Physically-based methods for improved high temperature creep performance of 9Cr steels and welds: nano-, micro- and macro-scale studies

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Physically-based methods for improved high temperature creep performance of 9Cr steels and welds: nano-, micro- and macro-scale studies


Supervisor: Prof. Padraic O’Donoghue
Co-supervisors: Prof. Sean Leen and Dr. Richard Barrett

Thesis submitted to the National University of Ireland Galway as fulfilment for the requirements for the Degree of Doctor of Philosophy

College of Engineering and Informatics, National University of Ireland Galway

September 2019
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Abstract

The reduction of emissions from fossil fuel power plants is essential to minimising the environmental impact of power generation and this can be achieved by higher temperature, with more efficient combustion of the fuel. This requires the development, testing and improved understanding of materials capable of resisting the creep deformation that occurs during long-term operation under high temperature and pressure conditions. 9Cr tempered martensitic steels have excellent creep resistant properties due in part to their hierarchical microstructure stabilised by multiple precipitate types. To obtain the maximum life from a 9Cr component, plant operators require accurate modelling and assessment methods to predict the remaining service life of a given component.

Thus, the thesis is concerned with the development of experimental small scale testing methodologies for component remnant creep life measurements and, the novel numerical modelling of microstructure evolution during high temperature creep. This numerical model utilises a physically-based continuum damage mechanics creep model, incorporating the mechanisms of (i) primary hardening, (ii) multi-precipitate type coarsening and (iii) cavitation damage. A novel multi-precipitate type term is developed, incorporating the thermal- and strain-induced coarsening behaviour of M23C6 and MX precipitates. The model is validated for current generation P91 materials at power plant conditions and accurately predicts the effect of altered composition on the creep strain behaviour. The production of a creep resistant microstructure in 9Cr components requires careful heat treatment to generate the precipitate strengthened hierarchical microstructure. As such, the effects of standard 9Cr, and elevated temperature heat treatments, on the microstructure and mechanical properties of the next-generation material MarBN are also investigated. This enables recommendations on the optimum heat treatment for MarBN components and these are also presented.

The enhanced creep strain model is implemented in a finite element creep subroutine to simulate the behaviour of welded tensile and piping components and this accurately predicts the behaviour of P91 welded tensile specimens from laboratory
to plant conditions. Literature data for precipitate and microstructural features, for the weld metal and the heat affected zones, are combined in a novel parameter identification approach to extract the necessary material terms for the model. Weld strength reduction factors are calculated, indicating that welded tensile results are conservative when compared to component level modelling.

Small scale testing of in-service component materials, sampled without the requirement to take plants offline, play an important role in estimating the remaining life of a component. A small punch creep (SPC) test is one such method and the material requirement here is very small in comparison to standard tensile testing – the specimen being 7 mm in diameter and 0.5 mm thick. It is shown here that this approach produces reliable and repeatable test data which, importantly, is in agreement with the published tensile test data. SPC tests of the un-aged and thermally aged P91 specimens are presented. The aged specimens demonstrate significantly reduced creep lives with little to no warning of failure occurring prior to disk rupture. Unaged specimens were considerably more ductile with accelerating displacement rates observed prior to failure. The multi-precipitate type creep subroutine predicts the punch minimum displacement rate trend in agreement with the experimental results.

In terms of the heat treatment of the next generation MarBN, normalisation was conducted at the (i) standard 9Cr temperature and (ii) a recommended elevated temperature for MarBN. The higher temperature normalisation is significantly different from the current standard for 9Cr materials. A softened region, observed in the sample normalised at the lower temperature, is investigated via micro-mechanical testing and electron microscopy. Lath size effects are correlated with the hardness data, indicating that decarburization potentially leads to softening after lower temperature normalisation. The higher temperature normalisation resulted in finer laths, which are indicative of a stronger material with a higher yield stress, it also prevents the formation of creep weak precipitates (BN) and promotes uniform mechanical properties. This work emphasises the requirement for elevated temperature normalisation of MarBN for component manufacturing.

For plant operators employing 9Cr precipitate strengthened steels, there now exists a multi-precipitate type based model with enhanced prediction of creep lives of welded and plain components using measured microstructural features. Coupled with the small punch creep test, the remaining life assessment of in service components can now be performed from minimal material samples.
Acknowledgements

Firstly I would like to thank my supervisors, Padraic, Sean and Richard, for their unflagging optimism, patience and guidance on all aspects of this work, you have my deepest thanks. To the IRC and the EPA for funding this project and to Stephen Scully at ESB for providing materials and advice whenever it was needed. Also many thanks to Dr. Mark Jepson of Loughborough University Dr. Scott Doak, Dr. Keith Yendall and Mr. Sam Davis of the Loughborough Materials Characterisation Center for their support during my time in Loughborough University.

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In particular I would like to thank my friends Matthew, Owen, Aidan, Pete, Agata and the rest of the NUI Galway Tae Kwon Do club for helping me vent my stress over the years and to my friends who supported me through all these years, my deepest thanks. To Coffee, may we never be parted.

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Finally, to Deborah, for the kindness, support and an endless supply of tea, I couldn’t have done this without you.

Thank You All.
List of Publications

The work presented in this thesis resulted in the following publications:


• C. ´O Murchú, S. B. Leen, R. A. Barrett, and P. E. O’Donoghue, ”A physically-based creep damage model for effects of different precipitate types,” presented at the 1st International Conference on Materials Design and Applications, Faculty of Engineering of the University of Porto, Portugal, 30th June – 1st July 2016. (Chapter 3)

• C. ´O Murchú, S. B. Leen, R. A. Barrett, and P. E. O’Donoghue, ”Effects of multiple precipitate types on high temperature creep damage evolution in welded 9Cr steels” presented at the 14th International Conference on Fracture, Rhodes, Greece, 18th – 23rd June 2017. (Chapter 4)

• C. ´O Murchú, S. B. Leen, R. A. Barrett, and P. E. O’Donoghue, ”Effects of multiple precipitate types on high temperature creep damage evolution in welded 9Cr steels” presented at IUTAM: Multi-scale Fatigue, Fracture & Damage of Materials in Harsh Environments, National University of Ireland, Galway, Ireland, August 28th – Sept 1st 2017. (Chapter 4)
• C. Ó Murchú, S. B. Leen, R. A. Barrett, and P. E. O’Donoghue, ”Small punch creep testing of power generation materials; Experimental and Numerical approaches”, presented at the BSSM 4th International Conference on Advances in Experimental Mechanics, Queens University, Belfast, UK, 10th-12th September 2019. (Chapter 5,6)
# Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>$A$</td>
<td>Norton creep material parameter</td>
</tr>
<tr>
<td>$A'$</td>
<td>Hyperbolic sine creep material parameter</td>
</tr>
<tr>
<td>$B'$</td>
<td>Material parameter</td>
</tr>
<tr>
<td>$B_C, B_M, B_L, B_Z$</td>
<td>$\text{M}_{23}\text{C}_6, \text{MX}, \text{Laves phase and Z-phase precipitate constant}$</td>
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<tr>
<td>$b$</td>
<td>Burgers vector</td>
</tr>
<tr>
<td>$b_{\text{cnt}}$</td>
<td>Micro-cantilever beam breadth</td>
</tr>
<tr>
<td>$b_o$</td>
<td>Small ring creep test ring breadth</td>
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<td>$b_1, b_2, b_3$</td>
<td>Chakrabarty load to stress conversion parameters</td>
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<td>$C_1$</td>
<td>Four precipitate state variable constant</td>
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<td>Monkman-Grant material constant</td>
</tr>
<tr>
<td>$C_{\text{MMG}}$</td>
<td>Modified Monkman-Grant material constant</td>
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<tr>
<td>$C_{\text{sp-MMG}}$</td>
<td>Small punch creep modified Monkman-Grant material constant</td>
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<td>$C_{\text{cer}}$</td>
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</tr>
<tr>
<td>$C_{\text{LM}}$</td>
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</tr>
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<td>$\text{CETOL}$</td>
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<tr>
<td>$\bar{C}$</td>
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<tr>
<td>$c_y$</td>
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<td>$D$</td>
<td>Hyperbolic cavitation damage term in three state variable model</td>
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<tr>
<td>$D_{i}$</td>
<td>Diffusion coefficient of element $i$</td>
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<td>$D_P$</td>
<td>Multi-precipitate type state variable</td>
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<td>$D_{CV}$</td>
<td>Cavitation state variable $i$</td>
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<tr>
<td>$D_{CR}$</td>
<td>Uniaxial cavitation state variable</td>
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<tr>
<td>$D_{OP}$</td>
<td>Thick walled pipe outer diameter</td>
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<tr>
<td>$d$</td>
<td>Current precipitate diameter</td>
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<tr>
<td>$d_{\text{imp}}$</td>
<td>Impression creep indenter depth</td>
</tr>
<tr>
<td>$d_g$</td>
<td>Grain size</td>
</tr>
<tr>
<td>$d_{\text{SRCT}}$</td>
<td>Small ring creep test ring thickness</td>
</tr>
</tbody>
</table>
$d_H$ Mean of indent diagonal measures
$d_0$ Initial precipitate diameter
$d_{C,0}, d_{M,0}, d_{L,0}, d_{Z,0}$ Initial $M_{23}C_6$, MX, Laves phase and Z-phase precipitate diameters
$d_k$ Precipitate diameter
$d_{nom}$ Nominal bolt diameter
$E$ Young’s modulus
$F_{\text{imp}}$ Impression creep indenter force
$F_{\text{SPCT}}$ Small punch creep indenter force
$F_{\text{SRCT}}$ Small ring creep tensile force
$F_{\mu H}$ Micro-hardness indenter load
$F_{\text{die}}$ Die clamping force
$f_p$ Precipitate volume fraction
$f_{C,0}, f_{M,0}, f_{L,0}, f_{Z,0}$ Initial $M_{23}C_6$, MX, Laves phase and Z-phase precipitate volume fractions
$f_{C,0}^{\text{max}}, f_{M,0}^{\text{max}}, f_{L,0}^{\text{max}}, f_{Z,0}^{\text{max}}$ Maximum $M_{23}C_6$, MX, Laves phase and Z-phase precipitate volume fractions
$H$ Primary hardening state variable
$H^*$ Primary hardening limit
$H_v$ Vickers hardness
$H'$ Current component hardness
$H_0$ Initial component hardness
$h$ Primary creep accumulation rate
$h_{\text{SPCT}}$ Small punch creep disk thickness at contact boundary
$h_0$ Small punch creep specimen thickness at clamp
$h_{\text{cnt}}$ Micro-cantilever beam height
$K_{\text{Ost}}$ Ostwald precipitate coarsening rate
$K_{\text{pc}}$ Single precipitate coarsening state variable rate
$K_k$ Multiple precipitate-type model coarsening rate of $k$ precipitate
$K_{\text{HP}}$ Temperature dependent Hall-Petch material constant
$K_{C}, K_M, K_L$ Thermal precipitate coarsening rates for $M_{23}C_6$, MX, Laves phase and Z-phase precipitates
$k_B$ Boltzmann constant
$k_{\text{bolt}}$ Correction factor for clamping force
$k_{\text{cnt}}$ Micro-cantilever curvature term
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<td>$k_N$</td>
<td>Creep ductility parameter</td>
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<td>$L_{HAZ}, L_{CW}$</td>
<td>Length of HAZ, cross-weld, weld and parent metal regions for strain compatibility equation</td>
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<td>$L_{WM}, L_{HAZ}$</td>
<td></td>
</tr>
<tr>
<td>$l$</td>
<td>Unit cell length</td>
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<tr>
<td>$l_{cnt}$</td>
<td>Micro-cantilever length</td>
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<tr>
<td>$M'$</td>
<td>Norton based single damage parameter model material constant</td>
</tr>
<tr>
<td>$M$</td>
<td>Taylor factor</td>
</tr>
<tr>
<td>MSR</td>
<td>Minimum creep strain rate</td>
</tr>
<tr>
<td>MDR</td>
<td>Minimum creep displacement rate</td>
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<tr>
<td>$m_{MG}$</td>
<td>Monkman-Grant material constant</td>
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<tr>
<td>$m_{MMG}$</td>
<td>Modified Monkman-Grant material constant</td>
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<tr>
<td>$\bar{m}$</td>
<td>Equivalent lath size</td>
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<tr>
<td>$n_{HP}$</td>
<td>Hall Petch material parameter</td>
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<td>$P_{imp}$</td>
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<td>Sub-grain growth material parameter</td>
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<td>$P_{LM}$</td>
<td>Larson-Miller parameter</td>
</tr>
<tr>
<td>$Q_c$</td>
<td>Creep activation energy</td>
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<tr>
<td>$r$</td>
<td>Small punch creep indenter radius</td>
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<td>$r'$</td>
<td>Precipitate radius</td>
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<td>$r_M, r_C, r_L, r_Z$</td>
<td>Rate controlling parameters for $M_{23}C_6$, MX, Laves phase and $Z$-phase volume fraction evolution</td>
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<tr>
<td>$R'$</td>
<td>Universal gas constant</td>
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<tr>
<td>$R$</td>
<td>Small punch creep distance from punch axis to clamp</td>
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<td>$R_{SRCT}$</td>
<td>Small ring creep test ring outer radius</td>
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<tr>
<td>$S_{ij}$</td>
<td>Deviatoric stress</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
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<tr>
<td>$T_W$</td>
<td>Thick wall pipe thickness</td>
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<tr>
<td>$T_{bolt}$</td>
<td>Torque on the upper die bolts</td>
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<tr>
<td>$t_f$</td>
<td>Time to failure</td>
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<tr>
<td>$t_r$</td>
<td>Rupture time</td>
</tr>
<tr>
<td>$t_{50,L}$</td>
<td>Time taken to precipitate 50% of maximum Laves phase volume fraction</td>
</tr>
<tr>
<td>$t_{50,Z}$</td>
<td>Time taken to precipitate 50% of maximum $Z$-phase volume fraction</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
</tbody>
</table>
$V_{\beta}^M$  Precipitate phase molar volume
\n\n$w$  lath width
\n\nw_{\text{imp}}  Impression creep indenter width
\n\nw_{\text{sg}}  Sub-grain growth
\n\nx_{i}^\beta  Mole fraction of element $i$ in a precipitate
\n\nx_{i}^{\alpha/\beta}  mole fraction of element $i$ at the precipitate/matrix interface
\n\na  Hyperbolic sine material constant
\n\na_1  Dislocation contribution to shear stress material parameter
\n\na_2  Low angle boundary contribution to shear stress material parameter
\n\na'  Rupture stress equation material parameter
\n\nb  Hyperbolic sine material constant
\n\nb_{\text{imp}}  Impression creep conversion parameter
\n\nb_{\text{SRCT}}  Small ring creep conversion parameter
\n\n\gamma  Inter-facial energy
\n\n\dot{\Delta}_{\text{imp}}^s  Impression creep indenter displacement rate
\n\n\dot{\Delta}_{\text{spc}}^s  Small punch creep indenter displacement rate
\n\n\Delta F  Helmholtz free energy
\n\n\delta_f  Small punch creep indenter displacement at failure
\n\n\dot{\varepsilon}_0  Temperature independent secondary creep constant
\n\n\dot{\varepsilon}_{\text{min}}  Minimum creep strain-rate
\n\n\dot{\varepsilon}_{\text{eq}}  Equivalent creep strain-rate
\n\n\dot{\varepsilon}_{\text{ss}}  Equivalent secondary creep strain-rate
\n\n\dot{\varepsilon}_{ij}^c  Creep strain-rate tensor
\n\n\varepsilon^c  Accumulated creep strain
\n\n\varepsilon_f  Creep strain at failure
\n\n\varepsilon_{\text{HAZ}}, \varepsilon_{\text{CW}}, \varepsilon_{\text{WM}},  Creep strain in HAZ, cross-weld, weld metal and parent metal regions for strain compatibility equation
\n\n\varepsilon_{\text{PM}}  Finite element equivalent creep strain-rate
\n\n\eta_{\text{imp}}  Impression creep conversion constant
\n\n\theta  Angle of $\varphi$ at the small punch disk clamp
\n\n\theta_0  Small punch geometric feature measure
\n\n\lambda  Inter-particle spacing
\n\n\lambda_{C}, \lambda_{M}, \lambda_{L}, \lambda_{Z}  Spacing of $M_{23}C_6$, MX, Laves phase and Z-phase precipitates
\n\n\lambda_{C,0}, \lambda_{M,0}, \lambda_{L,0}, \lambda_{Z,0}  Initial spacing of $M_{23}C_6$, MX, Laves phase and Z-phase precipitates
<table>
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<th>Definition</th>
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<td>$\lambda_{ob}$</td>
<td>Obstacle spacing</td>
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<tr>
<td>$\lambda_0$</td>
<td>Initial average precipitate spacing</td>
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<td>$\mu$</td>
<td>Shear modulus</td>
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<td>$\nu$</td>
<td>Triaxiality parameter</td>
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<td>$\rho$</td>
<td>Dislocation density</td>
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<td>Obstacle stress</td>
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<td>$\sigma_1, \sigma_2, \sigma_3$</td>
<td>Principal stresses</td>
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<td>$\sigma_{app}$</td>
<td>Applied stress</td>
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<td>$\sigma_{cnt}$</td>
<td>Micro-cantilever bending stress</td>
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<td>$\sigma_{eq}$</td>
<td>Equivalent or Von Mises stress</td>
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<td>Failure stress in tensile cross weld specimens for weld strength reduction factor calculation</td>
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<td>Failure stress in tensile parent material specimens for weld strength reduction factor calculation</td>
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<td>Failure stress in pipe weld specimens for weld strength reduction factor calculation</td>
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<td>Failure stress in pipe parent material specimens for weld strength reduction factor calculation</td>
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<td>$\sigma_{mem}$</td>
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<tr>
<td>$\sigma_{mdh}$</td>
<td>Mean diameter hoop stress</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Rupture stress</td>
</tr>
<tr>
<td>$\sigma_{trix}$</td>
<td>Stress triaxiality</td>
</tr>
<tr>
<td>$\sigma_{uni}$</td>
<td>Uniaxial stress</td>
</tr>
<tr>
<td>$\sigma_y$</td>
<td>Yield stress</td>
</tr>
<tr>
<td>$\tau_{Or}$</td>
<td>Shear stress due to dislocation pinning</td>
</tr>
<tr>
<td>$\tau_{bd}$</td>
<td>Shear stress due microstructural boundaries</td>
</tr>
<tr>
<td>$\tau_{HP}$</td>
<td>Shear stress due Hall-Petch effect</td>
</tr>
<tr>
<td>$\tau_{LAB}$</td>
<td>Shear stress due low angle boundaries</td>
</tr>
<tr>
<td>$\phi_k$</td>
<td>Effective strain-induced coarsening rate of precipitate $k$</td>
</tr>
<tr>
<td>$\phi_C, \phi_M, \phi_L, \phi_Z$</td>
<td>Effective strain-induced coarsening rate of $M_{23}C_6$, $MX$, Laves phase and Z-phase precipitates $k$</td>
</tr>
<tr>
<td>$\phi_2$</td>
<td>Single precipitate coarsening state variable</td>
</tr>
<tr>
<td>$\varphi$</td>
<td>Small punch specimen contact angle made by the surface normal with punch axis</td>
</tr>
<tr>
<td>$\chi$</td>
<td>Norton based single damage parameter model material constant</td>
</tr>
<tr>
<td>( \omega )</td>
<td>Norton cavitation state variable</td>
</tr>
<tr>
<td>------------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>( \omega_2 )</td>
<td>Hyperbolic sine cavitation state variable</td>
</tr>
</tbody>
</table>
Chapter 1

Introduction

1.1 Background

Until a flexible, clean and sustainable large scale power generation system is developed, fossil fuel plants will remain the mainstay of most modern power generation sectors across the planet. A direct consequence of this is the focus on improving efficiency in traditional fossil fuel power plants [1]. This objective is motivated by two factors; the first is a requirement to minimise the CO$_2$ emissions, reducing their contribution to global climate change and the second is to maximise the energy extraction from the fuel, minimising the fuel requirements and operational costs. Reduced operational costs are essential for consumers, as the demand for electrical energy is forecast to increase globally by 28% from 2015 to 2040 [2]. Improvements in fossil fuel generation technology will aid in minimising the quantities of fuels required to meet these demands, until the renewable sector becomes the dominant power producer. Higher temperature operation of fossil fuel plants holds the key to achieving these goals, by ensuring more complete combusting of the fuel. There are fewer pollutants released from the plant and, as per the Carnot relationship, the greater the increase in temperature the more work that can be extracted from the heat engine.

The heat engine in question here is a traditional power plant with steam as a working fluid. Here, the combustion of fossil fuels, biomass or nuclear fission generates steam which drives a turbine connected to an electrical generator. Increasing efficiency requires increasing the firing temperature for combustion generation, resulting in higher temperature steam. A higher operating temperature produces more complete combustion of the fuel, reducing the quantities of CO$_2$ produced [3]. For example, a 2% increase in plant efficiency produces a corresponding 5% reduction in CO$_2$. 
Figure 1.1 shows typical net efficiency ratings for three different types of power plant, sub-critical, supercritical and ultra-supercritical. The distinction between the three plant types is based on the thermodynamic properties of the working fluid, steam.

![Figure 1.1: Reductions in carbon dioxide emissions from power plants with increasing operational temperature ranges, from Abson et al. [3].](image)

All plant utilised steam as the working fluid, although the increasing temperature and pressures alter the characteristics of the fluid in each plant. Subcritical plant operate with a working fluid below the critical point, a temperature of 374 °C and pressures <22 MPa on each pass through the boiler-turbine system. In a supercritical plant the working fluid has a density similar to water with flow characteristics akin to that of a gas. The operational temperature range for these plants is 538-565 °C with pressures above 22 MPa. Finally, ultra-supercritical plants are aiming to operate at temperatures above 565 °C and pressures of up to 35 MPa [4]. Advanced ultra-supercritical plant operating above these ranges, at approximately 700 °C, are in the planning phases in Japan and Europe [5,6].

A typical plant layout of a coal fuelled power plant in shown in Figure 1.2 [7]. Powdered fuel is burned in the boiler to generate the required steam, which is then fed through the turbine to extract work from the fluid. The turbine powers the generator which produces the electricity, the remaining cooled steam condenses back into water and is pumped back into the boiler to start the cycle again. The boiler tubes, turbine blade and casings are therefore the materials exposed to the highest temperatures and pressures. These materials must also resist the largest forces, either from being pressurised (tubing and turbine case) or from centripetal forces generated from high rotation speeds in the turbine. In both cases, creep resistance of the component materials is the key design factor which controls their usable lifespan.
1.2 Energy in Ireland

The goal of increased firing temperature has been limited by the availability of materials capable of withstanding extended operation at high temperatures and pressures. Alloy design for long term operation has become a crucially important research topic globally, as fossil fuel based power generation is deemed a key technology for many decades to come. It is currently unrealistic to presume all global electrical power can be generated without some high temperature combustion or nuclear fuel generation system included within the energy mix. Therefore, improvements in alloy design must be pursued to minimise the effect of fossil fuel powered generation vis-a-vie CO₂ reduction.

1.2 Energy in Ireland

The CO₂ emissions from the Irish power generation sector are monitored by the Sustainable Energy Authority of Ireland (SEAI) in conjunction with the Environmental Protection Agency (EPA), who have made available their data since 1990. Figure 1.3 presents the CO₂ emissions from the EPA measurements of the power generation sector in Ireland, published in April 2019 [8]. The decreases since the beginning of the millennium have started to level out to similar levels as the 1990’s. Since 2012, the CO₂ levels have remained stable which is impressive giving the fact that the gross domestic product (GDP) of the country has increased by 80 % from 2013 [9]. Traditionally, increased GDP was linked with increased power generation capabilities being brought online to power the improved economic performance. The decoupling of the two is a sign of a movement towards a more carbon independent economy. The total potential electrical energy from all input fuels are shown to the left of Figure 1.4 with the outputs on the right and losses from extracting electrical
power shown at the top of the image. 44.9% of inputs are lost due to inefficiencies in
the power generation systems and this image highlights the urgent need to improve
the efficiency of our fossil fuel plants as quickly as possible.

Evidently, Ireland is a long way from its target for the Paris Climate Agreement, to
reduce greenhouse gas emissions to 40% of the 1990 levels [8]. The results presented
above are for the energy generation sector as a subset of the greenhouse gas (GHG)
producing sectors in the Irish economy. The break-down of power production in
Ireland historically is of interest to this project as there is limited benefit to improv-
ing fossil fuel plant efficiencies if they are systemically on the decline in the power
generation mix. Figure 1.5 presents the varying contributors to net energy input to
the national mix, from the SEAI 2018 annual report [10].
1.3 - High temperature power plant materials

The Irish power generation sector predominantly relies on fossil fuels, mainly gas and coal fired power plants and in recent years more sustainable generation methods such as a large quantity of wind farms. In 2017, approximately 18% of the electrical power generated came from renewables [10]. However, these sustainable green generation methods have their limitations, primarily that they are unreliable particularly for the case of wind generation. Without the inclusion of large battery storage solutions, some form of ”peaker” fossil plant is required, these are generally, gas powered plants which come online rapidly in response to peak demand periods. In the 12 years presented, the use of oil has effectively dwindled to nil, with a sizeable decrease in coal also. This gap has effectively been filled by renewable sources with reduced imports being utilised. Peat usage has remained largely stable, although the three remaining peat fired plants are scheduled to be closed in the coming decade [11]. The initial increase in natural gas corresponds with the global trend away from the use of coal for power generation [12]. Gas powered plants are significantly less polluting than their coal fired counterparts, generally operating at higher temperatures and are more flexible, having shorter start up times then their coal counterparts. Therefore, the goal of research in this field is to enable increased power plant operational temperatures and pressures, to ensure better resource utilisation and to minimise the levels of emitted CO$_2$ [13].

1.3 High temperature power plant materials

The history of commercial steam power is closely linked to the history of understanding creep in materials operating at high temperatures. Creep is a temperature
dependent phenomenon affecting metals once they reach 35% to 40% of the melting temperature [14]. Power plant materials must resist stresses imparted due to internal pressures and a common assessment criteria for comparing multiple different material types is the temperature at which a material can resist 100 MPa of stress for 100,000 hours. One example of such a comparison is made by Ennis et al. [15], which compares historic power plant materials with modern alloys. The results are presented here, in Figure 1.6 and these are used to briefly discuss the improvements to alloying technology.

![Figure 1.6: Comparing several different candidate materials for power plant applications, data from Abson et al. [3], Shingledecker et al. [16] and Di Gianfrancesco et al. [17].](image)

Form the 1970s, 1Cr0.5Mo steels were put into service with the Cr providing corrosion resistance and the Mo providing creep strengthening in the form of secondary phase precipitates. Additional Cr improved the corrosion resistance further in the 2.25Cr1Mo steels. Cr also forms a percentage of strengthening precipitates known as $\text{M}_2\text{C}_6$. The M can be Fe, Cr or Mo, all of which are considered as a single family of strengthening precipitates. A significant improvement to creep strength was made with the introduction of the tempered martensite 8.5-9 wt.% Cr materials [3]. While the stainless steel alloys (AISI grades in Figure 1.6) have similar operational temperatures, they are subject to other limitations. They are costly to manufacture with high concentrations of Cr and Ni in their composition and they also have proven to be challenging to integrate with 9Cr based components, requiring the use of buttressing type welds [18]. Buchkremer et al. [19] compared the coefficients of thermal
expansion for power generation austenitic stainless steels and tempered martensite steels, showing that the austenitic materials expand almost 50% more than tempered martensite steels. This limits their utility in plant which operate on a more flexible basis, and this is increasingly the case for these power plant, as a reaction to the inclusion of intermittent power sources to the grid. Thermo-mechanical fatigue of power plant components is rapidly becoming an area of concern for plant operators due the higher number of start-up and shut-down cycles [20]. Cyclic operation contributes to failures within power plant particularly in welded components and unexpected failures increase downtime and increase cost to the consumer.

1.4 Weld zone component failures

As the adoption of the 9Cr based materials became more wide-spread, a trend of unexpected failures began to occur within the welds of these materials [3]. This failure mode was denoted Type IV failure and occurs in the heat affected zone (HAZ) of the welded region. The HAZ region is generated during the welding procedure and can be subdivided into the following regions; coarse grained HAZ (CG-HAZ), fine grained HAZ (FG-HAZ) and inter-critical HAZ (IC-HAZ). A breakdown of the differing weld regions is shown in Figure 1.7. The creep strength mis-match between the various weld regions can exacerbates this failure mechanism, particularly as temperature increases [21]. Thus, the difference between plain and welded component life becomes larger [21]. Within the power generation sector, Type IV failure is viewed as a critical failure mechanism, whose precise cause of failure remains unclear.

1.5 Heat Treatments

Understanding the mechanisms contributing to weld failures requires an understanding of the material strengthening mechanisms and how they evolve during creep. The tempered martensite 9Cr steels are martensitic in nature, meaning they are heat treated to above the critical temperature $A_{c3}$ ($\sim 910^\circ$C, composition dependent) to fully dissolve all precipitates and transform the material to austenite completely.

After this, a rapid cooling is applied causing the material to attempt to revert to a body-centered-tetragonal (BCT) martensite, a very brittle phase with a hierarchical microstructure consisting of packets, blocks and laths. This material has a high concentration of microstructural boundaries which are essential to providing creep
strength needed for high temperature operations. The time temperature transformation curve for a P91 material (a 9Cr-1Mo steel that has been used by the power plant industry for some time) is presented in Figure 1.8 from Kirk et al. [23]. In their martensite phase, 9Cr steels do not have the necessary ductility to be of use and they are also lacking the majority of their strengthening precipitates. Without C diffusing into the secondary phase, there are few precipitates present in the material [24] and further heat treatment is required. A tempering heat treatment is applied to reduce the hardness of the component and to form the high volume fractions of precipitates necessary to resist creep deformation during high temperature operation [25]. The presence of precipitates along microstructural boundaries stabilises them against temperature activated degradation mechanisms. Post heat treating the two precipitate types formed are M$_{23}$C$_{6}$ carbides along boundaries and MX carbo-nitrides evenly dispersed through the microstructure.

Microstructural boundaries and precipitates are major contributors to the creep performance of the material and, as such, the loss of either of these features will diminish the overall creep performance of the alloy. The IC-HAZ is exposed to a temperature which causes partial austenisation resulting in partial recrystallisation, meaning the
1.6 Aim and Objectives

The primary aim of this thesis is to define, measure and model the effects of precipitates on the creep behaviour of 9Cr materials, through the development of: i) novel modelling methodologies including a mechanistic approach to simulating the effect of precipitate evolution on creep strength of 9Cr steels and ii) a small specimen high temperature creep test capability to minimise material requirements for experimental creep testing. There are four main components to the work:

1. The development of a physically based creep model for 9Cr materials for extrapolation from laboratory high stress conditions to lower stress levels for operational component over a range of temperatures applicable to current and next generation materials. The model includes physically based state variables, incorporating microstructure evolution mechanisms. As failures in welded components are of particular interest, the model is applicable to the welded regions.
for both tensile and internally pressurized components.

2. An understanding of the effect of precipitate morphology on the creep behaviour of 9Cr materials at high temperature is essential for the development of remnant life estimation systems. Materials containing differing precipitate distributions are to be assessed to understand the effect of alternate precipitate characteristics on the creep behaviour of the material.

3. A low cost, repeatable, creep test methodology is required by plant operators. Thus, small scale high temperature creep test apparatus is to be developed and applied to thermally aged material. The apparatus should operate independently from any other test equipment, i.e. be a stand-alone system, capable of maintaining the temperature within acceptable limits and producing creep data with similar or decreased scatter when compared with traditional tensile test data.

4. Next generation materials of industrial interest have been developed and are under consideration for plant improvements and an example is MarBN. However the novel materials require non-standard heat treatments to optimise their bulk creep response and the oxide formation during heat treatment can in some cases degrade the adjacent material to the oxide layer. The precise effect of this degradation is to be explored and quantified experimentally, with a view to recommending the retention or removal of this affected material post heat treatment.

1.7 Thesis Overview and Scope

A brief overview of the thesis contents is presented here to highlight the content within each chapter.

Chapter 2: Literature Review

This chapter contains an examination of the current state-of-the art in high temperature power plant materials available to plant operators and those under development for use in next generation advanced ultra-supercritical power plants. The physical basis of creep is discussed covering the atomic level diffusion processes and dislocation mechanics which occur during creep. The importance of heat treatment for the optimisation of material microstructure, to prevent Type IV failure from occurring
in new plant, is also discussed. The limitations of traditional creep testing and proposals for novel small specimen creep testing are examined also with particular focus on the small punch creep test methodology. Finally, a consideration of modelling methodologies is included as a prelude to Chapters 3 and 4. The importance of physically based models is explored, as they can provide more granular information on the processes leading to creep failure of these materials.

Chapter 3: Physically based, multiple precipitate type creep modelling

A novel creep modelling methodology is presented, including the effects of multiple precipitate types and physical descriptions of the steady state creep terms. A state variable approach is derived for materials containing multiple precipitate types with a focus on the tempered martensitic 9Cr based materials. A parameter identification methodology is presented with the model being fitted for wide stress and temperature ranges. Finally, the model is validated for the low creep strength Bar 257 9Cr material with physical justifications for the difference between this material and conventional P91.

Chapter 4: Precipitate based creep predictions for welds

The model of Chapter 3 is expanded to operate under the multiaxial stress condition by the inclusion of an additional cavitation damage parameter. A finite element (FE) approach is utilised to fit the parameter, based on notch tensile test modelling. A strain compatibility approach is applied to extract general HAZ creep strain data from several data sets available in the literature. Utilising this extracted data and measurements from welded 9Cr steels, the model parameters are identified and fitted for the HAZ and weld materials. A cross weld test specimen is then modelled using the ABAQUS finite element software, with the corresponding weld strength reduction factors (WSRFs) calculated from the cross weld and plane specimens. Similar modelling is performed for the thick walled piping components, where the hyperbolic sine model accurately predicts the stress redistribution which has been observed in real world components. Thick walled pipe WSRFs are compared with their tensile counterparts showing the tensile specimens to be highly conservative as a base to analyse heavy wall components.
Chapter 5: Experimental and numerical evaluation of a small punch creep test apparatus

In this chapter, details on the design, commissioning and validation of a small punch creep test (SPCT) apparatus at NUI Galway for testing of high temperature materials is presented. The apparatus is described along with the parallel development of a finite element model of the test set up, which includes the creep model of Chapters 3 and 4. Sample manufacture methodology and acceptance criteria, based on thickness and surface finish, are defined and applied. An analytical model for the conversion of SPCT load to membrane stress in the samples is presented also.

Chapter 6: Thermal ageing and small punch creep testing of P91

The results of a thermal ageing study of P91 material exposed to 600 °C for up to a year are presented. Transmission Electron Microscopy (TEM) images of the nano-scale precipitate evolution behaviour are presented. A thermal coarsening rate for the precipitates is calculated and compared with literature values. SPCT test results of un-aged and aged P91 material are included along with fractography of the failed specimen fracture surfaces. Differences in the failure behaviour of aged and un-aged materials are discussed in detail. Contour plots of FE results from modelling the SPCT test are compared with the experimental results. A discussion on the applicability of the creep model to the high stress SPCT experiment is included.

Chapter 7: Effect of heat treatment on sub-oxide MarBN characteristics

The next-generation MarBN material is heat treated at two normalisation temperatures, the P91/P92 recommended ASTM temperature and a MarBN specific higher temperature. The formation of an oxide affected zone is examined with micro-hardness testing and electron backscatter diffraction (EBSD) measurements of lath sizes also performed. An automated lath size detection tool is employed and two differing methods for measuring lath sizes are discussed: the line intercept method classically employed for comparison with other literature data and a point sampled method which produced a more physically representative measure of lath size. The connections between lath size, carbon content and dislocation density are discussed as a possible explanation for the degraded region which formed.
Chapter 8: Conclusions and Recommendations

This chapter presents the conclusions, limitations and a critique of the research conducted in this project. Recommendations on model improvements and future work to advance the experimental work are also detailed.
Chapter 2

Literature Review

2.1 Introduction

The high temperature creep behaviour of 9Cr power plant materials is reliant on a number of factors, including (i) constituent alloying elements, (ii) a complex hierarchical microstructure and (iii) heat treatment. The assessment of these materials in their as manufactured form and during service operation is as important as the quality of the material being assessed. In addition, a modelling methodology linking these factors with a physical basis is required to minimise operational expense to the plant operator and consumer.

The following chapter details; the development of power plant materials, the optimisation of their microstructure to maximise creep resistance, the development of small creep testing methods and numerical approaches to predicting their creep behaviour.

2.2 Development of creep resistant steel

2.2.1 CrMoV Alloys

Low alloy ferritic steels have been employed for power plant construction since the 1970’s leading to a focus on the repair and life extension of these plant components in recent years [27–29]. These materials are ferritic steels alloyed with Cr, Mo originally, where further development led to the addition of V, Nb and N to improve the creep performance of the material. This improvement in creep resistance can be attributed to increased quantities of precipitates formed. Cr and Mo form M23C6 precipitates while V, Nb and N form the MX family [30]. Cr also improves the corrosion resistance of these ferritic steels, which is vital for their use at higher steam temperatures and
pressures [31]. Appendix A contains a periodic table for reference when discussing the effects of composition in the following sections.

The historical development of high temperature steel alloys, such as for power plant applications has seen incremental changes to alloy compositions to continually improve the creep strength of a given material. As manufacturing technologies improve, greater control of alloying elements has produced a wide variety of creep resistant materials. The underpinning design objective is to increase the maximum allowable stress a material can withstand at a given temperature, typically with reference to 100,000 hours of creep life. Alternatively, maintaining the same stress level at a higher temperature for this time period is used as the target objective [15]. In either case, minor alterations to the composition or heat treatment can result in significantly different material properties. The design and characterisation process, for a novel material consists of a multi-step program, including but not limited to, microstructural analysis, experimental testing and numerical constitutive modelling. Component loading conditions and flexible operation of plant can also significantly alter the operational life of such a component.

The incremental improvements in material technology have led to the current suite of 9Cr based alloys employed in power plants world-wide. These materials consist of a hierarchical microstructure with complex strengthening mechanisms operating throughout the life of a component. The various creep mechanisms, at play within alloy steels are dependent on the presence of these microstructures within a component. Understanding and modelling the evolution of the microstructure during creep is a key focus of this work.

A schematic representation of the hierarchical microstructure present in martensitic precipitate strengthened materials is shown in Figure 2.1. The prior austenite grains (PAG’s) are subdivided into packets containing blocks, which contain a network of dislocations outlining the martensitic lath structures. PAG, block, packet and lath boundaries all serve to strengthen the materials against creep deformation. The strengthening mechanisms associated with these features are discussed in depth in this chapter.
2.2 - Development of creep resistant steel

2.2.2 P91

Abson and Rothwell [3] provide an in depth review of the development of 9% Cr containing steels for power plant. A current goal of high temperature materials research is to achieve an operational life of 100,000 hours at 650 °C for ultra-supercritical power plants. Table 2.1 highlights the incremental improvements of these steels since their inception in the 1960’s. Figure 2.1 presents a schematic layout of the material microstructure. This 9Cr-1Mo steel is frequently referred to as P91 for cast thick-walled components and this material is referred to as T91 when it is utilised for the manufacture of thin tubing sections. The composition of P91 and T91 are the same, the difference being the form factor.

2.2.3 P92

A reduction in the Mo content and a small percentage increase in the W content led to the development of the P92 material. W provides improved solid solution strengthening to the matrix material, due to it’s larger shear modulus $\mu$ [25, 32] (it should be noted standard P91 does not contain W). It also decreases the coarsening rate of $\text{M}_{23}\text{C}_6$, precipitates, due to its low diffusion coefficient in an iron based matrix (see Section 2.4.1), which in turn decreases the rate at which additional W can be absorbed into ripening precipitates under creep conditions [33]. However, increased concentrations of W can lead to the formation of additional intermetallic compounds such as Laves Phase $(\text{Fe,Cr})_2(\text{Mo},\text{W})$ for P92. This phase initially provides an improvement to the creep resistance of the steel by increasing the volume fraction of obstacles to deformation. However, the Laves phase itself has a much
higher coarsening rate, promoting an acceleration of creep rate towards the end of a creep test [30]. The allowable variations in composition of P91 and P92 are presented in Table 2.2 from the 2018 iteration of the ASTM standards [34]

Table 2.1: Development of 9-12%Cr steels from [3]

<table>
<thead>
<tr>
<th>Years</th>
<th>Alloy modification</th>
<th>600 °C/10⁵ hr creep rupture strength (MPa)</th>
<th>Example alloys</th>
<th>Max. use temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1960-1970</td>
<td>Addition of Mo or Nb, V to simple 12Cr and 9Cr steels</td>
<td>60</td>
<td>EM12, HCM9M, HT9, Tempaloy F9, HT91</td>
<td>565</td>
</tr>
<tr>
<td>1970-1985</td>
<td>Optimisation of C, Nb, V</td>
<td>100</td>
<td>HCM12, T91, P91, HCM2S</td>
<td>593</td>
</tr>
<tr>
<td>1985-1995</td>
<td>Partial substitution of W for Mo</td>
<td>130</td>
<td>P92, P122, P911 (NF 616, HCM12A)</td>
<td>620</td>
</tr>
<tr>
<td>Emerging</td>
<td>Increase W and addition of Co, B and controlled N</td>
<td>150</td>
<td>NF12, SAVE 12, MARN, MARB2, MARBN</td>
<td>650</td>
</tr>
</tbody>
</table>

### 2.2.4 Austenitic Stainless Steels

Austenitic stainless steels have also been developed in parallel with the 9-12Cr martensitic steels for power plant applications. Their high Cr and Ni contents, 15 to 26 wt.% and 5 to 37 wt.% respectively, ensure excellent corrosion and creep resistance at high temperatures, although it also significantly increases the cost of the components to produce [35]. Austenitic stainless steels show excellent potential for use in next generation ultra-supercritical power plant, operating in the 700 °C range. One of the factors limiting the application of austenitic stainless steels is their coefficient of thermal expansion in comparison with the martensitic based alloys [19]. Ennis et al. [15] state that the austenitic steels have thermal expansion coefficients up to 50% larger than their ferrite based counterparts. As a result of their higher expansion coefficients, during welding, austenitic steels experience higher thermal gradients, further diminishing their weld performance. Specifically during the post weld cool down, the contraction of the welded components induces stresses into the
joint leading to premature failures [36]. Plaut et al. [35] also highlight two other high
temperature properties of this class of material which could be of concern to plant
designers; these are the formation of undesirable intermetallic phases and signifi-
cant plastic deformation accumulation. Higher levels of plastic deformation within
a single material of a dissimilar metal weld could generate further internal stresses
causing a reduction in component life.

Table 2.2: ASTM allowable variations in composition in wt. % for 9Cr steels [34].

<table>
<thead>
<tr>
<th>Element</th>
<th>P91</th>
<th>P92</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Min</td>
<td>Max</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>0.08</td>
<td>0.12</td>
</tr>
<tr>
<td>Cb</td>
<td>0.06</td>
<td>0.10</td>
</tr>
<tr>
<td>Cr</td>
<td>8.00</td>
<td>9.50</td>
</tr>
<tr>
<td>Mn</td>
<td>0.30</td>
<td>0.60</td>
</tr>
<tr>
<td>Mo</td>
<td>0.85</td>
<td>1.05</td>
</tr>
<tr>
<td>N</td>
<td>0.030</td>
<td>0.070</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
<td>0.40</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
<td>0.020</td>
</tr>
<tr>
<td>S</td>
<td>-</td>
<td>0.010</td>
</tr>
<tr>
<td>Si</td>
<td>0.20</td>
<td>0.50</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
<td>0.01</td>
</tr>
<tr>
<td>W</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>0.18</td>
<td>0.25</td>
</tr>
<tr>
<td>Zr</td>
<td>-</td>
<td>0.01</td>
</tr>
</tbody>
</table>

### 2.2.5 CB2 & FB2 Alloys

The influence of boron on the long term behaviour of welded 9Cr steels has been
evaluated extensively such as by The Welding Institute (TWI), the COST program
in Europe [37] and by the National Institute for Material Science in Japan [38–40], as
it has a positive effect on the behaviour of $M_{23}C_6$ type precipitates. Boron addition
had been highlighted previously as a potential method for significantly improving the
Chapter 2 - Literature Review

High temperature performance of 9-12% Cr materials, specifically in retarding the onset of Type IV failure [41]. Rothwell et al. [37] generated a number of cross weld specimens from the boron containing 9Cr steel FB2. Specifically they focused on the most promising version of the material, containing 130ppm of B, when combined with an optimised concentration of N to produce a greater volume fraction of MX precipitates [25]. To ensure the prevention of detrimental phases, an optimised heat treatment is required for these materials, discussed previously [42].

2.2.6 MarBN

MarBN has been designed to maintain the hierarchical microstructure of the 9Cr steels during the welding process and hence try to mitigate Type IV failures (discussed more extensively in Section 2.9.3). To eliminate the causes of Type IV failure, the addition of B ensures the hierarchical structure is maintained through the weld process. The B segregates to the boundary regions forming $\text{M}_{23}\text{CB}_6$ precipitates, which have lower coarsening rates than $\text{M}_{23}\text{C}_6$ precipitates. The N composition is reduced to optimise the volume fractions of MX precipitates formed, to provide increased performance at higher temperatures and reduce the potential for BN formation. As a deeper understanding of alloy element contributions to creep strength has been achieved, the composition of the 9-12%Cr steels have become more refined. This, coupled with improved control of production methods, allows material scientists to specify alloying elements in the order of parts per million (ppm), as is the case in the next generation MarBN type materials. Specifically, in this case, the carefully controlled addition of N and B generates more thermally stable precipitates and also vastly improved weld material strength [38, 40, 41, 43, 44]. In Table 2.3, the Z-phase particles have the potential to form within MarBN material, however sufficiently long term testing of the material has not been completed yet to confirm when this phase will occur. The lower concentration of N is expected to limit the formation of Z-phase at these longer times.
2.3 Creep in Metallic Alloys

Creep is defined as \textit{the continuous deformation of a material under stress especially at high temperatures}. Detailed and careful consideration of creep is of critical importance in power plant steels. The mechanisms of creep at work within the various steel families can be separated into high and low stress regimes. Low-stress creep involves diffusion-based processes, while high-stress creep involves dislocation based processes. For longer term, lower stress testing, diffusion effects dominate the creep behaviour whereas during high stress testing dislocation processes dominate the creep behaviour. The two distinct stress regimes are clear in Figure 2.2, data from the work of Haney, Sklenicka, Milicka and Cerri [46–49]. During testing at intermediate stress levels, it is therefore important to consider the combined effects of diffusion and dislocation based creep effects.

A deformation mechanisms map for a generic material is presented in Figure 2.3 from Viswanathan [50]. Diffusion based creep dominates at lower stresses over a wide

<table>
<thead>
<tr>
<th>Steel</th>
<th>Precipitate</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>P91</td>
<td>M$_{23}$C$_6$</td>
<td>(Cr,Fe,Mo)$_{23}$C$_6$</td>
</tr>
<tr>
<td></td>
<td>MX</td>
<td>(Nb,V)(N,C)</td>
</tr>
<tr>
<td></td>
<td>Laves Phase</td>
<td>(Fe,Cr)$_2$Mo</td>
</tr>
<tr>
<td></td>
<td>Z-phase</td>
<td>Cr(V,Nb)N</td>
</tr>
<tr>
<td>P92</td>
<td>M$_{23}$C$_6$</td>
<td>(Cr,Fe,Mo,W)$_{23}$C$_6$</td>
</tr>
<tr>
<td></td>
<td>MX</td>
<td>(Nb,V)(N,C)</td>
</tr>
<tr>
<td></td>
<td>Laves Phase</td>
<td>(Fe,Cr)$_2$(W,Mo)</td>
</tr>
<tr>
<td></td>
<td>Z-phase</td>
<td>Cr(V,Nb)N</td>
</tr>
<tr>
<td>MarBN</td>
<td>M$_{23}$C$_6$</td>
<td>(Cr,Fe,W)$_{23}$(CB)$_6$</td>
</tr>
<tr>
<td></td>
<td>MX</td>
<td>(Nb,V)(N,C)</td>
</tr>
<tr>
<td></td>
<td>Laves Phase</td>
<td>(Fe,Cr)$_2$(W,Mo)</td>
</tr>
<tr>
<td></td>
<td>Z-phase</td>
<td>Cr(V,Nb)N</td>
</tr>
</tbody>
</table>

Table 2.3: Precipitate composition in 9Cr steels [25,30,45], Z-phase and Laves phase both form during long term creep exposure and are detrimental to creep strength.
Chapter 2 - Literature Review

Figure 2.2: Minimum strain rate versus applied stress for T91 at 600 °C from [46–49].

...temperature range and, as the stresses increase, the dislocation based mechanisms dominate the deformation behaviour.

Figure 2.3: Schematic deformation mechanism map with contours of constant creep rate from Viswanathan et al. [50].

2.3.1 Diffusion Creep Mechanisms

Diffusive creep is the process whereby the material microstructure is evolving into a more energetically favourable arrangement [51]. An example of this behaviour is seen within the alloy steels containing secondary phases, such as precipitates (the benefits of precipitate based strengthening are discussed later in this section). During solidification, a matrix of the primary alloying elements forms, via dendrite growth,
2.3 - Creep in Metallic Alloys

into solid grains, secondary phases are microstructure features which form separately to this matrix. The most commonly considered secondary phase consists of precipitates which deform the crystal lattice. A small number of large precipitates are more thermodynamically stable than widely dispersed smaller particles. The diffusion properties of the various elements, which form the precipitates within the iron matrix, dictate the rate at which these small precipitates grow.

Vacancy diffusion through the lattice also occurs, whereby individual vacancies migrate through the crystal lattice and conglomerate at grain boundaries at triple points in particular (see Figure 2.4). These vacancies coalesce to form cavities and provide energetically favourable paths for crack growth through a material [52]. Strain loading of a material provides additional energy for the diffusion of these vacancies while increasing stress triaxiality also enhances the rate of vacancy based damage accumulation [52, 53]. Triaxiality as defined by Watanabe et al. [53] as the sum of the principal stresses divided by the Von Mises equivalent stress:

\[
\sigma_{\text{trix}} = \frac{\sigma_1 + \sigma_2 + \sigma_3}{\sigma_{\text{eq}}} \tag{2.1}
\]

The strain mismatch between a precipitate containing matrix and a precipitate free boundary was utilised to develop the damage model as described by Cane [52]. Vacancy diffusion through the matrix obeys the same laws as those for alloying elements diffusing through the lattice under temperature and strain effects and Section 2.7.2 provides details on this process.

![Figure 2.4: Schematic of vacancy diffusion through crystal lattice forming cavities at boundaries, from [54].](image)

2.3.2 Dislocation Creep Mechanisms

A dislocation is an extra half plane of atoms within the crystal lattice of a metal, generating a stress field at the point where this half plane of atoms ends, between two
other full planes of atoms, see Figure 2.5. Here, the green line indicates the length of the Burger’s vector (\(b\)) and the dashed black line represents a microstructural boundary, which in this example is a grain boundary. They are defects in the material which allow deformation to occur in the lattice. Dislocation motion is the process by which macro-scale deformations are expressed at the atomistic level. Dislocations are of two types predominantly, either edge or screw, but can also be of mixed intermediate type between these two, Figures 2.5 and 2.6 show schematics of the edge and screw dislocations respectively. The description of dislocations was first proposed by Volterra [55] in 1907 and the term dislocation to describe the crystal lattice defect was first used by Taylor in 1934 [56]. Dislocation dominated creep occurs under high temperature and pressure conditions, (see Figure 2.3) and newer power plants aiming to operate under advanced ultra-supercritical conditions are more likely to encounter dislocation dominated creep effects. Much laboratory testing occurs under higher stress (or strain-rate) conditions as it allows a test program to be completed in a reasonable time frame. As such, the relationship between high and low stress conditions should be considered.

