



University of Leicester

Development of Advanced Ferritic Steels for
High Efficiency Power Generation Plant

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*A thesis submitted to the University of Leicester
for the Degree of Doctor of Philosophy
Submitted August 2009*

Acknowledgements

The work described in this dissertation was carried out in the Department of Engineering of the University of Leicester, between October 2005 and March 2009, under the supervision of Prof. S.V. Hainsworth. To my best knowledge, it is the original work of the author except where reference is made to the work of others.

Thanks are due to the EPSRC and CORUS for funding this research through CASE PhD studentship.

I must thank Prof. S. V. Hainsworth for her continual supporting, dedicated supervision, help and advice throughout this project. Thanks are also due to Prof. A. Strang for his supervision, great enthusiasm on this project, and for his renowned expertise on creep resistant steels. Dr. P. F. Morris (Corus) is particularly thanked for guidance, supervision and beneficial discussion throughout this project, and also for providing precious samples.

I would like to thank all the technical support staff in the Materials Lab, Department of Engineering. Graham Clark, he supported me almost everything from polishing, etching, RLM, SEM, TEM, even proofreading on my some writing pieces; Barry Kirkland, who helped me set up thermal ageing experiment work, and continued to look after my furnaces in long time running; Dipak Raval; Alan Wale; Peter Barwell, for his great help on looking after my furnaces when main electricity power shut down and gave me instruction on safety awareness in the Lab. We enjoyed many happy hours over past three years.

I would like to thank Prof. H. V. Atkinson for her long lasting support to me and lots of beneficial discussion on my project, especially on the Mechanics of Materials. Particular thanks are given to John Critchell for giving me dedicated training on TEM operation, his expertise on TEM and great patience inspired me very much. Special thanks to Prof. V. Vodarek at Technical University of Ostrava, Czech Republic, who helped me master the techniques of EDX by TEM when I despaired of carrying on minor phase analysis in TEM, also, he helped me on the interpretation of Electron Diffraction pattern. P.D. Clarke at Corus provided me precious E911 samples and four experimental cast alloy, without these time consuming and money consuming support, it is impossible to carry on this PhD project, these hard work would be greatly acknowledged. A.P. Backhouse at Corus also gave some helpful

discussions on this project. I must thank the project student, Tien Lam Lau, he conducted hardness testing on cast alloy samples of code 30 and 31 up to 5000 hours.

Finally, I am indebted so much to my family who have supported me through the course of my research.

Guixiang Qin

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Abstract

E911 creep samples exposed to temperatures of 600°C, 625°C and 650°C at differing stress levels were supplied by CORUS. The hardness of the gauge length that experienced both creep strain and temperature was found to be lower than that of the head where thermal softening only can be assumed. The changes in the morphology and size of precipitates were observed qualitatively by optical microscopy and Scanning Electron Microscopy. A creep fracture mechanism map of E911 steel was constructed with two modes of creep (transgranular and intergranular). A fitted ellipse shape was used to characterise the irregular block shape by Electron Backscattered Diffraction (EBSD). It showed that the width of the block inside a prior austenite grain increases more rapidly in the gauge length than in the head; subgrain growth was also observed by EBSD. Transmission Electron Microscopy studies indicate that at 600°C E911 steel can reach up to 75647 hours creep rupture life (108MPa), which is due to the relatively small size of $M_{23}C_6$, Laves and M_2X phases. However, Z phase precipitation results in a drop in creep resistance owing to the dissolution of fine MX phase and the transformation of M_2X phase. At 625°C and 650°C, the creep rupture life decreases owing to the coarsening of Laves, $M_{23}C_6$ and M_2X phases.

Four experimental steel casts were prepared with varying levels of Ni and Cr to investigate the effect of these elements on Z phase formation. After 10,000 hours exposure, there was little evidence of Z phase in the samples studied and therefore it is difficult to draw definitive conclusions about the role of Ni or Cr in promoting Z phase formation. It is possible that the casts studied here will allow better conclusions to be drawn after exposing the samples to longer durations.

Key words: E911, Creep, SEM, TEM, EBSD, Z phase

Publications

Some of the work described in this thesis has been presented previously in the following publications:

- 1. G. Qin**, S.V. Hainsworth, P.F. Morris, P.D. Clarke, A.P. Backhouse, A. Strang, TEM studies of microstructural evolution in creep exposed E911, in: I. A. Shibli, S. R. Holdsworth (Eds.), Proceedings of the European Creep Collaborative Committee conference, Zurich, DEStech Publications, Inc., 2009, pp 595-605.
- 2. G. Qin**, S.V. Hainsworth, P. F. Morris, P.D. Clarke, A.P. Backhouse, A. Strang, Effect of high temperature creep deformation on microstructural development of E911, in: A. Strang, W. M. Banks, G. M. McColvin, J. E. Oakey, R. W. Vanstone (Eds.), Proceedings of the Seventh International Charles Parsons Turbine Conference, Glasgow, IOM Communication Ltd, 2007, pp 441-452.

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Chapter 1 Introduction

1.1 Power generation plant

1.1.1 Power plant working flow

Power plants obtain energy by burning fossil fuels to generate thermal energy, then, the thermal energy is transferred to mechanical energy which is eventually converted to electrical energy as shown as Figure 1.1. The steam from the superheater (tube walls) in the boiler at high pressure and high temperature is piped into the high pressure (HP) turbine. The steam is exhausted from the HP turbine at reduced pressure and temperature and is returned to the reheater in the boiler, the reheated steam is passed to the intermediate pressure turbine (IP), and from there passed to the low pressure (LP) turbine. As steam moves through the system, the dynamic pressure from the steam drives the turbine. The mechanical energy is then converted to electrical energy at the generator. Exiting steam is passed through the condenser and the water is pumped back to the boiler. Exhausted gas is vented into air through the chimney stack.

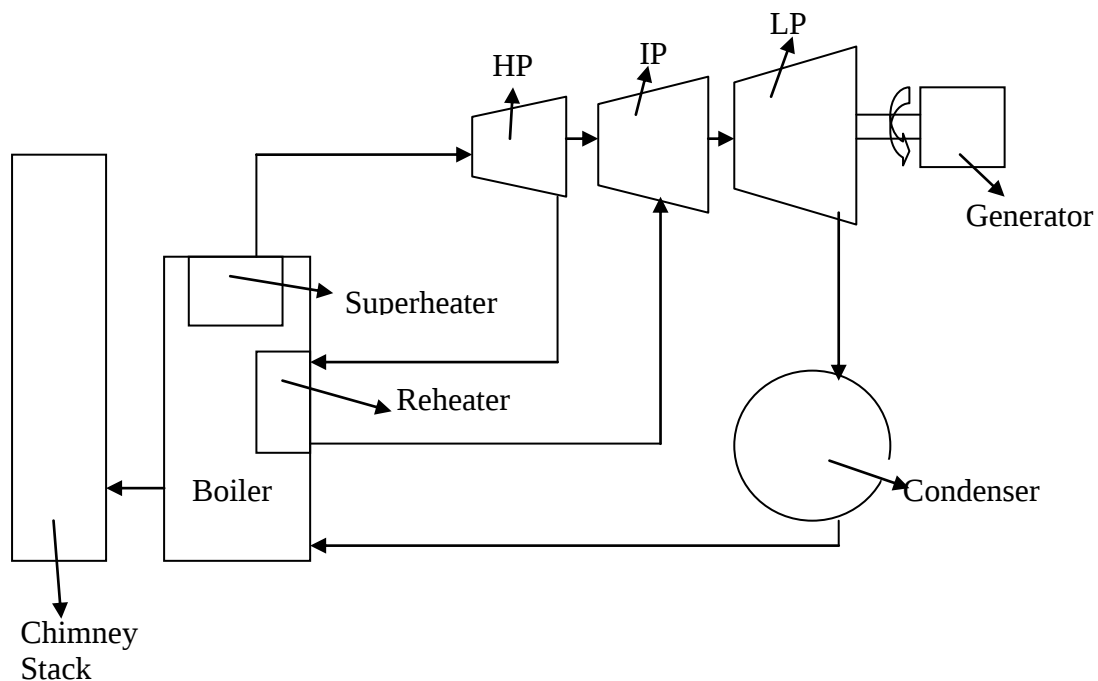
Coal and oil fired stations have poor thermal efficiencies (40%) and high emission and pollution levels (CO_2 , SO_x , NO_x and particulates) while combined cycle gas turbine-fired (CCGT) stations have higher thermal efficiencies, typically around 60% with reduced pollutant emission of NO_x and SO_x [1]. However, today, higher gas prices have made the CCGT less attractive and the need to minimise carbon dioxide emissions from fossil fuel plants is now widely accepted [1].

Research has indicated that an increased concentration of carbon dioxide in the atmosphere is correlated with a rise in mean global temperature, also known as climate change [2]. Acid rain is also caused by nitrogen oxides and sulphur dioxide.

Since there is a continuing increase in the demand for electrical power in Europe, USA, Japan and especially countries such as China, India and other emerging economies, steps need to be taken to reduce and/or eliminate the effects of the corresponding increases in CO_2 and other harmful emissions on global warming. Harmful SO_x emissions can be eliminated through the use of fluidised bed boilers burning a mixture of pulverised coal and limestone, thus fixing

the sulphur; limiting the combustion temperature below 1000°C also reduces NO_x formation; the use of cyclone traps reduces the emission of particulates into the atmosphere; CO₂ is still produced but plans are in progress to sequestrate this in exhausted oil and gas field reservoirs [3, 4].

Although the technology for carbon dioxide capture and storage, and for removal of emissions such as SO₂, NO_x and particulates from coal fired power stations is being developed, improving the efficiency of power plant can have a great impact on the reduction of emissions of carbon dioxide and other harmful gases.



HP: High pressure turbine

IP: Intermediate pressure turbine

LP: low pressure turbine

Figure1.1. Simplified schematic diagram of a power plant

1.1.2 Power plant efficiency

There is a strong driving force towards efficiency improvement in coal-fired steam power plant, both for economic and environmental reasons [5]. This can be achieved by improvements in the mechanical design of turbine blades and elimination of steam leaks between stages, all of which significantly improves the steam flow, as well as the overall

aerodynamic and thermal efficiency of the turbine. These improvements in thermal efficiency result in reduced CO₂ and other emissions since less fuel needs to be burned per MW of power generated. In addition to their use in new power generation plant the efficiencies of both existing fossil-fired and nuclear generating plant, built between the 1960's and 1980's can also be improved by retrofitting them with improved blading and inter-stage seals [6, 7, 8].

While improvements in mechanical design are beneficial, the major improvements in thermal efficiency can only be achieved by increasing the temperature and pressure of the incoming steam. On this basis modern plant is being designed to operate according to the Carnot Cycle under ultra supercritical [USC] steam conditions i.e. at inlet steam temperatures of up to 700°C and pressures in the range of 300-400 bar [9].

The efficiency of the cycle of a power plant can be presented by the Carnot Efficiency given in equation 1.1:

$$E = \frac{T_1 - T_2}{T_1} \quad (1.1)$$

where E is the efficiency,

T_1 is the temperature of steam turbine inlet and,

T_2 the temperature of exhaust.

According to the Carnot equation, use of inlet steam temperature in the range of 580 to 630°C should theoretically result in thermal efficiencies of between 64 to 65%. In practice, due to other losses in the power generation plant, increases of ~10% is still a marked improvement that results in significant reductions in CO₂ emissions per MW of power generated. In order to achieve this, a new range of high temperature 9-10%Cr creep resistant steels have been developed as a result of collaborative studies conducted in the European COST programme as well as in other Japanese and American research programmes. These new steels have found applications in boiler components as well as turbine blades, rotors, castings, valve bodies, bolting and main steam piping in advanced steam generation plant. The criterion for use of these advanced ferritic steels in modern USC steam generation plant is that at a stress of 100MPa they have a minimum creep rupture life of 100,000 hours at the required

operating temperature. On this basis the maximum temperature of operation for these advanced 9-10%Cr steels is 630°C thus limiting the thermal efficiency of plant using these alloys to a maximum of about 50% [10].

In order to achieve yet higher thermal efficiencies, such as the use of higher inlet steam temperatures greater than 630°C, high temperature creep resistant Ni-based alloys are required. A trial 400 MW demonstration plant with 300bar 700°C/720°C/720°C VHP/HP/IP inlet steam conditions is presently being developed in Europe and is expected to be commissioned in 2014 and achieve a thermal efficiency in excess of 60%. In addition design studies are presently in progress in the USA for a generating plant with an inlet steam temperature great than 760°C [11].

The present work reported in this investigation concentrates on an advanced creep resistant 9%Cr steel (E911) developed by Corus for steam generating boiler plant components operating at 600°C.

1.2 Some typical 9-12% Cr steel

Steam pipe and turbine rotor steels usually comprise of 0.1-0.2% C and Cr contents between 9-12%. Table 1.1 lists a range of typical compositions and typical heat treatment temperatures for a number of different steels used for power generation plant.

Table 1.1 shows that the 10^5 creep rupture strength (σ) of tempered martensitic 9-12 % Cr steels tested at 600°C has been doubled by the minor changes of chemical composition (from 59MPa to 125 MPa), especially in Mo, W, Ni and B. Over the last three decades, these developments in the strength of steels have formed the basis for efficiency improvement in power plants as the materials can be used at higher working temperatures.

The following section discusses why 9-12% Cr tempered martensitic steels possess good creep resistant properties.

Table 1.1 Steam pipe and turbine rotor steels [12]

	X20	P91	E911	P92	Steel E	Steel F	Steel B
C	0.2	0.1	0.1	0.1	0.1	0.1	0.2
Cr	11	9	9	9	10	10	9
Mo	0.9	0.9	1	0.5	1	1.5	1.5
W			1	1.8	1		
Ni	0.5	0.1	0.3	0.05	0.6	0.7	0.1
V	0.3	0.2	0.2	0.2	0.2	0.2	0.2
Nb		0.05	0.05	0.06	0.05	0.05	0.05
N		0.06	0.07	0.06	0.05	0.05	0.02
B				0.001			0.01
Austenitisation temperature	1050°C	1050°C	1060°C	1065°C	1070°C	1120°C	1120°C
Pre tempering treatment temperature					570°C	570°C	590°C
Tempering temperature	750°C	750°C	770°C	770°C	690°C	690°C	700°C
$\sigma_{10^5 \text{ h}/600^\circ\text{C}}$	59MPa	85MPa	98MPa	113MPa	95MPa	95MPa	125MPa

X20, P91, E911,P92 are production steels while Steel E, Steel F, Steel B are experimental steels developed in the COST programmes. Compositions expressed in wt %.

1.3 Phase transformation from austenite to martensite

Lath martensite appears in solution treated and quenched carbon steels with a carbon content less than 0.6 wt.% [13]. When the austenite (γ) phase with a face-centered cubic (f.c.c) structure in steels is quenched to low temperature or room temperature (9-12% Cr steel), a displacive transformation forms a new phase with a body centred cubic (b.c.c.) or body-centred tetragonal (b.c.t.) structure. This transformation is called the martensitic transformation and, the resulting phase is called martensite [13, 14, 15]. Figure 1.2 illustrates the displacive f.c.c. $\rightarrow$ b.c.c transformation in iron [16]. It shows that small lens-shaped

grains of b.c.c. nucleate at f.c.c. grain boundaries and grow almost instantaneously; the lenses stop growing when they reach the next boundary.

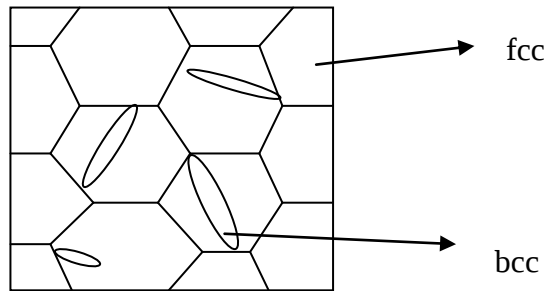


Figure 1.2. The displacive f.c.c. $\rightarrow$ b.c.c. transformation in iron.

B. c. c. lenses nucleate at f.c.c. grain boundaries.

Figure 1.3 shows that the details of the martensite formation process. Figure 1.3 (a) and (b) show the f.c.c unit cell and the formation of the b.c.t. cell from this. Figure 1.3 (c) and (d) show the transformation in the structure caused by 'Bain Strain'. There is a compression along the z axis and a uniform expansion along the x and y axis, this caused by 'Bain Strain'. When Bain strain happens, there must be a corresponding change in the macroscopic shape. Therefore, the martensite lath has been observed.

In low-carbon martensitic steels, the habit plane is $\{111\}_{\gamma}$, the orientation relationship between austenite (γ) and martensite (α') can be expressed with the Kurdjumov and Sachs (1930) relationship [17]:

$$\{111\}_{\gamma} \parallel (011)_{\alpha'}$$

$$\langle \bar{1}01 \rangle_{\gamma} \parallel \langle \bar{1}11 \rangle_{\alpha'}$$

The martensitic transformation stores strain energy, producing a martensite structure with high dislocation density within the martensite laths.

Martensitic steels with high strength have been used for a number of engineering applications. The following section considers why the Cr content is limited to the region 9-12% for the power generation plant applications.

