Microstructural evolution in high chromium steels

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Microstructural Evolution in High Chromium Steels

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Dr Geoff West

April 2013

Department of Materials
Loughborough University
I would like to thank my supervisors, Professor R.C. Thomson and Dr. G.D. West, for their guidance and support throughout the course of my PhD studies.

I am grateful to Loughborough University for the funds provided towards the realisation of this work.

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I must also thank my friends in the research group and all the staff in the department who have helped me a lot throughout my PhD studies.

Finally, I wish to thank my family and my girlfriend, X. Yan, for their unfailing support and encouragement.
List of Acronyms

AR: As Received
BCC: Body Centred Cubic
BCT: Body Centred Tetragonal
BSE: Backscatter Electron
CI: Confidence Index
CP: Central Pixel
EBIC: Electron Backscatter Induced Current
EBSD: Electron Backscatter Diffraction
ECCC: European Creep Collaborative Committee
EDX: Energy Dispersive X-ray
FCC: Face Centred Cubic
FEG: Field Emission Gun
FIB: Focused Ion Beam
IPF: Inverse Pole Figure
IQ: Image Quality
KAM: Kernel Average Misorientation
LAM: Local Average Misorientation
LOS: Local Orientation Spread
OIM: Orientation Image Microscopy
OM: Optical Microscopy
SE: Secondary Electron
SEM: Scanning Electron Microscopy
TEM: Transmission Electron Microscopy
Abstract

The 9 wt% Cr ferritic-martensitic steels with alloying additions of Mo, V and Nb have been widely used in the power generation industry for many years. The high temperature strength and creep resistance of the advanced high chromium steels come from the microstructure, which typically contains a tempered martensite matrix with a fine dispersion of secondary particles. However, the dislocation density and the type, size and distribution of second phase particles in the microstructure are functions of the applied heat treatments. The mechanical properties of these steels, in turn, can be very sensitive to the microstructure during high temperature service life and therefore it is important to understand both the microstructural evolution and mechanical properties of these steels as a function of service life.

This research project was focused on gaining a complete, quantified, understanding of microstructural changes, with respect to both the matrix microstructure and secondary phase changes, in high Cr Grade 91 and 92 tempered martensitic power plant steels, as a function of pre-service heat treatment, stress, time and temperature. The high chromium steels examined in this research were creep-tested at 650°C and then examined using a variety of experimental techniques, including optical microscopy (OM), hardness testing, field emission gun scanning electron microscopy (FEG SEM), focused ion beam scanning electron microscopy (FIB SEM), electron backscattered diffraction (EBSD) and transmission electron microscopy (TEM) to characterise the microstructural evolution characterisation.

The hardness values of Grade 91 and 92 steels changed as expected with different heat treatments, stresses, times and temperatures. The particle size distribution and chemical compositions of the MX phase which (includes VN and NbC) have been characterised with the use of energy dispersive X-ray (EDX) in the transmission electron microscope (TEM). The MX particle coarsening was only observed in 91 steels with varying heat treatment and applied stress conditions, which maybe an indicator of the better high temperature resistance and creep exposure resistance of 92 steels than 91 steels.
The particle size distribution of both M\textsubscript{23}C\textsubscript{6} and Laves phase particles have been characterised separately with focused ion beam images (FIB) and backscatter electron images (BSE) in the dual-beam scanning electron microscope (FIB SEM). The coarsening of M\textsubscript{23}C\textsubscript{6} particles was observed and quantified as the mean particle size increased and the number density decreased gradually in both the 91 and 92 samples as a function of pre-service heat treatment, stress, time and temperature. However, this coarsening effect was observed more significant in 91 samples than in 92 samples. The particle coarsening of the Laves phase (which was only observed in Grade 92 steels) was also observed, as the mean particle size increased gradually with varying heat treatments and applied stresses in all of the 92 samples. In addition, the Laves phase coarsening more significantly than the M\textsubscript{23}C\textsubscript{6} particles with varying heat treatments and applied stresses.

The grain and subgrain structure of grade 91 and 92 steels have been extensively characterised with the use of electron backscatter diffraction (EBSD) in the scanning electron microscope. It has been shown that a change in the low/high angle boundary ratio of EBSD boundary maps can provide a quantification of the matrix microstructural evolution of grade 91 and 92 steels as a function of pre-service heat treatment, stress, time and temperature. EBSD analysis as a general assessment tool for material microstructural evolution of Grades 91 and 92 steels was investigated. The average Kernel Average Misorientation (KAM) value was used as the assessment of recovery in steels to investigate the effects of stress relief heat treatment, long-term aging and creep stress on the microstructure recovery, the microstructural recovery increased as the decrease of mean KAM values of T91 and T92 samples after heat treatments or creep tests.
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Chapter 1. Introduction

1.1 Background of Project

Many developments have been progressed in the past fifty years to reach high thermal efficiency and hence low emission for fossil fuel power plants. Less fuel is required for a given power output by increasing the thermal efficiency of a power plant, and lower fuel consumption means less environmentally damaging gas emissions [1]. There are two major parameters which affect the thermal efficiency of a power plant; the temperature, and the pressure of the steam entering the turbine. The thermal efficiency of a power plant can be increased significantly by increasing these two parameters. When steam temperatures reach 600°C with pressures at 25-30 MPa, thermal efficiencies can reach about 42% in most modern steam power stations. This can be increased to around 45% in the next generation of power stations with steam temperatures of 625-650°C [1]. However, increasing the operating temperatures and pressures accelerates all degradation processes in steels, such as recovery and recrystallization, migration of atoms and dislocations, grain and subgrain coarsening, as well as coarsening of particles [2]. These phenomena lead to more demanding requirements on the high temperature mechanical properties of the materials. The 9 wt% Cr ferritic-martensitic steels with alloying additions of Mo, V and Nb have been widely used in the power generation industry where they are used in headers and steam piping, and boiler super-heater and re-heater tubes [3]. This is because these steels have excellent creep resistance, high corrosion and oxidation resistance, good thermal conductivity and a low thermal expansion coefficient [4]; all properties that are needed for a material to reach a long time service life in the high temperature and pressure environments found in power plants.

The high temperature strength and creep resistance of the advanced high chromium steels come from the microstructure, which typically contains a tempered martensite matrix with a fine dispersion of secondary particles [5-8]. Normally, prior to service these steels are given a two stage heat treatment that consists of normalizing and tempering to produce a tempered martensitic structure. This martensitic matrix has a high dislocation density, and the chemical composition of these steels contains
alloying additions such as Nb, V, Mo, and Cr, which are all strong carbide formers. After these heat treatments, complex carbide and nitride precipitate particles are formed and become distributed throughout the microstructure [7]. These various particles precipitate in different parts of the martensitic microstructure; chromium rich $M_{23}C_6$ particles are usually found in the prior austenite and lath boundaries and VN and NbC (all named as MX) can be found dispersed within the martensite laths. As a result, the microstructure of these steels has a high dislocation density, a fine dispersion of particles and solid solution strengthening elements present in the matrix. The three major strengthening mechanisms which enhance the creep strength of steels are: precipitate hardening derived from secondary phase particles; dislocation hardening derived from the high dislocation density in the tempered martensite matrix; and solution hardening derived from elements such as Mo and W [9, 10]. These strengthening mechanisms improve the mechanical and thermal properties of high Cr ferritic-martensitic steels, making them suitable for applications that require good creep resistance and which operate in relatively severe conditions requiring good corrosion and oxidation resistance. However, the dislocation density and the type, size and distribution of second phase particles in the microstructure are functions of the applied heat treatments, for example, those designed to relieve residual stresses which are applied before the steels enter service, often associated with welding procedures. In addition, the microstructures also change during the prolonged creep exposure. The recovery of the dislocation substructure and the coarsening of secondary phase particles during creep can both degrade the creep resistance of the material and limit the service life of these types of steels at high temperatures [11-14]. The mechanical properties, in turn, can be very sensitive to the microstructure and therefore it is important to understand both the microstructural evolution and mechanical properties of these steels as a function of service life.

1.2 Project Aims and Objectives

The aim of this research project was to gain a complete, quantified, understanding of microstructural changes, consisting of both matrix microstructure and secondary phase change, in high Grade Cr 91 and 92 tempered martensitic power plant steels, as a function of pre-service heat treatment, stress, time and temperature.
This thesis first presents a review of the primary and secondary phases of 9 wt% Cr steels from the literature, which includes the physical metallurgy and characteristics of precipitate particles of 9 wt% Cr steels, together with a brief section describing the influence of pre-service heat treatment on 9 wt% Cr steels, and also a section describing the creep behaviour and microstructural stability of these steels.

The following chapter discusses the experimental techniques used for this research. Firstly, a detailed description of the materials that were used, identifying the chemical compositions and conditions in which the investigated materials were processed is presented. Secondly, the sample preparation techniques consisting of cutting, polishing, etching and carbon replica processes are described and discussed. Finally, the rest of the chapter provides a brief explanation of the different microstructural characterisation techniques used, which include optical microscopy (OM), hardness tests, field emission gun scanning electron microscopy (FEG SEM), focused ion beam scanning electron microscopy (FIB SEM), electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM), in addition to a description of the instrument parameters used.

The effects of stress relief heat treatment on the microstructure and mechanical properties of grades 91 and 92 steels are discussed in chapter 4. This chapter begins with a discussion of the effects of stress relief heat treatment on the hardness of 91 and 92 steels, and then describes the influence of stress relief heat treatment on the matrix microstructure changes using EBSD maps. The rest of the chapter describes the effects of stress relief heat treatment on the secondary phase particles using FIB images to quantify the changes in the precipitate distributions.

The effects of long-term aging on the 91 and 92 steels focussed on three aspects which were investigated and discussed. Firstly, the hardness values of 91 and 92 steels were measured, and the changes of these hardness values due to varying long-term aging times discussed. Secondly, the grain and subgrain structure of grade 91 and 92 steels have been extensively characterised with the use of electron backscatter diffraction (EBSD) in the scanning electron microscope. The changes in matrix microstructure and low/high angle grain boundary ratio of 91 and 92 steels due to varying long-term aging times have been investigated. Thirdly, the particle size distribution and chemical compositions of MX (includes VN and NbC) have been
characterised with the use of energy dispersive X-ray (EDX) in the transmission electron microscope (TEM), and the particle size distributions of $\text{M}_{23}\text{C}_6$ and Laves phase particles have been characterised separately with focused ion beam images (FIB) and backscatter electron images (BSE) in the dual-beam scanning electron microscope (FIB SEM).

Similarly, the effects of creep stress on the 91 and 92 steels were investigated and discussed with respect to three aspects. Firstly, the hardness values of 91 and 92 steels were measured, and the changes of these hardness values due to varying creep stress discussed. Secondly, the grain and sub-grain structures of grade 91 and 92 steels have been extensively characterised with the use of EBSD maps. The changes in matrix microstructure and low/high angle grain boundary ratio of 91 and 92 steels due to varying creep stress have been investigated. Thirdly, the particle size distribution and chemical compositions of MX after creep failure have been determined with the use of EDX in the TEM and the particle size distributions of $\text{M}_{23}\text{C}_6$ and Laves phase particles after creep failure have been characterised separately with FIB and BSE images using FIB SEM.

Finally, EBSD analysis as an assessment tool for material microstructural evolution of Grades 91 and 92 steels was investigated in Chapter 7. The chapter begins with an overview of the possible assessment tools for the microstructural evolution, then explains and compares a hardness analysis tool, a grain size analysis tool and EBSD analysis tool. This is then followed with a description and investigation of Kernel Average Misorientation (KAM) analysis, and how this KAM method can be used as an assessment tool for material microstructure evolution with respect to different stress relief heat treatments, isothermal aging and creep tests. At last, the conclusions and further work in this project are discussed in Chapter 8.
Chapter 2. Literature Review

This review first gives a brief description of the development history for 9 wt% advanced chromium steels and is then followed with an introduction to the common chemical compositions for different types of advanced chromium steels. It then considers the literature relevant to the various factors which affect the microstructure and chemical and mechanical properties of 9 wt% Cr power plant steels. These factors include the physical metallurgy, the secondary phases present in the martensitic-ferritic matrix, the effects of pre-service heat treatments, and the evolution of the microstructure under creep stress conditions 9 wt% Cr steels.

2.1 The Development of 9 wt% Cr Steels

In 1936, the basic composition of 9Cr-1Mo steel, P9, which had a high corrosion resistance, was developed for the oil industry [15]. In the late 1950s, the first development led to the steel 9Cr-2Mo-Nb-V, named EM12 [16]. This steel had up to 40% δ ferrite and exhibited high strength, however, it became brittle and had low rupture ductility during service at ~550°C. In the middle of the 1970s, steel P91 was developed for nuclear applications by Oak Ridge National Laboratories and Combustion Engineering Company based on the basic composition of the 9Cr-1Mo steel P9 [17]. By optimising the alloy composition with the addition of 0.2 wt% V, 0.06 wt% Nb and 0.05 wt% N, the creep resistance was improved markedly. In the 1980s, steel NF616, a tungsten alloyed 9 wt% steel, was invented by Prof. T. Fujita at Tokyo University. This steel was further developed and became a new ‘P92’ steel developed by Tokyo University together with Nippon Steel Corporation [18]. By the addition of 1.8 wt% W and 0.001 wt% B, and reducing the Mo content from 1 wt% to 0.5 wt%, a further improvement in creep resistance was obtained in the P92 steel. In 1992, steel E911 was developed in the European COST (Co-operation in Science and Technology) Action 501 based on the turbine rotor steel E [18]. This steel contains 1 wt% Mo and 1 wt% W, and has a similar creep resistance to P92. Currently new steels such as NF12 and SAVE12 are under development [18]. In these steels the W content has been increased and Co has been added to improve the creep resistance, which it is hoped will increase maximum operating temperature...
of the steel. The year of development, modification procedure, steel types and the maximum use temperatures of the major 9 wt% Cr steels that have been used in the power generation industry are shown in Table 2.1.

Typical chemical compositions, production details and heat treatments for the various 9 wt% Cr steels are given in Table 2.2 [1]. With the development of 9 wt% Cr steels, the mechanical properties for different steel variants changed significantly. The stress rupture strengths of the currently used and the new power station steels are compared based on the maximum service temperature for a 100,000 h stress rupture strength of 100 MPa, as shown in Figure 2.1 [1].

Figure 2.1 shows that the stress rupture strengths increased from 1Cr, 2.25 Cr, 9 Cr, 12 Cr, P91, E911 to P92, and for the latest steels (E911 and P92), the stress rupture strengths are very similar.

![Figure 2.1: Stress rupture strengths of the currently used and the new power station steels [1].](image-url)
### Table 2.1: The development of the 9 wt% Cr steels used in the power generation industry [18].

<table>
<thead>
<tr>
<th>Years</th>
<th>Steel modification</th>
<th>Steel</th>
<th>Max use temp. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1940-1960</td>
<td></td>
<td>P9</td>
<td>520-538</td>
</tr>
<tr>
<td>1960-1970</td>
<td>Addition of Mo, Nb, V to simple Cr – Mo steels</td>
<td>EM12</td>
<td>565</td>
</tr>
<tr>
<td>1985-1995</td>
<td>Partial substitution of W for Mo and add Cu, B</td>
<td>P92,</td>
<td>620</td>
</tr>
<tr>
<td></td>
<td></td>
<td>E911,</td>
<td></td>
</tr>
<tr>
<td>Future</td>
<td>Increase W and add Co</td>
<td>NF12,</td>
<td>650</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SAVE12</td>
<td></td>
</tr>
</tbody>
</table>

### Table 2.2: Details of 9 wt% Cr steels, chemical compositions in wt% [1].

<table>
<thead>
<tr>
<th>Element</th>
<th>P9</th>
<th>P91</th>
<th>P92</th>
<th>E911</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>88.69-89.64</td>
<td>89.35</td>
<td>87.70</td>
<td>87.73</td>
</tr>
<tr>
<td>C</td>
<td>Max. 0.15</td>
<td>0.10</td>
<td>0.124</td>
<td>0.105</td>
</tr>
<tr>
<td>Si</td>
<td>0.20-0.65</td>
<td>0.38</td>
<td>0.02</td>
<td>0.20</td>
</tr>
<tr>
<td>Mn</td>
<td>0.80-1.30</td>
<td>0.46</td>
<td>0.47</td>
<td>0.35</td>
</tr>
<tr>
<td>P</td>
<td>Max.0.03</td>
<td>0.020</td>
<td>0.011</td>
<td>0.007</td>
</tr>
<tr>
<td>S</td>
<td>Max.0.03</td>
<td>0.002</td>
<td>0.006</td>
<td>0.003</td>
</tr>
<tr>
<td>Cr</td>
<td>8.5-10.5</td>
<td>8.10</td>
<td>9.07</td>
<td>9.16</td>
</tr>
<tr>
<td>Mo</td>
<td>1.70-2.30</td>
<td>0.92</td>
<td>0.46</td>
<td>1.01</td>
</tr>
<tr>
<td>W</td>
<td>-</td>
<td>-</td>
<td>1.78</td>
<td>1.00</td>
</tr>
<tr>
<td>V</td>
<td>0.20-0.40</td>
<td>0.18</td>
<td>0.19</td>
<td>0.23</td>
</tr>
<tr>
<td>Nb</td>
<td>0.30-0.45</td>
<td>0.073</td>
<td>0.063</td>
<td>0.068</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>-</td>
<td>0.003</td>
<td>-</td>
</tr>
<tr>
<td>N</td>
<td>-</td>
<td>0.049</td>
<td>0.043</td>
<td>0.072</td>
</tr>
<tr>
<td>Ni</td>
<td>Max.0.30</td>
<td>0.33</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>0.034</td>
<td>0.002</td>
<td>-</td>
</tr>
</tbody>
</table>

Form and dimensions (mm):
- Pipe, Ø159, 20 wall thickness
- Pipe, Ø300, 40 wall thickness
- Flat bar, 100x16

Heat treatment:
- 1h/1050°C + 2h/1070°C + 1h/1050°C +
- 1h/750°C, 2h/775°C, 1h/750°C,
- Air cooled, Air cooled, Air cooled
2.2 The primary and secondary phases in 9% Cr steels

2.2.1 The Physical Metallurgy of 9% Cr Steels

2.2.1.1 The Fe-C System

Without any alloying additions in the microstructure, the carbon steels have a range of different crystal structures which change as a function of both temperature and carbon composition. Figure 2.2 shows the iron-carbon binary phase system which consists of ferrite (α), austenite (γ) and cementite (Fe3C). In this phase system, when heating the iron above 723°C, the ferrite phase, which has a body-centred cubic structure (bcc), changes to the austenite phase, which has a face-centred cubic structure (fcc). By heating a pure hypo-eutectoid iron-carbon alloy (<0.8 wt% Carbon) to the austenite temperature range, the simplest carbide in steel, cementite phase (Fe3C) disappears as the solid solubility of carbon in iron increases [19].

2.2.1.2 The Fe-Cr-C system

After the addition of Cr into steel, a more complex Fe-Cr-C system is produced. In this system, different equilibrium phases can be present in the microstructure depending on composition and temperature. Figure 2.3 shows a vertical section through the Fe-Cr-C phase diagram. It is shown that chromium is a ferrite stabilizing element, and there is the possibility that a range of Cr-based carbides (M7C3, M23C6) may form in the microstructure [20].

Figure 2.2: The iron-carbon binary phase system [19].
The equilibrium microstructure consists of ferrite and carbides at the typical tempering temperature, ~750°C and the typical service temperature below 600°C. In the process of normalising at ~1050°C, the Cr-based carbides start to dissolve, the Fe phase transforms from $\alpha$ to $\gamma$ phase. To improve the stability of austenite or ferrite, or reduce the possibility of delta ferrite phase formation during normalizing, other alloying additions are added to this class of steels. These alloying additions are discussed in detail in Section 2.2.1.4.

2.2.1.3 Martensite
The matrix phase that is most widely used in service in 9 wt% Cr steel is martensite. The martensite phase is formed from austenite after rapid cooling (quenching), which traps carbon atoms that do not have time to diffuse out of the crystal structure. This martensitic transformation begins during cooling when the austenite reaches the
martensite start temperature ($M_s$) and the parent austenite becomes mechanically unstable [3]. The continuous cooling transformation diagrams of Grade 91 and 92 steels are shown in Figure 2.4, which describes the martensite transformation procedure relate to temperature and cooling time.

Figure 2.4: The continuous cooling transformation diagrams of Grade (a) 91 and (b) 92 steels [17,18].
Figure 2.5 shows the shape change of reference lines and crystal with martensite transformation [21]. If a small region ending inside the crystal is sheared as in Figure 2.5(b), there are two sources of strain energy. One is the strain set up in the matrix due to the shearing of only part of the cross section. The second is due to the mismatch of the two lattices across the martensite matrix interface. For the purposes of simplicity the first source has normally been ignored, since in principle it can be avoided by letting the interface cover the entire cross section, as is shown in Figure 2.5(c and d). The strain due to mismatch across the interface is unavoidable in a large piece and thus always influences the mode of transformation.

![Figure 2.5: Shape change of reference lines and crystal with martensite transformation [21].](image)

To explain this theory of the martensite habit plane, note first that the simplest lattice distortion which can accomplish the austenite-martensite transformation is shown in Figure 2.6 [22].
Figure 2.6: (a) fcc lattice showing alternative bct unit cell. The x’s mark the positions of interstitial atoms in the austenite and their locations in the martensite, (b) Austenite and martensite unit cells [22].

This figure illustrates how the martensitic body-centred tetragonal (bct) cell is produced from the austenitic fcc cell without rearrangement of the atoms. Figure 2.6(a) shows two unit cells of the fcc lattice with a bct cell inscribed as an alternative description of the lattice. Figure 2.6(b) shows the bct cell of austenite and the bct cell of martensite. The lattice distortion or deformation involved in going from austenite to martensite is the difference between the two cells in Figure 2.6(b). This is often referred to as the Bain distortion after the man who first suggested it [22].

Martensite is not as stable as the austenite phase, so the carbon will diffuse out of the lattice and form carbides with iron and/or other carbide forming elements on subsequent reheating. This process during reheating gives rise to precipitation strengthening and an improvement in creep strength. Conversely, the high dislocation density present in virgin martensite results in a high level of stored energy in the microstructure. This stored energy may promote the process of recovery when the materials are exposed to typical operating conditions for prolonged time periods. Recovery of the high energy dislocation structure is shown as subgrain formation and growth, which is discussed in more detail in later sections.
2.2.1.4 Alloying Addition Elements

The chemical composition range of grades P91 and P92 steel is shown in Table 2.2. Chromium is the major alloying element in this steel; the presence of Cr has several interesting effects. Generally, it greatly improves the hardenability of the steel to a point where 9 wt% Cr steels become air hardenable to achieve a fully martensitic structure. It is also a strong ferrite stabiliser, and also a very strong carbide former which encourages the strengthening of steels by precipitation hardening. It also forms the basis for the corrosion resistance of stainless steels, as it forms a protective oxide on the surface of steel, which self-repairs in the presence of oxygen if the steel is damaged mechanically or chemically, and thus retards the effects of high temperature oxidation and corrosion.

Carbon occupies interstitial sites in ferrite and austenite, with a much greater solubility in the latter. Increasing the carbon content strongly encourages the precipitation of carbide phases. In general, the higher the content of carbon in steel, the more difficulties which can arise when it comes to welding as it tends to promote cracking in the heat affected zone region. This is an important issue for 9 wt% Cr steel power station components.

Nitrogen is found in relatively high quantities and initially exists as an interstitial element like carbon. The main purpose of nitrogen is to combine with certain elements such as vanadium and niobium to form nitrides, which strengthen the steel by precipitation hardening. Nitrogen is also an austenite stabilizing element.

Molybdenum is a ferrite stabilizing element and carbide former. It increases the hardenability of steel and reduces the risk of temper embrittlement. It is present in 9 wt% Cr steels primarily to increase strength by solid solution strengthening. Figure 2.7 shows how the hardness of the Fe-C-Mo alloys varies with the molybdenum content [23]. Molybdenum also forms carbide particles that are stable at temperatures higher than those used in service and thus tends to yield a fine grain structure. Molybdenum is a favoured alloying element because it increases the strength at a relatively low cost.
Nickel is an austenite stabilizing element and, unlike the other metallic additions added to 9 wt% Cr steels; it does not tend to form carbides. It suppresses the formation of delta-ferrite at the high normalizing temperatures employed. Strang and Vodarek [24] found that increasing the nickel content caused an increase in the coarsening rate of M\textsubscript{23}C\textsubscript{6} particles in 12CrMoVNb steel.

Vanadium is one of the most widely used precipitation strengthening additions in steel, and like other micro-alloying elements, it has a strong affinity for carbon and nitrogen while at the same time it exhibits a high solubility in austenite at temperatures as high as 1150°C. This is important because it must remain in solution at normalizing temperatures, until it precipitates as carbon nitride particles during tempering, in order to maximize its contribution to precipitation strengthening. As it is a very expensive alloying element, its presence in the steel must be utilized effectively. It is also a ferrite stabilizing element.
Niobium can significantly increase the yield strength and slightly increase the tensile strength of carbon steel in small quantities. This element can also have a moderate precipitation strengthening effect. Its main contribution is to form carbide particles above transformation temperatures, and to retard the recrystallisation of austenite, thus promoting a fine-grained microstructure. It is also a ferrite stabilizing element.

2.2.2 The Secondary Phases Present in 9% Cr Steels

Pure binary carbides do not occur in steels due to the fact that there is always some solubility of the alloying elements in the various carbide phases [25]. There are many sites in the microstructure where carbide nucleation and growth can occur. These include dislocations in the martensite matrix or intra-lath boundaries, prior-austenite grain boundaries and even at pre-existing carbide particles, all of which are high energy sites that are energetically favourable for the formation of carbides, as they provide high diffusivity paths for the rapid diffusion of interstitial atoms such as carbon and nitrogen. Another peculiarity with carbides in steels is that they may not be thermodynamically stable [26], and so are referred to as metastable. As a consequence, during the initial stages of tempering the first carbides to form are not necessarily the most stable carbides, as on further heating, these may be gradually replaced by more stable ones at higher temperatures either at the same location of the less stable carbides or separately away from the dissolving carbides [25]. Table 2.3 shows the carbides in the Fe-Cr-C system.

2.2.2.1 M₃C Particles

M₃C, better known as cementite, is a chemical compound with the formula Fe₃C (or Fe₂C: Fe), and is an orthorhombic crystal structure with lattice parameters of a=0.4510 nm, b=0.5040 nm and c=0.6730 nm. It is a hard, brittle material, and in carbon steel, it either forms from austenite during cooling or from martensite during tempering. In 9 wt% Cr steel, the precipitation of fine (Fe, Cr)₃C particles within the martensite laths are formed as a result of air cooling from a normalizing temperature of around 1045°C [28]. Kuo [25] argues that the M₃C phase tends to be replaced by more stable carbides at higher temperatures, such as M₇C₃, M₇C₃ and M₂₃C₆, since chromium has a higher affinity for carbon than iron.
Table 2.3: Carbides in the Fe-Cr-C system. The composition of the metal portion, M, of the carbide is left unspecified. The density and the lattice parameter of different carbides will vary with respect to chemical composition [27].

