The effect of duration of stress relief heat treatments on microstructural evolution and mechanical properties in grade 91 and 92 power plant steels

This item was submitted to Loughborough University's Institutional Repository by the/an author.


Additional Information:

- Copyright 2011 ASM International, www.asminternational.org. This article was published in Advances in Materials Technology for Fossil Power Plants - Proceedings from the 6th International Conference and is made available as an electronic reprint with the permission of ASM International. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplications of any material in this article for a fee or for commercial purposes, or modification of the content of this article is prohibited.

Metadata Record: [https://dspace.lboro.ac.uk/2134/15339](https://dspace.lboro.ac.uk/2134/15339)

Version: Accepted for publication

Publisher: © ASM International and Electric Power Research Institute

Please cite the published version.
This item was submitted to Loughborough’s Institutional Repository (https://dspace.lboro.ac.uk/) by the author and is made available under the following Creative Commons Licence conditions.

For the full text of this licence, please go to:
http://creativecommons.org/licenses/by-nc-nd/2.5/
The effect of duration of stress relief heat treatments on microstructural evolution and mechanical properties in Grade 91 and 92 power plant steels

L. Li, P. Zhu, G. West and R. C. Thomson

Department of Materials, Loughborough University, Loughborough, LE11 3TU, UK

ABSTRACT

A detailed examination has been carried out of the microstructural evolution and mechanical properties of samples of T91 and T92 steels which have been subjected to both a ‘normal’ pre-service heat treatment and an extended stress relief heat treatment at 765°C for up to 16 hours. The samples have subsequently been creep tested to failure at different stresses ranging from 66 to 112 MPa. In each case, a reduction in rupture time was observed of 20-30% in the samples which had experienced the additional stress relief heat treatment compared to those which had not. It is shown that these data, when compared with the mean values expected from European Creep Collaborative Committee (ECCC) Datasheets, result in a reduction in stress of approximately 10% of the mean value predicted from the ECCC data, which is within the allowable scatter band.

In order to investigate the reasons behind this reduction in life, extensive analyses have been carried out using a range of advanced electron microscopy techniques. In particular, imaging using both ion and electron beams in combination with image analysis methods have been used to provide a rapid and accurate technique for quantifying the particle size distributions of the M23C6 carbides and also the Laves phase, which was found only in the T92 samples. Electron backscatter diffraction techniques have also been used to quantify the changes occurring in the martensitic matrix with respect to the nature and length of the grain boundaries and the grain size distribution.

The effect of the additional heat treatment on microstructural evolution is to coarsen the secondary phase particle distribution and enhance matrix recovery before the steel enters service, to the detriment of the hardness and creep fracture life. It is also demonstrated that there is a significant effect of applied stress on the particle size distributions and matrix recovery during creep testing.

1. Introduction

Advanced high chromium ferritic steels such as Grade 91 and Grade 92 are extensively used in the power plant industry. Components made from these types of steels, including headers, steam pipes and tubes, are required to provide reliable service at high pressures (20-30 MPa) and temperatures (550-610°C) for several decades\(^\text{[1]}\). Key properties which make Grade 91 and Grade 92 steels suitable for power plant applications include high thermal conductivity, low thermal expansion coefficient, good corrosion/oxidation resistance and relatively good creep resistance\(^\text{[1,2]}\).

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\(^\text{[3-6]}\). 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\(^\text{[7,8]}\). 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, for example those designed to relieve residual stresses, often associated with welding processes, which are applied before the steels enter service. 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 type of steels at elevated temperatures\(^9\)\(^{12}\). 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.

