strain hardening fit was calculated using
the continuously loaded bulk tests rather than the staircase loaded. The results show that strain
hardening values for surface and bulk are in good agreement with the exception of sample 4,
which shows strongly diminished strain hardening. A value of strength coefficient was
obtained by extrapolating the projected stress at 100% \( \varepsilon_t \), with maximum deviation from bulk
of 76 MPa in specimens 1-3 and -105 MPa for specimen 4. The deviation of the average
surface strength coefficient from bulk is 10±84 MPa.

A value of ultimate tensile strength was calculated using the Considère’s plastic instability
criterion. The assumption is that at the point of plastic instability, strain hardening saturates
and reduces to zero, where plastic instability occurs at a strain equal to the hardening exponent
(\( \varepsilon = n \times 100 \)) [27]. Therefore, it is possible to project a value of tensile strength (\( \sigma_{UTS} \)) using
the parameters from Table 1 and applying the Hollomon equation:

\[ \sigma_{UTS} = K n^n \]

Equation 4

The projected ultimate tensile strength follows the same trend as all other recorded parameters,
with specimen 3 and 4 deviating by 40 MPa positively and negatively, the average of surface
UTS varies by 3±53 MPa. Average values for surface properties are in consistent agreement
with those recorded in bulk, differing by under 5% in all cases except for strain hardening exponent having a ∼7% variation. With the exclusion of the anomalous strain hardening result provided by sample 4, the variation is reduced to less than 1%.

Discussion

The most consistent misrepresentation of bulk flow curves in the surface response is at the point of yield. Figure 2 illustrates the gradient of $\sin^2 \psi - d$-spacing plot ($m^*$), which can be considered a measure of lattice strain plotted against macroscopic applied stress. Lattice strain exhibits a non-linear response at the point of yield, with linearity returning as the plastic regime progresses. A similar behaviour can also be observed in the $m^*$ against stress plots in Aluminium, observed by Foecke et.al [253]. This non-linear response manifests in the experimental curves (recorded in the surface) as a dampened transition at yield rather than the sharp transition recorded using the standard method. Despite this discontinuity, it has been demonstrated that the response of this plane is sufficient for measuring stress in the elastic and plastic regime.

It is clear that all recorded surface properties consist of a higher degree of scatter to that present under standard loading conditions. This is considered to be due to a number of factors inherent to the technique. Due to the type of microtester used to apply load, slight variations in alignment are expected. With specimens mounted using fixed grips, rather than the universal joints used in standard tests, it is difficult to achieve a purely uniaxial loading condition. Consequently, specimens may be subjected to slight shear stresses that bias the flow curve. An additional factor is the limited sampling volume measured using x-ray diffraction. The 2mm aperture combined with a limited penetration depth results in a sampling volume in the order of 10s of cubic micrometres. In contrast, standard testing measurements can be considered as an average throughout the entire gauge volume, in the order of 100s of cubic millimetres. Due to the techniques high sensitivity to local inhomogeneities, sampling volume has a significant influence on individual measurements. Therefore, this is considered to be the largest contributor to the scatter. It has been demonstrated that individual errors are mitigated by performing multiple repeat measurements and averaging the results. This is evident in the good agreement of the fit with the experimental bulk curve, Figure 6. Fitting was achieved applying Hooke’s law and the power-law hardening model (Equation 3) to the average surface mechanical properties displayed in Table 1. The results of the fit are somewhat surprising in where it lies in relation to the staircase loaded curve. Due to measurements being taken at hold points under static load, specimens experienced a period of stress relaxation. It was therefore expected that the fit would intersect the stress relaxed minima of the serrations on the staircase
Accuracy in individual samples can be improved using longer count times, increased \( \psi \)-inclinations, improved surface quality and alignment. However, intrinsic material properties may affect the accuracy of the stress measurement in a given material. In addition to the standard requirements of XRD stress measurement, weak texture and small grain size, it must be reiterated that the most important parameter is the diffracting plane’s response to applied stress [184,261].

**Conclusion**

A method for recording uniaxial stress-strain curves of thin surface layers has been explored and validated against bulk flow curves using homogeneous specimens. The technique accurately describes both elastic and plastic regimes, with the transition between them less well represented due to the intrinsic interplanar response to applied stress in this range. The small sampling volume leads to variations between individual flow curves, which can be brought into good agreement with the standard bulk curve by averaging over repeat measurements. The new validated methodology enables now to record flow curves of altered surface layers as found for example after shot peening and machining as well as in material irradiated by low penetrating charged particles such as protons.
Figures:

(a) Schematic of technique, with surface measurement contributions from (a) sin2ψ stress and (b) DIC strain. (c) Depicts the combination of data sets to generate a flow curve.

Figure 1: Schematic of technique, with surface measurement contributions from (a) sin2ψ stress and (b) DIC strain. (c) Depicts the combination of data sets to generate a flow curve.
Figure 2: Gradient of $\sin 2\psi$ vs. $d$-spacing plotted against load cell engineering stress. Engineering stress is plotted rather than true stress since this is what it is calibrated against when obtaining the DECs, this best reflects the data as it was collected.

Figure 3: Comparison of the stress-strain behaviour in surface (a) i; (b) ii; (c) iii and (d) iv using the combined $\sin 2\psi$ & DIC method to the standard method
Figure 4: (a-d) Bulk elastic modulus of flow curves generated using $\sin^2\psi$ & DIC, with modulus calculated by least squares method.

Figure 5: (a-d) Flow curves plotted as log $\sigma$ – log $\varepsilon$ with strain hardening parameter ($n$) calculated by gradient of the region between 2% and 9% $\varepsilon_t$, applied to flow curves measured
by sin2ψ & DIC. The solid line represents an average of three bulk flow curves recorded using the standard method.

Figure 6: Bulk flow curve using standard technique (solid line) and flow curve fitted using Hooke’s Law and Hollomon equation for the elastic and plastic regimes using parameters recorded using XRD & DIC (dashed line).
4.2 Manuscript 2: On the application of Xe+ plasma FIB for micro-fabrication of small-scale tensile specimens

Albert D. Smith, Jack M. Donoghue, Alistair J.W. Garner, Etienne Bousser, Bartlomiej Winiarski, James Carr, Julia Behnsen, Tim Burnett, Robert Wheeler, Keith Wilford, Philip J. Withers, Michael Preuss

Named author contributions were as follows:

Albert D. Smith: Lead author, prepared specimens, assisted with all PFIB sessions in partnership with named operators, contributed to process development, carried out small-scale mechanical testing in partnership with Jack M Donoghue, assisted with pin fabrication & orientation mapping, SEM imaging, carried out FEA, digital image correlation, performed all analysis.

Jack M. Donoghue: Operated PFIB, contributed to process development, designed the pre-tilt holder and specimen mount, carried out small-scale mechanical testing, fabricated loading pin, carried out orientation mapping & SEM imaging and carried out XCT.

Alistair J.W. Garner: Operated the PFIB & contributed to process development.

Etienne Bousser: Operated the PFIB, fabricated loading pin & contributed to process development.

Bartlomiej Winiarski: Operated the PFIB in the preliminary stages of the project, results not included in the manuscript.

Julia Behnsen: Carried out XCT.

James Carr: Processed XCT data and meshed tomography based models.

Tim Burnett: Provided PFIB advice and assisted with allocation of time on the equipment.

Robert Wheeler: Gave advice on the tensile testing equipment and performed some preliminary work on the loading pin preparation.

Keith Wilford, Philip J Withers & Michael Preuss: Supervisors of Albert Smith.

The manuscript was internally reviewed by Prof. Michael Preuss, Dr. Alistair JW Garner and Dr. Jack M Donoghue.
On the application of Xe\(^+\) plasma FIB for micro-fabrication of small-scale tensile specimens

Albert D. Smith\(^1\), Jack M. Donoghue\(^1\), Alistair J.W. Garner\(^1\), Etienne Bousser\(^1\), Bartlomiej Winiarski\(^1\)\(^2\), James Carr\(^1\), Julia Behnsen\(^1\), Tim Burnett\(^1\), Robert Wheeler\(^3\), Keith Wilford\(^4\), Philip J. Withers\(^1\), Michael Preuss\(^1\)

The University of Manchester\(^1\), Thermo Fisher Scientific, FEI Czech Republic s.r.o.\(^2\), Micro Testing Solutions LLC OH USA\(^3\), Rolls-Royce plc, Derby UK\(^4\)

Keywords: Xe\(^+\) Plasma FIB-SEM Dual Beam Microscope, In-situ Mechanical Testing, Digital Image Correlation, X-Ray Computed Tomography, Finite Element Analysis, A508 Grade 4-N steel

Abstract

In order to perform site-specific mechanical studies to examine the contribution or interaction of a material constituent, a reliable methodology for the production of small-scale samples is required. The low milling rates of Ga\(^+\) focussed ion beams (FIBs), usually used for such sample preparation, limits the practically achievable scale of specimens, making results difficult to relate to current standards. With the high milling rates achievable with the newly developed Xe\(^+\) plasma FIB, it is now possible to manufacture specimens approaching the smallest representative volume (SRV). In this study, a methodology has been developed that allows for the manufacture of mesoscale-small-scale specimens to be tested in tension. It has been demonstrated that yield and tensile strength measured in specimens of this scale are representative of bulk behaviour, with the only size-dependent property being the strain hardening exponent. The work carried out has established that it is feasible to manufacture samples using Xe\(^+\) PFIB that are approaching the SRV in reasonable timescales.

Introduction

Small-scale mechanical testing of site-specific or limited-volume specimens is an attractive proposition for a wide range of different material investigations, including film/coatings [110,251], testing of phase/grain boundary interactions [262] and ion irradiated layers [82,112,124]. Many of such material investigations provide a composite problem when undertaking conventional mechanical tests with large samples that incorporate the region of interest, and attempt to separate the relevant component from the global response. Such approach becomes impractical when the region of interest becomes minimal in size relative to the bulk, with the situation complicated further by property gradients and interactions between constituent parts [93]. A more practical option is to reduce the size of the samples so that they
only contain the region or regions of interest. Unfortunately, testing at the length scale of 10s to 100s of microns introduces a number of challenges, including a well-documented size effect in metals, where an increasing in hardening is found to be inversely proportional to specimen diameter. This occurs due to the limited number of dislocation sources as the length scale is reduced, causing the material to approach its theoretical strength \[99,128,143,263,264\]. It has been suggested that the grain size has to be sufficiently small in small-scale specimens during plastic deformation to achieve the smallest representative volume (SRV to emulate bulk) \[111\], which is currently unknown. Perhaps the greatest challenge of testing at these small scales is the fabrication and testing of specimens. Previous studies have used Ga\(^+\) focussed ion beam (FIB) to machine specimens from regions of interest and utilised micro- and nano-indentation or piezo-actuated loading to perform tests on miniaturised specimens in bending \[265\], compression \[100,112,124,266\] and tension \[82,107,111\]. However, the limited milling rate of Ga\(^+\) FIBs restricts the practically achievable diameters of tensile specimens to \(\sim 10 \mu m\). For the large majority of engineering materials the sampled volume would be limited to only a single or a few grains and therefore the smallest representative volume (SRV) for bulk material properties is unlikely to be met. These types of samples are therefore better suited to the study of single and bi-crystal properties \[82,107\]. A further issue with Ga\(^+\) FIBs for microfabrication is the implantation and subsequent diffusion of Ga\(^+\) ions that can lead to phase changes and segregation to grain boundaries affecting mechanical properties, particularly in aluminium \[155\].

Both of these limitations are mitigated by the use of the relatively recently developed Xe\(^+\) plasma FIB (PFIB). In Ga\(^+\) FIBs the divergent nature of the point source results in a spherical aberrated non-gaussian beam profile, limiting currents to \(\sim 60 \text{ nA} \) \[149,150\]. Conversely, the larger virtual source of the PFIB results in a more collimated beam that retains focussed spot at milling currents as high as 3000 nA. The higher usable current combined with a heavier ion has a dramatic effect on milling rates increasing those by up to two orders of magnitude compared to a Ga\(^+\) FIB. This greatly improves the practically achievable scale of specimens \[156,267\]. In addition, by using an inert species, the Xe\(^+\) FIB does not promote phase changes due to micro-alloying as seen with Ga\(^+\) FIBs \[155\]. Furthermore, it has also been clearly demonstrated that despite having a higher mass, the use of Xe\(^+\) ions results in a smaller surface amorphisation zone due to a higher sputtering yield and lower penetration depth \[133,154\]. The efficient sputtering rate and relatively high operating currents make the Xe\(^+\) PFIB an ideal candidate for the microfabrication of larger small scale tensile specimens. By employing PFIB for the preparation of uniaxial tension mechanical test-samples, it is possible to achieve sample cross sections an order of magnitude greater in size than with conventional Ga\(^+\) FIB. With this increased specimen size, materials can approach the SRV, provided they have sufficiently fine
grains, which will allow these small-scale samples to give representative mechanical properties to bulk and thus mitigating the size effect [111].

The present study aims to develop a sample preparation methodology to explore the viability of applying the emerging PFIB technology to prepare and test tensile samples to contrast against the standard uniaxial flow curves gathered using a technique set out in ASTM E8 [260]. The material chosen for this study was SA508 Grade 4-N steel partly due to its relatively small grain size of ~5μm, allowing for the SRV to be approached, and due to its proposed use in the nuclear industry as a candidate reactor pressure vessel material. This type of small scale mechanical testing will be of great interest to the nuclear community, where ion irradiations with low penetration depths are increasingly used to simulate the effects of neutron irradiation.

**Experimental Methods**

*Material and Preparation*

The material used in this study was forged SA508-4N in the quenched and tempered condition supplied by Rolls-Royce plc. Rectangular specimens were firstly extracted by electrical discharge machining (EDM) with the forging transverse direction parallel to the face normal of the specimen (TD//33). Coupons of dimensions 27 x 3 x 1 mm³ were ground mechanically to remove the recast layer from all faces using 400 grit silicon carbide abrasive paper. Further mechanical grinding, through successive steps to 4000 grit, took the coupon from 1 mm to a final thickness of 80 µm. The resulting thin foil was polished with diamond paste, with a final polishing step using diluted colloidal silica. A standard TEM sample punch was used to prepare the foil into a 3 mm diameter disk. Burrs were carefully removed with 4000 grit abrasive paper. The foil disk was mounted in wax between two glass slides, ground into a ‘half-moon’ and attached to a brass sample mount using cyanoacrylate adhesive (Appendix Figure 1).