![Figure 2.5: Schematic of an edge dislocation motion through the crystal lattice due to the application of strain, in the directions indicated by the black half arrows. The green line indicates the length of Burger’s (\(b\)) vector for this dislocation type.](image)

When a plant component is pressurised or a test specimen is deformed, internal stresses are applied to the material matrix. Shear stress is applied to the crystal lattice causing the dislocation to jump from one crystal plane to another. It starts to the left of the crystal lattice in 2.5a, moves through the lattice, distorting it as in Figure 2.5b and finally the dislocation reaches a boundary it cannot cross and is locked in place, e.g. grain boundary, 2.5c. This jumping motion is known as slip, and occurs along a given slip plane within the material. Assuming that only single
atomic bonds are broken one at a time minimises the energy required for dislocation movement [24]. Dislocations can cross this grain boundary, provided the number of dislocations piled up at the boundary is large enough to meet the force requirement to overcome the boundary. The dislocation can then continue to move through the neighbouring grain.

Figure 2.6: Schematic of a screw dislocation showing the distortion of the crystal lattice due to the presence of the extra half plane. The green line indicates the length of Burger’s vector for this dislocation type.

2.4 Strengthening mechanisms

Deformation within materials under creep loading is primarily a function of dislocation movements through the crystal lattice and this in turn is a function of temperature and stress. Creep strengthening mechanism design is focused on the retardation of this movement through the crystal lattice. Substitutional solution strengthening provides opposition to this motion by placing large atoms within the lattice, generating fields of distortion which require additional energy to overcome, via the mechanism of dislocation climb. Interstitial strengthening inserts a secondary lattice of atoms within the interstitial locations of the primary matrix material, providing significant lattice distortion to the matrix material and martensitic materials take advantage of this behaviour. Secondary phase particles, such as precipitates and intermetallic phases, are formed within the matrix materials during heat treatment or in-service (e.g Laves and Z-phase precipitates, see Section 2.7.1). Further optimisation processes of the heat treatments, to generate the preferred material microstructure, have been widely researched [57–60]. The compositions of these phases have been optimised to provide long term precipitate stability, enhancing the creep properties of the parent alloy. Control of the precipitate coarsening rates has
been highlighted in the literature as a key area of research, essential to the future development of steels for use in next generation power plant [25].

2.4.1 Heat Treatment

The optimisation of steel properties using heat treatments has been of interest for almost as long as steels have been in use. Changes in duration, temperature and cooling rate can all have significant impact on the final properties of the steel. Broadly speaking, there are several heat treatment regimes available for carbon steels. The addition of alloying elements can have a significant impact on the temperature and time regimes required to perform the same heat treatment for different steels. The typical two stage heat treatment for the production of tempered martensitic steel is presented in Figure 2.7. The ASTM guidelines for heat treating of 9Cr steel require a normalisation heat treatment between 1040 °C and 1080 °C, and a tempering heat treatment between 730 °C and 800 °C [61]. The primary goals of normalisation and tempering heat treatments for 9Cr steels are relieving residual stress from the initial formation process and generating the precipitate strengthened hierarchical microstructure.

![Figure 2.7: Typical two stage normalisation and tempering for of a carbon steel to produce a tempered martensite material.](image)

Normalisation

Normalisation is the process by which the carbon steel alloy is heated above Ac₃ temperature to form austenite in Figure 2.8. The iron matrix converts from α-iron
2.4 - Strengthening mechanisms

(ferrite) a body-center-cubic (BCC) (below 910 °C) arrangement, to a face-center-cubic (FCC) arrangement known as γ-iron, during normalisation. This allows a higher concentration of carbon atoms to migrate into the matrix, providing interstitial solute strengthening to the steel. The formation of γ-iron allows the martensitic transformation to occur and, during cooling, the matrix reverts to α'-iron a body-centered-tetragonal arrangement.

During normalisation, the iron becomes fully austenitic and new grains form and a rapid cooling then induces a martensitic transformation. The martensite transition is a result of carbon dissolved in the matrix being unable to diffuse out of the matrix due to the rapid cooling, thus, pinning the crystal lattice in place and generating the hard brittle martensite phase. The newly formed martensite grains, with prior austenite grain boundaries (PAGBS), contain packets, subdivided into blocks containing laths. Grains, packets and blocks are all high angle boundaries (HABs)(see section 2.4.3), while the lath boundaries are regions of high dislocation density and are low angle boundaries (LABs) (see section 2.4.4). The tempering heat treatment is then applied to (i) recover ductility of the material, (ii) relieve residual stress from the normalisation process and (iii) generate precipitates.

![Figure 2.8: Typical heat treatment temperature regimes for a range of carbon steels, reproduced from Porter and Easterling [24].](image)

**Tempering**

Tempering is the process of recovering ductility, which is lost during the martensite transformation. The capturing of C in the iron matrix and the ensuing distortion of the lattice produce a hard brittle phase. Tempering can be performed at a range of
temperatures, depending on the alloy being heat treated. For example, Honeycomb [62] states that tempering can take place between 150 and 700 °C, for 0.3 % to 1.5% plain carbon steels, while in other work on 0.5Cr-Mo-V alloys, tempering at 775 °C is applied [63]. Meanwhile the ASTM standards for 9Cr based pressure vessels [61], recommend tempering heat treatments between 750 and 780 °C for creep resistant 9Cr materials. Tempering temperature is dependent on the alloy composition, here only tempering of 9Cr steels will be discussed. The P91 phase diagram calculated using thermodynamic software by Milović et al. [64], is shown in Figure 2.9,

![Image of P91 phase diagram]

Figure 2.9: Predicted phase diagram of P91, reproduced from [64].

This standard contains an addendum defining an alternative tempering temperature of under 730 °C, with the understanding that the purchaser must perform an additional tempering above 730 °C, before putting them into service. Of interest here are the mechanisms by which precipitates form during the tempering process as they are of particular importance when materials are under creep conditions. During tempering, the carbon interstitial atoms diffuse out of the matrix and begin to form nano-scale rods. For 0.1 % steels, cementite (Fe₃C) rods form which then become spherical after longer tempering periods [62]. Creep strengthening precipitates form in a similar matter to this. Initially C diffuses from the matrix and then combines with other elements such as Cr, Mo and W (for P92/MarBN) to form M₂₃C₆ precipitates, a similar process can form some MX carbides. Nitrogen percolates out of the matrix in a similar fashion forming MX precipitates with V and Nb throughout the microstructure. Abe et al. [25] observed the preferential formation of M₂₃C₆ along microstructural boundaries attributing this to higher diffusivity along these bound-
Table 2.4: Activation energy and diffusion coefficients required for diffusion to occur in an \( \alpha \)-iron matrix for some common alloying elements.

<table>
<thead>
<tr>
<th>Solvent Solute</th>
<th>Activation Energy (kJ/mol)</th>
<th>Diffusion coefficient ( (m^2/s) )</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )-iron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>80</td>
<td>( 1.79 \times 10^{-10} )</td>
<td>[62]</td>
</tr>
<tr>
<td>Co</td>
<td>226</td>
<td>( 2.05 \times 10^{-15} )</td>
<td>[62]</td>
</tr>
<tr>
<td>Cr</td>
<td>343</td>
<td>( 2.04 \times 10^{-4} )</td>
<td>[62,65]</td>
</tr>
<tr>
<td>Mo</td>
<td>226</td>
<td>( 9.32 \times 10^{-17} )</td>
<td>[65,66]</td>
</tr>
<tr>
<td>N</td>
<td>76</td>
<td>( 1.29 \times 10^{-10} )</td>
<td>[62]</td>
</tr>
<tr>
<td>Nb</td>
<td>215</td>
<td>( 4.3 \times 10^{-4} )</td>
<td>[67]</td>
</tr>
<tr>
<td>V</td>
<td>58</td>
<td>( 1.79 \times 10^{-20} )</td>
<td>[30,68]</td>
</tr>
<tr>
<td>W</td>
<td>293</td>
<td>( 1.49 \times 10^{-20} )</td>
<td>[30,62]</td>
</tr>
</tbody>
</table>

To avoid the detrimental presence of BN precipitates in MarBN steel, a novel heat treatment regime is required, as detailed by Li et al. [43]. This consists of a normalisation heat treatment between 1175 °C and 1200°C for 1 to 7 hours, which dissolves any previously formed BN precipitates and prevents further BN from forming during the heat treatment process. A standard 9Cr tempering (between 750 °C and 800 °C) is then performed afterwards, as per ASTM standards [61]. Li et al. [43] highlights the sensitivity of the BN particles to the heat treatment conditions, particularly if the 1200 °C limit is exceeded. Excessive BN particles formed when a normalisation between 1225 °C and 1250 °C was performed. Abe et al. [38] observed the effects of the B and N additions to 9Cr steels, the strengthening being imparted by the segregation of B to the grain boundaries during normalisation. During tempering \( M_{23}C_6 \) precipitates form on these boundaries and are now stabilised by the B present at the boundaries. The B surrounding the \( M_{23}C_6 \) retards the diffusion of additional alloying elements into the precipitate, preventing coarsening from occurring. Precip-
iterate strengthening is a key mechanism of creep resistance in these steels. The effect of differing heat treatments on MarBN is considered in greater detail in Chapter 7.

**Decarburisation during heat treatment**

A particular concern is the formation of oxide layers while heat treating 9Cr steels. At elevated temperatures (by elevated here the author refers to temperatures above 1080 °C the ASTM maximum for normalisation), 9Cr steels are prone to oxidation during heat treatment. The formation of an oxide layer can result in a decarburized region forming as a result of diffusion from the bulk material into the oxide layer. C, Co and Cr, all diffuse based on their relative diffusivity in martensitic iron. Aside from the local composition change caused by oxidation, there is also a net loss of bulk creep resistant material during oxidation [69]. During manufacturing, thicker tubes are therefore required to account for the loss of material due to oxide scale formation and loss of operational material, thus increasing manufacturing costs. It is reported that heat treatments to below 700 °C can cause carbon enrichment in the base material. This occurs when the iron oxidation rate is higher than the carbon oxidation rate. The non-oxidized carbon can be forced to re-diffuse into the base material surface layer adjacent to the oxide-base metal interface resulting in a harder region adjacent to the oxide-metal interface [70–72].

### 2.4.2 Precipitate strengthening

Figure 2.10 is a schematic illustration of the effect of precipitate coarsening on the pinning of dislocations, in terms of the formation of Orowan loops around the precipitate. During Ostwald precipitate coarsening, larger precipitates consume smaller precipitates increasing the average inter-particle spacing. Increased inter-particle spacing, reduces the effect of dislocation pinning and loop formation. The creep strengthening provided by dislocation pinning and bowing at precipitates was defined by Orowan [73] as:

\[
\tau_{Oo} = \frac{\mu b}{\lambda}
\]

(2.2)

where \(\mu\) is the shear modulus and \(\lambda\) is the inter-particle spacing. Increased spacing allows dislocations to bow through the larger gap more easily. Figure 2.10a shows the material condition with a fine dispersion of precipitates prior to creep exposure. Figure 2.10b shows the material post creep exposure where the pinning effect has been reduced due to the coarsening of pinning precipitates.
2.4 - Strengthening mechanisms

(a) 
(b)

Figure 2.10: Schematic of precipitate coarsening with resulting dislocation bowing and loop formation in a material (a) prior to creep test and (b) post creep test [74].

Optimum creep life can be expected from a high volume fraction of small precipitates, with low coarsening rates. MX precipitates are small (radius of 10-50 nm), thermally stable, V and Nb carbo-nitrides in both P91 and P92 steels. M$_{23}$C$_6$ precipitates are larger, less thermally stable Fe, Cr, Mo carbides in P91 and contain W in P92 and MarBN. MarBN also contains B enriched precipitates of the following form M$_{23}$(CB)$_6$ [25,30,75].

During high temperature creep conditions, the inter-metallic Laves phase also forms in both steels, consisting of (Fe,Cr)$_2$Mo in P91 and (Fe,Cr)$_2$(Mo,W) in P92 [30]. MX precipitates are less likely to thermally coarsen and are less susceptible to strain induced coarsening than the M$_{23}$C$_6$ precipitates, which show a strong effect of strain and temperature induced coarsening in 9Cr steels [76]. The Laves phase particles initially provide some creep strengthening to the steel. However, their rapid growth reduces their ability to pin precipitates and leads to enhanced cavitation type damage which can result in premature failure of components [77, 78]. After long creep exposure times (∼10,000 hours), Z-phase particles can begin to form by absorbing the V, Nb and N of MX precipitates. This drastically reduces the creep life of high Cr containing alloys [45]. 9Cr materials were shown to be less susceptible to the formation of Z-phase than the 11 % to 12 %Cr by Danielsen et al. [45].

2.4.3 High angle boundaries

During the solidification process, small dendrites of solidified metal form and grow to form larger grains. They form where the grains meet boundaries and unless further processing is performed, the grain structure will be based on this random
solidification. The normalisation process recrystallises the material generating prior austenite grain boundaries (PAGBs). Grains and their boundaries are found in all metals, aside from highly specialised cases such as single crystal blades for aerospace applications [79]. A high angle boundary is any boundary where the crystal orientations between the two adjacent grains have an angle greater than $15^\circ$ [80,81]. Plastic deformation in the form of dislocations cannot move through a HAB, unless sufficient dislocations pile-up increasing the force on the leading dislocation up to a critical value. Exceeding this critical force, the leading dislocation is pushed through the boundary. For the martensitic steels of interest to this project, the sub-grain packet and block structures both are delineated by HABs, causing dislocation pile-ups, hardening the material.

These are often treated as effectively the same type of HAB for calculations of mechanical properties, however there is a difference in the degree of mis-orientation associated with each hierarchical structure. Firstly it is widely agreed that PAGBs are boundaries with mis-orientations of $40^\circ$ to $65^\circ$, while the definition of packet and block boundary mis-orientations are less clear. Katharikeyan et al. [82] classified packet boundaries as ranging from $11^\circ$ to $20^\circ$ and from $49^\circ$ to $58^\circ$, with blocks between $53^\circ$ and $60^\circ$. The lower end of packet boundaries described in this work overlaps those defined by Chauhan et al. [80] and Zhang et al. [81].

### 2.4.4 Low angle boundaries

LABs define the martensitic lath structure in 9Cr alloys, where the boundaries themselves are regions of high dislocation density [20]. Martensitic laths are narrow elongated structures housed inside of the block structure in martensitic steels. Figure 2.1 presents a schematic of a martensitic steel containing precipitates. The block substructures are further split into laths by dense dislocation networks surrounding regions (laths) of low dislocation density. Inter-lath mis-orientation angles were identified by Apple et al. [83] as being of the order $3^\circ$ to $4^\circ$, however they are generally considered to be less than $15^\circ$ [80,81,84–86].

Lath growth and transformation to equiaxed sub-grains occurs due to the loss of pinning precipitates on the lath boundaries during high temperature exposure. The annihilation of lath boundaries can also occur due to dislocation annihilation removing dislocations from the network of lath boundaries. This increases the lath boundary width and hence reduces their effectiveness as obstacles to dislocation motion. $M_{23}C_6$ coarsening reduces their pinning effect on the lath boundaries [25,87].
2.5 Creep testing Methods

Multiple testing methodologies have been developed historically to test the creep behaviour of materials and the most well known and standardised version is the
plain tensile test methodology, defined most recently in ASTM E139 (2018) [95]. However there are some issues with this testing procedure and other approaches have been developed to address these issues which are discussed below. One of the primary concerns with standard tensile testing is the quantities of components required to manufacture test specimens. This is for the specific case of remnant creep life estimation, where ex-service materials are utilised to estimate the remaining operational life of a component. The other issue with standard tensile testing is the duration of the tests, some of which can last for more than 100,000 hours [96], which means they are extremely slow and costly to perform. The majority of laboratory testing is conducted at elevated stresses and temperatures to minimise the time taken for a given test. The limitation of this approach is relating the laboratory results to actual plant operational loads and, as such, models are required to relate the two loading conditions. Section 2.10 discusses different modelling approaches to this issue. The creep strain rate, \( \dot{\varepsilon}_{cr} \), extracted from any test method for all materials is a function of the applied stress, \( \sigma_{\text{app}} \), temperature, \( T \) and time, \( t \).

### 2.5.1 Standard tensile testing

A typical creep tensile test specimen is shown in Figure 2.13, where the sample can be threaded into the tension testing mechanism or it can be mechanically clamped. This requires a pipe component of thickness greater than 20 mm to allow for machining of test specimens and this pipe section must also be at least 145 mm long for a standard specimen [97]. The specimen is then put under tension with a constant axial force applied to the specimen, once the apparatus has reached the desired operating temperature. Testing can be performed in an inert atmosphere or in air.
as desired, oxidation will obviously occur in an air environment. The gauge length should at a minimum be equal to four times the gauge length diameter and all information on standard tensile testing is available in the ASTM E139 standard [98].

![Figure 2.13: Tensile specimen dimensions from ASTM EM\E8M standard [97, 98], all dimensions in mm.](image)

### 2.5.2 Notched tensile testing

The majority of high temperature operations occur in power plant within piping or tubing components. The uniaxial creep test does not elucidate the response of a material to the multi-axial loading conditions experienced in plant. Therefore, controlled multi-axial testing is required to further understand the behaviour of a material when exposed to multi-axial operational conditions. A multi-axial stress state is developed in the test specimen by the inclusion of a notch in the gauge length [99]. The effects of notch size and shape have been the subject of much research historically. Eggeler et al. [100] numerically examined the effect of notch geometry on the stress redistribution behaviour using finite element modelling. The presence of a notch can either increase or decrease the time to failure for a particular material and this behaviour is known as notch strengthening or weakening, respectively [100, 101]. Notched creep simulations have also been employed for parameter identification of continuum damage mechanics models which directly relate the stress state sensitivity index with cavitation damage accumulation [102,103]. Cane [52] developed the numerical framework highlighting the importance of the triaxial stress state to cavitation. In these approaches, the index value ($\nu$) controls the time to failure of the notched specimen, as it modifies the rate of damage accumulation ($\dot{D}_{cav}$), where the principal stress ($\sigma_1$) to equivalent stress ($\sigma_{eq}$) ratio is raised to this index $\dot{D}_{cav} \propto (\sigma_1/\sigma_{eq})^\nu$. The concentration of a high principal stress in a given region accelerates the damage accumulation in this area. Watanabe et al. [53] observed this trend in their FE simulations of welded P91 which predicted Type IV failure in regions of highest stress triaxiality. The primary limitation of tensile notched and plain creep testing is the requirement of larger quantities of material, necessitating the removal of entire components to manufacture test specimens.
This limits the components for which standard tensile creep testing can be performed on and as such, there has been much research into the viability of small scale creep testing. These alternative test methods are discussed below and the objective is to minimise the cost of creep testing, by minimising the material requirements. Ideally, there exists a minimally invasive creep test which can reliably estimate the remaining creep life of a power plant component, thus minimising the need for conservative steady state creep based life estimation methods. However such an approach has yet to be identified.

2.5.3 Thermal ageing

Strain free ageing or thermal ageing aims to examine the effect of temperature only loads on a material over a prolonged period of time. From high temperature creep tests, the effects of combined temperature and strain exposure are observed, although the effect of temperature only cannot always be easily extrapolated. In fact, in many creep studies, the comparison between material in the grip portion of a tensile test specimen is examined as extensively as in the gauge length, with the assumption of zero strain accumulation having occurred within the grip portion [96,104].

Thermally activated microstructural evolution processes are of most interest to these studies, given that for precipitate strengthened steels, the coarsening rates are of utmost importance. The formation of new phases due to diffusion of solute atoms out of the matrix and the creep performance of the material post thermal exposure are also of interest. For a P92 material, aged for 5,000 hr at 650 °C. Sakthivel et al. [105] observed the formation of Laves phase particles in the aged specimen, leading to decreased yield and ultimate tensile stresses.

For creep tests at 110 MPa, a reduction of 11% was observed in the time to failure of the aged material compared to the un-aged, for the 120 MPa test conditions, the reduction was on the order of 56 %, see Figure 2.14 [105].

The loss of solute strengthening atoms is offset by the benefit of additional precipitate strengthening. However at the higher stress range, the loss of these atoms appears to have had a far greater impact on the time to failure. The loss of Mo solute atoms allows for dislocation dominated (high stress) creep to occur more easily, causing the recovery of the equiaxed sub-grain structure from lath widening during creep.

Other works have examined the effects of thermal ageing compared against high temperature neutron bombardment to assess the formation of detrimental phases in
2.5 - Creep testing Methods

Figure 2.14: Creep testing results of un-aged and aged P92, from Sakthivel et al. [105].

stainless steels [106]. Understanding the stability of solution elements, while exposed to high temperature is essential to predicting long term behaviour for plant usage. In this case, thermally aged specimens exhibited the formation of $M_{23}C_6$ precipitates while the irradiated specimens contained Laves phase, $M_{23}C_6$’s, and the detrimental $\eta$ phase (a complex particle consisting of Cr, Mo, Ni, Fe, Si associated with irradiation damage in austenitic steels). The $\eta$ phase absorption of Si and Ni reduces the austenite stability of the material further weakening it against creep [106]. These experiments highlight the benefit of this type of testing as the formation of $M_{23}C_6$’s during irradiation experiments can be attributed to the temperatures and not the irradiation processes.

2.5.4 Small ring creep testing

Small ring creep testing (SRCT) is a relatively new creep test method comprising of either a circular or elliptical ring of material loaded diametrically in tension [107,108]. The ring sample provides primary and secondary creep data, converted from the load line deformation of the sample, with analytical solutions for the deformation of the sample developed to convert the small ring data to equivalent uniaxial data [107]. A key benefit of this approach is the generation of bulk material data from a relatively small test specimen, thus minimising the cost of performing the tests. In fact, in later work, the same research group highlight that they generated 6 samples from a single aero-engine gas turbine blade [108]. This allows significant repeat testing which is essential for developing reliable time to failure models. The size of the sample in Figure 2.15 ensures that microscopic defects will be less influential on the overall tests results as there is a larger quantity of material being tested than in the
impression or small punch creep test methods.

![Typical specimen dimensions for the small ring creep specimen from Hyde et al. [108]](image)

Figure 2.15: Typical specimen dimensions for the small ring creep specimen from Hyde et al. [108]

However one of the limitations of this test methodology is that it does not result in tertiary creep. While useful, the small ring test does not provide the complete creep strain profile that would be obtained had a regular tensile test been carried out. It should be noted that many modern 9Cr based power plant materials do not exhibit a steady state creep behaviour, rather they exhibit a prolonged primary creep phase with a continually decreasing creep rate until the onset of tertiary creep, where the creep rate accelerates towards the end of the test as in Figure 2.16. Many predictive models require information on both the minimum creep strain rate (MSR) and the time to failure to be of use, e.g. the Monkman-Grant relation [109]:

\[
\dot{\varepsilon}_{\text{min}}^{\text{MG}} t_f = C_{\text{MG}} \quad (2.3)
\]

where \(\dot{\varepsilon}_{\text{min}}\) is the minimum creep strain-rate, \(m_{\text{MG}}\) is a constant usually in the range 0.8 - 0.95 [109], \(t_f\) is the time to failure in hours and \(C_{\text{MG}}\) is a temperature dependent material constant.

![Schematics of creep strain accumulation curves for older generation power plant materials in a) and modern 9Cr based materials in b).](image)

Figure 2.16: Schematics of creep strain accumulation curves for older generation power plant materials in a) and modern 9Cr based materials in b).
2.5.5 Impression Creep Testing

Similar to ring creep testing, impression creep testing provides information about the primary and secondary creep behaviour of a material. It consists of a flat faced indenter pressing into a small square sample with dimensions on the order of 10 mm × 10 mm × 2.5 mm, supported on a rigid platen. Figure 2.17 presents a schematic of an impression creep test set up and note that the sample and indenter are the same width. A reference stress based approach is utilised to convert the average indenter pressure to an equivalent uniaxial stress and the displacement rate to an equivalent steady state strain rate. The reference stress approach relates the loading conditions on the indenter face to a nominal stress, in this case the equivalent uniaxial stress by the inclusion of two apparatus dependent parameters.

![schematic of impression creep test set up](image)

Figure 2.17: Sample and indenter arrangement for a small specimen impression creep test, all dimensions in mm.

The conversion from applied load to equivalent uniaxial stress is:

\[
\sigma_{\text{uni}} = \eta_{\text{imp}} \bar{p}_{\text{imp}} \tag{2.4}
\]

where \( \sigma_{\text{uni}} \) is the equivalent uniaxial stress, \( \eta_{\text{imp}} \) is an experimentally determined constant and \( \bar{p}_{\text{imp}} \) is the average indenter pressure equal to \( F_{\text{imp}}/(w_{\text{imp}}d_{\text{imp}}) \). The displacement to strain rate conversion is given as:

\[
\dot{\varepsilon}_{\text{cr ss}} = \frac{\dot{\Delta}_{\text{imp ss}}}{\beta_{\text{imp}} w_{\text{imp}}} \tag{2.5}
\]

where \( \dot{\varepsilon}_{\text{cr ss}} \) is the equivalent secondary creep rate, \( \dot{\Delta}_{\text{imp ss}} \) is the indenter displacement rate into the sample, \( \beta_{\text{imp}} \) is an experimentally determined constant and \( w_{\text{imp}} \) is the indenter width. This reference stress approach is relevant to materials which obey the Norton creep behaviour (see Section 2.10) and, for a 9Cr steel under high stress
laboratory conditions, the near vertical data set of Figure 2.2 obeys this behaviour. Provided the testing is performed at stress levels away from the transition region, e.g. around 100 MPa for 9Cr steels, this is a reasonable assumption for this material. A detailed description of this reference stress approach is available in the literature [110–112]. Evidently, low stress testing would be required to identify $\eta_{imp}$ and $\beta_{imp}$ for the low stress regime, limiting the usefulness of this due to the requirement for much longer test times. However, for the evaluation of steady state creep behaviour, this approach has proved useful by Hyde et al. [113] for the testing of heat affected zone material.

### 2.5.6 Small Punch Creep Testing

The small punch creep SPC test methodology utilises a spherical or hemispherical indenter to apply a constant load to a thin disk sample, creep deformation of the disk occurs leading to rupture failure. A smaller sized sample than either the ring or impression creep tests is required for a small punch creep test (SPCT). Here the specimen is 0.5 mm thick with a recommended diameter of 8 mm [114]. The apparatus set up is shown in Figure 2.18. An agreement on the general design principals and analysis methods for assessing SPCT data was developed in to 2006, titled: ”Small Punch Test Methods for Metallic Materials”. The report was intended as a first step to developing a standardised SPCT methodology in Europe [114].

![Figure 2.18: Sample, spherical indenter and die arrangement in a small punch creep test apparatus.](image)

The displacement-time curves from this type of test closely resemble the creep strain-time curves of traditional tensile testing [115], containing primary, secondary and...
tertiary creep. Of the small specimen test methodologies reviewed, this approach is the only one which produces tertiary creep or rupture data [114].

Samples can be removed from a component plant utilising a scoop sample extraction tool developed by Rolls Royce [116], a considerable benefit to this approach as entire components do not have to be removed to manufacture samples. A cup shaped cutter, which rotates along its central axis and around a perpendicular axis, removes a sample of material from a larger component, minimising the damage to the component and removing the requirement to shut down the plant for long periods to perform a remnant life assessment. A schematic of this type of cutter is provided in Figure 2.19. From this scoop of component material either impression or small punch creep samples can be manufactured. The SPC test apparatus is a relatively simple design and can be manufactured at reasonably low cost, according to Hyde et al. [107]. The equivalent grain length (EGL) for the SPCT should be on the order of 5 mm, based on the perimeter of the annular region in which failure occurs during SPC tests. For a different indenter or receiving hole diameter, the EGL will be different and, as such the value of 5 mm is an estimate at best. There are some challenges with this test methodology such as i) disk bending while primary creep occurs in the initial phase of testing and ii) conversion of the test load to an equivalent stress. During the initial load application, the disk deforms plastically in parallel with the primary creep phase. As such identifying the deformation due to plasticity during loading and primary creep is challenging.

The small punch testing of thin disks was originally developed for estimation of brittle to ductile transition temperature from components in service [117, 118]. Following on from this work, the test method was utilised to determine fracture toughness and the degradation of coatings [119]. The Monkman-Grant relationship (Equation 2.3)
between minimum creep rate (MCR) and time to failure was modified by Alegre et al. [120] for SPC test results, building on the work of Dobeš et al. [121]. Dobeš et al. demonstrated that a more accurate fit to experimental data could be achieved by:

\[
\frac{(\dot{\varepsilon}_{\text{cr}}^{\text{min}})^{m_{\text{MMG}}}}{\varepsilon_f} t_f = C_{\text{MMG}}
\]

(2.6)

where the original Monkman-Grant constant is divided by the creep strain at failure. The constants all hold their original meanings from Equation 2.3. However the constants will obviously have different values for the same input data and as such, they are denoted with the MMG subscript for Modified-Monkman-Grant model. This model has been recast using the steady state displacement rate and displacement at failure for SPCT purposes by Alegre et al. [120].

\[
t_f (\dot{\Delta}_{\text{ss}}^{\text{spc}})^{m_{\text{MMG}}} = C_{\text{MMG}}^{\text{sp}}
\]

(2.7)

Here \(\dot{\Delta}_{\text{ss}}^{\text{spc}}\) is the small punch steady state displacement rate, \(m_{\text{MMG}}\) was assumed to be 1 by Alegre et al. [120], and \(C_{\text{MMG}}^{\text{sp}}\) is the small punch creep modified-Monkman-Grant material constant. Assuming the exponent to have a value of unity is reasonable based on the values between 0.95 and 1.01 identified by Dobeš et al. [118] and Povolo [122] for a variety of materials and temperatures.

**SPCT analytical model**

The stress variation through the thickness of a thin disk specimen during small punch creep testing can be quite large. As such, identifying a single stress value for the disk has required the use of reference stress based approaches. Unlike the flat indenter where the contact area remains constant, the contact area between the punch and the sample increases over the duration of an SPC test [115]. Figure 2.20 shows the geometry utilised for the identification of the relationship between applied load and membrane stress developed with the relevant geometric features.
2.5 - Creep testing Methods

Figure 2.20: Reproduction of the membrane stretch forming over a hemispherical punch utilised by Chakrabarty to relate applied load to membrane stress [114,123].

An analytical solution to convert the applied load on the punch to a membrane stress in the disk thickness was developed by Chakrabarty et al. [123], based on membrane stretch forming over a hemispherical punch. The model neglects the bending stresses which initially provide the majority of the load resistance. This assumption is justified as these are quickly overcome by the membrane stress and, during steady state creep, the bending stresses are considered negligible [114]. Based on the geometry of Figure 2.20 the Chakrabarty formulation defines the membrane stress as [123]:

\[
\sigma_{\text{mem}} = \frac{F_{\text{SPCT}}}{2\pi hr \sin^2 \theta_0} 
\]

(2.8)

\[
h_{\text{SPCT}} = h_0 \left( \frac{1 + \cos \theta_0}{1 + \cos \theta} \right)^2 
\]

(2.9)

where \(\sigma_{\text{mem}}\) is the membrane stress, \(F_{\text{SPCT}}\) is the punch force, \(h_{\text{SPCT}}\) is the sample thickness at the contact boundary, \(r\) is the radius of the punch, \(\theta_0\) is the angle \(\varphi\) at the contact boundary with \((\theta_0 = \varphi_{\text{max}})\). \(\varphi\) is the angle made by the surface normal with the vertical axis and \(\theta\) is the angle \(\varphi\) at \(d = R\), \(R\) being the distance to the clamp edge from the centre of the punch. The central displacement of the punch \(u_1\) is defined as:

\[
u_1 = R \sin \theta \ln \left( \frac{\tan (\theta_0/2)}{\tan (\theta/2)} \right) + r(1 - \cos \theta_0)
\]

(2.10)

The relationship between \(\theta\) and \(\theta_0\) is

\[
\sin \theta = \frac{r}{R} \sin^2 \theta_0 
\]

(2.11)
Based on the regression analysis of Yang et al. [124] and the results of the round robin testing program performed by Bicego et al. [125], a general relationship between Equations 2.10 and 2.11 was developed. The general form is as follows:

\[
\frac{F_{SPCT}}{\sigma_{mem}} = b_1 R^{b_2} r^{b_3} h_0
\]  

(2.12)

Taking logarithms of both sides, gives:

\[
\log \left( \frac{F_{SPCT}}{\sigma_{mem}} \right) - \log (h_0) = \log (b_1) + b_2 \log (R) + b_3 \log (r)
\]  

(2.13)

Multi-variable least squares fitting was applied with the following physical bounds, based on the geometries of SPCT equipment in use; \(0^\circ \geq \theta_0 \geq 90^\circ\), \(2 \geq R \geq 3\) mm and \(1 \geq r \geq 1.5\) mm. This gives the generalised form of the relation between applied punch force and membrane stress as:

\[
\frac{F_{SPCT}}{\sigma_{mem}} = 3.333 R^{-0.202} r^{1.192} h_0
\]  

(2.14)

The authors then round the indices and include a correlation factor, to account for differing creep ductilities of materials or for differing ductility of the same material at different temperatures and stresses. The recommended relation from the CEN standard is as follows [114]:

\[
\frac{F_{SPCT}}{\sigma_{mem}} = 3.33 K_{sp} R^{-0.2} r^{1.2} h_0
\]  

(2.15)

The identification of the \(K_{sp}\) value is based on comparisons with uniaxial test data, the CEN document recommends that five repeat SPC tests should be performed at a given temperature. The requirement for a comparison with a uniaxial test of the same material undermines the primary benefit of the small punch approach. The basis for the inclusion of the \(K_{sp}\) term in the CEN agreement was to account for materials with differing ductilities at different temperatures. Here, testing is to be performed at a set temperature for a single material type. As such, the \(K_{sp}\) parameter will be maintained at a value of unity.

Hyde et al. [108] have developed a measure they refer to as EGL for comparing differing small scale test methods with the uniaxial full scale test. EGL measures for the test methods discussed in this section are presented in Table 2.5 for comparison. The impression and small punch EGL’s are based on the geometry of the indenter.
and the perimeter of the rupture surface. The EGL for the SPCT approach has not been related to the geometry of the test method, however the nominal stress defined by Hyde et al. [108] does not rely on any additional parameters outside of the geometry of the indenter and the sample. The Chakrabarty approach is a robust method for converting between the applied load and the membrane stress in the sample, which can be compared against tensile data.

Table 2.5: Comparison of equivalent gauge lengths for various small specimen creep tests, from [107], where the standard uniaxial length is given in Figure 2.13

<table>
<thead>
<tr>
<th>Geometry</th>
<th>$\sigma_{\text{nom}}$ (mm)</th>
<th>EGL (mm)</th>
<th>Dimensions</th>
</tr>
</thead>
</table>
| Ring         | $\frac{F_{\text{RSCT}} R_{\text{SRCT}}}{b_d d_{\text{SRCT}}^{2}}$ | $4R_{\text{SRCT}}^{2} \frac{b_{\text{SRCT}} d_{\text{SRCT}}}{d_{\text{SRCT}}}$ | $R_{\text{SRCT}} = 6$ mm  
$b_{\text{SRCT}} = 2$ mm  
$d_{\text{SRCT}} = 1$ mm  
$\beta_{\text{SRCT}} = 0.488$ |
| Impression   | $\frac{F_{\text{imp}}}{w_{\text{imp}} d_{\text{imp}}}$ | $\sim 2d_{\text{imp}}$ | $w_{\text{imp}} \sim 10$ mm  
$d_{\text{imp}} \sim 1$ mm  
$\beta_{\text{imp}} \sim 2$ mm |
| Small punch  | $\frac{F_{\text{SPCT}}}{2\pi R_{\text{ho}}}$ | $\sim 5$ | $R_{\text{SPCT}} = 1$ mm  
$h_{\text{ho}} = 0.5$ mm |

2.6 Micro-mechanical testing

Micro-mechanical testing holds the promise of extracting large quantities of micro- and macro-scale properties from small quantities of materials, either by indentation based methods using micro- or nano-hardness testing or by conducting miniaturised bending tests on micro-sized beams. The simplest of these is the micro-hardness test, in which the applied forces are far lower (0.01 N to 0.1 N) than for the standard Vickers test (50 N to 980 N) [?126].

At a smaller scale, nano-hardness indentation is also possible which allows the characterisation of block boundary strengthening in a high purity Fe-C alloy [127]. The micro-sized cantilever bend method is also discussed in relation to characterising the sub-grain boundary strengthening effect in 9Cr materials [128].


2.6.1 Micro-hardness testing

Vickers hardness testing was developed for materials with high hardesses, operating across a wider range of hardesses than the Brinell approach with a simpler conversion from indent size to hardness value [129]. Micro-hardness testing uses the same approach as standard hardness testing although it operates at lower loads with a smaller indenter [130]. The work hardening behaviour of the material and the load applied can affect the micro-hardness measurements [131,132]. Hardness values from the Vickers test are calculated based on the load applied and the surface area of the indentation [126]:

\[
\text{Hardness} = 0.1891 \times \frac{F_{\mu H}}{d_H^2}
\]  

(2.16)

where \(F_{\mu H}\) is the indenter load applied in N, and \(d_H\) is the mean of the two diagonal lengths of the diamond shaped indentation. Siefert et al. [133] examined Vickers hardness testing for the 9Cr family of steels. In particular they focused on the mapping of regions suspected of having variations in hardness. They identified an idealised load and spacing distance for generating hardness maps, 0.2 kg with a spacing of 1.6\(d_H\), respectively.

Hardness has been suggested as an indicator of material condition for 9Cr steels for in-situ component remnant life estimations [134]. However, to date there has been no definitive, physically-based explanation of the exact nature of the relationship between material condition and hardness [60,135]. Due to the complex microstructural evolutions which occur during creep in 9Cr steels, linking hardness to a specific mechanism of degradation has proved challenging. For example considering the heat treatment of 9Cr steels, changes in hardness can be attributed to precipitate volume fraction, dislocation density, lath martensite formation and grain size, many of which also evolve over time during creep exposure.

One of the most widely used applications of Vickers hardness testing is for the estimation of yield stress, developed by Tabor [136].

\[
H_v = c_y \sigma_y
\]  

(2.17)

where \(c_y\) has a value of around 3, and \(\sigma_y\) is the yield stress. Busby et al. [137], for example, identified values of 3.03 and 3.06 for irradiated ferritic and austenitic steels, respectively for \(c_y\). Zhang et al. [131] focused on the relationship between hardness and yield stress for work hardening materials (similar to those considered
by Tabor [136]), bulk metallic glasses (BMGs), coarse grained or ultra-fine grained materials, brittle BMG’s and ceramics. Of interest to this work is their observation of two distinct indentation types: "pile-up" or "sink-in" behaviours, for metallic materials.

The sink-in behaviour occurs when material near the indenter experiences hardening by plastic deformation, where ductile coarse grained materials exhibit this behaviour. Through further load application, the indenter extends the region of hardened material to a relatively large range around the indentation. This behaviour is characterised by the indentation mark edges bowing inward toward the centre of the indent and the presence of slip bands.

The pile-up type behaviour is characterised by plastic deformation being concentrated near the indenter tip. This indent shape is generated when obstacles in the material prevent dislocation movement through the material. The material near the indenter is continuously hardened during the indentation procedure but this plastically deformed region does induce further plasticity at greater distances from the indent. Zhang et al. [131] state that materials exhibiting the pile-up behaviour can be said to obey the Busby [137] type relationship between hardness and yield stress. Material exhibiting the pile-up type effect are fully hardened and this relationship represents an intrinsic material property. However, for material exhibiting the sink-in behaviour, the Busby approach to calculating yield stress from hardness is less reliable as it relates to a partially hardened state of the material, dependent on the load applied and, as such, is not an intrinsic material property.

Hardness testing has been employed by the power generation industry to evaluate the remaining lives of components for some time, as creep induced microstructural evolution softens the material [138,139]. Bhadeshia et al. [134] highlight that hardness information is only of use when detailed measurements are made prior to component installation and during secondary creep, as hardness does not relate easily to creep cavitation damage. More recently, a direct relationship between the hardness ratio (initial pre-creep $H_0$, over current $H'$) to the life fraction, for a modified 9Cr steel, was developed by Masuyama [135] through the following relationship.

$$\frac{H'}{H_0} = 0.98 - 0.15\frac{t}{t_r}$$  \hspace{1cm} (2.18)

where $t$ is the current creep exposure time and $t_r$ is the creep failure or rupture time. This method requires that the hardness measures should be made before a
component is put into service and is not traditionally part of pre-installation testing. As such, moving forward, this approach may be of use for newly installed components only.

2.6.2 Micro-cantilever testing

Micro-cantilever bending was developed for the semi-conductor industry to measure the Young’s modulus of extremely thin films [140,141]. This early work depended on selective etching to manufacture the beams and/or evaporation techniques to produce the required specimens. The introduction of focused ion-beam milling systems allowed a more traditional manufacturing approach to be applied, albeit at the micron scale. Much work to date, has focused on the behaviour of beams manufactured from single crystal copper [142–145]. Armstrong et al. [142] measured the effect of crystal orientation on the Young’s modulus extracted from the micro-cantilever results and obtained values in close agreement with bulk copper results.

The size effect on micro-cantilever behaviour has been examined in the work of Ding et al. [146]. Here an increase in rupture strength of polysilicon beams is related directly to increasing the surface-to-volume ratio of the beams. Motz et al. [143] highlight an increase in flow stress from 250 MPa to 1000 MPa for a thickness reduction from 7.5 µm to 1.0 µm for beams 20 to 25 µm long. Highlighted by Armstrong et al. [142] and Kiener et al. [145] is the requirement to have an aspect ratio (loaded length:width) of greater than 6 for the use of simple beam theory with an encastré end condition.

Robertson et al. [147] observed decreasing Young’s modulus with decreasing beam cross-sectional dimensions for silicon-carbide (SiC) micro-cantilever beams. This is attributed to gallium ion implantation damage occurring during manufacture. They also noted that their Young’s modulus values were above the values expected for SiC. This attributed to plastic deformation occurring in beams with a cross-section of 0.3 µm × 0.3 µm under high stress loading conditions. They propose that small deflection equations were unable to account for the plasticity observed and thus overestimated the Young’s modulus for those tests.

2.7 Microstructural Evolution During Creep

The following section focuses on the mechanisms of microstructural evolution during high temperature creep exposure. Long term deformation of early alloys was
relatively straightforward to predict based on experimental testing but, as the complexity of alloying increased, the nano- and micro-scale deformation mechanisms also increase in complexity.

### 2.7.1 Evolution of Precipitates

Second phase particles or precipitates provide obstacles to dislocation motion through the material. The normalisation dissolves all precipitates into the matrix, providing excess carbon for a martensitic transformation. During tempering, element diffusion through the matrix allows alloying elements to form secondary phase particles and longer term ageing allows spheroidizing to occur, leading to carbides and other precipitates forming. The fundamental process affecting precipitates during creep is the coarsening of individual precipitates, which has a concomitant effect of dissolving the smallest precipitates in favour of larger precipitates, increasing the average spacing between any given set of precipitates.

This mechanism is known as Ostwald ripening [148, 149] and, within a two phase system containing a matrix phase and dispersed second phase, thermodynamic equilibrium is always sought by the system. The governing factor is interfacial energy between the particle and the matrix [30, 148, 149]. The equation describing particle coarsening due to temperature exposure is:

\[
d = (d_0^3 + K_{Ost}t)^{1/3}
\]

where \(d\) is the current particle diameter, \(d_0\) is the initial precipitate diameter after tempering and \(K_{Ost}\) is the temperature dependent thermal coarsening rate for a particular precipitate type. Umantsev et al. [150] and Ágren et al. [151] expanded on the original work of Lifshitz et al. [148] and Vorhees et al. [149] to calculate the coarsening rate for multi-component systems, i.e., complex precipitates such as \(M_{23}C_6\)s and MXs. This results in the following equation for the coarsening rate of a carbon component system of \(\beta\) precipitates in an \(\alpha\) matrix:

\[
K_{Ost} = \frac{8}{9C} \frac{\gamma V_M^{\beta}}{\sum_{i=1}^{C} \frac{(x_i^\beta - x_{\alpha/\beta}^i)^2}{x_i^{\alpha/\beta} D_i/RT}}
\]

Here \(V_M^{\beta}\) is precipitate phase molar volume, \(x_i^\beta\) is the mole fraction of element \(i\) in the precipitate, \(x_{\alpha/\beta}^i\) is the mole fraction of element \(i\) at the precipitate/matrix interface,
$D_i$ is the diffusion coefficient of element $i$ in the matrix, see Table 2.4 for details. Hald et al. [30] state that the interface curvature has little effect on equilibrium solubilities for this approach, and the calculations of $x^{\alpha/\beta}$ were performed for a flat matrix/precipitate interface. This approximation holds, provided the precipitate in question, is significantly larger than the matrix atoms surrounding it. When considering diffusion from a single plane of matrix atoms into a spherical precipitate, the boundary between the two is effectively flat. Given the measurements of initial precipitate diameters as being in the tens of nanometre range, this is an appropriate assumption. The remaining unknown for this equation is the interface energy $\gamma$. Hald et al. [152] utilised this parameter as a fitting tool for comparison with their experimental data. Calculated coarsening rate values from this approach are reproduced in Table 2.6 for the P92 and P91 materials. The values of interface energy varied from 0.3 to 1 J/m², showing the relative insensitivity of the coarsening parameters to this variable in Equation 2.20. Table 2.6 is arranged by increasing coarsening rate and from this work we have a physical basis for the behaviour of precipitates due to exposure to heat.

Table 2.6: Precipitate coarsening values calculated by Hald et al. [152] for MX, $M_{23}C_6$ and Laves phase particles. See Table 2.3 for precipitate compositions.

<table>
<thead>
<tr>
<th>Precipitate</th>
<th>Steel</th>
<th>$T$ (°C)</th>
<th>$K_p$ (mm³ hr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MX</td>
<td>P92</td>
<td>600</td>
<td>3.09×10⁻²⁰</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650</td>
<td>2.36×10⁻¹⁹</td>
</tr>
<tr>
<td>Laves phase</td>
<td>P92</td>
<td>600</td>
<td>1.05×10⁻¹⁸</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650</td>
<td>1.50×10⁻¹⁷</td>
</tr>
<tr>
<td>$M_{23}C_6$</td>
<td>P92</td>
<td>600</td>
<td>6.84×10⁻¹⁹</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650</td>
<td>1.72×10⁻¹⁷</td>
</tr>
<tr>
<td></td>
<td>P91</td>
<td>600</td>
<td>2.76×10⁻¹⁷</td>
</tr>
<tr>
<td></td>
<td></td>
<td>650</td>
<td>2.15×10⁻¹⁶</td>
</tr>
</tbody>
</table>

Strain induced coarsening has been observed by Taneike et al. [104], within a 12Cr material for MX precipitates (Nb(C,N), V(C,N) and Ta(C,N)). The observed en-
hanced coarsening within the gauge length did not correlate with a purely thermally activated coarsening mechanism. The Ostwald ripening approach, outlined above, was modified with an additional diffusion term correlating with both time and creep strain exposure that captured the observed enhanced coarsening within the gauge length. Similar trends for M$_{23}$C$_{6}$ have been observed by Hättestrand et al. [76] in 9Cr steels, and based on this, the Ostwald coarsening rate can be adjusted as follows:

$$d = (d_0^3 + K_{Ost} t + \phi_k \varepsilon^{cr})^{1/3}$$  \hspace{1cm} (2.21)

$\varepsilon^{cr}$ being the accumulated creep strain and $\phi_k$ is the effective strain-induced coarsening rate. Hättestrand et al. [76] also reported increased Laves phase diameters in the crept samples over the thermally aged samples. Clearly strain accumulation affects all the precipitates to varying degrees in these materials.

### 2.7.2 Depletion of solutes

Precipitate growth is fuelled by solute atom diffusion from the matrix into the precipitates and by preferential growth of larger precipitates at the expense of the smaller precipitates. Here the focus is on solute depletion, which is particularly important for the Laves phase precipitates, as it initially provides additional strengthening by decreasing the average particle spacing. However the rapid coarsening of the Laves phase particles removes the additional benefit due to the larger diameters achieved by the intermetallic phase. This loss of strength is also coupled with a loss of the Mo or W solid solution strengthening due to the laves phase formation. Kipelova et al. [153] measured the evolution of Laves phase in creep tested P911 steels, with the maximum diameters reaching 400 nm, well above an effective creep strengthening size. Laves phase growth is driven by the diffusion of Fe, Cr, Mo (all 9Cr steels) and W (P92, MarBN only) from the matrix into new precipitates. Abe et al. [154] compared two steels with and without W solid solution strengthening. In the W free material, failure occurred after 1152 hours with an MSR of $2.46 \times 10^{-6}$ hr$^{-1}$, while the W containing material failed after 4239 hours with an MSR of $6.76 \times 10^{-7}$ hr$^{-1}$.

W solute atoms can strongly influence the creep behaviour as evidenced by the data discussed above. Based on the atomic radii of the common alloying elements, similar effects can be expected from the removal of Mo. However these elements are primarily utilised in the formation of precipitates, although some will remain in the matrix as solute strengthening. Table 2.7 shows the atomic radii for common alloying elements and some tramp elements commonly found in 9Cr steels. Generally
for substitutonal strengthening, the greater the difference in atomic radii the larger the effect is [62].

Table 2.7: Atomic radii of common alloying elements and the % difference with iron.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic radii (Å)</th>
<th>% Difference with Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.56</td>
<td>0</td>
</tr>
<tr>
<td>Al</td>
<td>1.18</td>
<td>-24</td>
</tr>
<tr>
<td>B</td>
<td>0.87</td>
<td>-44</td>
</tr>
<tr>
<td>C</td>
<td>0.67</td>
<td>-57</td>
</tr>
<tr>
<td>Co</td>
<td>1.52</td>
<td>-3</td>
</tr>
<tr>
<td>Cr</td>
<td>1.66</td>
<td>6</td>
</tr>
<tr>
<td>Cu</td>
<td>1.45</td>
<td>-7</td>
</tr>
<tr>
<td>Mo</td>
<td>1.90</td>
<td>22</td>
</tr>
<tr>
<td>N</td>
<td>0.56</td>
<td>-64</td>
</tr>
<tr>
<td>Nb</td>
<td>1.98</td>
<td>27</td>
</tr>
<tr>
<td>P</td>
<td>0.98</td>
<td>-37</td>
</tr>
<tr>
<td>S</td>
<td>0.88</td>
<td>-44</td>
</tr>
<tr>
<td>Si</td>
<td>1.11</td>
<td>-29</td>
</tr>
<tr>
<td>V</td>
<td>1.71</td>
<td>10</td>
</tr>
<tr>
<td>W</td>
<td>1.93</td>
<td>24</td>
</tr>
</tbody>
</table>

2.7.3 Sub-grain recovery

The loss of martensitic lath structure is also referred to in the literature as sub-grain recovery and describes, the process of LAB annihilation due to dislocation-dislocation interactions driven by strain and temperature application. Coupled with this process is the decrease in the particle pinning effect due to precipitate coarsening. As the number of precipitates located on lath boundaries decreases, sub-grain recovery can occur more easily [154]. Immobile dislocation annihilation is a separate damage mechanism where the pile-up of dislocations can reduce the overall immobile dislocation density. Without the presence of precipitates to pin lath boundaries, which are simply regions of high dislocation density, dislocation hardening cannot occur. This effect was observed by Maruyama et al. [155] and Nishimura et al. [156], based on
comparisons between bainitic and ferritic steels with and without secondary phase particles present.

Cerri et al. [49] observed sub-grain coarsening during creep testing of a 9Cr-1Mo material, and identified an empirical correlation between the sub-grain size at rupture with the inverse modulus compensated stress \( (\sigma_{\text{uni}}/E) \) of the following form:

\[
    w_{sg} \approx C_{\text{cer}} b \left( \frac{\sigma_{\text{uni}}}{E} \right)^{-P_{\text{cer}}}
\]  

(2.22)

where \( C_{\text{cer}} \) is a material constant, evaluated in their work as 1.39, \( w_{sg} \) is the sub-grain size at rupture and \( P_{\text{cer}} \) is a material constant weakly dependent on material and temperature, identified here as 1.09 and \( E \) is the Young’s modulus. While this approach allows a relation to be generated for the sub-grain size at failure with the flow stress applied, it is less useful for quantifying the rate at which sub-grains are recovered.