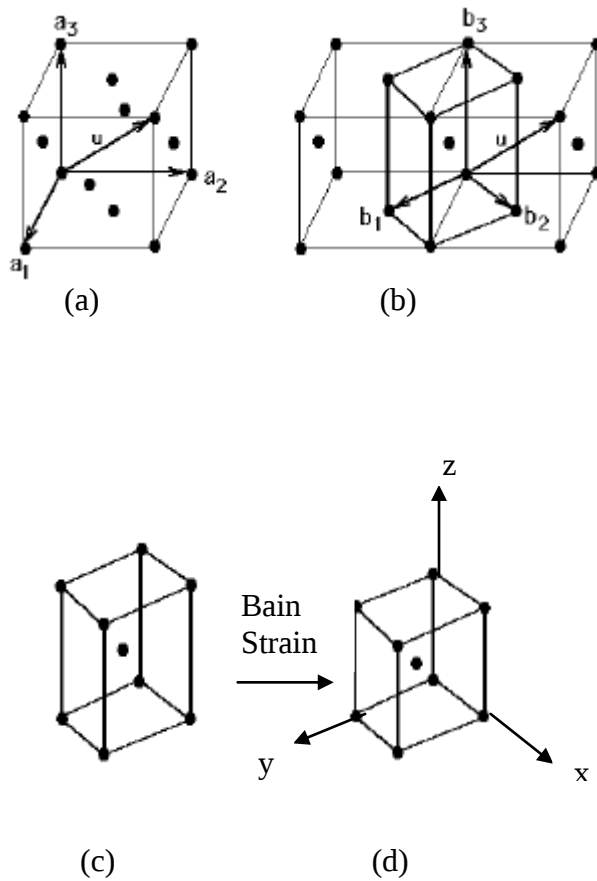


Figure 1.3. The Bain strain. After Bhadeshia [18].

(a) a f.c.c. cell. (b) two adjacent f.c.c. cells make a body-centred tetragonal austenite cell. (c) a body-centred tetragonal austenite cell (d) the 'Bain Strain' transforms the body-centred tetragonal austenite cell to body-centred cubic martensite cell.

1.4 Fe-Cr constitutional diagram

Figure 1.4 shows the Fe-Cr constitutional diagram. At compositions near to 9% Cr, the two-phase region between austenite (f.c.c) and ferrite (b.c.c) has a very narrow temperature range of 820 -1200°C. This means that it is possible to austenitise the steel in the temperature range of 820-1200°C, then just cool in air to produce a fully martensitic structure, with minimal amount of delta ferrite, which is regarded as detrimental for high temperature strength properties [19]. However, when the Cr content is more than 12-13%, the material does miss the f.c.c phase field and cannot be quenched to form martensite. The fundamental design concept is that the high creep strength of the 9-12% Cr steel relies on the martensitic transformation hardening.

Therefore, the feature of being able to produce a fully martensitic structure with air cooling (other than by quenching in water) is a key point for 9-12% Cr steel to be selected as power generation plant materials. Due to this property (slow cooling rate can be benefit in bulk material), the thick components in power plant could be made from 9-12% Cr steel. Additionally, the high Cr content gives good oxidation resistance at high temperatures.

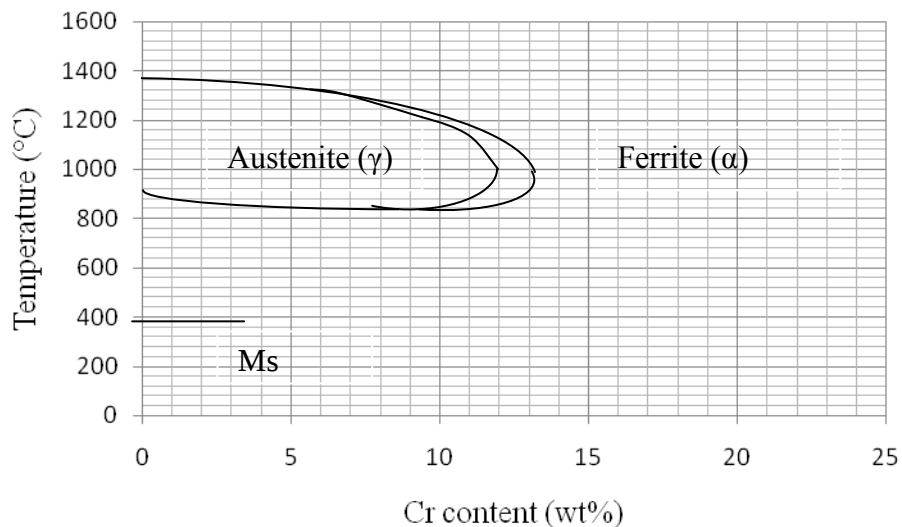


Figure1.4. Fe-Cr constitutional diagram [19].

The austenitisation temperature has a great influence on the dissolution of precipitates and the size of the prior austenite grains. In P92 [19], during austenitisation at 970°C, not all $M_{23}C_6$ particles are dissolved, whereas with austenitisation at 1070°C and above, $M_{23}C_6$ particles are dissolved completely. Nb(C, N) precipitates are observed in all specimens after austenitisation, this also was observed in E911 steel (Chapter 7 in this thesis). The different martensite lath width caused by different austenitising temperatures for P92 was described by Ennis et al. and Zielińska-Lipiec et al. [20, 21]. They showed that increased austenitisation temperature causes an increase in lath width and prior austenite grain size. Usually, the austenitisation temperature for this steel is in the region of 1050-1150°C.

1.5 Tempering of 9-12%Cr martensitic steel

In order to minimise the rate of degradation during exposure at elevated temperature and strain in power plant working conditions, tempering is designed to create a highly stable

microstructure, as close as possible to equilibrium [22]. Usually, the tempering temperature is about 20°C below A_{c1} , to produce fine carbides and reduce the stored energy from the martensitic transformation process. The stored energy of a power plant alloy in martensitic form is 1214 J mol⁻¹ greater than that in its equilibrium state, whereas the post-tempering microstructure is only 63 J mol⁻¹ above the equilibrium [23]. Therefore, tempering can reduce the stored energy and leaves only a small driving force for the microstructure evolution in long term service.

During tempering, two main processes take place, these processes are accelerated at the higher tempering temperatures.

Firstly, recovery causes a reduction in the high dislocation density. Therefore, in P92 [19], the tempering at 715°C leads to slightly higher dislocation density than standard tempering at 775°C. In the shorter term, the lower tempering temperature gives the high creep rupture strength, but this strengthening effect decreases rapidly in service; tempering at a higher temperature produces better long-term creep properties [24]. However, tempering at 835°C (just above A_{c1} transformation temperature of 825°C) causes a sharp reduction in the dislocation density. This effect is particularly critical for welding, because the temperature of the heat-affected zone is around 850°C. Therefore, this is the most likely site for creep rupture failure [25].

Secondly, precipitates of carbides, nitrides or carbonitrides occur during tempering [19]. In E911, P91 and P92, $M_{23}C_6$ carbides precipitate preferentially on the prior austenite grain boundaries and on the martensite lath boundaries. These precipitates retard the sub-grain growth and therefore increase the strength of the materials. In P92 and E911 steels, three types of MX (Nb(C, N), plate-like VN and small complex Nb(C, N)-VN) are found [19, 20, 21, 26, 27, 28]. The precipitates of fine MX phase in P92 are important for the mechanical properties [21]. MX is also a fine phase in E911 steel and aids in retaining strength for the long term service (Chapter 7 in this thesis).

1.6 Creep mechanism

Creep is the plastic deformation of a material when it is subjected to a stress below its yield stress. An indication of the tendency to creep is the homologous temperature. Homologous temperature is the ratio of a materials working temperature to its melting temperature. Figure 1.5 shows how creep is divided into three categories: primary, steady state and tertiary creep.

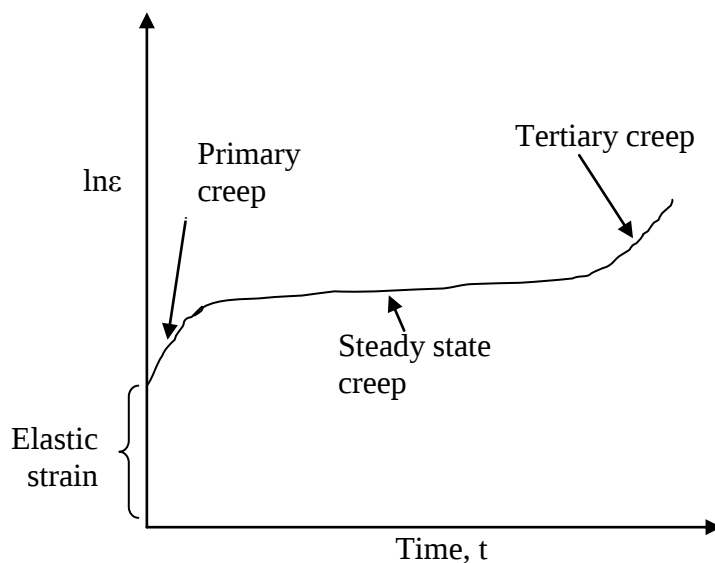


Figure1.5. Strain versus time creep behaviour [29].

Primary creep strain is usually less than one percent of the sum of the elastic, primary and steady state strains. The mechanism in the primary region is the climb of dislocations that are not pinned in the matrix [29].

The tertiary part is described by a sharp increase in creep rate, and terminates with material rupture.

The steady state creep rate is usually constant, the majority of the life of a power plant material is spent in this regime.

Both the temperature and stress determine the creep mechanism. The predominant mechanism can be determined by deformation mechanism maps, in which the stress normalized against the shear modulus is plotted against the homologous temperature T/T_m

[30, 31]. On considering the ratio of service temperature of power plant components (current is around 600°C, will be further improved to 650 °C) and the melting temperature of 9-12% Cr steel (above 1500°C), the ratio is around 0.4, therefore, the creep mechanism is dislocation glide and climb rather than bulk diffusion in power plant operation condition. This creep mechanism was also reported by Yardley [17].

In power generation plant, it is clear that the creep mechanism is dislocation climb and glide. Since creep cannot be avoided at high temperatures and high stresses it is very important to investigate the creep rupture properties at power plant working conditions.

1.7 Creep rupture properties

The secondary creep (steady creep) rates of P91, P92 and E911 have been plotted against the applied stress [19], as shown in Figure 1.6.

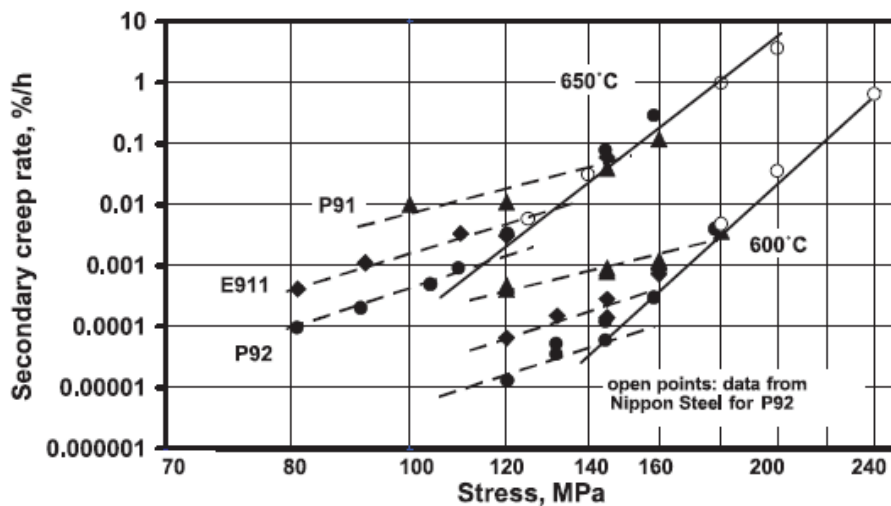


Figure1.6. Secondary creep rates for P91, P92 and E911, after Ennis [19].

According to the Norton equation (1.2), the secondary creep rate is proportional to the applied stress to the power of n .

$$\dot{\varepsilon} = C \sigma^n \exp\left(-\frac{Q}{RT}\right) \quad (1.2)$$

$\dot{\varepsilon}$ is minimum creep rate,

σ is measured in MPa,

T is temperature in Kelvin,

R is the universal gas constant ($8.314 \text{ J mol}^{-1}\text{K}^{-1}$),

C , Q and n are material constants, varying from one material to another material, and could be determined experimentally.

The value of n is around 16 at high stress while the n is 6 at low stress in this plot (Figure 1.6).

Figure 1.6 shows that at high stress, there is no obvious difference in secondary creep rate of the three steels, while at low stress, the differences among steels are more distinct. It was found that P92 has the smallest secondary creep rate.

Creep deformation behaviour is associated with the microstructural evolution which has been investigated extensively.

1.8 Microstructure evolution in service

1.8.1 The microstructure of tempered martensite 9-12% Cr steel

There have been a considerable number of publications [32, 33, 34, 35] describing the microstructure of tempered martensite in 9-12% Cr steels. The microstructure consists of a large number of $M_{23}C_6$ carbides distributed along lath, blocks, packet boundaries and prior austenite grain boundaries (PAGBs) while the MX carbonitrides are distributed at laths, blocks, packet boundaries and PAGBs as well as in the matrix within laths, as shown in Figure 1. 7.

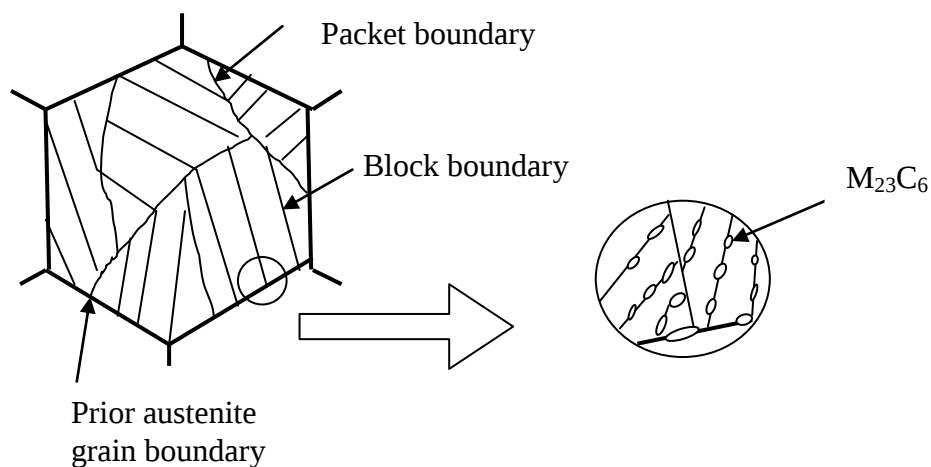


Figure1.7. Illustration of the microstructure of tempered martensitic of 9-12% Cr, after Abe [35].

However, after long term exposure to stress and temperature in service, an evolution in the microstructure has been observed.

1.8.2 Minor phase precipitates

Minor phase precipitation depends on the tempering temperature, the steel's chemical composition, service temperature and strain. There have been lots of papers that reported on the minor phase evolution in 9-12% Cr steel in service [36, 37, 38, 39] as shown in Table 1.2.

M₂₃C₆ phase

The prior austenite grain boundaries, packet, block and lath boundaries are decorated by M₂₃C₆ carbides, in the “as-received” (i.e. solution heat treated and annealed) condition [35]. As a fine phase, M₂₃C₆ contributes to creep strength due to its pinning effect in preventing dislocation climb. However, this phase grows with increasing exposure time at higher temperatures [19]. It also has been noticed that an applied strain accelerated the coarsening process. The carbides in the head of the creep ruptured specimen are smaller than those in the stressed gauge portion of the specimen [40, 41, 42].

MX phase

MX phase is regarded as a beneficial phase to creep properties due to its fine size (typically below 100 nm), fine distribution and stability in long term service. It is the most desired phase in 9-12% Cr steel. MX phase can be divided into primary MX (NbC) phase and secondary MX ((V,Nb)(C,N)) phase. Primary MX phase is rich in Nb while secondary MX phase is rich in V [36, 37]. VN has the following orientation relationship with the matrix by Baker and Nutting, reported by Golpayegani et al. [43]. Therefore, it is easy to identify both by electron diffraction and EDX in TEM.

$[110]_{\alpha}/[100]_{VN}$ and $[001]_{\alpha}/[001]_{VN}$

M₂X phase

In the as tempered condition, M₂X (Cr₂N) phase is a fine phase (Chapter 7 in this PhD thesis). However, after long term service in a power plant, M₂X phase becomes a coarser phase. The role of M₂X phase evolution in connection with the accelerated degradation of creep strength in 9-12% Cr steels was investigated by H. Chilukuru, K. Durst, M. Goken, W. Blum [44]. They found that M₂X phase coarsened much faster than VX, forming large M₂X

precipitates at subgrain boundaries at the expense of the M_2X precipitates in the subgrain interior. This reduces the precipitation hardening in the subgrain interior.

Laves phase

The presence of Laves phase $[(Cr,Fe)_2(Mo,W)]$ (by extracting Mo, W from the matrix) is observed after exposure to temperature and stress. For E911 at 625°C and 650°C after 1000 hours when the Laves phase has just precipitated, creep results show a higher creep resistance of this steel with respect to the P91 steel [45]. The presence of Laves phase lead to some arguments for the role of W. As suggested by Hald [46], the highest creep resistance cannot be associated with the solution strengthening of W but is due to the beneficial effect of the precipitation of Laves phase through an increase in the total volume fraction of secondary phase which can contribute to the precipitation strengthening.

However, the Laves phase precipitates are unstable at higher temperature. This results in extended phase growth and a larger particle size. In P92, at 650°C the Laves phase particles are about 60% larger than at 600°C, as reported by Korcakova [47].

Z phase

Investigations on minor phase evolution in martensitic 12CrMoVNbN steels using X-ray diffraction found a strong diffraction peak corresponding to an interplanar spacing of $d=0.226\text{nm}$ [48]. This X-ray diffraction line was only found to be present in the samples after long term exposures.