<table>
<thead>
<tr>
<th>Carbide</th>
<th>Structure</th>
<th>Lattice Parameters/Å</th>
<th>Formula Units/Cell</th>
<th>Density/ g·cm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td>M₃C</td>
<td>Orthorhombic</td>
<td>a=4.5241, b=5.0883, c=6.7416</td>
<td>4</td>
<td>7.704</td>
</tr>
<tr>
<td>M₇C₃</td>
<td>Trigonal</td>
<td>a=13.982, c=4.506</td>
<td>8</td>
<td>6.965</td>
</tr>
<tr>
<td>M₂₃C₆</td>
<td>Cubic F</td>
<td>a=10.638</td>
<td>4</td>
<td>6.996</td>
</tr>
<tr>
<td>M₆C</td>
<td>Cubic F</td>
<td>a=11.082</td>
<td>16</td>
<td>6.325</td>
</tr>
<tr>
<td>M₂C</td>
<td>Hexagonal</td>
<td>a=3.002, c=4.724</td>
<td>1</td>
<td>9.188</td>
</tr>
</tbody>
</table>

The dissolution of cementite occurs in two stages. Firstly, the composition of Cr in Fe₃C keeps increasing until reaching a saturation value of about 20 at%. Secondly, Fe₃C is replaced by Cr₇C₃ or Cr₂₃C₆, which is accompanied by a large increase of Cr in the carbide.

2.2.2.2 M₇C₃ Particles
M₇C₃ is a Cr-rich precipitate with a trigonal crystal structure with lattice parameters of a=0.1398 nm and c=0.4523 nm [29]. This phase is formed by the reaction of M₃C with the matrix at higher tempering temperatures due to the ready supply of chromium and carbon. However, it is difficult to find the presence of M₇C₃ in high Cr steels due to the fast transformation from M₇C₃ to M₂₃C₆.

2.2.2.3 M₂C Particles
M₂C, or Mo₂C is a molybdenum-rich carbide and has a close-packed hexagonal (cph) structure with a lattice parameter of a=0.3002 nm and c=0.4724 nm [27]. The M₂C particles reduce the creep resistance of the 9 wt% Cr steel by removing Mo from within subgrain regions, which would act as a solid solution strengthening element [30].
2.2.2.4 \textit{M}_6\textit{C} Particles

\textit{M}_6\textit{C}, like \textit{M}_2\textit{C}, is also a molybdenum-rich carbide and has a fcc structure with a lattice parameter of \(a=0.1108\) nm [25]. It tends to form at ferrite grain boundaries rather than transform from previous existing carbides. With different proportions of Mo, the phase can exist as \(\text{Fe}_4\text{Mo}_2\text{C}\), \(\text{Fe}_2\text{Mo}_4\text{C}\) and \(\text{Fe}_3\text{Mo}_3\text{C}\) in a simple Fe-Mo-C ternary system [26].

2.2.2.5 \textit{M}_{23}\textit{C}_6 Particles

\textit{M}_{23}\textit{C}_6 forms at higher tempering temperatures than \textit{M}_7\textit{C}_3 and Kuo [25] found it is the main or only carbide phase (out of \textit{Fe}_3\textit{C} and \textit{M}_7\textit{C}_3) to be present in 9 wt\% Cr steel at tempering temperatures higher than 700°C. This phase has a fcc structure and may vary in chemical composition depending on the different alloying elements in the steel. These \textit{M}_{23}\textit{C}_6 carbides contain Cr, and also may contain Fe, V, Mo and Ni [29].

\textit{M}_{23}\textit{C}_6 carbide does not form in the steel microstructure before the tempering heat treatment and only be transformed from less stable carbides such as \textit{M}_2\textit{X} and \textit{M}_3\textit{C}. After tempering heat treatment, \textit{M}_{23}\textit{C}_6 carbide forms from those unstable carbides on primary boundaries and some exist within laths or subgrains [31]. According to the position of \textit{M}_{23}\textit{C}_6 carbide formation, \textit{M}_{23}\textit{C}_6 particles may produce a hardening effect on the creep strength of the 9 wt\% Cr steel by the prevention of subgrain boundary motion, by impeding knitting reactions between free dislocations and subgrain boundaries, and also by pinning sub-boundary dislocations [32].

It has been shown that with increasing high temperature ageing and creep strain, the coarsening of \textit{M}_{23}\textit{C}_6 particles occurs in the creep experiments on 12 wt\% Cr steels [24]. The grain boundary pinning ability of these \textit{M}_{23}\textit{C}_6 particles is reduced as the creep exposure process advances, and therefore, reducing the mechanical properties of high temperature power plant components in service. In addition, these \textit{M}_{23}\textit{C}_6 particles are primarily responsible for the pinning of lath boundaries, so the lath interfaces mobility increases as the coarsening and spheroidisation of the \textit{M}_{23}\textit{C}_6 particles proceeds.

2.2.2.6 \textit{MX} Particles

\textit{MX} particles have a fcc crystal structure and can be either carbides or nitrides, depending on whether the “\textit{X}” is carbon or nitrogen, and the “\textit{M}” is normally chromium, vanadium or niobium. \textit{MX} particles also form during tempering, similar to
M\textsubscript{23}C\textsubscript{6} particles. Since MX particles only tend to dissolve at much higher temperatures than those experienced under typical power plant operating conditions, these particles are very important for the long-term creep strength of 9 wt% Cr steels. MX particles stabilise the subgrain boundary network and also impede knitting and absorption reactions at free dislocations and subgrain boundaries [33].

Both niobium and vanadium rich MX particles are known to be present in 9 wt% Cr steels such as grade 91 and 92, and the chemical compositions vary with the compositions of the steel and heat treatment cycles [33]. MX particles are referred to as (V, Nb)(N, C), and are normally classified into VN and NbC. VN has a lattice parameter of $a = 0.4139$ nm and NbC has a lattice parameter of $a = 0.4469$ nm [34]. However, some N atoms in VN and C atoms in NbC can be substituted with C and N, respectively, which results in the lattice parameter values changing slightly with varying compositions and heat treatments.

There are four types of MX particles, and as well as forming during pre-service heat treatments, MX particles also tend to form during the long-term or creep exposure to service conditions, known as secondary particles. Coarse primary NbX particles remain from the normalising heat treatment [35]. Fine platelet VX and fine spherical NbX particles form during tempering heat treatment [36]. The VX ‘wing-like’ particles, where plate-like vanadium carbonitride particles attach themselves to spherical Nb(C, N) particles, are formed during creep test procedure [36]. The MX particles, except the primary NbX, are typically fine and distributed uniformly within subgrains as well as on sub-boundaries.

2.2.2.7 Laves Phase

Laves phase is an intermetallic phase which particles most commonly in prior-austenite and subgrain boundaries, and also in areas near M\textsubscript{23}C\textsubscript{6} particles [37]. It has the composition Fe\textsubscript{2}M, where the ‘M’ can either be Mo, W or both. This phase tends to form during high temperature creep conditions, such as in high temperature service. It is found that the average size of the Laves phase particles increase sharply during the first 2,000h and then the growth rate retards over longer time periods [38].

Laves phase may have either an improved or reduced effect on the creep resistance properties of 9 wt% Cr steel. On the one hand, the formation of Laves phase
removes the Mo and W elements, which could be effective solid solution strengtheners, from the matrix phase. This can act as a softening process, which reduces the creep resistance of 9 wt% Cr steel. On the other hand, small Fe$_2$M particles which precipitate on subgrain boundaries can act as precipitation strengtheners to improve the creep resistance of 9 wt% Cr steel.

2.2.2.8 *Summary of Secondary Phases present in 9 wt% Cr Steels*

As discussed in the previous section, there are a number of precipitate phases present in 9 wt% Cr steels and certain characters, such as chemical composition, size, distribution and morphology, are important for determining creep strength and are very much dependent on varying temperature conditions, applied creep stress and different bulk material compositions. However, it was found that the major phases present after creep at 650°C, are M$_{23}$C$_6$ particles (mainly Cr$_{23}$C$_6$), MX particles (mainly V(C,N)) and Laves phase. In 9 wt% Cr creep resistant steels, increasing the working temperature reduces the long-term creep and mechanical properties, in particular due to coarsening of MX carbonitrides, as well as precipitation, growth and coarsening of Laves phase [39, 40]. A summary of the particles present in 9 wt% Cr creep resistant steels and stages of thermal history at which they form are shown in Table 2.4.

**Table 2.4:** Particles present in 9 wt% Cr creep resistant steels and remarks on their formation characteristics [13].

<table>
<thead>
<tr>
<th>Steel</th>
<th>Precipitate</th>
<th>Formula</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>P91</td>
<td>M$_{23}$C$_6$</td>
<td>(Cr,Fe,Mo)$_{23}$C$_6$</td>
<td>Particles during tempering</td>
</tr>
<tr>
<td></td>
<td>MX</td>
<td>(Nb,V)(C,N)</td>
<td>Undissolved during normalizing</td>
</tr>
<tr>
<td></td>
<td>MX</td>
<td>(V, Nb)(N, C)</td>
<td>Particles during tempering</td>
</tr>
<tr>
<td></td>
<td>Laves phase</td>
<td>(Fe,Cr)$_2$Mo</td>
<td>Particles during creep(T&lt;650°C)</td>
</tr>
<tr>
<td>P92</td>
<td>M$_{23}$C$_6$</td>
<td>(Cr,Fe,Mo)$_{23}$C$_6$</td>
<td>Particles during tempering</td>
</tr>
<tr>
<td></td>
<td>MX</td>
<td>(Nb,V)(C,N)</td>
<td>Undissolved during normalizing</td>
</tr>
<tr>
<td></td>
<td>MX</td>
<td>(V, Nb)(N, C)</td>
<td>Particles during tempering</td>
</tr>
<tr>
<td></td>
<td>Laves phase</td>
<td>(Fe,Cr)$_2$(Mo,W)</td>
<td>Particles during creep(T&lt;720°C)</td>
</tr>
</tbody>
</table>

2.3 *Influence of Heat Treatment on 9% Cr Steels*

Heat treatment is the controlled heating and cooling of metals to alter their physical and mechanical properties without changing the product shape. Heat treatment is often associated with increasing the strength of material, but it can also be used to alter certain manufacture objectives such as improved machining, improved formability, and to restore ductility after a cold working operation. Steels are particularly suitable for heat treatment, since they respond well to heat treatment and
the commercial use of steels exceeds that of any other material. Castings or forging based forming processes can be used to produce 9 wt% Cr steel components for high temperature power plant applications. After these processes the steel components are typically subjected to a two-stage heat treatment in order to improve the creep resistance. This heat treatment consists of a normalizing treatment and a tempering treatment. The changes in temperature and duration of this heat treatment process can affect the microstructure of 9 wt% Cr steels, such as the tempered martensite microstructure formed in the 9 wt% Cr steel, shown as Figure 2.8 [43]. These heat treatments are discussed in the following sections. For some 9 wt% Cr power plant steel components, a pre-service stress relief heat treatment is applied to remove or reduce the residual stresses, which are generated from permanent remaining strains during the steel components manufacturing process.

![Figure 2.8: Tempered martensite in steel P92. (a) Light optical micrograph of P92-AR-1 Sample; (b) Transmission electron micrograph [41].](image)

### 2.3.1 Normalizing

The normalizing treatment is applied to remove all of the particles which exist in the matrix from prior forming processes, then air cooling to produce a fully hardened martensitic structure. Due to the high chromium and molybdenum content, this microstructure can be formed in sections up to about 1000 mm in thickness [41]. The suitable normalizing temperatures have been suggested to be between 1050°C and 1100°C, and after air cooling, a hardness range of 400 to 420 HV is achieved [42,43]. The martensitic structure produced from the normalizing treatment is influenced greatly by the temperature, which means both under- and over-normalizing can
affect the creep properties, and reduce the service life of power plant components. Orr and Burton [42] observed that as the normalizing temperature increases from 1050°C to 1100°C, the strength of 9 wt% Cr steel increases by 10-15%. The reason is that at the higher temperature more carbides and nitrides are dissolved during the normalizing treatment. Figure 2.9 shows how the as-tempered hardness changes with the normalizing temperature [44]. Under-normalizing means less particles are dissolved during the normalizing process, and then retained in the new martensite microstructure. These retained particles can reduce the creep strength of the steel, and hence reduce the service life of power plant components. The effects of under-normalizing are difficult to detect due to the very small changes in the hardness values or the microstructure of the as-normalized sample.

However, over-normalizing may result in grain growth, heterogenous grain sizes and the formation of delta ferrite, which are considered to have a detrimental effect on the mechanical properties of the 9 wt% Cr steel. The effects of over-normalizing are thus very easy to detect by observing the grain sizes or delta ferrite phase using the Optical Microscope.

A study undertaken by Borggreen [45] on P91 steel showed that the relationship between ASTM grain size and normalizing temperature is almost linear, as shown in Figure 2.10. (The value of ASTM grain size, which decreases with the matrix grain

![Figure 2.9: The relationship between hardness of an as-tempered (1h/750°C) sample and normalizing temperature [44].](image-url)
size increase, is calculated by the number of grains within a square inch at 100X magnification). The normalizing temperature can also affect the width of martensite laths. Ennis et al [46] showed in their experiments on P92 steel that normalizing temperatures of 970°C, 1070°C and 1145°C resulted in lath widths of 0.38 nm, 0.42 nm and 0.58 nm respectively. However, the normalizing temperature affects the secondary phases in the 9 wt% Cr steel as well. Maile [6] observed that a high normalizing temperature is responsible for a reduction of M23C6 particles per unit area, but also for an increase in V-rich MX particles per unit area and the size of such particles, shown in Figure 2.11 (all results depicted in this graph have been normalised on the reference state).

![Figure 2.10: Effects of normalizing temperature on the ASTM grain size of P91 steel [45].](image)

![Figure 2.11: (a) Influence of normalizing temperature below standard value and (b) Influence of normalizing temperature above standard value on the mean size and particle density of M23C6 carbide and V rich-MX nitride in P91 steels [6].](image)
2.3.2 Tempering

Tempering is the second stage of the heat treatment cycle, and this process has two main benefits to the 9 wt% Cr steels. Firstly, it can diffuse out the carbon that is trapped in a supersaturated solid solution in the matrix phase of steel to relieve internal residual stresses in the material, which improves the ductility and toughness of the steel. Secondly, it can induce the precipitation of carbide and nitride particles with alloying elements such as chromium, vanadium and niobium.

A suitable tempering temperature has been suggested to be between 750°C and 800°C [6] in order to promote precipitation strengthening for most 9 wt% Cr steels. As the steel is reheated, the carbon that was trapped in the supersaturated solid solution diffuses and forms carbides. At the low temperatures, these carbides are unstable cementite particles. When the temperature increases to 500-700°C, the carbide forming elements such as chromium, vanadium, niobium and molybdenum diffuse into the particles and form fine and stable particles which then replace the less stable cementite particles.

As a result of the tempering process, a tempered martensitic structure is formed in the material. This microstructure is strengthened by M$_{23}$C$_6$ (Cr-carbide) and MX ((V,Nb)-nitride) particles precipitation on prior austenite grain boundaries, ferrite subgrain boundaries and on dislocations inside subgrains in the steels. The typical microstructure of a tempered 9 wt% Cr steel and the relative carbide and nitride particles are shown in Figures 2.12 and 2.13 [31].

Ennis found in his research that the hardness of P92 is insensitive to normalising temperature between 970 and 1145°C (~440 HV$_5$). The hardness of P92 decreases as the tempering temperature increases, the difference in the normalising temperature did very limited effect, as shown in Figure 2.14 [31].
Figure 2.12: Bright field TEM micrograph of a thin foil from a sample normalized at 970°C and tempered at 775°C showing large M$_{23}$C$_6$ particles on subgrain boundaries with a high dislocation density within the subgrains [31].

Figure 2.13: Bright field TEM micrograph of thin foil normalized at 970°C tempered at 775°C showing spheroidal Nb-rich M(C,N) and complex M(C,N) particles [31].
The tempering temperature also affects the carbide and nitride particles. Maile [6] found that a tempering temperature (850°C) exceeding the standard (750-800°C) increases the mean sizes of both the carbide and nitride particles. However, the V rich-MX particle density is reduced significantly, while only a limited change in the M$_{23}$C$_6$ particle density is observed, as shown in Figure 2.15 (all results depicted in this graph have been normalised on the reference state).

Figure 2.14: The relationship between hardness of P92 and various tempering temperatures [31].

Figure 2.15: The influence of tempering temperature on the mean size and particle density of M$_{23}$C$_6$ carbide and V rich-MX nitride in P91 steels [6].
2.3.3 Stress Relief Heat Treatment

Machining of large castings, complex parts or weldments induces a lot of residual stress, which can cause distortions during long-term service. If the parts are clamped in service, then cracking could occur. For these reasons, stress relieving is often necessary for these special components, such as 9 wt% Cr welds or bulk power plant components.

Residual stresses that remain locked in a structure as a consequence of manufacturing processes are most commonly reduced by heat treatment, and only in some special cases, can also be reduced by mechanical stress relieving (e.g. pre-stretching). P. Sekdek and J. Brozda [47] carried out an experimental study on welded joints of dissimilar steels and found that residual stresses in welded joints of dissimilar steels cannot be reduced by heat treatment due to the difference in the thermal expansion coefficients between ferritic and austenitic steels. The normal stress relief heat treatment procedure is to uniformly heat a structure to a sufficiently high temperature, but below the lower transformation temperature range, and then to uniformly cool it, which can then relax these residual stresses.

Stress relief heat treatment also offers several benefits. For example, when a component with high residual stresses is machined, the material tends to move during the metal removal operation as the stresses are redistributed. After stress relieving, however, greater dimensional stability is maintained during machining, providing for increased dimensional reliability. In addition, the potential for stress corrosion cracking is reduced, and the metallurgical structure can be improved through stress relieving. In this case, the steel becomes softer and more ductile through the precipitation of iron carbide at temperatures associated with stress relieving.

The temperatures used for stress relief heat treatment have important consequences for the mechanical properties and residual stresses. A. G. Olabi and M. S. J. Hashmi [48] studied the effects of various stress relief temperatures (550°C, 650 °C and 750 °C) on the mechanical properties and residual stresses of aircraft engine components made of AISI 410 high-chromium steel. In their study, it was found that the hardness values at the depth of 1 mm in the HAZ were reduced by about 10% after stress relief at 550°C, 35% at 650°C and 40% at 750°C, indicating that the
hardness decreases as the stress relief temperature increases [48]. It has also been found that the maximum residual stress level has been reduced by about 50% at 550°C, by about 70% at 650 °C and completely relieved at 750 °C, indicating that the reduction of residual stress increases as the stress relief temperature increases [48].

The mechanical properties and residual stresses are also affected significantly by the stress relief durations. G. Choudhuri and D. Srivastava [49] have found in their study that a progressive increase in coherent domain size and decrease in dislocation density occurred during extended stress relieving at 400°C (36 and 96h). A. G. Olabi and M. S. J. Hashmi [50] studied the effects of various stress relief durations (0.5 h, 2 h and 10 h) at 550°C on the mechanical properties and residual stresses of aircraft engine components made of AISI 410 high-chromium steel. In their study, it was found that the hardness values at the mid thickness is reduced from 410 HV to 380 HV to 320 HV as the stress relief durations increase from 0.5 h to 2 h to 10 h. This indicates that the hardness decreases as the stress relief time increases, as shown in Figure 2.16 [50]. It has been also found that the maximum residual stress level decreases as the stress relief time increases, as shown in Figure 2.17 [50].

![Figure 2.16](image_url)

*Figure 2.16: The hardness variation after stress relief over the sample thickness with three different time durations [50].*
2.4 Creep Behaviour and Microstructural Stability of 9% Cr Steels

The microstructure of 9% Cr steels is very complex, with carbide or nitride secondary phases contained within a matrix consisting of ferrite, martensite and possibly retained austenite. The microstructure formed is sensitive to various parameters, in particular the pre-service heat treatments and minor composition variations. In this section, the relationship between the creep rupture strength and microstructural stability of 9% Cr steels will be reviewed, as well as the creep strengthening mechanisms of 9% Cr steels.

2.4.1 Creep Behaviour

Creep is the tendency of a solid material to slowly move or deform permanently under the influence of stress. It occurs as a result of long term exposure to levels of stress that are below the yield strength of the material. The rate of this deformation is a function of the material properties, exposure time, exposure temperature and the applied structural load. Depending on the magnitude of the applied stress and its duration, the deformation may become so large that a component can no longer perform its function. For example, creep of a turbine blade could cause the blade to contact the casing, resulting in the failure of the blade. Therefore, a comprehensive database of long-term creep test results on industrial products was developed before using the 9 wt% Cr steels in power plant applications. In Europe long-term creep tests have been carried out and coordinated by the European Creep Collaborative
Committee (ECCC), and Table 2.4 shows worldwide data collations of E911, P91 and P92 steels resulting in extensive databases made by ECCC [41].

As already mentioned, the driving force in the development of 9% Cr steels is to achieve improved creep properties, it is therefore essential to understand the creep behaviour and the relationship between creep behaviour and related parameters, such as applied stress and service temperatures.

**Table 2.4:** ECCC database statistics of 91 and 92 steels, which showing creep performance as a function of temperature [41].

**P91-2005**

<table>
<thead>
<tr>
<th>Test temperature °C</th>
<th>Number of test results in time interval</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;10,000h</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------</td>
</tr>
<tr>
<td>500</td>
<td>71(6)</td>
</tr>
<tr>
<td>525</td>
<td>3(3)</td>
</tr>
<tr>
<td>550</td>
<td>262(11)</td>
</tr>
<tr>
<td>575</td>
<td>58(1)</td>
</tr>
<tr>
<td>600</td>
<td>524(7)</td>
</tr>
<tr>
<td>625</td>
<td>57(1)</td>
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<tr>
<td>650</td>
<td>358</td>
</tr>
<tr>
<td>675</td>
<td>6</td>
</tr>
<tr>
<td>700</td>
<td>40</td>
</tr>
</tbody>
</table>

Parentheses denote unbroken tests  Total testing hours: **17,852,130**

**P92-2004**

<table>
<thead>
<tr>
<th>Test temperature °C</th>
<th>Number of test results in time interval</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>&lt;10,000h</td>
</tr>
<tr>
<td>----------------------</td>
<td>----------</td>
</tr>
<tr>
<td>550</td>
<td>92</td>
</tr>
<tr>
<td>575</td>
<td>9(1)</td>
</tr>
<tr>
<td>600</td>
<td>196(3)</td>
</tr>
<tr>
<td>625</td>
<td>33</td>
</tr>
<tr>
<td>650</td>
<td>211(1)</td>
</tr>
<tr>
<td>675</td>
<td>18</td>
</tr>
<tr>
<td>700</td>
<td>122</td>
</tr>
<tr>
<td>750</td>
<td>17</td>
</tr>
</tbody>
</table>

Parentheses denote unbroken tests  Total testing hours: **7,036,945**
2.4.1.1 Steady State Creep Behaviour

The relationship between steady state creep strain rate $\dot{\varepsilon}$ and applied stress $\sigma_a$ at high temperatures of pure metals and solid solution alloys is shown by Dorn’s relationship [51]

$$\dot{\varepsilon} = AD \mu b/(kT) (\sigma_a /\mu)^n, \quad \text{(1)}$$

with $D=D_0 \exp(-Q/RT)$, where $D$ is the lattice self-diffusion coefficient, $D_0$ is the frequency factor, $Q$ is the activation energy, $R$ is the gas constant, $\mu$ is the shear modulus, $b$ is the Burgers vector, $k$ is Boltzmann’s constant, $n$ is the stress exponent, $T$ is the temperature and $A$ is a dimensionless constant. Further, the recovery creep theories are well interpreted by Eq. (1) when the observed value of $n$ is between 4 and 5 and the activation energy is nearly equal to that of the self-diffusion process. However, for particle and precipitation strengthened alloys, Eq. (1) gives rise to unrealistically high values of the stress exponent and apparent activation energy [51]. This can be solved by rationalizing in terms of effective stress using;

$$\dot{\varepsilon} = A_0D \mu b/(kT) [(\sigma_a - \sigma_R )/\mu]^{n_0}, \quad \text{(2)}$$

where $\sigma_R$ is the threshold or resisting stress associated with the operative particle-by-pass mechanism, $n_0$ is the modified stress exponent equal to about 4 and $A_0$ is a dimensionless constant.

2.4.1.2 Creep Rate and Relative Parameters

The creep strain rate $\dot{\varepsilon}$ as function of time $t$ under different stresses at 600°C on 9Cr-1Mo steel is shown in Figure 2.18 [52]. The creep rate decreases as the time increases until the minimum creep strain rate $\dot{\varepsilon}_m$ is reached, then increases sharply to rupture. At the same test time, the creep rate decreases as the stress reduces from 200 MPa to 130 MPa.
Figure 2.18: Strain rate $\dot{\varepsilon}$–time $t$ curve at 600°C on 9 Cr-1Mo steel [52].

Figure 2.19 shows the minimum creep strain rate as a function of the applied stress $\sigma$ at different temperatures. The $\dot{\varepsilon}_m$ dependence on $\sigma$ can be simplified as:

$$\dot{\varepsilon}_m = A(T) \sigma^n$$  \hspace{1cm} (3)

where $A(T)$ is a temperature dependent parameter and $n$ is the stress exponent. As the stress increases, the minimum creep strain rate increases with a gradient of 10. At the same stress, the minimum creep strain rate increases as the temperature increases from 848 K to 923 K.
2.4.2 Creep Strengthening Mechanisms

9% Cr steels have been used successfully under ultra-super critical steam conditions at 600°C, and have the potential to be used at 625°C, although further improvement of creep strength is necessary for this advancement. In the 9% Cr steels, there are several types of obstacles to dislocation motion, which are sub-boundaries, free dislocations within subgrains, and secondary carbide and nitride particles. In this section, three creep strengthening mechanisms, which are solution hardening, particle hardening and dislocation hardening attributed to these obstacles, are discussed.

2.4.2.1 Solution Hardening

Solution strengthening has often been referred to in discussions of the effect of Mo and W on creep strength of 9% Cr steels. In Maruyama’s studies, minimum creep rates of α iron (0.001% C) and Fe (0.001% C)-2.3% W alloy are compared in Figure 2.20 [53]. In this figure, the W addition reduces the creep rate by three orders of magnitude, which proves that the solution hardening is effective if the dislocation hardening and the particle hardening are absent. However, Hald [41] mentioned that

![Figure 2.19: Minimum creep rate $\dot{\varepsilon}_m$ as a function of the applied stress on 9 Cr-1Mo steel [52].](image)
during creep exposure at around 600-650°C most of the Mo and W in the steels will precipitate as the intermetallic Laves phase \(((\text{Fe,Cr})_2\text{(Mo,W)})\). This would cause creep instability in the steels because the solution strengthening effect from Mo and W would be lost, and the precipitation strengthening effect from Laves phase is believed to be insignificant.

**Figure 2.20:** Minimum creep rates of ferritic steels at 600°C [53].

### 2.4.2.2 Particle Hardening

There are many kinds of carbide and nitride particles in the 9% Cr steels; normally particle hardening is dominated by the MX particles within subgrains and M\(_{23}C_6\) and Laves phase on sub-grain boundaries. As is evident in Figure 2.20, the creep rate of α iron is reduced significantly by introducing MX particles into the FeVNbC steel. This result proves that particle hardening occurs from the MX particles within subgrains, however, two possible mechanisms for it have been proposed. The first theory is that MX particles themselves act as obstacles to dislocation motion [54], and the second is that they slow down recovery of the dislocation substructure and retain the dislocation hardening for longer durations [35].