*Plasma Focussed Ion Beam Milling*

A schematic of the PFIB preparation procedure is illustrated in Figure 1, all milling was performed at 30 kV using an FEI Helios FEG-SEM equipped with a Xe⁺ plasma ion beam column. The sample mount was fixed to a 45° pre-tilt holder using a grub screw and a 7° stage tilt was used to so that the ion beam (at 52°) would be incident normal to the specimen surface. All alignments were made relative to the sample mount since the sample mount attaches directly into a housing in the mechanical testing equipment. An initial cut was made to mill away the mechanically deformed layer on the top edge of the disk and to ensure the sample longitudinal axis ran parallel to the mount. Milling was performed using a cleaning cross section at 1.3μA, whereby the cut is made up of a series of successive line scans within the
reduced area, rather than a dynamic multidirectional scan. The z-depth of each line cut was set at 150 μm, where the PFIBs unit of depth is defined in terms of fluence required to mill through that depth of Si. The ratio of milling efficiency in steel to Si was found to be approximately 1:1 so no depth correction was required. Following the high current scan, a further cut was made at 0.18μA with the same dwell time. The lower current polishing step was intended to reduce the curtaining associated with high current milling and avoid the propagation of those curtains in subsequent steps.

An initial thinning step was made to align the lamellar with the specimen mount and to reduce the thickness to approximately 40 μm (Figure 1c). The 400 μm wide lamellar was milled at 1.3μA to a depth of approximately 500 μm using a dynamic scan in all directions. Such high current milling was observed to result in deep, pronounced curtaining approximately 2μm in width and 1μm deep. Platinum was therefore deposited on the outer edge in order to protect from further curtaining during the subsequent thinning stage (Figure 1d). Deposition at this stage rather than during the preceding high current thinning step prevented degradation of the Pt layer by the relatively broad beam profile at high currents. The Pt layer was deposited using the ion beam at 8 kV and a current of 0.13 μA, at a deposition rate of ~100 nm min⁻¹ until the layer reached a thickness of ~ 5 μm. Fiducial markers were placed on the top edge of the lamellar at 59 nA using cleaning cross section milling to ensure sharp edges and thus good contrast. These fiducials are used as positional markers by the automated serial sectioning tool in the FEI Auto Slice and View 4 software package during the next stage of preparation.

An automated routine was employed for the final thinning to reduce user error and increase repeatability. It incorporates a cross-polish, also referred to as rocking mill, cleaning cross section. At each step of the cross-polish, the specimen was tilted by 2° around the z-axis in order to intersect and eliminate any curtains generated by the previous step. Cross-polishing of a 350 μm wide region on each side was performed at 30kV and a current of 0.18 μA to produce a final lamellar of ~30 μm thickness (Figure 1e). Each line took approximately 7 minutes to complete after which the line was advanced 150 nm. Following completion of a line, a secondary electron (SE) image was acquired to monitor progress. Images were acquired at 8 kV, with a dwell time of 3x10⁻⁶ s taking approximately 10 seconds to collect each frame. An offset of 2° in the cross-polish limits fortification of preceding curtains generated by successive passes, maintaining as clean a surface as possible. Further detail on the automated rocking mill process is described in section 2.3 of [149]. The microscope stage possesses 2 degrees of freedom, with only a single tilt axis. With the tilt axis utilised for the 2° automated rocking mill, over tilt is not possible whilst performing a rocking mill. In an effort to mitigate the tapering inherent to FIB sample manufacture using a top-down approach [233], a bespoke pre-tilted specimen stub was prepared by EDM to provide 2° overtilt (Appendix Figure 2),
which was calculated in a tapered specimen by parallax. Two specimen batches were prepared in total, one prepared using the pre-tilt holder, and the other mounted vertically with no overtilt.

Milling of tension specimens from the thinned lamella required remounting to a 45° pre-tilted holder to orientate the ion beam normal to the sample surface. The width of the lamellar was sufficient to arrange 2-3 parallel samples (Figure 1f). Each cut was milled in series at 180 nA, with the gauge sections milled last to avoid redeposition of sputtered material biasing the sample cross-section measurements. All milling of the final specimen shapes was carried out using the cleaning cross section tool (individual cuts), which was found to be quicker than rectangular tool (dynamic all direction) and also provided clean, flat sides to the gauge length. The cuts were made with a width of 5 µm and a dwell time sufficient to mill through 300 µm. The excessive depth was intended to allow the beam tails to penetrate through the thickness due to overtilt not being possible at this step and was also found to produce the best possible surface finish. Rectangular cavities were milled into the tab to allow for pin insertion following orientation mapping to prevent excess redeposition.

The whole PFIB preparation process takes 2-3 days to complete, which depends on foil thickness and its alignment on the specimen mount. The automated routines do not require an operator to be present, which accounts for approximately 50% of the preparation time.

**Micromechanical Testing**

In-situ mechanical tests of PFIB machined samples were performed using a Microtesting Solutions (Hilliard, OH, USA) µ-Test Rig (MTR-3), mounted in a Zeiss Sigma FEG-SEM. A schematic of the piezo-actuated MTR is illustrated in Figure 2. Once the specimen was positioned onto the loop, decreasing the applied voltage causes the piezo actuator to contract and load the specimen via the pin. The quasi-static tests were performed using voltage control, which would correspond to displacement control in a conventional mechanical test. For these experiments, the displacement rate was ~100 nm s⁻¹ with hold points at 200 nm displacement increments. Secondary electron images were taken at each hold point at 8 kV in high current mode. Scans took approximately 4 seconds to complete, with a dwell time of 50 ns and line averaging x 4 to reduce noise from the rapid acquisition. Images were taken in order to record displacement by tracking two Pt fiducial markers which were deposited using the PFIB (Figure 3). Macroscopic strain was obtained utilising the Labview Insitu Test VI MTR control software, while strain localisation was calculated using the commercially available LaVision DaVis 8.4 digital image correlation software package. The applied load was recorded by the test rig using an internal load cell with a total capacity of 453 g. Further detail on the development of the piezo-actuated micromechanical testing rig can be found in refs. [252,268]
Orientation Mapping

Orientation mapping was performed using the FEI Helios FEG-SEM-PFIB equipped with an Oxford Instruments Nordlys Max2 EBSD detector operating at 20kV with a 0.1µm step size at ~50 Hz. Kikuchi patterns, taken at 8x8 binning, were indexed using AZtecHKL software. Separate maps were taken over the gauge section for each tensile sample post milling. It was found that samples tilted from the upright position resulted in poor quality Kikuchi patterns due to obstruction of the diffracted beam from the recessed specimens. The sample mount was therefore inverted in the same 45° pre-tilt holder used for the punching step, with a 25° stage tilt. Maps were processed using HKL Channel 5, with grain boundaries defined misorientation >10°.

X-ray Computed Tomography

X-ray computed tomography (XCT) was performed on specimens prepared by PFIB, with and without overtilt, to assess the degree of gauge section taper. This was carried out at The University of Manchester Henry Mosley X-ray Imaging Facility, using a Zeiss Versa XRM-520. An accelerating voltage of 100 kV was used with a current of 91 µA, equating to 10.2 W of power. 1601 projections were taken of each specimen, prepared with and without overtilt, with a 40 s exposure, using a low energy filter at the source (LE3). The source and detector were positioned 14.04mm and 37.02mm from the specimen respectively. Images were collected with an optical magnification of 20x with 2x camera binning; voxel size was 0.3693µm. Images were processed and reconstructed using Zeiss Scout and Scan. Analysis and visualisation was performed using Avizo 9.0.0 software.

Finite Element Analysis

Finite element analysis (FEA) was performed to differentiate the influence of geometry from scale. This was performed using Dassault Systemes SIMULIA Abaqus/CAE 6.14-2, with 2-D plane-strain models constructed using the software package. Synopsis Scan IP software package was used to reconstruct and apply an adaptive tetragonal-mesh to the tomography results. Figure 4 illustrates the meshing of each example, a) plane strain and b) based on XCT data. All models comprised of tetragonal meshes with approximate element sizes of 1.5µm and 1.6µm -1.8µm for 2D plane strain and tomography-based model respectively. The plane strain test contained 3 boundary conditions in order to best represent the experimental conditions: a static boundary at the right-hand y-surface and a displacement (25µm lateral) boundary condition at the left-hand y-surface. A symmetric boundary was applied to the lower x-plane. In the tomography-based model, they consisted of two in the X-Z-plane, a static boundary applied to all element nodes at the base to simulate the mount. Loading was applied to the same region as in the experiment and was achieved by a displacement boundary
condition at the loop interior (Figure 5), constrained in all but the displacement direction. Material properties were obtained experimentally in ref. [269] and the full flow curve applied as separate elastic and plastic parameters.

Results & Discussion

Microstructure and sample geometry

An example of the final geometry for specimens prepared with and without overtilt, as measured by XCT, are displayed in Figure 6 and SE micrographs of each batch are shown in Figure 7. The mean gauge section measurements for the sample with no overtilt were: 132µm (L); 17.5µm (W); 40µm (T). Each batch contained 2 samples, however, 1 of the specimens with no overtilt was lost to attrition during the experiment. No EBSD map was taken of this specimen due to redeposition degrading Kikuchi pattern quality. However, from the microstructure of the overtilted batch displayed in Figure 8, it is possible to estimate the approximate number of laths in its gauge length. The average lath size was of the order ~9 x 3 x 3µm³, which was calculated using the mean diameter and aspect ratio; this corresponds to ~1080 laths in the gauge volume. From the XCT results, the gauge section taper was observed to deviate by ±8% from the mean value, corresponding to an angle of 1.6°. Furthermore, the taper was discontinuous, visible by the mean value (0% deviation) being slightly off centre towards top tab in Figure 6. The discontinuity is also visible in the electron micrographs (Figure 7a), where the pronounced curtains are a result of the high current initial thinning step, which could not be removed during the lower current automated rocking mill process due to an insufficient line current density (dwell time). Both of the samples prepared using 2° overtilt were successfully tested, having mean gauge dimensions of: 151µm (L); 19µm (W); 32µm (T); with 8 and 10 visible prior austenite grains (PAGs). Despite the slight variation in gauge dimensions, the sampling volume remains approximately equal and consisted of ~1050 laths. An overtilt of 2° resulted in a reverse taper of -0.44°, with a ±2 % deviation from the mean. The mean cross section is situated at the centre of the gauge section indicating no discontinuity and an adequate line current density in the cross-polish step. Milling the T-bone geometry was performed with no overtilt for either preparation routes, resulting in a trapezoidal cross section. Measurement of the width of both sides of the sample was performed using Image-J [244] and used to calculate the cross-sectional area assuming an ideal trapezoid, however blunt edges and bowing were not accounted for.

Mechanical testing

Stress strain curves for the overtilted and non-over tilted specimens are displayed in Figure 9. For comparison, a flow curve (from ref. [269] – identical material) from a standard cylindrical specimen with a 7mm diameter is also shown. Due to a slight misalignment, the Youngs
modulus for all measured samples during the primary loading stage was far larger than would be expected: 254 ± 3 GPa compared to 189 ± 2 GPa for the bulk. A more accurate modulus was obtained during an unload cycle in one of the tests, which was more consistent with that of the bulk measured at 178±3GPa. Proof stresses (0.2% yield stress) were 622 MPa and 600 MPa for the overtilt and non-overtilted samples respectively and were in good agreement with the bulk value of 646 ± 9 MPa. The yield transition was dampened and gradual in the sample without overtillt, which is evident in the proportional limit; 540 MPa as opposed to 572 MPa for the sample with overtillt.

Strain hardening parameters were calculated by the gradient of the log-log stress-strain curve for the region between proof and peak stress [27]. The bulk strain hardening parameter was calculated as 0.122 [269], whereas the curves in the PFIB prepared samples were significantly lower. While the proof stress was well represented, the largest variation from the bulk properties was in the plastic regime, with a peak stress and strain hardening exponent of 0.094 and 0.083 for overtillt and no overtillt respectively. Peak stress and strain to failure follow the same under representative trend with respect to bulk. There is a possibility that this behaviour is due to gauge section aspect ratio (T/L) rather than scale or taper. Previous work by Zhao et.al found that the post necking strain to failure can be extended by increasing the ratio of gauge section thickness relative to its length [270,271]. Furthermore, their work on ultra-fine-grained Cu demonstrated that a larger aspect ratio increased the strain hardening rate while not affecting yield [271]. Due to the large difference between the grain size of that study (100nm - 1µm) and this study (~5µm), the gauge section aspect ratio is not considered to be the likely cause of the change in strain hardening behaviour observed here.

Figure 10 (a) shows a flow curve from a sample prepared with a 2° overtillt containing highly localised strain at a PAG boundary, which is highlighted on the micrograph and orientation map (Figure 10 (b) and (c)). The behaviour displays similar characteristics to the overtillted specimen shown in Figure 9, however a slightly diminished plastic response is observed due to a sharp loss in strain hardening at the peak stress. This test exhibited a slightly lower peak stress than either of the other tests, however, a similar strain hardening parameter was observed to the other specimen prepared with overtillt (0.092). The sudden drop is assumed to be due to a strain localisation manifesting at 1.76% global strain which was fully matured by the observable load drop at 4.4%. Localised shearing of this manner was not observed in any of the other tensile tests despite all containing a similar number of PAG boundaries, possibly due to the fact that this was the only specimen with a PAG boundary through the gauge thickness. However, the finite element modelling of tetragonal meshed XCT samples, displayed in Figure 11, indicate that the PAG boundary localisation is situated in a geometry dependent strain hotspot. It is therefore also possible that the other samples do contain PAG
boundaries that facilitate this mode of localisation, but are situated outside of this high strain region. The localisation is arrested at the neighbouring boundary with subsequent deformation occurring in the same homogeneous manner as the other tests. Arresting of strain localisation implies that the neighbouring PAG boundary does not span the entire gauge thickness.