Detailed analytical electron microscopy studies revealed that particles of this minor phase had a tetragonal unit cell with dimensions of $a=0.286\text{nm}$ and $c=0.739\text{nm}$ [40, 41]. The particles contained vanadium, chromium, niobium and nitrogen. This (V, Nb)CrN phase was referred to as modified Z phase [41].

Strang and Vodarek [41] published the original BCT structure for Z-phase. More recently, the relationship between the Z phase unit cell and the FCC subcell has been drawn by Danielsen [49] as shown in Fig.1.8.

Table 1.2 Summary of typical phases in 9-12% Cr steels

Phase	Formula	Precipitate time	Crystal structure	Phase evolution
Primary MX	(Nb, V)(C, N) Nb rich	Usually present in the initial steel cast	Face centred cubic	Fine-fine
Secondary MX	(V, Nb)(C, N) V rich	During tempering	Face centred cubic	Fine-fine
M ₂ X	Cr ₂ N	During tempering	Hexagonal close packed	Fine-coarse
M ₂₃ C ₆	(Cr, Fe, Mo, W) ₂₃ C ₆ for E911 and P92, (Cr, Fe, Mo) ₂₃ C ₆ for P91	During tempering	Face centred cubic	Fine-coarse
Laves	(Cr, Fe) ₂ (Mo, W) for E911 and P92, (Cr, Fe) ₂ Mo for P91	After short time thermal exposure and creep	Hexagonal close packed	Fine-coarse
Z phase	(V, Nb)CrN	After long time thermal exposure and creep	Modified Tetragonal	Fine-coarse Rapid coarsening rate
M ₆ C	(Mo, Cr, Ni) ₆ C (Not found in E911 in this PhD thesis)	After long time thermal exposure and creep	Face centred cubic	Fine-coarse Rapid coarsening rate

The modified Z-phase, which differs from original Z phase as it contains vanadium, is related to an FCC structure. The relationship between the coordinate axes of modified Z phase and the FCC phase has been expressed as follows [40]:

$$[100]_Z = 0.5[110]_{FCC}, [010]_Z = 0.5[110]_{FCC}, [001]_Z = 1.83[001]_{FCC}.$$

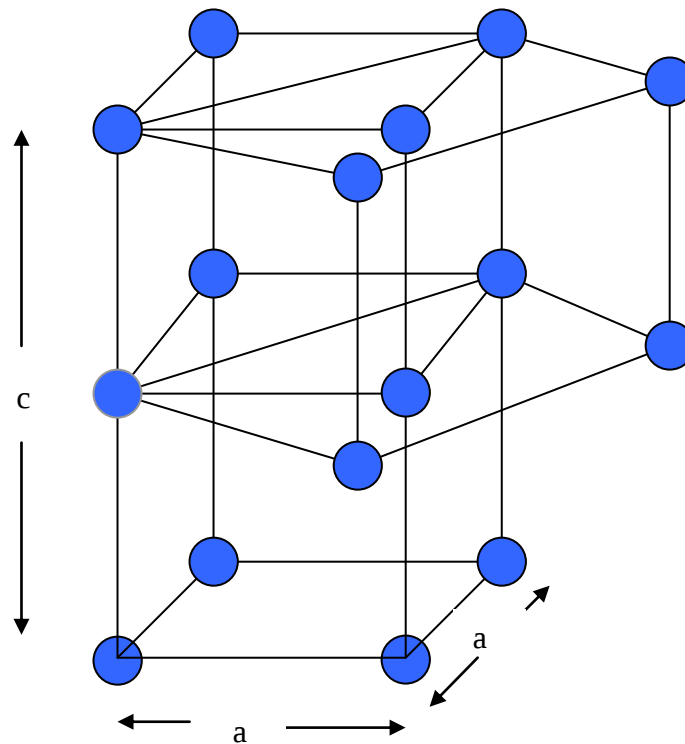


Figure 1.8. The relationship between the Z phase unit cell and the FCC subcell. Nitrogen and some metal atoms have been left out for clarity.

Sawada et al. worked out the inter-particle spacing of the Z phase of 9-12 % Cr steels [50], which was between 1.1 and 2.7 μm . However, it was reported that the typical inter-particle spacing of M_{23}C_6 , MX, and Laves phases is 0.26, 0.32, and 0.41 μm respectively [51]. According to the Orowan mechanism, Z phase formation cannot increase to the Orowan stress [50, 52], therefore, it is an undesirable phase in creep strength.

The coarsening of M_{23}C_6 , Laves phase, M_6C and Z phase brings a loss of long-term creep strength, because such coarsening consumes existing fine precipitates or solute-hardening atoms.

1.8.3 Dislocation density reduction

The dislocation density reduction in 9-12% Cr steel at the service temperature of 600°C was investigated by Ennis, Czyrska-Filemonowicz [19], Zielińska-Lipiec, Czyrska-Filemonowicz, Ennis, Wachter [42], and the results are shown in Table 1.3.

Table 1.3 Dislocation density evolution in creep tested P91, P92 and E911 steels at 600°C
(unit: m^{-2})

Steel	As received	1000h	10,000h	17,000h	22,000h
P91	$(7.5 \pm 0.8) \times 10^{14}$	$(4.8 \pm 0.5) \times 10^{14}$	$(1.1 \pm 0.4) \times 10^{14}$	No data	No data
P92	$(7.9 \pm 0.8) \times 10^{14}$	$(5.4 \pm 0.5) \times 10^{14}$	$(2.5 \pm 0.5) \times 10^{14}$	$(2.3 \pm 0.5) \times 10^{14}$	No data
E911	$(6.5 \pm 0.6) \times 10^{14}$	$(5.0 \pm 0.5) \times 10^{14}$	No data	$(2.2 \pm 0.4) \times 10^{14}$	$(2.1 \pm 0.4) \times 10^{14}$

Table 1.3 shows that after 22,000 hours, the dislocation density of steel E911 drops rapidly by more than 60% compared with the as received condition. The dislocation density reduction is connected with the creep strength loss.

1.9 Methods of strengthening creep –resistant steels

The methods of strengthening creep-resistant steels consist of solute hardening, precipitation hardening, dislocation hardening and the effect of grain boundaries, which can be achieved by the alloy design and heat treatment.

1.9.1 Solute hardening

The solute atoms such as Mo, W have been favoured as solid solution hardeners for ferritic steel due to their larger atomic sizes than that of the solvent iron [35]. The W effect on the creep rupture strength of 9Cr-(0-4)W-0.1C steels was investigated [35, 53]. It was found that the creep rupture strength (at 10,000 hours) linearly increased with increasing W concentration up to 3%. Then, the creep rupture strength remained unchanged for W concentrations greater than 3%.

However, in 9-12% Cr steel, the creep-resistant mechanism is complex. The coarsening of the Laves phase $((\text{Fe}, \text{Cr})_2(\text{Mo}, \text{W}))$ after long term service in power plant would cause creep instability in the steels because it leads to withdrawal of elements (Mo, W) from solid solution.

1.9.2 Precipitation hardening

How to control a fine particle size is very important in 9-12% Cr tempered martensite steel design.

In the service of 9-12% Cr tempered martensite steel, the dispersed fine precipitates act as obstacles to impede the dislocation climbing. However, particle coarsening of 9-12% Cr steel brings a loss of creep strengthening in long term service in power plant. Bhadeshia pointed out that in 9-12% Cr steel, the coarsening behaviour of precipitates is greatly affected by the presence of other phases [54].

In Fe-M-C alloys, the volume-diffusion-controlled Ostwald ripening of M_aC_b carbides is given by the following equation [55]:

$$r^3 - r_0^3 = k_3 t \quad (1.3)$$

$$k^3 = \frac{8(a+b)\sigma V D_M \mu_M}{9aRT(\mu_{pM} - \mu_M)^2} \quad (1.4)$$

where r and r_0 are the average particle radii at the time t and $t=0$,

σ is the interfacial energy of the carbides,

V is the molar volume of the carbides,

μ_{pM} and μ_M are concentrations of metal M in the carbides and matrix,

D_M is the volume-diffusion coefficient of metal M ,

R and T are gas constant and the temperature respectively.

After evaluation by the above equation and Thermo-Calc calculation [35], VC, VN, NbC, NbN and TiC exhibit a very low coarsening rate compared with Laves phase. Therefore, the fine particles of the above phases are the most desirable candidates in 9-12% Cr alloy design for the purpose of precipitation strengthening in long time service. On the other hand, by reducing the carbon concentration of 9% Cr steel (9Cr-3W-3Co-0.2V-0.05Nb-0.05N) to a very low level of 0.018%, the creep strength increased significantly; when the carbon concentration is down to 0.002%, the unstable $M_{23}C_6$ phase can be eliminated and the large number of nanosize MX nitrides (<10nm) are found distributed along lath, block, packet and prior austenite boundaries. This was reported by Abe [35].

However, the particle coarsening mechanism is extremely complex. It has been reported that the addition of W suppresses the coarsening of $M_{23}C_6$ carbides and lath subgrains, although the mechanism is not fully understood [35, 54].

Another element which can bring a good effect on the precipitation strengthening is B. The effect of boron on the distribution and size of $M_{23}C_6$ carbides has been examined for 9Cr-3W-3Co-0.2V-0.05Nb-0.08C steel containing boron with 0, 48, 92 and 139ppm respectively [35]. It was found that the suppression of $M_{23}C_6$ particle coarsening during creep and the maintenance of a homogeneous distribution of $M_{23}C_6$ near prior austenite grain boundaries, can be achieved by the addition of boron [35].

1.9.3 The grain boundaries

The grain size has an important influence on mechanical properties of polycrystalline materials. This can be expressed by the Hall-Petch relationship [56, 57]:

$$\sigma_0 = \sigma_i + kD^{-1/2} \quad (1.5)$$

where σ_0 is the yield stress,

σ_i and k are constant,

D is the grain diameter.

The Hall-Petch relationship applies for high angle boundaries, there is therefore an analogous expansion for packet diameter and block size. It would not apply for low angle boundaries such as subgrain boundaries. In addition, in martensitic steels a unique yield stress does not exist and usually yield stress is expressed in term of 0.2% proof stress.

A Hall-Petch relationship was found between σ_0 and packet size d_p and austenite grain size d_r [58]. All of these indicate that the smaller the grain size, the better the mechanical properties. In addition, a Hall-Petch relationship was also observed between σ_0 and block width d_b [59].

1.9.4 Dislocation hardening

In the just tempered condition, 9-12% Cr steel usually contains a high density of dislocations. After long term exposure to stress and temperature, the recovery of excess

dislocations and the recrystallization of the deformed microstructure cause a loss of creep strength [60]. In the short term, the dislocation hardening is beneficial for creep strengthening but it is not useful for increasing long-term creep strength at elevated temperature [35].

1.9.5 Roles of major alloying elements in high Cr ferritic steel

Through the analysis based upon above sections, the effect of elements in 9-12% Cr steel can be summarised in Table 1.5.

Although the effects of all kinds of elements in high Cr steel have been investigated in depth, there are still some creep strengthening mechanisms unclear at present.

Table 1.5 Roles of major alloying elements in high Cr ferritic steel [61]

Element	Merit	Demerit
B	Improve creep strength and quenching hardenability, stabilize $M_{23}C_6$ and delay their coarsening	Reduce impact toughness.
C	Necessary to make $M_{23}C_6$ and NbC.	
Co	Suppress δ -ferrite, decrease D (the diameter of grain).	
Cr	Improve oxidation resistance, lower M_s , raise A_1 , main element of $M_{23}C_6$.	Increase D
Cu	Suppress δ -ferrite.	Promote precipitate of Fe_2M
Mn		Increase D and reduce creep strength, lower A_1
Mo	Lower M_s , raise A_1 , solid solution hardening.	Accelerating growth of $M_{23}C_6$.
N	Make MX.	
Nb	Form MX and contribute to strengthening.	Promote precipitates of Z phase.
Ni		Increase D and reduce creep strength, lower A_1 .
Re	Prevent the loss of creep rupture strength, lower M_s .	Lower A_1 .
Si	Improve oxidation resistance.	Increase D and reduce creep strength.
V	Form MX and contribute to strengthening.	
W	Lower M_s , raise A_1 , delay coarsening of $M_{23}C_6$ particles, solid solution hardening.	

Note: M: Metal

X: Carbon or Nitrogen

A_1 : Austenite starting temperature

M_s : Martensite starting temperature

D: Diameter of grain

1.10 European COST 536 (Co-operation in the field of Science and Technology) program

Steam turbine and boiler manufacturers and steel makers, through the European COST (Co-operation in the field of Science and Technology) program, have been working towards the development of improved high temperature creep resistant 9-12 % Cr steels.

Through the past COST 501 and 522, the development of a range of cast and forged alloys for steam turbines has been carried out. This led to a series of COST alloys (such as: steel E, steel F, steel B etc.) [10].

The long term creep testing results on current used E911, P92 and COST alloys have been shown in Table 1.1. At 600°C, these alloys can reach 100,000 hours creep rupture life at a stress of between 98-125MPa.

However, when the creep temperature increases to 620-650°C, these steels were found to be ruptured rapidly. For example at 650°C, E911 ruptured at 14319 hours at 77 MPa (Chapter 2 in this PhD thesis); a large number of test alloys with 11-12% Cr show a severe breakdown in creep stability between 5,000 and 30,000 hours [62]. None of these can reach 100,000 hours creep rupture life at 650°C. This brings a big challenge to improve power plant efficiency.

Due to the large number of 9-12% Cr steels and experimental alloys needing to be investigated, a network called Nano Scale WP of COST 536 was created in 2004. The aim of this project is to improve the detailed understanding of metallurgical stability of 9-12% Cr steel under creep conditions, then to provide the evidence for the new alloy composition design or heat treatment, which can produce the improved creep properties for the material used at the temperature of 650°C [62].

Nano Scale WP of COST 536 was divided into the following three headlines [62]:

- Microstructure characterisation
- Modelling
- Alloy design.

Most of work presented in this Ph. D thesis falls into the Microstructure characterisation category. Prior to microstructural analysis, mechanical properties (hardness and creep) were obtained and analysed.

1.11 Scope of work in this thesis

Two types of 9-12% Cr tempered martensitic steel are examined in this work. They are E911 creep samples and four kinds of cast experimental alloys respectively.

1.11.1 9%Cr1%MoNbVNW creep resistant martensitic steel

E911 steel is a 9%Cr 1%MoNbVNW creep resistant tempered martensitic steel that is used for elevated temperature service application in high temperature power generation plant.

In this study, E911 creep exposed samples from three different temperature levels were supplied by CORUS. Long-term creep data obtained for E911 inevitably shows a reduction in creep resistance with increasing test temperature and exposure duration: at 600°C, the longest creep rupture life was 75647 hours at a stress of 108 MPa; however, at 625°C, the longest rupture life dropped down to 31198 hours at a stress of 93 MPa, at 650°C, even down to 14319 hours at a stress of 77 MPa. This degradation behaviour of creep resistant properties was investigated in this PhD work.

In this work, hardness testing was carried out to measure the creep samples' resistance to localised plastic deformation. A difference between the head and the gauge part was expected.

Metallographic examination by means of Reflected Light Microscopy and Scanning Electron Microscopy was carried out on all of the samples. Microstructural evolution during exposure at different temperatures and stresses was observed.

In order to investigate the microstructural evolution effects on the crystallography in samples of E911, Electron Backscattered Diffraction has been used to evaluate the changes in misorientation and grain morphology as a function of creep exposure.

Transmission Electron Microscope coupled with Energy Dispersive X-ray Analysis has been used to investigate the effects of precipitate evolution: the distribution, chemical composition and size evolution of the MX phase, Laves phase, $M_{23}C_6$ phase, M_2X phase and Z phase in E911 creep samples at three temperatures levels have been investigated and analysed with the aim of understanding the influence of factors in microstructural evolution of E911 steel.

Figure 1.9 shows the experimental program of E911 steel.

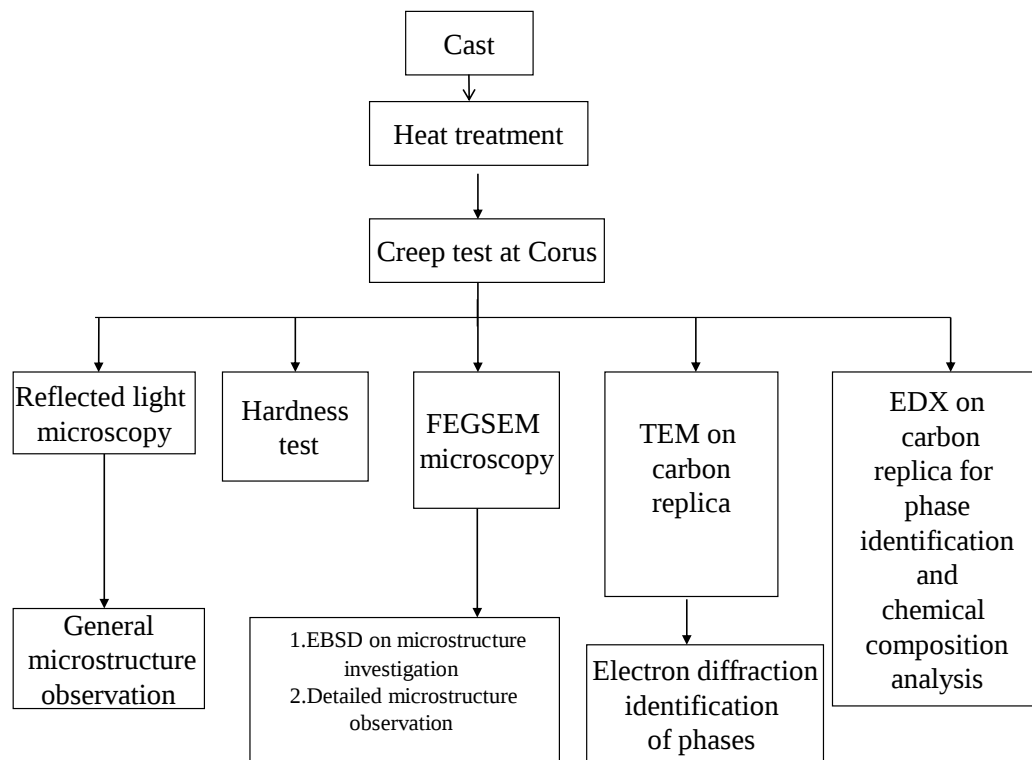


Figure 1.9. The flow chart showing the experimental program of E911 steel.