By comparing creep curves of 9Cr-0.1C steel having M\(_{23}C_6\) particles on sub-boundaries and of 9Cr-2Ni steel without particles, Maruyama [53] concluded that the M\(_{23}C_6\) particles improve creep resistance by slowing down the recovery of the dislocation substructure [54]. Igarashi and Sawaragi [55] have studied creep of 9%
Cr steel with Fe$_2$M particles but without M$_{23}$C$_6$ and MX particles, and have confirmed an increase in creep resistance by the Fe$_2$M particles.

2.4.2.3 Dislocation Hardening
Dislocation hardening is based on the presence of sub-boundaries and free dislocations. This hardening mechanism is confirmed by considering Figure 2.20 where Fe-9Cr-VNbCN with the dislocation substructure and Fe-VNbC without the dislocation substructure have widely different performance. However, Maruyama [53] also discussed that the dislocation substructure cannot reduce the minimum creep rate without particles and solute atoms, since the dislocation substructure cannot be retained during creep without these obstacles. Therefore, particles and/or solute atoms are necessary to enable the strengthening by the dislocation substructure.

2.4.3 Influence of Creep on Microstructure
The microstructure of the 9% Cr steels is tempered martensite formed during a final normalising and tempering heat treatment. During the tempering treatment, the dislocations and ‘ferrite’ subgrains are formed in the matrix phase, and various carbide and nitride particles precipitate on prior austenite grain boundaries, ferrite subgrain boundaries and on dislocations inside subgrains. The technically relevant stresses and temperatures for creep testing and service exposure of 9% Cr steels are in the range 300 MPa/500°C - 500 MPa/650°C. During creep testing, the temperature of which is below the final tempering temperature, changes to the subgrain structure, dislocations and precipitate particles occur.

2.4.3.1 Influence of Creep on Microstructure
The typical sub-grain structure of an as-received material is shown in Figure 2.21(a) [56]. The high density of excess dislocations, which can be observed clearly in the figure, were produced by martensitic transformation during quenching and were retained after tempering in martensite lath subgrains. After creep deformation, the resulting microstructure of 9% Cr steels is illustrated as Figure 2.21(b) [56]. The martensite lath structure can still be distinguished, but there is a reduction in the area fraction of martensite as is evidenced by the more equiaxed grain structure, which is essentially ferritic.
Ennis [38] found in his work that after creep deformation at 600°C the microstructure exhibited a subgrain structure which had a polygonal shape, replacing the original subgrain structure of as-received P91 steels. The mean subgrain width was determined as $0.7 \pm 0.1 \, \mu m$ (for 1502 h) and $1.4 \pm 0.2 \, \mu m$ (for 9775 h) which was more than twice the width of the subgrains in the unstressed sample head. However, Cerri [52] mentioned that when the subgrains grow during creep, the subgrain size at higher stress (175 MPa) is larger than that at lower stress (130 MPa) at 600°C, shown as Figure 2.22(a) and (b). At 650°C, the subgrain size is larger at any applied stress than at the lower temperature (Figure 2.22(c) and (d)).
2.4.3.2 Influence of the Creep on Precipitate Phases

Since carbide and nitride particles precipitate on prior austenite grain boundaries, martensite/ferrite subgrain boundaries and on dislocations inside subgrains, the size and distribution of these particles are also affected by creep test. Hald [41] has researched the evolution in mean particle sizes of particles in steels P91 and P92 at 600°C. The $M_{23}C_6$ showed significant coarsening in steel P91; while in steel P92 this carbide is highly stable. The MX carbonitrides show a very high stability against coarsening in both steels. There are large differences between the Laves particle
sizes in the two steels. After an initial growth phase of about 10,000 hours, the Laves phase particles are more stable in steel P92 than that in steel P91. However, in steel P91 these particles grow to very large sizes during an extended growth period, which lasts about 30,000 hours.

2.5 Summary

From the literature it can be seen that the high Cr steels are widely used in power generation and a series of Cr steels were developed to reach a long time service life in the high temperature and pressure environments found in power plants in the past fifty years. The high temperature strength and creep resistance of the advanced high chromium steels are derived from the microstructure, which typically exhibits a tempered martensite matrix with a fine dispersion of secondary particles. The three major strengthening mechanisms which enhance the creep strength of these steels are precipitate hardening derived from secondary phase particles, dislocation hardening derived from the high dislocation density in the tempered martensite matrix, and solution hardening derived from elements such as Mo and W. However, the precise nature of the microstructure, with respect to the dislocation density and the type, size and distribution of second phase particles, is a function of the applied heat treatments. In addition, the microstructures are also prone to change during the prolonged creep exposure. The recovery of dislocation substructure and the coarsening of secondary phase particles during creep can both degrade the creep resistance of the material and limit the service life of these types of steels at elevated temperatures. The mechanical properties, in turn, can be very sensitive to the microstructure and therefore it is essential to understand both the microstructural evolution and mechanical properties of these steels as a function of service life.

The overall aim of the work laid out in the following chapters is to gain a complete, quantified, understanding of microstructural changes, consisting of both matrix microstructure and secondary phase change, in high Cr 91 and 92 tempered martensitic power plant steels, as a function of pre-service heat treatment, stress, time and temperature. The following chapter gives a full description of experimental techniques used for this research and rest chapters investigated and discusses the microstructural evolution of grades 91 and 92 steels as a function of heat treatment, temperature and creep stress.
Chapter 3. Experimental Methodologies

3.1 Materials

Two types of steels, Grade 91 and 92, were provided by Doosan Power for this project. These steels were in the forms of tubes (T) and test bars machined from pipes (P) and hence referred to subsequently as T91, T92 and P91, P92. The chemical compositions of the samples are shown in Table 3.1. Both types of steel have very similar compositions and are representative examples of each Grade, however, the letters T and P have been kept in the material designation for each sample because the fact that they have experienced different processing conditions to make a pipe or tube is relevant to this research.

Table 3.1: Chemical compositions of the materials provided by Dooson Babcock Energy.

<table>
<thead>
<tr>
<th>Element</th>
<th>wt.% (balance Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>T91 0.106</td>
</tr>
<tr>
<td></td>
<td>Si 0.363</td>
</tr>
<tr>
<td>Mn</td>
<td>0.480</td>
</tr>
<tr>
<td>P</td>
<td>0.014</td>
</tr>
<tr>
<td>S</td>
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<tr>
<td>Cr</td>
<td>8.637</td>
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<tr>
<td>Mo</td>
<td>0.937</td>
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<tr>
<td>Ni</td>
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<td>N</td>
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<tr>
<td>Nb</td>
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<tr>
<td>V</td>
<td>0.215</td>
</tr>
<tr>
<td>W</td>
<td>-</td>
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<td>B</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>T92 0.128</td>
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<td>Si 0.318</td>
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<td>W</td>
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<tr>
<td>V</td>
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<tr>
<td>W</td>
<td>1.700</td>
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<td>0.003</td>
</tr>
</tbody>
</table>

After normalising and tempering at typical conditions (normalising at 1050°C, tempering at 750°C), a total number of 26 samples were made from the two grades of steels with different stress relief and creep test conditions. The details of all the heat treatment conditions and mechanical test conditions are given in Tables 3.2 and 3.3 respectively. The samples were denoted by their materials (label T91, T92, P91, P92) and suffixes indicating the heat treatment conditions. The suffix “AR” indicates that the sample is in the as-received state (only normalised and tempered). The suffixes “8 h” and “16 h” indicate that the samples had experienced an additional 8 or 16 hours stress relief at 765°C compared to the as-received state. The additional numbers indicate the creep test condition of the samples. For example, the suffixes “-1” and “-16-1” indicate that a 82 MPa stress rupture test has been applied on the as-received and the 16 hours stress relieved T91 samples respectively, and the suffixes “-2” and “-16-2” indicate a 66 MPa stress rupture test has been applied on the as-received and the 16 hours stress relieved T91 samples respectively.
Table 3.2: Heat treatment, stress relief and creep test conditions of T samples.

<table>
<thead>
<tr>
<th></th>
<th>Stress relief conditions</th>
<th>Creep test conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(The stress relief treatment was performed on the as-received samples)</td>
<td>(Load/ Temperature/ Rupture life)</td>
</tr>
<tr>
<td><strong>T91</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91-AR</td>
<td>As-received</td>
<td>N/A</td>
</tr>
<tr>
<td>T91-8 h</td>
<td>8 hours at 765°C</td>
<td>N/A</td>
</tr>
<tr>
<td>T91-16 h</td>
<td>16 hours at 765°C</td>
<td>N/A</td>
</tr>
<tr>
<td>T91-AR-1</td>
<td>2 hours at 765°C</td>
<td>82 MPa / 650°C / 1549 h</td>
</tr>
<tr>
<td>T91-16-1</td>
<td>16 hours at 765°C</td>
<td>82 MPa / 650°C / 992 h</td>
</tr>
<tr>
<td>T91-AR-2</td>
<td>2 hours at 765°C</td>
<td>66 MPa / 650°C / 5857 h</td>
</tr>
<tr>
<td>T91-16-2</td>
<td>16 hours at 765°C</td>
<td>66 MPa / 650°C / 4826 h</td>
</tr>
<tr>
<td><strong>T92</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T92-AR</td>
<td>As-received</td>
<td>N/A</td>
</tr>
<tr>
<td>T92-8 h</td>
<td>8 hours at 765°C</td>
<td>N/A</td>
</tr>
<tr>
<td>T92-16 h</td>
<td>16 hours at 765°C</td>
<td>N/A</td>
</tr>
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<td>T92-AR-1</td>
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<td>112 MPa / 650°C / 1649 h</td>
</tr>
<tr>
<td>T92-16-1</td>
<td>16 hours at 765°C</td>
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<td>T92-16-2</td>
<td>16 hours at 765°C</td>
<td>85 MPa / 650°C / 7965 h</td>
</tr>
</tbody>
</table>
Table 3.3: Heat treatment, stress relief and creep test conditions of P samples.

<table>
<thead>
<tr>
<th></th>
<th>Stress relief conditions (The stress relief treatment was performed on the as-received samples)</th>
<th>Creep test conditions (Load/ Temperature/ Rupture life)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P91</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P91-AR-1</td>
<td>2 hours at 765°C</td>
<td>78 MPa / 650°C / 2807 h</td>
</tr>
<tr>
<td>P91-16-1</td>
<td>16 hours at 765°C</td>
<td>78 MPa / 650°C / 1995 h</td>
</tr>
<tr>
<td>P91-AR-2</td>
<td>2 hours at 765°C</td>
<td>69.8 MPa / 650°C / 7684 h</td>
</tr>
<tr>
<td>P91-16-2</td>
<td>16 hours at 765°C</td>
<td>69.8 MPa / 650°C / 4819 h</td>
</tr>
<tr>
<td>P91-AR-3</td>
<td>2 hours at 765°C</td>
<td>74.4 MPa / 650°C / 4310 h</td>
</tr>
<tr>
<td>P91-16-3</td>
<td>16 hours at 765°C</td>
<td>74.4 MPa / 650°C / 2858 h</td>
</tr>
<tr>
<td><strong>P92</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P92-AR-1</td>
<td>2 hours at 765°C</td>
<td>107.2 MPa / 650°C / 2504 h</td>
</tr>
<tr>
<td>P92-16-1</td>
<td>16 hours at 765°C</td>
<td>107.2 MPa / 650°C / 2019 h</td>
</tr>
<tr>
<td>P92-AR-2</td>
<td>2 hours at 765°C</td>
<td>99.1 MPa / 650°C / 3854 h</td>
</tr>
<tr>
<td>P92-16-2</td>
<td>16 hours at 765°C</td>
<td>99.1 MPa / 650°C / 3883 h</td>
</tr>
<tr>
<td>P92-AR-3</td>
<td>2 hours at 765°C</td>
<td>91.8 MPa / 650°C / 3350 h</td>
</tr>
<tr>
<td>P92-16-3</td>
<td>16 hours at 765°C</td>
<td>91.8 MPa / 650°C / 5930 h</td>
</tr>
</tbody>
</table>

The effect of stress relief heat treatment was investigated by determining the microstructural evolution of non-creep tested samples. The influence of long-term aging was studied by determining the microstructural evolution of creep tested head section samples (which did not experience creep stress). The effect of creep stress in the rupture tested samples was studied by comparing the stressed gauge section (G) with the unstressed (isothermally aged) head section (H) of each sample. It should be noted that all the T samples, had dimensions of approximately 10×4×10 mm (L×W×H) and were cut from tubes made from T91 and T92 steels. The diameter of the T91 tube is 45 mm with a wall thickness of 9 mm, and the diameter of the T92 tube is 42 mm with a wall thickness of 5 mm. For the P samples, all the samples were in the shape of a test bar which had a diameter of 8 mm at gauge position and 12 mm at head position. The shapes of T and P samples are shown in Figure 3.1.
Figure 3.1: The shapes of (a) T and (b) P creep tested samples.

It should be noted here that for the as-received and stress relieved samples, surfaces which are parallel to the axis direction of the tube were examined in the subsequent microstructural characterisation; for the creep tested samples, surfaces which are perpendicular to the axis direction (the stress direction in the gauge portion) of the tube/bar were examined.

3.2 Sample Preparation

3.2.1 General Preparation
The general sample preparation procedure consisted of cutting, mounting, grinding, polishing and final polishing. Firstly, small sections at both the head and gauge positions of each sample were obtained using a Struers Accutom-5 circular saw,
equipped with an Al$_2$O$_3$ blade suitable for cutting metals with a hardness 500 HV or below.

These sections were then mounted in conductive Bakelite and subjected to metallographic preparation. Special attention was paid to the gauge portions of rupture tested samples. To avoid excess cracks, surfaces which are at least 10 mm away from the rupture point were examined.

After that, grinding was carried out on the sample using resin bonded diamond grinding discs, with grades Struers Piano 220, 600 and 1200. These sections were then polished using a typical procedure for microscopy image analysis. This includes 9 µm, 3 µm, 1 µm particle size diamond polishes and a final chemo-mechanical polish with Buehler non-crystallizing colloidal silica polishing suspension (particle size of 0.04 µm) to remove the deformation produced during the abrasive stages of preparation.

3.2.2 Carbon Extraction Replicas

The normal sample preparation technique for the secondary phase particles characterisation is the carbon extraction replica. The main advantage of this technique is that it can eliminate all the effects from the iron matrix, thus it allows a more accurate determination of the chemical composition of the precipitate phases. It also can avoid the problems associated with working with a magnetic material (ferrite) in the Transmission Electron Microscope (TEM). In addition, carbon extraction replicas can preserve the relative positions and orientations of secondary phase particles.

In this project, carbon extraction replicas were produced by lightly etching the surface of generally prepared metallographic samples. Chemical etching was carried out by using Villella’s reagent and etching time was restricted to a short period of 30 seconds, in order to remove the surface particles and expose the particles of interest. A thin carbon film was then deposited onto the etched metal with a Quorum Q150TES carbon vaporiser. In this investigation, a suitable carbon coating with dark brown colour and thickness of approximately 20~30 nm was used.

Once the carbon had been deposited, the coated surface was scored into approximately 3 mm squares with a razor blade (the diameter of a copper mesh grid
is 3 mm). To remove the replica from the surface, an electrolytic etch using 10% HCl in methanol was carried out, with a voltage of 5 V, and a current of 30~50 mA. The coated sample was then rinsed in a beaker of pure methanol to remove the electrolyte. Finally the sample was immersed in distilled water at a 45° angle, which removed the carbon film with the surface tension of water. Each replica was then collected with tweezers and deposited onto 400 mesh square copper grids. After drying, the replicas were ready for TEM examination.

3.3 Optical Microscopy

After metallographic preparation and etching using Villella’s reagent, the samples were examined in a Reichert MEF-3 optical microscope. The main aim of using optical microscopy was to provide an indication of the morphology and extent of all phases present in the samples.

3.4 Hardness Testing

Vickers hardness testing was carried out using a Reichert hardness tester. A weight of 10 kg was applied for 10 seconds on each of the tested samples. 5 Vickers indentations which crossed the sample surface uniformly were taken to calculate the mean value. The hardness values were then calculated from the following equation:

$$HV=1854.4P/d^2 \text{ [kg/mm}^2\text{]}$$

where HV is the micro-hardness number, P is the load in grams, and d is the diagonal distance of the indentation in millimetres.

3.5 Field Emission Gun Scanning Electron Microscopy (FEG SEM)

In this work, a Carl Zeiss 1530 VP FEG SEM was used to analyse the matrix microstructure of the samples. In this system, an electron beam is emitted and focused by the electron lenses to a very small spot, as the electron beam hits the sample surface, several types of signals are generated, such as secondary electrons,
backscattered electrons, and x-rays, as shown schematically in Figure 3.2. In principle, all these signals are the result of particular interactions between the incident electrons and the sample [57]. With these various signals, different imaging techniques can be used to provide the surface morphology of metallic, electronic and polymeric materials under high magnifications, such as secondary electron images (SE) or backscattered electron images (BSE).

**Figure 3.2:** Some of the signals which may be used in the SEM [57].

To determine crystallographic information, the electron backscatter diffraction (EBSD) technique was applied. In this work, the EBSD maps were taken to determine the crystal orientation, low angle boundary distribution for each sample, and this will be discussed in detail in Section 3.8.

**Figure 3.3:** The regions from which secondary electrons, backscattered electrons, and X-rays may be detected [57].
After the incident beam enters the sample surface, the electrons are scattered in the sample within a region shown in Figure 3.3[57]. Normally, when using SEM to determine the surface features of a sample, the SE image is used for the surface topography, and the BSE image is used for compositional information, according to the different depth they were scattered into the sample surface, as shown in Figure 3.3. In this work, SE imaging was used to image the topography of the sample surface, and BSE imaging was used to determine the size distributions of Laves phase in all the T and P steel samples.

In this project, the electron source was operated under high current mode with an accelerating voltage of 20 kV and a 30 µm aperture size, with a working distance of 5 mm and 25 x 22 µm² image sizes for SE images. For BSE images, the accelerating voltage was set to 10 kV with a 30 µm aperture. The backscattered electron coefficient varies monotonically with atomic number [57], which means different phases give rise to different contrast in the BSE images. Compared to the matrix phase, the Laves phase has a higher atomic number (rich in Mo and W), and as a result the Laves phase is brighter than the matrix. In this work, the BSE images were used to determine the differences between the Laves phase and matrix phase, and to analyse the size distributions of the Laves phase with a 6 mm working distance and 25 x 22 µm² image sizes.

3.6 Focused Ion Beam Scanning Electron Microscopy (FIB SEM)

In this work, a dual beam microscope, an FEI Nova Nanolab 600 FIB-FEGSEM equipped with a focused ion beam (FIB) column employing a Ga liquid metal ion source, combined with a high-resolution Field Emission Gun Scanning Electron Microscope (FEG SEM) was used to characterise the microstructural evolution of primary and secondary phases in the steels.

In this system, the FIB column is capable of both imaging and micro-milling depending on the beam current being used. In this work, the dual beam system was operated using the ion beam mode to generate ion-induced secondary electron images. The ion beam imaging contrast mechanism was used to discriminate secondary phase particles from the matrix. It should be noted that the contrast
mechanism used in this work was in fact a type of conductivity contrast. As the incident focussed Ga+ ion beam scans across the sample surface, positive charges accumulate on the surfaces of non-conductive secondary phase particles such as M$_{23}$C$_6$ or MX. This positive charge build-up on particles traps the emitted ion-induced secondary electrons. Therefore, as fewer ion-induced secondary electrons are emitted from the non-conductive particles than those emitted from the conductive metal matrix, particles have a lower brightness than the matrix in the image and are successfully discriminated from the matrix in the images. Due to the fact that the vast majority of secondary phase particles present after heat treatment are M$_{23}$C$_6$ and MX non-conductive particles, the conductivity contrast is considered suitable for the characterisation of secondary phase particles in T91 and T92 steels.

For ion beam images, the accelerating voltage was 30 kV and the current was 30 pA. When taking these images, the contrast (80-90%) and brightness (30-40%) (The higher percentage values mean the higher contrast and brightness values) of the image was set in a suitable range of values to get a high image intensity contrast between matrix and secondary phases. The working distance was 20 mm and the size of ion beam images was 25 x22 µm$^2$.

**3.7 Image Tool 3.0 as Particle Size Distribution Analysis Software**

For this research, the ion beam induced secondary electron images and BSE images of grades 91 and 92 steel samples were analysed using an image analysis software programme; Image Tool 3.0. The FIB and BSE images were first edited using Photoshop software, and transferred into grey-scale digital images consisting of an area of 1024 x 768 pixels. Using this Image Tool 3.0 software, several measurement options are available, such as feret diameter, length, width, area, perimeter and aspect ratio and so on. However, the feret diameter was used as the main factor to quantify the particle size distribution of the M$_{23}$C$_6$ particles. FIB and BSE images are ideal for automatic image analysis as the contrast between the particles and the matrix is achieved by conductivity contrast and chemical composition contrast, respectively. When using Image Tool 3.0 to analyse the particle size data of M$_{23}$C$_6$ particles and Laves phase, several factors which may affect particle size analysis results from FIB and BSE images are first considered and discussed.
Particle size distributions may be affected by “overlapping” particles, in which case two or more close particles may count as one when measured using the Image Tool 3.0 software. In general, the “overlapping” particles may decrease the interphase surface area per unit volume and the number density of the particles present in material microstructure, and at the same time increase the mean particle size in the microstructure [3]. Normally, these “overlapping” particles in the system had a very limited effect on the particle size distribution because of the small population; no more than 5 “overlapped” particles were observed in a FIB or BSE image. What is more, these “overlapped” particles typically occurred as a result of nucleation of particles on pre-existing particles, and thus they need not to be measured individually since the effective “obstacle” area should be considered as the sum of independent particles.

In FIB or BSE images, defects may also produce contrast, and if these defects were counted as particles when measurements are taking place, the particle size data may be affected. Normally, the defects like voids produce contrast, but exist as dark particles with bright edges which can be easily separated from the M23C6 particles which appeared as purely dark particles in FIB images or Laves phase which appeared as white particles in BSE images.

Figure 3.4 shows the image analysis procedure of a FIB image of M23C6 particles using Image Tool 3.0. Firstly, the FIB image was transferred into a grey-scale digital image consisting of an area of 1024 by 768 pixels using Photoshop software, shown as Figure 3.4 (a). A similar procedure is applied to the BSE images, the only difference is the Laves phase appeared as white particles and matrix appeared as a black area. This grey-scale digital image was then threshold according to the contrast between the matrix and particles, and changed into a white and black image, in which white parts are matrix phase and black parts are M23C6 particles, shown as Figure 3.4 (b). The size analysis was then taken on this threshold image, shown as Figure 3.4 (c) in which the different colours represent different size categories.

When using the grey-scale digital images to analyse the particle size distribution of M23C6 particles or Laves phase, the accuracy is greatly dependent on the number of pixels that can be assigned to any given particle, which means the greater the
number of pixels that can be assigned to any given particle the more accurate the measurement is going to be. For this research, the smallest detectable particle size was set as 5 pixels, which means that any particles present in the image smaller than 70 nm in diameter would remain as unmeasured. The reason for excluding the particles below 70 nm are because these particles are difficult to separate from dirty or other secondary particles such as MX particles and the absence of these particles in data analysis have a very limited effect on the particle size distribution of $\text{M}_{23}\text{C}_6$ particles or Laves phase.

**Figure 3.4**: a) FIB image of $\text{M}_{23}\text{C}_6$ particles in T91-AR-1 Gauge sample, b) the same image after threshold process and c) after size analysis. The different colours represent different size categories.
To improve the accuracy of the particle size distribution of the M$_{23}$C$_6$ particles and Laves phase particles in 91 and 92 steels, 5 FIB or BSE images in the scale of 25 × 22 µm$^2$ were analysed together to work out the mean particle size and number density of M$_{23}$C$_6$ particles or Laves phase particles in the same investigated area, 2750 µm$^2$. The mean particle size of M$_{23}$C$_6$ particles or Laves phase particles of individual images were investigated and compared with the mean particle size of all of the images, for the T92-AR-2 sample for example, as shown in Table 3.4.

Table 3.4: The mean particle size of M$_{23}$C$_6$ particles or Laves phase particles of individual images compared with total images and standard deviation of T92-AR-2 sample (Each image consists of more than 200 M$_{23}$C$_6$ particles or 100 Laves phase particles).

<table>
<thead>
<tr>
<th>Secondary Particles</th>
<th>Image Number</th>
<th>Mean Particle Size (nm) (Head)</th>
<th>Mean Particle Size (nm) (Gauge)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M$_{23}$C$_6$</td>
<td>1</td>
<td>133.0</td>
<td>165.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>127.1</td>
<td>173.0</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>126.6</td>
<td>172.3</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>126.9</td>
<td>163.7</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>129.6</td>
<td>163.1</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>128.6 ± 2.4</td>
<td>167.5 ± 4.3</td>
</tr>
<tr>
<td>Laves Phase</td>
<td>1</td>
<td>197.6</td>
<td>272.0</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>205.7</td>
<td>326.9</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>188.6</td>
<td>271.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>172.3</td>
<td>269.7</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>186.6</td>
<td>286.9</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>190.4 ± 11.2</td>
<td>285.1 ± 21.6</td>
</tr>
</tbody>
</table>

For all the samples, the standard deviation in mean particle size of M$_{23}$C$_6$ particles is in the range < 5 nm and that in the mean particle size of Laves phase particles ranged up to 25 nm. This standard deviation value calculated from individual images indicated the homogeneous nature of the particle size distribution of M$_{23}$C$_6$ or Laves phase particles in the 91 and 92 samples, the smaller value of standard deviation means that there is a more uniform particle size distribution. These standard deviation values were thus included into the investigation of the particle coarsening in M$_{23}$C$_6$ or Laves phase particles with different heat treatment or stress conditions, which proved very reliable because the change in the particle size was larger than the standard deviation values.
3.8 Electron Backscatter Diffraction (EBSD)

Electron backscatter diffraction (EBSD) is an important analytical tool which can provide crystallographic information about the sample. A schematic diagram of an EBSD system is shown in Figure 3.5 [58]. The polished sample which has a strain-free surface is tilted to an angle of 70 degrees by mounting on an angled sample holder. As the incident electron beam was emitted on the sample surface, the diffracted electrons are emitted onto the phosphor screen to form diffraction patterns. These patterns are recorded by the sensitive video camera and then analysed by the PC to form an EBSD map.

![Figure 3.5: A schematic diagram of an EBSD system equipped to a SEM [58].](image)

The EBSD pattern constitutes a number of Kikuchi bands; each band contains a pair of parallel Kikuchi lines, the formation of which is shown in Figure 3.6 [59] and the parallel Kikuchi lines map is shown in Figure 3.7 [60]. As the incident beam entered the tilted sample, some backscattered electrons, which satisfy the Bragg law, are diffracted to form a set of paired large cones corresponding to each diffracting plane. The pair of parallel Kikuchi lines is formed when these cones are intersected by the phosphor screen [61]. As discussed above, the different Kikuchi lines come from
different diffracting crystal planes, the positions and orientations of which can be determined through measuring and analysing the positions and the angles of corresponding Kikuchi lines. As a result, the crystallographic structures of the samples can be determined in the EBSD map.

Figure 3.6: The formation of Kikuchi lines [60].