**Finite Element Analysis**

The results of the FEA analysis from the tomography-based model agree well with the observable plastic deformation in the corresponding micrograph shown in Figure 11. A broader distribution of plastic strain is visible in the 2° overtilt sample, whereas, is highly localised in the sample with no overtilt. Figure 11c displays profiles of maximum shear strain measured by digital image correlation, which were taken from the centre of the entire gauge length. Both profiles were made at 8% total deformation and were normalised against the maximum value to allow direct comparison of distribution between specimens. No markers were applied, with correlation of raw surface features leading to significant noise in local strain measurements. Although it is possible to apply an array of markers to improve local strain measurement, the application process was not perfected before this study. The strain profile for the overtilted sample displays a broad distribution of strain gradually decaying from the neck region over the majority of the gauge section. Conversely, the specimen prepared with no overtilt displays a sharp peak in the region of the neck with steep decay. Despite the noise, the trend corroborates the normalised maximum principal strain measurements of the model. While it would be expected that the region of maximum strain lies at the narrowest point of the gauge length, this was not found to be the case experimentally or using the models. Since the FEA was modelled as isotropic solid in terms of mechanical properties, the region of maximum strain is not thought to be due to a microstructural effect. The narrowest point of the gauge length is “constrained” in plane by the immediately adjacent volume of material in the specimen tab, this is thought to extend the stress field further along the gauge length. Furthermore, although the fillets at either end of the gauge section to the tabs are angled at 45° there is a de facto notch at the transition between fillet and gauge section. This notch will instigate a more complex stress state in this region than would be expected in a specimen with a large radius fillet, this notching may also be contributing to the shift.

To assess the effect of varying taper geometry on plastic response, a plane strain model was constructed with the only varying parameter being the taper referred to in Figure 12 as thickness ratio (ratio of maximum to minimum thickness). Elastic and plastic stress strain input parameters were taken from the full flow curve of the bulk test [269]. Stress-strain data was extracted as the average of in-plane stress and strain for all elements in the model, which was strained to 10%. The results of the model showed good agreement with the experimental
observations (Figures 9 and 12). Increased taper suppresses the plastic response of specimens, which is in agreement with observations made by Singh et al. [146]. However, the observations are not consistent in the literature; Zhang et al. recorded an increase in plastic response in FEA modelling of pillar compression, where yield, strain hardening and peak stress were all increased as a function of tapering [272].

Figure 13(a) shows a comparison of the effect of thickness ratio on the maximum stress for the FEA and experimental results. The thickness ratios of the experimental results are taken from the XCT data for samples with and without overtilt; a dashed line represents the bulk stress at 10% applied strain recorded in ref. [269]. The maximum stress measured in tapered XCT and 2D FEA plotted as a function of taper converges with the bulk properties in a linear fashion. The results from the FEA modelled from the XCT geometry agree well with both the 2D plane strain FEA and the experimental results. Figure 13(b) shows the strain hardening parameter as a function of taper. A similar linear trend is observed with both FEA models with good agreement to bulk results at a thickness ratio of 1. The maximum stress recorded experimentally is in good agreement with the FEA results, however, the experimentally recorded strain hardening exponent is not so accurately represented by the models. The negative effect of specimen thickness on strain hardening in polycrystalline samples is well known [128]. This is thought to arise from the ratio of grains sitting within the volume to that of grains intersecting the free surface. Un-constrained grains at a free surface accumulate dislocation density at a lower rate during deformation, due to an easy path for annihilation, than those that are constrained in the bulk [129,132]. The build-up of back stresses is limited in those grains and therefore they do not inhibit the operation of dislocation sources to the same extent as a fully constrained grain. A recent study was performed into the effect of specimen geometry on bulk samples including the thickness to diameter ratio (t/d) for various steels [130]. It was demonstrated that the loss of strain hardening due to t/d was in the order of 0.03 for the most similar alloy (CrMoV) to that studied here. The measured loss of geometry-calibrated strain hardening (n(FEA)-n(exp)) in this study was ~0.02. It is clear that despite the large number of lath boundaries within a specimen, the strain hardening remains unrepresentative of bulk hardening. The tempered martensite laths share an orientation relationship within the prior austenite grains in groups referred to as blocks. It is understood that coherent boundaries, such as martensite laths, meeting the criteria for slip transmission provide less effective barriers to dislocation motion [273]. In the case of hardening it has been argued that the block size is the dominant effect, since it is the next largest incoherent boundary in the hierarchical structure [274,275]. Microbend testing performed by Shibata et al. shows that block diameters agree well with pure iron in Hall-Petch plots [274]. Therefore, a low t/d due to an insufficient number of fully constrained blocks is considered to be the likely
contributor to the degradation of strain hardening behaviour. Block and lath packet density has been demonstrated to be influenced by PAG size [276], hence the t/d ratio can be improved by increasing either specimen or decreasing PAG diameter.

Conclusions

A method for preparation of micro-scale specimens for mechanical testing by Xe+ Plasma FIB has been developed and tested. The main conclusions are as follows:

- The use of a Xe plasma FIB has allowed for the manufacture of samples at a scale approaching the smallest representative volume in a reasonable timescale of 2-3 days.
- A methodology has been developed that produces samples with a relatively parallel gauge length and a deformation-free, polished surface that can be used for subsequent EBSD analysis and also allows to apply patterns for DIC.
- By comparison with FEA modelling, it has been demonstrated that the observed yield dampening and reduction of peak stress are a result of slight taper rather than scale.
- Specimens exhibited no size dependent hardening with the only scaling effect being an intrinsic microstructural effect related to the t/d ratio, which could be overcome by grain size reduction or increasing gauge volume.
- In order to increase flexibility during sample preparation, a double axis tilt microscope stage would be beneficial.

Acknowledgements:

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Figures

Figure 1. Schematic of specimen preparation route, (a) mechanically thinned 3 mm diameter, 100 µm thick disk; (b) Mechanically cut into a half moon; (c) High current (1.2 µA) PFIB mill to remove cold worked layer; (d) Fiducial markers placed for automated positional correction; (e) 2° automated rocking mill both sides at 0.18 µA to a curtain free 380 x 500 x 30µm lamella; (f) Final milling of T-bone specimen geometry.

Figure 2. Schematic of piezo actuated µ-Test Rig used for in-situ testing within SEM
Figure 3. Secondary electron image used for strain measurement. Displacement is recorded by imaging at each hold point as the test progresses and images are later processed using digital image correlation to calculate strain.

Figure 4: Examples of meshes used for FEA analysis using, a) 2D plane strain & b) mesh modelled from XCT geometry

Figure 5: Schematic of boundary conditions for FEA simulation of meshed XCT measurements
Figure 6: XCT of samples prepared using (a) no overtilt and (b) 2° overtilt, coloured according to deviation from the mean cross section.

Figure 7: Secondary electron images of sample batches prepared (a) without overtilt and (b) with overtilt.
Figure 8: Orientation maps recorded using EBSD, displayed in Euler colours, showing typical microstructures in tensile samples, both orientation maps are taken from overtilted batch.

Figure 9. Flow curves of PFIB samples prepared with and without over tilt, bulk standard curve is overlaid [269]
Figure 10: a) Flow curve of specimen containing PAG running through the gauge section thickness; b) secondary electron image illustrating point of strain localisation prior to failure; c) Location of PAG boundary highlighted on EBSD orientation map.
Figure 11. (a) FEA modelled using XCT with secondary electron image of corresponding necked specimens, the strain distribution agrees well with the observable deformation in the secondary electron micrographs (b); (c) Normalised strain profiles generated by DIC of specimen surfaces at 8% strain.
Figure 12. 2D FEA of tensile stress strain curves for samples with varying thickness ratios.
Figure 13. (a) Peak stress and (b) Strain hardening exponent measured in the modelled 2D plane strain, modelled tomography and experimental data.
Appendix:

Appendix Figure 1: Completed specimen attached to sample mount, the sample mount is attached to the pre-tilt holders and directly into the microtest rig by grub screw.

Appendix Figure 2: Pre-tilted holder was designed with multiple tilt angles to provide an additional axis during the automated cross polish.
4.3 Manuscript 3: Novel Methods of Recording Flow Curves in Proton Irradiated Material

Albert D. Smith, Jack M. Donoghue, Alistair J.W. Garner, Keith Wilford, Philip J. Withers, Michael Preuss

Named author contributions were as follows:

**Albert D. Smith**: Lead author, prepared specimens, designed and carried out irradiation experiment, redesigned irradiated tensile specimens, performed XRD-DIC experiments, performed indentation testing, assisted with PFIB in partnership with named operators, carried out small-scale tensile testing in partnership with Jack M Donoghue, orientation mapping, digital image correlation, performed all analysis.

**Jack M. Donoghue**: Operated the PFIB, facilitated the tensile testing, orientation mapping.

**Alistair J.W. Garner**: Operated the PFIB

**Keith Wilford, Philip. J Withers & Michael Preuss**: Supervisors of Albert Smith

Additional contributions:

**David Lunt, Imran Bhamji, Allan Harte, Joseph Ward, Rhys Thomas & Felicity Baxter**: Attended proton irradiation experiment

The manuscript was internally reviewed by **Prof. Michael Preuss** and **Dr. Alistair JW Garner**
Novel Methods for Recording Flow Curves in Proton Irradiated Material

Albert D. Smith¹, Jack M. Donoghue¹, Alistair J.W. Garner¹, Keith Wilford², Philip J. Withers¹, Michael Preuss¹

The University of Manchester¹, Rolls-Royce plc²

Keywords: 3MeV Proton Irradiation, Diffraction Stress measurement, Xe+ Plasma FIB-SEM Dual Beam Microscope, In-situ Mechanical Testing, Digital Image Correlation, SA508 Grade 4-N steel

Abstract

Two novel methodologies have been developed to record stress-strain curves in thin proton-irradiated films of SA-508-4N ferritic steel. In the first case, in-situ loading experiments are carried out using a combination of X-ray diffraction and digital image correlation on the near surface region in order to measure stress and strain, thereby eliminating the influence of the non-irradiated volume. The second approach is to manufacture small-scale tensile specimens containing only the proton irradiated volume but approaching the smallest representative volume of the material. This is achieved by high-speed focused ion beam (FIB) milling though the application of a Xe+ Plasma-FIB PFIB. It was possible to demonstrate that both techniques are capable of recording the early stage of uniaxial flow behaviour of the irradiated material with reasonable accuracy providing a measure of irradiation-induced shift of yield strength, strain hardening and tensile strength. The work demonstrates that the two methodologies are capable of providing comparable results, which are consistent with the documented effects of irradiation damage on the tensile properties of metals.

Introduction

The expansion of the nuclear industry is being driven by increasing demand for low carbon, reliable energy [277]. In the UK, the increasing contribution of nuclear energy is intended to shift the national energy mix away from fossil fuels [13]. In order to increase power capacity and operational life in modern reactor designs, a better understanding of the performance of materials under high levels of irradiation damage and temperature is required. Displacement damage leads to a degradation of mechanical properties through irradiation-induced hardening, a reduction of strain hardening and reduction to strain to failure [46,59]. The most reliable method of testing material behaviour under reactor conditions is achieved by placing surveillance specimens within an operating or test reactor, which are removed and tested periodically [278]. However, the high level of financial commitment and long duration of
these tests is a restrictive barrier to entry [279]. The low displacement efficiency of neutrons leads to experiments running from months to years in order to reach relevant levels of damage. In addition, high post-irradiation activity requires a cooling off period to safely perform off-site examination, increasing test duration further [6]. This leads to a long turnaround time for specimens and can be prohibitive to studies requiring a wide range of irradiating conditions or new alloy designs. As a result, alternative forms of irradiation, particularly proton and heavy ion irradiation, have been developed in order to mimic the effects of neutron irradiation in shorter timescales.

Spallation source protons have an energy in the order of 100s of MeV, inducing a displacement damage similar to the effects of neutrons. Such high kinetic energy has the advantage of through thickness irradiation of bulk specimens, so can be analysed using standard mechanical testing [28,74,95,280–283]. However, this approach suffers from the same limitations as neutron irradiation, in terms of poor displacement efficiency and high residual post irradiation activity. This drives up experimental expense and limits the availability of equipment. Lower energy proton beams induce similar displacement damage with a reduced post irradiation activity, allowing for easy handling, transportation and testing [53,284]. The reduced energy of the incident beam is more efficient at generating displacement damage. Depending on the energy, low energy protons can attain damages in a matter of hours that would take months in a neutron test reactor or spallation beamline. However, the advantages enjoyed by low energy proton irradiation comes at the expense of penetration depth [5].

The limited penetration depth of proton irradiation makes measurement of changes in mechanical properties difficult using established techniques [93,285]. Over the last decade, the use Ga⁺ focussed ion beams (FIB) has allowed for the preparation of small scale samples from the proton irradiated layer [78–80,82,107,124]. The mechanical properties of these samples are then tested with an indenter tip or piezo actuated test rig without contributions from the non-irradiated volume. This development has allowed studies to take advantage of the increased dose rates and probe properties previously only attainable using indentation testing [84,89,286–288]. However, the useable currents are limited using Ga⁺ FIBs due to the point source of Ga⁺ ions, which limits milling rates. Consequently, specimen diameters achievable in a practical time frame are limited to ~10µm. For most materials, the maximum achievable scale is in the order of single to only a few grains. Hence, the technique is most applicable to single and bi-crystal investigations. Such a reduction in specimen scale is problematic when relating to a bulk response for polycrystalline specimens. It has been demonstrated that small scale specimens exhibit an increased hardening inversely proportional to specimen diameter [99,128,143,263,264]. In order to obtain a bulk response, specimens require a minimum length scale sufficient to inhibit size reduction effects. The optimum
specimen would be at the smallest representative volume (SRV), which would retain the benefits of scale reduction whilst exhibiting bulk behaviour [111].