### 2.7.4 Dislocations

Due to the application of strain, dislocations migrate through the material and pile-up at microstructural boundaries and this is enhanced with increasing temperature. Dislocations can glide through the material along the slip planes until they reach an obstacle, e.g. a large solute atom or precipitate. At this point, a dislocation can glide no further, however they can climb. Dislocation climb is facilitated by the diffusion of vacancies through the crystal to the obstacle and the dislocation then overcomes the obstacle, moving into the vacancy position and can then continue to glide along the new slip plane, Figure 2.21. By this mechanism, dislocation climb is controlled by the rate of vacancy diffusion through the crystal, which is heavily temperature-dependent. Taylor hardening is the process of mobile dislocations becoming immobile, thus decreasing the ability of materials to deform. The Taylor model for the contribution of dislocation immobilisation to shear stress is:

\[
    \tau_{\rho} = \alpha_1 \mu b \sqrt{\rho}
\]  

(2.23)

where \( \alpha_1 \) is a material constant, \( \mu \) is the temperature dependent shear modulus and \( \rho \) is dislocation density. Dislocation pile-up and immobilisation predominantly affects the primary phase of creep in 9Cr steels. The rapid deceleration in creep rate is a function of increasing immobile dislocation density compared with suppressed mobile dislocation generation. During the secondary creep phase, these two mecha-
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Figure 2.21: a) dislocation pinned by substitutional solute atom, b) vacancy diffusion to solute location and c) dislocation continues to glide on new slip plane.

Dislocation densities for 9Cr steels are in the $1.5 \times 10^{14}$ m$^{-2}$ to $7.5 \times 10^{14}$ m$^{-2}$ range [15,157,158], which accounts for both mobile and immobile dislocations. The majority of these dislocations are found in the lath boundaries with lath interior density being considerably lower [159] or devoid of any dislocations [160]. For a 12Cr material, the dislocation densities, prior to and post creep testing at 120 MPa and 550 °C and thermal ageing at the same temperature, were measured by Pešićka et al. [161]. The observed initial dislocation density was $1.02 \times 10^{14}$ m$^{-2}$ in the martensitic ferritic steel, with a factor of two reduction occurring during thermal ageing. For the crept specimen, they recorded an order of magnitude decrease to $1.16 \times 10^{13}$ m$^{-2}$, with continued long term creep reducing the density to $6.8 \times 10^{12}$ m$^{-2}$. Prior to ageing, considerable inhomogeneity is observed due to the lath martensite structure. However afterwards, a more homogeneous distribution was observed. For 9Cr materials creep for 100,000 hours at 600 °C under a stress of 80 MPa, Panait et al. [96] observed a decrease in dislocation density from $4.5 \times 10^{14}$ m$^{-2}$ to $2.2 \times 10^{14}$ m$^{-2}$ and $1.8 \times 10^{14}$ m$^{-2}$ for the head (thermally aged) and gauge sections, respectively.

A decrease in dislocation density represents a loss of plastic deformation transmission mechanism due to the balancing of dislocation generation and loss mechanisms. The recovery of sub-grains from laths, reduces the boundary density, decreasing creep resistance and increasing the effective grain size. This causes an increase in the strain accumulation leading to failure.
2.7.5 Oxidation

Oxidation during creep generates additional stresses at the surfaces of components exposed to harsh environments, such as superheater tubes utilised for steam generation. This is even more important for the Irish context, where some power plants are combusting peat which produces highly corrosive by-products [11, 162]. Oxygen combines with iron to form multiple forms of scale, such as hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) which can then spall or break off from the component, exposing fresh material to the corrosive atmosphere.

While oxides are forming at the surface, base material adjacent to the oxide layer can become depleted of strengthening elements, e.g. decarburisation can occur. Baud et al. [72] observed this phenomenon in an Fe-0.5C wt.% material at 700 °C and 735 °C and where they attributed the poor scale adherence to the presence of cementite precipitates.

Sawada et al. [69] compared T23 (2.25Cr-1.6W-V-Nb) materials crept at 625 and 650 °C in both air and helium environments. The T23 material is low-Cr, bainitic steel for USC power plant applications. At 625 °C, the samples crept in helium had comparable time to failure values with the in-air samples. For 650 °C, the samples crept in helium did not exhibit the abrupt drop in time to rupture that the in-air samples did, Figure 2.22. Oxide scale formation at 650 °C, contributed significantly to creep failure, with this effect becoming worse for longer exposure times, at lower stresses. The bainitic structure was observed to recover, causing softening of the material with increasing rupture time. The decrease in creep life was not correlated with the formation of oxide scale, rather they pointed to the possible loss of strengthening precipitates at higher temperatures.

![Figure 2.22: Rupture strength comparison of T23 sample crept in air and helium environments [69]](image)
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O’Hagan et al. [163] examined the effect of oxide formation on P91 super heater tubes based on thermal ageing experiments with synthetic salts of the same composition as flue ash found in Irish power plants. Multiple oxide layers formed and detached from the P91 as shown in Figure 2.23. Here, three types of oxide can be seen to have formed during the salt exposure thermal ageing experiments performed by O’Hagan et al. [163]. While not the same as creep specimens exposed to high temperature air these samples provide an indication of the type of oxide formation which can affect these materials. The hematite, magnetite layer has spalled off in Figure 2.23a with some Cr oxide mixed with it in the ”mixed oxide” layer, which is separated from the substrate completely.

![Figure 2.23: The iron-oxide layer is shown in a) with the chromium oxide is adhered to the substrate in b) with the oxygen dispersion through the various other oxides highlighted in c).](image)

The formation of oxides will reduce the effective stress resisting section of any given tensile specimen or piping component, increasing the stress levels within the remaining material. The oxide crack regions can provide initiation points for further cracking behaviour due to loading effects, such as cavitation damage.

### 2.7.6 Cavitation

The primary creep failure mode observed within plant components is cavitation induced failure due to the coalescence of individual crystal vacancies into larger voids, see Figure 2.4. This mechanism can be simulated using the Kachanov type damage model [164]. Crystal vacancies are an unavoidable fact of manufacturing metallic components. Other material alloying effects can lead to enhanced cavitation damage. Oversized precipitates can cause additional cavitation as observed by Tanieke et al. [165], who estimated that precipitates above 250 nm in diameter cause enhanced cavitation to occur in their vicinity.
Cane [52] identified the connection between cavity growth and the stress state of a material at any given grain boundary by examining a theoretical grain boundary with no precipitates present. The precipitate free material at the grain boundary promoted stable cavities and enhanced cavitation growth rate due to the differing strain rates between the precipitate containing matrix and the precipitate free grain boundary. This effect has been examined by Watanabe et al. [53] for a P91 weldment, where failure occurred in the heat affected zone adjacent to the parent material. They performed numerical creep simulations to estimate the stress distributions through the weld thickness. The creep failed weld is shown in Figure 2.24, where the cavities can be observed with increasing concentration near the failure location. The prediction of stress triaxiality concentration at the location of highest cavitation is shown in Figure 2.25. The inflection point between the two straight weld regions caused high levels of stress triaxiality to occur, accelerating the cavitation rate at this point.

Figure 2.24: Optical microscopy of a Type IV crack profile for a welded tensile creep test performed at 600 °C under a stress of 80 MPa [53].

2.8 Scatter in creep results

Repeatability of experimental results is essential to demonstrating material quality. Obviously, good control of the test conditions is also required. There is considerable scatter in the creep test data available for power generation materials and several historic and current material data sets are compared in this section to highlight this issue. All data was taken from the freely available National Institute of Material
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Figure 2.25: Finite element model predictions of the stress triaxiality within a welded 9Cr test specimen, from Watanabe et al. [53].

Science in Japan (NIMS) website, as they have amassed a large creep rupture time database at numerous temperatures for a variety of creep strong materials.

Figure 2.26: Creep time to failure data for four different creep resistant steels, demonstrating the scatter in failure times for each at varying temperatures, all data from NIMS [166].

For almost any given stress in each of the plots of Figure 2.26 a range of failure times have been observed. Although general trends are evident, there are few cases of
multiple results overlapping each other for a given test condition. The scatter in these results can be attributed to a number of factors; (i) variations in the composition (ii) variations in the heat treatments or (iii) temperature control of the experiment. Each of these factors can have significant effects on the microstructure of the material, which will directly affect the creep lives of a component. The most heavily studied material in Figure 2.26 is the 9Cr material and narrower scatter bands are observed here. However, given that the failure times are on log scales, there is frequently an order of magnitude scatter in the results for a given stress level.

Repeat testing at any stress level is cost and time prohibitive and, as such, microstructure-based models are under development in an attempt to predict this scatter in the test results for different material variations in heat treatment and composition. However, to make the utmost use of the results above, details on the precise composition, heat treatment, precipitates, laths and dislocation densities would be required to accurately correlate the test results to trends and variations in microstructural features. The manufacturing standards for the 9Cr materials have wide bands for the composition, as an example of the ”allowable” variations present for materials which fall under the P91 and P92 steel categories [34] (see Table 2.2).

The precipitate forming elements; Al, B, Cr, Mo, N, W and V will all directly affect the quantities and size distributions of precipitates during the manufacturing process. They will affect the lath martensite structure formed and, hence, will modify the creep performance and rupture life. A particularly detrimental element is Al, which forms AlN precipitates, at the expense of MX nitrides and severely decreasing the creep life of components manufactured from same [103]. Al was added to the 9Cr materials to improve their toughness [167]. Magnusson et al [168] examined the effect of Al concentration on the creep behaviour of the 9Cr steels. The offending alloy became known in the UK as Bar 257 material with an Al concentration of 0.028 wt.%. They modelled the concentration of MXs with increasing Al content in the material using ThermoCalc thermodynamic software and the results are summarised below in Figure 2.27. With increasing Al content comes a decrease in the MX precipitates and this results in a significant reduction in creep life. Hyde et al. [103] creep tested this material extensively at 650 °C to quantify the loss of creep strength when compared with standard P91.
Minor alterations in the Al content of the steel drastically change the composition of the MX precipitates and also the accelerated coarsening of the AlN precipitate during creep removes a key strengthening mechanism against creep deformation. Given that the MX precipitates largely do not increase significantly in diameter, any deviation from this general behaviour diminishes the creep rupture life. The ASTM standards for P91 were updated in 2006 to reflect the learnings from the research into Al effects on MX precipitates. The original maximum allowable limit for Al content was 0.04 wt.% [169]. In the 2006 version of the ASTM A335/A335M standard on ferritic steels for high temperatures, the Al limit was set to 0.02 wt.% [170].

The scatter observed in the data presented in Figure 2.26 should always be considered when performing any model fitting or when comparing test results against a single creep curve. The standardisation of creep test methods to date has allowed these large databases to be generated, however greater control over the material manufacturing process will be required as any deviation from the design composition can adversely affect the long term creep behaviour of the materials in question.

### 2.9 Creep in welded 9-12Cr

The majority of failures in power plant are observed in component welds as the hierarchical microstructure of the martensitic steels is lost due to the welding process, leading to underperforming welded components [3]. The development of creep resistant steels is as much controlled by improvements to the base material as it is by controlling the material properties post welding. The most recently developed materials have been focused on minimising the damaging effects of welding on the
2.9 - Creep in welded 9-12Cr microstructure [21]. Creep strain accumulates at differing rates within the different regions of a weld, with the heat affected zone the weakest region at resisting creep deformation, specifically in the fine-grained and inter-critical HAZ regions. The reader is referred to Figure 1.7 for a breakdown of the microstructures within welds.

2.9.1 Weld Microstructure

Examinations of welded sections prior to post weld heat treatment (PWHT) show columnar grains, formed due to directional solidification after welding. Lath martensite is formed within this material during cooling and high dislocation densities are observed within the laths along with lower volume fractions of carbides [171, 172]. Precipitate formation within the weld is attributed to auto tempering due to additional heating of individual weld beads during multi-pass welding. During PWHT, carbides and precipitates form in greater volumes and laths evolve into sub-grains [172].

2.9.2 HAZ Microstructure

The various HAZ microstructures are formed during welding, due to the temperature gradient occurring between the molten weld pool and parent material. The CG-HAZ region is exposed to temperatures exceeding Ac₃, leading to dissolution of precipitates and allowing large grains to form adjacent to the cooled pool of weld material. Adjacent to this is the FG-HAZ region where recrystallisation occurs along with partial dissolution of particles. Austenite is formed and then this transforms into martensite with coarsened carbides no longer distributed on the boundaries [172]. Subsequent tempering during post weld heat treatment may produce new precipitates and coarsen the un-dissolved pre-weld carbides [173]. The FG-HAZ blends into the IC-HAZ region of the weld immediately adjacent to the parent material. This region is widely reported as the most critical material in the weld [174, 175] and Type IV failures occur in this region of material. Figure 2.28 demonstrates the measured micro-hardness through the welded region, highlighting the softening which occurs in the IC-HAZ region (from Abd El-Azim [174] and from Laha et al. [175]).
2.9.3 Failure modes

Most failures have occurred within the IC-HAZ material and so the microstructure of this region is particularly important. Lee et al. [173] report increased precipitate diameters for both $M_23C_6$ and MX precipitates within the IC-HAZ region after PWHT for a 9Cr steel and similar results are observed by Paul et al. [171] and Vijayalakshmi et al. [176]. Vijayalakshmi et al. reported a significantly reduced volume fraction of $M_23C_6$ precipitates in the IC-HAZ compared to the parent material. This is due to partial dissolution and re-precipitation of the carbide during the welding process, not all precipitates reform during the re-precipitation phase, leaving a decreased volume fraction.

Failure location is utilised to classify the failure modes in welded connections as devised by Schüller et al. [3, 177], see Figure 2.29. Issues due to joint fabrication, such as solidification, hydrogen inclusion, improper reheating, embrittlement or on occasion creep induced failures are denoted as Type I-III, while Type IV failure occurs on the boundary between the HAZ and the parent material in the IC-HAZ.
2.9.4 Type IV failures

The prominent failure mode within power plant components is Type IV failure within the weldment [135, 178, 179], where failure occurs in the inter-critical heat affected zone (IC-HAZ). The exact causes of Type IV failure are unclear, however there are a number of compelling proposals in the literature. Grain refinement occurs and, as such, the smallest grains are present within the IC-HAZ region and the hierarchical microstructure of the martensitic grain with sub-boundaries and laths is lost. Oversized precipitates, from incomplete austenite transformation, can coarsen during the welding process, leading to large precipitates which are no longer able to pin the boundaries of newly formed grains [180].

The presence of delta ferrite and the effects this has on the weldment has been investigated by Li et al. [181]. The formation of the softer ferrite phase occurs within the IC-HAZ region, allowing additional creep strain to accumulate within the softer grains. The material in-homogenity between the ferrite and tempered martensite encourages increasing stress triaxiality. The material miss-match then drives higher stress triaxiality within the IC-HAZ, increasing the rate of cavity accumulation within this region [182]. Larger precipitates in the IC-HAZ will cause enhanced cavitation, as discussed previously, further weakening this material against the effects of creep.

Examining the successful retention of the hierarchical martensitic microstructure achieved in the MarBN steels, it can be observed that the boron enrichment of the $\text{M}_{23}\text{C}_6$ particles prevented their excessive growth during welding [21]. Coupled with this is the presence of the lath structure in place of highly refined grains classically formed within the IC-HAZ region [38]. The creep results of this material are very promising for preventing the Type IV failures from occurring in components of this material type [21]. The removal of the damaged material state and the corresponding lack of a Type IV failure further supports the conclusion that the loss of the hierarchical microstructure and the oversized precipitates are primarily responsible for Type IV failure. Figure 2.30 shows electron back scatter (EBSD) images of a MarBN weld and a P92 weld from Abe et al [21]. The MarBN material grain size is far larger than the P91.
2.10 Modelling visco-plastic deformation

Accurate models of creep behaviour are a crucial piece of technology required for plant operators. They are primarily focused on the precise prediction of failure times and are utilised to plan maintenance and inspections of plant components. A reliable creep model can minimise or mitigate the occurrence of unplanned plant failures and outages, thus minimising the operational cost of power plant and reducing power bills for consumers. Extrapolation from laboratory test conditions to real world operating ranges is the ultimate power of modelling. The goal of most researchers in this field is the development of a robust model capable of reliable extrapolation across a wide range of temperatures and stresses. This section will focus on two commonly used modelling methodologies for predicting creep behaviour; firstly the Norton power law model will be discussed followed by the hyperbolic sine model. Other modelling approaches exist but generally most modern creep models rely on versions or derivations of these two competing modelling approaches.
2.10 - Modelling visco-plastic deformation

2.10.1 Norton Models

The Norton model is a steady state visco-plastic model for time dependent material deformation, containing two material parameters $A$ and $n$. The creep strain rate equation is shown in multi-axial form in Equation 2.24.

$$
\dot{\varepsilon}_{ij}^{cr} = \frac{3}{2}A\sigma_{\text{eq}}^{n-1}S_{ij}
$$

(2.24)

Here, $\dot{\varepsilon}_{ij}^{cr}$ is the creep strain rate tensor, $\sigma_{\text{eq}}$ is the equivalent or Von Mises stress and $S_{ij}$ is the deviatoric stress. This model has been expanded to include a damage parameter capturing the characteristic tertiary phase creep strain acceleration seen in creep test data of high temperature steels. Hyde et al. [29] employed this model coupled, with a rupture stress equation to predict failures in repair welds of 0.5Cr0.5MoV main steam pipes. The time to failure equation is based on a ratio of the steady state, principal and Von Mises stresses within the pipes with a material constant describing the triaxial stress state in the pipe. The model is presented in Equations 2.25 and 2.26.

$$
t_f = \frac{1}{M'(\sigma_r)\chi}
$$

(2.25)

where, $t_f$ is the time to failure, $\chi$ and $M'$ are material constants and $\sigma_r$ is the rupture stress defined as:

$$
\sigma_r = \alpha'\sigma_1 + (1 - \alpha')\sigma_{\text{eq}}
$$

(2.26)

where $\alpha'$ is a material parameter. Kachanov developed a physically based damage parameter for creep failure of tensile test specimens [164], provided that damage from cavity formation is accurately represented by a ratio of areas. As cavities grow, the effective area resisting the applied load decreases, eventually leading to a rapid failure via crack growth connecting cavities along grain boundaries. This is known as a Continuum Damage Mechanics (CDM) approach to modelling creep as this represents a continuous damage evolution method. This cavitation has been included within the Norton model by Hayhurst for use in predicting failure in bi-axial tensile tests [183]. The creep rate and damage parameter are:

$$
\dot{\varepsilon}_{ij}^{cr} = \frac{3}{2}A'\left(\frac{\sigma_{\text{eq}}}{1 - \omega}\right)^n\frac{S_{ij}}{\sigma_{\text{eq}}}t_m
$$

(2.27)

$$
\dot{\omega} = B'\frac{\sigma_r^\chi}{(1 - \omega)^\phi}t_m
$$

(2.28)
where $A', n, m, B', \chi, \phi$ are material parameters which must be fitted to experimental creep data. This CDM model has been applied successfully to 9Cr alloys by Hyde et al. [103], Christopher et al. [184] and Nandi et al. [185]. However, one of the key issues with this model, is the lack of a physical basis, specifically to measurable quantities from test specimens. More physically based models are preferred as they predict the effects of stress and strain on observable microstructure. To this end, Spigarelli et al. [26,186] have developed a mechanistic modelling approach based on the intrinsic stress fields generated within a material due to the presence of fine and large precipitates and sub-grain. This approach is formulated within a Norton based framework. Their experimental work was focused on the high stress regime, and as such characterised only a single set of Norton parameters. However, they identified that the activation energy for creep within P91 material is variable, indicating the presence of a threshold stress intrinsic to the material.

### 2.10.2 Hyperbolic Sine Models

Dyson and Osgerby developed a three state CDM model for creep deformation and fracture in a 0.5Cr0.5Mo ferritic steel [102]. The model is based not on a Norton power law model but rather on a hyperbolic sine model. The justification for this approach is to allow for extrapolation from laboratory testing stress levels to actual plant operational range. The minimum strain rate (MSR) vs stress data from Sklencika [47], is shown in Figure 2.31. Both Norton and hyperbolic sine models have been fitted to this data set. The Norton model requires two parameter sets, for the high and low stress regimes. In comparison, the hyperbolic sine requires only a single parameter set to predict the entire data range. Thus, both short- and long-term tests are required to calibrate an accurate Norton based model, which is an expensive and time consuming process. However, for the hyperbolic sine model, short term tests will allow extrapolation to the low stress operational regime. Dyson and Osgerby’s three damage parameter CDM model, in multi-axial form, is given as:

\[
\dot{\varepsilon}_{ij}^{cr} = \frac{3}{2} \frac{S_{ij}}{\sigma_{eq}} \alpha \sinh \left[ \frac{\beta \sigma_{eq}(1 - H)}{(1 - \phi_2)(1 - \omega_2)} \right]
\]

where $\alpha$ and $\beta$ are material constants, while $H$, $\phi_2$ and $\omega_2$ are damage parameters relating to primary hardening, precipitate coarsening and cavitation damage.
respectively. Primary hardening is defined as:

\[
\dot{H} = \frac{h \dot{\varepsilon}_{cr}^{eq}}{\sigma_{eq}} \left(1 - \frac{H}{H^*}\right)
\]  

(2.30)

where, \( h \) is the rate controlling parameter, \( \dot{\varepsilon}_{cr}^{eq} \) is the equivalent creep strain and \( H^* \) is the maximum value of the primary hardening variable. Carbide precipitate type coarsening is defined as:

\[
\dot{\phi}_2 = \frac{K_{pc}}{3} (1 - \phi_2)^4
\]

(2.31)

where, \( K_{pc} \) is the damage rate controlling term. Cavitation damage is defined as:

\[
\dot{\omega}_2 = \frac{D}{\sigma_{eq}} \left(\frac{\sigma_1}{\sigma_{eq}}\right) \nu
\]

(2.32)

where, \( D \) is a material parameter related to the creep ductility, \( \nu \) is a material constant controlling the sensitivity of the material to the triaxial stress state. Dyson also produced a suggested table of damage mechanics terms for numerous deformation mechanisms known to affect the 9Cr family of steels [187]. The CDM parameters were subdivided into three distinct categories according to the dominant cause of the damage and these were i) strain-, ii) thermally- and iii) environmentally-induced damage. Damage parameter formulations, damage rates and their appropriate inclusion location within a hyperbolic sine based creep strain equation were all detailed in this work [187]. A term for dynamic sub-grain growth was included without the damage rate term. The stated reason of Dyson for this omission, was the lack of information available on the precise effect of sub-grain growth on the strain rate accumulation in these materials. As discussed previously, sub-grain recovery is heavily influenced by precipitate behaviour and dislocation mechanics.

The precipitate coarsening term, shown in Equation 2.31, was developed for a material containing a single precipitate type and the use of this model for other materials containing multiple precipitate families requires averaging the coarsening rate for all other precipitates present. Hayhurst et al. [188] applied this approach to a precipitate strengthened 0.5Cr material and Hyde et al. [103] applied it to the Bar 257 and P91 materials, assuming all precipitate behaviour was captured under a single carbide coarsening term. The effects of the MX precipitates are not expressly included in this approach and an empirical fit for the secondary creep constant \( \beta \) was employed in place of a more physically based definition of this parameter. The results of Hyde’s model fit to the two precipitate containing Bar-257 material are
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Figure 2.31: Comparison between Sinh and Norton based approaches to modelling minimum strain rates compared with T91 test data at 600 °C [47]

shown in Figure 2.32. This approach provided a good fit for the short term testing performed on the Bar 257 material, but the long term effect of multiple precipitate types evolving separately cannot be accounted for with this approach. Two set’s of material parameters were required to capture the behaviour of two similar P91 materials and the difference between the P91 and Bar 257 investigated was primarily the Al content. A physically based multiple precipitate containing model could potentially achieve the same level of agreement with the experimental results utilising fewer parameters.

Figure 2.32: Hyde single coarsening rate parameter based fitting to the Bar 257 creep test data at 650 °C, reproduced from [103].

2.10.3 Larson Miller Parameter

The Larson Miller parameter approach is a method of predicting service lifetimes for components based on the steady state creep rate and the failure time couched in a
temperature sensitive framework. The parameter has the following form [189]:

\[ P_{LM} = T(C_{LM} + \log t_f) \]  

(2.33)

where \( T \) is the temperature in K, \( C_{LM} \) is a material dependent parameter with a value typically on the order of 20. The parameter is most commonly calculated using a least squares fitting procedure to extrapolate from the laboratory conditions to longer lives. Larson and Miller assumed that creep is a rate controlled process with a minimum creep rate that was stress and temperature dependent. They also assumed that the minimum creep rate was proportional to the rupture life [189]. This is the observation of Monkman and Grant which gave rise to another life estimation procedure, discussed earlier (Equation 2.3) in relation to the small punch creep test method. The Larson Miller parameter can be derived from the continuum damage mechanics hyperbolic sine model, by applying some restrictions to this model, for the full description of this process see Dyson et al. [187]. The restrictions are as follows, no ageing of particles, constant ductility only, primary creep has reached a maximum value, i.e. \( H = H^* \).

### 2.11 Summary and Conclusions

At the smallest scales, creep deformation at high temperature relies on the twin processes of atomistic diffusion and dislocation movement through the crystal structures. To increase the creep resistance of a material, the rates of these two processes need to be reduced. Considering first the diffusion problem, the alloys in question are predominantly Fe, even for the stainless steels with 18-20 wt.% Cr and 8 wt.% Ni, with the remainder being Fe. As such, minimising the rate of elemental diffusion through Fe is challenging and is most effectively achieved with the addition of C to promote interstitial solution strengthening. Increasing C content proportionally increases the dislocation density, thus improving diffusion creep resistance while decreasing dislocation creep resistance.

Therefore, the remaining option to improve creep performance is impeding the dislocation movement through the lattice. Additional alloying elements can impart solid solution strengthening, while further interstitial strengthening above what the C addition produces, encourages the formation of precipitates. Heat treatments generate favourable microstructures with high boundary densities and the corresponding precipitate structures to reinforce the boundaries against recovery. The long term sta-
bility of the microstructure under plant operating conditions must be understood to make best use of these materials. Certain additions can improve the initial strength of a material, however, the long term effects may show a net negative result over the medium to long term testing. An example of this would be the addition of N to encourage additional MX precipitate formation. However, an abundance of N in a 9Cr steel can lead to the formation of the detrimental Z-phase precipitate (Cr(Nb,V)N), which absorbs the MX precipitate constituent elements decreasing the creep resistance of the material. As a result next generation materials such as MarBN have reduced the concentration of N within the alloy to avoid the formation of this and other detrimental precipitates e.g. BN [38].

Accurate physically based models, which include the effects of multiple precipitate types, are required to predict creep behaviour based on the condition of precipitates. The well-established thermally-activated coarsening constant of Ostwald has been given a physical-composition based meaning in the work of Umantsev et al. [150] and Ågren [190]. This has been extended to include strain induced coarsening by Hättestrand et al. [76]. However, this has not been implemented in a creep life prediction model to date, nor has a damage parameter for use in a continuum damage mechanics approach been developed from this coarsening formulation either. This project aims to develop a multiple precipitate based model including the effects of strain- and temperature- induced coarsening, which will allow for additional precipitates to be added to the formulation easily.

As cheaper and less material demanding test methodologies become more widespread, the quantity of useful creep data in the literature is expected to increase. The small punch creep methodology is being put forward in this project as the most promising of these small specimen type test methods for evaluating the creep behaviour of power plant materials. The application of this test to 9Cr-W (P92) material has been presented in the past by Komazai et al. [115] at 650 °C for both un-aged and aged material. However, for a P91 material, this has not been examined previously. A considerable issue for creep testing of any kind, but perhaps particularly important for a novel methodology, is the repeatability of the test method, since the scatter in available creep data can be up to an order of magnitude difference in the rupture times [166]. As such, the scatter in small punch creep data is to be investigated also, to examine whether it conforms to the behaviour for tensile creep results.

Novel 9Cr based materials are also of interest to this project as they hold the promise
of increased efficiencies and decreased emissions for power plant. While optimum heat treatments for the P91 and P92 materials are available in the literature [61], other new materials require further study of their heat treatments before they are installed in plant. As such the effect of the optimised 1200 °C heat treatment for MarBN, developed by Li et al. [43] is of interest to this project. The increased normalisation temperature prevents the formation of creep weak BN precipitates. This work aims to characterise the hardness profile with increasing distance from the oxide-base material interface and examine the microstructural features effecting these profiles for samples normalised at 1050 °C and 1200 °C.
Chapter 3

Physically based, multiple precipitate type creep modelling

3.1 Introduction

This chapter presents the derivation, calibration and validation of a new physically-based, continuum damage mechanics (CDM) creep model. This model simulates the Orowan precipitate strengthening due to the presence of multiple precipitate types in 9Cr steels under high temperature creep deformation. This incorporates two precipitate families present in as received 9Cr steels both MX and M$_{23}$C$_{6}$. The novel CDM state variable approach is presented including the effects of temperature- and strain-induced coarsening and this is embedded in a hyperbolic sine formulation for creep strain rate prediction.

This model was originally derived by Dyson and Osgerby [102] to predict failure of 1Cr0.5Mo ferritic steels undergoing creep at temperatures between 530 and 625 °C, for applied stresses of 65 to 320 MPa. These materials were strengthened against creep deformation by the inclusion of a single carbide precipitate family. As such the model was developed considering the evolution of this single precipitate type. The inclusion of carbide precipitate size and coarsening rate introduced a physical basis for the model predictions for the 1Cr0.5Mo material.

The model was subsequently applied to the 9Cr family of steels by Hyde et al. [103], who performed a similar comparison to Perrin and co-workers [191]. However Hyde employed the model in a finite element numerical modelling framework for P91 and Bar 257 pipes. This approach combines all precipitates under a singular precipitate coarsening based term which reproduced their test data to a high degree of accuracy. This approach required two constant sets due to the effects of the added Al, the
approach described here depends on the volume fraction of MX precipitates and the effect of this on obstacle spacing, while all other parameters stay the same.

Here the primary focus is to extend the modelling methodology of Perrin et al. [191, 192] to account for the multi-precipitate mechanisms present in 9Cr steels via the development of a new precipitate coarsening based model. This new model will capture the effect of different coarsening kinematics, inter-particle spacing and volume fraction on the creep life of multi-precipitate type strengthened alloys. The material model is successfully applied to 9Cr steels across a range of temperatures via the inclusion of temperature-independent steady-state creep constants. The role of Al content on creep performance is also simulated via a decreasing MX precipitate volume fraction, a variable which is identified in the present work as a critical value for creep life assessment of 9Cr steels.

3.2 Methodology

3.2.1 Hyperbolic sine creep model

In Chapter 2 the CDM hyperbolic sine flow rule with three material parameters was presented in multi-axial form, as developed by Dyson et al. [102]. The steady state material constants $\alpha$ and $\beta$ are replaced with temperature independent terms defined in the following section. The uniaxial implementation of this flow rule is as follows:

$$\dot{\varepsilon}^{cr} = \dot{\varepsilon}_0 \exp\left(\frac{-\Delta F}{k_B T}\right) \sinh\left[\frac{\sigma_{app}(1-H)}{\sigma_0(1-D_P)(1-D_{CR})}\right]$$

(3.1)

Where $\dot{\varepsilon}_0$ is the pre-exponential creep constant, $\Delta F$ is Helmholtz free energy, $k_B$ is the Boltzmann constant, $T$ is absolute temperature, $\sigma_{app}$ is applied stress and $H$, $D_P$ and $D_{CR}$, are the CDM state variables related to primary hardening, precipitate coarsening and intergranular cavitation, respectively. The creep constant, $\sigma_0$, is equal to the inverse of the $\beta$ term in Equation 2.29 and here is a stress quantity related to the key obstacles to deformation in the material and defined as [187]:

$$\sigma_0 = \frac{M k_B T}{b^2 \lambda_{ob}}$$

(3.2)

where $M$ is the Taylor factor, $b$ is the magnitude of the Burgers vector and $\lambda_{ob}$ is the mean spacing of obstacles. In the hierarchical precipitate-strengthened microstruc-
3.2 - Methodology

ture of 9Cr steels, the primary obstacles are (i) MX and M$_{23}$C$_6$ precipitates, (ii) high and low angle grain boundaries and (iii) dislocations, as illustrated schematically in Figure 2.1.

The mean obstacle spacing, $\lambda_{ob}$, is related to the mean spacing of (i) precipitates (M$_{23}$C$_6$, $\lambda_C$ and MX, $\lambda_M$), (ii) grain boundaries, $d_g$, (iii) laths (or subgrains), $w$, and (iv) dislocations, $\rho$. Using an approach similar to that of Roters et al. [1], $\lambda_{ob}$ is thus:

$$\frac{1}{\lambda_{ob}} = \sqrt{\frac{\lambda_C^2 + \lambda_M^2}{\lambda_C^2 \lambda_M^2}} + \frac{1}{w} + \frac{1}{d_g} + \sqrt{\rho}$$

(3.3)

Primary creep in 9Cr steels is related to hardening and microstructural evolution associated martensitic lath and subgrain strengthening, dislocation hardening and back-stresses associated with dislocation pinning at precipitates. The time derivative of primary hardening, $H$, is defined here, using the model of Hayhurst et al. [192,193], as:

$$\dot{H} = \frac{h}{\sigma} \left[ 1 - \frac{H}{H^*} \right] \dot{\varepsilon}^{cr}$$

(3.4)

where $h$ is a hardening modulus and $H^*$ is the saturated value of primary hardening. The creep damage term, $D_{cr}$, accounts for the formation and growth of creep cavities via the mechanism of vacancy diffusion (as illustrated schematically in Figure 2.4) in the material. The time derivative of cavitation, $\dot{D}_{cr}$, is defined here as:

$$\dot{D}_{CR} = C \dot{\varepsilon}^{cr}$$

(3.5)

where $C$ is a temperature-dependent constant related to creep ductility, $\varepsilon_f$. Vacancy diffusion through the crystal lattice to grain boundaries results in the individual vacancies coalescing and nucleating a cavity (Figure 2.4). Further growth of the cavity due to strain accumulation is included in the model via Equation 3.5 above as per the work of Cane [52].
3.3 CDM model for multiple precipitate types

In the initial microstructure, MX precipitates of type VN and NbC are distributed throughout the microstructure and $\text{M}_{23}\text{C}_6$ carbides, dominated by $\text{Cr}_{23}\text{C}_6$ carbides, are dispersed along boundaries. Thus, to account for the effects of coarsening related evolution of MX and $\text{M}_{23}\text{C}_6$ precipitates, it is necessary to extend the carbide coarsening precipitate CDM model of Dyson and co-workers [102, 192, 193] to include multiple precipitate types. Furthermore the volume fraction of both MX and $\text{M}_{23}\text{C}_6$ carbides are also incorporated as key variables as described below.

The precipitate spacing model is developed on the basis of a precipitate being present on every corner of a unit cell and the precipitate volume fraction is the ratio between the precipitate and unit cell volumes. Figure 3.1 shows this unit cell and precipitate arrangement.

![Figure 3.1: Unit cell and precipitate arrangement assumed for average precipitate spacing arrangement](image)

Utilising the volume fraction relation and the relationship between the unit cell length and precipitate radius $\lambda = l - 2r'$ with $d = 2r'$, the volume fraction of precipitates within a unit cell of material becomes

$$f_p = \frac{4\pi(d/2)^3}{(\lambda + d)^3}$$

where $d$ is the precipitate diameter (twice $r'$ in Figure 3.1) and $\lambda$ is the spacing of precipitates. Re-arranging for the spacing term and simplifying gives:

$$\lambda = d \left[ \left( \frac{\pi}{6 f_p} \right)^{1/3} - 1 \right]$$

This assumes a constant volume fraction of precipitates, while the precipitate diameters are able to coarsen during creep exposure. Previously, a schematic illustration of
the precipitate coarsening mechanism was presented in Chapter 2, (see Figure 2.10). It describes the formation of Orowan loops around the precipitate with increased inter-particle spacing due to precipitate coarsening during creep, reducing the effect of dislocation pinning and loop formation. The precipitate evolution term is defined as a function of the ratio of the mean inter-particle spacing for the initial, $\lambda_0$, and current, $\lambda$, microstructure:

$$D_P = 1 - \frac{\lambda_0}{\lambda}$$

(3.8)

with the mean inter-particle spacing defined, using the approach of Magnusson and Sandström [159, 194], which is based on the total number of precipitates per unit area.

$$\frac{1}{\lambda^2} = \frac{1}{\lambda_C^2} + \frac{1}{\lambda_M^2}$$

(3.9)

Where $\lambda_k$ is the mean inter-particle spacing of a type k precipitate and the subscripts 'C' and 'M' denote $\text{M}_2\text{C}_6$ and $\text{MX}$ precipitates, respectively. The mean spacing of precipitates is a function of the diameter and volume fraction of the precipitate, who’s derivation is covered in Chapter 1.

$$\lambda_k = d_k \left[ \left( \frac{\pi}{6 f_k} \right)^{1/3} - 1 \right]$$

(3.10)

Where $d_k$ and $f_k$ are precipitate diameter and volume fraction, respectively. The evolution of the mean precipitate diameter is defined via the Ostwald ripening process shown schematically in Figure 2.10. However, to account for strain-induced particle coarsening, the model of Taneike et al. [104] is used to define the mean precipitate diameter:

$$d_k^3 - d_{k,0}^3 = K_k t + \phi_k \varepsilon^\alpha$$

(3.11)

where $d_{k,0}$ is the initial precipitate diameter, $K_k$ is the thermal coarsening rate and $\phi_k$ is the strain-induced precipitate coarsening constant. Thus, the precipitate evolution term of Equation 3.8 becomes:

$$D_P = 1 - \frac{d_{C,0}^2 d_{M,0}^2}{d_{C}^2 d_{M}^2} \left( \frac{d_C^2 B_C + d_M^2 B_M}{d_{C,0}^2 B_C + d_{M,0}^2 B_M} \right)$$

(3.12)

where the parameter $B_k$ is defined as:

$$B_k = \left[ \frac{\lambda_k}{d_k} \right]^2 = \left[ \left( \frac{\pi}{6 f_k} \right)^{1/3} - 1 \right]^2$$

(3.13)
Chapter 3 - Physically based, multiple precipitate type creep modelling

For this work, the formation of Z-phase particles at the expense of MX carbonitrides, is omitted from the present study [45, 195] as is the loss of $M_23C_6$ carbides due to processes such as Cr depletion during oxidation. Then, it can be assumed that the volume fraction of precipitates remains constant during the Ostwald ripening process. Thus, the time derivative of 3.12 defines the precipitate evolution rate as:

$$\dot{D}_p = \frac{1}{3} \frac{d^3_{C,0}d^3_{M,0}}{d^2_{M,0}B_M} \left[ \frac{B_C}{d^3_C}(K_M + \phi_M \dot{\varepsilon}_{cr}) + \frac{B_M}{d^3_C}(K_C + \phi_C \dot{\varepsilon}_{cr}) \right] \frac{1}{(1 - D_P)} \quad (3.14)$$

where it can be shown that Equation 3.14 reduces to the more familiar model of Dyson and others [102, 192, 193] \((\dot{D}_p = (K/3d^3_b)(1 - D_P)^4)\) for a single precipitate type with no strain-induced coarsening.

3.4 Results

3.4.1 Model calibration

The CDM creep model is applied here to two Gr. 91 alloys, (i) conventional P91 alloy and (ii) Bar 257, a P91 alloy with increased Al content. The nominal compositions of the materials investigated in this study are presented in Table 3.1. The required material parameters are identified using a combination of creep and thermal ageing data, in conjunction with the results of published microstructural data.

Table 3.1: Chemical composition of P91 steels in wt.\% The P91 steel composition ranges are obtained from Abd El-Azim et al. [196], Magnusson and Sandström [168] and Orlová et al. [197], with the Bar 257 data taken from Magnusson and Sandström [168]. Note that trace elements such as Cu and S are not presented. The balance is Fe.

<table>
<thead>
<tr>
<th>Material</th>
<th>Al</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Mo</th>
<th>N</th>
<th>Nb</th>
<th>Ni</th>
<th>P</th>
<th>Si</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>P91</td>
<td>0.007-0.01</td>
<td>0.09-0.10</td>
<td>0.09-0.10</td>
<td>0.46-0.56</td>
<td>0.86-0.90</td>
<td>0.05-0.065</td>
<td>0.06-0.07</td>
<td>0.16-0.07</td>
<td>0.014-0.02</td>
<td>0.2-0.3</td>
<td>0.194-0.32</td>
</tr>
<tr>
<td>Bar 257</td>
<td>0.028</td>
<td>0.09</td>
<td>0.34</td>
<td>0.49</td>
<td>0.89</td>
<td>0.03</td>
<td>0.07</td>
<td>0.47</td>
<td>-</td>
<td>0.34</td>
<td>0.23</td>
</tr>
</tbody>
</table>

The temperature-dependent Young’s modulus is identified from the elastic region of monotonic tensile test data [198] and presented in Table 3.2. The magnitude of Burgers vector, $b$, and the Taylor factor, $M$, have values of 0.248 nm and 2.9, respectively, for body centre cubic materials, pure Fe values are utilised in this work.
for simplicity. The Helmholtz free energy, $\Delta F$, is calculated as $5.978 \times 10^{-19}$ J from Oruganti et al. [199].

Table 3.2: Identified temperature-dependent material parameters.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$E$ (GPa)</th>
<th>$H^*$ (-)</th>
<th>$\bar{C}$ (-)</th>
<th>$K_C$ (mm$^3$/hr)</th>
<th>$K_M$ (mm$^3$/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>144</td>
<td>0.450</td>
<td>8.5</td>
<td>$1.00 \times 10^{-15}$</td>
<td>$2.35 \times 10^{-18}$</td>
</tr>
<tr>
<td>625</td>
<td>125</td>
<td>0.131</td>
<td>7.5</td>
<td>$3.68 \times 10^{-15}$</td>
<td>$3.13 \times 10^{-18}$</td>
</tr>
<tr>
<td>650</td>
<td>110</td>
<td>0.090</td>
<td>2.5</td>
<td>$6.35 \times 10^{-15}$</td>
<td>$3.90 \times 10^{-18}$</td>
</tr>
</tbody>
</table>

The values for the initial precipitate diameters, $d_{M,0}$ and $d_{C,0}$, are taken from the data of Hald and Korcakova [30]. The volume fractions of the precipitates are obtained from Magnusson and Sandström [168], with a reduced value of $f_m$ for Bar 257, consistent with the formation of thermally unstable AlN nitrides at the expense of the MX precipitates. The thermal coarsening rates, $K_M$ and $K_C$, are identified via a least squares optimisation procedure, fitting Equation 3.11 to the experimental data of Hald and Korcakova [30] for P91 and P92 alloys thermally aged at temperatures of 600 °C and 650 °C, individually for both $M_{23}C_6$ and MX precipitates. A comparison with the experimental data is presented in Figure 3.2. The P92 data in Figure 3.2b is assumed to be applicable for the identification of $K_m$, as the MX precipitates are of similar composition in both materials, see Table 3.1 [30]. The identified coarsening rates are shown in Table 3.2, where the 625 °C values have been obtained by linear interpolation.

Figure 3.2: Identification of thermal coarsening rates of (a) $M_{\text{arg}23C_6}$ and (b) MX precipitates in 9Cr steels from the measured data of Hald and Korcakova [30] at temperatures of 600 °C and 650 °C.
The constants, $\dot{\varepsilon}_0$ and $\lambda_{ob}$, associated with the steady state creep behaviour of the candidate materials, are identified from minimum creep strain-rate (MSR) data. Using Equation 3.1, the MSR can be defined as,

$$MSR = \dot{\varepsilon}_0 \exp \left( \frac{-\Delta F}{k_B T} \right) \sinh \left( \frac{\sigma}{\sigma_0} \right)$$

Where representative values of $\dot{\varepsilon}_0$ and $\lambda_{ob}$ for P91 are identified using experimental data at temperatures of 600 °C and 650 °C, as presented in Figure 3.3.

The $\lambda_{ob}$ value of 31 nm identified, via the MSR data of Figure 3.3, is consistent with measured microstructural values of $w$ in the range of 0.3 to 1.5 $\mu$m [103, 158, 200], $d_g$ on the order of 4 $\mu$m [158] and a dislocation density of $1.6 \times 10^{14}$ to $7.5 \times 10^{14}$ m$^{-2}$ [15, 158] for P91 alloys, via Equation 3.10. The value of $\lambda_{ob}$ for Bar 257 is then identified retrospectively using Equation 3.10 in conjunction with a modified value of $\lambda_m$ to account for the decreased volume fraction of VN precipitates.

Finally, the primary creep constants $h$ and $H^*$, intergranular cavitation constant, $\bar{C}$, and the strain-induced precipitate coarsening constants, $\phi_k$, were identified using a least squares approach to minimise the difference between the model and experimental data. The optimised set of material parameters are presented in Table 3.2 and Table 3.3. From the work of Mustata and Hayhurst [201], the creep constant is related to creep ductility via the expression:

$$\bar{C} = \frac{k_N}{\varepsilon_f}$$

(3.16)
where \( k_N \) is a constant with a value of 1/3 for uniaxial loading, for a multi-axial implementation this value becomes unity. Using Equation 3.16, the optimised values of \( \bar{C} \) lead to creep ductility values of between 3.9 % and 13.3 % for temperatures increasing from 600 °C to 650 °C, values similar to the results of Klueh, who showed increasing specimen elongation from 4% at 400 °C to 10% at 600 °C [202]. Furthermore, the low value of \( \bar{C} \) is justified by the negligible increase in MX diameter measured by Hättestrand and Andrén [76] in crept specimens, compared to thermal aging data.

### 3.4.2 Modelling creep deformation in 9Cr steels

The ability of the proposed CDM model to predict creep deformation in conventional P91 steel (ASTM A335/ASME SA335), is presented in this section. Although data is obtained from different sources, potentially with small variations in composition and heat treatment, the alloys investigated fit within the composition range for Gr. 91 steel presented in ASME specifications [203]. Hence, these Gr. 91 alloys will be collectively denoted as ‘conventional P91’.

#### Table 3.3: Temperature-independent material parameters.

| Material | \( \dot{\varepsilon}_0 \) (hr\(^{-1}\)) | \( \Delta F \) (J) | \( h \) (MPa) | \( \lambda_{ab} \) (nm) | \( \delta_{M,0} \) (nm) | \( d_{C,0} \) (nm) | \( f_C \) (%) | \( f_M \) (%) | \( \phi_C \) (mm\(^3\)) | \( \phi_M \) (mm\(^3\)) |
|----------|-----------------|-----------------|-------|-----------------|-----------------|-----------------|--------|--------|-----------------|-----------------|      |      |      |      |
| P91      | \( 6 \times 10^{13} \) | \( 5.974 \times 10^{-19} \) | 0.07E | 31              | 36              | 100             | 2      | 0.5    | \( 1.04 \times 10^{-9} \) | \( 1.18 \times 10^{-14} \) |      |      |      |      |
| Bar 257  | \( 6 \times 10^{13} \) | \( 5.974 \times 10^{-19} \) | 0.07E | 38              | 36              | 100             | 2      | 0.1    | \( 1.04 \times 10^{-9} \) | \( 1.18 \times 10^{-14} \) |      |      |      |      |

Figure 3.4a presents a comparison of the predicted creep response against the measured data of Orlová et al. [200] at 600 °C for three different stresses. The predictions correlate closely with the experimental data for the intermediate stresses, viz. 110 MPa and 125 MPa, and reasonably closely for the higher stress, 175 MPa. A comparison of the predicted and measured creep rates is presented in Figure 3.4b for a stress of 125 MPa at 600 °C, showing very close correlation.

The comparison of predicted and measured responses at 625 °C is presented in Figure 3.5, showing close agreement of the model with experimental data. Similar results are obtained for two different applied stresses at a temperature of 650 °C, as illustrated in Figure 3.6. Figure 3.7 highlights the ability of the proposed model to predict creep rupture life via comparison with stress rupture data from the NIMS data sheet [166]. The model is shown to successfully capture the effect of temperature on the creep life.
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of conventional P91 and this is attributed to the inclusion of temperature-dependence in the steady-state creep constants.

Figure 3.4: Comparison of predicted (a) creep strain response and (b) creep-rate response of conventional P91 at 600 °C with experimental data of Orlová et al. [200].

Figure 3.5: Comparison of predicted creep response with the experimental data of Hyde et al. [103] at 625 °C.
3.4 - Results

Figure 3.6: Predicted and experimentally observed creep response for conventional P91 steel at 650 °C. The 70 MPa data is from the work of Abd El-Azim et al. [196] and the 98 MPa data is taken from Maruyama et al. [155].

Figure 3.7: Comparison of P91 predicted stress rupture life with experimental data. The experimental data is taken from the NIMS data sheet [202].

3.4.3 Simulating the effect of Al content on the performance of 9Cr steels

The effect of increased Al content in 9Cr steels causes a reduced volume fraction of the finely dispersed MX precipitates, leading to a reduced creep strength and, hence, decreased rupture time of the material [168]. Bar 257 is a P91 alloy with a high Al content, on the order of 0.028 wt.% [168], which has attracted some attention due the detrimental effect of the increased Al content on rupture life. The maximum allowable Al content prior to the discovery of Al nitride effects on creep life was 0.04 wt.%, until 2005 [169]. Based on the life limiting effects of the loss of MX precipitates due to N absorption during AlN formation the maximum Al content was lowered from 0.04 wt.% to 0.02 wt.% from 2006 onwards in the ASTM standards [170]. In the
present model, the effect of increasing Al content is simulated by reducing the volume fraction of MX precipitates, $f_m$. This leads to a concomitant reduction in the mean inter-particle spacing of MX precipitates (via Equation 3.10) and hence, a decrease in mean obstacle spacing, $\lambda_{ob}$, via Equation 3.3. The subsequent predicted effect on MSR is presented in Figure 3.8 for a temperature of 650 °C. Bar 257 is seen to exhibit a higher MSR for stresses above 20 MPa, with the effect predicted to increase with increasing stress. This reduced effect in the (lower stress) diffusional creep regime can be attributed to the reduced effect of MX precipitates in diffusion-based creep. A reduced volume fraction of MX precipitates allows increased dislocation motion through the lattice. Fewer mobile dislocations are pinned as a result allowing more dislocation based creep strain to accumulate, reducing the life of the materials at high stress. The process of vacancy diffusion through the crystal is not improved by a lower volume fraction of precipitates and as such little effect of the reduction in volume fraction is observed in Figure 3.8.

Figure 3.8: Predicted effect of Al content on the minimum creep rate at a temperature of 650 °C.

Figure 3.9 presents a comparison between the predicted and measured creep strain response in a Bar 257 alloy at 650 °C, for 70 MPa and 82 MPa, using the physically-based reduction in $f_m$. The key outcome here is the demonstrated ability to predict rupture life, based on composition induced alterations to the microstructure. Figure 3.10 shows the predicted and measured effect of increasing Al content in Gr. 91 alloys for 70 MPa at 650 °C. A creep life reduction factor of 5.8 is predicted for Bar 257, which is consistent with the test data. The proposed model is thus shown to be capable of predicting this detrimental effect of increasing Al content, highlighting the benefit of the physically-based precipitate modelling methodology.
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Figure 3.9: Experimental [103] and model predicted creep curves for Bar 257 at 650 °C.

Figure 3.10: Comparison of model and experimental data for Bar 257 and conventional P91 steel at 650 °C and an applied stress of 70 MPa. The Bar 257 data is from Hyde and co-workers [103] and conventional P91 data from Abd El-Azim et al. [196].

The predicted effect on stress-life rupture curves for Bar 257 and P91, at both 600 °C and 650 °C, is shown in Figure 3.11a and 3.11b respectively. Bar 257 is predicted to have a significantly lower creep life compared to conventional P91 across the full range of stress examined and for both temperatures.

The more general sensitivity of the model to increasing Al content on rupture life, via varying $f_m$ and $\lambda_{ob}$ independently, is presented in Figure 3.12. Figure 3.12a shows that for $f_m$ of 0.1 %, the predicted rupture life is reduced by a factor of $\sim 3$ compared to conventional P91 steel. Figure 3.12b shows the effect of increasing Al content via the $\lambda_{ob}$ parameter and the effect of such changes on the predicted time to failure, with an increasing $\lambda_{ob}$ value, predicted substantial reductions to creep life. However, neither variation of $f_m$ nor $\lambda_{ob}$ alone can predict the measured effect of increasing...
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Figure 3.11: Predicted creep rupture plot for P91 and Bar 257 alloys at (a) 600 °C and (b) 650 °C.