Figure 3.7: Typical processed EBSD diffraction pattern from an austenitic (FCC) steel [59].
In this work, the electron source was operated under high current mode with an accelerating voltage of 20 kV and the aperture size 50 µm in the EBSD analysis. A square area of 50×50 µm² was analysed in each scan with the step size of 0.1 µm. The crystallographic file loaded for indexing was the ferrite iron structure which has a body centred cubic structure with a lattice parameter a=0.287 nm. There are EBSD systems attached to both the FEG-SEM and FIB-FEGSEM; however, all the EBSD maps were collected by FIB-FEGSEM system due to the high speed EDAX-AMETEK camera on the FIB-FEGSEM dual beam system. The collection speed of camera on the dual beam system can obtain 250 frames per second (fps), which is nearly 3 times faster than that on the FEG-SEM. In this work, the collection speeds were 200-210 fps depending on the different samples, and the collection time for each image was around 20 minutes.

3.9 EBSD Analysis

Analysis of the EBSD maps was performed using EDAX Orientation Image Microscopy (OIM) analysis version 5 software. Firstly, the EBSD map was processed with clean-up step in OIM software before being used to determine the grain orientation and boundary information.

The pattern indexing in OIM is generally quite effective in identifying the orientation from a diffraction pattern. However, at times OIM has difficulty identifying some orientations such as at grain boundaries where the patterns often are made up of two superposed diffraction patterns from both crystal lattices separated by the grain boundary. OIM may index the pattern correctly for either grain or OIM may come up with an incorrect solution based on bands detected from both of the superposed patterns. This will lead to erroneous results near boundaries and triple points. OIM provides several clean-up methods, which attempt to "clean-up" the erroneous data. Grain Dilation and Neighbour CI Correlation are two most common clean-up methods. In the Grain Dilation method, the routine only acts on points that do not belong to any grains and removes these points, however, even these points have a very high confidence index (CI). The later method is only performed on data points with a CI less than some user defined value (0.2 in this work). If a particular point has a CI less than the minimum value, then the CI of the nearest neighbours are
checked to find the neighbour with the highest CI. The orientation and CI of the particular point are then reassigned to match the orientation and CI of the neighbour with the maximum CI. Due to the difference between these two methods, the Neighbour CI Correlation method was used to clean-up the EBSD map in this work. In this method, the grain tolerance angle is 5, minimum grain size is 2 (pixels) and minimum confidence index is 0.2.

The step size used to acquire the EBSD map is another factor which affects the quality of EBSD maps. A smaller step size means many more points are collected during EBSD map acquisition. This means more grain information from the material microstructure, however, it also means a much longer collection time. In this work, a 0.1 µm step size was chosen as a compromise between scanning accuracy and collection time.

In conventional metallography a grain boundary denotes the line separating two grains. Generally, in OIM a grain boundary refers to a line segment separating two measurement points in a scan. The misorientation angle is the minimum rotation angle (out of all symmetrically equivalent possibilities - based on the axis/angle description of orientation) required to bring two lattices into coincidence. For different features in the matrix phase, such as matrix grains, secondary particles and voids, the misorientations are very different, so it is possible to use a boundary misorientation map to describe and investigate the primary and secondary features distribution in material microstructure. In OIM, the user may specify the range in misorientation angle for boundaries. For example, Figure 3.8 is overlaid with boundaries ranging from 2 to 15 degrees in red, 15 to 25 in green, 25 to 45 in blue and greater than 45 degrees in black.

However, to study the boundary distribution of the primary phase (with high angle misorientation boundaries) and secondary phases typically (with low angle misorientation boundaries), the accurate definition of a boundary misorientation value, below which are mostly secondary boundaries and above which are mostly primary boundaries is very important, and this value can change with varying materials. To work out the suitable value for Grades 91 and 92 steel samples in this research project, the changes in ratios of low-angle to high-angle boundaries with different defined angle values are plotted in Figure 3.9.
The low/high angle ratios of all the samples changed significantly with misorientation angles when the defined angle value is below 10 degrees, which means there are a lot of secondary phases with a boundary misorientation below this value. However, there is still a gentle but continuous change in the low/high angle ratios of all the samples with misorientation angles when the defined angle values are in the range of 10 to 18 degrees. This change becomes quite limited in the range of 20 to 30 degrees, which means the number of features which have boundary misorientation angles in this range is very small. Therefore the boundary value is specified to be 15 degrees to involve both the large amount of secondary phases which have misorientation angles below 10 degree and the majority part of the secondary features which have misorientation angles in the range of 10 to 18 degrees.

Figure 3.8: The boundary mis-orientation map of P91-AR-1 Head samples with 2 to 15 degrees in red, 15 to 25 degrees in green, 25 to 45 degrees in blue and greater than 45 degrees in black.
3.10 Transmission Electron Microscopy (TEM)

3.10.1 Jeol 2000FX TEM

Transmission electron microscopy (TEM) was carried out in a Jeol 2000FX microscope operating at 200 kV equipped with an Oxford Instruments Inca EDX system. The Jeol 2000FX uses a tungsten thermionic source, and this microscope was employed primarily for quantitative EDX analysis and general microstructure characterisation. Images were captured using an Erlangshen ES500W digital camera. Carbon extraction replicas were used to obtain chemical composition information from the carbide particles without interference from the ferrous matrix.

3.10.2 Energy Dispersive X-ray Analysis (EDX)

The chemical composition of precipitate particles can be measured using Energy Dispersive X-ray Analysis (EDX). As an electron beam from the tungsten thermionic emitter strikes into the sample surface or a precipitate, electrons become excited to a higher orbital. As these electrons drop down from excited outer states to ground states, characteristic X-rays are emitted and can be used to identify different atoms.
In the TEM, quantitative EDX analysis were performed on carbon replicas using an Oxford Instruments Inca EDX system equipped with an ultra-thin polymer window, meaning that it can be used to detect light elements down to boron. For each sample, fifty particles were randomly chosen in a series of continuous TEM images. The spot size was set as 5 and the magnification was 100,000X to make sure the determined area was small enough to analyse the MX particles with a particle size down to 10 nm. An acquisition live time of 30 seconds was used for each precipitate in order to ascertain the chemical composition.

3.11 Summary
This chapter has presented full descriptions of the experimental procedures used for this project. Firstly, a detailed description of the materials that were used, identifying the chemical compositions and conditions in which the investigated materials were processed was presented. Then, the sample preparation techniques consisting of cutting, polishing, etching and carbon replica processes were described and discussed. In addition, the rest of the chapter provided a brief explanation of the different microstructural characterization techniques used. Optical microscopy (OM) was used to determine the matrix microstructure of 91 and 92 steels. Hardness tests were used to investigate the hardness values at different positions in samples from the 91 and 92 steels. Focused ion beam scanning electron microscopy (FIB SEM) was used to investigate the distribution of M23C6 particles and Laves phase. Electron backscatter diffraction (EBSD) was used to characterise the grain boundary maps, matrix recrystallisation maps and matrix recovery. Transmission electron microscopy (TEM) was used to investigate the size distribution and chemical composition of MX particles. These results are discussed in detail in the following results chapters.
Chapter 4. The Effects of Stress Relief Heat Treatments on the Initial Microstructural Evolution in Grade 91 and 92 Steels

4.1 Introduction

During the manufacturing process for steel components large stresses and plastic strains can be induced. Once the initial process is completed, these permanent strains generate residual stresses that limit fatigue life and performance during service [62]. These stresses can cause distortions in the components during long term service, cracking could occur if the components are clamped in service, and also void locations can change causing them to go out of tolerance. Some of the stress comes from the other parts in the bulk or shaped compress cannot be removed, however, those stress come from the matrix phase changes can be mostly remove by heat treatment. For these reasons, a stress relief heat treatment is often necessary for large and complex weldments, castings with a lot of machining, parts with tight dimensional tolerances and machined parts that have had a lot of stock removal performed.

In this study, a stress relief heat treatment was performed on both Grade 91 and 92 steels to investigate the effect of stress relief heat treatment on the subsequent microstructural evolution. Firstly, the hardness values of the 91 and 92 steels were measured using a Reichert hardness tester, and the changes of these hardness values due to additional stress relief heat treatment are discussed. Secondly, the grain and sub-grain structure of grade 91 and 92 steels have been extensively characterised with the use of EBSD maps in the scanning electron microscope. The changes in matrix microstructure and low/high boundary ratio of the 91 and 92 steels due to the additional stress relief heat treatment are discussed. Thirdly, the particle size and chemical composition distribution of MX particles have been determined with the use of TEM equipped with EDX. The particle size distributions of $M_{23}C_6$ and Laves phase particles have been characterised separately with the use of focused ion beam images and backscatter electron images in the dual-beam scanning electron microscope.
4.2 Stress Relieved Samples

Normally stress relief heat treatment is done by subjecting the components to a temperature of about 75°C below the transformation temperature, which is about 727°C (this value changes with different types of steel). Thus stress relief is typically carried out at ~650-750°C for about one hour or more until the whole part reaches the stress relief temperature. This stress relief procedure removes more than 90% of the internal stresses in the steel sample. In this study, the samples were examined in the as-received condition (denoted ‘AR’) which comprised a normalisation treatment at 1060°C for 20 minutes followed by a temper at 765°C for 80 minutes. Some of the samples then underwent an additional stress relief heat treatment for a further 8 h and 16 h at 765°C (denoted ‘16’).

4.3 Influence of the Stress Relief on the Mechanical Properties

4.3.1 Influence of the Stress Relief on the Hardness of 91, 92 steels

In this work, all the samples were tested using a Reichert hardness tester. A load of 10 kg was applied for 10 seconds on each of the tested samples and 5 Vickers indentations were taken uniformly cross the sample surface to calculate the mean hardness value and standard error. The mean values and standard deviations of as-received and stress relieved 91 and 92 samples are shown in Table 4.1.

Table 4.1: The mean values and standard deviations of AR and stress relieved 91 and 92 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Stress Relief Time</th>
<th>Hardness Data (Hv10)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td>As-received</td>
<td>225±5</td>
</tr>
<tr>
<td></td>
<td>8 h</td>
<td>212±3</td>
</tr>
<tr>
<td></td>
<td>16 h</td>
<td>205±4</td>
</tr>
<tr>
<td>T92</td>
<td>As-received</td>
<td>235±3</td>
</tr>
<tr>
<td></td>
<td>8 h</td>
<td>224±4</td>
</tr>
<tr>
<td></td>
<td>16 h</td>
<td>217±1</td>
</tr>
</tbody>
</table>

The hardness values of as-received and stress relieved samples were compared in this section to study the effect of stress relief on the hardness. Figure 4.1 shows the hardness value changes with stress relief time from 0 h to 8 h to 16 h for the T91 and T92 samples. For both the T91 and T92 samples, the hardness value was reduced
by around 5% after 8 h stress relief and reduced by around 8% after 16 h stress relief. In addition, T92 samples were approximately 10 HV higher in hardness values than T91 samples with the same stress relief time. The drop in hardness is a good indication of changes in microstructure during the stress relief treatment which may account for the different creep behaviour of stress relieved and non-stress relieved samples; these microstructural studies are discussed in detail in Chapter 6.

Figure 4.1: The hardness values of T91 and T92 samples with varying stress relief time at 765°C.

4.3.2 Influence of the Stress Relief on the Creep Properties of 91, 92 steels

The aim of this section was to investigate the effect of an additional 16 h stress relief heat treatment on the final creep properties. The creep test data have therefore been plotted in Figure 4.2 as the rupture stress as a function of time. Also shown are the mean lines from the European Collaborative Creep Committee assessments for Grade 91 [63] and Grade 92 [64]. It can be seen from the figure that the creep test data for both the T91 and T92 materials are close to the mean lines expected in the case of the samples which have received the conventional heat treatments, whereas for the samples which have received the additional 16 h at 765°C there is an earlier failure time, resulting in a lifetime reduction of approximately 10% of the mean value expected from the ECCC data in each case.
4.4 Influence of the Stress Relief on the Matrix Microstructure

Changes in the martensitic matrix as a result of the stress relief heat treatment were investigated by generating Image Quality (IQ) + Inverse Pole Figure (IPF) images and grain boundary misorientation maps using EBSD. The IQ + IPF images and grain boundary misorientation maps of as-received and 16 hours stress relieved T91 and T92 samples are shown in Figure 4.3 and 4.4, respectively. A well-defined martensitic matrix structure is evident in all maps. Comparison between the T91 as-received and 16 hours stress relieved maps show that there is very limited difference after the 16 hours stress relief at 765°C. However, the high angle boundaries reduce slightly as an effect of stress relief by comparing the grain boundary misorientation maps of T91 as-received and 16 hours stress relieved samples. In comparison, the recovery of matrix microstructure is also not significant in the T92 samples. There is very limited difference observed when comparing the IQ + IPF images and grain boundary misorientation maps of T92 as-received and 16 hours stress relieved samples.
Figure 4.3: Image quality plus inverse pole figure (a+b) and grain boundary misorientation EBSD detected (c+d) maps illustrating the microstructure evolution of the T91 as-received and 16 h stress relieved samples.
Figure 4.4: Image quality plus inverse pole figure (a+b) and grain boundary misorientation EBSD detected (c+d) maps illustrating the microstructure evolution of the T92 as-received and 16 h stress relieved samples.
A simple method of interpreting the changes in the matrix is to compare the ratio of low-angle (2-15°) to high-angle (15-180°) boundaries from the EBSD data, as illustrated in Figure 4.5. It is shown that the ratio increases after the 16 hours stress relief in both T91 and T92. For T91 samples, the low-angle/ high-angle boundary length ratio increases from 0.54 to 0.65, and for T92 samples the ratio increases from 0.57 to 0.8. The increase in the low/high angle boundary ratio may be explained by the effect of sub-grain formation. During the 16 hours stress relief at 765°C, free dislocations may tend to either be annihilated or to re-arrange themselves into low energy configurations (sub-grain boundary) which results in an increase in the proportion of low angle boundaries. Therefore, it can be speculated that a reduced free dislocation density in the 16 hours stress relieved samples reduces their resistance to creep and results in an earlier failure in the creep test compared to those not subjected to the stress relief treatment. It should be noted that this is further supported by the different matrix evolution behaviour exhibited by the non-stress relieved and stress relieved samples during isothermal aging, which is discussed in detail in the following Chapter.

Figure 4.5: The low/high angle grain boundary ratio of as received and 16 hrs stress relieved 91 and 92 steels.
4.5 Influence of the Stress Relief on the Secondary Phase Precipitation

To understand the influence of the additional stress relief heat treatment on the secondary phase precipitation, the particle size and chemical composition distribution of MX particles have been determined with the use of TEM equipped with EDX. In addition, the evolution of the particle size distribution of the $\text{M}_{23}\text{C}_6$ and Laves phase particles in As-received and 16 h stress relieved T91 and T92 samples has been investigated in order to determine whether the kinetics of particle coarsening are affected by the additional stress relief heat treatment.

4.5.1 Influence of the Stress Relief on MX Particles

The chemical composition of the MX particles was measured using EDX in the TEM in order to understand how these particles evolve during the additional stress relief heat treatment. In addition, the particle size distribution of the MX particles of T91 and T92 as-received and 16 h stress relieved samples was also determined using TEM.

4.5.1.1 Chemical Composition of MX Particles with Stress Relief Heat Treatment

Since the V(N,C) and Nb(C,N) are completely inter-soluble [65], the relative composition distributions of V, Nb and Cr in MX particles with respect to the as-received and 16 h stress relieved samples were examined. Figure 4.6 shows the average composition of the metallic elements V, Nb and Cr in the MX carbonitride particles of the T91 and T92 samples in the As-received and 16 h stress relieved condition. The chemical compositions were determined from carbon extraction replica samples using EDX in the TEM in order to eliminate interference from the Fe-rich matrix. The chemical compositions of one hundred individual and randomly sampled MX particles were measured.
Figure 4.6: A graph showing the mean chemical composition of MX particles present in T91 and T92 samples supplied in the as-received condition and 16 h stress relief at 765°C condition.

The reason for initially using mean values rather than the chemical compositions of individual particles, as shown in Figure 4.7, is that the composition of the metallic elements can vary to such an extent that it was difficult to distinguish between NbC and VN due to the fact that V and Nb are soluble in these phases respectively. The mean values thus give a good indication of the differences in particle compositions and types present in different samples. It can be seen that the mean composition of V for all the random MX particles increases slightly, as well as that of Nb decreases slightly, after 16 h stress relief. The changes in the mean composition of the metallic elements in the MX particles indicate that there were probably some more V-rich MX particles formed during the stress relief heat treatment. In addition, the mean composition of Cr is at nearly the same value before and after stress relief, around 15%. Figure 4.7 shows the chemical composition distribution of the measured particles, and each point represents the composition of a single measured particle. It can be seen that the particles measured in the T91 and T92 As-received samples are clustered in both the V-rich and Nb-rich regions, and the majority of particles measured in the T91 and T92 are in the V-rich region after the 16 h stress relief. Thus, the standard deviations for the mean composition compositions are over quite a wide range, as shown in Figure 4.6, due to the V-rich and Nb-rich MX particles which are both present in these samples and the measured particles are clustered in both the V-rich and Nb-rich regions.
Shanmugan [66] has said that the solubility of V is considerably higher than Nb in the iron matrix and therefore a significantly higher amount of vanadium would be left in solution in the iron matrix after initial heat treatment (tempering and normalizing). During the stress relief heat treatment at 765°C, the vanadium solution may start to come out of solid, forming more V(NC) particles. This results an increase in the V-rich MX particles with respect to a reduction in the Nb-rich MX particles after the 16 h stress relief heat treatment.
4.5.1.2 Particle Size Distribution of MX Particles with Stress Relief Heat Treatment

In addition to the measurement of compositional variations of MX particles, the particle size distribution of these particles was also investigated. To achieve this, carbon extraction replicas were studied using an Erlangshen ES500W digital camera in the Jeol 2000FX TEM. For this investigation, 5 random 1024x1024 pixel images at a magnification of x100,000, which was high enough to allow MX particles to be observed and detailed, yet low enough to analyse a large area, were acquired from the TEM and subsequently analysed with Image Tool 3.0. The TEM images of the T91 and T92 samples in the as-received condition and 16 h stress relief at 765°C condition are shown in Figure 4.8; the particles labelled with white arrows are MX particles, identified by their chemical signature.

Results of this investigation are presented in Figures 4.9 and 4.10, which show the measured particle size distribution and particle area distribution of T91 and T92 samples before and after 16 h stress relief heat treatment, respectively. In the T91 samples, there was a distinct difference in both the particle size and area distribution of MX particles with respect to stress relief heat treatment. The number of particles ranged in the sizes between 50 and 100 nm increased significantly as well as the number of particles ranged in the area above 3000 nm² increased significantly after the 16 h stress relief heat treatment. This particle coarsening is also evidenced as the mean particle size increased from 46 to 52 nm, as well as the mean particle area increased from 1826 to 2436 nm² after 16 h stress relief heat treatment. However, there was no such trend in T92 samples, which appeared reasonably consistent before and after heat treatment. There was no clear particle coarsening as the mean particle size changed from 49 to 48 nm, as well as the mean particle area changed from 2187 to 2126 nm² after the 16 h stress relief heat treatment.
Figure 4.8: TEM images of carbon extraction replicas showing the MX particles in (a) T91 As-received, (b) T91 16 h stress relieved, (c) T92 As-received and (d) T92 16 h stress relieved samples (white arrows indicate the MX particles).
4.5.2 Influence of the Stress Relief Heat Treatment on M23C6 Particles

Ion beam induced secondary electron images are presented in Figure 4.11 for both the T91 and T92 materials in the as-received condition and after the additional stress relief heat treatment at 765°C for 16 h. Coarsening of the M23C6 particles is clearly observable when comparing the ‘AR’ and the ‘16’ samples. The M23C6 particles appear dark in these images due to their lower electrical conductivity than the matrix.
The changes in the size and population of particles are a clear indication that the additional heat treatment is having a significant effect on the size of the $M_{23}C_6$ particles.

Figure 4.11: Focused ion beam induced secondary electron images for (a) T91-AR, (b) T91-16 (c) T92-AR and (d) T92-16 samples respectively. The particles visible in the image correspond to $M_{23}C_6$. (Laves phase may also present in the T92 samples, however, there is very limited effect from these very small amount of Laves phase).

Figure 4.12 shows the particle size distribution, the particle population and mean particle size of $M_{23}C_6$ particles in T91 and T92 high Cr steel samples with As-received condition and 16 h stress relief condition. In the particle size distribution figures, the particle size was plotted with number of particles per area, which consists of 5 FIB images with 25 x 22 µm in scale. The particle size distribution
curves show that there is an obvious increase in the number of large particles as well as decrease in the number of small particles, which forms cross point in the graph for both T91 and T92 steel samples after 16 h stress relief heat treatment. This cross point can be explained by the Ostwald ripening mechanism: during particle coarsening, small particles dissolve into solid solution and deposited on large particles, as a result, the number of small particles decrease and that of large particles increase. Quantification of the particle size distributions found that the mean particle size increased from 132 to 144 nm in T91 (as shown in Figure 4.12 (a)), and from 118 to 131 nm in T92 (as shown in Figure 4.12 (b)) as a result of the additional 16 h stress relief heat treatment. In addition, the number density of M$_{23}$C$_6$ particles reduced by about 28% for the T91 sample and by about 20% for the T92 sample after 16 h stress relief. The quantification of the M$_{23}$C$_6$ particle size distributions show that significant particle coarsening occurred in the 91 and 92 power plant steels after the 16 h additional stress relief heat treatment. There is some evidence that the particles in the Grade 91 steel were initially larger than those in the Grade 92 steel, although they appeared to coarsen at similar rates.
Figure 4.12: The particle size distribution of $\text{M}_2\text{C}_6$ particles of (a) T91 and (b) T92 samples with the As-received condition and 16 h stress relief condition.
4.5.3 Influence of the Stress Relief Heat Treatment on Laves Phase

To understand the influence of the additional stress relief heat treatment on the secondary phase precipitation, the evolution of the particle size distribution of the $\text{M}_{23}\text{C}_6$ particles in As-received and 16 h stress relieved 91 and 92 samples has been investigated using FIB images, as discussed in last section, whilst the evolution of the Laves phase particle size distribution was investigated using BSE images. However, no Laves phase was observed in the T91 material and it was only observed in the T92 samples which had been creep tested. This means no Laves phase was found using BSE images in the SEM in the T92-AR or T92-16 samples.

To investigate the reason that Laves phase was absent in these As-received and stress relieved T91 and T92 samples, thermodynamic calculation was used to predict the main phase present in these samples, and the results are shown in Figure 4.13. The main phases predicted to be present at thermodynamic equilibrium in both the T91 and T92 steels were the ferritic matrix, together with $\sim2\%$ by weight of $\text{M}_{23}\text{C}_6$ (Cr rich) and $\sim0.25\%$ by weight of $\text{MX}$ (V,Nb)(C,N). In addition, in the T92 steel, which has a significant addition of W, the Laves phase was predicted to be present below $700^\circ\text{C}$, rising to $\sim2.5\%$ by weight at $400^\circ\text{C}$. In conclusion, there is no Laves phase observed in any T91 samples at $650^\circ\text{C}$ due to the absence of W addition in matrix microstructure that Laves phase, and the Laves phase was not found in T92 samples in either the As-received or stress relieved ($765^\circ\text{C}$) condition. This is consistent with previous observations [67] in which Laves phase has only appeared after prolonged thermal/creep exposure at lower temperatures.
Figure 4.13: Equilibrium thermodynamic predictions in the temperature range 400-1200°C for (a) T91 and (b) T92.

4.6 Summary

This chapter has presented a study of the effects of stress relief heat treatment on the microstructural evolution of grades 91 and 92 high Cr power plant steels. Firstly, during the 16 hours stress relief at 765°C, free dislocations tend to either be annihilated or to re-arrange themselves into low energy configurations. This causes subgrains to form, which increases the proportion of low angle boundaries, an effect that was observed in both T91 and T92 samples. For T91 samples, a reduction in the area fraction of martensite laths due to matrix recrystallisation and slight grain coarsening led to a decrease in the total boundary length of the T91 samples that had received the 16 hours stress relief heat treatment. For the T92 samples only a very limited decrease in total grain boundary length after the 16 hours stress relief heat treatment was observed.

Secondly, the mean composition of V increases slightly, and that of Nb decreases slightly for MX particles in both T91 and T92 samples after 16 h stress relief heat treatment, which indicates that the V-rich MX particles increase in number and the Nb-rich MX particles decrease after the 16 h stress relief. In addition, the MX particle coarsening was observed significantly with the mean particle size and area increase in T91 samples after 16 h stress relief. However, there was no obvious change in MX particle coarsening in T92 samples after 16 h stress relief. The average particle size of M_{23}C_{6} particles increased while the number density of which decreased in both the
T91 and T92 samples after 16 hours stress relief at 765°C. The particle coarsening effect can be observed as the increase of the mean \( \text{M}_{23}\text{C}_6 \) particle size, due to the number of large particles increases gradually as the stress relief time increases in both the T91 and T92 samples and the decrease of the number density in total particles due to the small particles dissolved into solid solution. There was no Laves phase observed in both T91 and T92 samples in either the As-received or 16 h stress relieved conditions.

Thirdly, the hardness values of both the T91 and T92 samples decrease after the 16 hours stress relief at 765°C. The drop in hardness is a combined result of changes in matrix and secondary phase particle population. Both sub-grain formation and secondary particles coarsening reduce the free dislocation resistance, which results in the observed reduction in hardness. It has been demonstrated that the application of the 16 h stress relief heat treatment at high temperature results in a reduction of approximately 10% in the creep rupture life in both T91 and T92 materials examined compared to expected mean lifetimes.
Chapter 5. Effects of Long-Term Aging on the Microstructure Evolution in Grade 91 and 92 Steels

5.1 Introduction

The previous chapter has illustrated the importance of initial stress relief heat treatment on the grade 91 and 92 steels. The effects of stress relief heat treatment on the hardness, matrix microstructure and secondary particles distribution were discussed.

In addition to the important role of stress relief heat treatment, the effect of long-term aging heat treatment is also very important during the service life of 91 and 92 steel components. The advanced 91 and 92 steels are widely used in the electrical power generation industry where they are utilised in the construction of header and steam piping, and boiler super-heater and re-heater tubes in both advanced coal and gas fired power plants. For all these applications, the steel components experience high temperatures, which may cause the mechanical strength of these steels to decrease after long-term aging exposure due to microstructural evolution.

In this chapter, the effects of long-term aging on the 91 and 92 steels are investigated and discussed with respect to three aspects. Firstly, the hardness values of 91 and 92 steels were measured using a Reichert hardness tester, and the changes of these hardness values due to varying long-term aging time are discussed. Secondly, the grain and subgrain structure of grade 91 and 92 steels has been extensively characterised with the use of electron backscatter diffraction in the scanning electron microscope. The changes in matrix microstructure and low/high angle boundary ratio of 91 and 92 steels due to varying long-term aging times are discussed. Thirdly, the chemical composition distributions of MX particles have been determined with the use of TEM and EDX. In addition, the particle size distribution of M_{23}C_6 and Laves phase particles has been characterised separately with the use of focused ion beam images and backscatter electron images in the dual-beam scanning electron microscope.
5.2 Materials

The grade 91 and 92 materials used in this research are the same steels as used in Chapter 4, and the chemical composition of the investigated samples, T91, T92, P91 and P92, are shown in Table 3.1 (Chapter 3). The samples used in this investigation have previously been subjected to various initial heat treatments described in the previous chapter. In order to examine the effects of long term aging heat treatment only on the microstructural evolution of 91 and 92 steels, the head positions of creep tested samples, which were exposed at 650°C and were not subjected to stress, were investigated and described in this Chapter.