Recent work by the authors has explored two techniques to increase the sampling volume in low energy proton irradiated samples prepared for mechanical testing [269,289]. The first, an adaptation of the technique outlined by Foecke et.al [253], combines in-situ X-ray diffraction stress measurement and digital image correlation (DIC) to construct uniaxial flow curves [269]. Laboratory-based \( \sin^2 \Psi \) diffraction stress measurement relies on the limited X-ray penetration depth, which is in the same order as the proton irradiated layer. Calibration of the lattice response to applied stress allows for the calculation of stresses in the same material under the assumption the lattice response to applied stress is consistent. Strain is calculated using DIC on optical images collected in parallel to the stress measurements. Digital image correlation allows for non-contact measurement of in-plane strain on the surface. Therefore, both stress and strain data are collected from the near surface region that is affected by irradiation hardening. The second method utilises the recently developed Xe\(^+\) Plasma focussed ion beam (PFIB) technology. PFIBs do not suffer from the same current limitations of the Ga\(^+\) FIB, due to the increased relative size of the source which allows a focussed beam to be maintained at high currents [149]. It is therefore possible to perform large scale machining of material at mill rates exceeding 100 times that of Ga\(^+\) FIBs [156,267]. A methodology has been developed for the manufacture of samples with a gauge section in the meso-scale [289]. These specimens possessed a proof stress comparable to a standardised bulk test, however, did display a size dependent plastic response [289]. A methodology has been developed for the manufacture of samples with dimensions approaching the SRV, with a gauge section in the meso-scale exhibiting bulk behaviour in all aspects except strain hardening [289]. This study aims to apply both novel techniques for the first time to record the mechanical response of 3MeV proton irradiated SA508-4N steel, irradiated to a depth of approximately 30 \( \mu \)m.

**Experimental Methods**

*Material and specimen preparation*

The material in this investigation was SA508-4N martensitic-bainitic steel, supplied by Rolls-Royce plc. The material was forged, quenched and tempered and the composition is shown in Table 1. Dog bone tensile samples were prepared with a 27 mm x 2 mm x 1 mm gauge section by electrical discharge machining (EDM). Coupons for preparation of specimens by PFIB were also prepared by EDM to the dimensions 27mm x 3mm x 1mm. All specimens were ground to remove the recast layer and subsequently polished using a standard metallurgical preparation route.
Table 1: Composition of alloy [208]

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<tr>
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<th>C</th>
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</table>

Irradiation experiment

All irradiation experiments were carried out using the DAFNE 5MV Tandem Pelletron at the University of Manchester Dalton Cumbria Facility [221,290]. The specimen setup during irradiation is illustrated in Figure 1(a) and (b). A “jigsaw” configuration was designed to reduce leakage of the liquid indium eutectic heat sink during irradiation. Proton irradiation was carried out at 3MeV at a flux of $2.3 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$ to obtain a fluence of $8.43 \times 10^{17} \text{ cm}^{-2}$, with the beam rastered over a 5 x 25 mm$^2$ area. The beam was over scanned by 40% onto the aperture veins to produce hard edges in the irradiated region. Proton stopping range calculations were performed in SRIM [291] with the ‘quick Kinchin–Pease calculation’ [219]. The calculation predicted a stopping peak at ~36µm, with the damage at 60% of the penetration depth of the stopping peak taken as the nominal damage (Figure 1c). The temperature was monitored using a pyrometer, which was pre-calibrated according to the method outlined by Wady et.al [221]. The mean temperature was recorded throughout the experiment as $330\pm3^\circ\text{C}$. Following irradiation, specimens were lightly polished with colloidal silica in order to remove any surface implantation. The irradiated region was located by automated profile micro indentation testing, using a Struers Durascan automated indenter. A load of 0.005 kg was applied for 10 seconds; the use of a low load ensured indentations did not penetrate through the irradiated layer. Due to a slight aperture misalignment, the irradiated region over the sample set had a trapezoidal area. The area was measured and used to recalculate the nominal damage using the accumulated charge during irradiation. An average increase in hardness of 36 Hv was recorded in the irradiated region relative to the non-irradiated region, as shown in Figure 3.

Table 2: Proton irradiation conditions

<table>
<thead>
<tr>
<th>Energy</th>
<th>Flux</th>
<th>Dose Rate</th>
<th>Fluence</th>
<th>Nominal Dose</th>
<th>Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>3MeV</td>
<td>$2.3 \times 10^{14} \text{ cm}^{-2}\text{s}^{-1}$</td>
<td>$4.09 \times 10^{-3} \text{ mdp a s}^{-1}$</td>
<td>$8.43 \times 10^{17} \text{ cm}^{-2}$</td>
<td>15 mdp a</td>
<td>$330\pm3^\circ\text{C}$</td>
</tr>
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</table>

Combination of XRD and DIC

As the irradiated region in the gauge section was discontinuous, the specimen was further modified by EDM, as shown in Figure 2(a). The “double dog bone” geometry was designed
so the widest point of each radius leading into the second parallel intersected with the start and end of the irradiated region. The inner gauge section was 4mm x 1mm x 1mm, with a 0.5 mm radius in the transition region. Removal of the material ensured the experiment remained uniaxial whilst also removing the indentations used to locate the irradiated region. Samples were painted with a white anti-reflective coating and dusted over with black spray paint to apply a speckle pattern to be tracked by digital image correlation (DIC).

The in-situ X-ray stress measurement and image collection was carried out according to the methodology outlined in [269]. Quasistatic tensile loading was applied using a Kammrath Weiss 5 kN tension-compression microtester at a displacement rate of 5 μm s\(^{-1}\), which corresponds to \(1.25\times10^3\) s\(^{-1}\). The crosshead was frozen at numerous hold points throughout the test to allow for image acquisition and X-ray diffraction measurements. Optical images were analysed using the commercially available LaVision DaVis 8.1.5, image correlation software, with the total strain calculated in the region of the second gauge section.

Single peak X-ray stress analysis was performed using the sin2\(\Psi\) technique on the \{211\} reflection, with Cr K\(\alpha\) radiation giving a 20 of 155 degrees. Side inclination measurements were taken at 11 \(\Psi\)-tilt angles between \(\pm25^\circ\) with 10 exposures using a 1mm round aperture. Due to the reduced aperture, the counting times were increased to 3 seconds for each of the exposures and \(\pm2^\circ\) goniometer undulation was applied to increase counting statistics. Peak position and shape was determined using a gaussian fit, with stress calculated as follows:

\[
\sigma_x = \left( \frac{E}{1 + v} \right) \frac{\delta d_{hkl}^{\Psi=0}}{\delta \sin^2 \Psi} \frac{1}{d_{hkl}^{\Psi=0}}
\]

Equation 1

where \(d_{hkl}^{\Psi=0}\) is the inclined lattice spacing rotated around an axis normal to the loading direction, \(d_{\Psi=0}\) is the stress-free lattice spacing at \(\Psi = 0^\circ\) and \(\left( \frac{E}{1 + v} \right)_{hkl}\) are the effective elastic constants of the diffracting plane (1/2 S2) calculated to be 5.94 x 10\(^{-6}\) MPa\(^{-1}\) [269]. The diffraction elastic constants were assumed to be unchanged by irradiation for this calculation.

A linear response of the diffracting plane (211) to applied stress during plastic deformation [177] indicates that it is not sensitive to intergranular strain development or an increase in defect density.

**Plasma Focussed Ion Beam (PFIB) Milling and Piezo-Mechanical Testing**

A coupon was prepared for PFIB milling by grinding and polishing the non-irradiated face of the sample. It was mounted, with the irradiated face down and carefully thinned using silicon carbide paper until a thickness of \(\sim 60\mu m\) was achieved. After polishing, a 3mm disk was
extracted from the foil using a standard transmission electron microscope specimen punch, followed by grinding with fine grit silicon carbide paper to remove burrs. The foil was mounted between two glass slides with wax and ground to apply a straight edge. Attachment of the disk to a specimen mount using cyanoacrylate adhesive readied the specimen for preparation by PFIB. Specimens were prepared using the methodology outlined in [289], with all milling performed at 30kV and 2° overtilt using a PFIB equipped FEI Helios FEG-SEM. The high current (1.3µA) milling was carried out from the non-irradiated side to preserve as much irradiated material as possible. This high current thinning step continued until a thickness of ~40µm was reached. A subsequent automated cross polishing routine was performed using FEI Auto Slice and View 4 software package at 180 nA, removing approximately 5µm from each side. Therefore, the through thickness dimension contained only the flat portion of the dose profile with the Bragg peak removed (Figure 1c)). A final lamellar width of 400µm with a 30µm thickness provided sufficient area to prepare three parallel tensile specimens (Figure 2). The final specimen geometry was milled at 180 nA and the final gauge section dimensions were 150 µm x 30 µm x 30 µm, comprising of ~1600 laths, with an approximate lath of ~9 x 3 x 3µm³.

Two specimens were tested to failure using a Microtesting Solutions (Hilliard, OH, USA) µ-Test Rig (MTR-3), mounted in a Zeiss Sigma FEG-SEM. Loading conditions were the same as those applied in ref. [289], with specimens loaded using a diamond pin at a rate of ~100nm s⁻¹ and hold points at 200 nm increments. Secondary electron images were taken at each hold point to provide an accurate method of strain measurement. Strain was calculated by tracking platinum fiducial markers using digital image correlation, as outlined in [289].

Results

This section summarises the results obtained in the irradiated specimens measured using both techniques. Due to only two irradiated specimens being tested in both cases, the average values of properties are reported, with no treatment of error. All data for non-irradiated samples were collected in prior studies and is referenced accordingly. Data gathered from the stress strain curves is displayed in Table 3.

A comparison between the flow curves generated from the XRD/DIC technique in the irradiated region and from the non-irradiated material from ref. [289] is shown in Figure 4. The proof stress of the irradiated samples were obtained using the standard 0.2% offset, providing a median value of 770±9 MPa. The curve measured in the irradiated specimens displays clear irradiation hardening, with an increase in proof stress of 137±9 MPa. This value agrees well with the estimated yield shift of 110 MPa using indentation testing, which was calculated using the relationship from ref. [84]:

138
\[ \Delta \sigma_y = 3.03 \Delta H_V \] 

Equation 2

where, \( \Delta \sigma_y \) is the calculated yield shift; \( \Delta H_V \) is the measured increase in Vickers hardness due to irradiation damage and 3.03 is the correlation function for ferritic steel.

Strain hardening was calculated for the irradiated specimens using the log-log gradient of the plastic regime between proof and peak stress. Stress-strain curves exhibited a slight reduction of \( \sim 0.013 \) in strain hardening, relative to the non-irradiated material. Tensile strength, taken as the peak stress, remained unchanged at 875 MPa, while the strength coefficient was observed to decrease by 89 MPa. Fitted curves generated using Hooke’s law and a power law hardening model are shown in Figure 6, with plastic behaviour characterised by the Hollomon equation:

\[ \sigma_t = K \varepsilon^n \] 

Equation 3

where \( \sigma_t \) is true stress, \( K \) is the strength coefficient and \( n \) is the strain hardening exponent.

Figure 5 illustrates the flow curves recorded from microtensile specimens prepared from the proton irradiated region using the Xe\(^+\) PFIB method described previously. The measured proof stress was recorded as 807±9 MPa, exhibiting an irradiation hardening of 161±9 MPa. This is approximately 24 MPa higher than the median value of hardening reported using the XRD and DIC technique, and 52 MPa more than that calculated using indentation testing. The strain hardening exponent was calculated to be 0.06, a reduction of 0.034 relative to the non-irradiated state. It must be emphasised that the strain hardening exponent recorded in the non-irradiated specimen is already lower for the microtensile specimen than in the bulk samples [289]. The exponent is approximately 21% lower than that recorded using the XRD-DIC method and the standardised method [269]. Tensile strength was measured to be to 866±3 MPa using this technique, corresponding to an increase relative to the non-irradiated state of 135 MPa; furthermore, the strength coefficient was increased to 1093±11 MPa. Fits for the curves of irradiated and non-irradiated specimens using this technique are also shown in Figure 6.

SEM images (Figure 7a and b) of each specimen prior to failure, show some apparent differences between the non-irradiated and irradiated specimen. The irradiated specimen displays planar slip in the region of the neck which is indicative of dislocation channelling due to defect clearing during deformation [63]. Analysis of this behaviour using high resolution
digital image correlation could be applied in this case to quantify the observed change. Fracture surfaces for irradiated and non-irradiated specimens, tested using both techniques, are displayed in Figure 8. The region displayed for the irradiated sample, tested using the combination of XRD and DIC, is the flat portion of the dose profile. All examples illustrate that both non-irradiated and irradiated samples failed in the same mode, by ductile void coalescence. However, fractography of the microtensile samples effectively highlights the triaxial stress state at the neck during failure. This is amplified due to the removal of constraint, resulting in drawn out elongated cavitation, which extends in the direction of shearing. It is also notable that the reduction in area is significantly larger in the non-irradiated sample than the irradiated, corresponding to 95 % and 71 % respectively.

<table>
<thead>
<tr>
<th></th>
<th>XRD - DIC</th>
<th>Microtensile</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 mdpa [269]</td>
<td>15 mdpa</td>
</tr>
<tr>
<td>$\sigma_y$ (MPa)</td>
<td>633±74</td>
<td>770±51</td>
</tr>
<tr>
<td>$n$ (Unitless)</td>
<td>0.113</td>
<td>0.1</td>
</tr>
<tr>
<td>$\sigma_u$ (MPa)</td>
<td>875±53</td>
<td>872</td>
</tr>
<tr>
<td>$K$ (MPa)</td>
<td>1120±84</td>
<td>1209</td>
</tr>
</tbody>
</table>

**Discussion**

Both techniques have demonstrated that they are capable of recording a change in mechanical properties induced by displacement damage from proton irradiation. An increase in yield stress and decrease in strain hardening was documented using both XRD-DIC and microtensile testing.

**Yield Shift**

Due to the variance in relative sampling volumes for each technique, the recorded values of yield shift are slightly different despite being irradiated under the same conditions. This difference corresponds to a variation of nearly 40 MPa, with the specimens prepared using PFIB having the largest yield shift. Although the samples prepared using PFIB accumulate some surface damage due to ion beam milling, previous observations have shown that the damage layer is approximately 40% shallower to that induced using Ga$^+$ FIB, in the order of 10s of nano meters [133,154]. This would correspond to Xe$^+$ ion damaged region in the total gauge volume of approximately $5\times10^{-3}$ %, so is not thought to contribute significantly to the
measured shift. The relatively small differences between proof stresses in the non-irradiated dataset indicates that the variation evident in the irradiated sample is not a characteristic intrinsic to the method of preparation. This variation in yield stress is considered to be due to the difference in relative sampling volumes between the techniques, each effectively measuring a different dose. Figure 9 illustrates this; the area shaded in grey highlights the region sampled in the microtensile specimens and the plots shaded red through to black illustrate the attenuation of X-rays at each Ψ-tilt. The penetration depth as a function of tilt was calculated using [292]:

$$G_x = 1 - \exp\left\{ -\mu x \left[ \frac{1}{\sin(\theta + \psi)} + \frac{1}{\sin(\theta - \psi)} \right] \right\}$$

Equation 4

where $G_x$ is the total diffracted intensity at a depth of $x$; $\mu$ is the linear absorption coefficient; $\theta$ is the diffraction half angle and $\psi$ is the tilt angle relative to the sample surface.