2. Experimental Methods

2.1 Materials and Heat Treatments

Two types of steels, T91 and T92, were investigated in this study and their chemical compositions are shown in Table 1. The diameter of the T91 tube was 45 mm with a wall thickness of 9 mm, whereas the T92 tube was 42 mm in diameter with a wall thickness of 5 mm. Samples for microstructural examination of approximately 10×4×10 mm (L×W×H) were cut from both tube materials. Samples for creep testing were ‘dog bones’ of dimensions 200×36/13×9/5 mm (LxW (Head/Gauge) xH (T91/T92). The stressed gauge section (G) and the unstressed head section (H) were examined separately from the creep tested specimens. Cross-sections were examined from the gauge section perpendicular to the load direction and were at least 2 cm away from the fracture surface. The samples were examined in the as-received condition (denoted ‘AR’) which was a normalising treatment at 1060°C for 20 mins followed by a temper at 775°C for 80 mins. Some of the samples then underwent an additional heat treatment for a further 16 h at 765°C (denoted ‘16’), to simulate a post weld heat treatment, for example. Samples in each condition were creep tested at 650°C at stresses of 66, 82, 85 and 112 MPa. Table 2 provides a detailed listing of the sample designations with the corresponding heat treatment condition, creep test data and hardness values obtained.

Table 1: Chemical composition of materials investigated (wt.% and balance Fe).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Mo</th>
<th>Ni</th>
<th>Al</th>
<th>N</th>
<th>Nb</th>
<th>V</th>
<th>W</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91</td>
<td>0.106</td>
<td>0.363</td>
<td>0.480</td>
<td>0.014</td>
<td>0.003</td>
<td>8.637</td>
<td>0.937</td>
<td>0.230</td>
<td>0.012</td>
<td>0.0471</td>
<td>0.073</td>
<td>0.215</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T92</td>
<td>0.128</td>
<td>0.318</td>
<td>0.435</td>
<td>0.016</td>
<td>0.005</td>
<td>8.890</td>
<td>0.390</td>
<td>0.240</td>
<td>0.012</td>
<td>0.0381</td>
<td>0.054</td>
<td>0.211</td>
<td>1.790</td>
<td>0.0040</td>
</tr>
</tbody>
</table>

Table 2: Heat treatment conditions, creep test results and hardness values of specimens

<table>
<thead>
<tr>
<th>Sample designation</th>
<th>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>T91</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T91-AR</td>
<td>N: 1060°C/20 min T: 775°C/80 min</td>
<td>-</td>
<td>-</td>
<td>205±5</td>
</tr>
<tr>
<td>T91-16</td>
<td></td>
<td>16 h</td>
<td>82 MPa / 1549 hrs</td>
<td>H:194±3; G:162±3</td>
</tr>
<tr>
<td>T91-AR-1</td>
<td></td>
<td>16 h</td>
<td>82 MPa / 992 hrs</td>
<td>H:185±2; G:162±1</td>
</tr>
<tr>
<td>T91-AR-2</td>
<td></td>
<td>16 h</td>
<td>66 MPa / 5857 hrs</td>
<td>H:197±2; G:161±1</td>
</tr>
<tr>
<td>T91-16-2</td>
<td></td>
<td>16 h</td>
<td>66 MPa / 4826 hrs</td>
<td>H:188±3; G:154±1</td>
</tr>
<tr>
<td>T92</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T92-AR</td>
<td>N: 1060°C/20 min T: 775°C/80 min</td>
<td>-</td>
<td>-</td>
<td>218±2</td>
</tr>
<tr>
<td>T92-16</td>
<td></td>
<td>16 h</td>
<td>-</td>
<td>200±3</td>
</tr>
<tr>
<td>T92-AR-1</td>
<td></td>
<td>16 h</td>
<td>112 MPa / 1649 hrs</td>
<td>H:211±3; G:174±4</td>
</tr>
<tr>
<td>T92-AR-2</td>
<td></td>
<td>16 h</td>
<td>112 MPa / 1175 hrs</td>
<td>H:199±1; G:170±2</td>
</tr>
<tr>
<td>T92-16-2</td>
<td></td>
<td>16 h</td>
<td>85 MPa / 10172 hrs</td>
<td>H:226±4; G:166±3</td>
</tr>
</tbody>
</table>

*H and G in the Hardness column refers to the hardness value tested from head and gauge sections respectively
2.2 Thermodynamic Calculations
Thermodynamic calculations were performed for the compositions of the two steels to give an indication of the phases likely to be present at equilibrium using the software package MTDATA\[^{[13]}\] in conjunction with the critically assessed thermodynamic database for ferrous materials, TCFE\[^{[14]}\] version 1.22. Calculations were carried out over the temperature range 400 to 1200°C, and the phases liquid, ferrite, austenite, various carbides, Laves, sigma and AlN were allowed to exist.