5.3 The Effect of Long-term Aging on the Hardness of 91, 92 steels

In chapter 4, a methodology was described whereby the as-received materials were compared with those which had received a 16 h stress relief heat treatment in order to investigate the effects of stress relief heat treatment on the hardness of 91 and 92 steels. The same methodology was used to investigate the effects of long-term aging heat treatment on the hardness of 91 and 92 steel in this chapter. The mean hardness values and standard deviations of AR and stress relieved 91 and 92 samples with different aging time are shown in Table 5.1.

The effect of isothermal aging on the hardness of the T91, T92, P91 and P92 steels is shown in Figure 5.1. For the T91 and T92 samples, it can be seen that the hardness values of as-received samples decrease as the long term aging time increases for both samples, whereas there was no obvious trend in hardness values of 16 h stress relieved samples with different aging times. Similarly, it can be seen that the hardness values decrease as the long term aging time increases for P91 as-received samples, however, there was no such trend in the hardness values of P92 as-received samples, which may result from the quite limited range in aging time (2504 h to 3854 h). In additional, the change in hardness values was very limited with different aging times for both P91 and P92 16 h stress relieved samples.
Table 5.1: The mean values and standard deviations of AR and stress relieved 91 and 92 samples with different aging times.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Aging Time(h)</th>
<th>Hardness(Hv)</th>
<th>Sample</th>
<th>Aging Time(h)</th>
<th>Hardness(Hv)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td></td>
<td></td>
<td>T91-AR</td>
<td>0</td>
<td>225±5</td>
</tr>
<tr>
<td></td>
<td>T91-AR-1</td>
<td>1549</td>
<td>218±2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T91-AR-2</td>
<td>5857</td>
<td>215±2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>T92</td>
<td></td>
<td></td>
<td>T92-AR</td>
<td>0</td>
<td>235±3</td>
</tr>
<tr>
<td></td>
<td>T92-AR-1</td>
<td>1649</td>
<td>205±4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>T92-AR-2</td>
<td>10172</td>
<td>205±4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P91</td>
<td></td>
<td></td>
<td>P91-AR-1</td>
<td>2807</td>
<td>229±4</td>
</tr>
<tr>
<td></td>
<td>P91-AR-3</td>
<td>4310</td>
<td>218±4</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P91-AR-2</td>
<td>7684</td>
<td>213±2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P92</td>
<td></td>
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<td>P92-AR-1</td>
<td>2504</td>
<td>226±2</td>
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<tr>
<td></td>
<td>P92-AR-3</td>
<td>3350</td>
<td>225±2</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>P92-AR-2</td>
<td>3854</td>
<td>226±2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

During long term aging, the decrease in hardness values indicate that the isothermal aging heat treatment affects the microstructure evolution of both 91 and 92 steels, and thus accounts for the changes in mechanical properties. These effects of aging time on microstructure evolution, which consists of matrix microstructure evolution (characterised using EBSD analysis) and secondary particles evolution (characterised using TEM and FIB-FEGSEM), are discussed in the later sections.

In addition, the additional stress relief heat treatment affects the microstructure evolution by forming more sub-grains and increasing the secondary particle sizes, and thus reduces the hardness values of both 91 and 92 16 h stress relieved samples, as discussed in Chapter 4.
Figure 5.1: Graphs showing the effect of aging time at 650°C on the hardness of (a) the T91 and T92 and (b) the P91 and P92 samples subjected to different stress relief heat treatments. (As-received samples have taken an hour stress heat treatment at 765°C).
5.4 Effects of the Long-term Aging Heat Treatment on the Matrix Microstructure Evolution

Figures 5.2 to 5.9 show the microstructures, both in image quality plus inverse pole figure maps and boundary misorientation maps, of the T91, T92, P91 and P92 samples respectively that have experienced different aging times at 650 °C. It can be seen that in the as-received condition (no aging), the prior austenite grains, martensitic packets and the martensitic laths are well defined in all the four types of steel samples, and in the 16 h stress relieved condition (no aging), the well-defined martensitic matrix structure is also evident, however, there is an indication of some additional subgrain formation.

For all the as-received 91 samples (T91 and P91), the material matrix microstructure exhibited the presence of small equaxed grains within the martensite matrix after short term aging (1,549 h for T91 and 2,807 h for P91), as shown in Figure 5.2 and 5.6. After longer aging time (5,857 h for T91 and 7,684h for P91), all the as-received T91 and P91 samples show a large increase in low angle boundaries in the microstructure, which appear finer than that after shorter term aging. In contrast, such a defined subgrain structure is not evident in the as-received 92 samples after short term aging (1,649 h for T92 and 2,504 h for P92), as shown in Figure 5.4 and 5.8. After longer aging time (10,172 h for T92 and 3,854h for P92), the material matrix microstructure exhibited small equaxed grains within the martensite matrix, which are similar but in a lesser degree by comparing with the as-received 91 samples.

For all the 16 h stress relieved 91 samples, clusters of small equaxed grains within the martensite matrix were observed, which is a good indication of matrix recrystallisation after long term aging (4,826 h for T91 and 4,819 h for P91), as shown in Figure 5.3 and 5.7. However, the effect is not so significant in the 16 h stress relieved 92 samples because only a very small number of equaxed grains are present within the martensite matrix.

It is evident that the matrix recovery process during isothermal aging is greatly affected by the stress relief heat treatment. After 16 h stress relief heat treatment, the free dislocation densities may be reduced and thus undermines the isothermal aging resistance of both 91 and 92 steels, and as a result, there are more equaxed
grains within the martensite matrix of 91 and 92 16 h stress relieved samples with shorter aging time than those in as-received 91 and 92 samples with longer aging time. There are some small regions, which are identified as low angle boundaries (red lines in the boundary misorientation maps), and were found within the matrix of both the 16 h stress relieved 91 and 92 samples after long-term aging. These regions do not assume the shape of grains; instead, they appear as random fine scale undefined shapes, which may be interpreted as the onset of subgrain development that had occurred at the shorter aging time in the Grade 91 and 92 samples.

The normal and simplified method of interpreting boundary angle data is to compare the ratio of low angle (2-15º) to high angle (15-180º) boundaries, as shown in Figures 5.10 and 5.11. For all the 91 and 92 as-received steel samples, the low angle to high angle ratio increases with prolonged aging time, as shown in Figure 5.10, and for all the 91 and 92 16 h stress relieved steel samples, as shown in Figure 5.11, there is no such trend between the low angle to high angle ratio and aging time due to the prior effect of stress relief heat treatment on the microstructural evolution.
Figure 5.2: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the T91 as-received samples from no aging (left) to 5,857 h isothermal aging (right).
Figure 5.3: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the T91-16 h stress relieved samples from no aging (left) to 4,826 h isothermal aging (right).
Figure 5.4: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the T92 as-received samples from no aging (left) to 10,172 h isothermal aging (right).
Figure 5.5: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the T92 16 h stress relieved samples from no aging (left) to 7,965 h isothermal aging (right).

T92-16 (no aging)  T92-16 (1,175 h)  T92-16 (7,965 h)

2-15°  >15°
Figure 5.6: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the P91 as-received samples from 2,807 h (left) to 7,684 h isothermal aging (right).
Figure 5.7: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the P91 16 h stress relieved samples from 1,995 h (left) to 4,819 h isothermal aging (right).
Figure 5.8: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the P92 as-received samples from 2,504 h (left) to 3,854 h isothermal aging (right).
**Figure 5.9:** Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the P92 16 h stress relieved samples from 3,883 h (left) to 5,930 h isothermal aging (right).
Figure 5.10: Graph illustrating the ratio of low angle to high angle boundaries for 91 and 92 as-received steel samples subjected to different aging times.

Figure 5.11: Graph illustrating the ratio of low angle to high angle boundaries for 91 and 92 16 h stress relieved steel samples subjected to different aging times.
5.5 Effects of the Long-term Aging on the Secondary Phase Precipitation

To understand the influence of the long-term aging on the secondary phase precipitation, firstly the chemical compositions of MX particles as a function of aging time in 91 and 92 steels have been investigated. This was performed in order to identify whether the MX chemical composition changes occur during long-term aging, and thus determine whether such changes can be used as a method of assessing the condition, or thermal history, of high Cr ferritic-martensitic power plant steels. Secondly, the evolution of the particle size distribution of the M23C6 and Laves phase particles with respect to aging time has been investigated in order to determine how the kinetics of particle coarsening are affected with different aging times and temperatures.

5.5.1 Influence of Long-Term Aging on the MX Particles

The chemical composition of the MX particles was measured using EDS on the etching exposed MX particles in TEM carbon replica samples, in order to investigate how the chemical compositions of these particles change during long-term aging and also to determine any effects of the different chemical compositions of the bulk materials (T91 and T92 steels). It has previously been found that V(N,C) and Nb(C,N) are completely intersoluble [2, 3], and so it was interesting to examine the relative composition distributions of V, Nb and Cr in MX with different long-term aging times. Figure 5.12 shows the average composition of the metallic elements V, Nb and Cr in the MX carbonitride particles of the T91 and T92 samples with varying aging times. It is shown that a significant enrichment of V in MX particles occurs after 5,857 h aging in the T91 as-received sample whereas the chemical composition of metallic element Nb decreases in T91 as-received sample. In contrast, T92 as-received sample is shown to have a more stable composition of MX after long-term aging, as shown in Figure 5.12. With increasing aging time to 10,172 h, the mean chemical composition of V content and Nb content changed very slightly, which indicated that the mean compositions of these MX particles are moving towards their equilibrium values.
Figure 5.12: Plot showing the mean chemical composition of MX particles present in the T91 and T92 as-received samples supplied with different aging time.

Figure 5.13 shows the chemical composition distributions of V, Nb and Cr metallic elements of T91 and T92 as-received samples before and after long-term aging heat treatment. In Figure 5.13 (a, b), there appears to be a reduction in the amount of Nb-rich MX particles present due to significant increase in secondary precipitation of VN after 5,857 h aging (T91-AR-2) in T91 as-received sample. However, after 10,172 h aging (T92-AR-2) the composition distribution of MX particles in T92 as-received sample was separated into two distinct particle types, in this case either Nb-rich or V-rich particles, whereas before the aging stage, the composition distribution of the metallic elements in MX particles was more linear, as shown in Figure 5.13 (c, d).
Figure 5.13: EDX measurements from individual MX particles comparing their V, Nb and Cr content in the (a) T91 As-received, (b) T91 AR-2, (c) T92 As-received and (d) T92 AR-2 samples.
5.5.2 Effects of Long-Term Aging on the Particle Size Distribution of Secondary Phase Precipitation

Precipitation strengthening is one of the most important strengthening mechanisms in grade 91 and 92 high Cr ferritic-martensitic power plant steels, as explained in Chapter 2. In this mechanism, the stability of the steel microstructure is dependent on a fine dispersion of small particles which act as grain boundary pinning points, and also pin dislocations in the matrix to stop the motion of dislocations, and thus the process of recovery. Many studies of secondary particles in 91 and 92 steels have reported data from particle size measurements, but most of these are based on manual measurements on a limited number of particles. However, in order to link microstructural features to the creep properties and creep rupture time, a method that can accurately determine precipitate size, which can give the effects of particles on the strength of high Cr power plant steels was needed. The results of detailed particle size analysis of the different secondary precipitate phases in grade 91 and 92 steels with varying long-term aging times are discussed in the following sections.

5.5.2.1 Influence of Long-Term Aging on the Particle Size Distribution of M$_{23}$C$_6$ Particles

In this section, the effects of long-term aging on the precipitation behaviour of M$_{23}$C$_6$ particles are discussed. The particle size distribution of M$_{23}$C$_6$ particles was determined from FIB images, which were subsequently analysed with the Image Tool 3.0 analysis software (as shown in Figure 5.14). The methodology for particle size analysis has been described in Chapter 3.

It is evident from Figure 5.14 that the particles coarsen as the aging time increases from no aging to 5,857 h for the T91 as-received sample and to 10,172 h for the T92 as-received sample. To quantify this effect, the particle size distribution graphs, which plot particle sizes against the number of particles per unit area (2750 $\mu$m$^2$), are shown in Figure 5.15. In Figure 5.15 (a), the particle size distribution for T91 AR, AR-1 and AR-2 samples are displayed. The particle distribution change is very limited, and there is little particle coarsening in the T91 AR samples with different aging times. However, particle coarsening is observed in Figure 5.15 (b); the number of large particles increases as the aging time increases in the T92 samples. For T91, the average particle size increases from 132 nm (as-received state) to 135 nm after 5857 h isothermal aging, which is very limited. For T92, 10,172 h isothermal aging...
resulted in an increase in average particle size from 118 nm to 129 nm. At the same time, the number density of particles in the T91 as-received samples decreased from 3200 to 2605, however, there was very limited change in the number density of particles for T92 samples, from 4767 to 4724.

From Figure 5.16, the particle coarsening observed was very limited as the aging time increased from no aging to 4,826 h for T91 16 h stress relieved samples and to 7,965 h for T92 16 h stress relieved samples. To quantify this effect, the particle size distribution graphs were produced and are shown in Figure 5.17. It is evident from Figure 5.17 (a) that the particle size distribution for the T91 16, 16-1 and 16-2 samples changes only a small amount as a function of isothermal aging time, from 144 nm to 136 nm, then up to 151 nm, which indicated that there is no obvious trend between the T91 16 h stress relieved samples with different aging times. Similarly, there was no obvious trend in the particle size change of the T92 16 h stress relieved samples, as shown in Figure 5.17 (b). 7,965 h isothermal aging resulted in no significant change in the average particle sizes; both are 131 nm. At the same time, the number density of particles in the T91 16 h stress relieved samples increased from 2317 to 2948, however, that in the T92 16 h stress relieved samples decreases from 3787 to 3273. The mean particle sizes were, however, significantly larger than those in the samples which had not experienced the stress relief heat treatment.

It is evident from Figure 5.18 that the particles coarsen considerably as the aging time increases from 2,807 h to 7,684 h for the P91 as-received sample and changed very little as the aging time increases from 2,504 h to 3,854 h for the P92 as-received samples. To quantify this effect, the particle size distribution graphs were produced and are shown in Figure 5.19. In Figure 5.19 (a), the particle size distribution for the P91 AR-1, AR-2 and AR-3 samples are displayed. The particle coarsening effect can be observed as the number of large particles increases as the aging time increases. However, there is no obvious trend in the particle distribution change of the P92 AR-1, AR-2 and AR-3 samples, as shown in Figure 5.19 (b). For the P91 as-received samples, the average particle size increased from 117 nm to 135 nm with an isothermal aging time from 2,807 h to 7,684 h. For the P92 as-received samples, very small changes in the long-time aging time (from 2,504 h to 3,854 h) resulted in limited change of average particle size, from 136 nm to 132 nm. At the same time, the number density of particles in the P91 as-received samples
decreased from 3653 to 3052, and similar change in the number density of particles for the P92 as-received samples; from 3911 to 3657 was observed.

From Figure 5.20, the particles coarsen considerably as the aging time increases from 1,995 h to 4,819 h for the P91 16 h stress relieved samples and from 2,019 h to 5,930 h for the P92 16 h stress relieved samples. To quantify this effect, the particle size distribution graphs were produced and are shown in Figure 5.21. It is evident from Figure 5.21 (a) that the mean particle size for the P91 16-1, 16-2 and 16-3 samples changes slightly as a function of isothermal aging time; from 135 nm to 144 nm. A similar trend was observed in Figure 5.21 (b), which shows the change in the particle size of the P92 16 h stress relieved samples from 140 nm to 145 nm when the aging time changed from 3,883 h to 5,930 h (the head section of the P92 16-1 damaged during creep test). At the same time, the number density of particles in the P91 16 h stress relieved samples increased from 2445 to 3268, however, that in the P92 16 h stress relieved samples decreased from 3448 to 3251.
Figure 5.14: Focused ion beam plus IEE flow images illustrating the $\text{M}_{23}\text{C}_6$ particle size evolution of the T91 and T92 as-received samples from no aging (left) to 5,857 h (T91) / 10,172 h (T92) isothermal aging (right).
### Figure 5.15: $M_{23}C_6$ Particle size distributions of -AR, -AR-1 and -AR-2 head positions for T91 and T92 samples.

<table>
<thead>
<tr>
<th></th>
<th>Particle Number Density (2750 $\mu$m²)</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91-AR</td>
<td>3200</td>
<td>132</td>
</tr>
<tr>
<td>T91-AR-1 Head</td>
<td>2903</td>
<td>128</td>
</tr>
<tr>
<td>T91-AR-2 Head</td>
<td>2605</td>
<td>135</td>
</tr>
<tr>
<td>T92-AR</td>
<td>4767</td>
<td>118</td>
</tr>
<tr>
<td>T92-AR-1 Head</td>
<td>5559</td>
<td>118</td>
</tr>
<tr>
<td>T92-AR-2 Head</td>
<td>4724</td>
<td>129</td>
</tr>
</tbody>
</table>
Figure 5.16: Focused ion beam plus IEE flow images illustrating the $M_{23}C_6$ particle size evolution of the T91 and T92 16 h stress relieved samples from no aging (left) to 4,826 h (T91) / 7,965 h (T92) isothermal aging (right).
Figure 5.17: $\text{M}_{23}\text{C}_6$ Particle size distributions of -16, -16-1 and -16-2 stress relieved head positions for T91 and T92 samples.
Figure 5.18: Focused ion beam plus IEE flow images illustrating the $M_{23}C_6$ particle size evolution of the P91 and P92 as-received samples from 2,807 h (P91) / 2,504 h (P92) (left) to 7,684 h (P91) / 3,854 h (P92) isothermal aging (right).
Figure 5.19: \(\text{M}_{23}\text{C}_6\) Particle size distributions of -AR-1, -AR-1 and -AR-2 head positions for P91 and P92 samples.
Figure 5.20: Focused ion beam plus IEE flow images illustrating the $M_{23}C_{6}$ particle size evolution of the P91 and P92 16 h stress relieved samples from 1,995 h (P91) / 3,883 h (P92) (left) to 4,819 h (P91) / 5,930 h (P92) isothermal aging (right).
<table>
<thead>
<tr>
<th></th>
<th>Particle Number Density (2750 μm²)</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P91-16-1 Head</td>
<td>2445</td>
<td>135</td>
</tr>
<tr>
<td>P91-16-2 Head</td>
<td>2732</td>
<td>136</td>
</tr>
<tr>
<td>P91-16-3 Head</td>
<td>3268</td>
<td>144</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Particle Number Density (2750 μm²)</th>
<th>Average particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P92-16-1 Head</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>P92-16-2 Head</td>
<td>3448</td>
<td>140</td>
</tr>
<tr>
<td>P92-16-3 Head</td>
<td>3251</td>
<td>145</td>
</tr>
</tbody>
</table>

Figure 5.21: $M_{23}C_6$ Particle size distributions of -16, -16-1 and -16-2 stress relieved head positions for P91 and P92 samples.
The general conclusion that the $M_{23}C_6$ particles are coarsening can be made from most of results in the particle size distribution of $M_{23}C_6$ particles from the 91 and 92 long-term aged samples. Particle coarsening strictly occurs at a constant volume fraction and is characterised by a reduction in the overall number of particles and an increase in the mean size.

To investigate the effects of long-term aging on the $M_{23}C_6$ particle size distribution of the 91 and 92 samples with different aging times, the mean particle size and number density of $M_{23}C_6$ particles were plotted with varying aging times up to 10,172 h, as shown in Figures 5.22 and 5.24. The trend line for each 91 and 92 as-received and 16 h stress relieved samples was drawn according to the mean particle size data or number density data of $M_{23}C_6$ particles, and this trendline can be used to describe the changes in the mean particle size or the number density of $M_{23}C_6$ particles with varying aging times.

**Figure 5.22:** Plot illustrating the mean size of $M_{23}C_6$ particle for the 91 and the 92 steel as-received and 16 h stress relieved samples with varying aging time. The aging temperature was 650ºC.

To better explain the relationship between the mean particle size and long-term aging times, the mean $M_{23}C_6$ particle size was also plotted against the square and cube root of long-term ageing times, shown in Figure 5.23. From Figure 5.22 and 5.23, it can be seen that the mean particle size of $M_{23}C_6$ particles increases as the
aging time increases for all the 91, 92 As-received and 16 h stress relieved samples. They also show the effects of the 16 h stress relief heat treatment on the mean particle size of 91 and 92 samples. As discussed in Chapter 4, the mean particle size increased after the 16 h stress relief and this resulted in all of the 16 h series long-term aged samples having a larger mean $M_{23}C_6$ particle size than the As-received creep tested samples at the same aging time.

Figure 5.23: Plot illustrating the mean size of $M_{23}C_6$ particles for the 91 and the 92 steel as-received and 16 h stress relieved samples with (a) square root and (b) cube root of aging times. The aging temperature was 650°C.
Finally, by comparing the trendline of 91 and 92 long-term aged samples, the change rate of mean particle size with varying aging times for 92 creep tested samples is smaller than that for 91 creep tested samples, which means that when the aging time increases by the same amount, the mean M$_{23}$C$_6$ particle size changed much less for the 92 samples than that for the 91 samples. This means the 92 samples have much better long-term aging resistance, and thus potentially have longer service life at the same or even higher temperature than 91 samples.

![Figure 5.24](image_url)

**Figure 5.24**: Plot illustrating the number density of M$_{23}$C$_6$ particle for the 91 and the 92 steel As-received and 16 h stress relieved samples with varying aging time. The aging temperature was 650°C.

From Figure 5.24, the number density of M$_{23}$C$_6$ particles generally decreases as the aging times increase for all the 91, 92 As-received and 16 h stress relieved samples except for the 91 16 h stress relieved samples, which shows the opposite trend. This decrease in the number density of M$_{23}$C$_6$ particles is consistent with particle coarsening. Figure 5.24 also shows the effects of the 16 h stress relief heat treatment on the number density of M$_{23}$C$_6$ particles for creep tested samples. As discussed in Chapter 4, the number density of M$_{23}$C$_6$ particles decreased after the 16 h stress relief and therefore all the 16 h series creep tested samples have a smaller number density of M$_{23}$C$_6$ particles than As-received creep tested samples at same applied creep stress. This may also be the reason for the different trend in the 91 16
h stress relieved samples, because new particles may be formed during the long-term aging procedure, resulting in the increase in the number density of $\text{M}_{23}\text{C}_6$ particles. It can then be expected that after much longer aging times, these newly formed small particles will coarsen, resulting in an overall decrease in number density of $\text{M}_{23}\text{C}_6$ particles.

5.5.2.2 Influence of Long-Term Aging on the Particle Size Distribution of Laves Phase Particles

In this work, backscatter images were used to determine the difference between the Laves phase particles and the matrix phase, and then used to calculate the size distributions of Laves phase using a 6 mm working distance and 25 $\times$ 22 $\mu$m$^2$ image sizes. Laves phase is an intermediate intermetallic phase which particles most commonly in prior-austenite and subgrain boundaries, and also in the area near $\text{M}_{23}\text{C}_6$ particles. All the 91 and 92 samples were analysed using the BSE technique to examine the presence and distribution of Laves phase. However, there was no Laves phase in both the as-received 91 and 92 samples, and also in any of the 91 creep tested samples. In this section, therefore the effect of long-term aging on the Laves phase of the 92 samples was investigated.

It is evident from Figure 5.25 that the Laves phase particles coarsen considerably as the aging time increases from no aging to 10,172 h for the T92 as-received sample and slightly as the aging time increases from 2,504 h to 3,854 h for the P92 as-received sample. To quantify this effect, the particle size distribution graphs, which plot Laves phase particle sizes against the number of particles per unit area (2750 $\mu$m$^2$), are shown in Figure 5.26. In Figure 5.26 (a), the Laves phase particle size distribution for the T92 AR, AR-1 and AR-2 samples are displayed. The particle coarsening effect can be observed as the number density of Laves phase particles decreases from 2084 to 1227 as the aging time increases while mean particle size increases from 143 nm to 209 nm. This means the number density of large particles increases and that of small particles decreases during long term aging, which indicates the Laves phase particle coarsening. A similar trend was also observed in Figure 5.26 (b), which shows the coarsening of Laves phase particles in the P92 samples. As the aging time increases from 2,504 h to 3,350 h, the number density of Laves phase particles decreases slightly from 400 to 395 and the mean size of which increases from 206 nm to 254 nm. The P92-AR-3 sample shows a different trend in
particle coarsening due to the earlier failure during creep test process, and therefore the results are expected to be inconsistent for this sample.

From Figure 5.27, the particles were observed to coarsen considerably as the aging time increased from 0 h to 7,965 h for the T92 16 h stress relieved samples and from 3,883 h to 5,930 h for the P92 16 h stress relieved samples. To quantify this effect, the particle size distribution graphs were produced and are shown in Figure 5.28. It is evident from Figure 5.28 (a) that the Laves phase particle size distribution for the T92 16, 16-1 and 16-2 head samples changes significantly as a function of isothermal aging time, from 0 to 164 nm to 209 nm. A similar trend is observed in Figure 5.28 (b), which shows the change in Laves phase particle size of the P92 16 h stress relieved samples from 264 nm to 285 nm with aging time changed from 3,883 h to 5,930 h (the head section of P92 16-1 damaged during creep test). At the same time, the number density of Laves phase particles in the P92 16 h stress relieved samples increased slightly from 1627 to 2003, however, the P92 16 h stress relieved samples decreased from 535 to 435 as expected.
Figure 5.25: BSE images illustrating the Laves phase particle size evolution of the T92 and P92 as-received samples from 1,649 h (T92)/2,504 h (P92) (left) to 10,172 h (T92)/3,854 h (P92) isothermal aging (right).
Figure 5.26: Laves phase particle size distributions of T92–AR, -AR-1 and -AR-2 head and P92-AR-1, -AR-2 and –AR-3 head samples.
Figure 5.27: BSE images illustrating the Laves phase particle size evolution of the T92 and P92 16 h stress relieved samples from 1,175 h (T92) /3,883 h (P92) (left) to 7,965 h (T92) / 5,930 h (P92) isothermal aging (right).
Figure 5.28: Laves phase particle size distributions of T92-16, -16-1 and -16-2 stress relieved head samples and P-16-1, -16-2 and -16-3 stress relieved head samples.
The general conclusion that the Laves phase particle coarsening is considerable can be made from all the results of the particle size distribution of the Laves phase particles for all the Grade 92 long-term aged samples. There is a general decrease in the number density of the Laves phase particles in all the Grade 92 long-term aged samples, although there were some variations due to the samples used.

To investigate the effects of long-term aging on the Laves phase particle size distribution change of all the Grade 92 samples with varying aging times, the mean particle size and the number density of the Laves phase particles were plotted with varying aging time up to 10,172 h, as shown in Figure 5.29 and 5.31. The trendline for each 92 as-received and 16 h stress relieved samples was drawn according to the mean particle size data or the number density data of the Laves phase particles, and this trendline can be used to describe the change in mean particle size or the number density of the Laves phase particles with varying aging times.

**Figure 5.29:** Plot illustrating the mean Laves phase particle size for the 92 As-received and 16 h stress relieved samples with varying aging time. The aging temperature was 650ºC.