1.11.2 Four kinds of cast experimental alloys

In order to understand the Z phase behaviour in long term exposure at power plant working conditions, two levels of Ni (1% and 0.5%) and two levels of Cr (8.5% and 11.5%) 9-12% Cr tempered martensitic steels have been designed to produce four casts in total.

The thermal ageing testing was carrying out in the laboratory at University of Leicester.

Four thermal ageing temperatures were set as 625°C, 650°C, 675°C, 700°C while the sample thermal ageing durations were 500, 1000, 1500, 3000, 5000, 10,000 hours respectively. The

total of thermal ageing samples was 96. Thermal exposure tests were also carried out on samples of E911.

Hardness testing was carried out to measure the 96 thermal ageing samples' resistance to localised plastic deformation. The decrease of hardness was expected as exposure duration increase with the effect more profound with elevated temperatures.

The Transmission Electron Microscope has been used to investigate the precipitate evolution using carbon replicas. This work focuses on the presence of Z phase. Which element (Cr or Ni) has a great effect on Z phase presence will be unveiled.

Figure 1.10 shows the experimental program of thermally aged cast alloys.

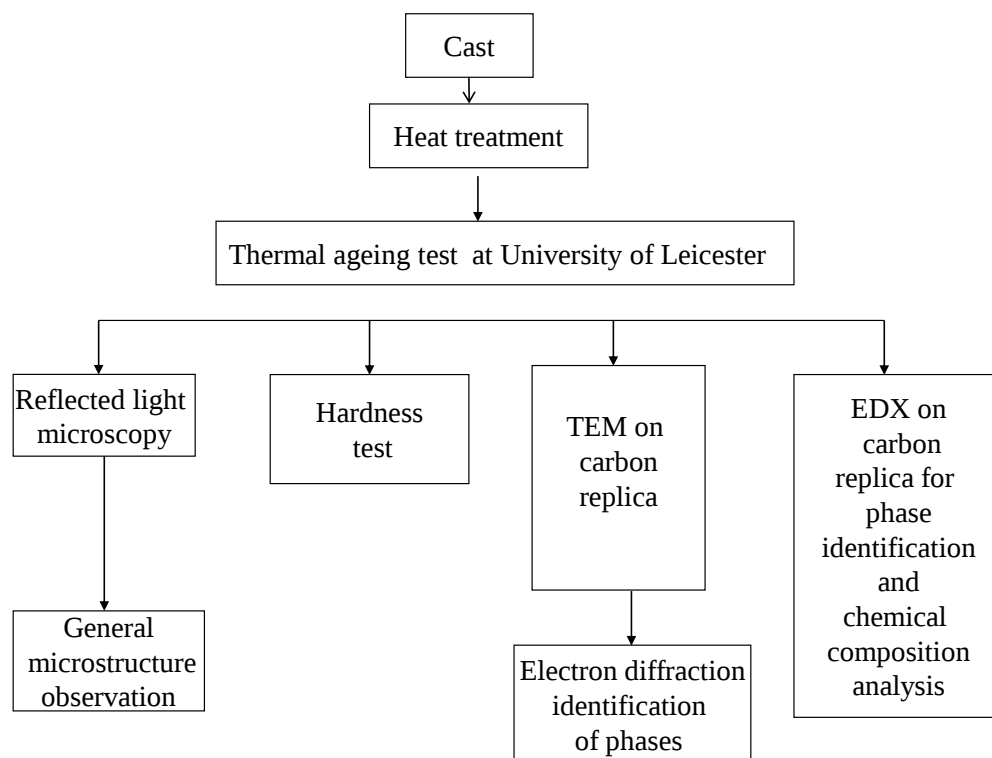


Figure 1.10. The flow chart showing the experimental program of thermally aged cast alloys.

Through this work, a valuable reference for the further new alloy design on this type of steel has been provided.

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Chapter 2 Materials

This thesis describes the results of studies on two different sets of steel materials. A major part of the study has involved investigating microstructural evolution in creep-exposed E911. A second area of study has been to investigate the microstructural evolution of a number of experimental casts that were produced by Corus UK Ltd. and that have subsequently been thermally aged. The experimental alloys were studied to determine the effects of nickel and chromium contents on microstructural stability and Z phase precipitation. This chapter gives the details of the material compositions and the creep exposure and ageing conditions for the materials.

2.1 E911 materials

The first material that has been studied is E911 steel, which has the composition given in Table 2.1. Tube samples were solution heat treated for 1 hour at 1100°C, air cooled and then tempered at 760°C for 2 hours and then air cooled. The microstructure was tempered martensite with a prior austenite grain size of $20.2 \pm 4.3 \mu\text{m}$ and a hardness of 269HV.

Table 2.1 Chemical composition of E911* (wt%)

C	Si	Mn	P	S	Cr	Mo	Ni	V	Al	Nb	W	N	Cu	Ti
0.115	0.19	0.35	0.007	0.003	9.10	1.00	0.22	0.23	0.006	0.069	0.98	0.069	0.08	0.002

*measured by Corus

Creep specimens of the geometry shown in Figure 2.1 were cut from the tube and long term creep testing was conducted at Corus, Swinden Technology Centre, Rotherham, UK.

Additionally, a number of E911 samples with 15 mm length were taken from the tube and thermally aged at the University of Leicester. The heat treatment of thermally aged E911 samples is a solution treatment at 1060°C for 1 hour and air cooling, followed by tempering at 760°C for 2 hours and then air cooling, which is different in term of the solution treatment temperature from the creep exposure samples.

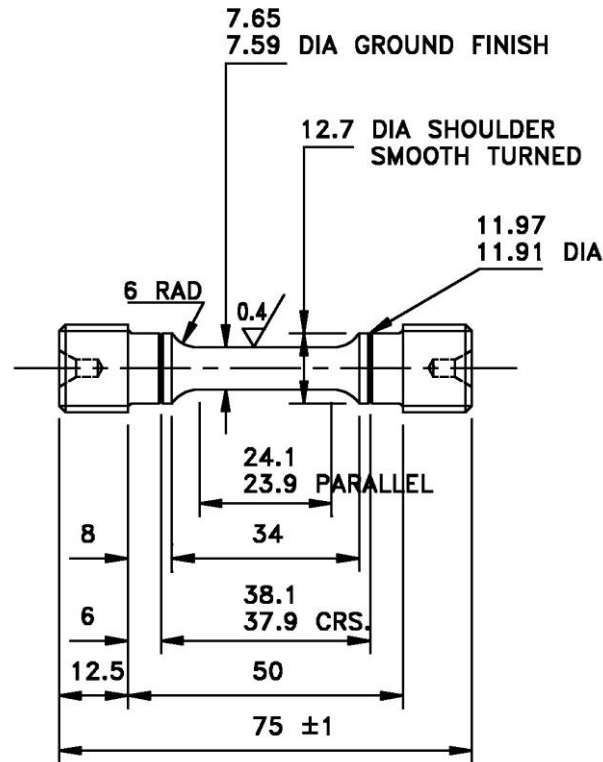


Figure 2.1 Dimensions (mm) of creep-rupture specimens

Table 2.2 shows the 12 creep rupture samples that were investigated in this work. The 600°C 13336 hrs sample gauge is quite short as it fractured close to the head, the other 11 samples fractured in the mid-section. The table shows temperature, stress, elongation, reduction in area and creep durations for the different samples.

2.2 Cast materials

Four experimental casts with different nickel and chromium levels were produced by vacuum induction melting at Corus UK Ltd. As-cast ingots were then subsequently processed by forging and rolling routes to 19 mm diameter bars. Five 250 mm lengths for each cast were then removed and subjected to ultrasonic testing to check for the presence of internal defects. Ultrasonic testing did not show any indications which would make the bars unsuitable for further testing; heat treatment was then carried out, five bars in the heat-treated condition (19 mm diameter bar, 250 mm length) were supplied for each cast by CORUS. The chemical composition of the four different casts is shown in Table 2.3.

Table 2.2 Details of E911 samples supplied (EL = elongation,
R of A = reduction of area)

Temperature	Stress (MPa)	Duration (h)	EL (%)	R of A (%)
600	200	1614	35	81
600	154	9800	23	63
600	139	13336	23	70
600	108	75647	10	12
625	154	1131	37	83
625	124	5487	26	69
625	108	13224	30	42
625	93	31198	15	22
650	124	849	36	83
650	108	2232	27	75
650	93	4530	27	69
650	77	14319	14	41

Table 2.3 Chemical composition of the four experimental casts

Code	C	Si	Mn	P	S	Cr	Mo	Ni	Al	B	Co	Cu	N	Nb	Ti	V	W
28	0.13	0.32	0.35	0.006	0.0031	8.50	0.59	1.04	0.007	-	0.003	<0.01	0.054	0.079	0.0010	0.25	0.002
29	0.145	0.31	0.35	0.007	0.0033	11.49	0.61	1.08	0.007	<0.0005	<0.01	0.02	0.069	0.080	<0.01	0.255	<0.01
30	0.14	0.33	0.34	0.008	0.0038	8.61	0.60	0.53	0.013	0.0005	0.005	<0.01	0.047	0.077	0.0011	0.25	0.005
31	0.135	0.32	0.34	0.006	0.0035	11.39	0.59	0.52	0.009	-	<0.01	<0.01	0.069	0.11	<0.01	0.25	<0.01
E911						9.10	1.00	0.22				0.08		0.069		0.23	0.98

The heat treatment of all bars consisted of a solution treatment at 1150°C for 1 hour and air cooling, followed by tempering at 700°C for 2 hours and then air cooling.

After the as received cast samples were supplied by CORUS in the heat treated condition, thermal ageing experiments were conducted at four different temperatures for time duration up to 10,000 hours. Cylinders 15mm length and 19 mm diameter were machined in Leicester

from the samples supplied by Corus. In order to control the temperature precisely, a thermocouple was inserted into a dummy sample to measure the temperature inside the sample, the dummy sample and thermally aged samples were put on the surface of a cast block in a furnace (The cast block was made of steel and its purpose was to ensure a homogeneous temperature for the specimens resting on it). Samples were removed from the furnaces at periodic intervals as outlined in the tables of heat treatment schedules and the microstructures and hardness were established.

Each of the four sample compositions was assigned a code as shown in Table 2.3. Each thermal ageing temperature and duration was then assigned a further code and the details of the different thermal ageing treatments and specimen codes are given in Tables 2.4-2.7.

Table 2.4 Code 28 (Cr: 8.5 Ni: 1.04) – specimen codes for thermal ageing

Temperature Duration	625°C	650°C	675°C	700°C
500 hrs	28A1	28 B1	28C1	28D1
1000 hrs	28A2	28B2	28C2	28D2
1500 hrs	28A3	28B3	28C3	28D3
3000 hrs	28A4	28B4	28C4	28D4
5000 hrs	28A5	28 B5	28C5	28D5
10000 hrs	28A6	28B6	28C6	28D6

Table 2.5 Code 29 (Cr: 11.49 Ni: 1.08) – specimen codes for thermal ageing

Temperature Duration	625°C	650°C	675°C	700°C
500 hrs	29A1	29 B1	29C1	29D1
1000 hrs	29A2	29B2	29C2	29D2
1500 hrs	29A3	29B3	29C3	29D3
3000 hrs	29A4	29B4	29C4	29D4
5000 hrs	29A5	29 B5	29C5	29D5
10000 hrs	29A6	29B6	29C6	29D6

Table 2.6 Code 30 (Cr: 8.61 Ni: 0.53) – specimen codes for thermal ageing

Temperature Duration	625°C	650°C	675°C	700°C
500 hrs	30A1	30B1	30C1	30D1
1000 hrs	30A2	30B2	30C2	30D2
1500 hrs	30A3	30B3	30C3	30D3
3000 hrs	30A4	30B4	30C4	30D4
5000 hrs	30A5	30B5	30C5	30D5
10000 hrs	30A6	30B6	30C6	30D6

Table 2.7 Code 31 (Cr: 11.39 Ni: 0.52) – specimen codes for thermal ageing

Temperature Duration	625°C	650°C	675°C	700°C
500 hrs	31A1	31B1	31C1	31D1
1000 hrs	31A2	31B2	31C2	31D2
1500 hrs	31A3	31B3	31C3	31D3
3000 hrs	31A4	31B4	31C4	31D4
5000 hrs	31A5	31B5	31C5	31D5
10000 hrs	31A6	31B6	31C6	31D6

2.3 Summary

For all of the samples investigated in this study the microstructure and hardness of the samples were investigated after either creep exposure or thermal ageing. Details of the techniques used for microstructural characterization are outlined in the following chapter.

Chapter 3 Microstructure Characterisation

In order to characterise the microstructure of the samples investigated in this thesis, a number of different sample preparation steps have been followed depending on whether the samples were being examined by optical microscopy, field emission gun scanning electron microscopy (FEGSEM) and electron backscattered diffraction (EBSD) or transmission electron microscopy (TEM). The details of the procedures followed are outlined in the following sections.

3.1 Specimen preparation

3.1.1 Metallographic specimen preparation

The following grinding and polishing procedures have been carried out on the BUEHLER METASERV Grinder-Polisher.

Table 3.1 shows the detailed grinding procedure used to produce flat samples. It was very important that, between steps, the sample was ultrasonically cleaned. For all grinding steps, the direction of the head rotation was the reverse of the direction of wheel rotation.

Table 3.1 Typical Grinding Procedure

	Silicon carbide paper grade	Duration (minute)	Force (N)	Wheel speed (r/min)	Coolant
Step 1	P240	2	111	180	water
Step 2	P400	1.5	111	150	water
Step 2	P600	1	97	150	water

After grinding, the specimens were polished following the route outlined in Table 3.2 below.

Table 3.2 Typical polishing procedure for metallographic specimen preparation

	Polishing cloth	Suspension	Coolant	Force (N)	Duration (min)	Rotation direction*
Step 1	6 micron DP-PAN	6 micron Diamond	Green	97	4	reverse
Step 2	3 micron DP-MOL	3 micron Diamond	Green	97	4	reverse
Step 3	1 micron DP-NAP	1 micron Diamond	Red	35	1	same
Step 4	Collin Silica OP-CHEM	No	White	35	1	same

* the specimen holder (head) and polishing cloth(wheel) were either rotated in the same direction (for the purpose of avoiding comet tails) or the reverse direction relative to each other at different polishing stages.

After final polishing, the samples were thoroughly washed using propanol, then dried. The etchant used for high Cr steel samples was Villella's reagent (5 ml HCl, 20 ml picric acid in saturated alcoholic solution, 80 ml ethanol). For the metallographic examination, the etching time is about 10-20 seconds. After etching, the samples were examined by reflected light microscopy (RLM) and scanning electron microscopy (SEM).

3.1.2 Sample preparation for hardness testing

Creep-rupture samples were sectioned longitudinally by wire cutting with an excess of cooling agent to avoid deformation of surfaces. One longitudinal section was mounted in cold-mounting resin and then ground to a 600 grit finish for hardness testing. Another longitudinal section was prepared for analysis by means of EBSD. Hardness surveys were taken using a Vickers macro-hardness tester with an applied load of 20kgf. The surveys were completed at 2 mm intervals along the length from the head to gauge.

The thermally-aged samples were sectioned, and then mounted in Bakelite in a Labopress-3 Struers automatic mounting press, and then ground to a 600 grit finish. Six indentations were

made at 20 kgf and the average hardness values obtained. It was important to ensure that indentations were made away from the decarburised zone.

3.1.3 EBSD sample preparation

EBSD Maps were obtained from the middle of the head and the middle of the gauge length (as shown schematically on Figure 3.1). The samples at the locations shown from Figure 3.1 were cut out from the section using diamond micro-cutting,

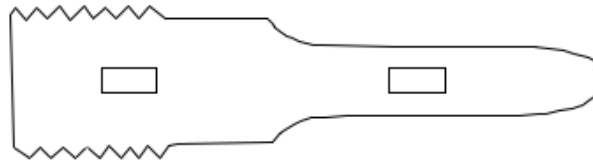


Figure 3.1 Sketch of a creep-ruptured sample showing the regions used for mapping.

Kikuchi patterns used for EBSD analysis are generated from the very near-surface and thus samples must be flat and distortion free [1]. In order to acquire sufficient flat and deformation free samples, the following procedures were applied after samples were cut from the designated area.

- Sample mounted in resin.
- Ground using 240, 400, 600, 800 and 1000 grit papers, 1 minute per step.
- Polished using 6 μm , 3 μm , 1 μm and 0.25 μm diamond suspension, 10 minutes each, low load and low speed.
- Finally polished using 0.05 μm colloidal silica for 10 minutes.
- The samples were then broken out of the bakelite mount and glued onto the FEGSEM stub with surface parallel to stub. Silver dag was applied to reduce image drift over the mapping period by giving good electrical conductivity between the sample and the SEM stub.

3.1.4 Carbon replica preparation for TEM

Figure 3.2 shows the essential steps for preparing TEM specimens. The specimens were polished and then etched with Villella's metallographic reagent; a layer of carbon was

evaporated onto the etched surface, finally, the specimen was etched again using the same reagent. Then, the carbon film was floated off into the reagent and washed, then collected on a nylon mesh grid [2], as illustrated in Fig. 3.2.