Al content, as presented in Figure 3.8, highlighting the requirement for the more mechanistic approach presented here, including separating the effect of $\text{M}_{23}\text{C}_6$ and MX precipitates and defining the $\sigma_{\text{ob}}$ creep constant from a physical basis.

Figure 3.12: Predicted effect of (a) reducing the volume fraction of MX precipitates and (b) varying the mean spacing of obstacles, $\lambda_{\text{ob}}$, on time to failure in P91 alloys for an applied stress of 90 MPa at 625°C.

3.5 Discussion

Presented here is a new CDM modelling methodology to predict microstructural degradation associated with different precipitate types in 9Cr steels. In particular, this new approach considers, for the first time, the key strengthening and degradation
mechanisms of these different precipitate types in the model of Dyson et al. [102, 191, 192]. The new methodology is able to predict the creep response of P91 alloys across a range of temperatures and stresses, as illustrated in Figure 3.4 to Figure 3.6, as well as rupture life as presented in Figure 3.7.

The inclusion of temperature-dependence in the model, in particular for the steady-state creep constants, is shown to be able to predict creep deformation, with only five temperature-dependent variables required. However, the temperature-dependent variables $K_C$, $K_M$ and $\bar{C}$ are determined using physical arguments (see Section 2.7 and Equation 2.20) and measured data, with the temperature-dependent Young’s modulus easily defined from monotonic tensile test data. The temperature-dependence of the $\bar{C}$ variable is consistent with ductility values at 600 ° presented in Klueh [202]. The decreasing $\bar{C}$ values with increasing temperature are also consistent with an increasing ductility with temperature. The final remaining temperature-dependent constant, $H^*$, is related to the back-stress in the material due to the key strengthening mechanisms of precipitates, laths and subgrains and immobile dislocations [159,186].

As illustrated in Figure 3.3, the use of a hyperbolic sine modelling methodology enables reliable extrapolation and interpolation of the MSR across a broad range of applied stresses. The relationship between microstructure and creep constants, presented here in Equation 3.2 and Equation 3.3, is key to the accurate prediction of the secondary creep response across a range of temperatures. This result also highlights the necessity to include microstructure in a modelling methodology for 9Cr steels to accurately predict creep behaviour.

Although the model predicts the creep response to a relatively high degree of accuracy in the 70 to 125 MPa stress regime, at higher stresses, the proposed modelling methodology is less accurate, by predicting the creep life at an applied stress of 175 MPa (see Figure 3.4a). It is argued here that this is possibly due to a change in primary mechanism of deformation under different stress regimes, further highlighting the requirement to include a more physically-based primary creep modelling methodology. For high stress modelling applications, in-elastic strain accumulation within the material is related to lath boundary hardening and conversion to equi-axed grains. Decreasing mobile dislocation densities due to dislocation pile ups at lath boundaries, serve to harden the material at high stress. High dislocation densities at the boundaries allow lath conversion to equi-axed grains to occur. This hardening due to a microstructural evolution lath strengthening mechanism, could be modelled using more physical models, such as proposed by Magnusson and Sandström [159],
Chapter 3 - Physically based, multiple precipitate type creep modelling

Spigarelli [186], Zhang et al. [204] or Barrett and co-workers [205].

Figure 3.9 presents application of the proposed model to Bar 257, including a comparison with creep test data from the literature [206]. Although the key point of this comparison is to demonstrate the ability of the approach to predict the detrimental effect of decreasing MX carbo-nitride volume fraction on rupture life for Bar 257, as compared to P91, it is worth noting that the model under-predicts strain at short times for the higher stress (82 MPa) and slightly over-predicts strain at long times for the lower stress (70 MPa). These deviations may be attributed to the fact that the primary and creep damage (cavitation) models do not explicitly account for the MX volume fraction.

The inclusion of MX precipitate behaviour within this model provides a more physical bases for the prediction of creep behaviour in high Cr containing material strengthened with precipitates. This improvement is an incremental step in the direction of a fully microstructure based creep model for power plant materials. For two similar materials, with minor differences in composition the two precipitate type model captured the differences in creep behaviour with a single parameter set, adjusting a single parameter in line with measured quantities. During long term operations (>100,000 hr) Z-phase ((Cr,Fe)(V,Nb)N) particles form at the expense of MX precipitates, causing a decrease in creep performance in 9Cr materials. This trend is also evident for newer 12Cr materials under development, as can be observed in Figure 2.26c. An evolving volume fraction approach could be coupled with the precipitate state variable presented here to account for this effect in future models. Additional precipitates can be included in this model by extending Equation 3.10 to include additional spacing terms for Laves or Z-phase. Appendix B contains a derivation of a four precipitate model with evolving volume fractions, based on the two precipitate approach presented here.

The results highlight the requirement to account for chemical composition and heat treatment when evaluating the performance of candidate materials. It is widely known that increasing the Al content has a detrimental effect on the high temperature creep performance of 9Cr steels, with a creep life reduction factor of 5.8 presented in Figure 3.10. This comparison clearly highlights the key role of precipitates, and in particular, of MX precipitates on the creep performance of 9Cr steels. Hence, it is necessary to (i) ensure strict control of chemical composition and careful heat treatment procedures are in place during component manufacture to optimise precipitate strengthening and (ii) develop material models capable of capturing the
key effects of such precipitates. In the present work, it is found that reducing the volume fraction of MX carbo-nitrides, consistent with the formation of AlN at the expense of more thermally stable VN, only captures this effect to a certain extent. The effect of increased mean spacing of obstacles associated with increasing Al content (as per Equation 3.3 with a reduced volume fraction of MX precipitates) on the creep constant, $\sigma_0$, must also be included to accurately capture the reduced creep performance due to loss of MX precipitates.

3.6 Conclusions

A continuum damage mechanics creep model for 9Cr steels, specifically designed to predict the key effects of precipitate-strengthening due to different precipitate types and microstructure-sensitivity of minimum creep strain-rate, has been developed. The model is applied here to P91 steel for $\text{M}_2\text{C}_6$ and MX precipitates, but the method is more generally applicable to multiple precipitate types, and indeed other alloy systems. The key conclusions are:

- The three state variable continuum damage mechanics model with multiple precipitate types is capable of predicting the creep deformation of 9Cr steels, incorporating the key role of MX carbo-nitrides on creep strength.

- Thermal ageing and strain-induced precipitate coarsening of MX and $\text{M}_2\text{C}_6$ precipitates represent key strengthening mechanisms to resist creep deformation in 9Cr steels. MX strengthening is dominated by thermal ageing, with strain-induced coarsening of $\text{M}_2\text{C}_6$ carbides necessary to predict the microstructural degradation and creep deformation in 9Cr steels.

- The multi-precipitate continuum damage mechanics model is capable of predicting the detrimental effect of increasing aluminium content, and associated reduction of MX precipitate volume fraction, on creep deformation and rupture life of 9Cr steels.

- MX carbo-nitride volume fraction is identified as a critical parameter for creep strength and life assessment in 9Cr steels operating in the target temperature range (above 600 °C) and in intermediate to higher applied stress regimes (approximately in the 70 to 100 MPa range). Aluminium content should be minimised to approximately 0.01 wt.% to ensure the formation of an optimum volume fraction of MX carbo-nitrides for high creep strength.
Chapter 4

Precipitate based creep predictions for welds

4.1 Introduction

The vast majority of power plant failures occur within welded connections often as Type IV failures which have been a source of major problems for power plant operators [21]. Type IV failures occur in the partially transformed inter-critical heat affected zone (IC-HAZ), (see Figure 1.7) which is a region of refined grains adjacent to the parent material within the HAZ [207]. Failure at this location has been attributed to multiple microstructural defects formed due to the weld process, including loss of the martensite hierarchical microstructure [21], loss or over-aging of precipitates [3], highly refined grains or the presence of delta ferrite [208]. This chapter presents the application of the multi-precipitate creep model, to an idealised three material cross-weld (CW) case. The expansion of the model from one dimension to a multi-dimensional case is required for applying the model to real world geometries. Here, welded tensile specimens are utilised for model validation, while welded thick-wall pipe components demonstrate a potential real world application of the model for comparing two 9Cr materials. The Fortran subroutine code utilised for this work is available in Appendix C.

The region in the vicinity of the weld is simulated using a three material approach consisting of parent (PM), weld (WM), and heat affected zone (HAZ) material, similar to that shown in Figure 2.29. In the modelled weld, considered for this work, the HAZ region is assumed to consist of fine-grained (FG-HAZ) or IC-HAZ material. Delineating these two regions with microstructural examinations is not always sufficient to distinguish between them. Hardness testing across the weld
region is often combined with microscopy techniques to identify the various HAZ regions as in Figure 2.28 [175, 196], where the IC-HAZ corresponds to in the region of minimum hardness. When examining the cross section of a weld there are no clear transitions between HAZ regions as there is only a gradient of material properties, which follows the temperature gradient experienced by the HAZ during the weld process.

The model is calibrated to Bar 257 material tested at 650 °C. Creep data sets are available in the literature for the PM, WM and CW specimens tested at the same temperature and stress levels [209]. A data extraction methodology using strain compatibility between the CW, PM and WM is presented and applied to identify explicit HAZ creep strain-time data following the work of Spigarelli et al. [210]. Averaged values are utilised for the microstructural parameters for the modelled HAZ region and it does not distinguish between CG, FG or IC-HAZ. Thus, the model is fitted for each of the three materials (PM, WM and HAZ) independently, then applied to an axi-symmetric CW test for P91 material. Utilising the modification of MX volume fraction and the corresponding change in average obstacle spacing, as discussed in the previous chapter, the creep behaviour can be altered from Bar 257 to standard P91. Validation of the CW model is demonstrated for welded P91 at 650 °C and compared against literature data [211,212]. The parameter fitting approach is also applied to a P92 material, with similar results for the P91 and Bar 257 data sets shown previously (see Figure 3.4).

The CW model is applied to a thick-walled pipe, using the same geometry as Hyde et al. [113]. The model solutions for stress redistribution through the pipe wall thickness are compared against analytical predictions at low and high stress levels showing good agreement. Weld strength reduction factors (WSRF) are calculated for the tensile CW specimens and welded thick-walled pipes for P91. Parent material and welded pipes of P92 are also modelled for comparison against P91 to demonstrate the expected improvement in WSRF between the two alloys.

### 4.2 Multi-precipitate type modelling methodology

The hyperbolic sine flow rule has been demonstrated by Barrett et al. [213] to give good agreement with experimental data for 9Cr steels tested at both high and low strain rates. Applied here is the model developed in Chapter 3 and this is expanded to include multi-axial stress conditions, with the details of this expansion discussed.
later in this chapter. The creep strain rate tensor is defined following the approach of Dyson and Osgerby [102], Perrin and Hayhurst [191] and Hyde et al. [103] for precipitate strengthened steels as follows:

\[
\dot{\varepsilon}_{ij}^{cr} = \frac{3}{2} \frac{S_{ij}}{\sigma_{eq}} \dot{\varepsilon}_0 \exp \left( -\frac{\Delta F}{k_B T} \sinh \left( \frac{\sigma_{eq}(1 - H)}{\sigma_0(1 - D_P)(1 - D_{CR})} \right) \right)
\] (4.1)

In this equation, \( S_{ij} \) is deviatoric stress tensor, \( \sigma_{eq} \) is equivalent (von Mises) stress and \( \dot{\varepsilon}_0 \) is a temperature-independent constant. All other symbols have their same meaning as in the one dimensional flow rule of Equation 3.1.

The other alteration to the model for operation under multi-axial conditions is the inclusion of the stress triaxiality effect in the cavitation damage parameter. The inclusion of this term for multi-axial stress states captures the observed phenomenon of cracking occurring within regions of high stress triaxiality, as follows:

\[
\dot{D}_{CR} = \bar{C}_{\varepsilon_{eq}} \left( \frac{\sigma_1}{\sigma_{eq}} \right) ^\nu
\] (4.2)

where \( \sigma_1 \) is the maximum principal stress and \( \nu \) is the triaxiality exponent. This is particularly relevant for welded connections as the material property mismatch within the weld region generates localised areas of high triaxiality as demonstrated by Watanabe et al. [53].

The CDM model is implemented within an explicit creep user subroutine for use with the non-linear, finite element code, Abaqus\textsuperscript{TM}, software version 6.14. A creep strain error tolerance (CETOL), of 6.66×10\textsuperscript{-6} [214] is used. The CETOL value is calculated using \( \sigma_{err}/E \), where \( \sigma_{err} \) is the allowable error in the stress calculation, and \( E \) is the Young’s modulus of the material. Mesh refinement studies were performed to ensure that results were mesh independent. The CW specimen and thick-walled pipes are modelled as 2D axisymmetric bodies.

4.3 Parameter identification and numerical modelling

In the model implemented here, the PM, WM and HAZ are considered as three separate materials with different sets of properties. For each material, there are seventeen input parameters that need to be determined. Twelve of these are microstructural
Chapter 4 - Precipitate based creep predictions for welds

and the remaining five are the pre-exponential constant, $\dot{\varepsilon}_0$, the primary hardening rate and limit, $h$ and $H^*$, respectively, the cavitation term, $\bar{C}$, and the triaxiality exponent, $\nu$. All constants are identified either directly or indirectly from published data. The following sections describe the process of identification of these parameters.

### 4.3.1 Identification of creep constants

Figure 4.1 shows the effect of stress on minimum strain rate (MSR) for both the PM and WM with the MSR experimental data from Hyde et al. [113]. The model calibration was performed for P91 and Bar 257 PM at 650 °C in Chapter 3. P91 and Bar 257 WM creep strain vs time data is obtained from the thesis of Agyakwa [209] for the 9Cr-1Mo weld consumable used in the fabrication of the Bar 357 CW tensile specimen. The Chromet 9MV consumable used is commercially available for use in P91 based fabrication from Metrode Products Ltd [209]. Being a standard consumable for P91 fabrication, it is assumed here that the same properties apply to WM formed in a P91 weld as in a Bar 257 weld. The model has also been calibrated to the P92 data of Ennis et al. [215] for P92 PM and to the data of Zhao et al. [216] for P92, WM and FG-HAZ materials. Table 4.1 shows the identified creep constants for the weld zones for the three materials, Bar 257, P91 and P92, including primary hardening and cavitation constants. The Helmholtz activation energy $\Delta F$ value of $1.04 \times 10^{-18}$ J for the P92 materials, is based on the creep activation energy data available for P91, $\Delta F \approx k_B Q_c / R'$ where $R'$ is the universal gas constant and $Q_c$ is the creep activation energy from Oruganti [199]. Equation 3.15 is fitted to the MSR-stress data shown in Figure 4.1 by optimising the $\dot{\varepsilon}_0$ and $\sigma_0$ terms with a least squares approach to minimising the difference between experimental data and model predictions, as in Section 3.4.1.

### 4.3.2 Calibration of primary hardening and cavitation constants

The identification of primary hardening variables, $h$ and $H^*$, and the cavitation constant, $\bar{C}$, from measured tensile creep strain curves for P91 and P92 materials, is performed utilising the automated least squares optimisation technique as in Chapter 3. Figure 4.2 shows the corresponding calibration fit of these three parameters for the P91 WM data of Agywaka [209], at 650 °C at 93 MPa and 100 MPa. The least squares parameter fitting was applied simultaneously using both creep strain
4.4 - Extraction of HAZ creep strain time data

![Figure 4.1: Comparison of predicted minimum creep strain rate with measured data from Hyde et al. [113] for PM and WM.](image)

### Table 4.1: Identified creep parameters for the three material zones in a 9Cr CW specimen.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Zone</th>
<th>$\dot{\varepsilon}_0$ (hr$^{-1}$)</th>
<th>$h$ (MPa)</th>
<th>$H^*$ (-)</th>
<th>$\bar{C}$ (-)</th>
<th>$\nu$ (-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM</td>
<td>HAZ</td>
<td>$1.02 \times 10^{12}$</td>
<td>2904</td>
<td>0.25</td>
<td>10</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>WM</td>
<td>$1.88 \times 10^{13}$</td>
<td>862</td>
<td>0.52</td>
<td>1.125</td>
<td>3.8</td>
</tr>
<tr>
<td>PM</td>
<td>HAZ</td>
<td>$6.2 \times 10^{25}$</td>
<td>8313</td>
<td>0.5</td>
<td>1.1</td>
<td>3.8</td>
</tr>
<tr>
<td>P92</td>
<td>HAZ</td>
<td>$8.0 \times 10^{25}$</td>
<td>188</td>
<td>0.084</td>
<td>1.52</td>
<td>3.8</td>
</tr>
<tr>
<td>PM</td>
<td>WM</td>
<td>$3.0 \times 10^{27}$</td>
<td>660</td>
<td>0.45</td>
<td>8</td>
<td>3.8</td>
</tr>
<tr>
<td>P91, Bar 257</td>
<td>WM</td>
<td>$6.00 \times 10^{13}$</td>
<td>7919</td>
<td>0.09</td>
<td>2.5</td>
<td>3.8</td>
</tr>
<tr>
<td>P91, Bar 257</td>
<td>PM</td>
<td>$1.02 \times 10^{12}$</td>
<td>2904</td>
<td>0.25</td>
<td>10</td>
<td>3.8</td>
</tr>
<tr>
<td>P92</td>
<td>WM</td>
<td>$1.88 \times 10^{13}$</td>
<td>862</td>
<td>0.52</td>
<td>1.125</td>
<td>3.8</td>
</tr>
<tr>
<td>P92</td>
<td>HAZ</td>
<td>$6.2 \times 10^{25}$</td>
<td>8313</td>
<td>0.5</td>
<td>1.1</td>
<td>3.8</td>
</tr>
<tr>
<td>P92</td>
<td>WM</td>
<td>$8.0 \times 10^{25}$</td>
<td>188</td>
<td>0.084</td>
<td>1.52</td>
<td>3.8</td>
</tr>
</tbody>
</table>

Curves to improve the stress range the model could operate over. The triaxiality exponent, $\nu$, was identified utilising the finite element methodology developed by Hyde et al. [103]. A range of exponent values were selected; based on the work of Hyde et al. [103] for a single precipitate type model, to calculate the corresponding time to failure. The calibration was performed for a net section nominal stress of 93 MPa at 650 °C.

### 4.4 Extraction of HAZ creep strain time data

Measured test data is available for the WM and PM, but not for the HAZ material. Thus, to obtain the HAZ creep response for identification of HAZ creep constants, a strain compatibility analysis of a CW specimen is employed. Figure 4.3 shows a
Chapter 4 - Precipitate based creep predictions for welds

Figure 4.2: Calibration of the primary creep constants via comparison with the experimental data of Agyawka [209] for P91 WM (Chromet 9MV consumable, Metrode Products Ltd.) at 650 °C.

schematic gauge length of a three-material CW creep test specimen, similar to the sample used by Hyde et al. [113] and Agywaka [209] for example. A creep strain curve can be extracted for the HAZ region using the strain compatibility approach suggested by Spigarelli and Quadrini [210], as follows:

$$\varepsilon_{HAZ} = \frac{1}{L_{HAZ}} (\varepsilon_{CW}L_{CW} - \varepsilon_{WM}L_{WM} - \varepsilon_{PM}L_{PM})$$  \hspace{1cm} (4.3)

where $L_{HAZ}$, $L_{WM}$, $L_{CW}$, and $L_{PM}$ are the representative lengths of the CW specimen as shown in Figure 4.3 and defined in Table 4.2. $\varepsilon_{HAZ}$, $\varepsilon_{WM}$, $\varepsilon_{CW}$ and $\varepsilon_{PM}$, are the corresponding creep strains in these regions. The CW, WM and PM responses are available from [113] and [209] as shown in Figure 4.4, for a stress of 93 MPa at 650 °C and the HAZ response is identified here using Equation 4.3. Clearly, the HAZ gives a significantly higher creep rate and strain accumulation than the CW, WM and PM. Figure 4.5 shows a comparison between the inferred HAZ response (via Equation 4.3) and the model predictions, demonstrating the capability of the model to represent the HAZ secondary creep response and rupture time. An elastic modulus of 110 GPa at 650 °C is assumed for each material [205].

4.4.1 Selection of Microstructural inputs

Details of the PM microstructure inputs are available in Chapter 3. Initial $M_{23}C_6$ diameters for the weld were selected based on the measurements of Lee et al. [173] and Arivazhagan et al. [172] on welded P91 (9Cr-1Mo) steels. Lee et al. investigated the microstructural degradation during creep of the HAZ material, concluding that
4.4 - Extraction of HAZ creep strain time data

Figure 4.3: Schematic of the three-material gauge length of CW specimen used in [209] and [113]. The specific dimensions are presented in Table 4.2.

Table 4.2: Dimensions of CW specimen utilised for HAZ creep strain versus time curve extrapolation [113, 209].

<table>
<thead>
<tr>
<th>Section</th>
<th>Dimensions (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent material ($L_{PM}$)</td>
<td>7.75</td>
</tr>
<tr>
<td>Heat affected zone ($L_{HAZ}$)</td>
<td>2.25</td>
</tr>
<tr>
<td>Weld material ($L_{WAZ}$)</td>
<td>6.00</td>
</tr>
<tr>
<td>Specimen diameter ($\phi D$)</td>
<td>8.66</td>
</tr>
</tbody>
</table>

coarsened $M_{23}C_6$ precipitates and a mixture of soft and hard ferrite grains within the ICHAZ lead to Type IV failure. Arivazhagan et al. [172] investigated the effect of Nb and V on the toughness of P91 WM post weld. Four welds with varying contents of Nb and V were subjected to Charpy V-notch impact testing, showing that a reduction of Nb and V increased the toughness of the weldment. A reduced volume fraction of MX is expected as a reduction in Nb and V concentrations. Transmission electron microscopy (TEM) images allowed the estimation of $M_{23}C_6$ precipitate size.

The HAZ precipitate diameters are selected based on the mean of measurements from TEM observations performed by Gaffard [217], Watanabe et al. [53], Lee et al. [173] and Vijayalakshmi et al. [176] on ICHAZ regions of welded P91 materials. Gaffard [217] noted a factor of two increase between the PM and ICHAZ $M_{23}C_6$ precipitate diameters, after post weld heat treatment (PWHT). Watanabe et al. [53] noted that this precipitate family experienced a qualitatively larger coarsening within the HAZ region due to exposure to temperatures below the $M_{23}C_6$ dissolution temperature allowing coarsening to occur. Lee et al. [173] published values for both $M_{23}C_6$
Chapter 4 - Precipitate based creep predictions for welds

Figure 4.4: Results of the creep strain extraction methodology for the HAZ region compared with the three data sets, PM, WM and CW utilised in Equation 4.3. MSR PM data from [103] while creep strain vs time data for PM, WM and CW is available in the thesis of Agyakwa [209].

Figure 4.5: Comparison of predicted and measured HAZ creep response for 93 MPa and 650 °C.

and MX precipitate families based on SEM based measurements of same, performed on sections increasingly further from the WM fusion line, capturing the diameter differences between WM, HAZ and PM regions. Milović et al. [218] observed decreased concentrations of MX precipitates within the ICHAZ, when investigating the reduced hardness occurring within this region, but did not measure precipitate diameters in the same manner as Lee et al. [173] or Gaffard [217]. Using thermodynamic modelling Svobodová et al. [219] predicted the MX and M23C6 formation temperature at 825 °C. El-Azim et al. [174] observed MX precipitates of a similar size to those observed by Lee et al. [173] in a post weld heat treated P91 HAZ material. Precipitates within the HAZ region form during PWHT or in some cases during multi-pass welding, where auto-tempering can occur due to repeated heating from later passes.
Precipitate volume fraction data for the HAZ region was obtained from the work of Vijayalakshmi et al. [176], showing significantly reduced volume fractions within the sub-regions of the HAZ compared with PM. Limited data are available for the precipitate volume fractions within the WM of a welded connection. Spigarelli and Quadrini [210] note that, during the rapid cooling of the weld and HAZ, new precipitates do not form leading to a low volume fraction of precipitates in these regions. The existing non-dissolved precipitates coarsen rapidly leaving a microstructure of large precipitates, widely dispersed. Barbadikar et al. [220] highlighted that an increase in normalising and tempering temperatures leads to a decrease in precipitate area fraction. They measured an increase in precipitate diameter when tempering temperature increased from 740 °C to 780 °C. Multi-pass welding causes high temperature tempering, potentially reducing precipitate area fraction further, via additional dissolution and partial re-precipitation of precipitates. Paul et al. [171] reported no carbides within the weld zone for a P91 multi-pass weld with five weld layers laid using twelve torch passes per layer. Microstructural characterization results were presented for the upper layer of WM, farthest from the HAZ material i.e. pure WM. This material, upon inspection after cooling, had not formed significant volume fraction of either precipitate families.

Elongated narrow prior austenite grains have been reported for the WM, due to rapid directional solidification post weld; grain size data was obtained from the work of Paul et al. [171], Vijayalakshmi et al. [176] and Vivier et al. [221]. Similar investigations of the HAZ region were performed by El-Azim et al. [174], Paul et al. [171] and Vivier et al. [221] to measure grain size in this region of welded 9Cr after PWHT. Lath widths were also presented for the weld and HAZ materials by Paul et al [171], Vijayalakshmi et al. (weld and HAZ), and Gaffard [217] (HAZ). Dislocation densities within the WM were qualitatively reported by Watanabe et al. [53] as significantly higher than for the PM. Table 4.3 contains the microstructural values utilised from these sources as detailed above, except in the case of the dislocation densities, where values are estimated from within an expected range.

The model has also been calibrated for P92 (detailed previously in Section 2.2.3). The P92 benefits from additional W, solid solution strengthening and considerably decreased precipitate thermal coarsening rates which improve its creep resistance. Literature data for 650°C creep tested P92 PM, WM and FG-HAZ were utilised, for this calibration. The MSR-stress and creep curve data used for the model calibration is from the work of Ennis et al. [215] and Zhao et al. [216]. The precipitate coarsening
rates identified by Hald et al. [30] were utilised for the thermal coarsening parameters, with the strain induced coarsening parameters for P91 used from Chapter 3. Table 4.3 contains the model parameter set for P92. Figure 4.6 presents the results of the parameter fitting to the P92 data of Ennis et al. [215] at 650 °C in the stress regime 81 to 110 MPa.

Table 4.3: Microstructural model parameters for the three material zones, for all three welded cases. Bar 257 for calibration, P91 for validation and P92 for thick-walled pipe comparisons.

<table>
<thead>
<tr>
<th>Material Zone</th>
<th>d_{M_23C_6,0} (nm)</th>
<th>d_{MX,0} (nm)</th>
<th>f_{M_23C_6} (%)</th>
<th>f_{MX} (%)</th>
<th>\lambda_{ob} (nm)</th>
<th>w (\mu m)</th>
<th>d_g (\mu m)</th>
<th>\rho (m^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>PM PM 100 36 2 0.1 38 0.4 40 3.66×10^{14}</td>
<td>Bar 257 HAZ 128 65 0.002 0.001 65 4 12 2.10×10^{14}</td>
<td>WM 200 55 0.05 0.0001 55 5 140 2.40×10^{14}</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PM PM 100 36 2 0.5 31 0.4 40 3.66×10^{14}</td>
<td>P91 HAZ 128 65 0.002 0.005 66 4 31.8 2.10×10^{14}</td>
<td>WM 200 55 0.05 0.0005 60 5 140 2.40×10^{14}</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>PM PM 100 36 2 0.5 50 0.4 40 1.00×10^{14}</td>
<td>P92 HAZ 128 65 0.05 0.0005 70 0.7 10 1.35×10^{14}</td>
<td>WM 200 65 0.002 0.005 60 6 100 2.47×10^{14}</td>
<td></td>
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</tr>
</tbody>
</table>

### 4.4.2 Identification of coarsening rates

The thermal coarsening rate constants $K_i$ for both MX and M$_2$C$_6$ precipitates are identified based on thermal ageing data from the grip region of a crept test specimen of Hald et al. [30]. Figure 4.7 shows a comparison between the thermal coarsening data at 650 °C and Equation 3.11 while $\phi_i$ is set to zero. Utilising these identified values of $K_i$, in combination with gauge section data from the same creep tests, the strain-induced coarsening constant $\phi_i$ is also been identified [54]. Figure 4.7 also shows the resulting comparison with the creep ageing data of Hald et al. [30] at 650 °C; a similar quality of fit is achieved for 600 °C [54]. Here, precipitate coarsening is assumed to be independent of material zone, as limited data is available on precipitate coarsening kinematics in weld and HAZ materials. Table 4 shows a summary of the identified coarsening rate constants for the M$_2$C$_6$ carbides and the
4.4 - Extraction of HAZ creep strain time data

MX precipitates. The additional W in P92 decreases the coarsening rate of M$_{23}$C$_6$ precipitates due to it’s low diffusion rate in Fe (see Table 2.4).

![Figure 4.6: Results of the model fitting for a P92 PM tested at 650 °C, experimental data from the work of Ennis et al. [215].](image1)

![Figure 4.7: Identification of strain and temperature induced coarsening parameters based on creep and thermal aging data at 650 °C from Hald et al. [30].](image2)

Table 4.4: Identified coarsening rates for M$_{23}$C$_6$ and MX families of precipitates at 650 °C, for P91, Bar 257 and P92

<table>
<thead>
<tr>
<th>Material</th>
<th>Zone</th>
<th>$K_{M_{23}C_6}$ (mm$^3$hr$^{-1}$)</th>
<th>$K_{MX}$ (mm$^3$hr$^{-1}$)</th>
<th>$\phi_{M_{23}C_6}$ (mm$^3$)</th>
<th>$\phi_{MX}$ (mm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bar 257, P91</td>
<td>PM, HAZ, WM</td>
<td>6.35×10^{-15}</td>
<td>3.90×10^{-18}</td>
<td>1.04×10^{-9}</td>
<td>1.18×10^{-14}</td>
</tr>
<tr>
<td>P92</td>
<td>PM, HAZ, WM</td>
<td>1.72×10^{-17}</td>
<td>2.36×10^{-19}</td>
<td>1.04×10^{-9}</td>
<td>1.18×10^{-14}</td>
</tr>
</tbody>
</table>
Chapter 4 - Precipitate based creep predictions for welds

4.4.3 Numerical modelling

The model has previously been validated uniaxially, for a P91 PM at 600 °C and 650 °C in Chapter 3 [54]. The FE creep integration scheme employed for the creep subroutine developed here, can select between implicit or explicit integration. As such, a converged maximum time increment size is required to ensure that there is no effect on the time to failure results. A maximum allowable time increment size of 5 hours is identified from Figure 4.8.

Figure 4.8: Time increment convergence plot, 5 hours is selected as the maximum allowable time increment. No significant effect on time to failure is identified for values between 0.05 and 10 hours.

Figure 4.9a shows the notched tensile specimen geometry and converged mesh from Abaqus™ developed for the multi-axial calibration of the $\nu$ term in Equation 4.2 (PM). Figure 4.9b shows the cavitation damage contours, for the 93 MPa condition, at failure after 1186 hours creep exposure at 650 °C. Iterative versions of this simulation are performed with varying values of the $\nu$ parameter at this stress level until agreement is achieved with the literature creep test data of Hyde et al. [103]. Once reasonable agreement is achieved for 93 MPa stress level the 82 MPa notched bar simulation is performed as a validation step. The results of this identification procedure are presented in Figure 4.10. Failure is deemed to have occurred when an integration point reached a cavitation damage ($D_{CR}$) value of 1. Validation is then performed for a net section nominal stress of 82 MPa at the same temperature of 650 °C. Figure 4.10 shows a comparison of the resulting predicted and experimental [103] rupture lives for notched and plain specimens, across a range of stresses. Clearly, the rupture life predictions correlate closely to the measured lives across the stress range of interest here for both plain and notched bar cases.
4.5 - Evaluation of precipitate effects in cross-weld specimens

Figure 4.9: Notched bar FE model geometry showing (a) Converged mesh with dimensions in mm and (b) cavitation damage contour at failure for nominal section stress of a 93 MPa at 650 °C, time to failure is 1186 hrs.

Figure 4.10: Comparison of predicted and measured creep rupture stress-time responses for plain (un-notched) and notched bar tensile tests at 650°C [103].

4.5 Evaluation of precipitate effects in cross-weld specimens

Figure 4.11 shows the predicted evolution of $M_{23}C_6$ precipitate diameter for the axisymmetric CW geometry, from Figure 4.3, for an applied load of 70 MPa at 650 °C, up to the time to failure of 1150 hr. Although the WM initially has the largest $M_{23}C_6$ precipitate diameter, the HAZ region experiences the most dramatic increase. The strain concentration within the HAZ leads to enhanced precipitate coarsening.
which accelerates the formation of creep cavities once precipitates exceed a critical size of about 250 nm [165]. This is consistent with experimental observations of enhanced cavity formation adjacent to large coarsened carbides [53, 173, 222], and illustrates the importance of including strain-induced carbide coarsening within the $D_p$ state variable.

Figure 4.11: Schematic of assumed CW geometry and predicted evolution of associated distributions of $M_{23}C_6$ precipitate diameter for 70 MPa at 650 °C, up to failure at 1150 hr.

Figure 4.12 shows the predicted evolution of cavitation damage for an applied stress of 70 MPa. A concentration of cavitation damage occurs at the centre of the HAZ, slightly biased towards the PM. Cavitation-induced failure within the HAZ is due to high strain accumulation and stress triaxiality occurring within this region, as observed by Watanabe et al. [53]. A high level of stress triaxiality, due to the geometry of the welded connection, is a contributor to Type IV failure. Figure 4.13 shows the evolution of triaxiality along the path of highest cavitation damage within the HAZ. The triaxiality is greater near the central axis leading to concentration of damage on this axis and hence, cracking is predicted to initiate here.

Figure 4.14a and Figure 4.14b show the predicted evolutions of $M_{23}C_6$ and MX diameters for sample points A, B and C in the PM, HAZ, and WM regions respectively (from Figure 4.12a). In Figure 4.14a, the PM $M_{23}C_6$ carbides remain the smallest until failure, while the HAZ carbides grow rapidly, reaching the proposed 250 nm [104]...
4.5 - Evaluation of precipitate effects in cross-weld specimens

Figure 4.12: Cavitation damage evolution for a load of 70 MPa at 650 °C. Maximum damage accumulates within the HAZ region leading to failure.

A threshold discussed previously in Chapter 3 for enhanced cavitation. WM carbides are predicted to be the most stable, coarsening slower than carbides in either PM or HAZ materials.

Figure 4.13: Evolution of radial distribution of stress triaxiality, across the centre of HAZ, for an applied load of 70 MPa at 650 °C. Maximum triaxiality occurs at the central axis in the HAZ where failure is predicted to occur.

The effect of stress on HAZ precipitate coarsening is demonstrated in Figure 4.15. A 33% increase in stress is predicted to lead to approximately 87% reduction in the time to reach an $M_{23}C_6$ diameter of 250 nm, i.e. a highly non-linear response due to combined strain and thermal coarsening effects of Equation 3.11. In contrast,
Chapter 4 - Precipitate based creep predictions for welds

Figure 4.14: Predicted evolutions of (a) $M_{23}C_6$ and (b) MX precipitate diameter for PM, WM and HAZ for the 70 MPa case at points A, B, C, in Figure 4.11.

Figure 4.14b demonstrates the stability of the MX precipitates in all three materials by their approximately flat coarsening curves for the short term 70 MPa tests. Thermally-induced coarsening dominates the growth characteristics of MX precipitates, as such short-term, high stress testing induces only minor coarsening of this family of precipitates [223].

Figure 4.15: Predicted effect of stress on $M_{23}C_6$ the precipitate coarsening dynamics within the HAZ region at point B, in Figure 4.11.

Figure 4.16 shows a close correlation of failure times between the multi-precipitate three material model with the PM and CW test data compiled by Tabuchi et al. [212] and Kimura and Takahshi [211] for P91 steels over a wide stress range at 650 °C. The model clearly captures the significant decrease in time to failure due to the weldment; a key objective of the present work. A slight overestimation of life for PM data is observed at high stress levels, with the PM model predicting failure occurring after 126 hours at 146 MPa compared with the experimental result of 64 hours. This may
be attributed to the lath growth and conversion to equi-axed grains which occurs under high stress conditions [96], as this mechanism is not accounted for in the model at present. However, as this is above typical plant operational ranges, it is perhaps of less interest to plant operators. The HAZ material parameters were calibrated for 93 MPa test data and the WM parameters from tests at 100 MPa and 93 MPa. Based on these calibration conditions, accurate stress-life predictions have been achieved for welded connections across a much wider stress range. This demonstrates the predictive capability of the hyperbolic sine based modelling approach for welded P91 creep behaviour. Creep tests are extremely time intensive and have high cost associated with them. By utilising the model presented here, accurate long-term predictions can be generated in conjunction with short term, low-cost laboratory tests.

Figure 4.16: Comparison between experimental data for P91 parent and CW specimens at 650 °C with model results [166, 211, 212].

4.6 Modelling thick-walled pipes

Based on the accurate model predictions from the parent and CW models compared to data in Figure 4.16, the model is applied to a thick-walled pipe geometry. In an actual plant, the vast majority of the component consists of PM, with a small percentage being weld and HAZ materials. Therefore the modelling of a thick-walled component is of interest to plant operators as it represents real-world conditions more accurately. The model geometry is of a typical thick-walled pipe found in power plants and is the same as utilised by Hyde et al. [113]. Increasing internal pressures were applied with proportional axial tensile loading appropriate for a pipe with closed ends, Figure 4.17 presents the axisymmetric geometry, loading conditions and an
appropriate converged mesh with 10500 quadratic elements. The element type was CAX8R, 8-node biquadratic axisymmetric quadrilaterals with reduced integration.

Figure 4.17: Geometry, loading conditions and converged mesh for the thick-walled pipe simulations, based on the work of Hyde et al. [224], dimensions in mm.

Different internal pressure scenarios, from 10 to 40 MPa were applied, where pressures above 25 MPa at 650 °C are considered ultra-super critical conditions [5]. Two pipe materials were investigated in this work, conventional P91 and P92 material. Increasing pressure shifts the location of failure from the internal wall of the pipe at low pressures, to the external surface of the pipe at high pressures. Pipe design codes generally rely on the mean diameter hoop stress [103];

\[
\sigma_{mdh} = \frac{p_i(D_{OP} - T_W)}{2T_W} \quad (4.4)
\]

where \(p_i\) is the internal pressure, \(D_{OP}\) is the outer pipe diameter, and \(T_W\) is the wall thickness. Overlaying the mean diameter hoop stress from three loading conditions; 10, 25 and 40 MPa on the minimum strain rate versus applied stress graph for P91 at 650 °C (from Figure 3.3b) gives the plot in Figure 4.18. It is seen that the 10 MPa internal pressure is below the transition region between the diffusion and dislocation dominated creep regimes, the 25 MPa case is slightly above the transition region and the 40 MPa is well into the dislocation dominated regime.

The Norton steady state creep equation requires two exponent values to fit the P91 MSR data in Figure 4.18. The equations of Lamé’s are combined with the
4.6 - Modelling thick-walled pipes

Figure 4.18: Increasing internal pressure migrates failure location in thick-walled pipes, from internal to external pipe wall. This is in line with the change from low stress, diffusion dominated creep to high stress, dislocation dominated creep.

Norton steady state model to predict the redistribution of stresses across the pipe wall thickness in Equation 4.5. Lamé’s equations for the stresses in a single material, thick-walled pipe with closed ends, under creep conditions, are defined through the wall thickness as:

\[
\begin{align*}
\sigma_r &= \frac{P_i}{(R_o/R_i)^{2/n} - 1} \left\{ \frac{1 - (R_o/r)^2}{1 + (R_o/r)^2} \right\} \\
\sigma_\theta &= \frac{P_i}{(R_o/R_i)^{2/n} - 1} \\
\sigma_z &= \frac{P_i}{(R_o/R_i)^{2/n} - 1} 
\end{align*}
\] (4.5)

where \(\sigma_r\), \(\sigma_\theta\) and \(\sigma_z\) are the radial, hoop and axial stress distributions respectively. \(R_o\) and \(R_i\) are the outer and inner radii of a thick-walled pipe, while \(r\) is any radial distance from the centreline of the pipe. Figure 4.19 compares the stress distributions through the thickness of a pipe, for elastic, low \((n = 1.6)\) and high \((n = 7)\) stress, creep conditions, using Equation 4.5 for the geometry described in Figure 4.17a. Increasing internal pressure causes the mean diameter hoop stress (Equation 4.4), to transition from the low to high stress regime, necessitating the use of a higher stress exponent term in Equations 4.5. Therefore, the location of highest stress is expected to migrate from the internal surface of the pipe, to the external surface for high stresses based on the analytical results. For a single material piping component this type of analysis could be sufficient for predicting failure locations. The inclusion of multiple materials in the weld requires the use of more complex modelling approaches. The hyperbolic sine model presented in this chapter allows failure predictions to be performed for welded pipes, revealing general trends in failure locations in welded pipes as in plain pipes.
Chapter 4 - Precipitate based creep predictions for welds

Figure 4.19: Stress distributions through the radial thickness of a single material, thick-walled cylinder under elastic and creep loading conditions, where two creep conditions are shown for Norton exponent values of 1.6 and 7.

Figure 4.20, shows the cavitation damage contours at failure for the 10 MPa, 25 MPa and 40 MPa thick wall, welded P91 pipe at 650 °C. The location of highest stress for this welded pipe migrates from the inner to outer surface of the pipe wall. Specifically for each pressure condition considered cavitation damage concentrates within the HAZ region in a similar manner to the CW specimens in Figure 4.12. At 10 MPa internal pressure, the failure occurs at the inner surface, while at 25 MPa and 40 MPa failure occurs at the outer surface of the pipe. These simulations have been performed with parent and welded pipes of P91 and P92 material to calculate weld strength reduction factors for the thick-walled pipes.

4.7 Weld Strength Reduction Factors

4.7.1 Tensile

The results in Figure 4.16 can now be used to investigate the weld strength reduction factor (WSRF). The WSRF is calculated according to ASME standards [203] and, for a particular time to failure, it is the ratio of CW to PM applied stress. In practice a vertical line is drawn on Figure 4.16 for the time to failure of interest and the ratio between the two stresses generates the WSRF.

\[
W_{SRF} = \frac{\sigma_{t, CW}}{\sigma_{t, PM}}, \quad t_{f, CW} = t_{f, PM}
\]  

(4.6)

WSRF values calculated in this work are in the range 0.5 to 0.9 and, these have been calculated for both the experimental data and the model tensile results, and
are presented in Figure 4.21. Tabuchi et al. [212] calculate WSRFs in the regime of 0.7 to 1 for P91 materials across a range of temperatures, and recommend a value of 0.7 being achieved at 650 °C for components operating up to 100,000 hours. The model is conservative compared to the experimental data.

4.7.2 Thick-walled pipes

The WSRF of thick-walled pipe and CW simulations are compared here to examine the effect of geometry and loading conditions. To this end the weld strength reduction factor for a thick-walled pipe is calculated using the same approach as for the tensile CW case, where the stress utilised is the mean diameter hoop stress of Equation 4.4, as such the pipe WSRF is defined as:

\[
WSRF_{pipe} = \frac{\sigma_{mdh}^\text{CW,f}}{\sigma_{mdh}^\text{PW,f}}
\]  

(4.7)

Figure 4.22 presents the results of the WSRF calculation for the modelled P91 thick wall pipes at 650 °C, compared against the uniaxial WSRF from Figure 4.21. The
Chapter 4 - Precipitate based creep predictions for welds

Figure 4.21: Experimental and model WSRFs for tensile tested and modelled P91 at 650 °C.

results from the pipe simulations show a significantly higher WSRF, indicating that the model results for welded pipes are closer to that of a plain PM pipe. This is inline with expectations, as the vast majority of the welded pipe is comprised of PM. For internal pressures between 15 and 30 MPa, the WSRF are in the 0.8 to 0.9 range and relatively stable. Outside of this range, for low or high pressures, the WSRF decrease indicates that the presence of a weld is reducing the life of the component to a higher degree.

Figure 4.22: Comparing FE predicted P91 tensile and thick-wall pipe WSRFs.

The thick-wall welded and plain pipes are modelled using the P92 parameters and compared against the P91 results in Figure 4.23. Here the improvement in performance achieved by P92 is evident, with the majority of the WSRF values being close to unity, there is little effect of the weld on component performance. A similar range of internal pressures were applied, between 10 and 40 MPa as for the P91 pipes. The additional W and subsequent reduced coarsening rates of the P92 contribute to extending the component life significantly. Comparing the time to failure for an
internal pressure of 20 MPa, the model predicts 6,953 hours to failure for the P91 weldment, while the P92 is 94,299 hours (see Figure 4.23), over an order of magnitude improvement. This is attributed to the significantly reduced coarsening rates of the precipitates within the P92 material. This can also be attributed to the lack of Laves and Z-phase particles which reduce the life of P92 components considerably, comparing P91 tensile, P91 and P92 thick-walled pipe WSRF. The P91 pipe shows considerable improvement over the tensile. The W containing P92, exhibits significantly improved WSRF above that of the P91 pipe or tensile results. The times to failure for the P92 pipes are also significantly improved at all pressure levels.

Figure 4.23: Comparing a)P91 tensile and thick-wall pipe WSRFs and b)P92 and P91 thick-wall pipe WSRFs.

4.8 Discussion

The model provides a predictive capability, calculating the life of welded component based on the evolving precipitate microstructure of 9Cr steels. Within this framework, the experimentally observed evolution of the microstructure experiencing creep has been predicted using a CDM physically based approach. The use of a CDM approach allows for the future addition of other microstructural degradation effects such as oxidation or fatigue loading effects with relative ease.

Ogata et al. [225] performed CW creep tests and welded pipe rupture tests using internal pressure with failure occurring in the HAZ. Creep voids were detected using detailed SEM observations. The number of voids per unit area was highest in the midsection of the HAZ region for both the tensile CW specimen and in the mid-thickness of the pipe. Using FE simulations, Ogata et al. [226] predicted high triaxiality at locations where tests showed a high density of creep voids. Micro-cracks
formed from the individual cavities at the mid-thickness of the pipe specimen, with these then growing towards the outer surface of the pipe. The present model predicts cavitation damage inducing failure at the midsection of the HAZ region where the triaxiality is high (see Figure 4.13). This is in line with the observations of Ogata et al. [225] and also similar to failures observed by Watanabe et al. [53].

As Figure 4.11 and Figure 4.14a show, the highest rate of $M_{23}C_6$ precipitate coarsening occurs within the HAZ region. Examining the carbide evolution plot in Figure 4.11 shows that although coarsening concentration is focused in the centre of the HAZ, this concentration of high precipitate diameter extends across much of the section.

While MX precipitates coarsen considerably slower than $M_{23}C_6$ precipitates, their contribution to the creep strength of the material, via extensive dislocation pinning, is significant. The addition of the MX coarsening kinematics to the model allows for the consideration of compositional variations on the time to failure of the material, i.e. modelling of P91 variants with different MX volume fractions [54].

Thick-walled pipe simulations utilising the hyperbolic sine model predict the expected failure location migration behaviour when compared with analytical creep steady state solutions from thick-walled cylinder theory. Low internal pressures lead to internal surface failures with high internal pressure leading to failure at the outer surface of the welded pipe, see Figure 4.20. Stress redistribution through the wall thickness occurs under low internal pressure. The lower stress regime allows significant precipitate coarsening to occur causing the cavitation damage to accumulate at the inner surface. At high internal pressure, cavitation damage begins to accumulate before the stress can redistribute leading to failure at the outer surface. Failure occurs within the HAZ region or at the HAZ-PM interface line for each of the simulated pipe conditions.

WSRF for the thick-walled pipes are higher at all failure times than the tensile simulations. This is attributed to the larger portion of P91 PM present in this simulation. The P91 uniaxial simulations exhibit WSRFs in the range of 0.5 to 0.68, compared to 0.7 to 0.9 for the thick-walled pipes. Figure 4.23 demonstrates the improvement in performance of P92 pipes against that of the P91 tensile and pipe WSRFs. Parameter identification for the P92 involved adjusting the original P91 parameters based on physical arguments and available data, particularly for the HAZ case, where FG-HAZ data is used in place of IC-HAZ data used for P91. As such the P92 results should be considered a good approximation of actual P92 thick
wall behaviour.

The parameter identification procedure presented here for the HAZ material is necessarily based on some simplifying assumptions. For example, the HAZ region is considered as a single homogeneous material while in fact, it is a more complex heterogeneous structure; consisting of the coarse-grain, fine-grain and inter-critical HAZ regions as shown schematically in Figure 1.7. Nevertheless, it is argued that the approach used here enables a reasonably accurate initial estimate of the HAZ material behaviour. The extraction of separate creep time curves for coarse grain, fine grain and inter-critical HAZ regions has proven challenging [227], as these are extremely narrow regions within the material. Some success has been achieved in the identification of creep properties of the various HAZ regions using indentation creep tests with small indenter’s, e.g. see Hyde et al [228]. In that work, two distinct material regions within the HAZ material were characterised as high temperature and low temperature HAZ, with these regions corresponding to HAZ adjacent to the weld and PM, respectively. Combining data from this type of testing with the strain compatibility technique described here could potentially produce a more refined modelling approach.

Hyde et al. [113] has employed an impression creep apparatus to the WM regions of welded Bar 257 materials to identify the minimum strain rate data for this material, but as discussed in Chapter 2 this does not provide failure times for the materials. While Agyakwa [209] performed full scale tensile tests on WM, this required large quantities of WM to be generated. A less materially demanding approach to testing the WM would have been to perform SPC testing on the WM, which would produce the same data as the tensile test for a fraction of the material requirements. Chapters 5 and 6 detail the development, calibration and application of an SPCT apparatus to P91 materials to explore the potential of this relatively new test as a means to validate multi-axial computational models.

4.9 Conclusions

Welded component life predictions have been calculated utilising a novel temperature- and strain-induced precipitate coarsening model, including both $M_{23}C_6$ and MX precipitate families in 9Cr steels, within a continuum damage mechanics creep model. This approach predicts welded component life for a relatively wide stress range, from typical laboratory tests to next generation ultra-super critical plant conditions.
A parameter identification methodology, previously presented for PM, is extended and applied here to weld and HAZ materials utilising published microstructural observations. The model has been expanded to include multi-axial effects, with calibration and validation against the notched bar test data.

Strain-induced coarsening is predicted to primarily affect $\text{M}_{23}\text{C}_6$ precipitates during creep which, when coarsened, enhance the rate of cavitation damage accumulation. An inhomogeneous evolution of $\text{M}_{23}\text{C}_6$ diameter is predicted within the HAZ region of a 9Cr steel weldment. The combined effects of high triaxiality, creep strain and precipitate coarsening accelerate the damage accumulation within the HAZ region leading to failure.

The inclusion of MX precipitate evaluation in the model, allows for compositional effects to be included. This can be coupled, in future work, with thermodynamic simulations for precipitate formation during heat treatments and manufacturing processes (e.g. welding), to predict through process component times to failure. The inclusion of W in P92 materials significantly improves the life of thick-walled pipe components, due to the decreased precipitate coarsening rates. P92 material owes much of its improved creep resistance to the presence of W and the model presented captures this effect through the reduced carbide coarsening rates. Also, the detrimental effects of Laves and Z-phase particles are not accounted here.

Thick wall pipe simulations of welded and plain P91 and P92 pipes highlight the importance of simulating real-world component geometries when calculating weld strength reduction factors. For the P91 material at 650 °C, the tensile factors were in the 0.5 to 0.6 range while the thick-walled pipe factors were in the 0.7 to 0.9 range. The uniaxial tensile weld strength reduction factors are more conservative than the thick-walled pipe factors, as they artificially emphasise the effect HAZ material has on the time to failure. The higher relative quantities of PM present in a component increase the weld strength reduction factors.

Two methods of increasing the life of welded components are suggested from this work, (i) reducing the initial carbide diameter within the HAZ region via careful heat treatment, and (ii) enhancing the thermal stability of precipitates by addition of new stabilising elements during manufacture and welding. One such example is the novel 9Cr material, MarBN, manufactured with controlled addition of B and N and up to 3% W to enhance the thermal stability of precipitates and retain the hierarchical microstructure of the PM post-weld.
Chapter 5

Experimental and numerical evaluation of a small punch creep test apparatus

5.1 Introduction

One method of extracting more accurate creep data from a welded specimen is to develop and utilise small scale creep testing. Here, thin slices or disks of material are extracted from the weld and tested to failure. Hyde et al. [113] employed this approach to identify the MSR data utilised here for the initial weld metal model calibration in Figure 4.2. Chapters 5 and 6 detail the calibration, validation and testing program for a small punch creep test developed to extract this type of material data explicitly.