2.3 Sample Preparation and Hardness Measurements
Samples were sectioned using a Struers Accutom saw, using an alumina slitting disk. The samples were subsequently mounted in conducting Bakelite, followed by grinding using 240 to 1200 grit SiC in a resin bond, and polishing on standard cloths with diamond suspensions down to 1 μm. Samples for examination using electron back scatter diffraction were further polished with a 0.02 μm colloidal silica suspension for 30 minutes which is considered to be effective in removing surface mechanical deformation and ensures the surface-sensitive EBSD analysis results are more representative of the bulk matrix\[^{[15]}\]. Macrohardness testing was carried out using a Mitutoyo AVK-C2 hardness tester with a load of 10 kg and a dwell time of 10 s.

2.4 Scanning Electron and Focussed Ion Beam Microscopy
An fei Nova 600 Nanolab dual beam field emission gun scanning electron microscope and ion beam system (FIBSEM) was also used for both characterizing the grain structure and the carbide population using ion beam etching\[^{[16]}\]. The FIBSEM was operated in the ion imaging mode, using a liquid metal gallium ion source to generate ion-induced secondary electron images. To achieve good contrast between the particles and the matrix, the imaging parameters were carefully adjusted. The optimum settings were found to be 30 pA for the ion beam current at 30 kV with a 150 μs dwell time at a magnification of 10,000 times and a working distance of 19.5 mm. An additional flow of insulator enhanced etch (IEE), XeF\(_2\), was used in order to distinguish between the Laves phase and the carbides. To achieve statistically valid data for particle size quantification, at least five images, covering a typical total sampling area of 2750 μm\(^2\), were collected for each specimen. In addition, the backscatter electron detector was used to generate images for each sample.

Measurement of the particle sizes and population were carried out by processing the ion beam images (1050×1050 pixels) using the UTHSCSA ImageTool 3.0 software. Due to the strong contrast between particles and the martensitic matrix, particles can be successfully distinguished from the matrix using a grey scale discrimination. The sizes and number density of the particles can then be measured by the software. It should be noted that particles which were less than 5 pixels on the image (equivalent to ~70 nm in diameter) were not included to avoid image noise and artifacts.

In order to quantify the changes in the matrix microstructure, electron back scatter diffraction (EBSD) analysis was performed on each specimen using an EDAX Pegasus system attached to a Zeiss 1530VP field emission gun scanning electron microscope (FEGSEM). In the EBSD analyses, the electron source was operated in high current mode with the accelerating voltage of 20 kV and an aperture size 60 μm. The specimen was pre-tilted to 70° with respect to the horizontal by mounting it on an angled specimen holder. A square area of 50×50 μm was analysed in each scan with a step size of 0.1 μm. The crystallographic file loaded for indexing was the ferrite structure, which has a body centred cubic structure with a lattice parameter a=0.287 nm.

2.5 Transmission Electron Microscopy
Transmission electron microscopy (TEM) was carried out in a Jeol 2000FX microscope operating at 200 kV equipped with an Oxford Instruments Inca EDX system. 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. Results and Discussion

3.1 Thermodynamic Calculations

The results of the thermodynamic calculations are presented in Figure 1. The main phases predicted to be present at thermodynamic equilibrium in both the T91 and T92 steels were the ferritic matrix, together with ~2 % by weight of M$_{23}$C$_6$ (Cr rich) and ~0.25 % by weight of 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°C, rising to ~ 2.5 % by weight at 400°C. The metallic content of the M$_{23}$C$_6$ phase was predicted to be ~60% Cr, 25% Fe and 15% Mo by weight in the T91 material, with W predicted to substitute for Mo in the T92 material, giving a predicted composition of ~58% Cr, 28% Fe and 14% W by weight.