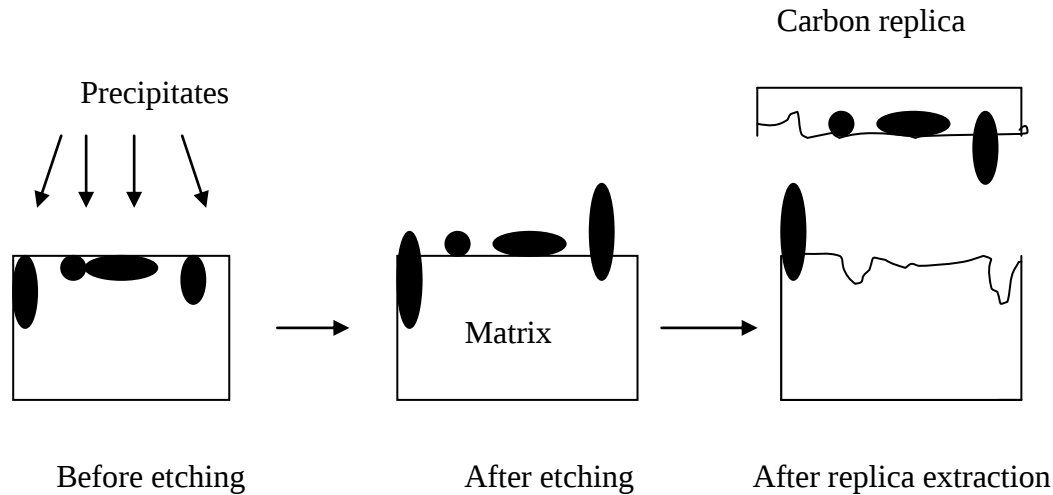


Figure 3.2. Schematic illustration of the carbon replica preparation route

The detailed route that was developed for carbon replica preparation for the 9-12 % Cr high temperature steel samples used in this study is outlined below. Before TEM sample preparation the samples were metallographically polished using the method outlined in Section 3.1.1. The following steps were then taken:

- The polished surface was etched using Villella's reagent. The etching time was extended until the surface appeared matt and no reflections could be seen. The estimated time was about 1 min for the samples that were creep-exposed for long durations and 30 seconds for short creep duration samples. The etching time depends on the particle size. Bigger particles could be extracted out by using a longer etching time. However, one must be aware that smaller particles would be dissolved by longer etching, so some compromise was needed to determine the optimum time.
- The carbon films were produced using an Emitech K950 evaporator. Carbon rods were used for preparing the coating and good carbon films were obtained if the point of one carbon rod was very sharp whilst the other was flattened. Carbon coating at about 1700 ms with a pressure of $\sim 1 \times 10^{-3}$ Pa gave a carbon film ~ 20 nm thick; the colour of the resultant carbon film was brown.

- The coating surface was lightly scored into squares of 3 mm side length.
- The bulk material was then immersed in Vilella's reagent until the replicas lifted off by metal dissolution. This procedure took 1-2 hours for long duration creep exposed samples and about 30 minutes for short duration creep exposed samples.
- The samples were then cleaned by immersing in methanol.
- The samples were then immersed in a beaker of 10% methanol/water to allow the replica to float off. If necessary, this step was repeated using a fresh solution until all the replicas floated off the sample. If the replica folded, it was put into deionised water to unwrap.

3.1.5 Thin film preparation for TEM

In some circumstances, where the detailed microstructure and the dislocation structures needed to be known, it is necessary to examine thin films rather than carbon replicas.

The first stage of preparation is that the bulk steel samples need to be cut into 3 mm diameter cylinders. The samples are then cut into 0.2 mm slices on a Struers Minutom. It was found that slow speeds and light loads gave best results.

3.1.5.1 Disk Grinding

The samples were then mechanically thinned using a Gatan Model 623 Disk Grinder. Prior to the procedure of disk grinding, the sample (200 μm slices) thickness was reduced to 140 μm by grinding the specimen on the grinding paper (600 grit). The specimens were then lapped according to procedures listed in Table 3.3.

After grinding and lapping on one side, the samples were turned over and the same steps were repeated on the second side. When the total specimen thickness was down to 50 μm , then lapping was stopped.

After mechanical polishing, the samples needed to be either electropolished or dimple ground or ion beam polished in order to continue to thin the disk to electron transparency. These procedures are outlined in the following sections.

Table 3.3 Disk grinding steps

Lapping disk	40 micron	15 micron	5 micron
Depth of material removed per stage	10microns /step	Start from 10microns /step Change to 5 microns/step	Start from 5microns/step Change to 2-3microns/step
Number of stages	3	3-4	3-4

3.1.5.2 Twin-jet Electropolishing

Samples were electropolished using a Fischione automatic twin-jet electropolisher. This could thin the samples from both sides. Electropolishing is faster than dimple grinding and ion beam polishing but it is difficult to control the current and voltage to obtain the optimum thinning result. The electrolyte solution that was used was 5% perchloric acid in 95% methanol. The optimum conditions (voltage and the current) for polishing need to be carefully obtained [3]. The optimum conditions vary with the electrolyte employed and the material being polished. In this work, typical values of 18-20V and 80-100 mA was used.

Cooling to between -40°C and -60°C has been introduced by Fischione [4] because it slows the electropolishing process. This could minimize the heat of reaction on the specimen and prevent vaporization of the electrolyte (electrolytes containing perchloric acid are volatile) [4].

When the optimum polishing conditions have been determined, polishing can be continued until specimen perforation occurs.

3.1.5.3 Dimple grinding

Dimple grinding is used prior to ion beam polishing to reduce the ion beam thinning time. For most metals, specimens of 20 µm thickness can be obtained from dimpling. The thick and supportive rim of the specimen can assist the handling of fragile TEM specimens. In this project, a Dimple Grinder, Model 656 has been used for the thinning process [5].

After dimple grinding, the specimens were ion beam polished to electron transparency. In this project, a Gatan 691 Precision Ion Polish System (PIPS) has been used.

3.2 Mechanical Testing Techniques

Hardness is a measure of a material's resistance to localized plastic deformation [6]. Quantitative hardness techniques have been developed over the years in which a small indenter is forced into the surface of a material, under controlled conditions of a load and rate of application. The depth or size of the resulting indentation is measured, which in turn is converted to a hardness number; the softer the material, the larger and deeper the indentation, and the lower the hardness index number and vice versa.

The Hardness test can be divided into two ranges: macrohardness testing and microhardness testing.

The surface of the sample generally requires very good final finishing; in this project, macrohardness testing has been used, so final grinding on 600 grit was enough. All indentations were made using a 20 kgf load. The standard indentation shape for a Vickers indenter is shown in Figure 3.3.

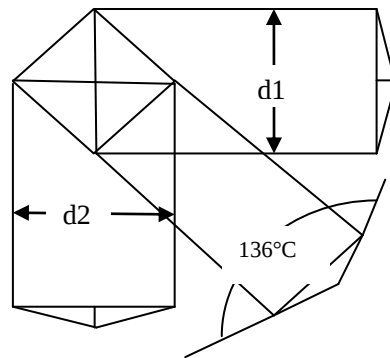


Figure 3.3. Vickers pyramid diamond indenter and indentation geometry, the diagonals of the diamond pyramid are represented by d1 and d2.

The Vickers diamond pyramid indenter is ground in the form of a squared pyramid with an angle of 136° between faces. The depth of indentation is $\sim 1/7$ of the diagonal length. When calculating the Vickers diamond pyramid hardness number, both diagonals of the indentation are measured and the mean of these values is used in the following formula with the load

used to determine the value of HV. Standard tables for Vickers hardness are usually a more convenient way to look up HV values from the measurements.

The Vickers diamond pyramid hardness number is the applied load divided by the surface area of the indentation.

$$HV = \frac{2F \sin \frac{136^\circ}{2}}{d} \quad (3.1)$$

where:

F =Load, kgf

d =Arithmetic mean of the two diagonals, mm

HV =Vickers hardness

A typical error in the hardness testing is between 2 and 6 HV (Chapter 4).

The hardness testing machine is routinely calibrated by a technician with a relevant steel.

3.3 Microscopy Techniques

3.3.1 Reflected Light Microscopy

Initial examination of the microstructure of all samples was undertaken using an Olympus Vanox BH-2.

The examination of material microstructures by reflected light microscopes is known as metallography. Contrast in the image of the specimen surface results from differences in reflectivity of the various regions of the microstructure. The reflected light microscope has come a long way over the years since it was invented [7], but the basic principle of focusing light by means of lenses remains the same. The microscope consists of a series of lenses which lead the light reflected from the observed object directly into the observer's eye or digital camera screen.

The main advantage of reflected light microscopy is that taking of the image is fast and easy, and does not require expensive parts and maintenance cost. Therefore, it is widely used.

One of the main limitations of reflected light microscopy is that this method has problems for imaging very small objects, because the ultimate resolution of the microscope is limited by the angular aperture of the objective lens (angle α) and the wavelength of light (λ) [8]. The resolution of the microscope is defined as the distance at which two point light sources can just be resolved at a separation δ , where $\delta = 0.61 \lambda / \sin \alpha$, δ is typically of the same order of magnitude as λ , and a theoretical resolution limit of about 200 nm [9] can only be achieved with a good optical microscope.

In the 1930s, electron microscopes were developed which use an electron beam, rather than light rays, focused by means of electric coils [10]. The resolution is greatly improved since the wavelength (λ) of electrons is much less than that of visible light.

3.3.2 Scanning Electron Microscopy

For detailed microstructural observation, scanning electron microscopy has great advantages over the reflected light microscope. In this project, two kinds of scanning electron microscopy (SEM) have been used: one, is environmental scanning electron microscopy (ESEM) equipped with energy dispersive X-ray analysis (EDX); another is an FEI Sirion 200 FEGSEM which is a an ultra-high resolution field emission gun (FEG) scanning electron microscope equipped with EDX and electron backscattered diffraction (EBSD).

A schematic diagram of an SEM is shown in Figure 3.4. The schematic working procedures of an SEM are as follows: At the top of the electron column within the chamber, a filament is heated (for the tungsten filament in the ESEM, the filament is heated to about 2700K until thermionic emission of electrons occurs) [11]. The electron gun emits a divergent beam of electrons. The beam diameter is controlled by a double condenser lens system, a first condenser lens (C1), is used to make a fine beam of electrons, the second condenser lens (C2) is to make the diameter of the beam smaller; the diameter of the beam as it hits the specimen is the main factor controlling the resolution of the microscope. An objective aperture (which is externally selectable) in the SEM can be used to control the convergence angle [12]. Scan coil energy is controlled by the scan generator, creating a magnetic field, which can deflect the beam back and forth. A final lens aperture can be used to focus the beam on the sample. The electron beam hits the sample and the electrons produced are collected by a detector, then converted to a voltage. This voltage is amplified and applied to the Cathode-ray tube (CRT), therefore causing the intensity of the spot of light to change. A large amount of spots

with varying intensities correspond to the topography of the sample and form the image on the screen of the CRT. In a FEGSEM, the source of electrons is from a Schottky thermal field emission gun and a better resolution can be achieved. The FEI Sirion 200 FEGSEM used in this project has the instrument resolution of 3.5nm at 500V, 2.5nm at 1kV and 1.5nm at 10kV respectively, which is ideal for obtaining the images for the application of high resolution.

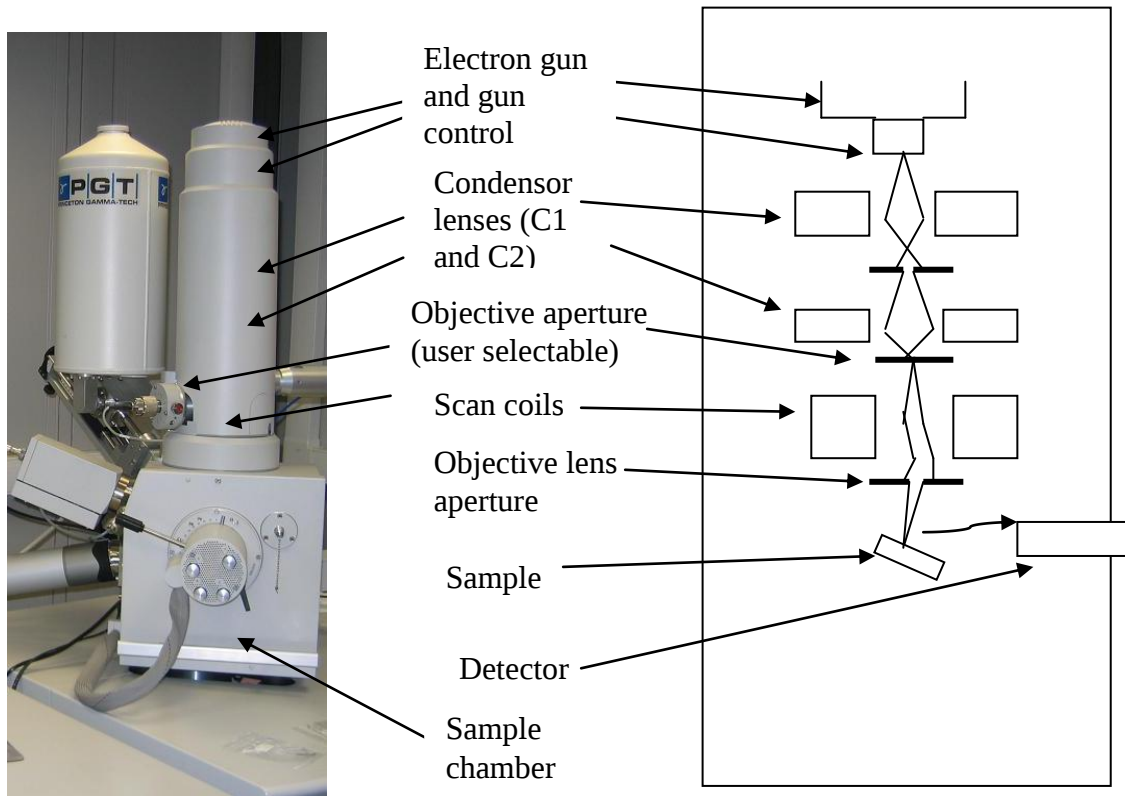


Figure 3.4. (a) A FEGSEM, (b) A schematic drawing of the electron column.

An illustration of the relationship between interaction volume and space resolution can be seen in Figure 3.5, which shows a typical pear-shaped interaction volume for an electron beam penetrating the surface and the depth from which the different signals arise.

Secondary electrons are detected from a near-surface region of interaction volume, while backscattered electrons can be detected from a much deeper region of the specimen. The sample volume for X-rays is similar in size to the interaction volume because X-rays are less easily absorbed by the material [13].

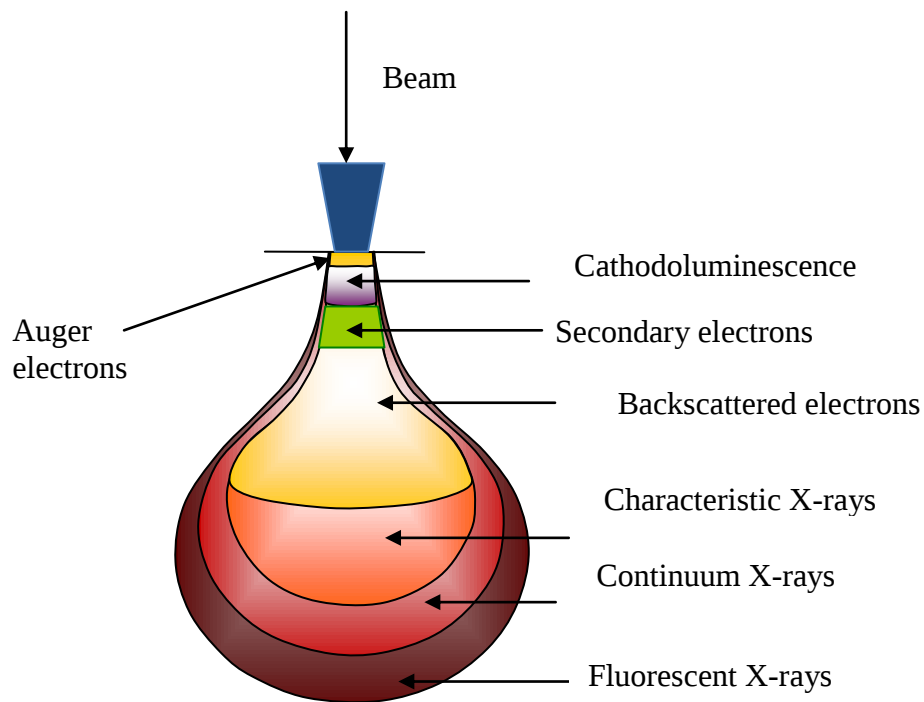


Figure 3.5. Relationship of reaction volume and space resolution

For the work in this thesis, secondary electron imaging has been used to evaluate the microstructure evolution.

3.3.3 EDX in the SEM

If the incident electrons have enough energy, an electron may be knocked out from the inner orbit. A hole in the orbit is formed and an electron from an outer orbit will fill in that hole. As it drops from an outer shell to an inner shell it loses energy (for example, from M shell to K shell) and an X-ray photon is emitted, which is shown in Figure 3.6.