The SPCT provides a low-cost and low-material demand creep test methodology for characterising the creep behaviour of materials, as discussed in section 2.5.6. The production of complete creep curves, comparable to tensile curves from a small volume of material is the primary objective of the SPCT based approach. Taking the example of the CW tensile test specimen in Figure 4.3, three SPCT disks could be extracted from the HAZ material for testing, providing a more direct assessment approach than the FE work of the previous chapter. This is in addition to the potential for creep testing of in-service components to estimate remnant life, for which the SPCT was originally developed.

The development, calibration and validation of a small punch creep test apparatus, for operation at high temperatures is now described. The sample manufacturing process is outlined along with acceptance criteria in relation to surface roughness and
Chapter 5 - Experimental and numerical evaluation of a small punch creep test apparatus

thickness. Calibration and validation test results are presented along with a brief description of some control issues which were solved during the initial operation of the device. To complement the experimental work, the development of an elastic-plastic-creep finite element model for the apparatus utilising the physically based two precipitate creep model from Chapters 3 and 4 is described. Model boundary conditions, geometries and contact considerations are presented, along with necessary convergence and sensitivity studies in this chapter.

5.1.1 Standards

The apparatus is designed to comply with the now expired 2006 European Committee for Standardisation (CEN) workshop agreement on small punch test methods for metallic materials [114] CWA 15627. The apparatus is shown schematically in Figure 5.1, reproduced from the standard here. Here, 1 is the sample with a height $h_0$

2 is the punch, 3 and 4 are the lower and upper dies, respectively and 5 is the extensometer. $D$ is the receiving hole diameter, $d$ is the specimen diameter and $r$ is the punch radius. $F$ is the applied load and $u_1$ and $u_2$ are the upper and lower sample face displacements where a difference between $u_1$ and $u_2$ post test indicates sample thinning. The standard requires samples to be 8 mm $\pm 1\%$ in diameter with

Figure 5.1: Recommended die, specimen, punch and extensometer placement for a small punch creep test apparatus from [114].
5.2 - Initial apparatus design

a thickness of 0.5 mm ±0.5%, with the thickness measured at four locations 90°
 apart on the outer edge and once in the middle. Specifications for the sample holder
dies are also supplied, namely the lower die receiving aperture of radius $R(= D/2)$
is recommended to be 2 mm with a 45° chamfer on the lower die aperture.

Where possible the guidelines in this standard are followed, the most significant
differences between the standard and the NUIG SPCT apparatus are the use of a
spherical indenter and the location of the extensometer. A spherical indenter is
employed to minimise the potential for rod misalignment to occur when loading the
sample, as, this effect had been investigated in the work of Cortellino [229]. Cortellino
highlights misalignment angles, between the push rod and specimen central axis, of
$<2^\circ$ which showed less than a 10% difference on the $MDR$ and $t_f$ results. Using a
sphere prevents this angle from forming between the push rod and specimen.

The inclusion of the extensometer within the lower die inside the furnace, requires
an active cooling system. This system requires a constant liquid supply which was
beyond the manufacturing capability available. As such the extensometer is placed
on the push rod above the furnace. A simple constant load system is employed using
weights applied to the push rod and released to begin the test, in place of using a
servo-controlled system. The dead load system is reliable and requires no additional
control system or power supply, making it ideal for this project.

5.2 Initial apparatus design

The NUI Galway SPCT apparatus was initially developed as part of a design project
for a group of masters students with this PhD candidate acting as supervisor for their
work. These students, working in conjunction with the PhD candidate, would have
built the rig as described in this section. The subsequent work, from section 5.3
onwards was carried out exclusively by the PhD candidate.

The SPCT consists of a frame stand, push rod-loading pan assembly, sample holding
die assembly, linear variable differential transformer (LVDT) displacement sensor
and a data logging PC. The LVDT is a Caldaro S8FLP-10A-10K±1% unit with a
stroke length of 10 mm and a resolution of ±1% supplied by Techni Measure Ltd.
The furnace is a TMS Europe tube MetTest1OTP unit controlled with two mineral
sheathed K-type thermocouples and the data acquisition (DAQ) system utilised is a
National Instruments USB-6009 DAQ. Figure 5.2 displays the original configuration
of the test apparatus.
Figure 5.2: Original NUI Galway SPCT apparatus layout, showing main features of the apparatus; push rod, loading pan and stopper assembly, frame structure, furnace and DAQ systems.

The internal layout of the push rod and die assemblies is presented in Figure 5.3. The pushrod and die assembly is shown in Figures 5.3a and 5.3b through 5.3d in image and schematic form respectively. The schematic shows the total height of the pushrod die assembly, with the lower die post having a narrower diameter to fit into the adjustment post in the base of the apparatus. The adjustment post is indicated on the base of the apparatus in Figure 5.2. Figures 5.3c and 5.3d show more details of the push rod, indenter sphere, specimen and die assembly. The spherical indenter insures the load is transmitted vertically into the specimen and pushrod alignment issues are minimised. This indenter however suffers from an aiming issue in that the sphere can move about the cavity when the pushrod makes contact with the specimen. The location of the indenter sphere is imaged and saved at the beginning of every test to minimise this effect as much as possible.
5.3 Design updates

At the conclusion of the masters project, a number of design improvements were identified in terms of safety and temperature isolation so that accurate creep data could be obtained. The LabVIEW (v17.1) virtual instrument (VI) system was focused on the development of an impression creep test apparatus and required updating. This system had initially been calibrated at room temperature and for LVDT voltage leads approximately 15 cm long with no interruption between the LVDT and the DAQ system.

The system is designed to operate without an operator constantly monitoring it. A guard was manufactured and mounted to the frame supports which holds the furnace in place, the primary goal of the guards is to prevent accidental contact with the furnace. During initial testing, the surface of the furnace reached a temperature of approx. 120 °C. An analogue thermometer was fitted to the external surface of
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the furnace behind the guard. Should a power failure occur during testing, this device will ensure that the temperature of the dangerous area of the furnace can be monitored. The DAQ system and thermocouple connections were mounted in a housing unit to isolate them from any sources of heat and prevent any interference with the wiring, as the DAQ was located on top of the apparatus frame exposed to the environment and potentially high temperature air rising from the furnace. The LVDT leads were extended significantly, requiring the re-calibration of the LVDT voltage to the displacement system. The presence of soldering joints in the LVDT cables causes a loss in voltage transmitted. Figure 5.4 shows the updated SPCT apparatus with additional safety features applied. The LVDT DAQ is isolated and a protective guard is fitted to prevent accidental contact with the hot surface of furnace. The analogue thermometer is located behind the warning sign on guard.

![Figure 5.4: SPCT apparatus with safety systems installed.](image)

To prevent high temperature air reaching the LVDT and potentially affecting the test results, the top of the furnace was covered with high temperature insulating rock wool material. Two ceramic insulating bricks with channels for the push rod were placed on top of the rock wool to keep it in place and to maintain a steady temperature in the furnace. The channels ensured that the push rod could move freely without interference. Forced air cooling across the LVDT was provided by a fan mounted to the rear of the apparatus and a heat sink mounted to the LVDT platen, Figure 5.5. This maintained the LVDT at room temperature for the duration of the tests, and prevented the upper portion of the furnace from becoming hot, providing some additional safety.
5.4 - Sample manufacture and inspection

Samples were taken from an as received T91 steel tube, supplied from the Aghada power plant in Cork, Ireland, (courtesy of Stephen Scully of ESB International) with the composition shown in Table 5.1. The tube is sectioned into 8 mm approx. wide rings see Figure 5.6a, and a flat face milled on one side, Figure 5.6b. A 7 mm diameter post is then machined from the wall thickness, and a hole drilled on the opposite side to the post shown in Figure 5.6c. The post is then cut into disks 0.55 mm thick, on a Struers Minitom low speed laboratory metallographic saw at 200 rpm. Figure 5.6d shows the cutting operation in progress. The low speed saw minimises the mechanical damage on the samples. Samples are then ground by hand on abrasive paper of 1200 grit to a thickness of 0.5 mm. 7 mm diameter samples are used in place of the 8 mm recommended by the CEN agreement [114] due to oxidation during testing causing the 8 mm samples becoming lodged in the lower die. The 8 mm sample was destroyed removing it from the lower die receiving hole. A reduced diameter sample prevented this from occurring in subsequent tests.

The thickness of the sample is then evaluated in line with the CEN standards, using a Mitutoyo micrometer accurate to 0.001 mm. The final quality check for the samples is whether surface roughness is at or below 0.4 µm (Ra). This value was selected as it was the smoothest finish which could consistently be achieved from this manufacturing process. The roughness measures were performed using a Mitutoyo Surftest 211 profilometer, with a profile length of 0.8 mm. Ra is a standard roughness measurement, it is the arithmetic mean roughness value or the mean of absolute values of profile deviations from the mean line of the roughness profile [230]. Roughness measures were repeated three times on the disks and rotated 90° then repeated a further 3 times at this new angle to the surface finish. The average values
Figure 5.6: Sample manufacturing procedure, firstly a) the tube ring is sectioned, b) one side is given a flat face, c) a cylindrical post is machined in the thickness of the pipe wall, d) the cylinder is sectioned into disks on a low speed laboratory saw.

of thickness and roughness for the calibration and validation samples are presented in Table 5.2.

Table 5.1: T91 composition in wt.%, the balance is Fe data from ESB International.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>As</th>
<th>Bi</th>
<th>C</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.018</td>
<td>0.035</td>
<td>0.011</td>
<td>0.070</td>
<td>0.057</td>
<td>9.050</td>
<td>0.089</td>
<td>0.472</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Mo</th>
<th>Nb</th>
<th>Ni</th>
<th>P</th>
<th>S</th>
<th>Si</th>
<th>V</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.951</td>
<td>0.819</td>
<td>0.105</td>
<td>0.010</td>
<td>0.062</td>
<td>0.329</td>
<td>0.259</td>
<td>0.036</td>
</tr>
</tbody>
</table>

5.5 Control Calibrations

5.5.1 LVDT

A LabVIEW programme was developed to calibrate the relationship between displacement and voltage emitted from the LVDT to the DAQ system. The previous calibration was performed for displacements of 0 mm and 10 mm. The LVDT voltage output was sampled at a rate of 50 Hz for 3000 samples then stored in a data file, where each data file represented a single minute of voltage readings. The LVDT is spring loaded to return to a displacement of 0 mm when uncompressed. Increments of 1 mm displacement were applied to the LVDT and the voltage recorded with the
Table 5.2: Thickness and roughness measures of all samples used for calibration and validation testing of the SPCT apparatus.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Thickness (mm) Average</th>
<th>Thickness (mm) Standard Deviation</th>
<th>Roughness (µm) Average</th>
<th>Roughness (µm) Standard Deviation</th>
<th>Use case</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>0.514</td>
<td>0.002</td>
<td>1.247</td>
<td>0.128</td>
<td></td>
</tr>
<tr>
<td>S2</td>
<td>0.502</td>
<td>0.011</td>
<td>0.640</td>
<td>0.118</td>
<td></td>
</tr>
<tr>
<td>S3</td>
<td>0.494</td>
<td>0.009</td>
<td>0.727</td>
<td>0.147</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>0.494</td>
<td>0.010</td>
<td>0.303</td>
<td>0.084</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>0.494</td>
<td>0.024</td>
<td>0.303</td>
<td>0.263</td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>0.505</td>
<td>0.009</td>
<td>0.565</td>
<td>0.065</td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td>0.492</td>
<td>0.001</td>
<td>1.407</td>
<td>0.217</td>
<td></td>
</tr>
<tr>
<td>S8</td>
<td>0.494</td>
<td>0.004</td>
<td>0.182</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>S9</td>
<td>0.492</td>
<td>0.188</td>
<td>0.188</td>
<td>0.040</td>
<td></td>
</tr>
</tbody>
</table>

above settings for three minutes at each displacement interval. Figure 5.7 shows the voltage recorded for the initial minute of a calibration test at a compression of 4 mm for 1 minute. There is some variation or noise in the voltage recorded but it is stable around an average value of 0.0587 V.

Figure 5.7: Voltage recorded for a compression of 4 mm recorded over the initial minute of the calibration test.

The LVDT compressed a total distance of 12.71 mm, although the operational range is reported at 10 mm. The calibration results are presented in Figure 5.8. A linear fit to the data between 1 mm and 11 mm was calculated and utilised for the
conversion between voltage and displacement in all other tests with this apparatus. This calibration was performed at room temperature. The 12 mm and 12.71 mm displacements are outside the design range of the LVDT and resulted in large voltage variations leading to the large error bars at these displacements. No change in voltage was detected from 0 to 1 mm displacement therefore the 0 mm, 12 mm and 12.71 mm values are all excluded from the calibration curve fitting.

Figure 5.8: Results from LVDT calibration testing, each voltage value was measured for 3 minutes and averaged, then plotted against the displacement values.

The voltage to displacement conversion was implemented through a new automated process to record voltage and save it to file during the test. As the creep tests were expected to last up to several weeks, a sample rate of a data point per minute provides good time resolution without producing an un-manageable quantity of data during longer term testing. This programme is presented in Figure 5.9, where the grey box is a ‘while loop’, inside which the DAQ assistant records voltage, feeding the results to a graph and a summation block. The equation from the fitting of Figure 5.8 is applied and the resulting displacements are displayed on screen and written to a text file.

5.5.2 Furnace

Due to difficulties machining the Nimonic 80A material used for the dies thermocouple placement on the sample was not possible. Thus, a relationship between the sample and top surface of the upper die is required to control the temperature of the test. The TMS furnace control system consisted of two mineral sheathed K type thermocouples; one is the control thermocouple used to set the target temperature in the chamber of the furnace. The second thermocouple is inserted into one wall of the furnace inside the heating coils. The maximum allowable temperature of the
heating coils is set from this thermocouple to prevent over-heating or damage of the system.

![Graphical representation of LabVIEW virtual instrument](image)

**Figure 5.9:** LabVIEW virtual instrument to collect LVDT voltage, convert it to displacement and plot on screen, writing to file every minute.

A series of high temperature calibration tests were performed with an additional K type thermocouple applied to the sample clamped as it would be during a creep test. The push rod is retracted from the die to allow space for the thermocouple. The furnace control thermocouple is placed in contact with the upper surface of the die, ensuring that it does not come in contact with the push rod or the clamping screws, as shown in Figure 5.10.

![Schematic layout of thermocouples](image)

**Figure 5.10:** Schematic layout of thermocouples during the furnace calibration tests.

The calibration curve relating sample temperature to upper die surface temperature is shown in Figure 5.11. Tests were performed at increasing durations up to 8 hours, the average heating rate was identified as 500 °C/hr. The furnace takes
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approximately 20 hours to return to room temperature once the target temperature is set to room temperature and no further heating occurs. The upper die temperature plotted in Figure 5.11 is the control thermocouple temperature, set using the furnace controller in Figure 5.4.

Figure 5.11: Results of the furnace temperature calibration to control the sample temperature inside the die.

5.6 Test procedure

The step-by-step standard operating procedure (SOP) for the safe operation of the SPCT apparatus for creep testing is included in Appendix D. For the purposes of clarity, a simplified version is included here. Initially the disk sample is loaded in the lower die, centred and imaged, the upper die is then applied and bolted in place with a torque wrench to apply a consistent load (for all tests 1 Nm torque is applied to each bolt). The ceramic indenter sphere is placed on the sample through the aperture in the upper die, imaged and the push rod is lowered to contact the indenter sphere (see Figure 5.3c). The stopper is then locked in position to prevent any additional load being applied to the sample. Thermocouples are positioned in contact with the upper die and insulating rock wool is placed in position at both ends of the furnace, which is then sealed.

The LVDT platen is then secured to the push rod in position to compress the LVDT greater than 1 mm. The insulation materials are placed on the upper opening of the furnace, insuring no contact is made with the push rod. The cooling fan is activated, all data loggers are activated and the furnace set to the required chamber (upper die) temperature. As the furnace heats, the push rod expands which moves the stopper upwards away from the head of the apparatus. When the apparatus has been at a
constant temperature for 40 minutes, the stopper is reset in position with the head and locked in place. The weights are then loaded onto the loading pan and the stopper is released; the test is now underway. The stopper is then locked in position on the push rod to a maximum allowable displacement of 2.5 mm.

Total LVDT displacement, chamber (upper die) temperature and LVDT temperature are all automatically recorded and saved to the data logging PC, the wall temperature from the furnace controller is recorded manually. All data is backed up to a cloud storage system once per day of testing to protect against data loss due to potential power cuts.

5.7 Preliminary results

Initial testing of the SPCT is performed with a load of 39.85 kg, consisting of 33 kg of weights on the loading pan, as shown in Figure 5.4, with the additional 6.85 kg from the mass of the loading pan, push rod, stopper and LVDT cooling assembly (Figure 5.5). Figure 5.12 presents these initial results, with the chamber temperature set to 643 °C and using the calibration curve in Figure 5.11 this results in a temperature of 600 °C on the sample. Wide scatter is observed with times to failure ranging from 0.5 to 90 hours.

![Initial test results](image)

Figure 5.12: Initial test results, showing a large scatter in time to failures for the T91 material tested at 39.85 kg and a chamber temperature of 643 °C.

The scatter in the results is due to the thermocouple placement within the chamber. The initial apparatus design did not have a method of securing the chamber thermocouple in place, the thermocouple was allowed to rest on the upper die and during testing it would become dislodged allowing it to approach the heated wall of
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the furnace. This caused the control unit to lower the furnace temperature to 600 °C, not at the upper die but at some arbitrary distance from the heating wall. The effect was identified by plotting the displacement of the push rod during the furnace heating stage. By subtracting the initial displacement when the apparatus was at room temperature from the displacements measured during heating, the thermal expansion of the push rod can be calculated. From this, the change in temperature of the push rod can be calculated using the coefficient of thermal expansion for Nimonic 80A, $1.60 \times 10^{-5}$ m/m°C. The 1D equation for expansion of a rod during heating is:

$$\Delta l = L_0 \alpha_{coe} (\Delta T)$$  (5.1)

where $\Delta l$ is the expansion of the push rod, $L_0$ is the heated length of the push rod inside the furnace, $\alpha_{coe}$ is the coefficient of thermal expansion and $\Delta T$ is the change in rod temperature. The results are presented in Table 5.3, for the creep tests of Figure 5.12. Confirmation of this effect is provided by plotting the push rod expansion temperature against the time to failure in Figure 5.13. There is a clear trend of increasing time to failure with decreasing expansion temperature indicating this to be the cause of the variation in time to failure.

Table 5.3: Initial calibration actual test temperature estimated from the push rod thermal expansion. All tests had the control thermocouple set to 643 °C.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>$\Delta l$ (mm)</th>
<th>$\Delta T_{rod}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>4.59</td>
<td>679</td>
</tr>
<tr>
<td>S2</td>
<td>5.40</td>
<td>800</td>
</tr>
<tr>
<td>S3</td>
<td>5.21</td>
<td>771</td>
</tr>
<tr>
<td>S4</td>
<td>4.99</td>
<td>739</td>
</tr>
<tr>
<td>S5</td>
<td>4.52</td>
<td>669</td>
</tr>
<tr>
<td>S6</td>
<td>4.67</td>
<td>659</td>
</tr>
</tbody>
</table>

5.8 Identification of minimum displacement rate

Two methods of identifying the minimum displacement rate (MDR) were developed in this project. The first being a graphical method and the second being a purely numerical method and both approaches generated similar results. The graphical
method requires the manual identification of the secondary creep behaviour in the
time displacement plots of Figure 5.12. For this method, a linear time-displacement
model is overlaid on the experimental results. Initial approximations of the slope
and intercept are applied as a first estimate for the optimisation approach. The time
data points are used as input to the linear model and a least squares optimisation
approach is applied to minimise the difference between the model and experimental
displacement data points. The Generalized Reduced Gradient (GRG) non-linear
solver in Microsoft Excel 2016 is employed to minimise the difference between the
linear model and the data thus optimising the displacement rate value.

Figure 5.13: Differing rod expansion temperatures indicate initial tests were per-
formed at different temperatures. Decreasing expansion temperature correlates with
increasing time to failure for the T91 material.

The numerical model extracts all data points for each hour of testing and averages
their displacement value for that hour. The change in this average displacement from
hour to hour is then calculated as the numerical displacement rate. This approach
requires no manual identification of the beginning and end of secondary creep and as
such is considered a more rigorous method of calculating displacement rate. Plotting
the two approaches produces a flat line for the least squares approach, by definition
as it produces a single value and a U-shaped curve for the numerical approach.
Figure 5.14 compares the two approaches for the test labelled S7. Similarly to the
creep strain rate curves for 9Cr materials, the displacement rate curve here shows a
distinct U-shape [200]. The U-shape is a product of decreasing displacement rate as
the initial bending and creep loading of the disk specimen gives way to steady state
creep, followed by an accelerating displacement rate due to tertiary creep occurring
prior to final failure. Microstructural hardening due to loss of mobile dislocations
and subgrain hardening during primary hardening contribute to this effect.
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Figure 5.14: Comparing results from the graphical and numerical approaches to identifying minimum displacement rate for S7.

5.9 Upgrades

5.9.1 Apparatus

To address the temperature control issue a thermocouple holder and mount assembly were designed, tested and improved upon to reach the final configuration presented here. The thermocouple mount consists of a collar placed on the lower die post, below the region where the sample is held. A bracket is mounted to this collar which holds the thermocouple in place in contact with the upper die. Two images of the thermocouple mount are presented in Figure 5.15. An extended thermocouple holder was installed to lower the collar away from the region where the upper die is applying load to the sample, shown in Figure 5.15b. Once this holder was installed a series of temperature calibration tests were performed and a relationship identified between the upper die and the sample temperatures.

The calibration curve for the upper die to sample temperature is presented in Figure 5.16 and compared with the original calibration. The identified new calibration curve in green here, has an improved fit to the calibration data and is utilised for all subsequent testing.

The relationship between rod expansion and sample temperature is required to calculate the sample temperature during the testing and not as a post processing exercise. Figure 5.17 displays the relationship between the expansion in mm and the sample temperature from the second calibration performed with the sample holder assembly fitted to the apparatus, as in Figure 5.15b. This equation is included in the upgraded LabVIEW programme.
5.9 - Upgrades

Figure 5.15: a) the original mount assembly and b) the extended holder in the assembly to prevent any further sticking of the push rod in the upper die aperture.

Figure 5.16: Comparing the original calibration without the control thermocouple mount with the upgraded apparatus calibration curve.

Figure 5.17: Relationship between the thermal expansion of the push rod and the sample temperature for the SPCT apparatus operating with the updated thermocouple holder.
5.9.2 LabVIEW virtual instrument

Voltage is sampled at the same rate as for the calibration work, averaged every minute and converted to displacement, as per the equation in Figure 5.8. To calculate the thermal expansion of the push rod, the initial displacement must be saved on the first iteration of the 'while loop' (the grey outer box indicates the 'while loop' in LabVIEW, see Figures 5.18 and 5.19) and passed through to each subsequent iteration of the while loop. The orange arrows on the grey 'while loop' surround indicate the variable is passed on to the next iteration of the loop. On each iteration of the loop the current displacement value is compared with the minimum displacement and the lower value of the two passed to the next iteration of the loop. The initial displacement value \( d_1 \) occurs when the system is at room temperature and as the furnace heats up the difference between this and the current displacement \( d_n \) is the thermal expansion of the push rod \( d_{z,n} \). This expansion value is used with the relationship identified in Figure 5.17 to obtain the current sample temperature \( T_{s,n} \). The equation of Figure 5.17 is only accurate prior to the application of the load as it is predicated on the sole displacement being due to the thermal expansion. The output from this programme is a series of text files for every day or part thereof containing initial displacement, current displacement, rod expansion and sample temperature calculated from rod expansion values.

![Updated SPCT VI for calculating and recording, displacement, minimum displacement and expansion temperature.](image)
5.9.3 Indenter damage

Before and after each test the indenter spheres are imaged on an Optiplex BX51M reflected light microscope to examine if any damage had occurred to the indenter sphere during the testing. The primary goal is to examine whether the indenter spheres could be reused. The indenter spheres are manufactured from a silica nitride (Si$_3$NO$_4$) ceramic material, with a Vickers hardness value of 1580 H$_v$ at room temperature. Figure 5.20a is a standard spherical indenter prior to any testing. During testing, some sample material adheres to the indenter and leaves a small layer of material on the sphere, as seen in Figure 5.20b. The depth of sphere implantation into the sample could be estimated from this image if required. These two images highlight why a disposable spherical indenter is preferable to a built-in hemispherical indenter. If a built-in indenter is applied, this sample material would need to be removed after each test. Material bonded to the sphere surface could alter the coefficient of friction in future tests if an indenter is reused. This material later could act as a stress concentration location on the surface of the sample during testing.

5.10 Validation tests

A further series of tests on T91 material are conducted to validate the new thermocouple holder design, and the upgraded LabVIEW system. The target temperature for this testing is 600 °C and the load applied in all cases was 39.85 kg. The ex-
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Figure 5.20: Comparing a silica carbide indenter a) before and b) after a 600 °C test with a load of 39.85 kg. Material from the sample adheres to the sphere during testing, increasing its surface roughness, the indenter is effectively no longer spherical when this occurs.

Expected time to failure for a test of T91 material is on the order of 30 hours, based on the results of Cortellino et al. [229]. The results are shown in Figure 5.21. Figure 5.22 shows the relationship between the minimum displacement rate and time to failure. Factors that could affect the results observed here are the temperature of the test, sample thickness, surface roughness or microstructural features through the thickness of the specimen. Tests 7-9 (Table 5.4) are within reasonable bounds of ±6 °C of the target temperature. Given the accuracy of the K type thermocouples at this temperature (±2.4 °C at 600 °C), the sensitivity of the furnace controller and the scatter discussed in Chapter 2 in creep test data, these bounds are deemed acceptable.

Table 5.4: Validation testing push rod thermal expansion temperature values and calculated sample temperatures from the relationship identified in Figure 5.17.

<table>
<thead>
<tr>
<th>Test</th>
<th>$\Delta l$ (mm)</th>
<th>$\Delta T_{rod}$ (°C)</th>
<th>$T_{sample}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S7</td>
<td>4.66</td>
<td>690</td>
<td>596</td>
</tr>
<tr>
<td>S8</td>
<td>4.65</td>
<td>689</td>
<td>595</td>
</tr>
<tr>
<td>S9</td>
<td>4.75</td>
<td>704</td>
<td>606</td>
</tr>
</tbody>
</table>
5.10 - Validation tests

Figure 5.21: SPCT validation for tests performed under a load of 39.85 kg.

Figure 5.22: Comparing minimum displacement rates with time to failure.

5.10.1 Chakrabarty theorem application

As discussed previously in Chapter 2, approximate analytical solutions for the calculation of stress in a disk specimen under going small punch creep are available in the literature. Of most interest is the approach of Chakrabarty et al. [123] which was developed based on a thin membrane stretching over a hemispherical dome. The equation for converting load to stress within a SPCT specimen is as presented in Chapter 2:

\[ \frac{F}{\sigma_{\text{mem}}} = 3.33K_{sp}R^{0.2}r^{1.2}h_{\text{disk}} \]  \hspace{1cm} (5.2)

Where \( F \) is the force applied to the indenter, \( \sigma_{\text{mem}} \) is the tensile radial membrane stress in the SPC specimen [114,125], \( K_{sp} \) is a conversion factor and set to unity here, \( R \) is the receiving hole radius, (2 mm here), \( r \) is the punch radius (2 mm for the spheres used in this apparatus) and \( h_{\text{disk}} \) is the thickness of the disk specimen. This conversion is applied using the sample thickness values from Table 5.2 for the
three validation tests, S7, S8 and S9 and the apparatus dimensions. The three tests experienced membrane stresses of \( \approx 207 \) MPa, which are compared against the P91 600 °C creep tensile data [166] in Figure 5.23. Bounds are overlaid on the tensile data and the SPCT results are clearly in line with the tensile results. Thus, the SPCT results show no greater scatter than that in the existing data for P91.

![Figure 5.23](image)

**Figure 5.23:** Comparison between SPCT validation results and literature data [166] for P91 tested at 600 °C.

### 5.11 Finite element model development

To estimate the stresses occurring within the disk sample during an SPCT, an FE model is developed here to numerically examine the factors affecting creep behaviour during SPCT of 9Cr steel. The two precipitate type physically based creep model from Chapters 3 and 4 can be applied to this SPCT simulation to examine the suitability of the model for predicting behaviour in this type of test. The SPCT model can be considered a further multi-axial validation of the model. The distribution of precipitate diameters can be predicted in particular in the region surrounding the failure locations, with a view to using precipitate diameters as an indicator of material condition.

#### 5.11.1 Geometry and Material properties

The model is developed using the same Abaqus\textsuperscript{TM} software as in Chapter 4. The geometry of Figure 5.3 is axi-symmetric consisting of the sample, dies and indenter sphere. The dies and indenter are all treated as rigid bodies, where the rigid body motion is constrained to a reference point. Loads and displacements are applied to the reference points for the punch and dies. The displacement of the punch
reference point is utilised for comparison with the experimental data. Figure 5.24 contains the boundary conditions and geometries for the model. Die-specimen, and indenter-specimen contact are defined, with a surface coefficient of friction included to replicate the real world conditions, from the work of Cortellino et al. [231]. Most notably absent is the push rod, as it is not necessary to model it as the load goes through the indenter. The compression of the indenter sphere is assumed negligible for this work.

The sample elastic and creep material properties for T91 material at 600 °C are presented in Tables 3.2 and 3.3. However, additional plastic material properties are required to facilitate the initial bending and indenter implantation into the sample prior to creep. Plasticity behaviour is defined based on the results of Barrett et al. [205] from initial cycle results of fatigue testing of P91 at 600 °C, under a strain rate of 0.1%/s. Figure 5.25 presents the elastic-plastic material stress strain curve utilised for this work. The plasticity behaviour is defined using a table in Abaqus populated with values from Figure 5.25.

Stresses up to 217 MPa, with corresponding plastic strains, are utilised to define the plasticity behaviour. At stresses above this level, a perfectly-plastic approach is
applied for further plasticity in the simulation. This plasticity model was applied to
cap the maximum stress which would occur in the model prior to the beginning of the
creep portion of the analysis. A stress level of 217 MPa generates a corresponding
creep strain of 0.228%, based on Equation 3.15. This is a significant amount of
creep strain in the initial increment of the creep step and, to mitigate this large
initial creep strain value, a small time increment is required. The automated time
incrementation size selection scheme is utilised with the CETOL parameter set at a
value of $6.86 \times 10^{-4}$ [214]. Large deformation theory was employed for this model using
the NLGEOM option in Abaqus™, as the modelling of non-linear type behaviours
such as user defined creep or contact necessitate its use. Here it is expected that
some form of necking will occur in the sample, due to the accumulation of damage
within the component. The NLGEOM will update the geometry accordingly as
elements effectively fail. The initial time increment applied is $1.0 \times 10^{-32}$ hr, with the
minimum allowable increment set to $1.0 \times 10^{-50}$ hr and the maximum being 5 hours.
The general solution controls were modified from the default to allow up to 30 time
increment sizes to be attempted before the simulation aborted. The selection of the
time increment size is based on the following equation from the Abaqus manual for
quasi-static analysis [214]:

$$
CETOL \geq (\ddot{\varepsilon}_{cr}|_{t+\Delta t} - \ddot{\varepsilon}_{cr}|_{t})\Delta t
$$

where $t$ is the time at the beginning of the increment, $\Delta t$ is the time increment
size and $\dot{\varepsilon}_{cr}$ is the equivalent creep strain rate. If CETOL is less than the right
hand side of the equation, then $\Delta t$ is reduced by 25% and the procedure begins the
next iteration. In this way, large initial creep strains corresponding to large initial
displacements can be accommodated using very small time increments. The side
effect of this approach is that simulations are time consuming to run and require large quantities of storage on computer systems.

5.11.2 Contact considerations

The contact between the die and the specimen is specified using normal and tangential behaviour, the normal behaviour being defined as "Hard" contact, where no over closure occurs between the die and the specimen. At the assembly stage of the model, the dies and specimen are set to be in contact before the application of the die load. The initial contact occurs between a single set of nodes, one on the indenter and one on the specimen. The constraint enforcement method is set to default and separation was allowed after contact had occurred. The tangential behaviour is defined using the penalty formulation for friction, with a coefficient of friction of 0.5 between the die and the specimen, from [231]. For the indenter-specimen contact definition the same settings were employed except with a coefficient of friction of 0.4. This value is based on the results of a numerical sensitivity study performed using a load of 320 N on the indenter, with the specimen die friction set constant at 0.5, with the results shown in Figure 5.26. The effect of indenter-specimen coefficient of friction has been examined in the literature by Ma et al. [232] and Zhai et al. [233], both concluding values less than 0.6 have no effect on the simulation. The same effect has been observed in this work.

Figure 5.26: Showing the effect of friction coefficient on the maximum Von Mises stress and creep strain during an SPCT finite element simulation.
5.11.3 Loads and boundary conditions

Utilising an axisymmetric model reduces the number of boundary conditions, with all geometries being constrained by this condition. The lower die is fixed in all directions allowing no movement or rotations. The upper die is constrained to only allow movement in the negative Z direction. The die force is applied through a reference point which is tied to the rigid body, no rotations are allowed at the reference point via application of a boundary constraint. The die force is calculated based on the applied bolt torque used on each of the upper die screws. The holes and screws are visible in Figure 5.3. The bolt calculation to convert from bolt torque to applied load is defined in Equation 5.4:

$$F_{\text{die}} = \frac{T_{\text{bolt}}}{k_{\text{bolt}} d_{\text{nom}}}$$  \hspace{1cm} (5.4)

where $T_{\text{bolt}}$ is the torque applied to single bolt (1 Nm for this work), $k_{\text{bolt}}$ is a correction factor of 0.2 for mild steel bolts [234] and $d_{\text{nom}}$ is the nominal outside diameter of the bolt (3 mm for this work). The total force from both bolts is equal to 3.33 kN.

For the indenter sphere quadrant shown in Figure 5.24, the same rigid body constraint type as for the dies is implemented, with the force applied to the reference point. At the beginning of the simulation, the reference point was moved to the centre of mass to prevent the generation of a torque. The simulation is separated into three steps, two static general steps, where the upper die clamps the specimen in the first step, followed by the second step where the indenter displaces a distance of 0.609 mm in the negative Z direction. This displacement is set based on the observed displacements in experiments S7 to S9. This plastically deforms the sample, embedding the indenter and increasing the contact area between the two. Finally, a viscous step is applied to calculate the creep behaviour of the disk specimen, wherein the precipitate based creep model of Chapters 3 and 4 is applied (see Appendix C for subroutine code).

5.11.4 Mesh

The specimen geometry is sectioned into three regions to allow the alignment of the master and slave surfaces for the contact boundary condition definition. A mesh refinement study is performed to identify the minimum number of elements required for a mesh independent solution, the results of which are shown in Figure
5.11 - Finite element model development

5.28. Previously published meshes for SPCT modelling, such as Ma et al. [232], highlighted the region of most interest, approximately 0.7 mm from the center of the disk specimen. As such mesh refinement is focused on this region in particular. Figure 5.27 shows three sample meshes utilised as part of the refinement process with Figure 5.27b being the mesh used for all future work, containing 4550 elements. Based on the results in Figure 5.28, both Von Mises stress and equivalent creep strain reach a constant level with this mesh design and no significant changes are observed for denser meshes than the 4550 element mesh.

![Figure 5.27: Meshes developed as part of the convergence study with a) 910, b) 4550 and c) 9675 elements. The converged mesh contained 4550 elements based on the results in Figure 5.28.](image)

![Figure 5.28: Mesh convergence study results, showing the effect of the mesh on the equivalent creep strain and Von Mises stress.](image)
Chapter 5 - Experimental and numerical evaluation of a small punch creep test apparatus

5.12 Discussion

The SPCT apparatus developed here has undergone extensive modification and testing. It is shown that reliable, repeatable results can be generated at high temperature. The results lie within the scatter bands observed from conventional tensile testing of modified 9Cr material from the literature. The reported scatter for P91 could be due to variations in heat treatments or compositions and as highlighted in Chapter 3, composition variations can have significant effects. The test variable with the greatest influence on the time to failure or MDR is the test temperature. As such, the sample temperature is set using the furnace control thermocouple in contact with the upper die and calibrated to the sample temperature. A secondary thermocouple is placed on the upper die to corroborate the control thermocouple readings and log it. Finally the thermal expansion of the push rod related to sample temperature is also calculated to ensure the test proceeds at the correct temperature. Even with these controls, a temperature variation of $\pm 6^\circ C$ occurs due to the combined sensitivity limits of K type thermocouples and the limits of the temperature control system. This variation is considered acceptable and tests which show temperatures outside of this measurement window are adjusted to bring the temperature under control, prior to the application of any load. The standard operating procedure of Appendix D reflects the steps to be taken to ensure the proper temperature.

Ideally the die arrangement could be modified to allow the direct application of a thermocouple to the sample being tested. Due to the work hardening nature of the Nimonic 80A during machining, this modification could not be performed without the risk of permanently damaging the die assemblies. In future, a new die assembly could be manufactured to include space for a thermocouple and potentially an extensometer inside the lower die post. The benefit of having a thermocouple on the sample is to minimise the errors which occur when estimating temperatures from relationships developed based on the calibration testing.

An iterative design, test and assessment approach was employed during the development of this apparatus. Thermocouple placement was identified as the root cause of temperature fluctuations during early testing and a simple holder was designed and tested showing much improved thermal control of the chamber. This approach proved effective for this work, the result being a fully functioning test apparatus. The update of the data logging system allowed the sample temperature to be calculated in real time, further improving the overall operation of the apparatus. The primary
issue with this approach is the time it takes to iterate and test the improvements made during each iteration. Following the various modifications and trial testing performed here, there is now confidence that the apparatus can be reliably used to carry out a more extensive programme of testing.

The effect of temperature on the LVDT has been negated by the inclusion of the forced air cooling system in Figure 5.5. A reasonable concern would be potential vibrations occurring from the air flow over the LVDT platen, however the averaging of the voltage over a minute for the calculation of displacement limits this effect. The averaged displacement every minute has some variation, as displayed in Figure 5.7 for example, although any effect of vibration is on the order of the inherent voltage variation and is minimal. Prior to each test the LVDT platen is securely fastened to the push rod to prevent any potential movement between the platen and rod.

A sample manufacturing and inspection process is presented in this chapter. The sample extraction method can reliably produce samples of the required thickness and roughness. Due to the final finishing process being performed by hand, the samples occasionally become slightly wedge shaped from the polishing process. However the variation in thickness is on the order of 0.04 mm from one edge to another and when this occurs the average thickness is not significantly affected. There is potential for an imbalance in the clamping load to occur on these specimens. However the effect of this potential imbalance is eclipsed by the effect of test temperature on the overall results of the test.

Indenter damage was expected to occur during the testing and the nature of this damage is of interest. Most indenter spheres showed an adherence of the sample material to the ceramic indenter. Figure 5.20 highlighted this behaviour and it should be noted that a rough estimation of the depth of indenter penetration can be gained from the material adhered to the sphere. In the case of Figure 5.20b from test S7, the indenter implanted itself in the sample to a distance of 0.79 mm. Comparing that against the total displacement of the push rod (3.37 mm) the indenter implantation accounts for 23 % of the total displacement measured. This measure is approximate at best, and only correlates with material which adhered to the sphere. Further implantation may have occurred however no material was deposited. The result of this material deposition is the modification of the coefficient of friction if a sphere was re-used without cleaning, with increasing surface roughness as material was sequentially deposited on the sphere. The sphere in this cases would no longer be uniform potentially leading to stress concentrations occurring around the regions of
the sphere where material is adhered.

The finite element model of the SPC apparatus uses an axisymmetric representation of the test set up. This assumes an ideal test configuration where the indenter sphere moves through the exact centre of the specimen. This assumption simplifies the simulation significantly as it avoids the requirement for a fully three dimensional model. However during the calibration and validation testing, it was observed that the indenter sphere could not be controlled to lie in the centre of the specimen. The clearances required for the push rod movement allow this movement of the sphere on the surface of the sample. The distance the sphere can move is on the order of 0.2 mm. For a misaligned indenter some concentration of force will occur on the segment of the disk supporting the majority of the load. Failure can be expected to begin at this location and extend in a ring like fashion through the most highly stressed region. A misaligned indenter will impart the same force as one centred on the specimen, as the force is transmitted from a flat push rod tip to a sphere. There may be some friction in the case of the indenter contacting the die aperture wall but the corresponding loss to overcome this friction is considered negligible in this work. The coefficient of friction between the ceramic indenter sliding tangentially by the metallic die is expected to be quite low. This is a limitation of this particular apparatus and should be considered in Chapter 6 when comparing the model results with the experimental results.

5.13 Conclusions

A small punch creep test apparatus and the accompanying finite element model have been calibrated, validated and checked for independence from numerical modelling issues. The SPCT apparatus is highly sensitive to test temperature and as such, additional thermocouples are in place for each test and an automated procedure for estimating the sample temperature based on expansion of the push rod is included. Disposable indenter spheres are employed to avoid issues of sample material adhering to the indenter on repeated testing. Utilising the Chakarbarty approach to estimate the membrane stress within the disk specimen allows comparisons between SPCT results and those of tensile creep tests. The scatter observed in the validation tests fall within the bands observed for conventional results for T91 steels at 600°C.

The finite element model has been developed to be both mesh and time increment independent. The effect of indenter-specimen friction settings has little to no effect on
the creep strains or Von Mises stresses developed within the disk specimens during the simulations, in line with findings from the literature. Extremely small time increments are required to mitigate the effect of testing at high loads, equivalent to above 200 MPa in a tensile test at 600 °C.

In the following chapter the SPCT apparatus is used to test the behaviour of T91 material which has been aged for up to 1 year at 600 °C. Comparisons between aged and un-aged material are made using the results of this testing. The finite element model is modified to reflect the aged condition and a similar comparison performed for the FE results.
Chapter 6

Thermal Ageing and Small Punch Creep testing P91

6.1 Introduction

This chapter presents the thermal ageing, SPC testing and modelling of aged and un-aged T91 materials using the two precipitate type creep model of Chapter 3 and 4. The samples were aged at 600 °C for increasing periods up to 8400 hours. The samples are then examined using transmission electron microscopy (TEM) to measure the two precipitate families, MX and M$_{23}$C$_6$. The TEM sample preparation is performed in Loughborough University at the Loughborough Materials Characterisation Center with imaging conducted at NUI Galway. Energy-dispersive X-ray spectroscopy (EDX or EDS) is performed at the University of Limerick with assistance from the Bernal Institute. The precipitate coarsening rates are measured using an automated procedure and, compared against literature data.

Following this, results of small punch creep tests using the apparatus of Chapter 5, at 600 °C on un-aged, 6 month and 1 year aged materials are presented. Repeat testing is performed to confirm the results where material quantities allowed. SPC testing of thermally aged material is a novel aspect of this project which has not been presented previously for T91 material.

Coupled with this experimental work is the application of the physically based two precipitate model of Chapters 3 and 4. Un-aged parameters are as defined for the P91 material at 600 °C in Chapter 3. The aged material is modelled utilising the coarsened precipitate diameters from the literature. Finally the experimental and model results are compared to examine the accuracy of the finite element modelling approach and the applicability of the material model for predicting SPCT results.
6.2 Experimental Methodology

This section presents the experimental set up of the thermal ageing study, sample extraction for the TEM examinations, calculation of precipitate coarsening rate, preparation of samples for SPC testing and finally examinations of failed SPC specimens.

6.2.1 Thermal ageing of T91

The specimens were removed from the as received Aghada plant tube (as described in Chapter 5) as small chunks of tube wall, which are then cut and ground into 10 mm $\times$ 8 mm $\times$ 3 mm small samples and numbered. Figure 6.1 shows the manufacturing process.

![Figure 6.1: Schematic sample manufacture process for the T91 thermal ageing samples. a) being the original tube with b) the rough specimen, which is then squared into the final sample geometry of c) a thermal ageing sample.](image)

A Nabertherm GmBH furnace is utilised for the thermal ageing study capable of maintaining temperatures up to 1100 $^\circ$C. The internal dimensions of the furnace are 205 mm $\times$ 180 mm $\times$ 170 mm. Three samples for each ageing time were utilised.

6.2.2 TEM sample preparation

Thermally aged samples are fixed in a bakelite thermosetting mounting agent using temperature and pressure, in a Struers ProntoPress-10 mounting device. Samples are ground and polished using a Struers Tegramin-30 automated polishing system. Resin bonded diamond pads of increasing equivalent grit are utilised in the following steps; 220 grit, 500 grit, 1200 grit with a water based lubricant. Samples are then polished to a progressively finer surface finish, with colloidal silica pastes appropriate to the polishing pad, initially to 9 $\mu$m and finally to 3 $\mu$m.
TEM carbon replica preparation is performed in line with recommendations from Mitchell et al. [235]. Samples are etched in Vilella’s reagent for 30 seconds, and immediately rinsed in methanol and water sequentially to prevent over etching, Figure 6.2 shows the precipitate carbon extraction process. The reagent dissolves the matrix material preferentially over the nano-scale precipitates, see Figure 6.2a. Care is required when handling and disposing of the reagent due to the presence of picric acid. Etched samples are then carbon coated, where-by a nano-scale layer of carbon is deposited on the samples on the order of 20 nm in thickness, Figure 6.2b. At this point, the carbon layer is bonded to the precipitates on the surface unaffected by the etchant. The carbon film is then scored using a razor blade to break the carbon into smaller pieces which can be transferred to 3 mm copper TEM grids.

![Figure 6.2: Precipitate carbon extraction replica sample preparation for TEM analysis of precipitate diameters. MX precipitates are shown in grey and M$_{23}$C$_6$’s in yellow. Showing a) initial etch, b) carbon coating, c) electrolytic etch, d) precipitate and carbon lifting and e) capture on TEM copper grid.](image)

Samples are further electrolytically etched to remove the matrix material from under the now exposed and coated precipitates. This is done in a 10% hydrochloric (HCl) acid in ethanol solution using two platinum electrodes with a voltage of 10 V set on a MetalThin etching apparatus. One electrode is placed in contact with the surface of the sample (see Figure 6.2c) and the other passed overhead 3 to 4 times. Hydrogen
off-gassing occurs and, as such, this procedure is performed under a fume hood. Following this second etching, the samples are rinsed gently in a bath of ethanol and transferred to a bath of de-ionized water as in Figure 6.2d. Upon breaking the surface tension of the water, the carbon films will begin to float on the surface of the water. The final step is to capture the films onto the 3 mm copper grids (Figure 6.2e) which are then allowed to air dry and these are stored for use in the TEM analysis.

During the final step of the carbon replication process, the thin foils can easily be damaged while attempting to capture them on the copper grids. Two forms of damage can occur, firstly the foils can tear and secondly the foils can become folded. Folded thin foils present a considerable concern as the accurate measurement of volume fractions and precipitate diameters depends on the assumption that only a single layer of precipitates is being measured. A TEM sample containing folded and unfolded regions is shown in Figure 6.3. It can clearly be seen that care is required when measuring precipitate diameters and that images containing only non-folded regions are utilised for the measurement process.

![Figure 6.3: TEM carbon replica sheet containing precipitates which has been folded during the sample preparation process.](image)

6.2.3 TEM observations

Aged samples are imaged at the Center for Microscopy and Imaging at NUI Galway using a Hitachi H700 transmission electron microscope. Imaging took place at multiple magnification levels between ×1000 and ×30000. Low magnification (x1000)
6.2 - Experimental Methodology

imaging is utilised in an attempt to observe preferential precipitate concentration locations; namely whether grain boundary locations could be estimated based on precipitate distributions. In some cases, strings of precipitates are observed, however this is not the case for all the TEM grids examined. Figure 6.4 shows one of the samples where microstructural features can be observed in the precipitate distributions. Some boundary marking rows of precipitates are highlighted in red to show potential microstructure boundary locations and this image is taken with a magnification of ×2000. Strings of large precipitates can be seen, assumed to be the larger $\text{M}_{23}\text{C}_6$, with smaller less populous collections of $\text{MX}$ within the interior regions in accordance with the reported observations of Abe et al. [25] and Mitchell et al. [235].

Figure 6.4: TEM image of carbon replica extracted precipitates from an un-aged sample of T91 material, imaged at ×2000 magnification.

Images taken at ×30000 magnification are utilised for the measurements of precipitate diameters as they provide a balance between precipitate definition and a large number of precipitates present in each frame. Images of regions containing precipitates are selected at random from the TEM copper grids and a series of four images are taken at each location. Portions of the copper grids contain either folded carbon films or no films. As such, the selection of regions to be imaged was a random sample from the regions containing a single layer of un-damaged carbon film. A new area is then selected randomly and the magnification set to the correct level and
another series of four images were obtained. The scans show the increase in average precipitate size and the density of precipitate distributions. The average total area captured for each ageing time is 484 µm².

Sample TEM images for each ageing time are presented in the following section, each heading title is the thermal ageing duration. For each ageing time, three samples were extracted, one was mounted, polished and used for precipitate measurements while the remaining samples were manufactured into SPCT specimens. MX precipitates are marked with green arrows and bubbles while M₂₃C₆ are marked with gold ones, in Figures 6.5 to 6.11.

0 hours (Un-aged)

Three sample images are displayed in Figure 6.5, showing dispersions of large, dense black precipitates and a wider dispersion of grey precipitates. The larger black precipitates are assumed to be M₂₃C₆, while the smaller grey ones are assumed to be MX precipitates based on the EDX results of Mitchell et al. [235], on precipitates in P91 prepared with carbon replicas. EDX characterisation of these two precipitates is discussed later in this chapter. In Figures 6.5a and 6.5c, there is a slight tendency for the larger precipitates to form in alignment with surrounding larger precipitates. This could indicate that the precipitates were lying on a boundary when they were removed from the matrix. Figure 6.5a contains some preferential regions of larger precipitates and they are widely dispersed through the imaged region in line with the MX candidate precipitates.

![Figure 6.5: Sample precipitate distributions from un-aged T91 material, at a magnification of x30000. These are typical input images utilised for automated precipitate size measurement.](image-url)
24 hours (1 day)

24 hours ageing did not have a significant obvious effect on the precipitates extracted in Figure 6.6. However there is some dark grey shading surrounding some of the precipitates in Figures 6.6b and 6.6c which, according to Mitchell et al. [235] could be iron oxide liberated from the surface during the production of the carbon replicas. It can be observed that there are a considerable amount of precipitates tightly clustered together in these images.

![Image](image_url)

Figure 6.6: Extracted precipitates from a sample which had undergone 24 hours ageing at 600 °C. Some shadowing is observed in figures a and b, which is related to the liberation of iron oxide during the etching process.

72 hours (3 days)

After three days ageing, another series of samples were removed from the furnace for microstructural analysis. Figures 6.7a through 6.7c show a reduced concentration of precipitates compared to Figures 6.5 and 6.6. Close clustering of the larger precipitates is again observed here, indicating that they preferentially form in proximity to each other, presumably in response to concentrations of Mo, Cr and C at these locations during the tempering process.
Figure 6.7: Precipitates after 72 hours of ageing showing a greater dispersion of large precipitates with few grey MX candidates in sight. Preferential formation of larger $M_{23}C_6$ grouped together in strings is further evidenced here.

168 hours (1 week)

Some potential oxide regions can be observed in Figure 6.8a, similar to those in Figure 6.7. Small grey MX precipitates can more readily be seen in these figures of samples aged for a week particularly in Figures 6.8b and 6.8c. Some v-shaped precipitates are also present in Figure 6.8c, which could potentially be V-rich MX’s [235].

Figure 6.8: Sample images of precipitates after a week of ageing at 600 °C, from the T91 material.

672 hours (1 month)

Qualitatively, the average precipitate size are observed to have increased in these images, Figure 6.9, compared with samples aged for 1 week or less and there is also
6.2 - Experimental Methodology

a considerable quantity of very light grey speckling in these images. These are not
considered to be precipitates but rather artefacts from the etching process which
were appended to the carbon layer. They are very evenly distributed throughout
these images and are not present in samples aged for other times. Clustering of
smaller precipitates can be observed in all three images. The results of Figure 6.9
indicate that, after a month of ageing precipitates have begun to coalesce and form
larger more thermodynamically stable configurations, as per the Ostwald ripening
process. The same can be seen of the larger dark precipitates.