To better explain the relationship between the mean Laves particle size and long-term aging times, the mean Laves particle size was also plotted against the square and cube root of long-term ageing times, shown in Figure 5.30. From Figure 5.29 and 5.30, it can be clearly seen that the mean particle size of the Laves phase
particles increases as the aging time increases for all the T92 and P92 As-received and 16 h stress relieved samples. However, the mean particle size coarsening rate of the P92 samples appears to be much higher than that of the T92 samples. The possible reason for this is the difference in bulk composition of the T92 and P92 samples. The
Mo concentration is 0.51 wt% in the P92 sample and 0.39 wt% in the T92 samples. The Laves phase has the composition Fe$_2$M, where the 'M' can either be Mo, W or both. The higher Mo concentration may cause the particle coarsening rate to increase, and the mean particle size of the Laves phase is much higher in the P92 samples than in the T92 samples, even with a shorter aging time. Figure 5.29 and 5.30 also show the effect of the 16 h stress relief heat treatment on the mean particle size of the Grade 92 samples in that all the 16 h series long-term aged samples have a larger mean particle size than the As-received creep tested samples at the same aging time.

![Figure 5.31](image.png)

**Figure 5.31:** Plot illustrating the number density of Laves phase for the 92 As-received and 16 h stress relieved samples with varying aging time. The aging temperature was 650ºC.

From Figure 5.31, there is no clear trend in the number density of Laves phase with varying aging times for all the 92 As-received and 16 h stress relieved samples. It is possible that the investigated sample area (µm$^2$) is not sufficient to properly quantify the number density of Laves phase since the particle size of Laves phase is much higher than that of M$_{23}$C$_6$ particles. However, this sampling area was appropriate to compare the same sampling areas for both the Laves phase and the M$_{23}$C$_6$ particles. The research in the number density change of Laves phase over a larger sampling area may be studied in future work.
5.5.2.3 Particle coarsening rate of secondary particles during long-term aging

In this study, the coarsening constant can be calculated from the equation 5.1

\[ k = \frac{(r^3 - r_0^3)}{t} \]  (5.1)

where \( r_0 \) is the initial mean particle radius and \( r \) is the mean particle radius at time \( t \). The coarsening constant is \( k \) and given in \( \text{m}^3\text{s}^{-1} \). There is no initial mean particle diameter for most samples in this study, however, there are varying aging or creep times for the same samples, so the equation 5.1 can be advanced into equation 5.2

\[ k = \frac{(r_2^3 - r_1^3)}{(t_2 - t_1)} \]  (5.2)

where \( r_1 \) and \( r_2 \) are the mean particle radius at times \( t_1 \) and \( t_2 \), respectively. The values of the coarsening constant of M23C6 particles and Laves phase for each 91 and 92 high Cr power plant samples at 650°C have been calculated and shown in Table 5.3.

**Table 5.3:** The values of the coarsening constant of M23C6 particles and Laves phase for each 91 and 92 high Cr power plant samples at 650°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat treatment</th>
<th>Coarsening Constant, ( K ), ( \text{m}^3\text{s}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M23C6 Precipitate</td>
<td>Laves Phase</td>
</tr>
<tr>
<td>T91</td>
<td>As-received</td>
<td>1.05 \times 10^{-26}</td>
</tr>
<tr>
<td></td>
<td>16 h Stress Relief</td>
<td>3.02 \times 10^{-26}</td>
</tr>
<tr>
<td>T92</td>
<td>As-received</td>
<td>7.39 \times 10^{-27}</td>
</tr>
<tr>
<td></td>
<td>16 h Stress Relief</td>
<td>2.78 \times 10^{-27}</td>
</tr>
<tr>
<td>P91</td>
<td>As-received</td>
<td>2.20 \times 10^{-26}</td>
</tr>
<tr>
<td></td>
<td>16 h Stress Relief</td>
<td>2.33 \times 10^{-26}</td>
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<tr>
<td>P92</td>
<td>As-received</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>16 h Stress Relief</td>
<td>1.86 \times 10^{-26}</td>
</tr>
</tbody>
</table>

From this table, it can be seen that the M23C6 particle coarsening rates of the T92 samples are both smaller than that of the T91 samples in the as-received and 16 h stress relief heat treatment conditions, indicating the better M23C6 particles coarsening resistance during long-term aging at 650°C. The M23C6 particle coarsening rates of the P91 and P92 samples are close and that of the P92 as-received samples is not calculated due to the very limited change in mean particle diameter.
size after short aging time (around 1,000 h). The Laves phase coarsening rates are significantly larger than the M\textsubscript{23}C\textsubscript{6} particles coarsening rates for both the T92 and P92 samples, indicating that the Laves phase coarsens more significantly than the M\textsubscript{23}C\textsubscript{6} particles during high temperature long-term aging.

5.6 Summary

This chapter has presented a study of the effects of long-term aging heat treatment on the microstructural evolution of grades 91 and 92 high Cr power plant steels. Firstly, the hardness values of all the as-received samples decreased as the long term aging time increased, except for the P92 as-received samples. There is no clear trend in hardness values in these samples, which may result from the quite limited range in aging time (2504 h to 3854 h). However, the change in hardness values was very limited with further aging time for all the 16 h stress relieved samples.

Secondly, during long-term aging, free dislocations tend to either be annihilated or to re-arrange themselves into lower energy configurations. This causes subgrains to form, which increases the proportion of low angle boundaries; an effect that was observed in both the 91 and 92 samples. For all the 91 and 92 as-received samples, the low/high angle boundary ratio increased as the aging time increased, indicating that there are more subgrains formed during long-term aging. For the 16 h stress relieved samples, there is no such trend between the low angle to high angle ratio and aging time due to the prior effect of stress relief heat treatment on the microstructural evolution.

Thirdly, the mean composition of V increased slightly, and that of Nb decreased slightly for MX particles in T91 samples after long-term aging heat treatment, which indicated that overall the number of V-rich MX particles increased and the Nb-rich MX particles decreased after long term aging. However, with increasing aging time to 10,172 h, the mean chemical composition of V content and Nb content changed very little in T92 samples. The M\textsubscript{23}C\textsubscript{6} particle coarsening effect can be observed as the mean particle size increases and the number density decreased gradually as the aging time increased in both the 91 and 92 samples. The particle coarsening of
Laves phase was also observed, as the mean particle size increases gradually as the aging time increases in all the 92 samples, however, there is no clear trend in the number density of Laves phase found in all the 92 samples. In addition, the Laves phase coarsened more significantly than the $\text{M}_{23}\text{C}_6$ particles at high temperature long-term aging. Differences in Laves particle size was also observed between the T92 and P92 samples sets, which could be linked to a difference in the bulk Mo content in the two sets of steels.
Chapter 6. Effects of Creep on the Microstructure Evolution in Grade 91 and 92 Steels

6.1 Introduction

The previous chapters have illustrated the importance of both stress relief and long-term aging heat treatments on Grade 91 and 92 steels. The effects of stress relief and long-term aging on the hardness, matrix microstructure and secondary particles distribution were discussed.

In addition to the stress relief and long-term aging heat treatment, the effects of creep stress on the microstructural evolution is also very important during the service life of Grade 91 and 92 steel components. The advanced 91 and 92 steels are widely used in the electrical power generation industry where they undergo creep stress at high temperature, which will cause the strength of these steels to deteriorate and hence reduce the service life. This breakdown is caused by the loss of the major strengthening mechanisms, which can include the tempered martensite lath (sub-grain) structure, $\text{M}_2\text{C}_6$ precipitates, MX precipitates or Laves phase precipitates which can occur in such steels.

In this chapter, the effects of creep stress on the 91 and 92 steels have been investigated and discussed with respect to three aspects. Firstly, the hardness values of 91 and 92 steels were measured using a Reichert hardness tester, and the changes of these hardness values due to varying creep stress have been discussed. Secondly, the grain and subgrain structure of grade 91 and 92 steels has been extensively characterised with the use of electron backscatter diffraction in the scanning electron microscope. The changes in matrix microstructure and low/high angle boundary ratio of 91 and 92 steels due to varying creep stress have been investigated. Thirdly, the chemical composition distribution of MX particles has been determined with the use of TEM equipped with EDX. In addition, the particle size distribution of both $\text{M}_2\text{C}_6$ and Laves phase particles has been characterised separately with the use of focused ion beam images and backscatter electron images in the dual-beam scanning electron microscope.
6.2 Materials

In order to examine the effects of creep stress on the microstructural evolution of 91 and 92 steels, the head positions of the creep tested samples, which were exposed at 650°C and have not been subjected to stress, and the gauge positions which were exposed at 650°C and failed under various creep stresses were both investigated for.

6.3 The Effect of Creep on the Hardness of 91, 92 steels

In chapter 4, a methodology was described whereby the as-received materials were compared with those which had received a 16 h stress relief heat treatment in order to investigate the effects of stress relief heat treatment on the hardness of 91 and 92 steels. The same methodology has been used to investigate the effects of creep stress on the hardness of 91 and 92 steel in this chapter.

6.3.1 The Results of Hardness Data for 91 and 92 Creep Tested Samples

The mean hardness values and standard deviations of AR and stress relieved 91 and 92 samples with different creep stresses are shown in Table 6.1. Figures 6.2 and 6.3 show the hardness differences between the head (unstressed) and gauge (stressed) positions of the investigated 91 and 92 samples. For all the T91, T92, P91 and P92 creep tested samples, Figure 6.2 and 6.3 show that the mean hardness value of gauge position decreased after creep testing compared to the head position for both As-received and 16 h stress relieved samples.
Table 6.1: Heat treatment conditions, creep test results and hardness values of creep tested samples
(This table is reference to table 5.1, which are different characterised positions in the same samples).

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>Initial Heat treatment conditions</th>
<th>Additional stress relief at 765°C</th>
<th>Creep test results at 650°C (Load / Rupture Life)</th>
<th>Hardness /HV 10 kg Load</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>T91</strong></td>
<td></td>
<td></td>
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<td>-</td>
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<td>85 MPa / 7965 h</td>
<td>H:218±2; G:176±1</td>
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</tr>
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*N is normalising heat treatment and T is tempering heat treatment

*H and G in the Hardness column refers to the hardness value tested from head and gauge sections respectively
Figure 6.1: Plots showing the effect of creep testing at 650°C on the hardness of (a) the T91 and (b) the T92 samples subjected to different stress relief heat treatments.
Figure 6.2: Plots showing the effect of creep test at 650°C on the hardness of (a) the P91 and (b) the P92 samples subjected to different stress relief heat treatment.
6.3.2 Discussion

The 91 and 92 samples were tested to failure at a temperature of 650°C and at different constant stress values, ranging from 66 to 112 MPa. Accordingly, the test duration ranged from 10,172 h to 992 h at different stress conditions. Figure 6.3 shows the effect of creep stress on the rupture time of the investigated 91 and 92 samples. For the 91 creep tested samples, Figure 6.3 (a) shows that the creep rupture time increased as the creep stress value decreased for both the 91 as-received and 16 h stress relieved samples. For 92 creep tested samples, Figure 6.3 (b) shows similar trend in that the creep rupture time increased as the creep stress value decreased for both the 92 as-received and 16 h stress relieved samples. By comparing Figure 6.3 (a) and (b), it can be seen that the applied creep stress for the 92 steel samples are much higher than those for the 91 steel samples, and even the smallest creep stress in the 92 samples, 85 MPa, is higher than the highest creep stress in 91 samples, 82 MPa. However, the rupture life of the 92 samples is commonly longer than that of 91 samples with higher creep stress, which means 92 samples have much better mechanical properties (higher creep rupture life, hardness values, etc.) than the 91 samples.

The relationships between the creep stress and hardness values of the creep tested samples are plotted in Figure 6.4. For all the 91 and 92 as-received and 16 h stress relieved creep tested samples (gauge positions), the similar trend can be observed is that as the creep stress increased, the mean hardness values of gauge samples also increased (except some special values, such as the hardness value of P92-AR-3 gauge sample, the earlier failure in creep test experiment results in the hardness value of which is much higher than the rest of the samples in same series). This relationship between hardness and creep stress can be explained in two ways, firstly, the material failure due to creep testing increases the formation of defects, voids and cracks in the material microstructure near the failure surface, which decreases the mechanical properties (such as hardness) of these areas. Secondly, as discussed in Chapter 5, the long-term aging heat treatment also has some effects, which is that the mean hardness value decreases as the long-term aging time increases, on the hardness of 91 and 92 samples. However, Figure 6.3 shows that the higher the creep stress, the shorter the rupture time. Therefore, the conclusion can be made that at higher creep stresses, the creep tested samples fail earlier, and the shorter
aging time makes the failed creep tested samples have higher hardness values on
gauge positions. After creep testing, the decrease in hardness value indicates that
the creep stress affects the microstructure evolution of both 91 and 92 steels, and
thus accounts for the changes in mechanical properties. These effects of creep
stress on microstructure evolution were characterised using EBSD analysis, and are
discussed in the following section.

Figure 6.3: Plot illustrating the stress versus the rupture time of (a) the 91 and (b) the 92 steel As-
received and 16 h stress relieved samples subjected to accelerated creep testing. The test
temperature was 650 °C.
Figure 6.4: Plot illustrating the applied creep stress versus the mean hardness values of the 91 and the 92 steel As-received and 16 h stress relieved samples subjected to accelerated creep testing. The test temperature was 650°C.

6.4 Influence of the Creep Stress on the Matrix Microstructure Evolution

Figures 6.5 to 6.12 show the microstructures, both as image quality plus inverse pole figure maps and boundary misorientation maps, of the T91, T92, P91 and P92 samples respectively that have experienced different creep stresses at 650°C. All the maps of the gauge positions were taken at 10 mm away from the fracture surface. It can be seen that in the gauge positions (creep tested), an obvious microstructural recrystallization from the amount of equiaxed grains formed in the matrix microstructure was observed in all the four types of steel samples.

For all of the as-received 91 samples (T91 and P91), a heterogeneous distribution of grain sizes is observable, as shown in Figures 6.5 and 6.6, which contain grains that are clearly larger and more equiaxed than the laths present in the head (unstressed) position of creep samples. As the creep stress values increase (from 66 MPa to 82 MPa for the T91-AR samples and from 69.8 MPa to 78 MPa for the P91-AR samples), the amount of martensite laths decreases and the amount of equiaxed grains increases. In contrast, such a defined subgrain structure is not significant in
the as-received 92 samples after creep test, as shown in Figure 6.7 and 6.8. For the entire gauge (creep tested) positions of as-received 92 samples, the martensite laths are still present, however, more equiaxed grains formed in the matrix microstructure than that of head (unstressed) positions of creep samples. As the creep stress values increased (from 85 MPa to 112 MPa for T92-AR samples and from 91.8 MPa to 107.2 MPa for P92-AR samples), the amount of martensite laths decreased and the amount of equiaxed grains increased. It is clear therefore that microstructural change (the reduction in martensite laths and formation of equiaxed grains) is happening faster in the 91-AR samples in comparison with the 92-AR samples.
Figure 6.5: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the T91 as-received samples subjected to accelerated creep tests to failure under different stress ranging from 66 (left) to 82 MPa (right) at 650°C. $t_r$ = time to rupture.
Figure 6.6: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the P91 as-received samples subjected to accelerated creep tests to failure under different stress ranging from 69.8 (left) to 78 MPa (right) at 650°C. $t_r$ = time to rupture.
Figure 6.7: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the T92 as-received samples subjected to accelerated creep tests to failure under different stress ranging from 85 (left) to 112 MPa (right) at 650°C. $t_r$ = time to rupture.
Figure 6.8: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the P92 as-received samples subjected to accelerated creep tests to failure under different stress ranging from 91.8 MPa to 107.2 MPa at 650°C. $t_r =$ time to rupture.
For all of the 16 h stress relieved 91 samples, a heterogeneous distribution of grain sizes was also observable, as shown in Figure 6.9 and 6.10, which contain grains that are clearly larger and more equiaxed than the laths present in the head (unstressed) positions of creep samples. As the creep stress values increased (from 66 MPa to 82 MPa for T91-16 samples and from 69.8 MPa to 78 MPa for P91-16 samples), the amount of martensite laths decreased and the amount of equiaxed grains increased. However, the amount of equiaxed grains in the 16 h stress relieved 91 samples is larger than that in the as-received 91 creep tested samples due to the 16 h stress relief prior-heat treatment. In contrast, such a defined subgrain structure is not evident in the 16 h stress relieved 92 creep tested samples, and the similar but more limited change was observed in Figure 6.11 and 6.12. In conclusion, microstructural change (the reduction in martensite laths and formation of equiaxed grains) in 91-16 samples is faster than that in 92-16 samples, and the 16 h stress relief prior-heat treatment results in the amount of equiaxed grains in the 16 h stress relieved samples is larger than that in the as-received creep tested samples.
Figure 6.9: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the T91 16 h stress relieved samples subjected to accelerated creep tests to failure under different stress ranging from 66 (left) to 82 MPa (right) at 650°C. $t_r$ = time to rupture.
Figure 6.10: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the P91 16 h stress relieved samples subjected to accelerated creep tests to failure under different stress ranging from 69.8 (left) to 78 MPa (right) at 650°C. $t_r =$ time to rupture.
Figure 6.11: Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the T92 16 h stress relieved samples subjected to accelerated creep tests to failure under different stress ranging from 85 (left) to 112 MPa (right) at 650°C. $t_r =$ time to rupture.
**Figure 6.12:** Image quality plus inverse pole figure maps and boundary misorientation maps illustrating the microstructure evolution of the P92 16 h stress relieved samples subjected to accelerated creep tests to failure under different stress ranging from 91.8 (left) to 107.2 MPa (right) at 650°C. $t_r =$ time to rupture.
The normal method of interpreting boundary angle data is to compare the ratio of low angle (2-15°) to high angle (15-180°) boundaries, as illustrated in Figure 6.13. For all of the 91 and 92 as-received steel samples, the low angle to high angle ratio of gauge (creep tested) samples is smaller than that of head (not creep tested) samples, and similarly, the low angle to high angle ratio of gauge (creep tested) samples is smaller than that of head (not creep tested) samples for all the 91 and 92 16 h stress relieved samples, although the reduction in this ratio of 16 h stress relieved creep tested samples is lesser significant than that of as-received creep tested samples.

Figure 6.13: Graph illustrating the ratio of low angle to high angle boundaries for the head and gauge positions of the AR and 16 hrs stress relieved -1 and -2 creep tested T91 and T92 samples.

6.5 Influence of Creep Testing on the Secondary Phase Precipitation

To understand the influence of the creep stress on the secondary phase precipitation, firstly the chemical composition of (V,Nb)X particles as a function of creep stress in 91 and 92 steel samples has been investigated. This was performed in order to understand whether MX chemical composition changes after creep testing, and thus determine whether such changes can be used as a method of assessing the stress condition, or creep history, of high Cr ferritic-martensitic power plant steels. Secondly,
the evolution of the particle size distribution of the M$_{23}$C$_6$ and Laves phase particles with respect to creep stress has been investigated in order to determine whether the kinetics of particle coarsening are affected by different creep stresses.

6.5.1 Influence of Creep Testing on the Chemical Composition of MX Particles

The chemical composition of the MX particles was measured using EDS on the etching exposed MX particles in TEM carbon replica samples, in order to investigate how the chemical compositions of these particles change with different creep stresses and also to determine any effects of different chemical compositions of the bulk materials (T91 and T92 steels). Figure 6.14 shows the average composition of the metallic elements V, Nb and Cr in the MX carbonitride particles of the T91 and T92 samples with varying creep stress (AR-2 samples of T91 and T92 samples were chosen due to the similar change in low/high angle ratio after creep testing). It is shown that a significant enrichment of V in MX particles occurs in the gauge positions of both T91 and T92 as-received samples whereas the chemical composition of metallic element Nb decreases in these samples.

![Figure 6.14: Plot showing the mean chemical composition of MX particles present Head (unstressed) and Gauge (stressed) positions in T91 and T92 as-received samples.](image)

Figure 6.15 shows the chemical composition distribution of the V, Nb and Cr metallic elements of head (unstressed) and gauge (stressed) positions in the T91 and T92
as-received samples. In Figure 6.15 (a) and (b), there appears to be a reduction in the fraction of Nb-rich MX particles present due to a significant increase in secondary precipitation of VN by comparing head (unstressed) and gauge (stressed) positions in T91 as-received sample. Similarly, the reduction in the fraction of Nb-rich MX particles as well as the increase in the fraction of V-rich MX particles was observed by comparing head (unstressed) and gauge (stressed) positions in the T92 as-received sample, as shown in Figure 6.15 (c) and (d).

Figure 6.15: EDX measurements from individual MX particles comparing their V, Nb and Cr content in the (a) T91 AR-2 Head, (b) T91 AR-2 Gauge, (c) T92 AR-2 Head and (d) T92 AR-2 Gauge samples.
6.5.2 Influence of Creep Testing on the Particle Size Distribution of M$_{23}$C$_6$ Precipitate Precipitation

The same image analysis software, which has been described in Chapter 4 and 5, was used to perform the detailed particle size analysis of the M$_{23}$C$_6$ precipitate phases in grade 91 and 92 steels with varying creep stress, and the results are discussed in the following sections.

6.5.2.1 The Results of Particle Size Distribution of M$_{23}$C$_6$ Particles

In this section, the effects of creep stress on the precipitation behaviour of M$_{23}$C$_6$ particles are discussed. The particle size distribution of M$_{23}$C$_6$ particles was determined from FIB images, which were subsequently analysed with the automatic image analysis software. The methodology for particle size analysis has been described in Chapter 3.

It is evident from Figure 6.16 that the M$_{23}$C$_6$ particles coarsened considerably after creep testing by comparing the particle sizes of the head position (not creep tested) and gauge (creep tested) of the T91 as-received samples. There was a slight increase in M$_{23}$C$_6$ particle sizes as the creep stress decreased from 82 MPa to 66 MPa (creep time increases from 1,549 h to 5,857 h) for the T91 as-received sample. To quantify this effect, the M$_{23}$C$_6$ particle size distribution graphs, which plot particle sizes against the number of particles per unit area (2750 $\mu$m$^2$), are shown in Figure 6.17. In Figure 6.17, the M$_{23}$C$_6$ particle size distribution for the head positions and gauge positions of T91 As-received samples are displayed. The particle distribution change was considerable for both T91-AR-1 and T91-AR-2 creep tested samples, and the average M$_{23}$C$_6$ particle size increased from 128 nm (not creep tested) to 164 nm (creep tested) after 1,549 h creep time at 82 MPa stress for T91-AR-1 creep tested samples (shown in Figure 6.17(a)) and increased from 135 nm (not creep tested) to 185 nm (creep tested) after 5,857 h creep time at 112 MPa stress for T91-AR-2 creep tested samples (shown in Figure 6.17(b)). At the same time, the number density of M$_{23}$C$_6$ particles in the T91-AR-1 creep tested sample decreased from 2903 to 1292, and that in T91-AR-2 creep tested sample decreased from 2605 to 1478.
Figure 6.16: Focused ion beam plus IEE flow images illustrating the $\text{M}_{23}\text{C}_6$ particle size evolution of the head and gauge sections of T91 as-received samples subjected to creep stress of 82 MPa (left) and 66 MPa (right).
Figure 6.17: The particle size distribution of $\text{M}_{23}\text{C}_6$ particles of head and gauge sections for (a) T91-AR-1 and (b) T91-AR-2 samples.
From Figure 6.18, the considerable $M_{23}C_6$ particle coarsening after creep testing can be observed by comparing the particle sizes of the head position (not creep tested) and gauge (creep tested) of T92 as-received samples. There was a slight increase in $M_{23}C_6$ particle sizes as the creep stress decreases from 112 MPa to 85 MPa (creep time increases from 1,649 h to 10,172 h) for the T92 as-received samples. To quantify this effect, the $M_{23}C_6$ particle size distribution graphs were produced and are shown in Figure 6.19. It is evident from Figure 6.19(a) that the $M_{23}C_6$ particle size for T92-AR-1 creep tested sample has coarsened considerably from 118 nm to 142 nm by comparing the head (no creep tested) position and gauge (creep tested) position. Similarly, there is an obvious trend in the $M_{23}C_6$ particle size change of T92-AR-2 creep tested sample that particle size increased from 129 nm to 168 nm for head (no creep tested) position and gauge (creep tested) position, are shown in Figure 6.19(b).