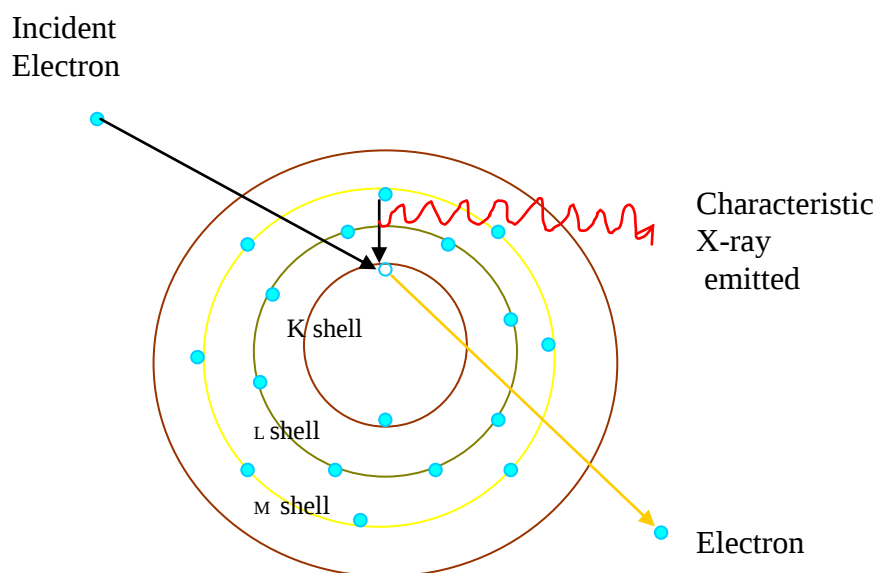


Figure 3.6. Schematic diagram showing the principle of characteristic X-ray emission.

The energy of the photons is characteristic of the element, and these characteristic X-ray energies can be found on an energy table for EDS analysis and used to identify the elements in the sample.

In this project, a Princeton Gamma Technology Avalon EDX system is used as a tool to determine the chemical composition analysis of different phases in samples. Further details on qualitative and quantitative analysis X-ray analysis can be found in references [11, 15].

It is important to understand that the depth in the sample from which X-rays are generated and the lateral resolution of X-rays is different to the secondary electron image and this must be appreciated in interpreting information from X-ray mapping and analysis for samples.

3.3.4 EBSD in FEGSEM

Electron backscattered diffraction patterns from the scanning electron microscope are widely used for characterizing the crystallographic structure of metallic samples. EBSD has been used in this thesis for studying the evolution of microstructure in the tempered martensitic 9-12% Cr steel. The basics of EBSD are explained in the following sections.

3.3.4.1 Basics of EBSD set up

System components

An EBSD system (Figure 3.7) comprises of

- A sample tilted at 70° from the horizontal level in the chamber.
- A phosphor screen to form the diffraction pattern.
- A sensitive charge coupled device (CCD) video camera to capture the diffraction pattern which is fluoresced by electrons from the sample.
- FEGSEM system to provide the necessary electron-sample interactions.

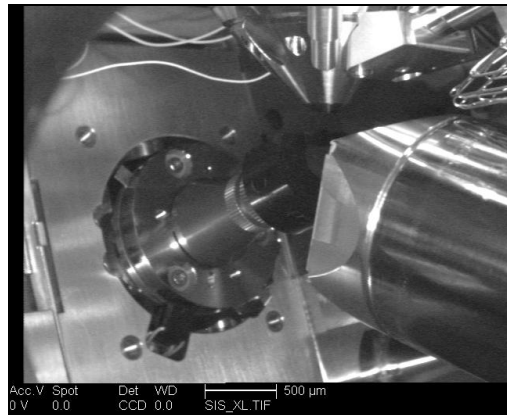


Figure 3.7. EBSD geometry

Pattern formation and collection

The FEGSEM is used to focus a beam of electrons at a point on a tilted crystalline sample. The atoms in the tilted material scatter a fraction of the electrons which forms a divergent beam of electrons. Some of these divergent electrons which are incident on atomic planes have angles satisfying the Bragg equation [16].

$$n\lambda = 2d \sin \theta \quad (3.2)$$

where n is an integer,

λ is the wavelength of the electrons, depends on accelerating voltage,

d is the spacing of the diffracting plane,

θ is the angle between incidence of the electrons and the diffracting plane [16].

A set of large paired angle cones has been formed by the above electrons which are satisfying the Bragg equation, thus, on the fluorescent screen, Kikuchi bands are formed as shown as Figure 3.8.

Interpreting diffraction patterns

Each Kikuchi band can be indexed by the Miller indices of the crystal plane while the intersections of the Kikuchi bands can be interpreted as zone axes (Figure 3.9).

The width w of the Kikuchi bands is given by [16]

$$w \approx 2l\theta \approx \frac{nl\lambda}{d} \quad (3.3)$$

where l is the distance from the sample to the phosphor screen, and the other terms are defined in equation 3.2. From equation 3.3, it is quite clear that crystal planes with wide d-spacings give narrow Kikuchi bands. The diffraction patterns also change as the corresponding crystal orientation changes [16].

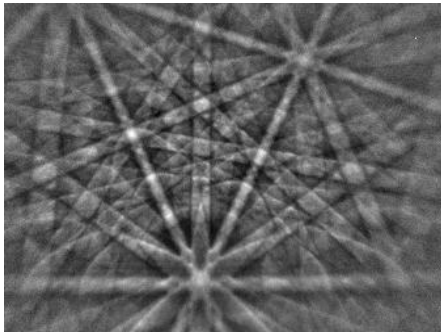


Figure 3.8. A diffraction pattern from iron bcc collected at 20KV accelerating voltage.

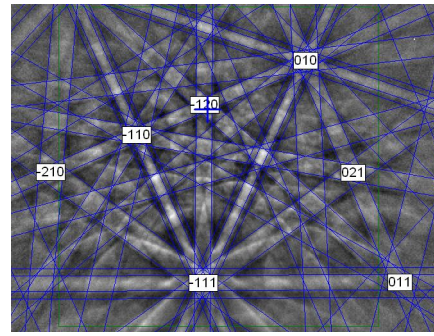


Figure 3.9. The diffraction pattern shown in Figure 3.8 was indexed.

3.3.4.2 Basic terminology needed to understand EBSD

Crystal orientation

The following matrix represents the relationship between a crystal coordinate system and a sample system [16].

$$\mathbf{r}_c = \mathbf{G} \mathbf{r}_s \quad (3.4)$$

$$\mathbf{G} = \begin{bmatrix} \cos \alpha_1 & \cos \beta_1 & \cos \gamma_1 \\ \cos \alpha_2 & \cos \beta_2 & \cos \gamma_2 \\ \cos \alpha_3 & \cos \beta_3 & \cos \gamma_3 \end{bmatrix}$$

$\mathbf{r}_c$ is the crystal system,

$\mathbf{r}_s$ is the sample coordinate system,

$\alpha_1, \beta_1, \gamma_1$ are the angles between the crystal direction [100] and the sample rolling direction (RD), transverse direction (TD), and normal direction (ND) respectively;

$\alpha_2, \beta_2, \gamma_2$ are the angles between the crystal direction [010] and RD, TD, and ND respectively;

$\alpha_3, \beta_3, \gamma_3$ are the angles between the crystal direction [001] and RD, TD, and ND respectively.

Euler angles

Euler angles also can be used to describe the relationship between the sample coordinate system and the crystal coordinate system (Figure 3.10).

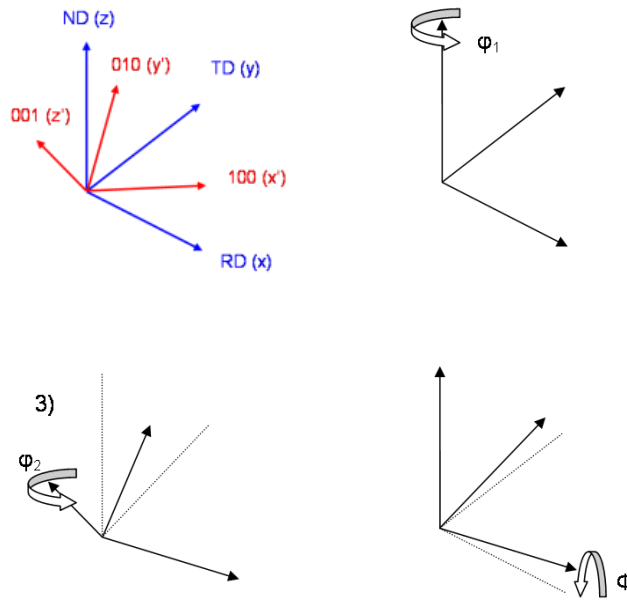


Figure 3.10. The two coordinate systems [17].

The three Euler angles $\phi_1\Phi\phi_2$ have been used to rotate one of the coordinate systems around three axes until it comes into coincidence with the other.

- The first orientation ϕ_1 is about the z axis, then followed by
- The second orientation Φ is about the new x axis, then followed by
- The third orientation ϕ_2 is about the new z axis.

In this thesis, Euler maps have been used as these are the most commonly used coordinate system for EBSD maps.

Misorientation

The orientation between two crystal coordinate systems can also be defined by the form of angle-axis pair, for example, $60^\circ[111]$. The angle-axis pair notation is normally used to describe grain boundary misorientations [16].

3.3.4.3 Microscopy conditions and parameters used for EBSD mapping

An FEI Sirion 200 FEGSEM was used in the work, and HKL CHANNEL 5 EBSD software was used for the analysis. The aperture size on the microscope was selected as 30 μm to allow good probe currents to be obtained. The working distance is defined as the distance between the specimen and the bottom of the pole piece and was set as 14 mm for this work. The spot size used was 5 which gives a probe current of approximately 2.2 nA. The exact probe current is dependent on accelerating voltage and working distance, and also filament source dependent. In general, under optimum SEM conditions, for the example of iron bcc, the effective spatial resolution is 10 nm for EBSD in FEGSEM.

For normal mapping, the band detection (i.e. the discrimination of the edges of the Kikuchi bands) was selected as minimum 5 and maximum 6 in order to get a good balance between speed and accuracy. For refining of the electron backscattered diffraction pattern (EBSP) calibration, it is very important to repeat a refinement procedure with a strong EBSP and with more detected bands between 8 and 12. Ideally, for the Mean Angular Deviation (MAD) which represents the goodness of fit of the solution, the smaller the number, the better the match between the actual detected bands and the system software simulation. A MAD below 0.5 is acceptable. The maximum number of reflectors tells the system the number of bands that have been used in indexing. 61 has been selected in this work to achieve a good balance between the acquisition speed and the index rate. Also, for the camera controls, the binning was set at 4×4 and the gain was low. Binning allows several pixels to be processed simultaneously as a unit and helps reduce data processing times. The time per frame was adjusted until a suitable value was obtained to achieve good background image intensity.

Full automatic indexing of the microstructure was achieved using proprietary system software: Flamenco was used for image acquisition and indexing; Tango was used to display maps and conduct EBSD measurements, such as: the crystal orientation, the grain boundary distribution, the subgrain boundary distribution, the phase distribution and the pattern quality; Mambo was used to obtain pole figures and inverse pole figures; Salsa was used to display the orientation distribution function. A grid size of 202×151 pixels was used for

obtaining maps at a microscope magnification of 2000. The maps contained 30,502 data points. A step size of 0.3 μm was used and, therefore the martensite lath and subgrain sizes below 0.3 μm cannot be indexed. A step size of 0.3 μm gave a good compromise for investigating the recrystallisation process of martensite laths or blocks within the creep-exposed samples. Indexing was performed using an iron bcc structure with a lattice parameter $a = 0.287 \text{ nm}$. The indexing rates (proportion of the map indexed) for all the samples were greater than 90%. Low angle boundaries were defined as those having misorientations between 2 and 15° (the standard cut-off is 15° [18]) and high angle boundaries were between 15 and 180°. Due to crystal symmetry, no two cubic lattices can be different by more than 62.8°, therefore, the high angle boundaries are in the range of 15°-62.8° in iron bcc.

3.3.5 Transmission Electron Microscopy

3.3.5.1 Introduction to TEM

The transmission electron microscope is an essential tool in this project for the identification of the various precipitates that are found within the microstructures of the steels. The microscope that has been used for this project is the JEOL 2100 TEM shown in Figure 3.11. The signals generated as a result of the interaction between a high-energy electron beam of electrons and a thin specimen are shown in Figure 3.12 [19].

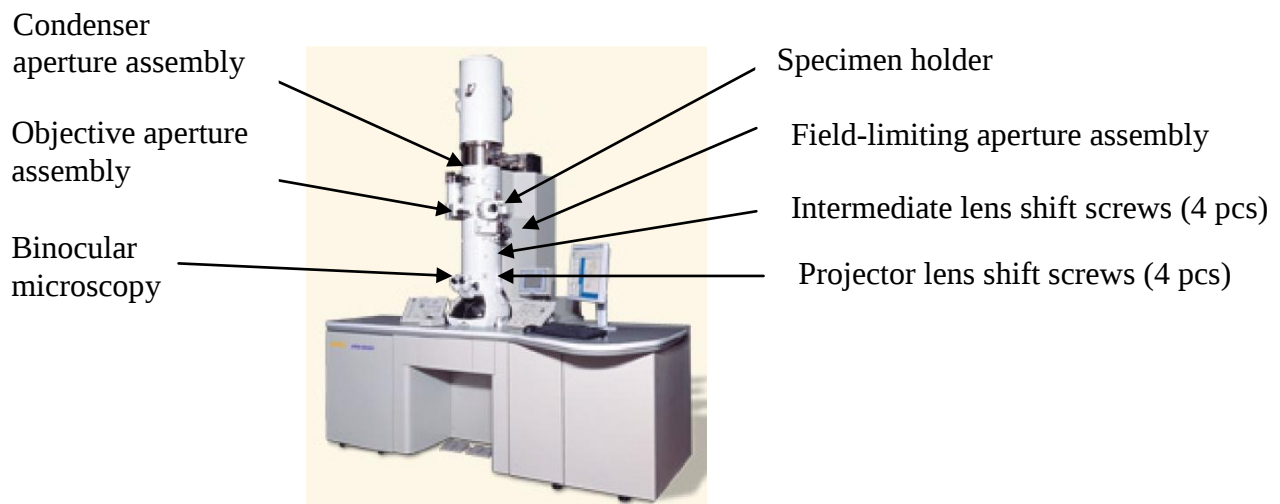


Figure 3.11. JEOL 2100 LaB6 TEM

The JEOL 2100 transmission electron microscope (TEM) permits characterization of samples with very high magnification (up to 1.5 million) and lattice resolution of 0.14 nm. The TEM used in this project is equipped with a Gatan 2k x 2k digital camera and a LaB₆ filament.

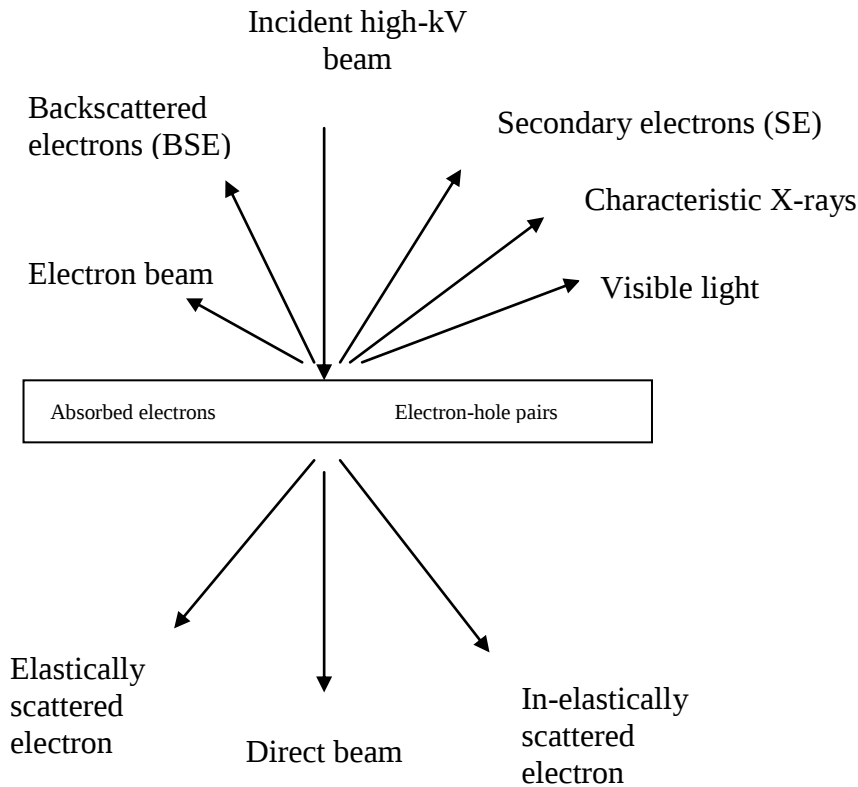


Figure 3.12. The signals generated as a result of the interaction between a high-energy electron beam of electrons and a thin specimen [19].

TEM requires that the beam can be transmitted through the sample. Samples for TEM observation have been prepared by a number of methods such as carbon replicas and thin films and these methods are outlined in the previous sections. Both of these methods allow the production of electron transparent samples.

In order to understand how the information from TEM allows identification of precipitates, the following sections outline the background to TEM with emphasis on image forming and diffraction patterns.

3.3.5.2 Geometry of diffraction

Diffraction: In general, if we see spots, then the specimen is at least partly crystalline. The ability to determine crystallographic orientation locally (down to the nm level) gives TEM its great advantage over SEM and reflected light microscopes. The precision is even greater using convergent-beam patterns [20].

Reciprocal lattice and direct lattice

The following basis of the reciprocal lattice vectors are defined by Bhadeshia [21]:

$$\mathbf{a}_i \cdot \mathbf{a}_j^* = \delta_{ij} \quad (\delta_{ij}=0 \text{ if } i \neq j, \delta_{ij}=1 \text{ if } i=j) \quad (3.5)$$

where the $\mathbf{a}$'s are the vectors of the direct lattice, the $\mathbf{a}^*$'s are then called the fundamental vectors of the reciprocal lattice.