In contrast, the sampling volume of the microtensile specimens were sampled from the region ranging from 3µm – 33 µm, with uniform sampling over this segment of the dose profile. Weighted dose ($D_w$) was calculated by integration to take account of both the non-linear sampling of XRD and the non-linear dose profile simulated using SRIM:

$$D_w = \frac{\sum D_i G_i}{\sum G_i}$$

Equation 5

and

$$D_w = \frac{\sum D_i}{N}$$

Equation 6

where $D_i$ and $G_i$ are dose and diffracted intensity diffracted intensity respectively at each bin and $N$ is the number of bins. Bins were set at 500 nm increments, with $D$ and $G$ calculated as a trapezium to increase accuracy.

Each dose, weighted for $\Psi$-tilts, gave an average of 9.9 mdpa calculated for those samples measured using XRD. Dose was found to be inversely proportional to $\Psi$-tilt angle due to the larger penetration depth at lower angles and ranged by 0.5 mdpa from 10.2 mdpa at $\Psi = 0^\circ$ to 9.7 mdpa at $\Psi = 27^\circ$. The range of doses were relatively narrow due to the exclusion of the stopping peak. Samples prepared using PFIB included some of the base of calculated damage.
peak, this gave a weighted dose of 15.6 mdpa. Given the weighted dose is 37% larger and the yield shift measured was greater in the specimens prepared by PFIB, the difference is most likely due to the sampling volume. It must be stated that studies have demonstrated that the SRIM profile, while accurately predicting stopping range, is not as accurate in predicting the magnitude of damage [3,81,288,293,294]. The non-linear characteristic of the dose profile is a characteristic of charged particle irradiation, with dose increasing up to a maximum at the stopping peak.

**Strain Hardening**

Both techniques revealed a measured decrease in strain hardening due to irradiation damage. This behaviour is consistent with previous observations that show that irradiation has a deleterious effect as a function of dose up to the critical value where strain hardening drops to zero and necking occurs at yield [60,214]. Strain hardening in the irradiated PFIB prepared specimens is much lower than that recorded by XRD and DIC, however this is not thought to be due to differences in the sampling volumes as with the yield shift.

The strain hardening exponent measured from stress strain curves recorded by XRD-DIC in the non-irradiated condition is comparable to bulk [269]. However, when considering the differences in yield points and hardening rates of the non-irradiated “substrate” and irradiated layer, there may be some deviation between the surface measurement and would be measured in material irradiated through thickness. The lattice response of dual-phase or composite materials during in-situ loading is analogous to the current study. Tensile deformation of these dual property materials will exhibit a linear response to applied stress up to the yield point of the softest constituent. Beyond which, load is understood to partition and will be transferred onto the harder of the constituents [295–298]. Hence, this will result in a larger stress recorded in the harder constituent of a dual property material than would be the case at the same level of strain if the same constituent were isolated. This has implications on the validity of the measured strain hardening in the irradiated layer. Due to partitioning, each increment of strain would result in a larger level of stress, which in turn will affect the calculated strain hardening parameter and is further complicated when considering the property gradients present in proton-irradiated material. A good indicator of the presence of load partitioning is the linearity of the elastic range for the irradiated layer, which would result in an inflection upon the yielding of the non-irradiated substrate [298]. Although this inflection was not observed, it is difficult to state whether or not partitioning is occurring with any certainty, as there is only one measurement point between the proportional limits of each layer. It may well be the case that the effect of partitioning is diminished due to the low volume fraction of irradiated material (~4 %). An in-situ study of dual phase 737-DP and 775-DP steels has reported the
effect of load partitioning on strain hardening was lesser in the alloy with a lower volume fraction of the harder martensite phase [299].

The strain hardening parameter of non-irradiated small-scale specimens, prepared using PFIB, has already been demonstrated to be far lower than that of bulk tests [289]. This is thought to be due to the high ratio of grains intersecting the surface to those fully constrained in bulk. In this study, the relative volumes of the irradiated specimens are approximately 50% larger than the non-irradiated. Under the assumption that prior austenite grain (PAG) boundaries control the hardening parameter to a larger extent than lath boundaries [289], the ratio of specimen thickness to grain diameter \((t/d)\) is 0.58 and 0.91 for non-irradiated and irradiated samples respectively. Specimens with a higher \(t/d\) ratio will harden at a higher rate due to the contributions of back stresses generated by dislocations accumulating in the larger fraction of fully constrained grains [79,132]. It has been shown that the strain hardening parameter \((n)\) raises with increased \(t/d\) before stabilising and accurately reflecting bulk hardening [300], the position and shape of this threshold value can vary considerably between materials [130]. Since the larger, irradiated samples have a \(t/d\) ratio that is far below the threshold value for all alloys outlined in refs. [300] and [130], it is not thought that they satisfy the requirement for bulk hardening behaviour. Despite being below the reported threshold for stabilisation (~3.75 in CrMoV steel [130]), there will still be an increase in hardening due to the increased \(t/d\) ratio. Quantification of the relative hardening variances requires tests to be carried out on non-irradiated control samples of the same scale and geometry.

**Ultimate Tensile Strength**

Work by Byun and Farrell illustrates that irradiated materials possess a UTS \((\sigma_u)\) that is typically in the range of that found in non-irradiated materials [71,74,76,214,301]. As dose is increased, the yield stress \((\sigma_y)\) increases and is coupled with a reduction of strain hardening, at the critical point satisfying \(\sigma_y \geq \sigma_u\) a specimen will experience prompt necking at yield. Whilst the yield shifts in the current work were insufficient to exceed this threshold value, UTS measured in specimens using both approaches were within 10 MPa as bulk (non-irradiated) in all but the non-irradiated samples prepared using PFIB. Specimens prepared by top-down PFIB milling invariably exhibit side-wall tapering due to Xe\(^+\) ion beam profile and material redeposition. UTS has been shown to be inversely proportional to gauge section taper in non-irradiated samples tested in tension [289]. This implies that taper may have been significantly lower in the microtensile irradiated specimens, however, they were prepared using the same methodology as in ref. [289]. It may also be the case that stress has been raised above the threshold regardless of the geometric constraints, providing an accurate UTS.

**Possible Sources of Error**
The presented techniques are subject to intrinsic and extrinsic sources of error, some of which have already been discussed, including geometry, scale and load partitioning. Misalignment of samples in the 5 kN loading rig used in the XRD-DIC experiments, as with all griped sample loading rigs, can introduce scatter in recorded properties. This scatter is due to a strain gradient placing the sample in shear as a result of off axis loading [302]. At the larger scale, this can be minimised by the use of guide pins, specialised grips or calibration, outlined in ASTME1012-05 [303]. However, at the sub-millimetre length scale, specimen alignment becomes a significant issue [304]. In order to ensure accurate alignment with the loading axis, specimens were prepared within the fixture that was directly attached to the tensile testing apparatus and milling was performed with care to ensure the samples remain parallel with the external fixture [111,289]. Even with a well aligned gauge length, off axis loading may result from a mismatched pair of loading contact surfaces. In a compression test this would correspond to the punch and the top of the specimen and in tension would be the loading pin and loop interior. Due to the aforementioned sidewall tapering arising from FIB milling, mismatched surfaces are inevitable without employing overtilt during preparation [111].

The damage profile that is intrinsic to proton irradiated materials is also likely to introduce errors in the measured properties. Each approach samples a non-linear dose which can be considered as a property gradient over the sampling range. As the softer regions near the proton-beam entry surface yield, localised deformation will occur and the test will no longer be truly uniaxial. In order to avoid this localisation, the use of a significantly smaller specimen diameter relative to the irradiation stopping range has been suggested, which would require a higher energy proton beam to achieve a representative volume [92]. Although the sampling volume of XRD stress measurement has been shown to be more heavily weighted to the flatter region of the dose profile in this study, property gradients within the measured volume may also contribute to the error in the measurement. Non-zero out of plane shear stresses can introduce a phenomena referred to as psi-splitting, which is a breakdown in the linearity of the \( \sin^2 \psi \) plot [292]. The split manifests as an upwards and downwards deviation from the centre line at positive and negative tilts, its presence will increase errors in the gradient used to calculate stress. This was not observed in the present work; however, it may become apparent in specimens that possess a steeper gradient. Therefore, it may not be suitable to apply the technique to lower energy proton, He⁺ or heavy ion irradiation.

**Conclusions**

Two novel methods for testing the mechanical properties of thin layers was applied to proton irradiated material have been applied for the first time to measure changes in yield and strain hardening behaviour and the invariance of UTS. The main conclusions are as follows:
• The combination of XRD and DIC has been provides a low-cost method that replicates standardised testing techniques.
• PFIB manufacture of mesoscale polycrystalline proton irradiated specimens has allowed the testing of a length scale previously unattainable using Ga’ FIB.
• It is clear that further experimentation is required to further calibrate both techniques, the most important of which are: an investigation into load partitioning between non-irradiated/irradiated layers and a systematic assessment of the smallest volume required to represent bulk behaviour.
• Both techniques provide a method of obtaining data from the proton irradiated layer and recorded irradiation hardening and the reduction in strain hardening.

Figures

Figure 1 a) Schematic of proton irradiation set up, b) thermal image of specimens mounted on the end station during irradiation, arrows indicate beam position and c) SRIM simulation for current collected on stage during proton irradiation to achieve nominal damage level of 10 mdpa.

Figure 2: Specimen geometry for tensile samples tested using both techniques (a) XRD-DIC and (b) PFIB –microtensile [289].
Figure 3: Typical indentation profile of irradiated region taken at 0.05 \( H_v \), with an average irradiation hardening of 36 \( H_v \); shaded area denotes the irradiated region.

Figure 4: Flow curves generated by XRD/ DIC technique for irradiated and non-irradiated specimens, error bars are gradient error in \( \sin^2 \Psi \) vs. d-spacing plot. Red markers are irradiated, black markers are non-irradiated collected in ref. [269], with crosses and open circles representing different flow curves.
Figure 5: In-situ testing of small-scale specimens prepared by PFIB. Red markers are irradiated and black markers are non-irradiated collected in ref. [289].

Figure 6: Fitted curves assuming power-law hardening from each technique for irradiated and non-irradiated states. Non-irradiated data taken from [269,289] were used to generate fits by applying a power-law hardening model.
Figure 7: Post necking behaviour of non-irradiated and irradiated microtensile specimens. (a-b) Secondary electron images taken prior to failure; (c-d) EBSD Orientation maps of non-irradiated and irradiated specimens, displayed in the IPF colour scheme projects plane normal parallel to the loading direction; a & c are adapted from [289].

Figure 8: Secondary electron images of fracture surfaces for each sample (a) non-irradiated XRD/DIC; (b) irradiated XRD/DIC; (c); microtensile (PFIB) non-irradiated (d) microtensile (PFIB) irradiated. Clear evidence of failure by ductile void coalescence using both techniques.
Figure 9: Technique dependent sampling depth relative to the SRIM damage profile for both techniques; shaded region corresponds to sampling range of PFIB microtensile specimens.
4.4 Manuscript 4: High Resolution Plastic Strain Mapping of 100 mdpA Proton Irradiated Polycrystalline Austenitic Stainless Steel

Albert D. Smith, David Lunt, João Quinta da Fonseca, Keith Wilford, Philip J Withers, Michael Preuss

Named author contributions were as follows:

**Albert D. Smith**: Lead author, prepared specimens, designed and carried out irradiation experiment, SEM analysis carried out in partnership with David Lunt, performed mechanical testing & indentation testing, carried out vapour assisted remodelling in partnership with David Lunt, carried out orientation mapping, performed all analysis.

**David Lunt**: Assisted mechanical testing, attended irradiation experiment, assisted in vapour assisted remodelling, SEM analysis, orientation mapping, developed python script to extract frequency plots.

**João Quinta da Fonseca**: Provided additional supervision for the HRDIC study, developed Python script for processing displacement maps

**Keith Wilford, Philip. J Withers & Michael Preuss**: Supervisors of Albert Smith

Additional contributions:

**Imran Bhamji, Allan Harte, Joseph Ward, Rhys Thomas & Felicity Baxter**: Attended proton irradiation experiment

The manuscript was internally reviewed by **Prof. Michael Preuss** and **Dr. David Lunt**
Nanoscale plastic strain mapping of proton irradiated austenitic stainless steel

Albert Smith¹, David Lunt¹, João Quínta da Fonseca¹, Keith Wilford², Philip J Withers¹, Michael Preuss¹

The University of Manchester¹, Rolls-Royce plc²

Keywords: Strain localisation, High Resolution Digital Image Correlation, 316L, Proton Irradiation.

Abstract

Metals and alloys in an irradiating environment experience a degradation in their plastic response due to localised deformation. This has been attributed to dislocation channelling in defect free channels that provide a low resistance path for deformation. This study investigates the effect of proton irradiation (100 mdpa) on the strain localisation behaviour in 316L austenitic stainless steel using High Resolution Digital Image Correlation (HRDIC). Electron micrographs, collected at progressive strain increments, were correlated and then the deformation behaviour was compared in a non-irradiated and irradiated region. A key observation from the strain maps was the presence of diffuse strain plumes near grain boundaries and several grains showing multidirectional slip for the non-irradiated region compared to wider spaced planar traces with less slip directions within each grain for the irradiated region. Fast Fourier Transform (FFT) analysis of the strain maps and slip band profiling for the two regions showed that the irradiated region exhibited a suppression of cross slip, which resulted in an increase in slip planarity. This was linked to strain hardening behaviour by the broadening of slip trace profiles.