Examination of carbon extraction replica specimens in the TEM confirmed that the majority carbide was indeed M$_{23}$C$_6$, with compositions determined by EDX analysis agreeing very well with those predicted. A smaller number of fine V-rich MX particles were also observed. It should be noted that no Laves phase was identified in the T91 material, as expected, and in the T92 material the Laves phase was only observed in the specimens which had been creep tested – i.e. no Laves phase was found using either back scatter imaging in the SEM or on carbon replicas in the TEM in the T92-AR or T92-16 samples. This is consistent with previous observations\cite{2,4,7-11} in which Laves phase has only appeared after prolonged thermal / creep exposure at lower temperatures.

![Figure 1](image.png)

**Figure 1:** Equilibrium thermodynamic predictions in the temperature range 400-1200°C for (a) T91 and (b) T92.

3.2 Influence of the Additional Stress Relief Heat Treatment

Hardness data are presented in Table 2 which show that the hardness dropped from 205 to 192 H$_v$ in T91 and from 218 to 200 H$_v$ in T92 as a result of the additional 16 h heat treatment. Ion beam induced secondary electron images are presented in Figure 2 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 M$_{23}$C$_6$ particles is clearly observable when comparing the ‘AR’ and the ‘16’ samples. The particles appear dark in these images due to their lower electrical conductivity than the matrix. The drop in hardness and changes in particle size are a clear indication that the additional heat treatment is having a significant effect on the microstructural evolution. Quantification of the particle size distributions found that the mean carbide size increased from 123 to 141 nm in T91 (see Table 3), and from 117 to 131 nm in T92 (see Table 4) as a result of the additional heat treatment.
Changes in the martensitic matrix as a result of the stress relief heat treatment were investigated using EBSD, and Figure 3 presents the resulting grain boundary maps. A well-defined martensitic matrix structure is evident in all four images, however, there is an indication of some additional sub-grain formation after 16 h. Quantification of these boundary maps in terms of the fraction of low:high angle boundaries shows that there is a slight increase from 0.54 to 0.65 in T91, and from 0.57 to 0.80 in T92 respectively.
Figure 3: EBSD derived boundary maps for (a) T91-AR, (b) T92-AR, (c) T91-16 and (d) T92-16. Low angle boundaries, defined to be from 2-15° are shown in red, and high angle boundaries, 15-180°, are shown in blue.

3.3 Effect of Isothermal Ageing on Microstructural Evolution

The effect of isothermal ageing at 650°C was investigated on samples taken from a position within the head of the creep test samples which was subjected to very low stresses. The hardness data (Table 2) showed small additional reductions as a consequence of ageing, with the T91 remaining softer than T92. Using back scatter electron imaging, a bright phase was clearly visible in the T92 samples only after prolonged thermal exposure, as presented in Figure 4. This was identified using EDX to be rich in both Mo and W, and was assumed to be the Laves phase.

Careful quantification of the sizes and distributions of the two types of particles, M23C6 and Laves, was carried out. In the case of T91, which contained primarily the M23C6 phase, ion induced secondary electron images in conjunction with image analyses were used to quantify the M23C6 particles. For the T92 samples, the black particles in the ion induced secondary electron images were a combination of both M23C6 and the Laves phase. Therefore, a different technique was utilized in which an additional flow of insulator enhanced etch (IEE) was used to ‘remove’ the Laves phase particles from the images, allowing separate quantification of the carbide phase only.
The Laves phase is the only phase appearing bright in conventional back scatter images (see Figure 4 for example), and therefore quantitative image analysis was carried out on these type of images to determine the Laves phase particle size distribution. It was therefore possible using a combination of imaging methods, over an appropriate number of fields of view to obtain a full, accurate and statistically significant quantification of both the M23C6 carbide and the Laves phase populations.

Figure 4: Back scattered electron images of the T92 samples (a) T92-AR-1Head, (b) T92-16-1 Head, (c)T92-AR-1 Gauge and (d) T92-16-1 Gauge showing substantial precipitation and coarsening of Laves phase during creep testing.