Figure 6.9: Precipitates beginning to coalesce into larger clusters after a month of
ageing at 600 °C.

4702 hours (6 month)

No obvious shading or over etching features is observed in the samples aged for just
over six months (six months and two weeks). Clustering of the larger precipitates are
observed in Figure 6.10a, along with some string like distributions above the scale
bar. There are regions devoid of the large precipitates in Figures 6.10b and 6.10c, 
indicating that precipitates prefer to grow along boundaries as opposed to within
in the matrix material. Fewer smaller grey precipitates are observed in the three
images shown here.
Figure 6.10: After 4702 hours ageing some clustering of M\textsubscript{23}C\textsubscript{6} precipitates is evident.

8400 hours (1 year)

After a further six months of ageing, samples were removed after a total ageing time of 8400 hours, slightly less than a year. Far greater concentrations of precipitates can be observed in Figures 6.11a through 6.11c and clustering is evident in each of the images. These large clusters are expected to act as single large obstacles to dislocation movement. The average spacing between the clusters increases as a result. Figure 6.11b has a considerable space left of centre where very few precipitates are observed. These large gaps provide easier paths for dislocation movement through the material, decreasing the creep resistance of the material.

Figure 6.11: Precipitates after 8400 hours of ageing showing significantly higher concentrations of precipitates in general and also generally larger precipitates clumped together.
6.2.4 Identification of precipitate composition

A Joel 2100 TEM is utilised with an Oxford instruments detector for the collection of emitted X-rays. The TEM is configured to operate in scanning mode with an accelerating voltage of 200 KeV to generate compositional maps of the replicas. The dwell time is set to 8 ms and the magnification set to ×150,000. The TEM beam rasters across the image area, generating X-ray spectra for each element present. This data is then composed into the maps shown in Figures 6.12 to 6.15. The expected precipitate compositions from the literature are provided in Table 3.1 of Chapter 2. Small areas are scanned comprising of only few precipitates to ensure multiple areas could be examined. The areas mapped are on the order of 3 µm².

During EDX spectroscopy, the emitted x-ray spectra are searched by the software to identify peaks corresponding to particular elements. This method is effective provided there is no significant overlap between the spectra peaks of interest. In this work the closest two peaks are the Mo and Nb peaks at 17.48 and 16.62 KeV from excited electrons returning to the K shell emitting x-rays of these energy levels. For Nb, Mo and Fe peaks, the L-alpha shell spectra are examined and no significant difference in the concentrations of these elements was detected over the K shell emissions.

The TEM images cover much larger areas than the TEM-EDX images, obviously many more precipitates are examined for the diameter work than for the EDX analysis. Two different TEM machines are utilised using differing methodologies and the TEM images are obtained in a static mode with the electron beam passing through the thin carbon replica film, leaving a white background with denser precipitates being in varying shades of grey to black. The EDX results are obtained by moving the TEM beam (STEM) over smaller areas and reading the x-ray spectra emitted from the precipitates in the carbon film. Therefore, the x-ray detector which forms the compositional maps only highlights regions which emit enough x-rays to give a spectra, as such a dark field image is produced. The oxide scales observed in some TEM figures will therefore not be detected by the EDX-TEM as they are not of sufficient thickness to generate a detectable spectra.

Precipitates with high concentrations of Cr, Fe or Mo are identified as M₂₃C₆ and those with high concentrations of V, or Nb are identified as MX precipitates. For the specimens aged for 8400 hours, Laves phase (Fe₂Mo) may have formed in small quantities. However without lattice diffraction based observations of these precipitates they are challenging to identify compared to the M₂₃C₆ family. Figures 6.12
to 6.15 contain the scanning electron (SE) images of precipitates on the left (a), followed by the Cr, Fe, Mo maps composited over the SE image in middle (b) and finally images to the right (c) contain the Nb, V concentration overlaid on the SE image. Three randomly selected positions where scanned for each ageing time and a single position for each time is shown. In all images, Cr is green, Fe is blue, Mo is yellow, Nb is maroon and V is red.

![Figure 6.12: Precipitate composition maps for the un-aged specimen.](image1)

![Figure 6.13: Precipitate composition maps for the specimen aged for 1 month (672 hours).](image2)

A number of trends can be extracted from these images. The large black precipitates are associated with one or more of Cr, Fe and Mo constituent elements, while the Nb and V are generally associated with the grey smaller precipitates. In Figures 6.13c and 6.15c, some of the small black precipitates are Nb and V rich, for the majority of the other images the grey precipitates are Nb and V rich indicating MX
6.2 - Experimental Methodology

Figure 6.14: Precipitate composition maps for the specimen aged for 6 months (4702 hours).

Figure 6.15: Precipitate composition maps for the specimen aged for 1 year (8400 hours).
precipitates. In Figure 6.15b after 8400 hours of ageing, there are large regions of
Cr and Fe around the precipitates due to long term diffusion from the matrix to
surround the precipitates. The images are taken as dark field images (background in
black, precipitates in white) in scanning transmission electron microscopy (STEM)
mode and these are then processed using FIJI imageJ (version v1.52o) software to
invert these images, i.e background in white precipitates in greys and blacks. This
inversion converts the images to a similar format to those in Figures 6.5 to 6.11, and
allows comparisons to be drawn between the two sets of images.

In the un-aged sample of Figure 6.12b there is an even distribution of Cr and Fe
with less Mo present and after a month of ageing, the Fe eclipses all other precip-
itate forming elements in Figure 6.13b. Fe clearly is the fastest element to diffuse
towards the precipitates, which is expected with the matrix being predominantly
Fe. In Figure 6.14b, Cr is the most predominant and an even spread of Fe points is
observed also, again the 9 wt.% of Cr in the material provides ample opportunity for
Cr to migrate into the precipitates during ageing. Mo does not appear to accumulate
in the precipitates until after 8400 hours of ageing. Figure 6.15b shows higher con-
centrations of Mo within the precipitates than in the surrounding area, while in the
maps at earlier times, the distribution of Mo is reasonably uniform. This indicates
that Mo is the slowest alloying element to diffuse into the precipitates, which follows
from the atomic radii differences between Mo and Fe in Table 2.7, only W should be
slower at diffusing through the matrix of which there is little in the material.

For the MX precipitates, Figures 6.12c, 6.13c and 6.14c all show concentrations
of predominantly V in the small precipitates with a uniform distribution of V an
Nb throughout the imaged areas. For the sample aged 8400 hours, this is not the
case as the regions surrounding the grey precipitates (in Figure 6.15a) have high
concentrations of both V and Nb in Figure 6.15c. Between 4702 hours and 8400
hours these elements have migrated to surround the precipitates and enhance their
coarsening. While the MX precipitates are almost too faint to be seen in the SEM
image of Figure 6.15a they are clearly highlighted in Figure 6.15c. In the upper left
corner of Figure 6.15a there is a shadowed region with high concentrations of Fe,
Cr and Mo but also several bright red V spots and this region is housing both large
M_{23}C_{6} and MX precipitates nearly hidden beside them.

Cr, Fe and V are the most obvious elements which are observed in the EDX exami-
nations of the samples and this is as expected from the composition of the material
in Table 5.1. They form the majority of the precipitates observed in this work and
are key to distinguishing between the two precipitate families of interest. Figure 6.13 is the lowest resolution image from the EDX analysis. However, it still contains valuable information, chiefly that the dim grey precipitates certainly contain Nb and V. There is also little Fe detected in this un-aged sample. However longer aged samples show large concentrations of Fe throughout the images. The Fe is migrating into the precipitates as the material is aged for longer and thus increased Fe content at longer ageing times could be an indicator of the presence of Laves phase Fe$_2$Mo.

6.2.5 Identification of thermal coarsening rate

An automated precipitate measurement system is developed for identifying the precipitates present in the TEM images of Figures 6.5 to 6.11 using FIJI open source software (version v1.52o) and post processing in Excel 2016 and Matlab R2018a. Initially a background smoothing is applied to remove the effects of uneven lighting, a circle of 200 px is utilised to average the grey value inside the sphere and subtract this from the intensity of the rest of the pixels in the circle, this then rasters over the entire image. An appropriate threshold setting was selected from all available options by utilising the automated settings in Fiji, which sequentially applies the 16 available methods to the original image. The Renyi Entropy method highlighted the maximum number of precipitates as such it was applied for all future images. A watershed segmentation was then applied to differentiate between adjacent regions of similar grey values. This process treats all local minimums as sources and "fills" upward until a neighbouring source is met, the boundary is considered as the point when two sources meet. The measurement macro was developed to minimise the subjective input of the operator, and was applied to all x30000 images with no modifications for samples of differing ageing time. The complete step by step procedure is available in Appendix E.

The TEM images from un-aged to samples aged for 8400 hours, are analysed using this automated tool and the results are a distribution of precipitate areas from each ageing time. These area results are then converted into equivalent circle diameters. The precipitate diameter distributions are presented in Figure 6.16 and log-normal distributions are fitted to this data using the Matlab R2018a distribution fitter tool, shown in Figure 6.17. The x-axis in Figure 6.17 is reduced to more clearly show the decrease in the smallest diameter bins, where the effect of ageing is most pronounced. No other diameter ranges show significant increases, as the effect of coarsening is dispersed throughout the range of precipitate diameter bins, for the aged results.
Decreasing relative frequency within the smaller diameter bins is an indication of increasing average size with longer ageing time. In Figure 6.16 prior to ageing, the majority of precipitates are within the <10 bin while, after ageing the distribution is shifted to the right, with significantly more precipitates residing in the overflow bin.

The mean values of precipitate diameter at each ageing time are then extracted from the identified distributions and utilised to identify the thermal coarsening rate. The Ostwald ripening equation of equation 2.19 is employed with a least squares approach to optimise the coarsening rate term \( (K_P) \), by minimising the difference between the experimentally measured diameters and the Ostwald modelled values. This provides an average precipitate diameter for both MX and \( \text{M}_{23}\text{C}_6 \) precipitates, a method for discerning between the two in TEM images is under development and discussed in Chapter 5.
6.2.6 SPC testing of un-aged and aged T91

To assess the degradation of creep strength of the materials, SPC testing is performed on disks manufactured from the aged samples. Un-aged samples and samples aged for 6 months and 1 year are tested at 600 °C under loads of 40 and 35 kg and compared against the validation results from Chapter 5 in the 40 kg case. Additional testing of un-aged material is performed at a load of 35 kg.

Sample fracture surfaces are imaged using a Hitachi S4700 scanning electron microscope (SEM), at the Center for Microscopy and Imaging at NUI Galway. The samples are mounted on carbon tabs and images are taken from the underside of the sample, in order to examine the fracture surface of the samples. The SEM was operated at 15kV, at a working distance of 12 mm.

Sample Manufacture

The sample manufacturing method utilised previously is modified, as the thermally aged samples are not pipe ring segments. Samples are epoxied to the head of a bolt, and then mounted on the low speed laboratory saw. Thin slices, on the order of 0.5 mm, are then cut at a disk speed of 200 rpm, with no additional weight added to the system to minimise mechanical damage. From the thin square samples, disks are manufactured by hand grinding and final polishing on 1200 grit polishing paper. The thickness and roughness acceptance criteria from Chapter 5 are applied to ensure samples are of sufficient quality. Table 6.1 contains details of the manufacture of the samples for the SPC test program.
Table 6.1: Sample and test details for both un-aged and aged specimens SPC tested at 35 and 40 kg at 600 ±6°C.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Ageing time (hr)</th>
<th>Thickness (mm)</th>
<th>Roughness (µm)</th>
<th>Test load (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S10</td>
<td>0</td>
<td>0.499</td>
<td>0.245</td>
<td>35</td>
</tr>
<tr>
<td>S11</td>
<td>0</td>
<td>0.495</td>
<td>0.488</td>
<td>35</td>
</tr>
<tr>
<td>S12</td>
<td>4702</td>
<td>0.500</td>
<td>0.308</td>
<td>35</td>
</tr>
<tr>
<td>S13</td>
<td>4702</td>
<td>0.503</td>
<td>0.215</td>
<td>40</td>
</tr>
<tr>
<td>S14</td>
<td>8400</td>
<td>0.503</td>
<td>0.400</td>
<td>35</td>
</tr>
<tr>
<td>S15</td>
<td>8400</td>
<td>0.495</td>
<td>0.307</td>
<td>40</td>
</tr>
<tr>
<td>S16</td>
<td>8400</td>
<td>0.501</td>
<td>0.220</td>
<td>40</td>
</tr>
</tbody>
</table>

6.3 Results

6.3.1 Coarsening Rates

The results of the TEM image analysis are presented in Figure 6.18, showing the average diameter from each set of TEM images. The Oswald ripening model is fitted to the data to identify the average thermal coarsening rate defined as;

$$d^3 - d_0^3 = K_P t$$

Here, as in Equation 2.19, $d$ is the precipitate diameter at a given ageing time $t$, $d_0$ is the initial diameter prior to any ageing and $K_P$ is the thermal coarsening rate. This is the average precipitate coarsening rate for both MX and M$_{23}$C$_6$ combined, which is compared against the identified values of Hald et al. [30], in Table 6.2. The value identified from this experimental work is in line with those of Hald. It is closer to the value for the MX precipitates due to the far larger quantities of MX precipitates measured, compared with the M$_{23}$C$_6$ precipitates. The precipitate diameters, measured in this work, follow typical Ostwald ripening behaviour for particle coarsening.
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Figure 6.18: The precipitate diameters measured with TEM analysis with the Ostwald particle coarsening curve fitted to identify the thermal particle growth rate $K_P$.

Table 6.2: Comparing identified coarsening rate from literature [30] against values obtained in this work.

<table>
<thead>
<tr>
<th></th>
<th>Ó Murchú Rate ($\text{mm}^3/\text{hr}$)</th>
<th>Hald M$_{23}$C$_6$ Rate ($\text{mm}^3/\text{hr}$)</th>
<th>Hald MX Rate ($\text{mm}^3/\text{hr}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$1.37 \times 10^{-17}$</td>
<td>$1.00 \times 10^{-15}$</td>
<td>$2.35 \times 10^{-18}$</td>
</tr>
</tbody>
</table>

6.3.2 SPC Testing for Un-aged T91

The 35 kg load results for the SPC tests on the un-aged T91 material are shown in Figure 6.19 (S10, S11) and the expected three stage creep curves are observed for both tests. After the primary creep portion of the curve, a steadily increasing displacement is observed for approximately 40 to 50 hours and after this, the displacement curve takes on a slightly wavy form. This is attributed to cracking occurring through the disk thickness, which in turn corresponds with an increasing contact area between the sphere and the specimen.

There is a distinct corner observed at the transition between secondary creep and tertiary creep, indicating that once tertiary creep began, final failure occurred shortly afterwards. Tertiary creep began at approximately 275 hours for the S10 case, with final failure occurring at 280 hours; this portion of the creep curve accounts for 1.8% of the total creep life of the specimen.

The MDR and time to failure data of the 40 kg validation results (already presented
in Chapter 5) are compared against the 35 kg test results of Figure 6.19, in Figure 6.20. Decreasing load, decreases the MDR and increases the time to failure as expected. The variation in the 40 kg results has been discussed previously as being within the observed scatter bands creep testing of P91 and T91 materials, as such similar scatter can be expected at the 35 kg load testing. Across all specimens tested, decreased MDR results in increased time to failure and the scatter observed in Figure 6.20 could be a result of microstructural features through the thickness of a sample influencing the test behaviour.

Figure 6.21: The time-displacement curve for the 6 month aged specimens, shows the 40kg test to be consistent with the results for the un-aged material in Figure 6.21 with, the three un-aged material tests having failure times of 27, 36
and 50 hours respectively (see Table 6.3). This indicates that 6 months of thermal ageing has not significantly affected the creep resistance of the material under high load conditions. However, once the load is decreased to 35 kg a decrease in creep life of approximately 60 hours occurs between the S11 un-aged and the S12 6 month result. The decrease is even more apparent comparing the S12 aged material with the S10 un-aged material, where a decrease of 173 hours is observed.

![Figure 6.21: Time-displacement data for the samples aged for 6 months.](image)

The lower load test allows more time for the influence of coarser particles to affect the creep behaviour of the material. The average particle diameter, from Figure 6.18 has increased from 11 nm to 27 nm over the course of 6 months thermal exposure. A particle diameter increase of 145% contributes to a decrease in creep life on the order of 36 to 62%, other ageing effects could also influence this behaviour e.g. subgrain coarsening or loss of mobile dislocations.

Figure 6.22 contains the results of testing performed on the samples aged 1 year. The 40 kg test is repeated to provide additional confidence in the results for material aged for 1 year. The two 40 kg tests show failure times significantly less than for the un-aged, with failure times of 12 and 13 hours for the S16 and S17 tests respectively. Evidently the additional ageing from 6 months to a year with the corresponding growth of the precipitates from 26 nm to 55 nm, has further reduced the creep resistance of the material at the 40 kg load case. Although the 35 kg test results show little deterioration in comparison with the material aged 6 months as is highlighted in Figure 6.23. The 1 year aged material failed at 91 hours compared with the 107 hours for the 6 month aged specimen. The S12-35 kg test, of 6 month aged material, failed sooner than expected, a proportional increase in failure time between the 40 kg and 35 kg was expected similar to that of the 1 year aged specimens. There
were relatively few MX precipitates evident in the TEM results for this ageing time and it was proposed that this was a sampling effect. This result could indicate that the particular disk in question may have a diminished creep resistance due to a low concentration of MX precipitates. Examining Figure 6.18 shows that, for this ageing time, the average precipitate was smaller than expected from the Ostwald predicted behaviour, which would indicate that lack of small precipitates did not cause this early creep failure. A defect in the thickness of the disk may have led to this early failure and additional testing of this material may indicate that this result is an anomaly.

![Figure 6.22: Time-displacement data for the samples aged for 1 year.](image)

![Figure 6.23: Minimum displacement rate vs time to failure for all aged T91 specimens tested at 600 °C.](image)

### 6.3.4 Post-test microscopy

The fractured surfaces of un-aged and 1 year aged samples are examined for both test loads, 40 and 35 kg. Figure 6.24 shows a schematic of an SPCT sample and indenter
6.3 - Results

Table 6.3: A summary of all T91 SPCT results at 600 °C, showing test loads, times to failure and the minimum displacement rates.

<table>
<thead>
<tr>
<th>Sample Number</th>
<th>Ageing time (hr)</th>
<th>Test load (kg)</th>
<th>( t_f ) (hr)</th>
<th>MDR (mm/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S7</td>
<td>0</td>
<td>40</td>
<td>27</td>
<td>( 1.84 \times 10^{-2} )</td>
</tr>
<tr>
<td>S8</td>
<td>0</td>
<td>40</td>
<td>36</td>
<td>( 1.22 \times 10^{-2} )</td>
</tr>
<tr>
<td>S9</td>
<td>0</td>
<td>40</td>
<td>51</td>
<td>( 1.20 \times 10^{-2} )</td>
</tr>
<tr>
<td>S10</td>
<td>0</td>
<td>35</td>
<td>281</td>
<td>( 2.31 \times 10^{-3} )</td>
</tr>
<tr>
<td>S11</td>
<td>0</td>
<td>35</td>
<td>167</td>
<td>( 3.46 \times 10^{-3} )</td>
</tr>
<tr>
<td>S12</td>
<td>4702</td>
<td>35</td>
<td>107</td>
<td>( 5.78 \times 10^{-3} )</td>
</tr>
<tr>
<td>S13</td>
<td>4702</td>
<td>40</td>
<td>57</td>
<td>( 9.85 \times 10^{-3} )</td>
</tr>
<tr>
<td>S14</td>
<td>8400</td>
<td>35</td>
<td>91</td>
<td>( 5.46 \times 10^{-3} )</td>
</tr>
<tr>
<td>S15</td>
<td>8400</td>
<td>40</td>
<td>13</td>
<td>( 3.42 \times 10^{-2} )</td>
</tr>
<tr>
<td>S16</td>
<td>8400</td>
<td>40</td>
<td>12</td>
<td>( 5.09 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

in the pre- and post-test conditions. As the sample ruptures, a ring fracture grows around the indenter sphere until, finally, the cap hinges downward. The location of the arrow in Figure 6.24b highlights the orientation of the SEM images in Figures 6.25 to 6.27.

Figure 6.24: Schematic of SPCT die specimen locations a) pre-test, indenter is on top of sample and b) indenter has pushed through sample. In the majority of testing the failure condition in image b) is observed.
Figure 6.25a shows the fractured surface of the S8-40 kg specimen. The edge of the fractured surface shows scratches perpendicular to the edge of the specimen which then reach a series of fractures parallel to the fracture edge. The fracture begins as a series of micro-cracks on the opposite to the indenter side of the specimen. As the indenter deforms the specimen, a network of fractures form on this side of the specimen and evidence of this network of microcracks is provided in Figure 6.25b. This series of parallel, tear-like, fractures slowly grow during the SPC test eventually connecting into larger fractures. The top left corner of Figure 6.25b is an example of this behaviour. These cracks connect together forming a continuous ring fracture which eventually results in tertiary failure of the specimen via the formation of perpendicular cracks adjacent to the final edge of the cap.

For the S10-35 kg of the un-aged specimen in Figure 6.26 the crack formation behaviour is altered from that of the 40 kg loaded specimens. Firstly, the indenter sphere is still adhered to the specimen at the end of the test as is seen in this image. Any attempt to remove the sphere would led to non-creep induced damage being imparted to the sample. As such, the indenter is left in position; attached to the cap region. un-agedic of the sphere is non-conducting and as a result, during SEM imaging electron charge builds up on un-agedic causing the cap portion of the image to be over-exposed. In Figure 6.26a, there is clear evidence of oxide having formed on the sample due to the longer test duration and oxide spalling can be observed on the cap. There is considerably less evidence of the network of cracks as observed for the 40 kg test in Figure 6.26b. The surface of the specimen is highly pitted, possibly from the oxide formation. Figure 6.26a shows a large crack parallel to the edge of the cap, followed by the wider region of perpendicular cracking similar to Figure 6.25a. However, the width of the 35 kg perpendicular region is greater than that of the 40 kg test, on the order of 500 µm compared with 200 µm respectively. This can be attributed to the tertiary creep phase occurring over a longer time period for the lower loading case, see Figure 6.19 for the relevant S10 creep curve.
Figure 6.25: Fracture surface of the S8-40kg test of un-aged material, a) shows an overview of the cap having hinged as in Figure 6.24b and b) shows a zoomed in area highlighting the widespread micro-cracking which occurred adjacent to the final fracture location.
Figure 6.26: Images of fracture surface from the S10-35 kg test of un-aged T91 material, a) shows the fractured surface with the indenter still in place, b) shows a magnified view of cracking and oxide spalling.

The fractured surface of the S14 test at 35 kg of material aged for 1 year is presented in Figure 6.27. The surface has a distinctly different morphology compared with the tests performed on un-aged material as described above. There is little evidence of the parallel crack region adjacent to the edge of the cup as seen in Figures 6.25a and
6.4 - SPCT FE Results

6.26a, indicating non-ductile cracking of the material. In fact the fracture surface appears to be entirely comprised of a crack that grew parallel with the cup edge. There is also a noticeable lack of tear-like surface features observed for the un-aged material. This suggests that the aged material is distinctly less ductile than the un-aged material. What is similar between the aged specimen results and the un-aged results is the pitted surface in Figure 6.27d. This again can be linked to oxidation at longer durations of testing, however no obvious spalling features are observed in this sample. Therefore oxidation had begun to affect the sample although it had not generated sufficient thickness to flake off, as seen in Figure 6.26. Also featured in Figure 6.27d are two tear like fractures but there is no evidence of these being as wide-spread as in Figure 6.25b.

6.4 SPCT FE Results

Finite element simulations are performed at loads of 20, 25 and 26.5 kg. As discussed in Chapter 5 due to the high stress sensitivity of the model, loads above these levels resulted in immediate failure of the simulation due to excessively high values of creep strain occurring during the initial increment. Further reduction of the increment size is not possible, as the minimum time increment size had been reached, while the creep strain increment was above the CETOL limit set. The material parameters for P91 at 600 °C are as presented in Chapters 3 and 4, the aged material is simulated by increasing the initial precipitate diameter in line with the coarsening curves in Figure 3.2. The precipitate input parameters are given in Table 6.4. Increasing initial diameters increases the average spacing of obstacles as per Equation 3.3, which in turn will decrease the effectiveness of particles to resist creep deformation.

6.4.1 Un-aged and Aged T91

Computed time-displacement curves for the indenter movement during the FE simulations are presented for the un-aged and aged materials in Figures 6.28a and 6.28b respectively. The aged specimens last for slightly longer durations, in contrast to what is observed from the experimental work, due to the formulation of the two precipitate state variable, discussed later in this section. In the un-aged sample simulation with a load of 26.5 kg, the M\textsubscript{23}C\textsubscript{6} precipitates started with a simulated uniform size of 100 nm and at failure the maximum precipitate size is predicted to be almost 16 times larger. However, the aged specimen under the same conditions, with
Figure 6.27: The fractured cap of the S14-35 kg 1 year aged specimen in a) and b) showing a magnified image of the cracked surface with dispersed cracks.
an initial diameter of 214 nm, showed coarsening to only 8 times larger. Table 6.4 contains the minimum and maximum precipitate diameters from the FE simulations.

Figure 6.28: FE simulation results for a) un-aged and b) 1 year aged T91 material at 600 °C, showing little difference between the two material conditions.

Figure 6.29: Experimental and FE results for the SPCT of T91 1 year aged and un-aged materials at 600 °C, comparing the applied load with the time to failure.
Figure 6.30: Experimental and FE results for the SPCT of T91 1 year aged and un-aged materials at 600 °C, comparing the minimum displacement rates with the applied loads.

Table 6.4: Maximum precipitate diameters from the FE SPCT simulations of un-aged and 1 year aged T91 material.

<table>
<thead>
<tr>
<th>Material</th>
<th>Load (kg)</th>
<th>(d_{M23C6,\text{max}}) (nm)</th>
<th>(t = 0)</th>
<th>(t = t_f)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-aged</td>
<td>20.0</td>
<td>100</td>
<td>1736</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>100</td>
<td>1636</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>26.5</td>
<td>100</td>
<td>1583</td>
<td>36</td>
</tr>
<tr>
<td>Aged 1 year</td>
<td>20.0</td>
<td>214</td>
<td>1578</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>25.0</td>
<td>214</td>
<td>1695</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>26.5</td>
<td>214</td>
<td>1725</td>
<td>40</td>
</tr>
</tbody>
</table>

The FE results are plotted against the experimental results in Figures 6.29 and 6.30, where the applied load is shown against time to failure and MDR. There is little to distinguish between the aged and un-aged FE results in the time to failure plot, especially for the 20 kg load simulation, although there is more deviation between the un-aged and aged at the higher loads. The experiments and simulations do not obey the same relationship between load and failure time. For example, the experimental un-aged test at 35 kg fails around 200 hours while the FE analysis is predicting a similar failure time for a load of 25 kg. Thus, the FE model is underpredicting the experimental failure times and this is likely evidence of a missing strengthening mechanism or the over prediction of damage leading to early failure in the simulations.
The MDR plot of Figure 6.30 shows the FE results following very similar trends to the experimental results. The steady state behaviour is utilised to calculate the minimum displacement rate, therefore while the model is undergoing steady state creep, it is behaving in line with the experimental trend. The model therefore is over-predicting damage leading to failure, or a strengthening mechanism is missing from the model for high stress operation. Extrapolating a log curve fit from the FE aged results generates a curve which passes through the aged experimental results. Under experimental loads, the un-aged material has a lower MDR. However, the FE results show the un-aged material having a higher MDR than the aged material. At the lowest simulated load of 20 kg the experimental trend is evident again, where the un-aged material has a lower MDR than the aged material.

### 6.4.2 Cavitation Damage

The contour plots of the cavitation damage evolution at three different times during of the 20 kg load simulation are presented in Figure 6.31. Figure 6.31a shows the condition post the elastic-plastic embedding of the indenter. Figure 6.31b presents failure beginning approximately 0.7 mm from the indenter centreline and Figure 6.31c shows the damage distribution at failure, where elements have failed through the disk thickness. It is assumed the initial elastic-plastic bending does not contribute to the creep induced damage from the hyperbolic sine model, thus no damage is observed at the beginning of the creep step in Figure 6.31a. Examining the damage contour plot in Figure 6.31b shows a number of elements having reached the maximum allowable level of damage, in line with the leading edge of the indenter-specimen interaction zone, at the mid-point \((t = t_f/2)\) of the simulation. A secondary region of high damage is forming above the chamfer on the lower die also. Damage is also predicted to spread to the free surface to the right of the primary damaged region. This is similar to the observations of the fractured samples in Figure 6.25, where widespread tearing has occurred in the region surrounding the primary crack.

Finally in Figure 6.31c the sample has fully failed although, the FE simulation does not generate the hinge type failure condition observed in the experiments. This is due to the axisymmetric formulation of the simulation. The necked region has failed and has become highly distorted, the NLGEOM option allows for the reorientation of the elements to include the effects of this thinning of material during the simulation. The creep subroutine tracks the values of cavitation damage in each element, once the maximum value of 0.95 was reached it is maintained at this level for the remainder of
the simulation. It is assumed, based on the final contour plots of cavitation damage, that the simulation ended due to the formation of a connected string of elements with maximum damage having formed through the thickness of the specimen. Elements in which cavitation damage reached a maximum are in the path of failure growth through the thickness of the specimen, similar to the experiments where failure grows gradually through the thickness of the specimen.

![Simulation snapshots](image)

Figure 6.31: Evolution of cavitation damage for the 20 kg simulation, with $t_f = 1976$ hr.

A 20 kg SPCT at 600 °C is also carried out where the cap and hinge type failure did not occur and the axi-symmetric features of the resultant specimen allowed qualitative comparison with the computational cavitation damage results. This is shown in Figure 6.32 with the FE cavitation plot overlaid on the left hand side of the SEM image. Experimentally, an annular type crack is observed with some oxide spalling in evidence on the slope away from the fractured surface in the top right of the image. The regions of highest damage correlate closely with the centre of
the fracture surface. A green lower damage ring corresponds with material from the upper surface which is pushed down during the test, in this image, this direction is out of the page. The yellow cavitation damage ring aligns closely with the free surface side of the cone pushed out of sample, indicating significant damage occurred here. This region aligns with the densely fractured region of the caps in Figure 6.25b. However, without the ability to safely tilt the sample in situ, examination of the fractures on these sloped regions is not possible. The fracture surface from this low load test is expected to be similar in form to the 35 kg test results in Figure 6.26, indeed evidence of oxide spalling is present in Figure 6.32.

Figure 6.32: FE cavitation plot overlaid on an SEM image of a sample tested at 20 kg for 600 °C.

### 6.5 Discussion

This chapter presents the thermal ageing of T91 material to explore the effect of high temperature ageing on precipitate diameters and the corresponding creep lives of these aged materials using the SPCT apparatus described in the previous chapter. The finite element simulation developed in Chapter 5 is also utilised to examine the accuracy of the material model developed in Chapters 3 and 4 under SPCT conditions.

To measure the precipitate diameters, carbon extraction replica’s are manufactured following a similar process to that described by Mitchell et al. [235] developed for P91 material. Carbon replica films of 9Cr materials are an effective method of
extracting precipitates from a material for quantitative microscopy although there are some issues with this approach. Setting aside the requirement for the use of dangerous and potentially explosive chemicals (dried picric acid is a precursor for many explosives), this methodology is entirely manual and the consistency of the etched surface achieved can differ from one sample to the next with no variation in the approach taken. A prime example of this would be the oxide films adhered to the carbon film in Figure 6.6, which did not occur for the majority of other samples. A background subtraction was performed prior to the measurement of precipitate diameters, as part of the automated measurement system developed. This removed the faint oxide regions from the images by averaging the grey intensity in a region surrounding any given pixel and subtracting the average grey intensity from the pixel in question. This cleaned the grey oxide coatings from the TEM images providing better contrast between the white background and dark precipitates.

Provided all previous steps are completed optimally, the physical capture of the carbon films onto the copper grids can cause significant damage to the replicas, either tearing or folding as in Figure 6.3. Other sample preparation methods include focused ion beam (FIB) milling or twin jet polishing. FIB removes a thin electron transparent piece of material, which is a time consuming and expensive process requiring complex dual beam SEM equipment. Twin jet polishing can completely grind away the sample material of interest and generally requires some experimentation to optimise the system for a particular material. Given the limited quantities of materials available twin jet polishing was deemed potentially too high a risk of losing aged material while optimising the approach and FIB based methods are too costly to pursue. Compared to these two alternate approaches, the carbon replica based approach provided an in-expensive and efficient means of liberating large quantities of precipitates for microstructural analysis. Combined with the automated measurement system statistically significant numbers of precipitates were measured and contributed to the precipitate coarsening rate identification.

The presence of oxide shadows in the images utilised for particle measurement necessitated the use of a background averaging macro in the automated system, see Appendix E. When utilised, this macro can reduce the grey intensity of isolated individual precipitates in the TEM images. Figures 6.12 to 6.15 contain some low grey intensity precipitates which correlate well with Nb and V concentrations. As such the faintest grey precipitates may not have been recorded by the measurement system. However, given the considerably high concentration of these particles the effect
of this loss is deemed as acceptable. The identified coarsening rate is still strongly influenced by the large number of smaller precipitates detected, as is shown in Table 6.2 when comparing the identified averaged coarsening rate with that utilised in the modelling of Chapter 3 and 4.

While the smaller grey precipitates in Figures 6.12 to 6.15 are positively identified as MX precipitates, applying this information on a mass scale to differentiate between $\text{M}_{23}\text{C}_6$ and MX precipitates has proven to be quite challenging. The average or mean equivalent circle diameter values, of the log-normal distributions which were fitted the precipitate diameter data were utilised to identify the thermal coarsening rate. These provide the most accurate measurement of the average precipitate diameters for the different ageing times. The long tails in the diameter data fit the log-normal distribution well. These values do not help in discerning between the two precipitate families of interest. Ideally a limit diameter above which a particle could be considered an $\text{M}_{23}\text{C}_6$ and below an MX would be applied to the precipitate data and two distinct coarsening rates could then be extracted. However, it would be difficult to say that initially small $\text{M}_{23}\text{C}_6$ precipitates which are consumed by larger precipitates during Ostwald ripening are not smaller than average to large MX precipitates.

The SPCT results for the un-aged material tested at 600 °C show scatter in the results in the time-displacement plot of Figure 6.19, however, when compared with the 40 kg results in Figure 6.20 the scatter is of a similar degree as the 40 kg tests. The S11 sample is slightly rougher, than the other samples (see Table 6.1). Previously, no significant effect of roughness had been observed and, as such, this level of variation was deemed acceptable for this test. As the S11 test temperature was within the acceptable limit but at the other end of the limit compared to the S10 test, it was expected to last longer than the S10 test. This indicates that, in this instance, the temperature effect was over ridden by another effect. Throughout the S11 test appears to have a higher displacement than the S10, pointing toward an effect which was present for the entire duration of the test. It is postulated here that a defect of some description may have been present in the sample and caused early failure. Defects through the thickness of SPC specimens will always be a concern for this test methodology, the apparatus developed here has shown itself to potentially be sensitive enough to allow identification of these types of effects.

The samples aged for 6 months, whose time-displacement curves are shown in Figure 6.21, both display a similar displacement rate with differing failure times consistent with their applied loads. A 5 kg reduction in load resulted in a factor of two increase
in time to failure for the 6 month aged material. The MDR and the failure time for the 35 kg test is also consistent with the S14 (1 year aged) material, shown in Figure 6.23. However the behaviour of the two materials immediately prior to failure differs.

Comparing the 35 kg time-displacement curves for the un-aged, 6 month and 1 year aged material highlights the effect ageing has on the failure of the materials. The S10 and S11 curves show the most pronounced tertiary creep curves lasting approximately 5 hours before final failure and the S12 (6 month aged) specimen shows a similar slight upward turn prior to failure. However, no such gradual upward turn is observed for the S14 (1 year aged) material. For this case there is a sharp turn from the secondary creep to final failure. The thermal ageing has diminished the creep ductility of the material, the degraded microstructure allowed the failure to rapidly propagate through the thickness of the sample. A coarser microstructure of recovered subgrains and larger precipitates do not resist fracture as effectively as the ductile un-aged material does. Here, we see a more brittle failure occurring for the 1 year aged specimen compared with the others. Examining the fractured surfaces of S13 (un-aged) and S14 (1 year aged) demonstrates this also. Figure 6.26 shows a wide area with perpendicular scratches from crack edge to the annular crack region for the S10 un-aged test. However, while in Figure 6.27, for the S14 (1 year) aged case, only a very small amount of perpendicular scratches or lines are observed, while most of the cracked region consists of the annular parallel type crack. This suggests that once the outer free surface of the sample begins to fail, the rest of the specimen will quickly follow afterwards, with less ductile deformation occurring (as is seen for the S10 test).

In Figure 6.29 the there is little difference in the time to failure for the FE aged and un-aged samples, indicating that the initial precipitate diameters for the aged specimen (see Table 6.4) did not have a significant impact on the time to failure. The root cause of this is the formulation of the two precipitate based state variable approach which is proportional to the increase in precipitate diameter, and not the absolute values of precipitate diameter. The aged specimens experience less particle coarsening during simulation and hence the state variable induces less degradation of the material. Table 6.4 shows the increase in precipitate diameters for the un-aged and aged simulations. The aged material experiences half the coarsening the un-aged material experiences for the \( M_{23}C_6 \) precipitates in the region surrounding the failure. The MX coarsening is of a similar order in both cases, indicating the
thermal stability of these precipitates. One possible solution to this is the inclusion of some initial precipitate softening for the two precipitate state variable term, derived in Chapter 3, proportional to the precipitate diameter increase. To represent the effect of thermal ageing, the precipitate state variable of Equation 3.14 can be re-formulated to include only thermal effects, where all terms have the same meanings as in Chapter 3.

\[
\dot{D}_P = \frac{1}{3} \frac{d_{c,0}^2 d_{m,0}^2}{B_c + B_m} \left[ \frac{B_c}{d_m^5} (K_m) + \frac{B_m}{d_c^5} (K_c) \right] \frac{1}{(1 - D_P)} \tag{6.2}
\]

The initial damage from thermal ageing has a value of approximately 0.03 after 8400 hours of ageing and inserting this damage into the 26.5 kg simulation resulted in a failure time of 143 hours, compared with the original aged simulation result of 190. The evolution of precipitate induced softening within the most highly affected element was plotted to compare the three simulation versions; un-aged, aged and aged with thermal softening in Figure 6.33.

![Figure 6.33: Evolution of precipitate state variable for un-aged, aged and aged with thermal softening FE simulations.](image)

The inclusion of an initial softening value, resulted in the aged specimen behaving similarly to the un-aged specimen. This inclusion did not result in a reduced time to failure for aged material, however the aged material behaviour is now closer to that observed in the experimental results. Additional microstructural evolution mechanisms are required to capture the effects of thermal ageing in the modelling of SPCT on aged P91.

Clearly, the failure times of the simulations do not coincide with the experimental results, with the FE analysis under predicting the time to failure. The sample
region of tensile deformation where failure occurs in both experimental and modelling results can be considered as, undergoing similar loading conditions to a tensile test. Kachanov damage, developed based on the reduction of area due to cavity formation under tensile loads, is therefore applicable to this loading condition. While the simulation and experimental failure times do not agree the results are more positive when comparing the minimum displacement rates. Particularly for the aged material, the simulation and experimental results do align and, at the 20 kg load the un-aged shows an MDR slightly less than the aged, as in the experimental work. At high loads, the model predicts a greater effect of precipitate diameter on the MDR, a trend that could be said to match that of the experimental results. The scatter in those MDR results however makes it difficult to say this with full confidence.

Cavitation damage evolution through the thickness of the disk specimen is presented in Figure 6.31, with the maximum damage occurring where experimental failure is observed. Specifically, this damage occurs in line with the leading edge of contact between the indenter and the specimen. At this location, the compressive load of the indenter is decreasing and transitioning to a tensile load from the disk bending/stretching. This inflection point has been highlighted previously by Ma et. al. [232] as the weakest point where failure can be expected to occur. Of particular interest is the distribution of damage on the lower surface of the disk surrounding the main crack, in Figure 6.31c, where a large network of tears have appeared indicating a high level of damage occurring at this location (as shown in Figure 6.25b). Comparison between these two sets of images indicates that the model has qualitatively captured the experimental behaviour. The inclusion of pre-creep thermal ageing softening to the $D_p$ term indicates that the model has the potential to effectively capture both un-aged and aged material behaviour, provided a mechanics based approach to reducing the value of the equivalent stress term is identified and incorporated.

The corroboration of this assertion is the comparison between the annular cracked region of a specimen tested at 20 kg at 600 °C. The damage contours from the 20 kg un-aged simulation overlay the regions of maximum damage with a high degree of accuracy, and also the cone region where large concentrations of tear-like cracking is expected to have occurred. Further long-term, low-load testing would provide the required time-displacement curve and more useful interpretations can be made about the behaviour of the material.

The finite element simulations are performed at a lower load than the experimental
work due to limitations in the formulation of the creep model from Chapters 3 and 4. The hyperbolic sine model is effectively a modified exponential based equation and, as such, the model creep strain rate is highly sensitive to high stress levels. To combat this, a limited plasticity model was implemented to ensure the maximum stress did not increase to values where the model would no longer function. A more robust solution would be the inclusion of an athermal viscous stress parameter which would be subtracted from the applied equivalent stress term. Such an approach could effectively unify short and long term creep predictions within a single model, and is of particular interest to modelling SPCT experiments.

6.6 Conclusions

Thermal ageing of T91 material for up to 1 year, coupled with TEM based microscopy and image analysis, allowed an average precipitate coarsening rate to be calculated for this material. Fe, Cr, and Mo diffuse towards the precipitates during ageing, and concentrate around $M_{23}C_6$ precipitates at all ageing times. For the MX precipitates, this concentration of Nb and V only occurred between the 6 month and 1 year ageing periods. The differentiation of the $M_{23}C_6$ and MX families requires further development of the image analysis software to screen for precipitates of a certain size and grey intensity in the micrographs. The identified rate sits in between literature values for coarsening rates in these materials, favouring the rate value for MX precipitates due to the significantly higher number detected in the micrographs.

Aged SPC specimens were successfully manufactured using a modification to the methodology presented in Chapter 5. Small punch creep testing of aged and un-aged T91 material revealed the degradation of creep performance which occurs with increasing ageing time. The 1 year aged specimens exhibited the shortest failure times and highest minimum displacement rates at both 35 kg and 40 kg. The un-aged specimens exhibit considerably more cracking, decreasing with increasing distance from the final crack region. The 1 year aged specimen exhibits very little cracking away from the main crack area in the hinged cap, indicating that significant deformation did not occur during testing. The aged specimen time-displacement curves show a sudden onset of failure from the secondary creep phase with almost no tertiary creep being observed. The un-aged and 6 month aged materials both experienced more obvious conversion from secondary to tertiary creep than the 1 year aged specimen.

The two precipitate creep model predicts the minimum displacement rates for low
load conditions which are in agreement with the trends observed experimentally at higher loads. Given that no modifications are made to the model prior to it simulating the SPCT conditions, the calibrated values of the multi-axial parameters in Chapter 4 have proven to be robust enough to provide reasonable agreement for displacement rates. While the formulation of the precipitate based state variable does not account for the degradation of the material due to strain free ageing, by including some initial softening due to the ageing, the model is closer to the experimental behaviour. Comparing the failure locations between the model and experiment shows good agreement between the model and the experimentally observed fracture behaviour. The distribution of cavitation damage correlates closely with images of the fractured surfaces, which is direct result of Equation 4.2. This equation effectively provides an element deletion function to the model which represents fracture growth through the specimen thickness, by removing elements once maximum damage is achieved. Maximum cavitation damage in an element is limited to 0.95 at which point the element can no longer resist any stress and it is no longer contributing to the specimen behaviour. In the experimental time-displacement curves fracture growth can be observed by jumps in the curve, similarly the model time-displacement curves exhibit this behaviour also. Modelling of the SPCT experiment with the hyperbolic sine model has highlighted a potential avenue for unifying long and short term creep simulations via the inclusion of an athermal viscous stress term.

Additional strengthening mechanism terms could be added to the multi-precipitate model, particularly to aid in simulating high load ranges, which include in-elastic strain hardening due to lath conversion to equiaxed grains and the loss of dislocation density. These terms would take the place of the primary creep model as discussed in Chapter 5. Additional imaging of the failed samples, especially the cross section of the failed specimens, could be used to examine directly the failure behaviour for un-aged and aged specimens. Some additional repeat SPC testing would be beneficial to corroborate the trends observed in this work, the SPCT apparatus has previously demonstrated it’s reliability so significant variations on these results are not expected.

Of particular interest would be a comparison between the SPCT results presented here and those from the MarBN material. MarBN is proposed as a successor to the P91 material investigated here and has proved in early testing, to have an enhanced creep resistance over P91 [41]. Additional data on the behaviour of this material is required prior to it being put into service within power plants. One significant
difference between the two materials is the requirement to normalise MarBN at 1200 °C compared to the 1050 °C required for P91. The effect of this higher temperature normalisation on MarBN is discussed in the following chapter.
Chapter 7

Effect of heat treatment on sub-oxide MarBN characteristics

7.1 Introduction

In earlier chapters, this project has focused on the testing and modelling of current generation 9Cr steels, e.g. P91 and P92. However, equally of interest is the behaviour of next generation materials for use in the Irish power generation sector. The modified 9Cr material, denoted as MarBN and discussed in Chapter 2, consists of additional Co and W, with controlled additions of B and N and it is now of particular interest to plant operators. The retention of the hierarchical microstructure during welding retards [21] the formation of Type IV cracks within the welds, the B concentration in MarBN ensures the beneficial hierarchical microstructure is formed again during weld cooling, coupled with more thermally stable M$_{23}$(CB)$_6$ carbides [38]. One of the key strengthening mechanisms provided by strict B and N composition control is the formation of creep strong precipitates, also one of the key themes of this work. To ensure only creep strong precipitates are formed, a different normalisation heat treatment is required for MarBN, at a temperature of 1200 °C [43], significantly higher than the ASTM standard for 9Cr of 1050 °C [61]. This higher normalisation temperature ensures the dissolution of all B into the matrix and prevents the formation of BN precipitates. When BNs form within MarBN, they sequester N from the matrix preventing the formation of creep strong MX precipitates and also prevent B segregation to grain boundaries to provide enhanced carbide strengthening. Chapters 3 and 4 both highlighted the importance of these precipitates for long term operation of any 9Cr steels under creep exposure. The work here focuses on the effects of this elevated normalisation temperature on the micro-mechanical properties of regions adjacent to the oxide layer, via micro-hardness
testing and micro-structural examinations.

MarBN is a potential material for use in super-heater tubes which are exposed to the highest temperature environments within power plants. The super-heater is comprised of multiple thin walled tubes designed to transfer energy from combusted fuel to water to generate steam. Heat treating thin walled MarBN tubes will result in oxide formation which is removed post heat treatment. However, for the sub-oxide zone material immediately adjacent to the oxide-metal interface, it is not clear if this material has reduced mechanical properties compared to the bulk material and if it should be removed along with the oxide. A layer of lower quality material, present on the inner and outer surface of a pipe, could provide an easy pathway for failure to occur within a component. As observed in the literature on welded 9Cr steels, the weakest HAZ region dictates the useful life [212] of a component. The analogy to this work is clear; should the outer surface of the material be significantly degraded, it will control the life of a parent material component manufactured from the same.

In this study, a micro-mechanical testing approach is undertaken, consisting of micro-hardness mapping and micro-cantilever testing. Scanning electron based characterisation is performed using electron back-scatter diffraction (EBSD) and automated lath size detection tool is applied from the literature.¹

### 7.2 Experimental Methods

#### 7.2.1 Materials

Cast 9Cr-3W-3Co-V-Nb (MarBN) material manufactured as part of the UK multi-partner, industry–academic project entitled IMPACT were heat treated previously in a manner similar to Li et al. [43]. Previously, material from the same melt has undergone low cycle fatigue testing at NUI Galway [236]. The material composition is the proprietary information of the industrial partners and is not available for publication. However, the material is from the same casting as utilised by Li et al. [43].

¹This work was performed at Loughborough University, under the co-supervision of Dr. Mark Jepson in collaboration with the Loughborough Materials Characterisation Centre (LMCC).
7.2.2 Heat treatment

The samples are machined into cubes of length 10 mm with a ground finish and heat treated according to Table 7.1. All samples were normalised at standard and non-standard temperatures, followed by an in air cooling afterwards, denoted by their normalisation temperatures in Table 7.1. Half of the samples were then given a further tempering heat treatment at 780 °C, which is within the normal tempering range for 9Cr materials [61].

Table 7.1: Sample numbers and applied heat treatments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Normalisation</th>
<th>Tempering</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1050</td>
<td>1050</td>
<td>-</td>
</tr>
<tr>
<td>N1200</td>
<td>1200</td>
<td>-</td>
</tr>
<tr>
<td>N1050T780</td>
<td>1050</td>
<td>780</td>
</tr>
<tr>
<td>N1200T780</td>
<td>1200</td>
<td>780</td>
</tr>
</tbody>
</table>

7.2.3 Micro-hardness testing

Automated micro-hardness mapping is performed on the samples utilising a Struers DuraScan-70, with a Vickers hardness indenter tip, and a 0.2 kg load. Hardness maps with an area of 2 mm x 3.5 mm and an indentation spacing of 0.1 mm, are generated following ISO 6507-1 [126] and Seifert et al. [133]. The hardness maps are arranged such that the effects of oxidation on a single side of the sample cubes is only considered. Hardness mapping is performed a sufficient distance from the other exposed sides of the samples to ensure the sub-oxide zone from a different free edge is not tested, e.g. see Figure 7.1.

7.2.4 Electron microscopy

Electron Backscatter Diffraction (EBSD) is the process by which a beam of electrons strike a material’s surface, which is angled at 70° to a secondary electron detector. The incident beam of electrons are scattered by elastic collisions with atoms within the material and are rebounded back out of the sample, some are forward-scattered and some are backward-scattered. The back-scattered electrons contain information
about the crystal orientation of the material. The back-scattered electrons have been diffracted to differing degrees depending on the orientation of the crystal impacted by the incident beam. The detector then collects the diffracted electrons which form Kikuchi patterns, the Kikuchi patterns for iron-based alloys have been well established and are saved in a type reference library in the detector computer. These are then compared against the patterns generated by the diffracted electrons and an orientation is identified. To improve the speed of this process binning is applied whereby several pixels in the detector are averaged and the averaged patterns utilised for identification of crystal orientation. Smaller binning significantly increases the duration of each scan, by orders of magnitude, depending on the area being scanned [237].

Figure 7.1: Schematic of sample hardness mapping layout.

EBSD scans are performed at increasing distances from the oxide-base metal interface with a Joel 7800F FEG SEM system equipped with an Oxford backscatter detector running Aztec 3.1 software. Areas of 120 µm × 90 µm are scanned with a probe current of approximately 29 nA with an accelerating voltage of 20 KeV and at a working distance of 16 mm. The scan resolution was set to 0.1 µm with 6x6 pixel binning being applied. Scan areas are sufficiently far from indented regions to avoid any strain induced localised re-orientation of grains.

7.2.5 Micro-cantilever manufacture and testing

To investigate the effect of oxide scale formation on the strength of the sub-oxide zone, micro cantilever samples were manufactured at increasing distances from the oxide-base material interface namely; 0.05 mm, 0.85 mm and 2.35 mm. Spacing was selected based on hardness testing results, to provide material from regions of differing hardness. Figure 7.2 shows a sample SEM image of the oxide interface.
region in the N1050 sample showing two rows of indents, with the initial indent being in the oxide region in both cases.

Figure 7.2: N1050 sample showing two rows of indents with the left most indent in the oxide region, shadowed square regions are caused by EBSD scanning.