Introduction

Increased strain localisation of in service nuclear materials due to displacement damage is well documented [46,59]. It is currently understood to be a contributor to the loss of ductility that materials suffer in an irradiating environment [305]. A suspected connection between transmission electron microscopy (TEM) observations of defect free channels in irradiated material [63] and the degradation of plastic performance was formed relatively early on [73]. Studies by Farrell et.al [64] on neutron irradiated structural alloys demonstrated that there is a critical dose for which the channelling deformation mode activates, which linked the mechanical response to early TEM observations. This behaviour is interesting in austenitic stainless steel, where these alloys maintain mechanical stability at relatively high doses while experiencing a transition to channelling at a relatively low dose of ~100 mdpa. Slip
localisation increases as a function of dose, and is therefore an important consideration for future reactor designs, where lifetime doses are expected to reach in excess of 100 dpa [25]. Improving the understanding of the influence of micromechanics on mechanical properties will improve tailoring of materials and refine selection for in service components.

Proton irradiation has been widely used to emulate in service neutron irradiation damage, with the advantage of reduced irradiation times, low sample activation and significantly less financial expense [5]. The method provides a high degree of control on experimental parameters allowing for fundamental studies into individual effects. However, a pelletron operated at 2-3 MeV (typical energy level before activation becomes an issue) results in proton penetration in the order of a few tens of microns. This complicates studies probing the mechanical properties and requires the application of surface sensitive techniques.

Advances in the field of High Resolution Digital Image Correlation (HRDIC) have enabled full field surface displacement mapping at nanoscale resolution [69,70,192–195,241,306,307]. Fine speckle patterns (<100 nm) are used in conjunction with electron microscopy to achieve a high enough resolution that individual slip bands can be analysed. This methodology not only facilitates the resolution of features obscured in standard imaging [187] but gives detailed information for each of the in-plane strain components [192]. Previous studies have applied HRDIC to irradiated stainless steels by precipitation of gold nano particles (~ 45 nm) from a supersaturated solution [69,70]. Typically, patterns applied using this method are low density [70], though, this has been improved in subsequent studies [307]. The spatial resolution of HRDIC maps depend not only on feature size but mean spacing, where an optimal spacing is roughly equal to the feature diameter [192]. These studies, on irradiated stainless steel, have been exclusively applied to the investigation of slip transfer due to its relevance to irradiation assisted stress corrosion cracking [69,70,306,307]. An alternate method of pattern application involves vapour-assisted remodelling of a sputtered film. Remodelled patterns are consistently dense with minimal particle diameter of 20-30 nm [195] providing exceptionally high spatial resolution for strain mapping. When combined with the use of automated imaging software it is possible to investigate large areas, i.e. hundreds of grains, and therefore map areas that are representative of the overall material response [192–195]. Hence, developments in statistical interpretation of high resolution strain maps provides a method of quantifying strain heterogeneity over multiple grains [193,241].

This study aims to utilise vapour assisted remodelling of gold nano-particles in order to apply HRDIC to mapping localised strain in proton irradiated austenitic stainless steel. Quantification of strain localisation using this technique will help improve understanding of deformation mechanisms and the effect an irradiating environment has on them.
Experimental Methods

Material and Specimens:

The material used in this study was 316L austenitic stainless steel, supplied by Rolls-Royce plc., that had been forged into a 50 mm thick plate, solution annealed and quenched. The forging comprises predominantly austenite phase (~1% ferrite phase) without any noticeable crystallographic texture (maximum intensity of 1.5x random). Tensile-test and characterisation specimens were Electric Discharge Machined (EDM) from the forging to produce specimens with their loading direction parallel to the forging direction. The dog-bone shaped tensile specimens were 50 mm long and 1 mm thick with gauge dimensions of 27 mm x 2 mm x 1 mm. In addition, coupon specimens (27 x 3 x 1 mm³) were prepared for characterisation. For both types of samples the recast layer from EDM was removed by mechanical grinding. Surfaces were further ground to #2500 grit paper, followed by diamond polishing and further hand polishing on an OPS cloth with colloidal silica.

Proton Irradiation

The specimen set-up for the proton irradiation experiment is shown in Figure 1a. The ‘jigsaw’ arrangement was chosen instead of machining samples post irradiation to avoid damaging the irradiated surface during the EDM process. As good temperature control during irradiation requires the application of a liquid eutectic tin-indium alloy between the backside of the samples and the cooling block, small inserts were fitted between each of the tensile specimens to provide a continuous seal. All irradiation experiments were carried out on the DAFNE 5MV Tandem Pelletron at The University of Manchester’s Dalton Cumbria Facility [221,290]. A summary of the proton irradiation conditions is given in Table 1. The beam was rastered over a 3 x 25 mm² rectangular area illustrated in Figure 1a. A 40% over-scan onto the aperture veins eliminated beam tails, providing hard edges to the irradiated area. Specimens were irradiated with 3MeV protons at a flux of 1.55x10¹⁴ cm²s⁻¹ to a fluence of approximately 5.75x10¹⁷ cm⁻². Stopping range calculation was performed using the ‘quick Kinchin–Pease calculation’ [219] in SRIM [291] (Figure 1b). The predicted stopping peak was calculated to be at 36µm and the nominal damage was selected at 22 µm, corresponding to 60% the depth of the peak damage. It was calculated to be 100 mdpa using the calculation outlined in section 6 of [221]. The irradiation temperature was monitored by a pyrometer, after calibration of the sample surface emissivity prior to irradiation. This was achieved by heating up to the target temperature and then monitoring using thermocouples spot-welded to the matchstick samples. The mean temperature throughout the experiment was recorded as 348 ± 15 °C. Following irradiation, specimens were lightly polished with diluted colloidal silica in order to remove any surface implantation.
Table 1: Irradiation conditions

<table>
<thead>
<tr>
<th>Energy</th>
<th>Flux</th>
<th>Nominal Dose Rate</th>
<th>Fluence</th>
<th>Nominal Dose</th>
<th>Temp</th>
</tr>
</thead>
<tbody>
<tr>
<td>3MeV</td>
<td>$1.55 \times 10^{14}$ cm$^{-2}$s$^{-1}$</td>
<td>$2.7 \times 10^{-3}$ mdpa s$^{-1}$</td>
<td>$5.75 \times 10^{18}$ cm$^{-2}$</td>
<td>100 mdpa</td>
<td>$348 \pm 15^\circ$C</td>
</tr>
</tbody>
</table>

Gold Remodelling

To track the local deformation, a gold speckle pattern was applied to the surface using the vapour assisted remodelling technique originally developed by Luo et. al [243] and further developed for the purpose of HRDIC by Gioacchino and Fonseca [192]. In this work, a thin gold film was applied to the sample surface using an Edwards S150B sputter coater, sputtering for 3 minutes at a deposition rate of 5-8 nm min$^{-1}$ [193]. Prior studies [192–194] utilising water vapour as a solvent to promote remodelling of the gold coating by Ostwald ripening requires relatively high temperatures (250-300 °C). Recent work by Orozco-Caballero et. al [195] utilises a closed system of styrene vapour and argon in order to avoid sample surface oxidation. However, it also provides the significant advantage in terms of irradiation studies, in that it allows remodelling at a lower temperature at the expense of time. The specimens were remodelled for a period of 168 hours at 120 °C, a schematic of the experimental setup can be found in section 2.1 of [195]. Although no TEM analysis was performed to observe the evolution of defect structure at 120 °C, work in Zr alloys suggests that temperatures below 200 °C show minimal defect density variation [308]. In the absence of TEM analysis, the net effect of possible annealing was measured using Vickers micro-indentation testing with a Struers Durascan automated indenter. Indentations were made for a period of 10 seconds with 0.005 kg. Irradiation hardening was measured at 20 ΔHv (Figure 1c) prior to and 17 ΔHv following remodelling. Although, there may have been some unobserved effect on defect structure, the resultant effect on mechanical properties can be considered negligible; the hardness drop is well within the standard error of 8 Hv.

High Resolution Digital Image Correlation (HRDIC) and orientation mapping

Micrographs were acquired using an FEI Magellan FEG-SEM (Field Emission Gun – Scanning Electron Microscope) using an insertable Circular Backscatter detector (CBS) in order to provide a good compositional contrast for gold markers. A 5 kV, 0.8 nA beam was used with a working distance of 4.6 mm to maximise spatial resolution and resolve the fine surface nano-particles. Each image was acquired at a horizontal field width of 19 µm. To cover a large area, the FEI MapsTM automated mapping software was utilised. A 15 x 15 map was
taken with a 40% overlap resulting in a 178 µm horizontal field width for the full montage. Each frame was taken at 2048 x 1768 pixels\(^2\), with a 5 second pause punctuating each image following stage movement to allow stabilisation. An interpolated focus function was employed to limit defocussing of the outer extremities of the map; the position of each map is indicated by arrows on the indentation profiling in Figure 1c.

Tensile deformation was performed using a Kammrath-Weiss 5 kN tension-compression microtester at room temperature and at a displacement rate of 5 µm s\(^{-1}\). The loading phase was essentially a quasistatic ex-situ test with the specimen removed from the apparatus for SEM mapping at each load increment. A total of 4 strain increments were measured for both the non-irradiated and irradiated regions. The average in-plane \(\gamma_{\text{max}}\) strain is indicated on the flow curve (Figure 1d) for each region and shows a lagging disparity in the average strain calculated in the irradiated maps. This can be attributed to the increased yield point due to irradiation hardening. Following mechanical testing the gold pattern was removed by polishing with colloidal silica for orientation mapping of the specimen.

Orientation mapping was performed in a CamScan FEG-SEM equipped with an Oxford Instruments Nordlys Nano EBSD detector and with diffraction patterns indexed using Aztec HKL. All maps were taken at 20kV. Texture was measured on a matchstick specimen over a 2 x 2 mm\(^2\) area with a step size of 1.5 µm, and the pole figures are displayed in the appendix. The regions analysed by HRDIC were mapped by EBSD for orientation imaging at a step size of 0.4 µm. The data were analysed using HKL Channel 5. Indexing rates were very high for both conditions with only 0.4% and 0.5% non-indexed solutions for the non-irradiated and irradiated areas, respectively.

Displacement calculations were performed using DaVis 8.1, acquired maps were stitched and cross correlated to the corresponding regional un-deformed maps. Vectors were calculated in multiple passes by Fourier transform for decreasing interrogation window sizes. Single passes were performed at incrementally reducing interrogation window sizes starting at 1000 x 1000 pixels\(^2\) and reducing down to 5 passes at the final interrogation window size of 8 x 8 pixels\(^2\). No overlap between each window was employed to avoid propagation of errors generated by noise; giving a final spatial resolution for each map of 74 x 74 nm\(^2\).

**Results**

*Speckle Pattern Morphology*

The remodelled speckle pattern morphology for the non-irradiated and irradiated region is displayed in Figure 2. The micrographs reveal a tri-modal pattern structure, with the largest of the features being coarse, non-spherical, unfaceted particles surrounded by a region clearly
depleted of gold. Tendrils can be observed forming connections with smaller particles in the midst of consumption that has been interrupted by halting the remodelling process. The next largest structures appear to be better defined, being roughly spherical with fewer interconnections with the surrounding particles. Small, well defined and interconnected particles make up the remainder, which is the majority of the surface. There is a clear variation in mean diameter between non-irradiated (Figure 2a) and irradiated (Figure 2b) regions; 14 nm and 11 nm respectively. In the irradiated region, the pattern is better defined, with larger depleted regions surrounding large particles. This variation can be attributed to the different polishing rate of the irradiation hardened region with previous studies having highlighted the impact of surface finish on final pattern morphology [192,193]. Due to the slightly different pattern morphology a noise analysis was carried out using the same sub window size to ensure the results yielded similar results. Strain was calculated by correlating the overlapping sections of images forming the mosaic. This was repeated 5 times for different regions and averaged for both irradiated and non-irradiated regions. Noise was calculated as $3.9 \times 10^{-3} \pm 2.5 \times 10^{-3}$% in the non-irradiated and $5.6 \times 10^{-3} \pm 4.6 \times 10^{-3}$% in the irradiated regions, and is therefore considered comparable.

**Strain Mapping & Microstructure**

The full field displacement data is differentiated to enable the maximum shear strain component ($\gamma_{\text{max}}$) to be calculated using Equation 1. The strain maps in this work are displayed as maximum shear strain, as this takes into account all of the in-plane components [194]. Due to the max shear calculation consisting of only in-plane components, the max shear ($\gamma_{\text{max}}$) is considered to be an effective shear ($\gamma_{\text{eff}}^{(\text{max})}$) [27,194,195]:

$$\gamma_{\text{eff}}^{(\text{max})} = \sqrt{\left(\frac{\partial u_1}{\partial x_1} + \frac{\partial u_2}{\partial x_2}\right)^2 + \left(\frac{\partial u_1}{\partial x_2} + \frac{\partial u_1}{\partial x_2}\right)^2} = \sqrt{\left(\frac{\epsilon_{xx} - \epsilon_{yy}}{2}\right)^2 + \left(\gamma_{xy}\right)^2}$$

Equation 1

where $\frac{\partial u_1}{\partial x_1}$, $\frac{\partial u_2}{\partial x_2}$ and $\frac{\partial u_1}{\partial x_2} + \frac{\partial u_1}{\partial x_2}$ differentiate to $\epsilon_{xx}$, $\epsilon_{yy}$ and $\gamma_{xy}$, respectively.

Figure 3a and Figure 4a show $\gamma_{\text{max}}$ strain maps of non-irradiated and irradiated regions at the most directly comparable strain increments, i.e. an averaged full-field $\gamma_{\text{max}}$ of 2.4% (S2 in Figure 1d) and 2.5% (S3 in Figure 1d), respectively. The development in strain maps taken at each hold point for both regions is displayed in the Appendix. The corresponding orientation map for the non-irradiated region and irradiated region are displayed in Figure 3b and
Figure 4b in the IPF-X colour scheme, with the X-plane normal running parallel to the loading direction. While the global texture in the material is weak, locally, slight variations of easy to activate slip due to variations in Schmid or Taylor factor might exist. Indeed, in the present case the irradiated region showed on average slightly higher standard deviation in Schmid factors for \{111\}(110) type slip (0.46±0.04) than the non-irradiated region (0.46±0.03).