Table 3: Particle size data for the M23C6 carbides in the T91 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Head</th>
<th>Particle population (3775 μm²)</th>
<th>Average size (nm)</th>
<th>Gauge Length Particle Population (3775 μm²)</th>
<th>Average Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T91-AR</td>
<td></td>
<td>3865</td>
<td>123.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T91-16</td>
<td></td>
<td>4467</td>
<td>141.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>T91-AR-1</td>
<td></td>
<td>4359</td>
<td>127.6</td>
<td>2131</td>
<td>162.6</td>
</tr>
<tr>
<td>T91-AR-2</td>
<td></td>
<td>5109</td>
<td>130.5</td>
<td>1882</td>
<td>185.1</td>
</tr>
<tr>
<td>T91-16-1</td>
<td></td>
<td>4136</td>
<td>150.9</td>
<td>1956</td>
<td>172.8</td>
</tr>
<tr>
<td>T91-16-2</td>
<td></td>
<td>3085</td>
<td>141.9</td>
<td>1505</td>
<td>182.1</td>
</tr>
</tbody>
</table>
The detailed number of particles observed in a given area, together with their mean size, are presented in Tables 3, 4 and 5 for the $M_2\text{C}_6$ particles in T91, the $M_2\text{C}_6$ particles in T92 and the Laves particles in T92 respectively. Considering the effect of ageing during the creep test for the $M_2\text{C}_6$ particles in the T91 material, it can be seen that the average particle size in the as-received material changed from 123 nm to 130 nm after 5857 h exposure at 650°C, indicating a relatively slow coarsening rate of only 0.001 nm h$^{-1}$ (assuming a crude linear rate). In the samples which had received the additional 16 h ageing at 765°C, although the starting size was larger at 141 nm, there was insignificant change during further exposure at 650°C for up to 5857 h during the creep test. A possible explanation for this is that the initial additional ageing at 765°C gives a Larson-Miller parameter (LMP) of 22,010, based on $LMP = T(20+\log t)$ where $T$ is the absolute temperature and $t$ is the time in hours. In order to achieve the same LMP at 650°C, an ageing time of over 7,000 h is required. Therefore, it appears that the higher temperature stress relief heat treatment dominates over the carbide sizes, with little further change being observed in the mean size during subsequent creep testing at the lower temperature.

**Table 4:** Particle size data for the $M_2\text{C}_6$ carbides in the T92 samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Head</th>
<th>Particle population (2750 $\mu$m$^2$)</th>
<th>Average size (nm)</th>
<th>Average Size (2750 $\mu$m$^2$)</th>
<th>Average Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T92-AR</td>
<td>4767</td>
<td>117.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T92-16</td>
<td>3787</td>
<td>131.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>T92-AR-1</td>
<td>5559</td>
<td>118.4</td>
<td>2864</td>
<td>142.4</td>
<td></td>
</tr>
<tr>
<td>T92-AR-2</td>
<td>4724</td>
<td>128.6</td>
<td>2214</td>
<td>167.5</td>
<td></td>
</tr>
<tr>
<td>T92-16-1</td>
<td>3726</td>
<td>128.2</td>
<td>2463</td>
<td>155.2</td>
<td></td>
</tr>
<tr>
<td>T92-16-2</td>
<td>3273</td>
<td>130.5</td>
<td>1771</td>
<td>168.6</td>
<td></td>
</tr>
</tbody>
</table>

In the case of the T92 samples, the population of $M_2\text{C}_6$ particles behaved in a similar manner to those in the T91 materials. The carbides changed in size from ~118 nm in the AR material, to ~129 nm after the ageing at 650°C associated with the creep test for 10,172 h, again indicating a relatively slow coarsening rate of only 0.001 nm h$^{-1}$. The carbides all had a mean size of ~130 nm in the samples which had received the additional ageing treatment for 16 h.