**Manufacture**

Focused Ion Beam (FIB) milling, was utilised to manufacture micro-cantilever samples. A Xe\(^+\) plasma ion source dual beam system was employed allowing welding and milling operations to be performed in situ. Initially a 70 µm × 100 µm × 30 µm blank was removed from the sample, see Figure 7.3a, utilising an automated macro developed in house at the Loughborough Materials Characterisation Center (LMCC). Blanks were removed from the sample and welded to the corner of a silicon platen, to provide the required clearance for milling. The cantilever beams are machined a distance of 12 µm from the surface of the blank, with the ion beam aligned perpendicular to the top surface of the blank and the width of the beam removed via milling, see Figure 7.3b. Next, the blank was rotated such that the wedge cut from the previous milling operation is made perpendicular to the ion beam and the cantilever beam is cut from the wedge shape. Blanks containing the cantilever beams were then removed from the post and mounted on a slot milled in the side of the silicon platen and welded in place, Figure 7.3c. Table 7.2 contains the dimensions of the cantilever beams manufactured for the N1050 and N1200 samples.
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![Image](image1)

Figure 7.3: Micro-cantilever manufacturing steps, a) Initial chunk liftout (oxide on left), b) mounted on silicon platen after initial beam width milling and c) final mounting position prior to test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distance from oxide (mm)</th>
<th>Height (µm)</th>
<th>Breadth (µm)</th>
<th>Length (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1050</td>
<td>0.05</td>
<td>3.90</td>
<td>3.80</td>
<td>40.0</td>
</tr>
<tr>
<td></td>
<td>0.85</td>
<td>3.20</td>
<td>3.66</td>
<td>60.0</td>
</tr>
<tr>
<td></td>
<td>2.35</td>
<td>3.17</td>
<td>3.66</td>
<td>60.3</td>
</tr>
<tr>
<td>N1200</td>
<td>0.05</td>
<td>2.97</td>
<td>3.62</td>
<td>59.3</td>
</tr>
<tr>
<td></td>
<td>2.35</td>
<td>3.05</td>
<td>3.64</td>
<td>60.0</td>
</tr>
</tbody>
</table>

Table 7.2: Dimensions of micro-cantilever beams manufactured for test program.

Testing

The platen containing the cantilever beam was then placed in a gallium source FEI Nova 600 Nanolab dual beam FIB system fitted with a micro probe (FMT 120, Kleindiek, Nanotechnik, Germany). Once mounted, the force probe was aligned with the beam, 60 µm from the root of the beam (40 µm for the initial N1050 0.05 mm test). A macro for continuously moving the sample stage in increments of 100 nm/s is then applied and the beam was imaged with the SEM camera every 2 seconds during the test. Three typical SEM images of the beam during the test are shown in Figure 7.4. Figure 7.4a shows the force sensor in contact with the beam at the beginning of the test, Figure 7.4b is the beam mid-way through the test procedure and Figure 7.4c is the beam plastically deformed at the end of a test.
7.3 - Data Analysis

7.3.1 Relating hardness and yield stress

The relationship between hardness and yield stress is of particular interest to plant operators, much work has been performed linking the two, particularly by Busby et
al. [137]. The viability of hardness based assessments of materials had previously been assessed by Tabor [136], who linked the plastic deformation during indentation directly to the plasticity properties of the material and not to the elastic recovery which occurs once the indentation tip is removed. From the work of Busby et al. [137], the change in yield stress of a steel can be calculated from change in hardness data using Equation 2.17, with $c_y$ having a value of 3.03.

$$\Delta H_v = c_y \Delta \sigma_y$$ (7.1)

### 7.3.2 Lath size measurements

Grain or sub-grain size measurements based on the linear intercept method, are calculated utilising the ASTM standard E1382-87: "Standard test methods for determining average grain size using semi-automatic and automatic image analysis" [238]. A series of lines at varying angles are overlaid on the image and the number of intersections are counted and converted into an average size. Appendix E of the standard details a modification for the measurement of narrow elongated grains, such as the lath tempered martensite structures of 9Cr steels. Lehto et al. [239] developed an automated MATLAB code based on this standard for heterogeneous distributions of grain sizes in welded structural steels.

Along with the EBSD orientation maps, showing the crystal orientation of the microstructure at any given point in the material, it also produces a band contrast (BC) image where regions of identified orientation are coloured in shades of grey and regions where no discernible orientation are denoted in black. Figures 7.5a and 7.5b are examples of this type of image, the corresponding orientation maps are included in the results section below. While samples are subjected to a beam of electrons, an electrical charge can build up on the sample surface, which distorts the image captured in the backscatter detector of the system. The longer a sample is exposed, then the more charge that can build up, further degrading image quality. Figure 7.5 contains samples of an image from the beginning of an imaging session and one from the end of a session, showing the difference in definition of the boundaries.

In order to utilise the automated approach of Lehto et al. [239], the band contrast images must be converted to black and white images, with grain interiors in black and boundaries in white. This process is performed here utilising the ImageJ software (v1.52o) and the Renyi Entropy threshold method developed by Kapur et al. [240]. In grey scale images such as the BC images in Figure 7.5, each pixel is assigned an
intensity value from 0 to 255, where 0 is pure white and 255 is pure black, details on the threshold tool are available in [241]. The selection of threshold limits is vitally important to accurately identify boundaries which will be utilised to estimate grain size. As such, a range of threshold grey intensity limits is tested for each image to identify the limit value which identifies the maximum number of boundaries.

Figure 7.5: Band contrast images from the samples normalised at (a) 1050 °C 0.8 mm from the oxide and (b) 1200 °C 1.4 mm from the oxide. In a) no charging occurred during imaging while in b) charging occurred causing a slight loss of focus.

Figure 7.6 contains a series of images at differing threshold limits from 30 to 80 for Figure 7.5a. For this image, limit values below 60 do not define the majority of the boundaries present, likewise comparing Figure 7.6d with Figure 7.5a not all boundaries are present in the image post threshold application. For the limit of 80, some finer boundaries are lost due to overlapping boundaries eclipsing the interior of the smaller laths. Therefore, for this case the image resulting from a threshold limit of 70 is utilised. This process is repeated for each of the EBSD scans presented in this chapter.

Once the images of the threshold application are assembled, the Lehto grain size tool [239] is applied to each image. As the EBSD scan settings are optimised to detect the lowest mis-orientation angles, boundaries with mis-orientations above 2° are detected. Therefore, application of the grain size tool will in fact be detecting lath, packet, block and grain boundaries. The average grain size is therefore considered to be the average lath size, as there are many more lath boundaries than any other types within each scan image. Lath boundaries occur on the boundaries of grains, packets and blocks, resulting in both high and low angle boundaries being present in certain cases. The average lath size is calculated utilising the method described in ASTM...
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E1382 linear intercept method [238]. Four sets of parallel lines are overlaid (0°, 40°, 90°, 135°) on the image and the boundary intersections counted, lines were drawn with a spacing of 7 pixels. All intercept lines are considered as a single distribution for the calculation of average lath size. As the dispersion of lath size is of interest, the value is also reported as a measure of the variation in sizes detected.

![Images showing effect of increasing threshold limit value on the number of boundaries included for grain size detection.](image)

Figure 7.6: Effect of increasing threshold limit value on the number of boundaries included for grain size detection. Images for the N1050 sample, 0.8 mm from the oxide.

The distribution of lath sizes from the application of threshold levels, 20, 70 and 80 for the N1050 sample, at a distance of 0.8 mm from the oxide, were extracted from the automated tool using the MATLAB Distribution Fitter tool (MATLAB version R2018a). Log-normal distributions are fitted to the results for these three threshold levels and are presented in Figure 7.7. Increasing the threshold level reduces the influence of smaller laths smoothing the density curve. At 80 intensity, the distribution shows the loss of smaller laths due to the increased boundary widths, effectively removing them from the image for measurement consideration.

The second method of lath size measurement, recommended for materials with heterogeneous grain sizes by Lehto et al. [239], is the point sampled intercept length approach defined by Gundersen et al. [242,243]. Here a random distribution of points is overlaid on the image and a line with a random orientation selected from 0°, 40°,
90°, 135° is extended until it meets a boundary. 5000 points are applied to each image, as this is above the recommended number from the standard and is identified as supplying a converged solution in the literature [239]. As the points are distributed randomly, laths are measured a proportional number of times to their surface area. The larger a lath is, the greater the number of points applied to that lath, increasing the effect of this lath on the resulting average measure.

![Graph](image)

Figure 7.7: Three sample distributions of lath size density functions for threshold grey levels of 20, 70 and 80, corresponding with Figures 7.6a, 7.6e and 7.6f respectively.

The point sampled lath size is reported as always being larger than the line sampled method, for welded materials. From Figure 7.8 the grey point sampled measures are lower than the empty circles for the linear intercept. Evidently for tempered martensitic materials, this is not the case. The point sampled lath sizes are less than the linear intercept sizes, the point sampling randomly places the points to be measured and, as such some very small laths may have been excluded. Lehto recommends the reporting of all three measures in the literature, as the line intercept and dispersion results allows comparison with other literature data and a good description of the distribution of lath sizes. The volume weighted results provide an effective lath size parameter which is more useful for estimation of mechanical properties [239, 244].
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Figure 7.8: Effect of increasing the grey intensity limit for threshold application on the lath measurement results, for the band contrast image in Figure 7.5a, and the corresponding EBSD map in Figure 7.9c.

7.3.3 Lath-yield stress relationship

Barrett et al. [32] developed a physically based yield strength model for 9Cr steels at high temperature. This model includes contributions from solute strengthening atoms, precipitates, dislocations and microstructural features i.e. low and high angle boundaries. Of interest to this work is the estimation of the lath contribution to yield stress. The model decomposes the microstructural boundary strengthening effect in contributions from high angle boundaries (HABs), i.e. the Hall-Petch relationship [245] and the contribution from low angle boundaries (LABs), which is inversely proportional to the dimension of the LAB [155]. The contribution to yield stress from high and low angle boundaries is described as follows:

\[ \tau_{bd} = \tau_{HP} + \tau_{LAB} \]  

where, \( \tau_{bd} \) is the contribution to yield stress from microstructural boundaries, \( \tau_{HP} \) is the conventional Hall-Petch effect for HABs and \( \tau_{LAB} \) is the contribution from LABs.

\[ \tau_{HP} = \frac{k_{HP}}{d_g^{n_{HP}}} \]  

where \( k_{HP} \) is a temperature dependent Hall-Petch constant, \( d_g \) is the minimum HAB dimension present, (for MarBN here it is assumed to be the block width), and \( n_{HP} \) is the Hall-Petch exponent with a value of 0.5. The contribution to yield stress as
described by Maruyama et al. [155], is:

\[ \tau_{\text{LAB}} = \frac{\alpha_2 \mu b}{\bar{m}} \]  \hfill (7.4)

where \( \alpha_2 \) is a material parameter valued between 2 and 3, \( \mu \) is a temperature dependent shear modulus and \( b \) is the burgers vector, on the order 0.248 nm, for bcc iron. \( \bar{m} \) is the equivalent lath width. In the EBSD scans below, the laths in MarBN are long narrow tempered martensitic laths with occasional equi-axed sub-grains spaced sporadically throughout the microstructure.

### 7.3.4 Application of small displacement theory to micro-cantilevers

A linear trend line is fitted to the force-displacement results, by incrementally increasing the number of data points included in this procedure the transition point from linear-elastic to plastic behaviour is identified. Yielding is deemed to have occurred when the inclusion of additional force-displacement data points caused a decrease in the \( R^2 \) measure of agreement between the fitted linear trend-line and the data. Examining the linear portion of the curve allows the stress-strain behaviour to be calculated with small displacement theory.

Using cantilever beam bending theory the stress-strain behaviour for the linear portion of the test is estimated. However it should be noted that cantilever beam bending theory has inherent assumptions, such as: the beam being uniform in cross section, the material obeys Hookes law, only small deflections are applied (small displacement theory), the material is isotropic, and plane sections remain so during bending [234]. The validity of this approach to micro-cantilevers manufactured from polycrystalline materials is discussed in Section 7.5.2.

From beam theory for a rectangular beam with cross-section dimensions of width \( b_{\text{cnt}} \), height \( h_{\text{cnt}} \) and a length \( l_{\text{cnt}} \), the stress \( \sigma_{\text{cnt}} \) at the outer fibre at the support location is:

\[ \sigma_{\text{cnt}} = \frac{6F_{\text{cnt}} l_{\text{cnt}}}{b_{\text{cnt}} h_{\text{cnt}}^2} \]  \hfill (7.5)

where \( F_{\text{cnt}} \) is the applied load. Deflection at the tip of a cantilever due to a point load is:

\[ \delta_{\text{cnt}} = \frac{F_{\text{cnt}} l_{\text{cnt}}^3}{3EI} \]  \hfill (7.6)

where \( I \) is the second moment of inertia and \( E \) is the elastic modulus, rearranging...
then gives:

\[ E = \frac{4k_{\text{cnt}}l_{\text{cnt}}^3}{b_{\text{cnt}}h_{\text{cnt}}^2} \]  

(7.7)

where \( k_{\text{cnt}} \) is the slope of the force-displacement curve. Equations (7.5) and (7.7) are then utilised to calculate the strain in the outer fibre of the beam at the support location, where the beam emerges from the chunk in Figure 7.3c.

### 7.4 Results

The following section presents the EBSD scan results, hardness distributions, lath size and micro-cantilever bending test results, for tempered and untempered materials. The grain orientations can be observed for each material at increasing distances from the oxide layers. Following on from these results are the micro-hardness results which have the extracted equivalent lath sizes overlaid for comparison. The lath sizes presented here are obtained utilising the linear intercept method. This study seeks to quantify the volume weighted lath sizes (from the point sampling approach), the linear lath size dispersions, threshold limits selected and the calculated contribution to shear stress from low angle lath boundaries. Also included is a comparison of the micro-cantilever and hardness based yield stress estimations.

#### 7.4.1 EBSD scans

Figures 7.9 to 7.12 show the EBSD scans at increasing distances from the oxide layer, for all samples in Table 7.1. For all image sets, the sub-labels represent the distance from the oxide-base interface at the centre of the scan area, and the oxide is to the direct left of the initial image (a), (aside from the N1050T780 sample where a wider spacing of EBSD scans is applied to this sample).

The white pixels in the EBSD results are regions where the crystal lattice was too disordered for the software to identify a singular orientation, the Aztec software deems these regions to be boundaries and attempts to draw boundaries over the EBSD orientation maps. As such in some EBSD results, small black pixels denote where an attempt was made by this software to denote a boundary.

Figure 7.9a exhibits a distinctly disorganised orientation map, compared to Figure 7.9b where there are regions of parallel laths in the same orientation and an evident HAB. Distinct colour changes are observed here, particularly for the 7.9b and 7.9d denoting high angle boundaries. Figure 7.9e contains some large white areas, which
are inclusions near the surface of the material, which absorbed the backscattered electrons preventing an orientation being detected.

![Sample normalised at 1050 °C, EBSD scans performed at increasing distances from the oxide-base metal interface.](image)

Figure 7.9: Sample normalised at 1050 °C, EBSD scans performed at increasing distances from the oxide-base metal interface.

The sample normalised at 1200 °C shows the $<101>$ (green) orientation to be prevalent for portions of the orientation maps presented here, particularly in Figures 7.10c and 7.10e. However, for the 0.35 mm case, a clear shift in orientation is observed, indicating a region of differing orientation is adjacent. Thus, this location is not considered to favour a particular orientation. As the material is cast and not rolled, it is expected that the material should not favour one particular orientation over another. Figures 7.10d and 7.10e present orientation maps with particularly wide boundary regions. This is attributed to two factors: (i) charging of the sample during SEM imaging, whereby an electrical charge builds up on the sample causing the backscatter electrons to be deflected, and (ii) at varying times during the imaging at Loughborough University, vibrations due to construction decreased the resolution of the SEM systems at erratic intervals. The combination of these two factors results in slightly blurry image, see Figure 7.5.

EBSD orientation maps of the sample normalised and tempered at 1050 °C and 780 °C respectively are presented in Figure 7.11. The sample shows a slight trend
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of favouring the \( <001> \) orientation (near the oxide) and, the \( <111> \) orientation (which becomes more prevalent with increasing distance from the oxide layer). The untempered samples (N1050 and N1200) showed clear evidence of distinct HABs, possibly at grain boundaries, away from the oxide. Similarly here in the 1.4 mm case, two regions of distinct lath orientations meet, indicating the presence of a HAB. Generally, for this case, the orientations from lath to lath appear more randomly orientated, than for the normalised only samples, possibly due to the tempering process.

Figure 7.10: Sample normalised at 1200 °C, EBSD scans performed at increasing distances from the oxide-base metal interface.

For the sample normalised and tempered at 1200 °C and 780 °C respectively, near the oxide in Figure 7.12a there is a distinct shift from a disordered nearly equi-axed region to the left of the image while the rest of the map consists of elongated laths. The map at a distance of 0.93 mm is the lowest quality of all EBSD scans obtained, as it suffered from a large quantity of charging, which occluded smaller laths, such as those in the bottom right corner. Measurement results from this image should be viewed in light of the quality of this image. The two maps furthest from the oxide highlight the overall lack of any texture or favoured direction of the material, Figure 7.12d heavily favours the \( <111> \) direction while Figure 7.12e almost exclusively favours the \( <101> \) direction. Given the scale of the images, the results here may
represent a texture within a single prior austenite grain. Both images contain clear martensitic laths with few sub-grain type structures.

Figure 7.11: EBSD scans from the sample normalised and tempered at 1050 °C and 780 °C respectively.
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Figure 7.12: Crystal orientations at increasing distances from the oxide for the sample normalised at 1200 °C and tempered at 780 °C.

7.4.2 Hardness

Vickers hardness test data are converted into 3D maps, see Figure 7.13 for the N1200 case. Examining the map, the oxide interface is evident on the left of the plot as a "wall" of low hardness in dark blue. As distance from the oxide increases, the predominance of a darker green region with few yellow peaks (400 - 410 Hv) can be observed until approximately 2 mm from the oxide. From 2 mm to 4 mm from the oxide more higher hardness, yellow peaks appear representing the 420 to 430 Hv range, indicating an increase in the average hardness. The oxide-base material interface is imaged optically to plot the profile between the oxide and sample, compared to the initial indent in each row.

This profile is then utilised to calculate an average distance from the oxide. This approach is applied to each sample to identify an average distance from the oxide. The hardness maps are then compressed from a three dimensional plot to a two dimensional plot by averaging the hardness at equal distances from the oxide interface. The equivalent lath sizes are then overlaid to compare with the hardness at increasing distance from the oxide.
Figure 7.13: Typical hardness map output for the sample normalised at 1200°C from automated hardness mapper.

Figure 7.14 highlights the softening observed in the sample normalised at 1050 °C, in the initial 1 mm adjacent to the oxide-base metal interface. A distinctive decrease in hardness is observed starting at the interface, continuing to a minimum at 0.3 mm and followed by a general increase saturating at a distance of 1.2 mm from the oxide. The lath size plot does not follow the hardness trend, as it initially increases while the hardness decreases, followed by a stable region and unlike hardness, it decreases in the bulk material. The initial inverse behaviour between lath size and hardness can be explained partially by the inverse relationship between lath size and yield stress of the material. A false zero is utilised on the primary vertical (left) axis in the following images, where the chart begins at a hardness value of 190 H_v.

In contrast to the N1050 sample, the N1200 sample shows no obvious softening adjacent to the oxide layer in Figure 7.15, remaining constant across the whole hardness profile. The equivalent lath sizes are relatively stable also ranging in size from a maximum of 0.86 μm 0.1 mm from the oxide to a minimum of 0.71 μm 0.8 mm from the oxide. For the N1050 case the maximum occurs 1.4 mm from the oxide with a size of 1.13 μm to a minimum of 0.71 μm in the bulk material. The mean lath size for the five positions is 0.772 μm, with a standard deviation of ±0.06 μm, widths for all locations are close to this value. The hardness is mean value for the width of the region tested is 410 H_v ±12 H_v.
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Similar to the untempered case, the tempered N1050T780 material exhibits a dip in hardness adjacent to the oxide layer. The recovery of ductility which accompanies tempering does not completely remove the sub-oxide softening material behaviour. In the tempered case, the decreased hardness affects a narrower region less than 0.5 mm compared with the 1 mm for the untempered, case in Figure 7.14. Adjacent to the oxide, a hardness of 202 H\text{v} is detected with a maximum in the bulk of 235 H\text{v}, while in the untempered case the minimum is 371 H\text{v} with a maximum of 411 H\text{v}. Tempering has reduced the dispersion of hardness by 7 H\text{v}, indicating the material hardness becomes slightly more uniform as a result of tempering. However, given the error bars this effect is probably negligible. The inherent softening of the N1050 region adjacent to the oxide layer is reduced by tempering.

Figure 7.14: Hardness and equivalent lath size from Lehto et al. [238, 239] plotted against distance from the oxide-base material interface N1050 sample.

Figure 7.15: Hardness and equivalent lath size from Lehto et al. approach [238, 239] plotted against distance from the oxide-base material interface N1200 sample.
7.4 - Results

Figure 7.16: Hardness and equivalent lath size results for the N1050T780 sample, similar to the results of Figure 7.14.

No obvious softening is observed in the hardness mapping of the N1200T780 sample and the trend is the same as observed for the normalised only sample. The same cannot be said of the equivalent lath size as this is largely due to the charge affected image 0.93 mm from the oxide. Ignoring this point as an outlier gives a range in lath sizes of 1.29 to 1.6 µm, which is larger than for the untempered case but below the range for the N1050 sample. This is also in line with observations of Morito et al. [246,247].

Figure 7.17: Hardness and equivalent lath size results for the N1200T780, hardness trend similar to Figure 7.15.

Linear intercept based equivalent lath sizes have been reported in the preceding figures. The point intercept volume weighted size measures are included in Table 7.3 below, utilising the linear-intercept based values and Equation 7.4. The contribution to yield stress is calculated for these materials, as per the recommendations of Lehto
et al. [239]. Barrett et al. [32] identified a value of 39 MPa for the contribution to yield stress from the low angle boundaries in a MarBN material. Utilising Equation 7.4 here, lath contribution to yield stress values are obtained based on the lath equivalent size measures from both point sampling and linear intercept methods. When equivalent lath size measures from the linear-intercept method are utilised to calculate $\tau_{LAB}$ the resulting values are, on average, 54% larger than those calculated using the point sampled results. Linear intercept based results significantly overestimate the contribution of laths to the yield stress, when compared against the work of Barrett et al. [32] as an initial estimate. This reinforces the observations of Lehto et al. [239] and Gunderson et al. [243], stating that the line intercept based measurements are not ideal for the estimation of macro-scale properties. The results from the point sampled methodology are more appropriate for this type of analysis.
Table 7.3: Volume weighted lath sizes, dispersions, threshold limits applied and the contribution to yield stress for normalised only and normalised and tempered samples, with distance from the oxide.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Distance from oxide (mm)</th>
<th>Volume weighted lath size (µm)</th>
<th>Size dispersion (linear)</th>
<th>Threshold limit</th>
<th>( \tau_{\text{LAB}} ) (MPa)</th>
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<tr>
<td>N1050</td>
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<td>1.43</td>
<td>2.80</td>
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<td>31.28</td>
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<td></td>
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<td>1.75</td>
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<td>70</td>
<td>25.56</td>
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<tr>
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<td>0.80</td>
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<td></td>
<td>1.40</td>
<td>1.71</td>
<td>3.09</td>
<td>70</td>
<td>26.16</td>
</tr>
<tr>
<td></td>
<td>2.35</td>
<td>1.09</td>
<td>3.24</td>
<td>70</td>
<td>41.04</td>
</tr>
<tr>
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<td>3.46</td>
<td>70</td>
<td>32.89</td>
</tr>
<tr>
<td></td>
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<td>1.04</td>
<td>3.10</td>
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<td>43.01</td>
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<tr>
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<td>3.28</td>
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<td>3.63</td>
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<td>3.44</td>
<td>70</td>
<td>32.18</td>
</tr>
<tr>
<td>N1200T750</td>
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<td>2.95</td>
<td>90</td>
<td>27.11</td>
</tr>
<tr>
<td></td>
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<td>3.78</td>
<td>60</td>
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<td>1.66</td>
<td>3.29</td>
<td>90</td>
<td>26.95</td>
</tr>
</tbody>
</table>

7.4.3 Micro-cantilever bending

Figure 7.18 presents the force-displacement curves obtained during the micro-cantilever tests of samples normalised at temperatures of 1050 °C and 1200 °C at different locations across the samples. The 1050°C 0.05 mm sample was the initial specimen

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tested and, as this had a shorter length, this generated a force in excess of the maximum allowable load in the force sensor. As a result the cross sections of future test specimens were reduced to avoid this issue. Table 7.2 contains the dimensions of each micro-cantilever tested.

![Figure 7.18: Comparing a) 1050°C and b) 1200°C micro-cantilever force-displacement curves. Note the N1050 0.05 mm beam dimensions are greater than the other tested beams.](image)

The outputs from the data extraction procedure and conversion to stress-strain response (as outlined in Section 7.3.4), are shown in Figure 7.19. Only the elastic portion of the curves are shown. Under both normalisation temperatures, an increased Young’s Modulus is calculated within the cantilever extracted 0.05 mm from the oxide-base material interface. Normalisation at both temperatures also shows a trend of decreasing slope or Young’s Modulus with increasing distance from the oxide interface.

The decrease in Young’s Modulus and yield stress with increasing distance from the oxide layer is presented in Figures 7.20 and 7.21 respectively. It can be seen for all cases, the Young’s modulus and yield stress follow the same decreasing trend with increasing distance from the oxide-base material interface. Furthermore the bulk material behaviour has not been significantly altered by increasing the heat treatment temperature. Figure 7.22 compares the micro-cantilever and hardness approaches to estimating yield stress for the two untempered materials. Both approaches show values in reasonable agreement with each other, however the micro-cantilever results show more variation with increasing distance from the oxide.
7.4 - Results

Figure 7.19: Extracted stress-strain curves from the micro-cantilever testing showing a) the 1050 °C and b) 1200 °C cases.

Figure 7.20: Change in Young’s Modulus with increasing distance from the oxide layer, from micro-cantilever testing performed at room temperature.

Figure 7.21: Decreasing yield stress observed with increasing distance from the oxide for samples normalised at 1050 °C and 1200 °C.
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Figure 7.22: Comparison of the yield stresses calculated utilising the micro-cantilever beam and hardness data (Busby et al. [137]) for the samples normalised at a) 1050 °C and b) 1200 °C.

7.5 Discussion

7.5.1 Hardness and lath size

Based on the observed orientation maps of the tempered and untempered materials, there is no obvious texture to the microstructure of the material in any crystallographic orientation. Generally, nearer to the oxide region the material contains higher concentrations of equi-axed sub-grains in place of martensitic laths. For the untempered material, this is explained by the lack of precipitates present in the micro-structure. As discussed in earlier chapters, precipitates, particularly of the M$_{23}$C$_{6}$ type, provide a pinning force on martensitic laths and stabilise the microstructure during high temperature exposure. However, during normalisation all precipitates are dissolved into solution leaving only solutes and interstitial atoms to strengthen the material. A loss of carbon to the oxide during the oxidation process will reduce the lattice distortion caused due to martensite transformation (see section 2.4.1). Reduced carbon content could have an affect on the amount of lath martensite formed and hence an affect on the material strength. Coupled with this is the affect on dislocation density, which decreases with decreasing carbon content, as observed in α-iron carbon alloys [32, 246]. Decreases in hardness after normalisation at 1050°C could potentially be a result of the migration of carbon from the bulk material into the oxide layer, but is more likely to be the lath size effect which is linked to the carbon concentration.

The decrease in hardness at the 1050 °C normalisation temperature is of concern due
to the thickness of the section affected and also the degree of softening which occurs. Thin super-heater tubes manufactured from MarBN are a particular industrial use case of concern here, on the order of 6 mm thick. If the oxide affected material region generated by heat treatment at 1050 °C is of decreased or unusual quality, this will significantly increase the cost inherent in employing this material in future plant or for upgrading existing plant.

A decrease in hardness has been detected through the cross weld region for P91 measured at increasing distance from the fusion line is reported by Ab el Azim et al. [174]. The maximum hardness in the weld was 235 Hv and the softest in the FG-HAZ of 200 Hv, where failure is reported to have occurred during creep testing. Hongo et al. [182] report a similar trend of minimum hardness of 210 Hv in the FG-HAZ/IC-HAZ regions to a value of 240 Hv in the tempered region. They also report failure occurring within this region of minimum hardness during creep exposure. Obviously, the stress regimes within welded P91 component will differ considerably with those in a plain MarBN component. However, should the component in question consist of sub-par material on the exterior and interior of the tube or pipe specimen, early failures could occur if the softer material is not removed from the component before service.

The thinner the component pipe, then greater an affect sub-par material will have on the behaviour of the pipe. Considering a thick walled pipe, as modelled in Chapter 4, (wall thickness of 33.8 mm and a $D_{OP}$ of 143.8 mm) and, assuming the softened MarBN is considered non-load bearing material, the loss in functional pipe area is approximately 5 % of the cross section. For a thin pipe, say on the order of the P91 tube whose material was tested in Chapter 6, with an outer diameter of 32 mm and a thickness of 5 mm, the loss of 1 mm of material on the internal and external faces equates to 40 % of the pipe cross sectional area being lost.

The lath measurement methodology presented here depends on a number of factors, the first being the quality of the EBSD maps produced. Charging of the sample occurs due to exposure to the electron beam over time, utilising lower energy electron beams may reduce the effect. However, in order to identify low angle boundaries higher energy beams are required with small binning applied. Smaller binning causes order of magnitude increases in the scan time for EBSD mapping, novel detectors recently released by Oxford Instruments utilising higher fidelity detectors can significantly speed up these types of scans in the future.

Based on the majority of maps being of good quality, the selection of the boundary
grey intensity level is the next factor which directly affects lath size measures. The boundary grey intensity level will greatly influence the number of boundaries detected for a given map, as highlighted in Figure 7.6a and in the lath size dispersion detected in Figure 7.7. Increasing the grey intensity for the application of a threshold limit to generate the boundary maps controls the influence of smaller laths. If the material in question was rather homogeneous in respect to microstructure feature size, then this would be a moot point. Although, for martensitic lath containing materials, the lath sizes will always follow some version of a log-normal distribution. Manual selection of grey intensity level is still required for the use of the automated linear intercept method or the volume weighted point sampled method. It should be noted that prior to the automated method presented by Lehto et al. [239] this type of analysis was performed by hand and extremely labour and time intensive.

7.5.2 Micro-cantilever bending

The response of the micro-cantilever beam testing demonstrates the classical ductile material type curve expected in a macro scale test. There are initial linear elastic regions until the critical force for yielding is obtained, followed by a slowly increasing force requirement to cause significant plastic deformation. The exception to this behaviour is the 2.35 mm material normalised at 1200°C, where a nearly perfectly plastic type behaviour is observed post yielding.

Figure 7.20 shows a consistent value of 130 GPa approx. for the Young’s modulus with the exception of the N1050 0.05 mm beam, from the micro-cantilever tests. This beam has a reduced length and increased cross-sectional area, meaning additional prior austenite grains may have been present to resist the applied load. Armstrong et al. [142] characterised the relationship between crystal orientation and modulus using micro-cantilever tests of single orientation containing beams. Their measured modulus values ranged from 60 GPa to 180 GPa for copper with a macro scale modulus of 117 GPa [142]. As such the lower value of modulus observed in these tests may be a result of the particular orientations present in the region of the beam which was most highly stressed. EBSD examinations of these locations pre and post test are recommend for any future testing to examine this potential effect.

Figure 7.21 presents a trend of decreasing yield stress with increasing distance from the oxide layer, evidently the material in all cases near the oxide layer has been considerably altered during the normalisation process for the two temperatures. While softening is observed in the near oxide material in the N1050 sample from the inden-
tation test results, the cantilever tests show a stiffer material at this location.

The yield stresses were calculated from the hardness test results, using Equation 2.17 and compared against those calculated from the micro-cantilever data, shown in Figure 7.22. Converted hardness data are denoted as Busby in this plot, in line with the approach of Hosemann et al. [248]. In their work Hosemann et al. compare micro-compression testing, with the Busby approach and the Dao model approach, for both irradiated and un-irradiated ferritic materials. The differences between these two testing methodologies may provide some insight into the microstructural mechanics at governing the behaviour of the materials.

7.5.3 Hardness and micro-cantilever test comparison

In terms of loading conditions, indentation testing produces a fully compressive stress field in the region surrounding the indentation, whereas the micro-cantilever produces localised tension and compression at the root of the beam. The addition of tensile forces in the micro-cantilever test could have removed the effect of the softened region. A softer region during indentation testing is indicative of a lower resistance to dislocation movement.

The other consideration is the quantity of material tested. The micro-cantilevers provide a considerably smaller amount of material to be tested, on the order of 600 $\mu$m$^3$, compared with the hardness testing where by large hemisphere of material surrounding the indentation is effected by the testing. The Vickers hardness test can generate two distinct indentation types in non ceramic materials, as defined by Zhang et al. [131] who analysed the relationship between hardness testing and strength for wide variety of materials.

Applying this information to the yield stress comparison plot in Figure 7.22, the close agreement for the 1200°C near the oxide layer, can be explained by this material exhibiting the pile-up type behaviour. Meanwhile the 1050°C sample near the oxide layer demonstrates the sink-in behaviour, causing the greater disagreement between the yield stress from the micro-cantilever and the hardness-Busby approach.

7.6 Conclusions

The novel 9Cr based power plant material MarBN has been heat treated in accordance with ASTM standards at 1050 °C and at 1200 °C, based on previous experi-
ence in the literature, to optimise precipitate formation for creep resistance. Detailed hardness mapping is performed with increasing distance from the oxide-base material interface to quantify hardness changes in the region adjacent to the oxide scale. SEM based microstructural investigations were performed to measure equivalent lath size in this region.

Hardness was seen to be lowered in the region adjacent to the oxide for the tempered and untempered samples normalised at 1050 °C, while showing little variation for the 1200 °C normalisation case. Lath sizes follow a clear inverse trend with hardness for the N1050 case and, to a lesser extent, the same is seen for the tempered N1050T780 case. The N1200 lath sizes remain relatively stable at or near 0.77 µm through the oxide affected and bulk material regions, showing no significant affect of lath size on the hardness behaviour. There is no significant variation in hardness for this material either and both measures can be considered constant. Similar hardness behaviour is observed for the N1200T780 sample, although the lath width results at 0.93 deviate from this trend. This deviation is attributed to a poor quality EBSD scan, rather than a very localised region of larger laths. The EBSD result of Figure 7.12b shows few fine laths in comparison with all other results and large boundaries were also detected unlike the other results.

The use of an automated system for lath size measurements requires the careful selection of limits for the conversion of band contrast images into black and white boundary containing images, i.e. thresholding. Incorrect selection of threshold limits will significantly alter the results of the automated grain size measurement tool. Utilising a linear intercept based measurement system allows comparison with other measured microstructural features in the literature. However, when calculating mechanical properties, this leads to overestimation. For this work the prediction of lath boundary contribution to the yield stress was over estimated by approximately 50 %, when utilising the linear intercept method compared to results of the point sampled method. To combat this effect, the use of a point sampled volume weighted lath size provided more accurate estimates of yield stress contribution, as it limits the effect of small laths on the equivalent lath size value. This is in line with previous reported work from the literature for estimating macro-scale properties from micro-scale measurements.

Initial exploratory work on the micro-cantilever testing of the oxide-affected and base MarBN materials was performed as part of this project, with the objective of identifying the softening mechanism operating of N1050 material and an explanation for its
absence at N1200. The initial results indicated that for both N1050 and N1200 samples the oxide affected zone materials were stiffer than the base material behaviour. The base material behaviour, 2.35 mm from the oxide interface, for N1050 and N1200 are quite similar. Micro-cantilever and hardness based measurements of yield stress are in reasonable agreement, indicating that the micro-cantilever beam tests capture the bulk materials response, with some variations between each test location. The Young’s modulus estimated values are lower than the macro scale response, potentially due to the small number of grains resisting the loading. Armstrong et al. [142] have demonstrated a dependence of micro-cantilever based Young’s modulus values on the specific crystal orientation of grains being tested. Additional repeat testing and analysis of these results is required to obtain more definitive conclusions, it remains a potential area rich for future studies.
Chapter 8

Conclusions and Recommendations

8.1 Summary

A novel physically-based creep model has been developed for multiple precipitate types, that incorporate thermal- and strain-induced coarsening parameters. This model successfully predicts the literature trends in both P91 parent and cross weld tensile creep tests. Increases in Al content reduces MX precipitate volume fraction, causing a significant reduction in the time-to-failure of such Al rich steels. The novel approach developed here demonstrates this ability to capture standard and non-standard P91 behaviour using a single parameter set combined with composition measurements.

Utilising weld metal, heat affected zone and parent material creep data from Bar 257 (increased Al version of P91), with microstructural measurements from similar welded 9Cr materials, the Bar 257 cross-weld behaviour was accurately predicted. Incorporating the appropriate P91 volume fraction data, in place of the Bar 257, allowed the prediction of standard P91 cross-weld time-to-failure, from laboratory test conditions to plant operational levels. The characteristic drop in creep life observed in P91 experimental data was emulated in the model results, in Figure 4.16. For plant managers the approach is shown to be conservative at plant operational stress levels.

Thick walled, plane and welded piping components were modelled for P91 and P92 materials. Tensile weld strength reduction factors from the model are conservative when compared with predictions from the thick walled pipes due to the large percentage of parent material present compared with the tensile specimens. The P92 weld strength reduction factors are higher than the P91 material for the thick walled piping components, due to the reduced precipitate coarsening rates of P92.
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The multi-axial implementation, is a robust approach for simulating complex loading conditions such as those occurring in welded components or during small punch creep testing.

A small punch creep test apparatus has been developed, generating results consistent with the tensile test time-to-failure data for P91 at 600 °C. The Chakrabarty conversion method was applied to converted the SPCT loads to membrane stresses in the disk samples. The SPCT system has demonstrated the same level of variability in repeat testing as observed from the tensile test data. A thermal ageing experiment was performed to age T91 material, (thin-walled tubing form of P91), at 600 °C for up to a year. Transmission electron microscopy combined with automated image analysis allowed the measurement of precipitate diameters at increasing ageing times. The thermally induced coarsening rate was identified as being in line with literature results. Cr, Mo and Fe elements all accumulate rapidly around the existing M23C6 precipitates, while Nb and V only diffuse towards the MX precipitates after six months to a year of ageing.

SPCT results of aged specimens demonstrate a significant reduction in creep life, un-aged specimens exhibited creep lives approximately three times longer than the 1 year aged specimens. Aged specimen fracture surfaces revealed little ductile fracture growth, indicating a more brittle and rapid propagation of failure through the specimen thickness. For plant operators greater levels of coarsening are expected than observed in this study due to strain and temperature effects. During operation at 600 °C strain enhanced coarsening will further embrittle a P91 component, due to increased precipitate diameters reducing the creep resistance and ductility of the material.

The SPCT has been simulated utilising a finite element approach which is independent from time increment and mesh density effects. The physical creep model captures the trend of minimum displacement rate which aligns with the experimental results, however it requires further development to operate successfully at higher stress ranges. The inclusion of some precipitate softening proportional to the aged precipitate diameters ensures greater alignment of the simulation results with the experimental results.

Normalisation of MarBN at 1200 °C generates a homogeneous microstructure from the oxide-metal interface to the bulk material, with a lath width of approximately 0.77 µm throughout. Smaller laths formed at 1200 °C which resulted in a greater contribution to yield stress than the 1050 °C samples. The initial yield stress micro-
cantilever test results indicate that the bulk materials in both cases are similar. For component manufacturers, utilising a standard 1050 °C normalisation on MarBN, will result in reduced creep performance and increased cost, as the softened region must be removed with the oxide after heat treatment.

8.2 Discussion

The constant volume fraction approach employed for the development of the novel multi-precipitate model is in line with literature observations of long-term creep behaviour. The results show good agreement with long-term data up to 100,000 hours, the design case for power plant materials. To capture the behaviour of current and next generation materials (MarBN), additional precipitates can be included within the framework developed here. For example, Laves phase and Z-phase precipitates form at the expense of Mo, W solutes and MX precipitates, respectively, in 9Cr materials. As the precipitate volume fractions are interdependent, they require the use of evolving volume fractions. One such time-dependent volume fraction formulation was suggested by Spigarelli et al. [186]. A four precipitate state variable is derived in Appendix B utilising this formulation, and can easily be implemented in the CDM approach developed in Chapter 3. The parameters of interest for this approach are the times required to precipitate 50% of the maximum precipitate volume fraction \( t_{50,i} \). These can be estimated using thermodynamic simulation software and the four precipitate model can be evaluated with these values.

The primary creep model, \( \dot{H} \), is effective for predicting both PM and CW behaviour across laboratory and plant stress ranges, as part of this research and so also in work of Dyson et al. [102], Perrin et al. [191] and Hyde et al. [103]. This model is an empirical fit to control the rate of creep strain accumulation during the initial phase of creep loading. The combined reaction of the various creep strengthening mechanisms to the initial loading during a creep test cause the primary creep decelerating strain rate behaviour. The material then creeps at a steady rate due to continual microstructural evolution. Eventually the material’s strengthening mechanisms are exhausted from these evolutionary mechanisms which leads to the onset of enhanced cavitation and final failure. The inclusion of additional strengthening mechanisms which resist high stress deformation would be particularly useful for modelling high load applications such as the SPC experiments, where plasticity is important during the initial indenter application.
Accurate precipitate creep modelling provided insight into the effects of material composition variations. The modelling of these compositional dependencies has been enhanced by the developments of this project. The inclusion of the separate MX precipitate coarsening parameters allowed the extrapolation of standard P91 cross-weld performance from Bar 257 test data. The primary difference in the two materials is the increased Al content in Bar 257. The reduction in volume fraction of MX precipitates, due to increased Al content, was applied to the model in line with literature observations. This allowed the standard P91 constants to predict the Bar 257 behaviour by applying a composition based alteration to the model, which accurately captured the effect of Al on creep life in P91.

The input data for the microstructural measures (precipitate diameters, volume fractions, dislocation densities, packet and lath sizes) were collected from multiple sources with slightly different P91 material variations. The argument being that an average value for a given microstructural feature, from a wide range of P91 source materials, will represent the most realistic measurement for this material. The resulting model is expected to produce the nominal response to a given stress and temperature input. For intermediate stress levels, the model curve passes through the centre of the P91 PM scatter in Figure 4.16. A large portion of data points utilised to fit the secondary creep constant $\dot{\varepsilon}_0$ are at this intermediate level, see Figure 3.3. The model predicts low to intermediate effects well (see Figure 4.16), while slightly over predicting the time to failure at high stresses. In this stress regime, creep behaviour is governed by dislocation dominated mechanics, i.e. the lath width and dislocation density evolutions under high stress, which will be considered in future work.

The FE results for cross weld tensile specimens showed the highest precipitate coarsening and cavitation damage occurring within the HAZ region. This is attributed to the strain-induced coarsening term which accelerated the growth of $M_{23}C_6$ precipitates in particular for this region. Maximum cavitation damage occurred in this region as a result of the coarsened precipitates and high stress triaxiality due to the material creep strain mismatch. These factors contribute directly to the Type IV failure observed in literature experiments [53]. At the low stress, plant operational range, the model is slightly conservative which is more appealing to operators. Conservatism in modelling is always preferable to over estimation, as it provides additional factors of safety for design.

Combined microstructural data from the IC-HAZ and FG-HAZ regions, for the nu-
merically modelled HAZ material, was utilised as complete data sets for both are not available in the literature. This approach was effective as the model cross-weld tensile results show. Ideally a study to measure the dislocation densities, precipitates, laths and packet sizes in each area of a weld would be performed. The resulting measures would remove some of the scatter which was introduced by including data from multiple sources.

The difference in WSRFs between the P91 tensile and thick walled results is attributed to the ratio of materials present in the two simulations. The majority of a thick walled pipe is parent material with a small amount of HAZ and weld material, so as such, the WSRF are close to unity for a thick wall welded component. This is in part borne out by experimental testing of welding using electron beam (EB) welding, whereby a narrow welded region is formed with single pass welding. Rothwell et al. [37] observed significantly improved cross-weld creep performance from the narrow EB welding process, compared with the traditional arc welding process. From these, it can be concluded that narrower welds are preferable. Smaller HAZ regions reduce the volume of damaged material, meaning less coarsened precipitates and unpinned boundaries in partially recrystallised material. Similarly, the delta ferrite issue was not observed in the EB welded specimens tested by Lawler et al. [249].

The prediction of P92 behaviour presented is based on the precipitate coarsening behaviour available for this material in the literature.

During SPCT modelling, high stresses due to plastic disk bending occur once the load is applied and on completion of the loading phase these high stresses are passed to the creep model. Numerically, this issue was minimised by limiting the maximum stress occurring during the indenter loading of the sample. A perfectly-plastic material model limited the maximum stress at the beginning of the creep step. This numerical control allowed the multi-precipitate type creep model to be utilised successfully, predicting failure concentrations at similar locations to those observed in experiments. No additional terms were added to the multi-precipitate type model and the same material parameters for the tensile materials were applied to capture the SPC behaviour. The approach of Yadav et al. [250] may be of use here which includes the effects of an internal stress mechanism utilised to reduce the effective stress causing creep. In their work, an internal viscous stress is calculated based on contributions from mobile dislocations and dipoles. The evolutions of both parameters were modelled also. This model was then combined with a precipitate coarsening term and a cavitation damage term using a CDM approach similar to this work.
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This formulation may provide a more realistic estimation of the remaining stress activating precipitate dominated creep during the small punch testing.

As precipitates coarsen, the growth in diameter decreases at longer ageing times, as the precipitates become more thermodynamically stable. The multi-precipitate state variable is proportional to the change in precipitate diameter over time, larger initial diameters will result in lower values of the precipitate state variable. This is the effect observed when comparing the modelled SPC results for un-aged and aged P91 materials. The aged materials are predicted to exhibit larger times to failure, when compared to the un-aged materials, in Figure 6.29. An initial thermal ageing precipitate softening value was calculated based on a modified state variable term and utilised as an initial value for the precipitate state variable. A 26.5 kg simulation was performed which showed the aged material, with initial softening, exhibited a time to failure similar to that of the un-aged material. The SPC simulation, with initial precipitate softening, is a more accurate simulation of the aged material than the material with only coarsened initial diameters. The predicted effect of thermal ageing on lath width and dislocation density could be included in future simulations. For example, Panait et al. [96] observed a 50% reduction in dislocation density within sub-grains after 100,000 hours thermal ageing.

The thermally aged P91 suffers from significantly degraded creep performance. This can be attributed to coarsened (larger) precipitates, with the resulting increase in spacing decreasing the obstacle stress in the matrix. Some sub-grain recovery may have occurred, based on observations reported in the literature, although this was not confirmed in this work. The fracture surfaces of the aged materials showed little evidence of ductile fracture growth, no fractures parallel to the loading direction were observed, rather, the entire thickness of the specimen seems to have failed at once.

The reduction in creep rupture life due to thermal ageing is not proportional to loads applied in the small punch creep tests. At lower loads the creep behaviour is dominated by precipitate controlled mechanisms; mainly diffusion processes. For the higher stress, shorter term, creep testing, the behaviour is dominated by plasticity effects such as dislocation and sub-grain hardening. For plant operators, the onset of brittle type failure after a year of ageing at 600 °C is a cause for concern. In a component, the combined effects of temperature and strain will coarsen the precipitates more so than reported here from thermal ageing alone. This could cause unexpected fractures. The operational loads are far lower than the stresses imparted
in the SPCT condition, as such, lower stress tests are required to examine the failure behaviour at load levels closer to the operational regime. Brittle type failures caused by higher temperature operation could be prevented by the use of novel, more creep resistant, materials.

If the SPCT approach is to gain wider adoption, a database of small punch creep test results for materials should be developed. This would allow trends to be identified between the SPC database and the vast amount of tensile data previously developed for materials such as 9Cr and stainless steels. The evolution of the microstructure under creep conditions, regardless of the method employed, is essential to understanding where and how these materials will fail in future. The behaviour of MarBN material should be investigated with SPCT testing to compare with P91 material. SPCT provides a method of characterising the material without requiring large quantities to be made available.

MarBN developed a softened region during normalisation at 1050 °C, concluded to be due to an increase in the lath size. No softening occurs at 1200 °C normalisation. The softening mechanism does not activate during the oxide formation after the 1200°C heat treatment. Factors effecting lath size are dislocation density, C content and prior austenite grain size. After normalisation, no precipitates are present as they dissolve into the matrix at these temperatures and hence, excess C is available for martensitic transformation. Potentially, due to decarburisation there may exist a region with depleted C and hence decreasing C content causes a decrease in dislocation density and a slight increase in lath width [32,246]. Furthermore, lower dislocation density provides the potential for more plasticity to occur, as there are fewer barriers to dislocation motion, resulting in lower hardness readings. The lack of softening occurring at the higher temperature indicates that the mechanism at play is not directly coupled with normalisation temperature.

A series of preliminary micro-cantilever tests were performed during this project. The initial results indicate that the bulk of materials normalised at 1050 °C and 1200 °C have very similar behaviours, this is in line with the lath width measures in Figures 7.14 and 7.15. The yield stress values are in line with those based on the micro-hardness testing results. However the Young’s modulus is under predicted at approximately 130 GPa, considerably lower than that of the macro modulus at 210 MPa. This is potentially due to the orientation of the specific grains resisting the load at the root of the cantilevers, this effect has been identified in the literature for copper by Armstrong et al. [142]. Further research is needed on the behaviour
of poly-crystalline micro-cantilevers to characterise the mechanisms at play during this test method. Micro-cantilever based testing is appealing for the same reason as small punch creep tests, they require minimal material samples. They have the added benefit of allowing the testing of singular microstructural features e.g. low or high angle boundaries and as such deserve more attention in future work.

8.3 Key Conclusions

- The novel physically-based creep damage model, including MX and M$_{23}$C$_6$ thermally- and strain-induced precipitate coarsening, successfully predicts effects of chemical composition on life.
- This model accurately predicts the detrimental effects of welding on creep life, via MX and M$_{23}$C$_6$ precipitate coarsening, for a wide range of applied loads.
- Thermal ageing at 600 °C significantly reduces the creep life of T91 due to the presence of coarsened precipitates with diminished creep strain resistance.
- The small punch creep test results, when combined with the Chakrabarty membrane stress equation, show no additional scatter above that observed in the tensile creep results of P91.
- MarBN material normalised at 1200 °C is harder and shows more uniform properties through the sample thickness than those normalised at 1050 °C.
- For power plants aiming to operate reliably in the ultra-super critical range, more stringent control of material composition is required for 9Cr materials. Minor alterations to precipitate composition can dramatically reduce the creep life of components due to the loss of precipitate strengthening over time.
- Failure prediction models must incorporate the majority of microstructural evolution mechanisms, if they are to be effective for this family of precipitate strengthened materials.

8.4 Recommendations for future work

The multiple precipitate type creep model should be expanded to include the effects of viscous stress, and an evolution mechanism for the same, which is proportional to the applied stress. This viscous athermal stress term should account for the intrinsic creep resistance of the matrix material, independent of precipitates. The evolution of
which is strain dependent, accounting for the recovery of sub-grains and dislocation behaviour which contribute to primary creep behaviour. This stress term should be implemented in the model by subtracting it from the equivalent stress term, reducing the stress which activates the other strengthening mechanisms. This novel model would also benefit from a physical dislocation based description of primary creep evolution to improve the high stress performance of the model. A version of the primary creep model of Yadav et al. [250] could be an interesting starting point for this work. Another avenue for consideration is the inclusion of time-dependent precipitate volume fractions, coupled with a three or four precipitate state variable. Initially, an approximation of the volume fraction behaviour could be utilised to expand the precipitate state variable followed by a more complex approach similar to the solution of Spigarelli [186]. A four precipitate state variable term with evolving volume fractions, has been derived and is presented in Appendix B.

The feasibility of measuring two precipitate type diameters, based on the grey intensity levels of each in the TEM images of Figures 6.5 to 6.11, should also be investigated. As mentioned previously, developing the relationship between grey intensity and identified composition is the first step in constructing this tool. Based on this, the threshold settings for identifying only one set of precipitates in an image would be selected and applied. The previously developed code for precipitate size measurement (available in Appendix E) can then be applied and the process repeated for the second or subsequent precipitate families. An averaged precipitate coarsening rate was identified from the thermal ageing results.