The strain map of the non-irradiated region, Figure 3a, displays clear strain heterogeneity through a combination of planar, diffuse and wavy slip; with a variety of clearly discernible ‘hot spots’. There are a small number of coarse slip bands with a background of lesser intensity, diffuse and multi directional slip within most grains. In addition, there are apparent strain hot-spots that correlate with the convergence of high intensity slip bands, the intersection of an annealing twin boundary and grain boundary triple point (Figure 3b). A region of low intensity, densely packed slip can be observed in the upper left quadrant. It contains no discernible planar slip bands, yet there is clearly a dominating slip direction with undulations tracing in unison with neighbouring bands. Large plumes of strain are observed projecting into neighbouring grains from coarse strain bands arrested at grain boundaries. Some regions in the upper right quadrant are devoid of any strain accumulation, it appears that the surrounding grains deform as normal and the central grain remains strain free. However, processed displacement maps in terms of rotation, displayed for reference in the appendix, reveals slip bands not visible in the γ\text{max} maps. Small slip bands can be observed around the boundary of this low strain grain, with the majority of deformation being rigid body clockwise rotation.

In the map of the irradiated region (Figure 4a), there is an absence of the deformation mode heterogeneity that is present in the shear strain maps for the non-irradiated condition in that deformation is limited to highly planar slip. Planar shear bands characteristically display high shear strains and are widely spaced with a lesser density of ‘background’ slip systems occurring in fewer directions. In addition to limited slip directions, there are also far fewer diffuse slip events recorded in the irradiated region. The upper right quadrant expresses slip changing direction, rather than the undulating deflections observed in the non-irradiated region, with a ‘saw-toothed’ configuration. In the local vicinity, the orientation map clearly exhibits an annealing twin of a similar configuration, containing a serrated boundary with the parent grain (Figure 4b). It clearly generates a complex loading state on the parent grain influencing local slip events. Arrested slip bands appear to have a diminished plastic effect on neighbouring grains, with scarcer hot-spots and plume-like phenomena. It should be noted that there are two areas in the irradiated region that show a high level of noise, which is not related to the deformation behaviour and have been excluded from the data analysis.
Both maps of non-irradiated and irradiated regions show slip readily transmitting through annealing twins in the cases where shear bands impinge the twin boundary at a high angle of attack. Similar strain patterns around annealing twins have been observed in a $\gamma''$ strengthened Ni-based superalloy [309] (fine $\gamma''$ also enhances slip localisation). In cases where a twin bisects a parent grain, slip is deflected to a common orientation within the twin before continuing its original path upon exiting. Twins at the edge of a grain show a similar behaviour, yet upon exiting, transmitted slip is deflected to a dissimilar orientation within the neighbouring (non-parent) grain, in one case it can be seen in excess of 120°. While the high angle slip deflection is observed less in the irradiated specimen, this could be a result of the limited sampling area of the strain maps rather than an effect of irradiation damage.

**Strain ‘lag’**

Unlike metals/alloys with a BCC and HCP crystal structure that experience prompt necking at yield within the dose range of this study, this does not occur for 316L where immediate plastic instability is observed at a dose approaching 300 times larger than in the present work [59,74,214]. Since the strain-hardening exponent remains positive, it is possible to use the difference between average strain for non-irradiated and irradiated regions ($\gamma_{\text{max}}$ strain-lag) to extrapolate a flow curve for the proton irradiated region. The idea was initially proposed by Ohr [60], who noted for neutron irradiated ferritic steel that stress strain curves could be superimposed on a damage free stress-strain curve by shifting it along the strain axis. By fitting the standard power function to account for the strain hardening contribution to yield stress increase, it was concluded that a value of equivalent pre-strain raised proportionally with irradiation dose. This was expanded in a more recent study to a multitude of materials, including austenitic stainless steels, experiencing irradiation hardening at a wide range of doses [59,74]. Beyond doses where instantaneous plastic instability occurs at yield, a curve for non-irradiated material cannot be superimposed. Hence, it is impossible to apply this formulation beyond the critical dose at which the yield point is shifted above the ultimate tensile strength of the non-irradiated material. The red plot in Figure 5a illustrates the blue plot for the non-irradiated transposed along the strain axis by the average plastic strain lag, measured using HRDIC for the first displacement increment. Accuracy of the transposed curve was validated using the method for calculating yield shift by indentation testing proposed by Busby et.al [84], using the correlation:

$$\Delta \sigma_y = 3.06 \Delta H_V$$

Equation 2
where, $\Delta \sigma_y$ is the calculated yield shift; $\Delta H_V$ is the measured increase in Vickers hardness due to irradiation damage and 3.06 is the correlation function for austenitic steel.

The calculated yield shift via hardness correlation (52 MPa) is in the same order as that calculated using transposition of non-irradiated flow curve assuming radiation-strain equivalence (~60 MPa). Since the yield shift is comparable, it can be assumed that the calculated value of strain hardening exponent using the transposed curve is of similar order. The strain hardening exponent for non-irradiated and transposed (pseudo-irradiated) material is measured as 0.28 and 0.23 respectively.

**Frequency plots**

The high spatial resolution of HRDIC not only allows for a statistical determination of slip mode type, but also an analysis of the relative intensities between and within sample regions. Therefore, frequency distributions of maximum shear strain (Figure 6) provides a quantitative method of comparing the strain heterogeneity between the non-irradiated and irradiated region. The maximum shear strain has been normalised against the average strain ($\gamma_{\text{max}}$) in the loading direction for each strain increment. This enables all strain steps to be compared and to minimise the impact of the non-irradiated and irradiated region being deformed to slightly different strains at each increment. The values of normalised shear strain were binned in 0.5 intervals beginning at 0.25. Frequency distributions have been plotted on a log-log scale to highlight the differences in strain localisation between the two regions. The frequency distributions corresponding to the non-irradiated regions are displayed in Figure 6a. At 1% applied strain, a deflection is evident in the range of ~8-15% maximum shear strain. This deflection is suppressed in subsequent applied strains. Frequency plots of the irradiated region comprise of a distribution which are for the most part linear although a change in gradient can be observed at 0.7% applied strain. As for the non-irradiated regions, the plots become more continuous for the proceeding steps (Figure 6b). Lunt.et.al [193] proposed a system of indexing to quantify the degree of heterogeneity within a specific range on the log-log frequency plots. It is based on the principal that a lower gradient relates to increased slip planarity, due to being weighted towards higher strains. The plots are displayed in Figure 6c as a function of average $\gamma_{\text{max}}$ strain in the loading direction. There is a clear variation between gradients at the initial stages of the test which moderates as a function of applied strain towards a convergence point at ~2.5% average strain.

**Full Field FFT**

Fast Fourier transforms (FFT) were applied to the strain maps and polar transforms were obtained from the FFTs, Figure 7a-d. All transforms were performed using image-j [244]. The
FFT for the strain map of the non-irradiated region comprises of fine intense lines and a diffuse background. The high intensity lines represent the contributions from the slip planarity. It can be noted that the majority of the lines are close to a 45/135° angle in accordance with maximum shear stresses. The diffuse background conveniently represents diffuse slip, where the transform derives little periodicity due to the slip bands being near or below the resolution limit of HRDIC. Conversely, the FFT of the irradiated sample shows a greater frequency of high intensity bands with very little diffuse background. As for the non-irradiated sample, the majority of the lines are close to a 45/135° angle. Some “packets” of high intensity appear somewhat broader towards the centre but at the radial extremities they can be seen to comprise of multiple fine lines. A lower intensity background is evidence of the suppression of cross slip with the majority of strain in the irradiated region being most likely confined to dislocation channels. Profiling the polar transforms of the FFT were performed in order to quantify intensity variation around the radius (Figure 7). These profiles are displayed as 180 degrees of the transform, due to the rotational symmetry around the x-plane, Figure 7e. The plots were integrated in the region illustrated in Figure 7b and Figure 7d to improve separation of the individual lines (compared to more central positions) together with good signal to noise ratio. Intensity was normalised against the summed intensity of each transform to allow direct comparison of peak minimum and maximum, with background characterised using High Score Plus and peak shape using Fityk. As pointed out earlier, the highest peak intensities are around 45° and 135° but with slight variations between the two patterns due to slight differences in local crystallographic orientations. In general, the profile recorded on the irradiated sample display far more high intensity peaks than the profile for the non-irradiated sample. The plot for the irradiated region contains a large number of overlapping intense peaks. While the non-irradiated region displays clear planar slip, the background, particularly around 45° and 135°, is higher due to contributions by diffuse slip. Development of FFTs at successive strain maps are displayed in Figure 8, all radial profiles of FFTs show only peak intensity grows with increasing applied strain without the occurrence of new peaks.

**Slip Band Spacing**

Multiple strain profiles from individual grains were investigated in the maps recorded for the two sample conditions with all profiles running normal to the dominant, planar slip traces; Figure 9a-d are representative examples of what was observed in most cases. Measured profiles were smoothed due to the relative size of the subset to profile length and plotted for each strain increment. Locations of profiling in non-irradiated and irradiated regions are displayed in Figure 10a&b, with FWHM plotted as a function of average $\gamma_{\text{max}}$ strain in Figure 10c. Peak centres were located by the local maxima, with peaks defined using a minimum prominence of 10-15. FWHM of peaks in all profiles were measured around the peak centres,
rather than FWHM of a gaussian fit which may account for some of the scatter that is present. Profiles of the non-irradiated region comprise of blunt peaks, which tend to broaden as the test progresses. In contrast, peaks from the irradiated region were better defined, increasing in magnitude with increasing applied load. They also displayed very little in the way of “new” distinct peaks forming. In both cases, profiling of slip bands shows mean spacing trending towards the positive, which is due to the gradual coalescence of peaks as some slip bands mature and composite peak centres begin to shift. Spatial resolution in all DIC is ultimately dictated by the size and density of the pattern and despite interpolation of grayscale enabling sub-pixel resolution [186], some diffuse slip bands are inevitably below the spatial resolution limit for this pattern. However, multiple slip bands in close proximity will cause peak broadening in a similar manner to the effect of defect density on X-ray diffraction peaks [310]. Therefore, a peak broadening measurement is better suited at this resolution to record the reduction in slip band spacing and are displayed as a function of applied strain in Figure 10c. The broadening increases at a rate of 14.3±2.0 in the non-irradiated profiles with an R2 of 0.96, whereas for the irradiated the broadening rate is 5.8±2.6 with an R2 of 0.7, with an irradiated to non-irradiated ratio of 0.41.

Discussion

Comparison of representations of slip localisation

The various analysis techniques applied to the strain maps of non-irradiated and irradiated regions quantify the observations made on the raw maps. A typical example of progression is illustrated in Figure 11 for grains in the non-irradiated and irradiated regions with a Schmid factor in both cases of ~0.43 for \{111\}(1\overline{1}0) type slip. The progression shows planar slip in both cases, with the non-irradiated region developing additional fine slip traces with increasing applied strain whereas the irradiated region progresses with increasing intensity of slightly more coarsely spaced slip bands, with near zero strain between each slip band. In the current work, frequency distribution, FFT analysis and slip band profiling has been attempted to provide a quantitative description of these differences in slip patterns.

Indexing heterogeneity using the distribution plots allows for analysis of the full field of the strain maps and shows promise in the early stages of the tensile test. However, as mentioned earlier, the convergence shown in Figure 6c would indicate that both regions eventually comprise of a similar level of strain heterogeneity. While it is possible that due to the relatively low dose in the irradiated region, and its proximity to the critical dose for dislocation channelling, a reversion to non-irradiated deformation mode is observed, in accordance to observations by Okada et.al in low dose Ni & Au [58] and also by Lee et.al in austenitic
stainless steel [311,312], this behaviour was not measured by the other techniques and also does not agree with Figure 10.

At the most directly comparable level of applied strain (2.5%), the FFTs and the strain profiling are complementary. The FFTs have the advantage of taking the full field into account, since intensity contributions are based on periodic repetition, so they are able to highlight the distribution of slip directions in the entire strain map. Profiles of the FFTs show a distribution of diffuse and planar slip in the non-irradiated region, evident as a slightly lower intensity background (2.5x10^{-3}) with broader peaks (an average HWHM of 2.0°±1.0°). In contrast, the irradiated region is made up of sharper peaks (1.6°±0.9°) and displays less background (2.4x10^{-3}) due to contributions weighted towards planar slip. This is a good representation of differences in development which can be observed in Figure 8. The weakness of this approach is that the FFT only selects repeating structures and is a convolution of the entire map. While it is possible to extract specific segments of the FFT and relate it to the map, it is based on periodic repeats, which makes it difficult to relate FFT features to individual features in the strain map. Figure 8 displays an intensity change as the test progresses. It would indicate that all planar slip systems at the highest strain were formed at the onset of plasticity [313]. However, this does not exclude the possibility that the regions between planar slip bands are not activated at the onset of plasticity and new co-planar slip forms through a process of refinement between existing slip bands [314]. Both contributions would be measured as a change in intensity as the test progresses, so would be difficult to confirm with this approach.

It must be stated, the profiling of FFTs at some angles display a decrease in intensity as a function of applied strain, although it does seem more evident in the non-irradiated specimen. The origin of this behaviour is not understood.