In two dimensions, we have:

$$\mathbf{a}_1 \cdot \mathbf{a}_1^* = 1, \quad \mathbf{a}_2 \cdot \mathbf{a}_2^* = 1 \quad (3.6)$$

In three dimensions, we define the fundamental reciprocal lattice vector as:

$$\begin{aligned} \mathbf{a}_1^* &= (\mathbf{a}_2 \wedge \mathbf{a}_3) / (\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3), \\ \mathbf{a}_2^* &= (\mathbf{a}_3 \wedge \mathbf{a}_1) / (\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3), \\ \mathbf{a}_3^* &= (\mathbf{a}_1 \wedge \mathbf{a}_2) / (\mathbf{a}_1 \cdot \mathbf{a}_2 \wedge \mathbf{a}_3), \end{aligned} \quad (3.7)$$

The reciprocal lattice is a useful tool in TEM; the components of any vector in the reciprocal lattice represent the Miller indices of a plane whose normal is the same direction as that vector while the spacing of the plane is given by the inverse of the magnitude of that vector.

3.3.5.3 Intensity of diffraction

Diffraction from primitive lattices is easier to index, because the reciprocal lattice construction gives all the possible diffracted beams. In non-primitive cells such as fcc, bcc etc. scattering from one atom in the cell can interfere with scattering from another to reduce or increase the intensity of diffraction.

For the instance of body-centred cubic [20]:

$$F = f \{ 1 + e^{\pi i(h+k+l)} \} \quad (3.8)$$

$F=2f$ if $h+k+l$ is even;

$F=0$ if $h+k+l$ is odd.

From the above analysis, we know that some diffractions are of zero intensity, they are known as forbidden reflections. These reflections are usually omitted from the reciprocal lattice.

3.3.5.4 Electron diffraction

Most electron diffraction is carried out with high energy electrons whose wavelengths are orders of magnitude smaller than the interplanar spacings in most crystals. The wavelengths of high energy electrons are also dependent on the accelerating voltage, which is shown in Table 3.4. The lattice parameter of Aluminum, the value of 0.405 nm, was calibrated in room temperature. In tempered 9-12% Cr martensitic steel, the Fe b.c.c lattice parameter is 0.287 nm. Electrons are charged, light particles and their ability to penetrate into solids is very limited. Therefore, the specimen thickness is limited usually to below 100 nm in TEM applications.

Table 3.4 The Correlation between Energy and Wavelength [22]

Accelerating voltage (kV)	100	200	500	1000
Wavelength: λ (Å)	0.0370	0.0251	0.0142	0.0087

3.3.5.5 Indexing the pattern

The indexing methods of diffraction patterns (DPs) can be found within several references [20], [22], [23], [24]. Also, an electron microscopy analysis software website (*Web Electron Microscopy Applications Software (WebEMAPS)*) (<http://emaps.mrl.uiuc.edu/>) has been used for the simulation and comparison of the diffraction patterns [25].

3.3.6 The Analytical TEM (AEM)

3.3.6.1 Why use X-ray analysis in the TEM rather than in the SEM?

A PGT Avalon EDX X-ray detector has been used in this project. Energy dispersive X-ray Analysis (EDX) in the TEM has marked differences from EDX analysis in the Scanning Electron Microscope (SEM).

When we investigate the chemical compositions of particles in high Cr steel why do we use EDX in the TEM on a carbon replica rather than bulk material in the SEM? Why do we need to put more effort into the TEM sample preparation?

EDX in the TEM has several advantages over EDX in the SEM.

The electron beam-sample interaction in the TEM and SEM is shown schematically in Figure 3.13.

Figure 3.13 shows that the considerable difference in the spatial resolution of EDX in the SEM and EDX in the TEM. Normally, SEM samples are thick enough for the focussed beam to be contained within the sample. The X-ray escape volume is larger than that of the backscattered electrons while the escape volume of backscattered electrons is larger than that of secondary electrons. So, it is apparent from this figure: **if a particle volume is smaller than the X-ray escape volume, the microanalysis on this particle in SEM will have influences from the matrix.**

So, it is vital to know the spatial resolution (thickness or depth is often used instead of volume because it is easier to visualize) of a specific sample in SEM.

According to Castaing's formula [14], the analytical area can be calculated.

$$Z_m = 0.033(E_0^{1.7} - E_c^{1.7}) \frac{A}{\rho Z} \quad (3.9)$$

E_0 : Accelerating voltage (kV)

E_c : Minimum emission voltage (keV)

A: Atomic mass

ρ : Density(Kg/m³)

Z: Atomic number

From Castaing's formula, one can understand that the X-ray range depends on the nature of the specimen and the over-voltage between accelerating voltage and minimum emission voltage, so it is possible to decrease the accelerating voltage to achieve better resolution.

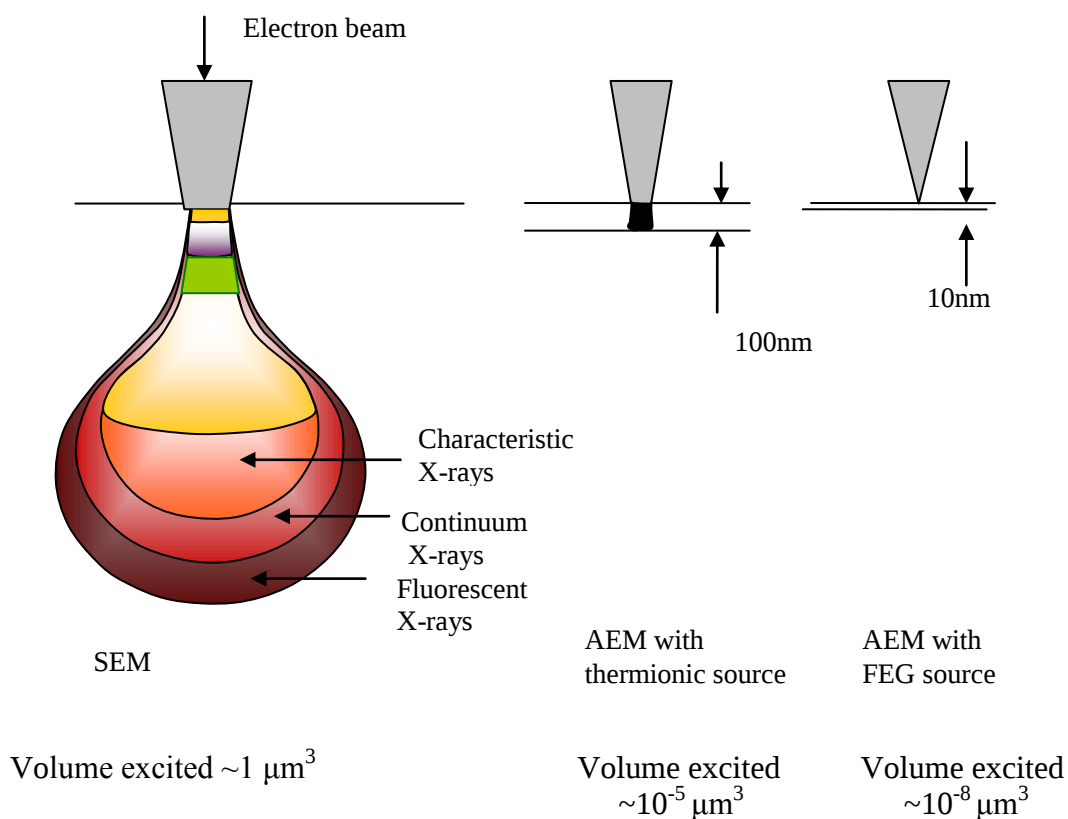


Figure 3.13. Comparison of the relative size of the beam-specimen interaction volumes in an SEM with a bulk specimen, a thermionic source AEM with a thin specimen, and a FEG AEM with an ultra thin specimen respectively [26], after minor modification.

For example, the analytical area of iron at 25kV is $\sim 1.8 \mu\text{m}$. Therefore particles which contain Fe and which are smaller than $1.8 \mu\text{m}$ cannot be analysed accurately using EDX in the SEM. One also must be aware that in a specimen containing light and heavy elements, each one has its own escape volume.

From Figure 3.13, the relative X-ray volume excited in the SEM is $\sim 1 \mu\text{m}^3$ while the X-ray volume excited in the TEM is $\sim 10^{-5} \mu\text{m}^3$ (using a thermionic source) and $10^{-8} \mu\text{m}^3$ (FEG source) respectively. The spatial resolution has been improved vastly. With respect to a high Cr steel sample, most of the particles are quite small, usually below $1 \mu\text{m}$ in diameter. Therefore it is impossible to perform accurate analysis in the SEM on bulk material samples.

TEM coupled with EDX has been applied to perform microanalysis to allow phase identification (ID) and determine the chemical compositions of precipitates without the problem of interference from the matrix provided analyses are carried out on carbon extraction replicas.

In order to improve spatial resolution and minimize the electron scattering in the TEM, the TEM sample should be thin enough (usually below 100 nm) to be beam transparent and a high beam energy has been used (200 kV) in this work.

3.3.6.2 The EDS –TEM interface

The column of a TEM is a harsh working environment; a high energy beam hits a specimen and scatters the electrons. The specimen, sample grids and column of the microscope (including the sample holder) which are hit by electrons emit both characteristic and Bremsstrahlung X-rays [26]. These X-rays accumulate energy from the electron beam, so such X-rays can penetrate into the material. The radiation from the microscope is known as ‘system X-rays’ while the X-rays from regions of the specimen (not the chosen area for analysis) are known as ‘spurious X-rays’. An example is the Cu K α peak resulting from copper sample support grids and other components from the sample holder. These artefacts can be blamed for large errors in quantification analysis and, sometimes, may cause the microanalysis work to be impossible. As an analyst, it is very important to identify them and find solutions to minimize their effects on microanalysis.

Figure 3.14 shows that a collimator has been installed to prevent the undesired radiation from the column of the microscope and to minimize the system X-rays. The collimator also defines the collection angle of the detector and the take-off angle of X-rays entering into the detector. Optimizing the take-off angle can maximize the count rate. In the TEM that we used the take-off angle is set to 18.3°.

In order to minimize the Bremsstrahlung X-rays generated in the specimen, beryllium grids (or nylon grids) have been used instead of copper grids, since the Be K α line is not routinely detectable. Be is highly toxic and must be handled carefully. Although nylon grids are safe and cheap, the orientation of the detector to the specimen and position of sample in column need to be adjusted frequently due to the low rigidity of material which results in the movement of sample Z height.

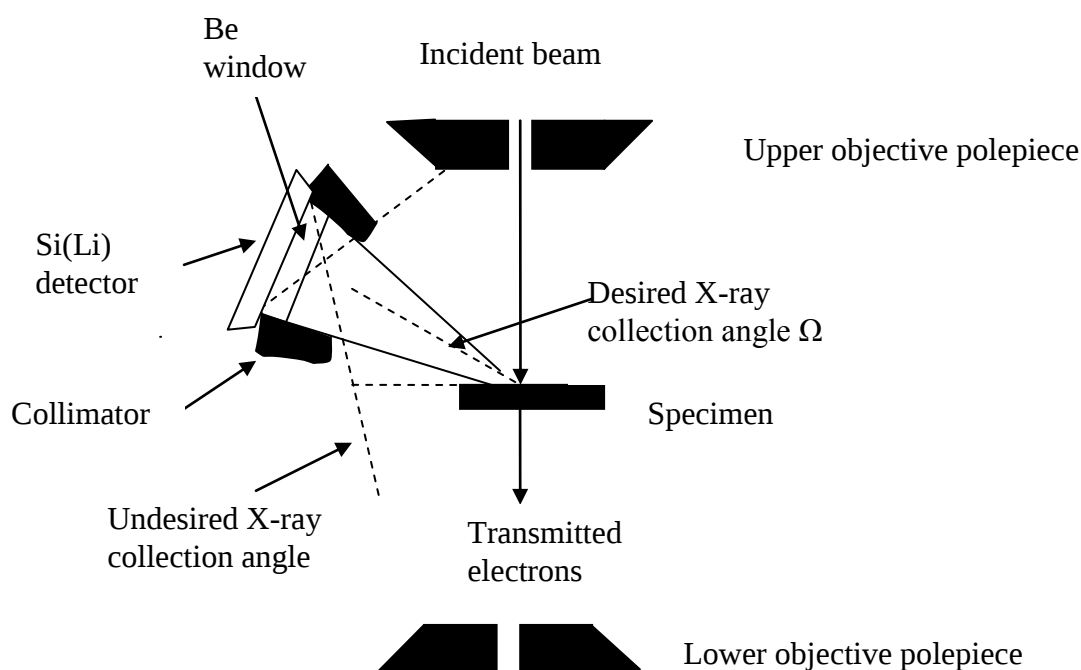


Figure 3.14. The interface between EDS and TEM (after Williams and Carter 1996) [27].

In order to continue to minimize the Cu $K\alpha$ line, one should keep the specimen close to zero tilt. The Bremsstrahlung effect is further reduced by using thin foils such as evaporated films rather than self-supporting disks.

The best index to indicate the performance of an EDX interfaced to a TEM is the peak-to-background ratio (P/B) in a standard specimen. In a well calibrated AEM, the P/B ratio will increase with the accelerating voltage [26].

3.3.6.3 Qualitative X-ray Analysis

Before performing particle analysis it is important that you acquire a spectrum across the complete X-ray energy range. In this work, a Si (Li) detector has been used, and an energy range 0-20 keV is sufficient because the specimen composition to be analysed is already known.

When acquiring the spectrum the dead time should be kept below 50%, with around 30% dead time a good choice for the maximum counting rate and resolution. In order to decrease dead time below 50%, one or all of the following methods can be applied:

- Choose a thin area of the specimen.
- Using a smaller condenser lens aperture.
- Using a smaller spot size.

In order to achieve an output count rate more than 4000 cps in this work, the spectrum should be acquired for at least 50 seconds.

The basic rule for peak identification is that one should look for families of peaks; if a family member is missing the phase identification may be wrong. In this work, there were a few elements overlapping for some phases and the ways in which these peaks were identified will be explained in detail in the following sections.

3.3.6.4 Quantitative X-ray Analysis

For EDX analysis in the SEM, owing to the thickness of the sample, matrix corrections including atomic analysis (Z), absorption (A) and fluorescence (F) effects have been applied. This correction method does not apply for thin TEM specimens. Consequently, a simple method had been developed by Cliff and Lorimer at the University of Manchester Institute of Science and Technology (UMIST) in the 1970's [27]. By using this method, the effects of specimen thickness have been removed, and the following equation was developed:

$$C_A / C_B = K_{AB} \cdot I_A / I_B \quad (3.14)$$

where C_A is concentration ratio in mass fraction for element A,

I_A is the peak intensity for element A,

K_{AB} relates to the intensity ratio and concentration ratio.

The K factor is not a standard value; each pair of elements has a different K-factor which depends on the detector efficiency, ionization cross section and fluorescence yield of both of the elements involved. It is vital that empirically obtained K-factors are system specific [27]. Also, both theoretically calculated and experimentally obtained K-factors are accelerating voltage dependent [27].

In practice, a single element (such as Fe or Si) has been set as a ratio standard element and all ratios have been taken with respect to that element. In this way, the Cliff and Lorimer ratio (CL ratio) has been determined experimentally.

For instance, in the AEM used in this work, CL ratios of high Cr steel have been calibrated at 200kV as shown in Table 3.5. The selected standard element is Si.

Table 3.5 CL ratios for Quantitative X-ray Analysis in TEM on 200kV
used for the analysis

Element	Cr	Fe	Mo	W	Nb	V
CL ratio	1.2	1.35	2.633	2.38	2.543	1.16
Line	K	K	L	M	L	K

After the AEM has been aligned correctly, microanalysis can be carried out on high Cr steel TEM samples.

The following chapter will show how these experimental techniques have been used for the analysis of specimens in this thesis.

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Chapter 4 Evaluation of the mechanical properties of creep-exposed E911

The mechanical properties of the creep exposed E911 samples are analyzed in this chapter.

4.1 Larson-Miller Parameter

In order to extrapolate experimental data on creep rupture life of materials, an equation was developed by Larson and Miller to predict rupture lives that would be impractical to reproduce in the laboratory [1]. This equation is known as the Larson and Miller equation (equation 4.1). This equation can also be used to relate the difference in rupture life to difference in temperature.

$$LMP = \frac{T(C + \log(t_r + t))}{1000} \quad (4.1)$$

where T is the temperature,

C is a constant, usually 20 is used for steels,

t_r is the compensation time of tempering,

t is the creep time.

To find the compensation time t_r , we have to take into account the 2 hrs tempering treatment at 760°C:

$$LMP = (760 + 273) (20 + \log 2) / 1000 = 20.97$$

If the LMP at tempered condition is 20.97, we then calculate the equivalent time at 600°C, 625°C, 650°C.

$$\text{at } 600^\circ\text{C: } 20.97 = (600 + 273) (20 + \log t_{600})$$

$$t_{600} = 10513 \text{ (hrs)}$$

$$\text{at } 625^\circ\text{C: } 20.97 = (625 + 273) (20 + \log t_{625})$$

$$t_{625} = 2254 \text{ (hrs)}$$

$$\text{at } 650^\circ\text{C: } 20.97 = (650 + 273) (20 + \log t_{650})$$

$$t_{650} = 525 \text{ (hrs)}$$

The calculated Larson-Miller parameters at three levels of temperatures are listed in Table 4.1.