As MX precipitates do not coarsen significantly, the $M_23C_6$ precipitate coarsening rate could be identified from the measured, average coarsening rate in Table 6.2 assuming MX precipitate coarsening did not occur. These two coarsening rates should be inserted in the creep subroutine and the simulations performed to examine if any significant change in rupture time or MDR occurs.

SPCT FE analysis should be performed accounting for the prior thermal history of the material. This has proven effective at reducing the overestimation of time to failure for the 26.5 kg simulation of 1 year aged material, as shown in Figure 6.33. Precipitate state variable predictions, for aged materials with initial softening are close to those for un-aged materials. Modifications to the dislocation density and lath width parameters in line with literature observations, from thermal ageing, should also be investigated. The current subroutine should be updated with an input parameter for values of pre-creep ageing $D_P$. These parameters also influence the
obstacle back-stress term which adjusts the creep strain-rate. Following on from
this, the updated creep model with a physical description of primary creep should
be implemented in the subroutine and applied to the SPCT simulations.

Further fractography should be performed on all failed SPC test samples to examine
additional trends in fracture surface features. Following this, the samples should
be sectioned and mounted to examine the cross section of failed samples. The cross
section mounted samples can then be examined for the presence of cavitation damage
and potentially region specific carbon replicas could be produced in the vicinity of
the fractured surfaces. The previously developed precipitate measurement system
would then be applied similarly for the TEM images from the fractured region. The
limitation with this approach is that the fracture surface is no longer available for
examination once the sample is either sectioned or polished to the mid thickness of
the sample. No further fracture surface imagery is possible after this point. The FE
predictions of particle size could then be compared with the experimental results.
However, the potential for more rapid carbide coarsening and subsequent additional
potential sites for cavitation needs to be investigated to enhance the understanding
of the key role of carbide coarsening on creep failure.

There are also some modifications and enhancements to the SPCT that can be consid-
ered. The apparatus should have the sample holder assembly replaced with a system
that more closely resembles that described by the CEN standard [114]. Specifically,
the depth of the receiving hole in the lower die should be reduced to provide a more
precise method of loading and unloading the samples, reducing the risk of imparting
non-creep damage to the samples. The inclusion of a second displacement sensor
beneath the sample would enable sample thinning to be measured during the test.
A new die arrangement would allow a thermocouple to be placed in contact with the
specimen, allowing direct measurement of sample temperature to be performed. As
the new displacement sensor is mounted inside the lower die rod, a high temperature
displacement sensor will be required for this location.

Lower load SPCT experiments should be performed with repeat testing, beginning
with a third 35 kg experiment for un-aged material. The experimental scatter is of
particular interest at all load levels, as it has led to order of magnitude differences
in failure times for given load levels. The physical reason for this scatter should also
be investigated, to develop correlations between time-to-failure and microstructure.
A test regime for P91 and MarBN materials should be embarked upon to begin
the process of building a database of creep data coupled with measurements of the
physical features of interest. Measurements should be performed prior to, during and after testing, to categorise the evolution of these features. Precipitate sizes and volume fractions, dislocation densities, lath geometry, grain and packet sizes should all be measured for this test regime. It may be possible then to identify the trends in microstructural features which lead to the scatter in the creep data.

EDX analysis of the MarBN samples mounted in a carbon free medium would provide clarity on the issue of C concentration effecting the lath width and subsequent softening behaviour in the N1050 and N1050T780 samples. Coupled with this, an examination of the dislocation densities in each region may provide insight into the hardness results observed. Further micro-cantilever testing is required, particularly for the N1050 0.05 mm sample, as later tests utilised longer and narrower cantilevers to reduce the forces applied to the test apparatus. EBSD scanning of the cantilevers before and after future testing would provide more insight into the influence of boundaries on the test behaviour. FE based analysis of the micro-cantilever testing should be performed to identify the stresses which occurred within the beams. EBSD scans of the tested cantilevers should also be performed, to assess the effect of plastic deformation on the lath structure during bending. Further examinations of C concentration within the softened regions should be performed as a next step to examine the possibility of decarburisation as a damage source. For MarBN components normalised at 1050 °C, the additional affected material should be removed from components. This additional process will increase manufacturing costs, but it is necessary to remove this potential failure initiation location, if normalisation at 1050 °C is performed.
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Appendices
Appendix A

Periodic table of elements
Figure A.1: Periodic table of elements
Appendix B

Four precipitate damage with evolving volume fraction

Multi-precipitate state variable:

\[ D_P = 1 - \frac{\lambda_0}{\lambda} \]  \hspace{1cm} (B.1)

\( \lambda \) being average precipitate spacing for all precipitates and \( \lambda_0 \) is the initial average precipitate spacing. Precipitate spacing defined as:

\[ \frac{1}{\lambda^2} = \frac{1}{\lambda_M^2} + \frac{1}{\lambda_C^2} + \frac{1}{\lambda_L^2} + \frac{1}{\lambda_Z^2} \]  \hspace{1cm} (B.2)

Each subscript represents the precipitates present in the material at any given time, MX (M), M23C6 (C), Laves phase (L) and Z-phase (Z). Individual precipitate spacing is described as in Chapter 3:

\[ \lambda_n = d_n \left[ \left( \frac{\pi}{6f_n} \right)^{1/3} - 1 \right] \]  \hspace{1cm} (B.3)

\( d_n \) is the precipitate diameter at any time, where \( n \) represents any of the four precipitates present. The initial spacing is given by:

\[ \lambda_{n,0} = d_{n,0} \left[ \left( \frac{\pi}{6f_{n,0}} \right)^{1/3} - 1 \right] \]  \hspace{1cm} (B.4)

A useful constant utilised for the two precipitate type derivation is now time dependent with the inclusion of volume fraction evolution:

\[ B_n = \left( \frac{\lambda_n}{d_n} \right)^2 \]  \hspace{1cm} (B.5)
Chapter B - Four precipitate damage with evolving volume fraction

And the initial value for any precipitate is:

\[ B_{n,0} = \left( \frac{\lambda_{n,0}}{d_{n,0}} \right)^2 \]  \hspace{1cm} (B.6)

The average spacing then becomes:

\[ \frac{1}{\lambda^2} = \frac{\lambda_C^2 \lambda_L^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2}{\lambda_M^2 \lambda_C^2 \lambda_L^2 \lambda_Z^2} \]  \hspace{1cm} (B.7)

Rearranging to bring the average spacing at any time to the numerator of the left hand side:

\[ \lambda = \left( \frac{\lambda_M^2 \lambda_C^2 \lambda_L^2 \lambda_Z^2}{\lambda_C^2 \lambda_L^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2 + \lambda_M^2 \lambda_C^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2} \right)^{1/2} \]  \hspace{1cm} (B.8)

The initial value of spacing is:

\[ \lambda_0 = \left( \frac{\lambda_M^2 \lambda_C^2 \lambda_L^2 \lambda_Z^2}{\lambda_C^2 \lambda_L^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2 + \lambda_M^2 \lambda_C^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2} \right)^{1/2} \]  \hspace{1cm} (B.9)

Utilising the definition of the damage term and substituting Equations B.8 and B.9 in:

\[ \left( \frac{\lambda_0}{\lambda} \right)^2 = \left( \frac{\lambda_M^2 \lambda_C^2 \lambda_L^2 \lambda_Z^2}{\lambda_C^2 \lambda_L^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2 + \lambda_M^2 \lambda_C^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2} \right) \]  \hspace{1cm} (B.10)

The top line of this equation is a constant, being simply the initial spacing terms. Inverting the bottom line and multiplying gives:

\[ \left( \frac{\lambda_0}{\lambda} \right)^2 = \frac{(\lambda_M^2 \lambda_C^2 \lambda_L^2 \lambda_Z^2)(\lambda_M^2 \lambda_C^2 \lambda_L^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2 + \lambda_M^2 \lambda_C^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2)}{(\lambda_M^2 \lambda_C^2 \lambda_L^2 \lambda_Z^2)(\lambda_M^2 \lambda_C^2 \lambda_L^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2 + \lambda_M^2 \lambda_C^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2)} \]  \hspace{1cm} (B.11)

Expanding the numerator and simplifying allows many terms to cancel out and the result is as follows:

\[ \left( \frac{\lambda_0}{\lambda} \right)^2 = \frac{\lambda_M^2 \lambda_C^2 \lambda_L^2 \lambda_Z^2}{(\lambda_M^2 \lambda_C^2 \lambda_L^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2 + \lambda_M^2 \lambda_C^2 \lambda_Z^2 + \lambda_M^2 \lambda_C^2 \lambda_L^2)} \]  \hspace{1cm} (B.12)
Re-organising Equation B.1 and substituting into Equation B.12 results in the following term with the constant initial spacing terms replaced with $C_1$:

$$(1 - D_P)^2 = C_1 \left[ \frac{1}{\lambda_M^2} + \frac{1}{\lambda_C^2} + \frac{1}{\lambda_L^2} + \frac{1}{\lambda_Z^2} \right]$$ \hfill (B.13)

Differentiating with respect to time to derive the accumulation rate term generates:

$$\frac{dD_P}{dt} = \frac{C_1}{-2(1 - D_P)} \left[ \frac{d}{dt} \left( \frac{1}{\lambda_M^2} \right) + \frac{d}{dt} \left( \frac{1}{\lambda_C^2} \right) + \frac{d}{dt} \left( \frac{1}{\lambda_L^2} \right) + \frac{d}{dt} \left( \frac{1}{\lambda_Z^2} \right) \right]$$ \hfill (B.14)

The differentiation of the spacing term is described next generally in a similar manner to that in Chapter 3. Using Equation B.5

$$\frac{d}{dt} \left( \frac{1}{\lambda_n^2} \right) = \frac{d}{dt} \left( d_n^2 B_n \right)^{-1}$$ \hfill (B.15)

$$\frac{d}{dt} \left( d_n^2 B_n \right)^{-1} = -\frac{1}{(d_n^2 B_n)^2} \left[ \frac{d}{dt} (d_n^2 B_n) + d_n^2 \frac{d}{dt} (B_n) \right]$$ \hfill (B.16)

From Chapter 2 the rate of precipitate coarsening due to thermal and strain effects is:

$$\frac{d}{dt} (d_n^2) = \frac{2}{3d_n} \left( K_n + \phi_n \frac{d}{dt} (\varepsilon^{cr}) \right)$$ \hfill (B.17)

The $B_n$ term is time dependent due to the inclusion of the evolving volume fraction, using the chain rule the differentiation of this term w.r.t time is as follows:

$$\frac{d}{dt} B_n = \frac{d}{dt} \left[ \left( \frac{\pi}{6f_n} \right)^{1/3} - 1 \right]^2$$ \hfill (B.18)

$$\frac{d}{dt} B_n = 2 \left[ \left( \frac{\pi}{6f_n} \right)^{1/3} - 1 \right] \frac{d}{dt} \left[ \left( \frac{\pi}{6f_n} \right)^{1/3} - 1 \right]$$ \hfill (B.19)

$$\frac{d}{dt} \left[ \left( \frac{\pi}{6f_n} \right)^{1/3} - 1 \right] = \frac{1}{3} \left( \frac{\pi}{6f_n} \right)^{-2/3} \frac{d}{dt} \frac{1}{f_n}$$ \hfill (B.20)

Using the volume fraction evolution from Spigarelli [186] which are subtly different for the four precipitate types. Specifically the MX and $M_{23}C_6$ obey one volume fraction equation and the Laves and Z-phase particles obey a separate equation.
Chapter B - Four precipitate damage with evolving volume fraction

This derivation will begin with the MX and M$_{23}$C$_6$ equation which is defined as:

$$f_j = \frac{f_j^{\text{max}}}{[1 + (t/t_{50,j})^{r_j}]} \quad (B.21)$$

Where the subscript $j$ can represent either the MX or M$_{23}$C$_6$ precipitates for simplicity. $t_{50,j}$ is at time constant for the time when depletion of this precipitate begins to occur, $f_j^{\text{max}}$ is the maximum volume fraction for a given precipitate type and $r_j$ is a rate controlling parameter which is precipitate dependent. As Laves phase increases in volume fraction it will deplete the M$_{23}$C$_6$, likewise for the Z-phase to MX ratio. The consequence of this is that the same $r_j$ value is used for Laves and M$_{23}$C$_6$ while the same value is also used for the MX and Z-phase precipitates. The differentiation of this term w.r.t time following on from Equation B.20:

$$\frac{d}{dt} \left( \frac{1}{f_n} \right) = -\frac{1}{f_n^2} \frac{df_n}{dt} \left( \frac{f_n^{\text{max}}}{[1 + (t/t_{50,n})^{r_n}]} \right) \quad (B.22)$$

$$\frac{d}{dt} \left( \frac{1}{f_n} \right) = -\frac{f_n^{\text{max}}}{[1 + (t/t_{50,n})^{r_n}]} \frac{df_n}{dt} \left( \frac{1}{1 + (t/t_{50,n})^{r_n}} \right) \quad (B.23)$$

$$\frac{d}{dt} \left[ 1 + \left( \frac{t}{t_{50,n}} \right)^{r_n} \right] = \frac{r_n}{t_{50,n}} \left( \frac{t}{t_{50,n}} \right)^{r_n-1} \quad (B.24)$$

Substituting Equations B.23 and B.24 into Equation B.22 gives:

$$\frac{d}{dt} \left( \frac{1}{f_n} \right) = -\frac{1}{f_n^2} \frac{f_n^{\text{max}}}{[1 + (t/t_{50,n})^{r_n}]} \frac{r_n}{t_{50,n}} \left( \frac{t}{t_{50,n}} \right)^{r_n-1} \quad (B.25)$$

Which can be simplified by rearranging the volume fraction equation and isolating the $t$ term on the left as so:

$$t = t_{50,n} \left( \frac{f_n^{\text{max}}}{f_n} - 1 \right)^{1/r_n} \quad (B.26)$$

Combining this with Equation B.25:

$$\frac{d}{dt} \left( \frac{1}{f_n} \right) = \frac{r_n}{f_{n} t_{50,n} \left( \frac{f_n^{\text{max}}}{f_n} - 1 \right)^{1/r_n}} \left( 1 - \frac{f_n}{f_n^{\text{max}}} \right) \quad (B.27)$$
This term is then inserted into Equation B.19 which gives:

\[
\frac{d}{dt}B_n = 2 \left[ \left( \frac{\pi}{6f_n} \right)^{1/3} - 1 \right] \left[ \frac{r_n}{f_n t_{50,n} \left( \frac{f_{\text{max}n}}{r_n} - 1 \right)^{1/r_n}} \left( 1 - \frac{f_n}{f_{\text{max}n}} \right) \right] \quad (B.28)
\]

Simplifying this term and substituting out the constant terms generates the evolution term for the \( B \) variable for MX and M\(_{23}C_6 \) precipitates:

\[
\frac{d}{dt}B_n = C_n \left[ 1 - \pi^{-1}(6f_n)^{1/3} \right] \left( f_{\text{max}n} - f_n \right) \frac{r_n - 1}{r_n} \quad (B.29)
\]

\[
C_n = \frac{2r_n 18^{2/3}}{f_{\text{max}n} (6\pi)^{1/3} t_{50,n}} \approx 5.1615 \left( \frac{r_n}{f_{\text{max}n} t_{50,n}} \right) \quad (B.30)
\]

Combining Equation B.29 with Equation B.17 and substituting back into Equation B.16 gives the definition of precipitate spacing evolution including evolving precipitate volume fraction for a single precipitate:

\[
\frac{d}{dt} \left( \frac{1}{\lambda_n^2} \right) = -\frac{1}{(d_n^2 B_n)^2} \left[ 2B_n \left( K_n + \phi_n \frac{d}{dt}(\varepsilon^{\text{cr}}) \right) \right. \\
+ \left. d_n^2 C_n \left[ 1 - \pi^{-1}(6f_n)^{1/3} \right] \left( f_{\text{max}n} - f_n \right) \frac{r_n - 1}{r_n} \right] \quad (B.31)
\]

This can then be simplified slightly to:

\[
\frac{d}{dt} \left( \frac{1}{\lambda_n^2} \right) = -\frac{1}{\lambda_n^2} \left[ \frac{2}{3d_n^3} \left( K_n + \phi_n \frac{d}{dt}(\varepsilon^{\text{cr}}) \right) \right. \\
+ \left. \frac{C_n}{B_n} \left[ 1 - \pi^{-1}(6f_n)^{1/3} \right] \left( f_{\text{max}n} - f_n \right) \frac{r_n - 1}{r_n} \right] \quad (B.32)
\]

The same approach was applied to the Z-phase and Laves phase particles with some minor adjustments. The volume fraction evolution is defined very similarly to Equation B.21. Here the subscript "o" is used as a placeholder for either L or Z terms used previously to represent the Laves and Z-phases.

\[
f_o = \frac{f_{\text{max}o}}{\left[ 1 + (t/t_{50,o})^{-r_o} \right]} \quad (B.33)
\]
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The resulting average spacing evolution rate for both of these particles are:

\[
\frac{d}{dt} \left( \frac{1}{\lambda_o^2} \right) = -\frac{1}{\lambda_o^2} \left[ \frac{2}{3d_o^3} (K_o + \phi_o \frac{d}{dt} \varepsilon^{cr}) + \frac{C_o}{B_o} \left( (6f_o)^{1/3} - \pi^{1/3} \right) \left( f_{o}^{\max} - f_o \right)^{1+r_o} \right] \frac{1}{f_{o}^{\max} f_o}
\]

(B.34)

Where the constant \( C_o \) is:

\[
C_o = \frac{2r_o \pi^{1/3}}{108^{1/3} f_{o}^{\max} t_{50,0}} \approx 0.6151 \frac{r_o}{f_{o}^{\max} t_{50,0}}
\]

(B.35)

These four terms are then substituted back into Equation B.14 to assemble the precipitate damage term for \( \{M_{23}C_6, MX, \text{Laves and } Z\text{-phase particle softening with evolving volume fractions.} \)

\[
\frac{d}{dt} D_P = \frac{C_1}{1 - D_P} \left[ -\frac{1}{\lambda_C^2} \left[ \frac{2}{3d_C^3} (K_C + \phi_C \frac{d}{dt} \varepsilon^{cr}) + \frac{C_C}{B_C} \left[ 1 - \pi^{-1} (6f_C)^{1/3} \left( f_{C}^{\max} - f_C \right)^{r_C-1} \right] \frac{f_{C}^{\max} f_C}{2^{2+r_C-3}} \right] 
\]

\[
+ -\frac{1}{\lambda_M^2} \left[ \frac{2}{3d_M^3} (K_M + \phi_M \frac{d}{dt} \varepsilon^{ct}) + \frac{C_M}{B_M} \left[ 1 - \pi^{-1} (6f_M)^{1/3} \left( f_{M}^{\max} - f_M \right)^{r_M-1} \right] \frac{f_{M}^{\max} f_M}{2^{2+r_M-3}} \right] 
\]

\[
+ -\frac{1}{\lambda_L^2} \left[ \frac{2}{3d_L^3} (K_L + \phi_L \frac{d}{dt} \varepsilon^{ct}) + \frac{C_L}{B_L} \left( (6f_L)^{1/3} - \pi^{1/3} \right) \left( f_{L}^{\max} - f_L \right)^{1+r_L} \right] \frac{f_{L}^{\max} f_L}{2^{2+r_L+1}}
\]

\[
+ -\frac{1}{\lambda_Z^2} \left[ \frac{2}{3d_Z^3} (K_Z + \phi_Z \frac{d}{dt} \varepsilon^{ct}) + \frac{C_Z}{B_Z} \left( (6f_Z)^{1/3} - \pi^{1/3} \right) \left( f_{Z}^{\max} - f_Z \right)^{1+r_Z} \right] \frac{f_{Z}^{\max} f_Z}{2^{2+r_Z+1}}
\]

(B.36)
Appendix C

Precipitate based creep subroutine

*******************************************************************************
**SINH CREEP SUBROUTINE 3MATERIAL 3 DAMAGE PARAMETER  **
**LAST EDITED 12/04/2019 **
**EDITED BY CATHAL O` MURCHU` **
**VERSION 8 **
*******************************************************************************

SUBROUTINE USDFLD(FIELD,STATEV,PNEWDT,DIRECT,T,CELENT,
1TIME,DTIME,CMNAME,ORNAME,NFIELD,NSTATV,NOEL,NPT,LAYER,
2KSPT,KSTEP,KINC,NDI,NSHR,COORD,JMAC,JMATYP,MATLAYO,LACCFLA)
C
INCLUDE 'ABA_PARAM.INC'
C
CHARACTER*80 CMNAME,ORNAME
CHARACTER*3 FLGRAY(15)
DIMENSION FIELD(NFIELD),STATEV(NSTATV),DIRECT(3,3),
1 T(3,3),TIME(2)
DIMENSION ARRAY(15),JARRAY(15),JMAC(*),JMATYP(*),COORD(*)
C
C Calling the value of Max principal stress from input file
C
CALL GETVRM('SP',ARRAY,JARRAY,FLGRAY,JRCD,JMAC,JMATYP,
1 MATLAYO,LACCFLA)
C
C Use the value of Principal stress as a field variable
C
FIELD(1)=ARRAY(3)
C
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C Assigning the value to a solution dependant state variable
C
STATEV(2)=FIELD(1)
C
IF(JRCD.EQ.1)THEN
WRITE(6,*), 'GETVRM ERROR OCCURS AT EL NUM',NOEL,'INT POINT',NPT
Call XIT
ENDIF

RETURN
END
C
C CREEP SUBROUTINE
SUBROUTINE CREEP(DECRA,DESWA,STATEV,SERD,ECO,ESWO,P,QTILD,
1 TEMP,DTEMP,PREDEF,DPRED,TIME,DTIME,CMNAME,LEXIMP,LEND,
2 COORDS,NSTATV,NOEL,NPT,LAYER,KSPT,KSTEP,KINC)
C
INCLUDE 'ABA_PARAM.INC'
C
CHARACTER*80 CMNAME
C
DIMENSION DECRA(1),DESWA(1),STATEV(*),PREDEF(*),DPRED(*),
1 TIME(2),COORDS(*),EC(2),ESW(2)
C
REAL::XALPH,XBTA,SMH,HSTR,DTRM,CAVMX,TRI,TT,DENOM,PRE,CAV,H,S,
1 T1,T2,XDC,XDMO,XKM,XKC,XPHIM,XPHIC,EPS0,DELF,LAMOB,
2 XTEMP,XM,XKB,XBURG,XLAMC,XLAMM,XLAMPRE,XLAMOBINV,T,XLAMOBVR,
3 SIGOBVR,SIG_SIG0
C
REAL,PARAMETER:: PI=3.14159
REAL,PARAMETER:: XR=8.314
INTEGER:: FAIL_IPT,FAIL_EL_OLD,FAIL_EL_NEW,NUM_FAIL_EL
C
INTIALISE CREEP STRAIN VARIABLES AND SWELLING AS ZERO
C
DO I=1,5
DECRA(I)=0.0D0
DESWA(I)=0.0D0

ENDDO

C
C RECALL STATE VARIABLES
C
CAV=STATEV(1)
s=STATEV(2)
H=STATEV(3)
TT=STATEV(4)
TEST=STATEV(5)
DP=STATEV(6)
XDC=STATEV(7)
XDM=STATEV(8)
P=STATEV(9)
PRE=STATEV(10)
XALPH=STATEV(11)
XBTA=STATEV(12)
XDCT=STATEV(13)
XDMT=STATEV(14)
FAIL_EL_OLD=STATEV(15)
FAIL_EL_NEW=STATEV(16)
NFAIL_EL=STATEV(17)
FAIL_IPT=STATEV(18)
BTASIG=STATEV(19)
SIGtriax=STATEV(20)
XLAMC=STATEV(21)
XLAMM=STATEV(22)
XLAMPRE=STATEV(23)
XLAMOBINVT=STATEV(24)
XLAMOBVR=STATEV(25)
SIGOBVR=STATEV(26)
SIG_SIG0=STATEV(27)

C
C**Input material constants******************************************************************************
C DAMAGE CONSTANTS FOR THREE DAMAGE PARAMETER

IF (CMNAME(1:7) .EQ. "SINH-PM") THEN
C**PARENT MATERIAL******************************************************************************
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C PRIMARY HARDENING
SMH=0.07199152*144000 !0.07199152*110000 !125000
HSTR=0.45 !0.09 !0.131
C
C CAVITATION DAMAGE
DTRM=8.5 !2.5 !7.5
C
TRI=3.8
C
C PRECIPIATE COARSENING
C M23C6
XDC0=100.0E-6 ![mm]
XKC=1.0E-15 !6.35E-15 !3.68E-15 [mm^3/h]
XPHIC=1.04E-9 ![mm^3]1.041179E-9
XFC=0.02 ![-]
C
C MX
XDM0=36.0E-6 ![mm]
XKM=2.35E-18 !3.9E-18 !3.13e-18 ! [mm^3/h]
XPHIM=1.18132E-14 ![mm^3]
XFM=0.005 !P91 !0.001!Bar257 ![-]
C
C TEMPERATURE INDEPENDENT VARIABLES
EPS0=6.0E13 ! [1/h]
XQC=360000 ! [J]
LAMOB=31.8437E-9!P91 !3.7987083686E-8 ! ! [m]
!898.15 !873.15 ! [K] !
C
ELSE IF(CMNAME(1:7) .EQ. 'SINH-WM') THEN
C**WELD MATERIAL*************************************************************************
C PRIMARY HARDENING
SMH=0.0264*110000 !125000 !0.07199152*144000
HSTR=0.25 !0.131 !0.45 !
C
C CAVITATION DAMAGE
DTRM=10 !7.5 !8.5 !
TRI=3.8
C
C PRECIPIATE COARSENING
C M23C6
XDC0=200.0e-6 ! [mm]
XKC=6.35E-15 ! 3.68E-15 ! 1.0E-15 ! [mm^-3/h]
XPHIC=1.04E-9 ! [mm^-3]
XFC=2.0E-5 ! [-]
C
C MX
XDM0=65.0E-6 ! [mm]
XKM=3.9E-18 ! 1.3E-18 ! 2.35E-18 ! [mm^-3/h]
XPHIM=1.18E-14 ! [mm^-3]
XFM=1.0e-5 ! Bar257 ! 5.0e-5 ! P91 ! 0.005 ! [-]
C
C TEMPERATURE INDEPENDENT VARIABLES
EPS0=1.05644088655804E12 ! [1/h]
XQC=360000 ! [J]
LAMOB=6.2E-8 ! P91 ! 60.85e-9 ! ! [m]
C
ELSE IF(CMNAME(1:8) .EQ. 'SINH-HAZ') THEN
C**HAZ MATERIAL******************************************************************************
C PRIMARY HARDENING
SMH=0.00784*110000 ! 125000 ! 0.07199152*144000
HSTR=0.52 ! 0.131 ! 0.45 !
C
C CAVITATION DAMAGE
DTRM=1.125 ! 7.5 ! 8.5 !
C
TRI=3.8
C
C PRECIPIATE COARSENING
C M23C6
XDC0=128.0E-6 ! [mm]
XKC=6.35E-15 ! 3.68E-15 ! 1.0E-15 ! [mm^-3/h]
XPHIC=1.04E-9 ! [mm^-3]
XFC=5.0E-4 ! [-]
C
C MX
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XDM0=55.0E-6 ![mm]
XKM=3.9E-18 !3.13e-18 !2.35E-18 ![mm^-3/h]
XPHIM=1.18E-14 ![mm^-3]
XFM=1.0E-6 !PM!5.0E-6 ![mm^-3]

C
C TEMPERATURE INDEPENDENT VARIABLES
EPS0=1.87811713165874e13 ![1/h]
XQC=360000 ![J]
LAMOB=6.66759136478928E-08 ![m]

ELSE
WRITE(6,*),'INCORRECT MATERIAL NAME,ONLY SBR-PM,SBR-WM,SBR-HAZ'
CALL XIT
ENDIF

C
C**********************************************************************
C
C CAVITATION DAMAGE LIMITS DEPENDING ON MODEL TYPE.
C FOR 1D MODELS
CAVMX=0.333
C FOR ANY HIGHER DIMENSION MODELS
CAVMX=0.95
C
C PRECIPITATE DAMAGE CONSTANTS
C
XBC=((PI/(6.0*XFC))**(1.0/3.0))-1.0)**2.0 ![mm]
XBM=((PI/(6.0*XFM))**(1.0/3.0))-1.0)**2.0 ![mm]
DPRE1=((XDC0**2.0)*(XDM0**2.0))/(3.0*((XDC0**2.0)*XBC)+
1*(XDM0**2.0)*XBM) ![mm^-2]

C
C MICROSTRUCTURAL CONSTANTS
C
XM=2.9 !TAYLOR FACTOR
XKB=1.38064852E-23 !BOLTZMANN CONSTANT [N.m/k]
XBURG=2.48E-10 !BURGERS VECTOR [m]
XTEMP=873.15!923.15 ![K]!
XW=4.0E-7  !LATH WIDTH [m]
XDG=4.0E-6  !GRAIN SIZE [m]
XRHO=4.8E14  !DISLOCATION DENSITY [m]
DELF=5.978E-19  ![J]

C
C INITIALISE STATE VARIABLES
C
C for SPCT work change KSTEP Check to 3, Creep step is 3rd step
IF ((KSTEP.EQ.3).AND.(KINC.EQ.1)) THEN
XDC=XDC0  ![mm]
XDM=XDM0  ![mm]
DCAV=0.0
ELSE
XDC=XDC  ![mm]
XDM=XDM  ![mm]
ENDIF

C
C BETA EVOLVING WITH SPACING VERSION
C
C PRECIPITATE SPACINGS
XLAMC=XDC*(((PI/(6.0*XFC))**(1.0/3.0))-1.0)  ![mm]
XLAMM=XDM*(((PI/(6.0*XFM))**(1.0/3.0))-1.0)  ![mm]

C
C AVERAGE PRECIPITATE SPACING TERM
XLAMPRE=(SQRT(((XLAMC**2.0)+(XLAMM**2.0))/((XLAMC**2.0)*
1(XLAMM**2.0))))*1E3  ![1/m]

C
C INVERSE AVERAGE OBSTACLE SPACING
XLAMOBINVT=XLAMPRE+(1.0/XW)+(1.0/XDG)+(SQRT(XRHO))  ![1/m]

C
C AVERAGE OBSTACLE SPACING
XLAMOBVR=1/XLAMOBINVT  ![m]

C
C EVOLVING OBSTACLE SPACING STRESS TERM
SIGOBVR=((XM*XKB*XTEMP)/((XBURG**2.0)*(XLAMOBVR)))*(1.0E-6)  ![MPa]

C
C STEADY STATE CREEP CONSTANTS
C

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\[ \text{XALPH} = \text{EPS0} \times \exp\left(\frac{-\text{DELF}}{\text{XKB} \times \text{XTEMP}}\right) \quad \text{[1/hr]} \]

\[ \text{XBTA} = \left(\frac{\text{XBURG}^{2.0} \times \text{LAMOB}}{\text{XM} \times \text{XKB} \times \text{XTEMP}}\right) \times (1.0 \times 10^6) \quad \text{[1/MPa]} \]

C

\[ \text{IF} \quad ((\text{KSTEP} .EQ. 2) .AND. (\text{KINC} .EQ. 1)) \quad \text{THEN} \]

\[ \text{STATEV(1)} = 0.0 \]
\[ \text{STATEV(3)} = 0.0 \]
\[ \text{STATEV(6)} = 0.0 \]
\[ \text{STATEV(9)} = 0.0 \]
\[ \text{STATEV(10)} = 0.0 \]
\[ \text{STATEV(21)} = \text{XLAMC} \]
\[ \text{STATEV(22)} = \text{XLAMM} \]
\[ \text{STATEV(23)} = \text{XLAMPRE} \]
\[ \text{STATEV(24)} = \text{XLAMOBINVT} \]
\[ \text{STATEV(25)} = \text{XLAMOBVR} \]
\[ \text{STATEV(26)} = \text{SIGOBVR} \]
\[ \text{STATEV(27)} = \text{SIG.SIG0} \]
\[ \text{FAIL_IPT}=0 \]
\[ \text{FAIL_EL}=0 \]
\[ \text{ENDIF} \]

C

C Calculation of total time

C

\[ \text{TT} = \text{TIME(1)} \quad \text{!STEP TIME AT BEGINNING OF STEP} \]

\[ \text{IF} \quad (\text{LEND}.=0) \quad \text{THEN} \]

\[ \text{TT} = \text{TIME(2)} - \text{DTIME} \]

\[ \text{ENDIF} \]

\[ \text{STATEV(4)} = \text{TT} \]

C

C CALCULATION OF STRAIN INCREMENT EXPLICIT

C

C \text{SINH} WITH 3 DAMAGE VARIABLES

C

\[ \text{DENOM} = (1.0 - \text{PRE}) \times (1.0 - \text{CAV}) \]

\[ \text{DECRA(1)} = \text{XALPH} \times \left(\text{SINH}((\text{XBTA} \times \text{QTILD} \times (1.0 - \text{H})) / \text{DENOM})\right) \times \text{DTIME} \]

C EQUIVALENT PLASTIC STRAIN RATE

\[ \text{DP} = \text{XALPH} \times \left(\text{SINH}((\text{XBTA} \times \text{QTILD} \times (1.0 - \text{H})) / \text{DENOM})\right) \times \text{DTIME} \]

C

C \text{SINH} WITH 3 DAMAGE VARIABLES & EVOLVING SIG0 TERM
C
DENOM=(1.0-PRE)*(1.0-CAV)
DECRA(1)=XALPH*\left(\sinh\left(\frac{QTILD*(1.0-H)}{(SIGOBVR*DENOM)}\right)\right)*DTIME
C EQUIVALENT PLASTIC STRAIN RATE
DP=XALPH*\left(\sinh\left(\frac{QTILD*(1.0-H)}{(SIGOBVR*DENOM)}\right)\right)*DTIME
C
P=DP+P
C
C TEST QUANTITIES
BTASIG=XBTA*QTILD
SIG_SIG0=QTILD/SIGOBVR
C
C Defining DECRA(5) for implicit integration
C
IF (LEXIMP.EQ.1) THEN
C
C SINH WITH 3 DAMAGE VARIABLES
C
DENOM=(1.0-PRE)*(1.0-CAV)
DECRA(5)=XALPH*\left(\sinh\left(\frac{XBTA*QTILD*(1.0-H)}{DENOM}\right)\right)*DTIME
C EQUIVALENT PLASTIC STRAIN RATE
DP=XALPH*\left(\sinh\left(\frac{XBTA*QTILD*(1.0-H)}{DENOM}\right)\right)*DTIME
C
C SINH WITH 3 DAMAGE VARIABLES & EVOLVING SIG0 TERM
C
DENOM=(1.0-PRE)*(1.0-CAV)
DECRA(5)=XALPH*\left(\sinh\left(\frac{QTILD*(1.0-H)}{(SIGOBVR*DENOM)}\right)\right)*DTIME
C EQUIVALENT PLASTIC STRAIN RATE
DP=XALPH*\left(\sinh\left(\frac{QTILD*(1.0-H)}{(SIGOBVR*DENOM)}\right)\right)*DTIME
C
P=DP+P
C
C TEST QUANTITIES
BTASIG=XBTA*QTILD
SIG_SIG0=QTILD/SIGOBVR
C
ENDIF
C
C PRINCIPAL STRESS FROM USDFLD ABOVE
Chapter C - Precipitate based creep subroutine

C
S=STATEV(2)
C
C DAMAGE CALCULATED AT END OF INCREMENT
C
IF (LEND.EQ.1) THEN
C
**PRIMARY HARDENING*******************************************
C
DH=((SMH*DP)/QTILD)*(1.0-(H/HSTR))
H=H+DH
IF (H.GE.HSTR) H=HSTR
C
C **PRECIPITATE COARSENING**************************************
C
M23C6 STRAIN AND TEMPERATURE
XDC=((XDC0**3.0)+(XKC*TT)+(XPHIC*P))**(1.0/3.0)
C M23C6 TEMPERATURE
XDCT=((XDC0**3.0)+(XKC*TT))**(1.0/3.0)
C
MX STRAIN AND TEMPERATURE
XDM=((XDM0**3.0)+(XKM*TT)+(XPHIM*P))**(1.0/3.0)
C MX TEMPERATURE
XDMT=((XDM0**3.0)+(XKM*TT))**(1.0/3.0)
C
C **PRECIPIATE DAMAGE*******************************************
C
DPRE=DPRE1*(1.0/(1.0-PRE))*(((XBC/(XDM**(5.0)))*((XKM*DTIME)+
1(XPHIM*DP)))+((XBM/(XDC**(5.0)))*((XKC*DTIME)+(XPHIC*DP))))
PRE=DPRE+PRE
C
C **CAVITATION DAMAGE*******************************************
C
IF (S.LT.0/D0) S=0.D0
DCAV=DTRM*DP*((S/QTILD)**TRI)
TEST=DCAV
IF (DCAV.LT.0.D0) DCAV=0.D0
C
CAV=CAV+DCAV

IF (CAV.GE.CAVMX) THEN
CAV=CAVMX
STATEV(1)=CAV

C          CALL XIT
C          RECORD ELEMENT NUMBER AND INT POINT NUMBER OF FAILURE
C          FAIL_IPT=NPT
C          FAIL_EL_OLD=FAILED_EL_NEW
C          FAIL_EL_NEW=NOEL

C          COUNT NUMBER OF FAILED ELEMENTS
C          IF (FAIL_EL_NEW.NE.FAIL_EL_OLD) THEN
C          NFAIL_EL=NFAIL_EL
C          ENDIF
C          GO TO 10
ENDIF

C
C          triaxiality assigned to sdv
SIGtriax=S/QTILD

C          CODE TO EXIT SUBROUTINE IF MORE THAN 2 ELEMENTS FAIL
C          IF (NFAIL_EL.GE.2) THEN
C          GO TO 10
C          ENDIF
C END IF

C
STATEV(1)=CAV
STATEV(2)=S
STATEV(3)=H
STATEV(4)=TT
STATEV(5)=TEST
STATEV(6)=DP
STATEV(7)=XDC
STATEV(8)=XDM
STATEV(9)=P
STATEV(10)=PRE
Chapter C - Precipitate based creep subroutine

STATEV(11)=XALPH
STATEV(12)=XBTA
STATEV(13)=XDCT
STATEV(14)=XDMT
STATEV(15)=FAIL_EL_OLD
STATEV(16)=FAIL_EL_NEW
STATEV(17)=NFAIL_EL
STATEV(18)=FAIL_IPT
STATEV(19)=BTASIG
STATEV(20)=SIGtriax
STATEV(21)=XLAMC
STATEV(22)=XLAMM
STATEV(23)=XLAMPRE
STATEV(24)=XLAMOBINV
STATEV(25)=XLAMOBVR
STATEV(26)=SIGOBVR
STATEV(27)=SIG_SIG0

c
RETURN
10 STOP
END
Appendix D

Small Punch Creep Rig Operational Documents

D.1 Standard Operating Procedure

<table>
<thead>
<tr>
<th>Subject - PhD Research Project</th>
<th>College of Engineering and Informatics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title: High temperature small punch creep testing of polymers and metals</td>
<td>Lab number: ENG-G037, ENG-G002</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Objective</th>
<th>Construction and testing of a high temperature small punch creep test rig</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Test 9Cr steels at high temperature</td>
</tr>
<tr>
<td></td>
<td>Determine creep properties of 9Cr steels at different temperatures</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Health &amp; safety Documents</th>
<th>Refer to the Safety Statement for the Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NUI Galway Health and Safety Statement</td>
</tr>
<tr>
<td></td>
<td>Standard Operating Procedures in place for lab experiments</td>
</tr>
<tr>
<td></td>
<td>High temperature small punch creep test risk assessment</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>New safety hazards</th>
<th>Refer to high temperature small punch creep test risk assessment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>- Burns from furnace</td>
</tr>
<tr>
<td></td>
<td>- Pinching/ crushing from weights and punch</td>
</tr>
</tbody>
</table>

| Additional PPE Required | Lab coat, safety shoes, safety glasses during operation and maintenance of rig |

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# Additional Engineering Controls

Refer to high temperature small punch creep test risk assessment

- Manual handling
  - Signage
  - Guard around rig

## Special Handling

- See above, PPE requirement
- Weights should be added/removed one at a time
- Ensure personnel involved are trained in manual handling

## Accident and Injury procedures

The following procedure should be employed when injuries due to the hazards mentioned in the 'New Safety Hazard’ section occurs

- See above, PPE requirement
- See emergency procedure on the door of room ENG-G037
- Report the accident to the Safety Representative detailed below
- In the event of injuries which result in bleeding, seek assistance in dressing the wound using the materials found in the First Aid kits located around the engineering building at NUI Galway

### Overall Risk Level

| Low/Med/High | Medium - see Risk Assessment |

### Report all accidents to:

| Lab Champion: | - Mr. Pat Kelly |
| Safety Representative: | - Mr. Aodh Dalton |

### SOP prepared by:

| Cathal Ó Murchú | Contact Details: c.omurchu3@nuigalway.ie | Approved By: Aodh Dalton | Date: 01/2018 |

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#1 **Scope of Work/Activity:** State the process/operation/equipment that will be used
- Set up the test rig
- Placing sample in holder, setting up weights on loading pan
- Perform experiments to determine the creep behaviour materials for a range of different loads and temperatures

#2 **Reference Documents:** Include any relevant documents (for example manuals, MSDS).

#3 **Environmental or Waste Management Impacts and procedures**
- CEN - CWA 15627 'Small punch test method for metallic materials
- High temperature small punch creep test - Risk assessment
- HSA manual handling guidelines
- SDS rocol copper grease (available in lab SDS folder)

#4 **Other Equipment:** List all items needed to run a process, e.g. tweezers, vials, drill, lathe, et
- N\A Laptop/computer with LabView SPCT VI software
- Weights
- Thermal insulation bricks
- Insulating rockwool
- Tweezers
- 2 mm silicon nitride indenter spheres
- Allen keys
- Torque wrench with 3\8” to 3 mm hex head converter
- Disk samples
- M3 bolts

#5 **Materials:** List all source material, gases, or chemical used to operate the system
- Steel weights
- Rocol copper grease
#6  **Maintenance:**  
- Within Equipment Calibration date- Yes: ×, No: n/a  
- Within Preventative Maintenance due date- Yes: ×, No: n/a  
- Within PAT testing due date- Yes: ×, No: n/a

#7  **Procedure:** Include or reference instructions on programming and/or operating all equipment  

**Safety Briefing:**  
- Be aware of emergency exits and evacuation notice  
- Read the prepared Risk Assessment  
- Be aware that the departmental safety statement is available for viewing in the main floor of the Highway Laboratory  
- Know where first aid kits are located and how to contact the first aid responder  
- If for some reason any employee or student wishes to perform a function that differs from the procedural methods summarised in the protocol below, they must consult Prof. Sean Lean and/or Dr. Richard Barrett initially and subsequently with members of the technical staff.
#8 Apparatus

- Ensure furnace is at room temperature, check both thermocouples to confirm chamber temperature.
- Ensure there are no weights on the loading pan.
- Remove thermal insulating bricks and wool from top of furnace.
- Open furnace by rotating both top and bottom furnace brackets, not the furnace case itself.
- Release LVDT platen from push rod by loosening 4 mm hex head bolt in holding collar, slide collar to rest on top of furnace.
- Carefully remove chamber thermocouple from holder and rest on head of SPCT rig.
- Grasp loading pan firmly and retract the push rod from the upper die, release the stopper and lock in place once the pushrod is 30 to 40 cm above the upper die.
- Using the torque wrench with 3\(\frac{\pi}{8}\)” to 3 mm hex head converter release both clamping screws.
- Using a 4 mm allen key release the lower die clamping grub screw located in the alignment post on the base of the apparatus.
- Remove the lower die rod and using the bench vice gently remove the upper die. Gently rotate the upper die and pull up gently, it should release easily. Care should be taken not to invert the die post.
- The test specimen can now be removed using a tweezers and placed in storage for further study.
- Once the specimen is removed carefully invert the lower die post over a tray to capture the indenter sphere for further study.
- The lower die post should be returned to the alignment post and tightened back in place with the 4 mm allen key.
• The next specimen can be loaded into the lower die with a tweezers, center the specimen in the lower die and apply the upper die in place.
• Tighten the loading screws to the required torque for each clamping screw with the torque wrench
• Insert indenter sphere into aperture in upper die and image to ensure sphere is in place on sample
• Align secondary thermocouple to be in contact with upper die.
• Release stopper and gently lower push rod in to contact with indenter, care is needed to ensure pushrod assembly does not impact sample in any way. To ensure good alignment the push rod may require some rotation to ensure it enters the upper die cleanly.
• Lock stopper in place with 3 mm allen key.
• Position lower insulating rock wool in contact with furnace walls and lower die post.
• Place chamber thermocouple in contact with upper die avoiding clamping screws and push rod, check for good contact between die and thermocouple.
• Close furnace and using all four clasps.
• Move LVDT platen up push rod and depress LVDT a minimum of 1 mm and tighten platen in place, using 4 mm allen key. LVDT arm should not be depressed more than 3 mm as thermal expansion requires up to 5 mm of further stroke length of LVDT.
• Place rockwool in upper aperture of furnace, cover with two insulation bricks, ensure no contact occurs between bricks and push rod.
• Start LVDT VI on data logging PC to verify LVDT is not overly compressed beyond limits set above.
• Set digital thermometer to PC mode and turn on data logger on PC, occasionally software will need to be restarted when it does not detect the digital thermometer.
• Ensure all warning signs are in place on guard and lab door
• Switch on cooling fan at wall socket behind apparatus, set target temperature chamber and upper die on furnace controller.
• Manually record furnace chamber and wall temperature, displacement, expansion temperature, zeroed displacement at regular intervals.
• for a 600 °C a heating time of 2 hours and 40 minutes is recommended and thermal expansion of 4.7 mm should have occurred.
• Once test temperature is reached and stabilised, the stopper is released and dropped to contact the head and locked in position.
• The test load is then placed on the loading pan, the apparatus system load is 6.85 kg which is added to the load applied to the loading pan.
• Release the stopper and set the maximum displacement distance using a 2.5 mm allen key to set the height at which the stopper is locked to the push rod. The test is now underway, the time should be logged manually at this point.
• Periodic inspections of the device are recommended for the duration of the test, twice daily to record the chamber thermocouple and displacement readings.
• The testing logbook should be filled in at the end of each experiment with a comment stating if there were any issues with the operation of the apparatus. Any issues should be reported to Prof. Sean Leen and/or Dr. Richard Barrett.
Appendix E

Automated Measurement System Codes

E.1 Precipitate measurement tool

Developed for Fiji ImageJ software (version v1.52o) using Java, this code requests a directory containing the images to be measured, reads in the file names and generates a list. The image footers are removed and the cropped image is saved. Next a scale bar overlay is placed on the image, the background is then removed, using a rolling sphere technique of radius 200 px, the average pixel intensity inside this circle is identified and subtracted away from the rest of the image, this smooths the background removing large spatial variations of background intensities, minimising the effects of uneven lighting. Again this smoothed image is saved with a new name.

A threshold is then applied to the image to create a binary image from the greyscale original. ImageJ provides a function where all possible automated threshold settings are shown in a single image to select the optimum result. Based on this the Renyi Entropy [240] threshold method was selected as it outlined the maximum number of precipitates of all the possible options. Next a watershed segmentation is preformed on the image, essentially the image is treated as a topographical map containing hills and valleys corresponding with the maximum and minimum grey intensities of the image. The process treats all local minimums as sources and "fills" upward until a neighbouring source is met, the boundary is considered as the point when two sources meet. Further boundaries can be applied by giving the process a mask of previously identified boundaries in this case the result of threshold processing provides the mask. Figure E.1 contains a schematic explaining the watershed process and the identification of boundaries when two sources reach each other. Following the watershed process the Analyze Particles macro was applied to the images using...
Figure E.1: Watershed based boundary identification between sink regions

a size range of 0 to infinite with a circularity of 0.5 to 1. These settings instruct the package to include all particles of any size detected, with a circularity or roundness defined as: $4\pi Area/\pi Max Diameter^2$ by Russ [251]. The results are then saved in text file format. This process is then looped over the entire directory of images.

Each result file contains a list of all particles measured including the area, mean intensity value and perimeter. An equivalent circle diameter is extracted from the area value for each particle, and the average diameter is calculated based on the global average for each precipitate measured.

```
//developed By Cathal O'Murchu'
//Civil Engineering Department, NUI Galway, Ireland
//Developed for 9Cr steel precipitate measurements
//**************************************************
//get file list in folder
inputdir=getDirectory("Choose a Directory")
outputdir=inputdir+"/measurements/";
setBatchMode(true);
Dialog.create("Set Scale");
Dialog.addMessage("Please insert image scale");
label="scale";
default=2000;
Dialog.addNumber(label, default);
Dialog.show()
scale=Dialog.getNumber();
//print(scale);
imglist=getFileList(inputdir);
```
for (i = 0; i < imglist.length; i++) {
    print(imglist[i]);
    // get last opened file directory
    open(imglist[i]);
    // dir=getDirectory(imglist[i]);
    // extract name without file extension
    name=File.nameWithoutExtension;
    // extract image dimensions
    getDimensions(width, height, channels, slices, frames);
    // set line and background colours
    run("Colors...", "foreground=white background=black selection=yellow");
    // set image height to exclude information at based of image
    imgheight=width;
    makeRectangle(0, 0, width, imgheight);
    roiManager("add");
    // crop image
    run("Crop");
    path=inputdir+name+"measure.tiff";
    // save cropped image as measure version
    save(path);
    close();
    open(path);
    name1=File.nameWithoutExtension;
    // Set scale bar
    if(scale==5000){
        makeLine(590,1040,663,1040);
        run("Set Scale...", " known=2000 pixel=1 unit=nm");
    }else if(scale==8000){
        makeLine(590,1040,708,1040);
        run("Set Scale...", " known=2000 pixel=1 unit=nm");
    }else if(scale==10000){
        makeLine(590,1040,737,1040);
        run("Set Scale...", " known=2000 pixel=1 unit=nm");
    }else if(scale==30000){
        makeLine(590,1040,700,1040);
        run("Set Scale...", " known=500 pixel=1 unit=nm");
    }
Chapter E - Automated Measurement System Codes

```java
} else if (scale == 40000) {
    makeLine(590, 1040, 737, 1040);
    run("Set Scale...", "known=500 pixel=1 unit=nm");
} else if (scale == 60000) {
    makeLine(590, 1040, 811, 1040);
    run("Set Scale...", "known=500 pixel=1 unit=nm");
} else {
    exit("scale out of bounds");
}

run("Clear");
// Scale bar location
// Where to put it?
x = 10;
y = 1000;
// How wide (in units) should the scale bar be?
barwidthUNIT = 500;
// How wide (in pixels) should the scale bar be?
getPixelSize(unit, pWidth, pHeight);
barwidthPX = barwidthUNIT / pWidth;
// How thick (in pixels) should the scale bar be?
barheightPX = 5;
// Which color?
color = "red";
// The scale bar
makeRectangle(x, y, barwidthPX, barheightPX);
run("Add Selection...", "stroke=" + color + " width=1 fill=" + color);
// The label
text = "" + barwidthUNIT + " " + unit;
// set font size
fontSize = (getValue("font.size"))*2;
// Generate label
textposx = (((barwidthPX + x) / 2) - getStringWidth(text));
textposy = y - fontSize - 10;
makeText(text, textposx, textposy);
run("Add Selection...", "stroke=" + color + " font=" + fontSize + "
    fill=none");
run("Select None");
```
E.1 - Precipitate measurement tool

//end scale bar placement

//reduce background effects
run("Subtract Background...", "rolling=200 light sliding");
//Save background subtracted Image
path0=inputdir+name1+"minusbackground.tiff";
save(path0);
//Mask development
setAutoThreshold("RenyiEntropy");
//run("Threshold...");
setThreshold(0, 213);
setOption("BlackBackground", false);
run("Convert to Mask");
//Watershed conglomerated particles
run("Watershed");
run("Watershed");
path3=inputdir+name1+"watershed.tiff";
save(path3);
//Begin Particle analysis
run("Analyze Particles...", "size=0-infinite circularity=0.5-1.00
    show=Outlines display exclude clear include in_situ");
//Save masked image
path1=inputdir+name1+"mask.tiff";
save(path1);
//save results file
updateResults;
path2=inputdir+name1+".csv";
//save profile
saveAs("Results",path2);
run("Clear Results");
roiManager("delete");
run("Close All");
}
print("Data analysed Sir")