However, it is interesting to note from the data presented in Table 5 that significant differences were observed in the size of the Laves phase particles as a result of isothermal ageing. In the head of the creep samples, the particles grew from 143 nm to 210 nm as a result of exposures for 1,649 and 10,172 h respectively in the ‘AR’ series. Although the initial size was bigger in the ‘16’ series, they similarly grew from 164 nm to 210 nm as a result of exposures for 1,175 and 7,965 h respectively. These changes are illustrated quantitatively in the graphs presented in Figure 5 in which the particle size distribution plots are presented for both the $M_2\text{C}_6$ particles (a) and the Laves phase (b) in which it can be clearly seen that there is a significant difference in the size distributions and mean sizes between the two particle populations.
Changes in the martensitic matrix were also examined using EBSD by generating grain boundary maps as a result of the isothermal ageing in the head of all of the creep tested samples. The low:high angle grain boundary ratio derived from the data was again used to quantify the matrix ‘recovery’. These data are compiled in Figure 6 for all of the samples examined. Focussing on the results for the head sections (white bars), it can be seen that in the AR sample series, there is a small increase in the ratio with increasing thermal exposure, whereas in the 16 sample series there is a much smaller change, with some evidence of a slight decrease in the ratio. This decrease may be an indication of enhancement in the matrix recovery for the samples which have received the additional 16 h heat treatment.
3.4 Effect of Stress on Microstructural Evolution

The microstructures of the gauge sections of the creep tested samples have also been compared with the head sections in order to study the effect of stress on microstructural evolution. The samples were examined in a consistent position 2 cm away from the fracture surface. The hardness data (Table 2) consistently showed that the hardness in the gauge length was typically ~ 40 H, lower than the corresponding head section, indicating a degradation as a function of the applied stress. Ion induced secondary electron images are presented in Figure 7 which compare the particle size distribution in the head and gauge length for the AR-1 series of samples for both materials. It is clear that there is significant coarsening in the gauge length compared with the head sections in both materials.

![Figure 7: Focused ion beam induced secondary electron images for (a) T91-AR-1 Head, (b) T91-AR-1 Gauge, (c) T92-AR-1 Head and (d) T92-AR-1 Gauge illustrating the significant particle coarsening as a result of creep. The particles in the T91 steels correspond to the distribution of M$_{23}$C$_6$ whereas the particles shown in the T92 steels are a mixture of both M$_{23}$C$_6$ and Laves phase particles.](image-url)
Figure 8: Particle size distribution plots for (a) M\textsubscript{23}C\textsubscript{6} particles and (b) Laves phase particles in the gauge sections of the T92 creep tested samples.

The mean particles sizes in the gauge length are presented in Tables 3, 4 and 5 for the M\textsubscript{23}C\textsubscript{6} and the Laves phase separately. There is some systematic additional coarsening of the M\textsubscript{23}C\textsubscript{6} in the gauge length compared to the head, for example, ~118 nm in T92-AR-1 (head) to 142 nm in the gauge. This effect is more pronounced in the case of the Laves phase, which changes in size from ~209 nm in the head of T92-16-2 to ~289 nm in the gauge length. Particle size distribution plots are presented in Figure 8 for the M\textsubscript{23}C\textsubscript{6} (a) and the Laves phase (b) separately. These graphs show clearly that there is an effect of the applied stress and thermal exposure on the coarsening rate. For both the Laves phase and the M\textsubscript{23}C\textsubscript{6} carbides, there is also a significant reduction in the particle population in the gauge length compared with the head, indicating true coarsening is occurring.

It is also interesting to note that at failure, the carbide and Laves particles had reached similar average size values in the same creep test condition. For example, comparing T92-AR-2 with T92-16-2, the carbides had average sizes of ~168 nm and ~169 nm respectively, and the Laves particles ~285 nm and ~289 nm. These data therefore indicate that fracture is associated with a certain critical size distribution of particles, and therefore this is a possible explanation of the earlier failure of the samples which have received the additional 16 h heat treatment. Again determining a crude linear coarsening rate for the samples which have been creep tested, for the M\textsubscript{23}C\textsubscript{6} particles rates of 0.015 nm h\textsuperscript{-1} for T92-AR-1 and 0.021 nm h\textsuperscript{-1} for T92-16-1 can be determined respectively, and for the Laves phase, corresponding rates of 0.135 nm h\textsuperscript{-1} and 0.171 nm h\textsuperscript{-1}. Similar trends are observed for the T92-AR-2 and T92-16-2 samples, which have rates of 0.005 nm h\textsuperscript{-1} in both cases for M\textsubscript{23}C\textsubscript{6} and rates of 0.028 nm h\textsuperscript{-1} and 0.036 nm h\textsuperscript{-1} for the Laves phase. Therefore, given that there are very similar particle coarsening rates and similar particle size distributions at failure, it can be assumed that the samples which have not received the additional 16 h heat treatment at 765°C will take a longer time to reach the critical microstructural condition.