At the same time, the number density of $M_{23}C_6$ particles in T92-AR-1 creep tested samples decreased from 5559 to 2864 after 1,649 h creep time at 112 MPa, and that in T92-AR-2 creep tested sample decreased from 4724 to 2214 after 10,172 h creep time at 85 MPa by comparing the head (no creep tested) position and gauge (creep tested) position.
Figure 6.18: Focused ion beam plus IEE flow images illustrating the $\text{M}_{23}\text{C}_6$ particle size evolution of the head and gauge sections of T92 as-received samples subjected to creep stress of 112 MPa (left) and 85 MPa (right).
Figure 6.19: The particle size distribution of $\text{M}_{23}\text{C}_6$ particles of head and gauge sections for (a) T92-AR-1 and (b) T92-AR-2 samples.
It is evident from Figure 6.20 that the M_{23}C_6 particles coarsened considerably after creep testing by comparing the particle sizes of the head position (not creep tested) and gauge (creep tested) of the T91 16 h stress relieved creep tested samples. To quantify the particle coarsening, the M_{23}C_6 particle size distribution graphs, which plot particle sizes against the number of particles per unit area (2750 μm²), are shown in Figure 6.21. In Figure 6.21, the M_{23}C_6 particle size distribution for head positions and gauge positions of the T91 16 h stress relieved creep tested samples are displayed. The particle distribution change was considerable for both T91-16-1 and T91-16-2 creep tested samples, the average M_{23}C_6 particle size increased from 136 nm (not creep tested) to 181 nm (creep tested) after 992 h creep time at 82 MPa stress for the T91-16-1 creep tested samples (shown in Figure 6.21(a)) and increased from 151 nm (not creep tested) to 206 nm (creep tested) after 4,826 h creep time at 66 MPa stress for the T91-16-2 creep tested samples (shown in Figure 6.21(b)). At the same time, the number density of M_{23}C_6 particles in the T91-16-1 creep tested sample decreased from 2544 to 1789, and that in T91-16-2 creep tested sample decreased from 2948 to 913.
Figure 6.20: Focused ion beam plus IEE flow images illustrating the M$_{23}$C$_6$ particle size evolution of the head and gauge sections of T91 16 h stress relieved samples subjected to creep stress of 82 MPa (left) and 66 MPa (right).
Figure 6.21: The particle size distribution of $\text{M}_{23}\text{C}_6$ particles of head and gauge sections for (a) T91-16-1 and (b) T91-16-2 samples.
From Figure 6.22, the \( \text{M}_{23}\text{C}_6 \) particle coarsened considerably after creep testing by comparing the particle sizes of head position (not creep tested) and gauge (creep tested) of the T92 16 h stress relieved creep tested samples, and there was an increase in \( \text{M}_{23}\text{C}_6 \) particle sizes as the creep stress decreased from 112 MPa to 85 MPa (creep time increases from 1,175 h to 7,965 h) for the T92-16 creep tested samples (gauge positions). To quantify this effect, the \( \text{M}_{23}\text{C}_6 \) particle size distribution graphs were produced and are shown in Figure 6.23. It is evident from Figure 6.23(a) that the \( \text{M}_{23}\text{C}_6 \) particle size for the T92-16-1 creep tested sample coarsened considerably from 128 nm to 155 nm by comparing the head (no creep tested) position and gauge (creep tested) position. Similarly, there was a significant increase in the particle size of the T92-16-2 creep tested sample that \( \text{M}_{23}\text{C}_6 \) particle size increased from 131 nm to 169 nm, are shown in Figure 6.23(b). At the same time, the number density of \( \text{M}_{23}\text{C}_6 \) particles in the T92-16-1 creep tested samples decreased from 3726 to 2463 after 1,175 h creep time at 112 MPa, and that in the T92-16-2 creep tested sample decreased from 3273 to 1771 after 7,965 h creep time at 85 MPa by comparing the head (no creep tested) position and gauge (creep tested) position.
Figure 6.22: Focused ion beam plus IEE flow images illustrating the M$_{23}$C$_6$ particle size evolution of the head and gauge sections of T92 16 h stress relieved samples subjected to creep stress of 112 MPa (left) and 85 MPa (right).
Figure 6.23: The particle size distribution of $M_{23}C_6$ particles of head and gauge sections for (a) T92-16-1 and (b) T92-16-2 samples.
It is evident from Figure 6.22 that the M$_{23}$C$_{6}$ particles coarsened considerably after creep testing by comparing the M$_{23}$C$_{6}$ particle sizes of head position (not creep tested) and gauge (creep tested) of the P91 as-received samples. There was an increase in M$_{23}$C$_{6}$ particle sizes as the creep stress decreased from 78 MPa to 74.4 MPa and to 69.8 MPa (creep time increases from 2,807 h to 4,310 h and to 7,684 h) for the P91 as-received samples. To quantify this effect, the M$_{23}$C$_{6}$ particle size distribution graphs, which plot particle sizes against the number of particles per unit area (2750 $\mu$m$^2$), are shown in Figure 6.24. In Figure 6.25, the M$_{23}$C$_{6}$ particle size distribution for head positions and gauge positions of the P91 As-received samples are displayed. The M$_{23}$C$_{6}$ particle distribution change was significant for all the P91-AR-1, P91-AR-2 and P91-AR-3 creep tested samples; the average M$_{23}$C$_{6}$ particle size increased from 117 nm (not creep tested) to 165 nm (creep tested) after 2,807 h creep time at 78 MPa stress for the P91-AR-1 creep tested samples (shown in Figure 6.25(a)), increased from 131 nm (not creep tested) to 175 nm (creep tested) after 4,310 h creep time at 74.4 MPa stress for the P91-AR-2 creep tested samples (shown in Figure 6.25(b)) and increased from 135 nm (not creep tested) to 177 nm (creep tested) after 7,684 h creep time at 69.8 MPa stress for the P91-AR-3 creep tested samples (shown in Figure 6.25(c)). At the same time, the number density of M$_{23}$C$_{6}$ particles decreased from 3653 to 1923 in the P91-AR-1 creep tested samples, decreased from 3566 to 1580 in the P91-AR-2 creep tested samples and decreased from 3052 to 1395 in the P91-AR-3 creep tested samples.
Figure 6.24: Focused ion beam plus IEE flow images illustrating the M$_{23}$C$_6$ particle size evolution of the head and gauge sections of P91 as-received samples subjected with creep stress from 78 MPa (left) to 69.8 MPa (right).
### (a) Particle Number Density and Average Particle Size

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From Figure 6.26, the $M_{23}C_6$ particle coarsening can be seen to be considerable after creep testing by comparing the particle sizes of head position (not creep tested) and gauge (creep tested) of the P92 As-received creep tested samples. There was a slight increase in particle sizes as the creep stress decreased from 107.2 MPa to 99.1 MPa (creep time increased from 2,504 h to 3,854 h) for the P92-AR creep tested samples (gauge positions). The P92-AR-3 samples which had been tested at 91.8 MPa stress shows different trend of particle size due to the earlier failure. To quantify this effect, the $M_{23}C_6$ particle size distribution graphs were produced and are shown in Figure 6.27. It is evident from Figure 6.27(a) that the $M_{23}C_6$ particle size for the P92-AR-1 creep tested sample shows considerably coarsening from 136 nm to 155 nm by comparing the head (no creep tested) position and gauge (creep tested) position. However, there was a limited increase in the $M_{23}C_6$ particle size for both the P92-AR-2 and P92-AR-3 creep tested samples in which the particle size increased

**Table 6.25:** The particle size distribution of $M_{23}C_6$ particles of head and gauge sections for (a) P91-AR-1, (b) P91-AR-2 and (c) P91-AR-3 samples.
from 135 nm to 143 nm for head (no creep tested) position and gauge (creep tested) position of the P92-AR-2 creep tested sample, are shown in Figure 6.27(b), and increased from 132 nm to 149 nm for head (no creep tested) position and gauge (creep tested) position of the P92-AR-3 creep tested samples, are shown in Figure 6.27(c). At the same time, the number density of particles decreased from 3911 to 2013 after 2,504 h creep time at 107.2 MPa in the P92-AR-1 creep tested samples, decreased from 3651 to 2484 after 3,854 h creep time at 99.1 MPa in the P92-AR-2 creep tested sample and decreased from 3657 to 2544 after 3,350 h creep time at 91.8 MPa in the P92-AR-3 creep tested sample by comparing the head (no creep tested) position and gauge (creep tested) position.
Figure 6.26: Focused ion beam plus IEE flow images illustrating the $\text{M}_{23}\text{C}_6$ particle size evolution of the head and gauge sections of P92 as-received samples subjected with creep stress from 107.2 MPa (left) to 91.8 MPa (right).
### (a)

![Graph](image)

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### (b)

![Graph](image)

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Figure 6.27: The particle size distribution of M$_{23}$C$_6$ particles of head and gauge sections for (a) P92-AR-1, (b) P92-AR-2 and (c) P92-AR-3 samples.

It is evident from Figure 6.28 that the M$_{23}$C$_6$ particles coarsened considerably after creep testing by comparing the M$_{23}$C$_6$ particle sizes of head position (not creep tested) and gauge (creep tested) of the P91 16 h stress relieved creep tested samples. There was a slightly increase in M$_{23}$C$_6$ particle sizes as the creep stress decreased from 78 MPa to 74.4 MPa and to 69.8 MPa (creep time increased from 1,995 h to 2,858 h and to 4,819 h) for the P91-16 creep tested samples. To quantify this effect, the M$_{23}$C$_6$ particle size distribution graphs are shown in Figure 6.29. The M$_{23}$C$_6$ particle distribution change was significant for all the P91-16-1, P91-16-2 and P91-16-3 creep tested samples; the average M$_{23}$C$_6$ particle size increased from 135 nm (not creep tested) to 180 nm (creep tested) after 1,995 h creep time at 78 MPa stress for the P91-16-1 creep tested samples (shown in Figure 6.29(a)), increased from 144 nm (not creep tested) to 189 nm (creep tested) after 2,858 h creep time at 74.4 MPa stress for the P91-16-2 creep tested samples (shown in Figure 6.29(b)) and increased from 136 nm (not creep tested) to 199 nm (creep tested) after 4,819 h

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creep time at 69.8 MPa stress for the P91-16-3 creep tested sample (shown in Figure 6.29(c)). At the same time, the number density of $M_{23}C_6$ particles decreases from 2445 to 2245 in the P91-16-1 creep tested samples, decreased from 3268 to 1293 in the P91-16-2 creep tested samples and decreased from 2732 to 1277 in the P91-16-3 creep tested samples by comparing the head (no creep tested) position and gauge (creep tested) position.
Figure 6.28: Focused ion beam plus IEE flow images illustrating the M$_{23}$C$_6$ particle size evolution of the head and gauge sections of P91 as-received samples subjected with creep stress from 78 MPa (left) to 69.8 MPa (right).
(a)

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(b)

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<td>P91-16-2 Gauge</td>
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Figure 6.29: The particle size distribution of M$_{23}$C$_6$ particles of head and gauge sections for (a) P91-16-1, (b) P91-16-2 and (c) P91-16-3 samples.

From Figure 6.30, the M$_{23}$C$_6$ particle coarsening was significant after creep testing by comparing the particle sizes of head position (not creep tested) and gauge (creep tested) of the P92 16 h stress relieved creep tested samples. There was a slight increase in particle sizes as the creep stress decreased from 107.2 MPa to 99.1 MPa and to 91.8 MPa (creep time increased from 2,019 h to 3,883 h and to 5,930 h) for the P92-16 creep tested samples (gauge positions). To quantify this effect, the M$_{23}$C$_6$ particle size distribution graphs were produced and are shown in Figure 6.31. From Figure 6.31(a), due to head position of the P92-16-1 sample was damaged during creep test, only the gauge position of the P92-16-1 sample was investigated. The mean M$_{23}$C$_6$ particle size for gauge position of the P92-16-1 creep tested sample was 148 nm and the number density of which was 2125. It is evident from Figure
6.31(b) that the $M_{23}C_6$ particle size for the P92-16-2 creep tested samples coarsened considerably from 140 nm to 158 nm by comparing the head (no creep tested) position and gauge (creep tested) position, and the $M_{23}C_6$ particle size for the P92-16-3 creep tested samples also increased from 145 nm to 171 nm for head (no creep tested) position and gauge (creep tested) position, as shown in Figure 6.31(c). At the same time, the number density of particles decreased from 3448 to 1804 after 3,883 h creep time at 99.1 MPa in the P92-16-2 creep tested samples, decreased from 3251 to 1823 after 5,930 h creep time at 91.8 MPa in the P92-16-3 creep tested samples by comparing the head (no creep test) position and gauge (creep tested) position.
Figure 6.30: Focused ion beam plus IEE flow images illustrating the $M_{23}C_6$ particle size evolution of the head and gauge sections of P92 as-received samples subjected with creep stress from 107.2 MPa (left) to 91.8 MPa (right).
(a)

<table>
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(b)

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6.5.2.2 Discussion of Particle Size Distribution of $M_{23}C_6$ Particles

The general conclusion that the $M_{23}C_6$ particle coarsening is considerable as the mean particle size increases and number density of $M_{23}C_6$ particle decreases, can be made from all the results of the particle size distribution of $M_{23}C_6$ particles from head and gauge sections for all the 91 and 92 creep tested samples. For all the creep tested samples, one of the main reasons that cause the sample failure is the large secondary particles in the matrix phase. During creep testing, the large particles keep growing and when reach certain values, it may be possible that they can initiate the formation of creep cavities.
To investigate the effects of creep stress on the M$_{23}$C$_6$ particle size distribution change of 91 and 92 creep tested samples with varying applied creep stress, the mean particle size and number density of M$_{23}$C$_6$ particles are plotted with varying constant stress values, ranging from 66 to 112 MPa, as shown in Figure 6.32 and 6.33. The trendline for each 91 and 92 as-received and 16 h stress relieved creep tested samples was drawn according to the mean particle size data or number density data of M$_{23}$C$_6$ particles, and this trendline can be used to describe the rate of change in the mean particle size or number density of M$_{23}$C$_6$ particles with varying applied creep stress.

**Figure 6.32:** Plot illustrating the applied creep stress versus the mean size of M$_{23}$C$_6$ particle for the 91 and the 92 steel As-received and 16 h stress relieved samples subjected to accelerated creep testing. The test temperature was 650 °C.

From Figure 6.32, the mean particle size of M$_{23}$C$_6$ particles decreased as the applied creep stress increased for all the 91, 92 As-received and 16 h stress relieved creep tested samples (gauge positions). This decrease in mean M$_{23}$C$_6$ particle size can be explained in two ways. On one hand, the larger creep stress may have enhanced diffusion to the M$_{23}$C$_6$ particles, making it easier for small particles to merge together to form large particles; on the other hand, the larger creep stress means a shorter rupture life, and the larger particles coarsening also increased as the long-term aging time increased (the creep test undergo at 650°C, which means the creep
tested sample also go through long-term aging), as discussed in Chapter 5, and so the mean particle size of $\text{M}_{23}\text{C}_6$ particles decreased as the rupture life decreased. However, in the case of the T92-AR-2 creep tested sample, the applied creep stress increased from 85 to 112 MPa, around 30% stress increased, and the same time, the rupture life (long-term aging) decreased from 1,0172 h to 1,649 h, around 84% time decreased. The much greater change in creep time than that in applied creep stress means the long-term aging effect the mean particle size more than creep stress does, which results in the mean particle size of $\text{M}_{23}\text{C}_6$ particles decreased as the creep stress increased.

Figure 6.32 also shows the effects of the 16 h stress relief heat treatment on the mean particle size of creep tested samples. As discussed in Chapter 4, the mean particle size increased after 16 h stress relief and this results in all the 16 h series creep tested samples having a larger mean $\text{M}_{23}\text{C}_6$ particle size than the as-received creep tested samples at same applied creep stress.

Finally, by comparing the trendline of the 91 and 92 creep tested samples, the change rate of mean particle size with varying creep stresses for the 92 creep tested samples was smaller than that for the 91 creep tested samples, which means when applied creep stress changed in same range value, the mean $\text{M}_{23}\text{C}_6$ particle size changed much less in the 92 samples than that in the 91 samples. As discussed earlier, the creep failure occurs when the mean particle size reaches certain value, and it can be predicted that the creep rupture life of the 92 samples is much longer than that of the 91 samples since the mean $\text{M}_{23}\text{C}_6$ particle size of the 92 samples increased more slowly than that of the 91 samples at high creep stress.
From Figure 6.33, it can be seen that the number density of $\text{M}_2\text{C}_6$ particles increased as the applied creep stress increased for all the 91, 92 as-received and 16 h stress relieved creep tested samples (gauge positions). This increase in the number density of $\text{M}_2\text{C}_6$ particles can also be explained in two ways as per the discussion about the particle size data. However, as discussed earlier, the change in creep time is much larger than that in creep stress, which implies that the effects from long-term aging are larger than that from applied creep stress, thus the number density of $\text{M}_2\text{C}_6$ particles increased as the applied creep stress increases.

Figure 6.33 also shows the effects of 16 h stress relief heat treatment on the number density of $\text{M}_2\text{C}_6$ particles for the creep tested samples. As discussed in Chapter 4, the number density of $\text{M}_2\text{C}_6$ particles decreased after 16 h stress relief and this results in all of the 16 h series creep tested samples having a smaller number density of $\text{M}_2\text{C}_6$ particles than the as-received creep tested samples at same applied creep stress.

Finally, by comparing the trendline of the 91 and 92 creep tested samples, the change rate of number density of $\text{M}_2\text{C}_6$ particles with varying creep stresses for the 92 creep tested samples was smaller than that for the 91 creep tested samples,
which means when applied creep stresses change in same range value, the number density of $M_{23}C_6$ particles change much less for the 92 samples than that for the 91 samples.

6.5.3 **Influence of Creep Testing on the Particle Size Distribution of Laves Phase Particles**

In this project, the BSE images were used to determine the difference between Laves phase particles and matrix phase, and then used to calculate the size distributions of Laves phase with a 6 mm working distance and $25 \times 22 \ \mu m^2$ image sizes. All the 91 and 92 creep tested samples were analysed using the BSE technique to examine the presence and distribution of Laves phase, however, there was no Laves phase in the 91 creep tested samples as a result of the bulk chemical composition of the steel. Therefore, in this section, the effects of creep testing on Laves phase of creep tested 92 samples were investigated.

6.5.3.1 **Results of Particle Size Distribution of Laves Phase**

From Figure 6.34, the Laves phase particle coarsening can be seen to be considerable after creep testing by comparing the particle sizes of the head position (not creep tested) and gauge (creep tested) of the T92 as-received samples. There was a slight increase in Laves phase particle sizes as the creep stress decreased from 112 MPa to 85 MPa (creep time increased from 1,649 h to 10,172 h) for the T92 as-received sample. To quantify this effect, the Laves phase particle size distribution graphs were produced and shown in Figure 6.35. It is evident from Figure 6.35(a) that the Laves phase particle size for the T92-AR-1 creep tested sample coarsened considerably from 143 nm to 222 nm by comparing the head (not creep tested) position and gauge (creep tested) position. Similarly, there was a significant change in the Laves phase particle size of the T92-AR-2 creep tested sample that particle size increased from 190 nm to 285 nm for the head (not creep tested) position and gauge (creep tested) position, was shown in Figure 6.35(b). At the same time, the number density of Laves phase particles in the T92-AR-1 creep tested samples decreased from 2084 to 759 after 1,649 h at 112 MPa, and that in the T92-AR-2 creep tested sample decreased from 1102 to 388 after 10,172 h at 85 MPa by comparing the head (not creep tested) position and gauge (creep tested) position.
Figure 6.34: BSE images illustrating the Laves phase particle size evolution of the head and gauge sections of T92 as-received samples subjected to creep stress of 112 MPa (left) and 85 MPa (right).
Figure 6.35: The particle size distribution of Laves phase particles of the head and gauge sections for the (a) T92-AR-1 and (b) T92-AR-2 samples.
It is evident from Figure 6.36 that the Laves phase particle coarsened considerably after creep testing by comparing the particle sizes of the head position (not creep tested) and gauge (creep tested) of the T92 16 h stress relieved creep tested samples. There was a slight increase in Laves phase particle sizes as the creep stress decreased from 112 MPa to 85 MPa (creep time increased from 1,175 h to 7,965 h) for the T92-16 creep tested samples (gauge positions). To quantify this effect, the Laves phase particle size distribution graphs were produced and shown in Figure 6.37. It is evident from Figure 6.37(a) that the Laves phase particle size for the T92-16-1 creep tested sample increased from 164 nm to 200 nm by comparing the head (not creep tested) position and gauge (creep tested) position. Similarly, there was significant change in the particle size of the T92-16-2 creep tested sample that Laves phase particle size increased from 208 nm to 289 nm for the head (no creep tested) position and gauge (creep tested) position, was shown in Figure 6.37(b). At the same time, the number density of Laves phase particles decreased from 1627 to 1080 after 1,175 h at 112 MPa in the T92-16-1 creep tested samples and decreased from 2001 to 482 after 7,965 h at 85 MPa in the T92-16-2 creep tested sample by comparing the head (not creep tested) position and gauge (creep tested) position.
Figure 6.36: BSE images illustrating the Laves phase particle size evolution of the head and gauge sections of T92 16 h stress relieved samples subjected to creep stress of 112 MPa (left) and 85 MPa (right).
Figure 6.37: The particle size distribution of Laves phase particles of the head and gauge sections for (a) T92-16-1 and (b) T92-16-2 samples.
From Figure 6.38, there was no particle coarsening trend in the Laves phase after creep testing by comparing the particle sizes of the head position (not creep tested) and gauge (creep tested) of the P92 as-received creep tested samples. There was a very little increase in particle sizes as the creep stress decreased from 107.2 MPa to 99.1 MPa (creep time increased from 2,504 h to 3,854 h) for the P92-AR creep tested samples (gauge positions). The P92-AR-3 sample had been tested at 91.8 MPa stress showed different trend of particle size due to the earlier failure. To quantify this effect, the Laves phase particle size distribution graphs were produced and shown in Figure 6.39. It is evident from Figure 6.39(a) that the Laves phase particle size for the P92-AR-1 creep tested sample increased slightly from 206 nm to 224 nm and the number density for which changed very limited from 400 to 443 after 2,504 h at 107.2 MPa by comparing the head (not creep tested) position and gauge (creep tested) position. However, there was no particle coarsening in the Laves phase particle size for the P92-AR-2 creep tested sample that the particle size changed from 244 nm to 236 nm and the number density changed from 809 to 734 after 3,854 h creep time at 99.1 MPa for the head (not creep tested) position and gauge (creep tested) position of the P92-AR-2 creep tested sample, as shown in Figure 6.39(b). For the P92-AR-3 creep tested sample, shown in Figure 6.39(c), the particle size changed from 254 nm to 203 nm (due to the earlier failure) and the number density changed from 395 to 143 after 3,350 h at 91.8 MPa.
**Figure 6.38:** BSE images illustrating the Laves phase particle size evolution of the head and gauge sections of P92 as-received samples subjected with creep stress from 107.2 MPa (left) to 91.8 MPa (right).
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It is evident from Figure 6.40 that there was no particle coarsening in the Laves phase after creep testing by comparing the particle sizes of the head position (not creep tested) and gauge (creep tested) of the P92 16 h stress relieved creep tested samples. There was a very little increase in Laves particle sizes as the creep stress decreased from 107.2 MPa to 99.1 MPa and to 91.8 MPa (creep time increased from 2,019 h to 3,883 h and to 5,930 h) for the P92-16 creep tested samples (gauge positions). To quantify this effect, the Laves phase particle size distribution graphs were produced and shown in Figure 6.41. From Figure 6.41(a), due to head position of the P92-16-1 sample was damaged during creep testing, only the gauge position of the P92-16-1 sample was investigated. The mean Laves phase particle size for the gauge position of the P92-16-1 creep tested sample was 220 nm and the number density of which was 554. It is evident from Figure 6.41(b) that the Laves phase particle size for the P92-16-2 creep tested sample changed very little from 264 nm to
267 nm by comparing the head (not creep tested) position and gauge (creep tested) position, and the Laves phase particle size for the P92-16-3 creep tested sample also changed very little from 285 nm to 293 nm for the head (not creep tested) position and gauge (creep tested) position, shown in Figure 6.41(c). At the same time, the number density of Laves phase particles decreased from 535 to 461 after 3,883 h at 99.1 MPa in the P92-16-2 creep tested sample and decreased from 435 to 397 after 5,930 h at 91.8 MPa in the P92-16-3 creep tested sample by comparing the head (not creep tested) position and gauge (creep tested) position.
Figure 6.40: BSE images illustrating the Laves phase particle size evolution of the head and gauge sections of P92 as-received samples subjected with creep stress from 107.2 MPa (left) to 91.8 MPa (right).
(a)

![Graph showing Particle Size (nm) vs. Number of Particles per Area 2750 μm² for P92-16-1 Gauge.]

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(b)

![Graph showing Particle Size (nm) vs. Number of Particles per Area 2750 μm² for P92-16-2 Head and P92-16-2 Gauge.]

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### Figure 6.41: The particle size distribution of Laves phase particles of the head and gauge sections for (a) P92-16-1, (b) P92-16-2 and (c) P92-16-3 samples.

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#### 6.5.3.2 Discussion of Particle Size Distribution of Laves Phase

The general conclusion that the Laves phase particle coarsening is considerable, from the results showing that the mean particle size increased and the number density of Laves phase particles decreased, can be made from the Laves particle size distribution in the head and gauge sections of all the T92 creep tested samples. However, it was interesting to note that this Laves phase particle coarsening was not significant for the P92 creep tested samples. After creep testing, the mean particle size changed very little by comparison of the head and gauge positions (the mean Laves phase particle size even decreased significantly after creep testing for the earlier failed P92-AR-3 sample) and the reduction in number density could not be observed in all the P92 creep tested samples. The reason for this phenomenon is that the failure times of all of the P92 creep tested samples were between 2,000 and 4,000 h (except the P92-16-3 sample which failed at 5,930 h). It was found that Laves phase showed a rapid size increase in the 92 samples when they undergo long-term aging at 650°C. It would therefore appear that the long-term aging heat
treatment had much more effect on the Laves phase particle coarsening than the creep stress, which resulted in quite a limited change in the mean particle size and number density of Laves phase comparing the head and gauge positions of the P92 creep tested samples.

To investigate the effects of creep stress on the Laves phase particle size distribution of all the 92 creep tested samples with different applied creep stresses, the mean particle size and number density of Laves phase were plotted with varying constant stress values, ranging from 85 to 112 MPa, shown in Figure 6.42 and 6.43. The trendlines for each 92 as-received and 16 h stress relieved creep tested samples was drawn according to the mean particle size data or number density data of Laves phase, and this trendline can be used to describe the change rate of mean particle size or number density of Laves phase with varying applied creep stresses.

From Figure 6.42, the mean particle size of Laves decreased as the applied creep stress increased for all the 92 as-received and 16 h stress relieved creep tested samples (gauge positions). Figure 6.42 also shows the effects of the 16 h stress relieved heat treatment on the mean particle size of Lave phase for the creep tested samples. It has been shown earlier that the 16 h stress relief heat treatment did have a significant effect on the mean particle size for $M_{23}C_6$, however, there is no clear
difference in the results for Laves phase. It is therefore concluded that the initial additional 16 h heat treatment, during which time no Laves phase was present, has not had an influence on the subsequent precipitation and coarsening of Laves phase. Similar results were observed for the number density data which are shown in Figure 6.43.

![Figure 6.43: Plot illustrating the applied creep stress versus the number density of Laves phase for the 92 As-received and 16 h stress relieved samples subjected to accelerated creep testing. The test temperature was 650ºC.](image)

From Figure 6.43, the number density of Laves phase increased as the applied creep stress increased for all the 92 as-received and 16 h stress relieved creep tested samples (gauge positions). The larger creep stress means the shorter rupture life (long-term aging), thus the number density of Laves phase increased as the rupture life decreased. However, as discussed earlier, the change in rupture life is much larger than that in the creep stress, indicating that the effects from long-term aging change were larger than from applied creep stress change.
6.6 Summary

This chapter has presented a study of the effects of different creep stresses on the microstructural evolution of Grades 91 and 92 high Cr power plant steels. Firstly, the hardness values decreased significantly after creep testing by comparing the head (unstressed) and gauge (stressed) positions of all of the samples. The creep rupture time increased as the creep stress values decreased for all of the 91 and 92 as-received and 16 h stress relieved samples, which correlates with the mean hardness values change.

Secondly, matrix recrystallization was observed in all of the creep tested samples by observing more equiaxed grains in the matrix microstructure and a decrease in the low/high angle boundary ratio after creep testing. The reduction in the low angle to high angle ratio of 16 h stress relieved creep tested samples was less significant than that of the as-received creep tested samples.

Thirdly, the mean composition of V increased slightly and that of Nb decreased slightly for MX particles in both the T91 and T92 samples after creep testing, which indicates that the V-rich MX particles increased and the Nb-rich MX particles decreased with applied stresses. M_{23}C_6 was clearly observed as the mean particle size increased together with a decrease in the number density with applied creep stress. The particle coarsening increased as the applied creep stress decreased was also observed in the gauge length of the crept samples. The additional 16 h stress relief heat treatment was also found to have a significant influence on the coarsening of the M_{23}C_6 particle. Laves phase coarsening was also observed, although there was no significant difference between the as-received and 16 h conditions. The influence of thermal ageing also appeared much more significant than the influence of applied stress in this case.
Chapter 7. Crystallographic Orientation Analysis for the Assessment of Microstructural Recovery

7.1 Introduction

Advanced 9–12% chromium heat resistant steels have been used extensively in ultra-supercritical fossil fired power plant at temperatures in excess of 500°C because of their enhanced creep strength, high corrosion resistance and reasonable cost [68]. It has been found that the creep strength of these steels decreases significantly after long-term creep exposure [69] and ultimately leads to failure. This creep failure is caused by the loss of a major strengthening mechanism, which is suggested to be the loss of solution strengthening elements through the precipitation of $\text{M}_{23}\text{C}_6$, MX, Laves phase or other particles in such steels [70, 71]. Recent results, however, suggest that the recovery of subgrains that takes place during long-term creep exposure could be an additional cause of creep failure [72]. Since the recovery of a martensitic structure is an important factor for creep failure, it is necessary to find a suitable method for the assessment of both particle precipitation and microstructural recovery during creep, which ultimately will contribute to the production of a model which can accurately predict creep behaviour in power plant steels and hence determine the expected service life of a component either before or during service.