Direct measurements of slip band spacing by strain profiling might be the most straightforward way to analyse the strain maps to identify differences in strain localisation. However, it is vulnerable to biasing due to the manual placement of profiles and does not take advantage of all the data available through the strain map. Therefore, the strain profiling provides data from specific locations rather than a statistical analysis. In that, peaks from the irradiated specimen are sharper with a lesser background than that of the non-irradiated region, which is indicative of the suppression of diffuse slip and dislocation channelling. This correlates well with the results of the FFT analysis, which also shows promotion of planar slip in the irradiated region. The FFT provides insight into the overall average response and mitigates the possible biasing of profiling, it is complemented by the results of site specific nature of profiling, which allows direct measurement of slip characteristics.
Effect of irradiation on strain localisation for different applied strain levels

Non-irradiated stainless steel is known to deform in a mixed mode with dominance of planar slip, due to the relatively low stacking fault energy (SFE) suppressing cross slip [315,316] and promoting slip planarity [317]. However, the SFE is not low enough to completely eliminate wavy diffuse slip bands (mode heterogeneity) [318]. Above a critical irradiation dose (Dc), diffuse slip is suppressed with dislocation channelling dominating, taking the form of single-mode highly-planar slip [59]. In the present case, the strain maps provide evidence that 100 mdpa has been sufficient to suppress diffuse slip in 316L. Planar slip, in the absence of diffuse slip, is indicative of defect clearing during yielding, providing an easy path for subsequently mobile dislocations [32,62]. Work carried out by Jiao & Was (2010) demonstrated that the only defect that correlates to this manner of localised deformation in irradiated austenitic steel is dislocation loops [319]. This implies that the increased slip planarity in the irradiated sample at the onset of plasticity is due to the presence of irradiation-induced loops. It has been proposed that the defect clearing within dislocation channels drops the hardening capacity within them to near zero, which contributes to the macroscopic drop in strain hardening behaviour [61]. Strain hardening contributes to flow stress as the sum of the strain hardening contribution and the initial yield stress. Historically, the strain hardening contribution has been described in terms of an increase in dislocation density. Recent work carried out by Welsch et.al in high Mn steel verified that the stress contribution due to strain hardening is inversely proportional to mean slip band spacing [314]. In the present work, measurements of average FWHM of slip bands increase at a higher rate in the non-irradiated than the irradiated. The implication is that mean spacing is decreasing at a higher rate in the non-irradiated sample set, due to overlapping contributions generated at a higher rate in the non-irradiated leading to the broadening of the peaks. Therefore, the non-irradiated region has a higher strain hardening rate than irradiated region. This is consistent with observations on the effect of irradiation damage on the strain hardening capacity of materials where irradiation damage is known to impede strain hardening as a function of dose ultimately limiting overall ductility [73]. The measured ratio of FWHM broadening rate was 0.4 of irradiated to non-irradiated condition. Measurement of the strain hardening rate in ref. [61] provides approximate strain hardening exponents of 0.4 in non-irradiated 316LN and 0.25 for the same alloy at 500mdpa, this giving a ratio of 0.62. Although the FWHM implies a difference in strain hardening and is trending in the correct direction, the broadening is clearly not directly comparable.

Conclusions

This study utilised a combination of high spatial resolution of a vapour remodelled gold pattern and an automated mapping technique to obtain high resolution strain data over large
regions of 316L austenitic stainless steel before and after irradiation during tensile loading. The strain maps have been analysed applying a range of methodologies.

- While the non-irradiated region showed some degree of diffuse slip amongst planar slip after plastic deformation, the irradiated region only displayed highly planar slip. This is consistent with literature stated behaviour and is indicative of slip channelling behaviour that clears out irradiation induced dislocation loops for the irradiated condition.

- Simple frequency plots of the maximum shear strain distribution did provide some quantitative analysis of strain localisation but lacked sensitivity at higher applied strains. In contrast FFT analysis and more manual slip band profiling of the strain maps were better suited to identify subtle differences in slip planarity/strain localisation.

- The reduction in strain hardening due to irradiation damage has been recorded and an attempt made to quantify in terms of slip band profile width. Measurement of slip band width describes a difference in strain hardening behaviour consistent with the trends of literature reported behaviour. While an absolute value of strain hardening was not calculated, the technique shows promise in this regard.

- Recording irradiated and non-irradiated behaviour on a single specimen provided the opportunity to generate flow curve for the irradiated region. Under the assumptions of Ohr [60], the variation in average strain between non-irradiated and irradiated regions provides a value of equivalent pre-strain. This allowed a flow curve to be generated by transposition of the non-irradiated flow curve along the strain axis.

Where prior studies have used HRDIC in irradiated materials to observe individual events [69,70], we have employed prominent analysis techniques to quantify slip characteristics in non-irradiated and irradiated 316L. By confirming the established understanding of deformation behaviour in irradiated material, the technique has been validated as an effective tool in this field. Furthermore, by investigating a low dose at the threshold for dislocation channelling, the high sensitivity of the technique has been demonstrated by observing properties that previously required TEM analysis. In contrast to more established microscopy techniques, large scale mapping allows larger areas to be subject to detailed analysis.
Figures:

Figure 1: (a) Specimen setup and geometry for irradiation experiment, red area denotes beam raster; (b) SRIM calculation of damage as a function of penetration depth. Nominal damage of 100 mdpa corresponds to 60% the depth of Bragg peak maxima; (c) Indentation profiling of specimen through 7mm wide irradiated region, red and blue arrow denote position of strain maps for irradiated and non-irradiated respectively; (d) True flow curve of non-irradiated specimen with average max shear for each strain increment for both non-irradiated and irradiated maps.
Figure 2: (a&b) Vapour remodelled gold particles in each region of the sample, particle diameter in non-irradiated and irradiated regions were 14nm and 11nm respectively.
Figure 3: (a) Strain map of 0 mdpa region at global max shear strain of 2.39%; (b) orientation map of corresponding region displayed in IPF X.
Figure 4: (a) Strain map of 100 mpda region at global max shear of 2.45%; (b) orientation map of corresponding region displayed in IPF X.
Figure 5: (a) Flow curve for non-irradiated 316L and extrapolated flow curve using the lag between the first displacement increment assuming radiation-strain equivalence, equivalent plastic strain and correlated hardness yield shift are indicated on the plot.

Figure 6: Frequency plots of full field max shear strain for each average $\gamma_{\text{max}}$ strain (a) non-irradiated and (b) irradiated regions; (c) gradients of each plot in a&b plotted in terms of average $\gamma_{\text{max}}$. 
Figure 7: (a & b) FFT and polar transform of non-irradiated full field maps at 2.5%; (c&d) FFT and polar transform of irradiated full field maps at 2.4%; (e) Normalised profiling of the region marked in red of polar transformed FFT, the width of the profile is in order to reduce noise.

Figure 8: Radial profiling of FFTs for each strain increment for both regions.
Figure 9: (a&b) Plot position for typical example of slip in both non-irradiated and irradiated maps; (c&d) Corresponding intensity plots for marked profiles in non-irradiated and irradiated maps at all strain increments.
Figure 10: (a&b) Profiling locations on maximum shear strain map at the two most similar global $\gamma_{\text{max}}$ strains; (c) FWHM of all profiles for each strain increment.
Figure 11: Progression of strain in non-irradiated and irradiated regions with comparable Schmid factors (~0.43).
Appendix:

Appendix Figure 1: (a) Dose rate frequency, with an average current of 6.10 nA; (b) Temperature frequency, with an average temperature of 348 ± 15°C

Appendix Figure 2: Average Vickers hardness of 316L specimen in undamaged region, irradiated to 100mdpa before and after gold remodelling
Appendix Figure 3: Pole figures collected by EBSD for (a) 2x2 mm of substrate; (b) NI region; (c) Irradiated region
Appendix Figure 4: Strain progression for both regions throughout the entire test.
Appendix Figure 5: Rotation map, displayed in radians, highlights low intensity slip bands that are not visible when displayed in $\gamma_{\text{max}}$. 
5 Conclusions

In the present work, a range of techniques were applied to non-irradiated and irradiated material to record or derive flow curves. Manuscripts 1-3 were direct measurements, Manuscript 4 gave insight into flow behaviour without providing a flow curve other than the derived strain-lag pseudo-flow-curve. While all techniques demonstrate capability to produce flow curves, the combination of XRD and DIC is clearly the most favourable in terms of logistics for implementation in future studies. The technique requires the least investment in terms of capital costs and relies on technology that is commonplace in laboratories, therefore also requires little in the way of specialised training. Sin²Ψ stress measurement can be performed using most commercially available diffractometers, hence would only require the procurement of a microtester and camera to utilise this technique. Furthermore, digital image correlation software can be obtained commercially, scripted in MatLab and Python or obtained for free as pre-programmed plugins. Surface flow curves provided bulk representative data during elastic and plastic deformation, however, the relationship broke down during the elasto-plastic transition at yield. This is attributed to favourably orientated grains deforming plastically while unfavourably orientated grains deform elastically [177]. Tests performed on irradiated samples exhibited the same blunted yielding during the transition to plastic deformation, but the measured yield shift was comparable to that estimated using indentation testing. To summarise, the combination of XRD and DIC has provided flow curves in proton irradiated material that are consistent with literature reported behaviour in irradiated metals. This technique is intrinsically linked to the requirements for diffraction stress measurement, as such is currently limited to texture free, sufficiently fine-grained material and those with a diffracting plane exhibiting a linear response to applied stress.

In contrast to the XRD/DIC technique, preparation of specimens using Xe⁺ plasma FIBs requires specialised equipment and the associated training to complement it. Due to the high operating currents, the PFIB suffers from an exaggerated form of the inherent characteristics of Ga⁺ FIB high current milling, specifically: curtaining and taper. While automated cross-polishing eliminates the majority of curtaining, the tapering is more of an issue in the absence of double tilt microscope stage. The use of a pre-tilted specimen mount mitigated the tapering to some extent, however, the lack of fine control restricted its effectiveness at completely eliminating the taper. Using finite element analysis, it was possible to attribute the reduction in UTS and the dampened yielding to the specimen taper. By elimination, the reduction in strain hardening was shown to be dominated by a non-geometric effect and was understood to be due to scale; the proof stress was demonstrated to be bulk representative. The effect of specimen tapering on mechanical response could be reduced by preparing specimens with a decreased length. Specimens were prepared from proton irradiated material and exhibited a
slightly larger yield shift to that measured using indentation testing and XRD and DIC. The increased hardening was attributed to the relative sampling volume using this technique, where the 30 μm thick specimens comprise of region of the higher damage in the dose profile. Tests on the irradiated material also exhibited a response that is consistent with the reported behaviour: positive yield shift, reduction in strain hardening and a reduced strain to failure. The irradiation hardening raised the tensile strength relative to the non-irradiated specimens prepared by PFIB. However, it did not exceed the tensile strength recorded in bulk tests, which is consistent with the understood response in irradiated materials. Although Xe⁺ PFIBs are currently unconventional, it must be stated that this technology is being produced by an increasing number of companies, which will certainly lead to decreasing costs and increased proliferation. Broader availability will increase the viability of wider implementation as more operators are trained and understanding of the mill rates and overtilt conditions for different materials are improved.

High resolution digital image correlation was applied to non-irradiated and irradiated 316L stainless steel using styrene remodelled gold as markers. It was demonstrated that the styrene remodelling process did not significantly anneal the proton irradiation damage. The motivation for this study was to apply the relationship between strain hardening contribution to flow stress and slip band spacing to construct a flow curve [314]. Unfortunately, the spatial resolution provided by the remodelled pattern proved to be insufficient to resolve the fine slip required to perform this calculation. By using the variation of strain between the non-irradiated and irradiated regions, it was possible to obtain a value of equivalent pre-strain. This allowed a flow curve to be constructed by transposition along the strain axis using the assumption outlined by Ohr [29]. The pseudo-flow curve provided a yield stress in the order of that estimated by indentation testing. Application of a host of analysis techniques offered insight into the irradiation induced strain localisation just beyond the critical dose for dislocation channelling (100 mdpa) [64]. Of the analysis techniques applied, FFT analysis and slip band profiling were complementary, while frequency analysis appeared to lack the sensitivity at this level of damage.
6 Future Work

In addition to the broader application of the techniques to different metals and a wider range of damages, the present work has highlighted a number of potential subjects for future research. As discussed in Manuscript 1, the combination XRD and DIC has potential in the field of coatings. It is arguable that application of the technique to ceramic coatings, such as oxides or thermal barrier coats, would be less challenging than in metallic systems. The purely elastic response leading up to fracture is advantageous in that no specific plane is required for stress measurement, provided the elastic constants are known. Figure 66 is an example stress strain curve of a magnetite oxide formed during the carburisation of 316N ex-service AGR ducting material. The stress strain curve can provide an understanding of the failure in the oxide layer, which is evident in the stress relief as the test progresses.

As stated throughout this thesis, stress measurement using diffraction is sensitive to the presence of texture. This is due to the nature of the 1D detector, where diffracted spots, rather than a ring, have a limited probability of detection at all tilt angles. It is possible to mitigate the effect of texture by performing stress measurements using an area detector. By integration around the diffracted ring the contributions at each $\Psi$-tilt can be maximised. This widens the scope of the technique to a broader range of materials and conditions, which are often textured when in service.

Currently, specimen preparation using the Xe$^+$ PFIB takes 2-3 days depending on the starting thickness of the foil. The vast majority of time is devoted to thinning material, with specimen shaping taking just a few hours. As highlighted in preceding Ga$^+$ FIB work in the field of small
specimen testing, the Xe$^+$ PFIB preparation process would also benefit from pre-thinning with a more efficient technique such as using a femtosecond laser [151] or micro EDM [129]. This bulk removal step would be followed by an automated cleaning cross section to remove the damage layer, followed by specimen shaping – drastically reducing preparation time. This would also allow specimens to be manufactured with larger gauge dimensions or fabricate more specimens to improve statistics. The preparation of specimens with differing dimensions would also be beneficial. Samples were prepared during this work with the 5:1 gauge section ratio recommended in bulk tests, which may not have been suitable using this preparation route, where gauge length taper is more common. It is clear that the smallest representative volume was not fully realised, however, it is understood that this value is a function of material and microstructure. The work would benefit from a systematic study of a range of specimen dimensions in a single-phase material with an equiaxed, texture free microstructure. This study would preferably be carried out on a material that can be milled with ease, possibly copper. Furthermore, SRV may not be achievable using only a PFIB, in such a situation mechanical grinding may be required followed by the use of a femtosecond laser to roughly shape specimens, with the PFIB only used to clean the sample edges. Repeating the study with a fixed geometry at a range of grain sizes would also clarify the effect of grain diameter. This project would most likely require a considerable time and financial commitment.

Figure 67: (a) The spatial resolution of strain maps can be increased in PFIB prepared specimens by application of a Pt speckle pattern by electron beam, where the optimal diameter was found to be ~150 nm, EBSD orientation maps taken prior to pattern application allows strain localisation to be related to microstructural features. Application of Pt markers using an automated script [238] can provide markers over the entire gauge length, enabling high resolution digital image correlation (Figure 67). The improved spatial resolution of the strain maps, coupled with EBSD orientation mapping can provide
insight into deformation mechanisms throughout the test. Although the pattern does not provide the same resolution as the gold pattern, strain maps at this resolution measure grain to grain interactions at a resolution that is not possible when correlating the raw surface.

Slip band profiling using HRDIC, highlighted the difference in the rate of new slip band formation in non-irradiated and irradiated 316L. Recent work by Welsch et al [314] calculated the strain hardening contribution to flow stress using the distance between slip bands. Although HR-DIC lacked the resolution to measure the absolute distances as the test progressed, it is viable to replicate their work and apply to proton irradiated material using electron channelling contrast imaging.
References


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