The grain boundary maps obtained from the gauge sections of both the T91 and T92 samples in the AR-2 and 16-2 test conditions are presented in Figure 9. It can be seen that there has been significant change in the matrix microstructure, and in the T91 samples there is little evidence of the original martensitic structure remaining after the creep test. It is also apparent that the T92 material is more resistant to these recovery processes, with some evidence of the original martensitic structure remaining.
Figure 9: EBSD Boundary maps of (a) T91-AR-2 Gauge, (b) T91-16-2 Gauge, (c) T92-AR-2 Gauge and (d) T92-16-2 Gauge specimens. Low angle boundaries (2-15°) are shown in red and high angle boundaries (15-180°) are shown in blue.

The observations from the grain boundary maps can also be quantified using the ratio of low:high angle grain boundaries, and the data from the gauge sections have also been presented in Figure 6 along with those for the head sections. In all cases, there is a significant reduction between the values determined for the gauge length compared to the head sections. This decrease is associated with the formation of larger equiaxed grains which increases the number of high angle boundaries, and further coarsening of the dislocation substructure reduces the number of low angle boundaries. It is therefore apparent that there is a significant effect of the applied load on the matrix recovery, in addition to its related effect on the size and distribution of the second phase particles.
3.5 Mechanical Properties
The aim of this research was to investigate the effect of an additional extended pre-service heat treatment, for example, during fabrication, on the final creep properties. The creep test data have therefore been plotted in Figure 10 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\(^{[17]}\) and Grade 92\(^{[18]}\). 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\(^\circ\)C there is an earlier failure time, resulting in a reduction in stress of approximately 10\% of the mean value expected from the ECCC data in each case. However, this is nevertheless within the ±20\% scatter in stress allowed by ECCC on which safety factors are derived for design purposes. It should also be noted from Figure 10 that this difference is indeed reducing at longer times and lower stresses more typical of those experienced in service.

Figure 10: The rupture stress data at 650\(^\circ\)C obtained for both the T91 and T92 steels in both the normal condition and after the additional 16 h heat treatment at 765\(^\circ\)C plotted as a function of time. The values are compared against the mean lines for Grades 91 and 92 respectively, as assessed by the ECCC\(^{[17,18]}\).

4. Conclusions
It has been demonstrated that the application of an extended pre-service tempering heat treatment at high temperature results in a reduction of approximately 10\% in the creep rupture stress in both T91 and T92 materials examined compared to expected mean lifetimes. Advanced characterisation techniques have been employed to separately quantify the size distributions of both the carbide and Laves phase particles present in these two materials. The Laves phase was only present in the T92 grade, and indeed was only observed after extended ageing at low temperature. The effect of a 16 h heat treatment at 765\(^\circ\)C is to coarsen the M\(_{23}\)C\(_6\) particles significantly, such that they undergo little further subsequent coarsening after extended ageing during creep testing at 650\(^\circ\)C for up to ~10,000 h. However, the Laves phase which forms during the lower temperature creep tests, was found to coarsen significantly in the T92 material. It is postulated that there is a critical particle size distribution at which failure occurs, and therefore that the effect of the additional heat treatment is to bring the samples closer to that critical size distribution, such that the samples fail in a shorter time compared to those which have not received the additional heat treatment. It has also been shown, by comparison of the head and gauge sections of the creep samples, that there is a significant effect of stress on both the coarsening of the particles and also on the recovery of the martensitic matrix.
5. Acknowledgements
The authors would like to acknowledge the support of the Technology Strategy Board (Project Number TP/5/MAT/6/I/H0101B) and the following companies: Alstom Power Ltd., E.ON Engineering Ltd., Doosan Babcock, National Physical Laboratory and QinetiQ for their valuable contributions to the project.

References
[18] European Creep Collaborative Committee (ECCC) Datasheet on Steel ASTM Grade 92 (BS PD6605), 2005