The most common method for measuring the recovery of the microstructure of these steels is to use a hardness measurement as it can be used as a simple mechanical, non-destructive test method to estimate the loss of mechanical resistance and creep resistance in steels [73]. In actual plant installations, hardness is used to determine and assess degradation for materials currently in service [74]; however, although hardness testing can provide a reasonable assessment of expected creep life, it is the combination of both the matrix microstructure and the particle distributions within the steel which contribute to the measurement. In order for successful predictive models to be developed, it is necessary to model changes in both the particle distributions and the matrix during creep exposure independently.
Recently it has been shown that through the use of focused ion beam (FIB) and scanning electron microscope (SEM) imaging, it is possible to identify and individually measure both the M\textsubscript{23}C\textsubscript{6} and Laves phase particles in power plant steels exposed to creep conditions [75]. In order to produce a complete descriptive model of creep behaviour in these steels it is necessary to investigate methods which are capable of determining the evolution of the matrix microstructure of these materials during the creep process. Electron backscatter diffraction has been successfully used to identify and to measure the lengths per unit area of low and high angle grain boundaries within high Cr steel matrix microstructures [76]. Comparing the density of each of these boundary types gives a measure of matrix recovery. This method was used in previous chapters to give a brief description of how matrix recovery changed with different heat treatment, ageing time and applied creep stress. However, this approach has not been demonstrated for conditions between which only small differences in microstructure would be expected. Recently, EBSD has been successfully applied to an investigation of crystallographic morphologies of dislocation substructures and grains [77] through the use of the orientation analysis technique of kernel average misorientation (KAM) and relating the results to remnant creep life of a creep sample.

In this chapter, three different crystallographic orientation analysis procedures in a commercially available EBSD collection and analysis software package were investigated and compared to find out the best orientation analysis technique for the assessment of the evolution of the matrix microstructure of grade 91 and 92 steel with different heat treatment and creep conditions. This orientation analysis technique was then compared with the method that measuring low/high angle grain lengths to determine microstructural recovery, to detail the different benefits of these two techniques.

### 7.2 Experimental Procedure

The samples analysed for this chapter are shown in Chapter 3 (Table 3.2 and 3.3), and they consisted of either 91 or 92 grade 9 wt% Cr steels. All samples were subjected to creep testing at 650°C at varying creep stress, except the T91 and T92
as-received and 16 h stress relieved sample. Both the heads and the gauge positions of creep tested samples are examined.

For EBSD data analyses, Tex-SEM laboratories OIM data analysis software was used. In order to study the effect of different kernel analysis techniques, kernel average misorientation (KAM), local average misorientation (LAM) and local orientation spreads (LOS) were used. The kernel size was varied between 1 and 10 neighbours and the maximum kernel misorientation value was 5°. Figure 7.1 gives details on the three types of kernel averages compared in this study.

A kernel is defined as a central pixel (CP) surrounded by a number of layers of pixels. The orientation relationships between the different pixels within the kernel can be analysed in a number of different ways when using the OIM software:

1) Local average misorientation, LAM: This procedure compares the orientation of each pixel within the kernel to each of its immediate neighbours. An average of each comparison is made and is plotted at the CP.

2) Kernel average misorientation, KAM: Compares the orientation of the pixels at the perimeter of the kernel to the orientation of the CP. An average of the misorientations is taken and then plotted at the CP.

3) Local orientation spread, LOS: Here the orientation of each pixel is compared to every other pixel within the kernel. The average misorientation is then plotted at the CP.

Figure 7.1: Schematic of the different kernel orientation analysis procedures used.
To detail the different benefits of these analysis procedures, 3 different samples were examined which were known to be in different stages of recovery: a gauge length of a creep tested P91 steel (P91-AR-1 G – 167 Hv\textsubscript{10}), the head portion of the same creep sample (P91-AR-1 H – 229 Hv\textsubscript{10}) and a head sample of a creep tested steel which had undergone an additional 16 hours of stress relief heat treatment (P91-16-1 H – 204 Hv\textsubscript{10}). The microstructural recovery, as assessed by the hardness of these samples can be ordered as follows: P91-AR-1 G > P91-16-1 H > P91-AR-1 H where the gauge length sample is the most recovered.

Figure 7.2 shows the effect of this microstructural recovery on the LAM, KAM and LOS data collected and for the KAM, LAM and LOS data, the mean misorientation together with the skew (a measure of the asymmetry of a distribution) and kurtosis (a measure of peak of a distribution) for the three recovery conditions. All three of the orientation analysis techniques show a decreasing average misorientation as microstructural recovery increases, as shown in Figure 7.2(a). LAM only has small differences in the mean value. KAM and LOS show large differences between the head and gauge portions and small differences between the head and the 16 hour heat treated sample. This is reasonably representative of the differences in recovery that could be expected within the microstructure based on their measured hardness values. The values of the skew of the data (Figure 7.2(b)) show that for all of the analysis procedures there is an increase in skew, as the expected extent of recovery increases. This indicates that each of the procedures is sensitive to the recovery of the microstructure. The kurtosis of the data also increases with expected recovery with KAM showing the most measurable change with extent of recovery, as shown in Figure 7.2 (c). The kurtosis of the LOS data is less predictable with the P91-16-1 H sample (with a moderate expected recovery) having the lowest kurtosis value. In addition, as LOS compares every pixel within a kernel, it requires significantly more processing time than KAM or LAM. For this reason and the fact that KAM shows decreasing mean value and an increasing skew and kurtosis with recovering microstructure, it is recommended that KAM is used as the analysis technique.
Figure 7.2: Mean misorientation, kurtosis and skew values for KAM, LAM and LOS for P91 steel samples with differing levels of microstructural recovery.

Figure 7.3 shows the effect of changing the kernel size on KAM data through both increasing the step size and the number of pixel layers within the kernel. It can be seen that the average KAM of a set of data increases as the kernel area increases,
the skew decreases with increasing kernel area and the kurtosis also decreases. This means that as the kernel area increases, the KAM values within the plot become closer to a normal distribution and that the peaks become less sharp. Importantly, these plots indicate that increasing the kernel layer or the step size of the data has the same effect on the data and it is the kernel area that is important. The fact that an increase in kernel area increases the average KAM is perhaps unsurprising. It would be expected that in a high dislocation density material such as this, sampling a larger kernel area would see more variation in orientation than when sampling a smaller kernel area. So in this study, EBSD data were collected from an area measuring 50 x 50 µm using a step size of 0.1 µm giving a total number of data points of ~290,000 with an exposure time of 3.72 milliseconds for each pixel in the map to reach enough kernel area and data points. During KAM analysis procedure, the kernel layer 7th (the KAM values calculated from comparing each perimeter pixel at 7th layer to the central pixel) was used for all the samples to increase the kernel area of determined samples and also increase the KAM sensitivity in microstructural recovery.

**Figure 7.3:** The effect of kernel area on mean KAM value (top), kurtosis (left) and skew (right) of data in a KAM map.
7.3 KAM Analysis Assess the Effect of Stress Relief on Microstructural Recovery

The resulting KAM maps of T91 and T92 samples with as-received and 16 h stress relieved heat treatment conditions are shown in Figure 7.4. The KAM values for collected points in the maps increase as the colour changes in the orders blue < green < yellow < orange < red in maps. It can be seen that after the 16 h stress relief heat treatment, the maps appear closer to blue than red, indicating a lower average KAM for both T91 and T92 samples.

![KAM maps](image)

**Figure 7.4:** The KAM maps of (a) T91-AR, (B) T91-16, (c) T92-AR and (d) T92-16 samples (The KAM values for collected points increase as the colour changes in the orders blue < green < yellow < orange < red in maps).
This trend is more apparent in Figure 7.5 where the KAM plotted with number of points to show the KAM distribution of T91 and T92 samples with as-received and 16 h stress relief heat treatment conditions. For each EBSD map, 289,289 data points were collected and the KAM values for each point were determined, these values were then counted within certain ranges (from 0 to 5 degree, and 0.2 degree for each bit) and analysed. It can be seen that after the 16 h stress relief heat treatment, the range of KAM distribution curve moves to lower values, which indicates that the average KAM reduced, the same time, the skew and kurtosis value increased for both T91 and T92 samples. However, it should be noted that, the change in the KAM distribution is more limited in T92 sample than that in T91 sample, and this indicates there is less microstructural recovery in the T92 sample after the 16 h stress relief heat treatment.

Figure 7.5: KAM distribution of (a) T91 and (b) T92 as-received and 16 h stress relieved samples.
Since average KAM values reduce as the microstructural recovery increases, the change in KAM values for different samples and conditions can be used to quantify the microstructural recovery. Figure 7.6 shows the mean KAM values of the T91 and T92 samples with as-received and 16 h stress relieved heat treatment conditions.

![Mean KAM values for T91 and T92 samples](image)

**Figure 7.6:** (a) Mean KAM values for T91 and T92 samples with as-received and 16 h stress relieved conditions.

The decrease in mean KAM values of T91 and T92 samples proved the microstructural recovery occurs after 16 h stress relief heat treatment. The same conclusion was obtained by using boundary length method which showed that the low/high angle ratio increase after 16 h stress relief heat treatment for both 91 and 92 steels, as discussed in section 4.4. In addition, this reducing in mean KAM value is 0.32 degrees in T91 sample and only 0.08 degrees in T92 sample, which indicates the microstructural recovery of T91 is much higher than that of T92 samples. However, the low/high angle ratio method shows the opposite result that the increase in low/high angle ratio of T92 samples is more significant than that of T91 samples. As discussed in Chapter 4, the hardness values reduced about 20 Hv for both T91 and T92 samples after 16 h stress relief heat treatment. This reduction in hardness values was from the combination of both the matrix microstructural recovery and the secondary particle coarsening within the T91 and T92 samples.
The reduced microstructural recovery of the T92 sample (KAM method) is consistent with the conclusion that particle coarsening in M$_{23}$C$_6$ particles of T92 sample is more significant than that in T91 sample after a 16 h stress relief heat treatment. This means both the KAM analysis and boundary length measure techniques can be used to identify the microstructural recovery, however, the KAM analysis technique is more sensitive when there is small difference in microstructural recovery.

### 7.4 KAM Analysis Assess the Effect of Long-term Aging on Microstructural Recovery

The resulting KAM maps of 91 and 92 samples with varying aging times are shown in Figures 7.7 and 7.8. It can be seen that as long-term aging times increase, there are more red parts than blue parts indicating a lower average KAM value for all the 91 and 92 as-received samples. However, there are more blue parts than red parts indicating a higher average KAM value for all the 91 and 92 16 h stress relieved samples as long-term aging times increase.

This trend is more apparent in Figure 7.9 where the KAM is plotted with number fraction to show the KAM distribution of 91 and 92 samples with varying aging times. It can be seen that as long-term aging times increase, the range of the KAM distribution curves move to lower KAM values, which indicates that the average KAM reduced for both 91 and 92 as-received samples. However, it can also be seen that as long-term aging times increase, the range of the KAM distribution curve moves to higher KAM values for all the 16 h stress relieved samples, which indicates that the average KAM increase for both 91 and 92 16 h stress relieved samples. This means there is no microstructural recovery in these 16 h stress relieved samples during long-term aging, which is consistent with the conclusion in Chapter 5, that there is no trend between the low angle to high angle ratio and aging times in 16 h stress relieved samples. This means the grain boundary measurement technique is very limited when investigating the microstructural recovery during long-term ageing procedure.
Figure 7.7: The KAM maps of T91 and P91 as-received and 16 h stress relieved samples with varying aging time at 650°C (The KAM values for collected points increase as the colour changes in the orders blue < green < yellow < orange < red in maps).
Figure 7.8: The KAM maps of T92 and P92 as-received and 16 h stress relieved samples with varying aging time at 650°C (The KAM values for collected points increase as the colour changes in the orders blue < green < yellow < orange < red in maps).
Figure 7.9: KAM distribution of (a) 91-AR, (b) 91-16, (c) 92-AR and (d) 92-16 samples with varying aging time at 650°C.
Figure 7.10 shows the change in mean KAM values with varying aging times for 91 and 92 samples with as-received and 16 h stress relieved heat treatment conditions. For all the as-received 91 and 92 samples, the mean KAM values decrease as the long-term aging times increase, this reduction in mean KAM values of 91 and 92 as-received samples proved the microstructural recovery occurs during long-term aging procedure. On the contrary, the mean KAM values increase slightly as the long-term aging times increase for all the 91 and 92 16 h stress relieved samples. This is because after the 16 h stress relief heat treatment, there are some unstable sub-grains formed at 765°C and these sub-grains may coarsening and emerge together, which decreases the total length of sub-grain boundary during long-term aging procedure at lower 650°C.

In addition, the KAM change rate which is calculated by $KAM_{mean} / aging$ time are analysed and listed in Table 7.1. As the aging times increase, the KAM change rates are all negative values for 91 and 92 as-received samples, which indicates the microstructural recovery increases, and positive values for 91 and 92 16 h stress relieved samples, which indicates there is no microstructural recovery. It has been discussed in Chapter 5 that the change in hardness values of 16 h stress relieved

![Figure 7.10: Mean KAM values of 91, 92 as-received and 16 h stress relieved samples with varying aging time at 650°C.](image-url)
samples was very limited with varying aging times for both 91 and 92 samples. The increase in mean KAM value of 91 and 92 16 h stress relieved samples during long-term aging indicates the reduction in subgrains, and thus due to hardness increase. This is consistent with the conclusion in Chapter 5 that particle coarsening of secondary particles in 91 and 92 16 h stress relieved samples during long-term aging result in the reduction in hardness values.

The KAM change rate is \(-4.65 \times 10^{-5} \, ^\circ / h\) for T91 as-received sample and \(4.31 \times 10^{-5} \, ^\circ / h\) for T91 16 h stress relieved sample, and is \(-0.64 \times 10^{-5} \, ^\circ / h\) for T92 as-received sample and \(0.76 \times 10^{-5} \, ^\circ / h\) for T92 16 h stress relieved sample, which indicate and quantified the change in microstructural recovery of T91 and T92 samples, the recovery change in T91 sample is much higher than that in T92 sample. The KAM change rate is similar for P91 and P92 as-received samples; however, the change in microstructural recovery in P91 16 h stress relieved sample is much higher than that in P92 16 h stress relieved sample. The limited change in microstructural recovery for 92 samples indicates the better high temperature resistance of 92 Cr steels than 91 Cr steels.

Table 7.1: The KAM change rates (calculated by KAM\(_{\text{mean}}\) /aging time) for 91, 92 as-received and 16 h stress relieved samples.

<table>
<thead>
<tr>
<th>As-received Sample</th>
<th>KAM(_{\text{mean}}) change rate (10(^{-5}) °/h)</th>
<th>16 h Stress Relieved Sample</th>
<th>KAM change rate (10(^{-5}) °/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91-AR</td>
<td>-4.65</td>
<td>T91-16</td>
<td>4.31</td>
</tr>
<tr>
<td>T92-AR</td>
<td>-0.64</td>
<td>T92-16</td>
<td>0.76</td>
</tr>
<tr>
<td>P91-AR</td>
<td>-1.96</td>
<td>P91-16</td>
<td>6.31</td>
</tr>
<tr>
<td>P92-AR</td>
<td>-2.16</td>
<td>P92-16</td>
<td>1.55</td>
</tr>
</tbody>
</table>
7.5 KAM Analysis Assessment of the Effect of Creep Stress on Microstructural Recovery

The resulting KAM maps of the head and gauge positions in 91, 92 as-received and 16 h stress relieved creep tested samples are shown as Figure 7.11. It can be seen that after creep test, the majority of the gauge position maps appear in blue rather than only a small part of the head position maps in blue, indicating a much lower average KAM value for all the 91 creep tested samples. In addition, nearly half part of the gauge position maps appear in blue rather than only a small part of head position maps in blue indicating a lower average KAM value for all the 92 creep tested samples after creep test. The increase in low KAM areas after creep test indicates the increase in microstructural recovery consists of subgrains formation and recrystallization (equaixed grains formation).

Figure 7.12 shows the KAM distribution of head and gauge positions in 91 and 92 creep tested samples. For 91 samples, it can be seen that most part of KAM distribution curve move to lower KAM values after creep testing, which indicates that the average KAM reduced for all the 91 creep tested samples. In addition, it can also be seen that the range of KAM distribution curve moves to lower KAM values slightly after creep testing for 92 samples, which indicates that the average KAM reduced for all the 92 creep tested samples. The change in KAM distribution of 92 creep tested samples is less than that of 91 creep tested samples indicates there is less microstructural recovery in 92 samples after creep testing.
Figure 7.11: The KAM maps of head and gauge positions in 91, 92 as-received and 16 h stress relieved creep tested samples (The KAM values for collected points increase as the colour changes in the orders blue < green < yellow < orange < red in maps).
Figure 7.12: KAM distribution of head and gauge positions in (a) T91, T92 and (b) P91, P92 –AR-1 creep tested samples.

Figure 7.13 shows the change in mean KAM values of head and gauge positions for 91 and 92 as-received and 16 h stress relieved samples with varying creep stress. For all the 91 and 92 creep tested samples, the mean KAM values decrease significantly by comparing the head and gauge positions and this reduction in mean KAM values of 91 and 92 samples proves in a quantitative way that the microstructural recovery occurs during the creep test procedure. In addition, the reduction in the mean KAM values of gauge positions in 92 creep tested samples is less than that in 91 creep tested samples; especially for P92 creep tested samples. However, there is no obvious trend in the mean KAM values of gauge positions for all the creep tested samples with varying creep stress. This is consistent with the result of the grain boundary length measure technique discussed in section 6.5, that
the entire low/high angle boundary ratio decrease remarkable after creep testing for all the 91 and 92 samples. This means both of these two techniques are suitable for identifying the changes in microstructural recovery when there is significant difference expected, such as result of creep testing.

![Graph showing mean misorientation values](image)

**Figure 7.13:** Mean misorientation values of (a) 91 and (b) 92 as-received and 16 h stress relieved samples with varying creep stress at 650°C.

In order to test KAM as a viable microstructural recovery assessment tool for creep tested samples, the gauge length of a creep tested T92 steel sample was examined. Figure 7.14 is a hardness profile taken along a longitudinal cross-section of the
gauge length of the sample. It can be seen that there is a gradual decline in hardness towards the fracture where a sudden drop in hardness is observed. This gradual decline in hardness is indicative of microstructural recovery during creep testing with the region closest to failure being the most recovered. Six positions along this length were examined using EBSD and the KAM maps were plotted.

![Figure 7.14: Hardness as a function of distance from fracture of the gauge length of creep tested T92 steel](image)

The resulting KAM maps and accompanying average KAM values of the positions are shown in Figure 7.15. It can be seen that as the distance from the fracture increases, the maps appear closer to red than blue indicating a higher average KAM. As shown in Figure 7.16 (a), there is a clear trend of increasing area percentage of high KAM areas (red) with distance from the fracture, and the overall trend of the low KAM areas (blue) is the inverse of the high KAM curve but there are a number of anomalous points. When the average KAM is plotted as a function of the distance from the fracture, as shown in Figure 7.16 (b), there is a clear trend of increasing mean KAM values with distance from the fracture to head section. This example of a creep tested sample demonstrates that the average KAM values can be used to effectively rank the recovery of microstructures of steels which have been exposed to creep conditions.
Figure 7.15: KAM maps (top) collected from varying distances from the fracture of a creep tested T92 sample together with corresponding threshold to retain red (middle) or blue (bottom) pixels.

Figure 7.16: (a) a measure of the area percentage of red and blue pixels (relating to high and low KAM values respectively) and (b) mean KAM values from varying distances from the fracture of a creep tested T92 sample.
7.6 Summary

It has been shown that kernel average misorientation (KAM), local average misorientation (LAM) and local orientation spread (LOS) analysis of power plant steel using electron backscatter diffraction (EBSD) can vary significantly with different kernel sizes. However, from the results obtained using a standardised analysis procedure, it is concluded that when taking account of the extremely intensive processing time of LOS analysis, the less sensitive to microstructural recovery of LAM, KAM is the most favourable orientation analysis technique out of the three presented here as it shows a trend of reduce in average KAM value as the pre-service martensitic structure recovers. Dislocations within the surface and strain caused by the martensitic structure of the steel means that there are small local variations in orientation. When the microstructure recovers, these small variations reduce and so kernel orientation analyses show a reduced level of variation within them. In this chapter, the average KAM value was then used as the assessment of recovery in steels to investigate the effects of stress relief heat treatment, long-term aging and creep stress on the microstructural recovery.

It has been shown that the reduction in mean KAM values of the T91 and T92 samples proved the microstructural recovery occurs after the 16 h stress relief heat treatment. In addition, the increase in microstructural recovery of T91 16 h stress relieved samples was much higher than that in T92 16 h stress relieved samples.

For all the as-received 91 and 92 samples, the mean KAM values decreased as the long-term aging times increased, this reduction in mean KAM values of the 91 and 92 as-received samples proved the microstructural recovery occurs during long-term aging procedure. On the other hand, the mean KAM values increased as the long-term aging times increased for all the 91 and 92 16 h stress relieved samples. This is because most of matrix recovery happened during the 16 h stress relief heat treatment, and there are some unstable sub-grains formed at 765ºC which may disappear during long-term aging procedure at lower 650ºC. As a result, the 16 h stress relieved samples have better matrix stability during the long-term aging procedure than As-received samples. In addition, the limited change in microstructural recovery for all the 92 samples indicates the better high temperature resistance of Grade 92 steels than Grade 91 steels.
For all the 91 and 92 creep tested samples, the mean KAM values decreased significantly by comparing the head and gauge positions and this reduction in mean KAM values of 91 and 92 samples proved the microstructural recovery occurs during creep test procedure. In addition, the reduction in the mean KAM values of gauge positions in 92 creep tested samples is less than that in 91 creep tested samples, indicating the better creep exposure resistance of 92 steels. It has been also shown that through the use of the average KAM value of a region it is possible to rank regions of the gauge length of a creep tested sample in order of recovery. As well as this there is an excellent correlation with hardness which varies as a function of distance from the point of fracture.

This KAM orientation analysis technique as assessment of microstructural recovery is also compared with the boundary length measure technique. When there is significant difference expect in microstructural recovery, such as creep test, both of these two techniques are suitable and alternatively. However, the KAM orientation analysis technique is more sensitive and accurate than boundary length measure technique for conditions between which only small differences in microstructure would be expected, such as stress relief heat treatment and long-term aging procedure.

A technique such as this, when used in conjunction with other techniques such as ion beam imaging for particle size analysis, can provide a full description of the microstructural evolution of high Cr steel during creep. Knowledge of this process will ultimately enable the production of a fully descriptive model of the microstructural effect of creep during high temperature service. A tool such as this will be invaluable for industries where creep can lead to costly failures such as the power generation industry.
Chapter 8. Conclusions and Further Work

8.1 Conclusions

The main objective of this research was to develop a complete understanding of the microstructural evolution, consisting of both the microstructural recovery and secondary particle coarsening, of Grades 91 and 92 high-Cr ferritic-martensitic steels as a function of stress relief heat treatment, long-term aging and creep stress conditions.

The effects of stress relief heat treatment, long-term aging and creep stress on the microstructure are summarized in the flow diagram in Figure 8.1. The 16 h stress relief heat treatment, which can remove most of the residual stresses from manufacturing processes, is a very important and necessary initial heat treatment for both the Grade 91 and 92 steels in the welded condition. During long-term ageing, the 16 h stress relieved 91 and 92 samples had less change in hardness values, limited matrix recovery and similar particle coarsening rates compared with the as-received 91 and 92 samples. It has been demonstrated that the application of the 16 h stress relief heat treatment at high temperature results in a reduction of approximately 10% in the creep rupture life in both the T91 and T92 materials examined compared to expected mean lifetimes. However, this is nevertheless within the ±20% scatter in stress allowed by ECCC on which safety factors are derived for design purposes.

Grade 92 steels appear to have better mechanical properties, long-term aging resistance and creep resistance than Grade 91 steels. The Grade 92 steels have approximately 10-20HV higher hardness values than the Grade 91 steels for both the as-received and stress relieved long-term ageing and creep tested samples. The matrix recovery occurred in both Grade 91 and 92 steels during the long-term ageing process; however, this matrix recovery in Grade 92 steels was very limited in comparison to that in Grade 91 steels. The Grade 92 steels have much longer creep failure time than the Grade 91 steels with similar creep stress, for example, the T92 as received sample failed at 10,172 h with 85 MPa creep stress and the T91 as received sample failed at 1,549 h with 82 MPa creep stress.
Figure 8.1: A flow diagram summarizing the effects of the 16 h stress relief heat treatment and the microstructural changes that occur in grade 91 and 92 steels subjected to prolonged aging/creep at 650°C.
The Kernel Average Misorientation (KAM) method was also used in this project to investigate the effects of stress relief heat treatment, long-term aging and creep stress on the microstructural recovery. The reduction in mean KAM values of the T91 and T92 samples proved the microstructural recovery occurs after the 16 h stress relief heat treatment. As the long-term aging times increased, the mean KAM values of all the as-received 91 and 92 samples decreased. For all the 91 and 92 creep tested samples, the mean KAM values decreased significantly by comparison of the head and gauge positions, and this reduction in mean KAM values of the 91 and 92 samples proved the microstructural recovery was significant during creep testing. It has been also shown that through the use of the average KAM value of a region that it is possible to rank regions of the gauge length of a creep tested sample in order of recovery.

8.2 Further Work

It has been mentioned in Chapter 7 that the matrix recovery had an excellent correlation with hardness when ranking regions along the gauge length of a creep test sample. In addition, there was also a relationship between hardness and secondary particle size from the results and discussions in other chapters. The data now available are comprehensive, and therefore it is worth researching the overall relationship between the hardness values, matrix recovery and secondary particle coarsening and to develop an integrated model which is capable of predicting future behaviour. The hardness values, matrix recovery (KAM value) and mean particle size (\(M_{23}C_6\) for 91 steels, and both \(M_{23}C_6\) and Laves phase for 92 steels) of a series points along the creep tested sample can be determined and calculated, and these data can be used to build up a model to describe the relationship between hardness, matrix recovery and secondary particle coarsening.

The Grade 92 steels appear to have better mechanical properties and longer service lives than Grade 91 steels. The most significant difference between these two steels is the fact that the Laves phase is only present in 92 steels after long-term ageing. It may worth to study in more detail of the particle coarsening of the Laves phase during long-term ageing and creep exposure out to longer times than were available for the samples investigated in this research. There is some evidence in the literature that Laves phase is associated with the formation of creep cavities, therefore the
fracture surface of a creep-tested sample could also be investigated. The cavities in the fracture surface, or in sectioned samples, can be investigated using FIB and TEM to investigate the tomography and composition of any particles associated with these cavities. The number density and particle size of secondary particles, especially Laves phase, associated with these cavities can also be investigated, to work out the effect of Laves phase on mechanical behaviour in these creep-tested samples.
References


34. The International Centre for Diffraction Data, Joint Committee on Powder Diffraction Standards


60. V. Randle, Electron backscatter diffraction: Strategies for Reliable Data Acquisition and Processing, Materials Characterization, 60(9), (2009), pp.913
64. European Creep Collaborative Committee (ECCC) Datasheet on Steel ASTM Grade 92 (BS PD6605), (2005)
67. F. Masuyama, ISIJ international, 41(6), (2001), p.612
68. R. Viswanathan, J. Shingledecker and J. Hawk, ECCC Creep Conference, Zurich, (2009), p.31
77. K. Fujiyama, K. Mori, T. Matsunaga, H. Kimachi, T. Saito, T. Hino and R. Ishii,