4.2 Hardness analysis

The Vickers hardness was measured in the head and gauge length of the samples as outlined in section 3.1.2. Table 4.2 shows the average hardness value and corresponding standard deviation. The values of standard deviation of hardness for all of the samples are between 1.62 and 6.66, which was considered acceptable. The data from the head and gauge lengths of the different creep-exposed samples is shown in Figure 4.1. The data points show the average hardness measured in the head and the gauge length of the fractured samples plotted against the Larson-Miller Parameter (LMP) with a constant of 20, which is usual for steel of this type. The hardness of the gauge length that experienced both strain and temperature was found to be lower than that of the head where thermal softening only can be assumed. In both cases, the hardness of the samples had decreased substantially from the original solution heat treated and tempered “as-received” sample shown by the red circle on Figure 4.1.

Table 4.1 The calculation of Larson-Miller parameter

	t(h)	t _r (h)	LMP
600°C	1614	10514	21.03
	9800	10514	21.22
	13336	10514	21.28
	75647	10514	21.77
625°C	1131	2254	21.13
	5487	2254	21.45
	13224	2254	21.72
	31198	2254	22.02
650°C	849	525	21.36
	2232	525	21.64
	4530	525	21.88
	14319	525	22.31

Table 4.2 The Hardness value and corresponding standard deviation. For reference, the as-received hardness was 269 HV $\pm$ 2.

		Head		Gauge	
	Exposure duration (hrs)	Hv20	Standard Deviation	Hv20	Standard Deviation
600°C	1614	264.4	1.6	233.3	6.0
	9800	258.5	3.2	221.2	3.6
	13336	257.5	3.8		
	75647	246	3.4	192.8	1.6
625°C	1131	250.5	3.2	223.7	2.2
	5487	245.8	4.5	201.5	3.9
	13224	241.8	3.8	198.3	3.5
	31198	242	3.1	193	3.0
650°C	849	251.1	3.4	198.5	2.3
	2232	249.8	3.3	208.4	6.7
	4530	243.2	3.9	193.5	4.7
	14319	234.4	5.1	189.7	3.8

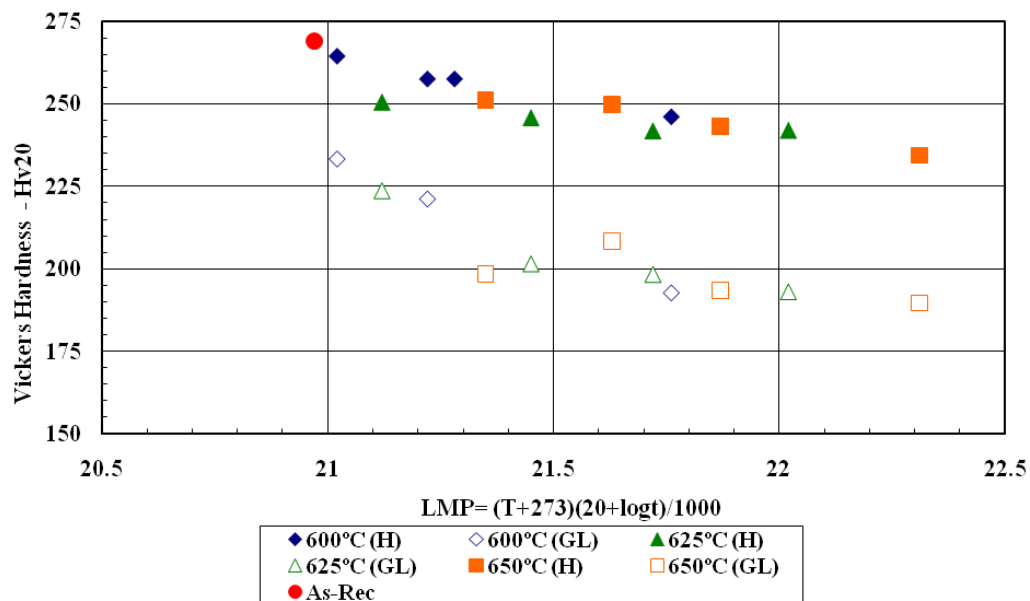


Figure 4.1. Vickers hardness versus Larson-Miller parameter for the creep-exposed samples.

H and GL denote head and gauge length respectively. Note that t_r is allowed for.

4.3 Creep rupture data analysis

Creep rupture testing was conducted at Corus UK Ltd. The stress versus creep rupture duration results are shown in Figure 4.2. The creep rupture data shows that stresses below

100MPa give significant creep durations, generally over 30,000 hours. The creep strength is lower at 650°C than 625 and 600°C, as would be expected. (Full creep rupture ductility data was given in Table 2.2).

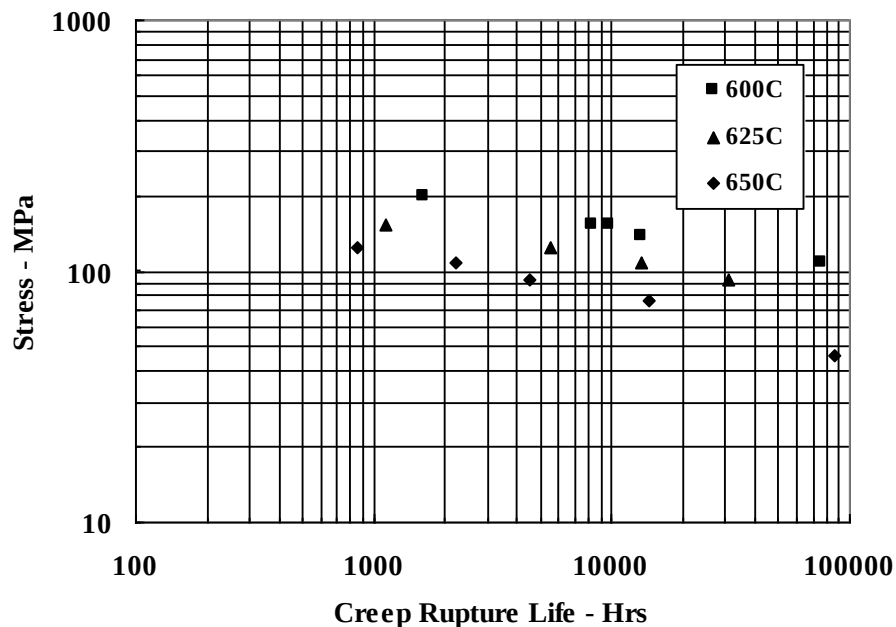


Figure 4.2. Applied stress versus creep rupture life as a function of temperature.

4.4 Summary

Long term creep data for E911 steel shows a general reduction in mechanical properties with increasing test temperature and exposure duration. This behaviour is connected with microstructural changes in service. Although we have not directly examined service material, the information here can be correlated with changes in creep strength with observed microstructure and should be useful for service life predictions. The following Chapters will investigate the microstructure evolution by a range of material characterization techniques: RLM, SEM, TEM, EBSD, EDX.

4.5 References

[1] F. R. Larson, J. Miller, A Time-Temperature Relationship for Rupture and Creep Stresses, Trans. ASME (1952), vol. 74, pp. 765–775.

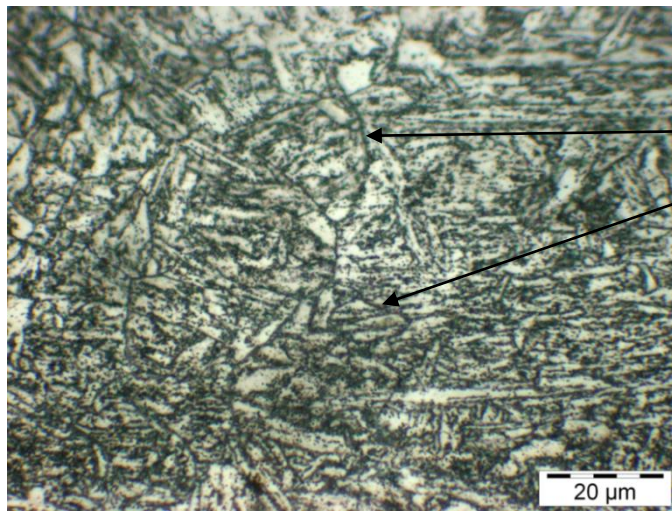
Chapter 5 Microstructure Evolution and Analysis of Fracture Mechanisms by RLM and SEM

This chapter shows reflected light microscopy and scanning electron micrographs of the creep exposed E911 samples. Additionally, the creep failure mechanism of the different samples has been investigated and a fracture mechanism map has been constructed from the creep failure mechanisms that were observed.

5.1 Microstructure analysis by Reflected Light Microscopy (RLM)

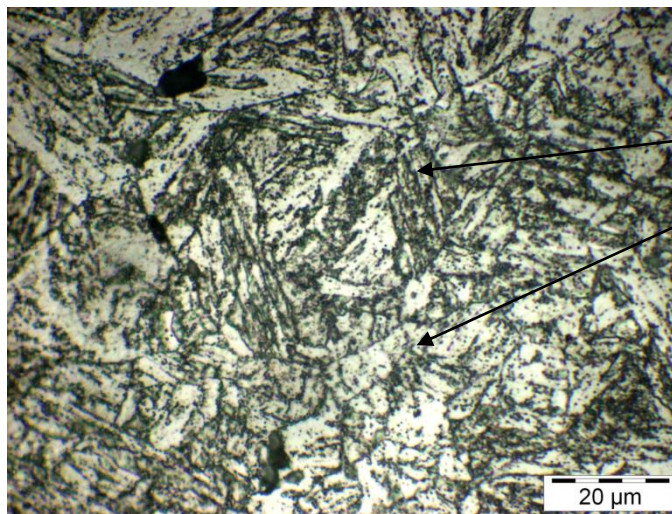
Figure 5.1 shows reflected light micrographs of the creep exposed E911 samples (all of the micrographs were taken at a magnification of 1000). The general microstructure of tempered martensite was described in section 1.8.1. From Figure 5.1 (a) to (f), the microstructural changes as a result of creep exposure can be observed. The position of prior-austenite grain boundaries are clear at the lower temperature (600°C) up to 75647 hours exposure (see Figure 5.1 (a), (b), (c)) and at higher temperature (650°C) for the shorter creep exposures (e.g. Figure 5.1 (d)). However, after longer exposure at higher temperatures of 650°C, the positions of prior-austenite grain boundaries are obscured and not easy to be distinguish owing to the resolution and etching limitations of reflected light microscopy. According to Kimura *et al.* [1], the observed boundaries consist of precipitates ($M_{23}C_6$, MX and Laves phase etc.) in high chromium tungsten strengthened ferritic steel. The observation of the shape of precipitates and occupancy on prior-austenite grain boundaries requires SEM (see section 5.2). Phase identification and the chemical composition of the precipitates was carried out by TEM coupled with EDX (Chapter 7).

Inside prior-austenite grain boundaries, the elongated martensite lath structure was observed. From Figure 5.1 (a) to (f), the degree of elongation of martensite structure decreased. This morphology evolution will be discussed in detail in Chapter 6. The lines enclosed martensite laths consist of precipitates ($M_{23}C_6$, MX, or Laves etc.), which will be investigated in Chapter 7 by TEM.



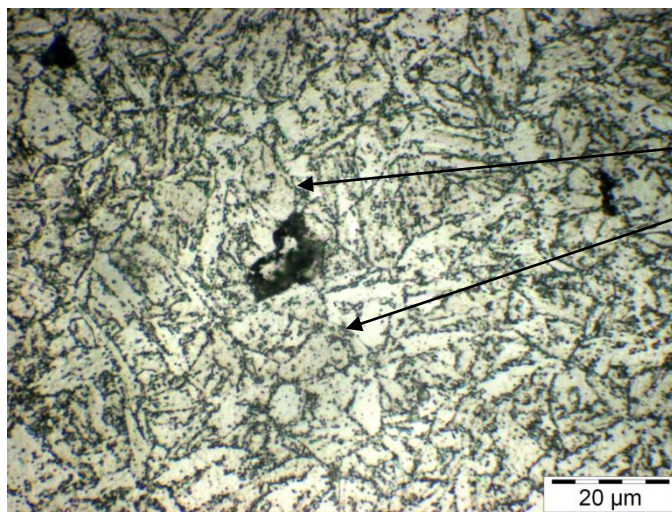
Prior austenite grain
boundaries

(a) 600°C 1614 hours gauge



Prior austenite grain
boundaries

(b) 600°C 13336 hrs gauge



Prior austenite grain
boundaries

(c) 600°C 75647 hrs gauge

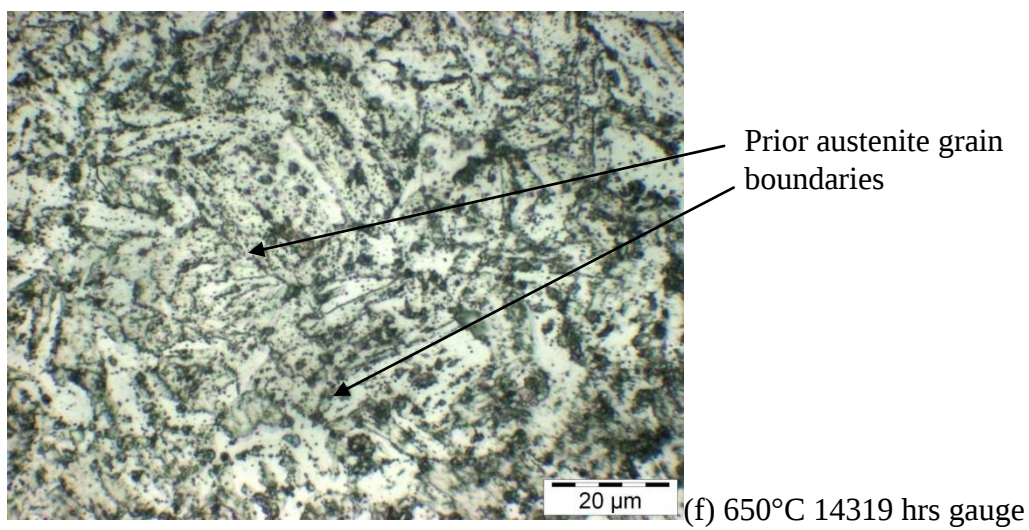
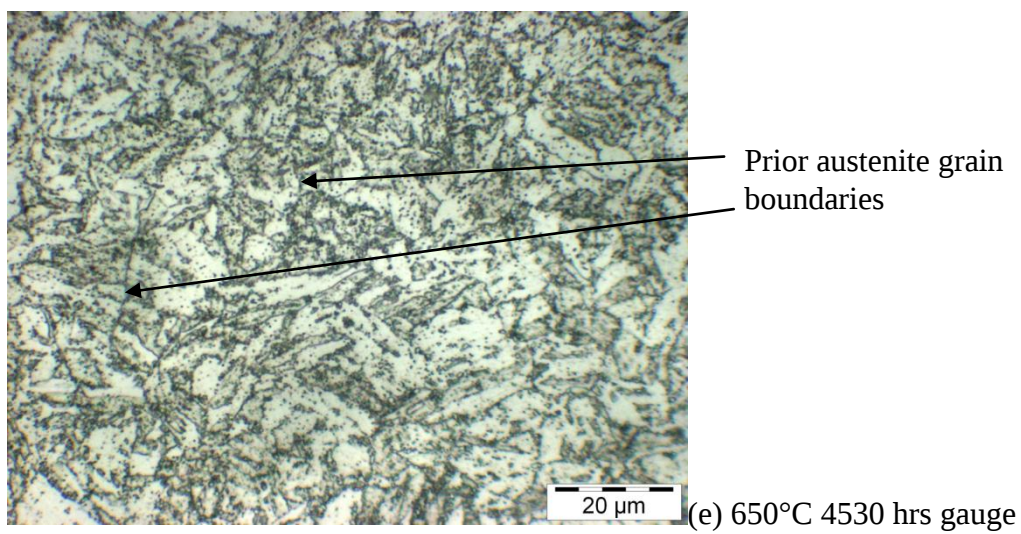
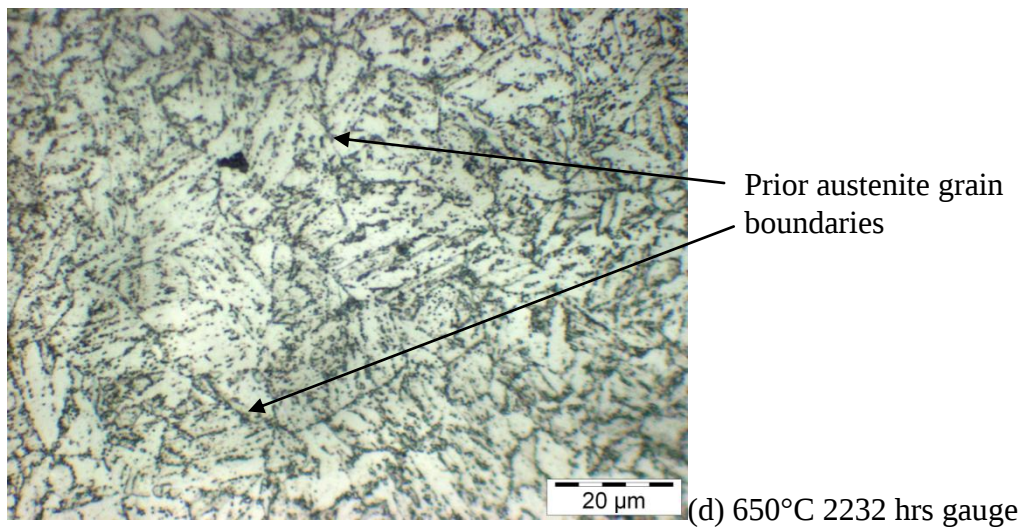
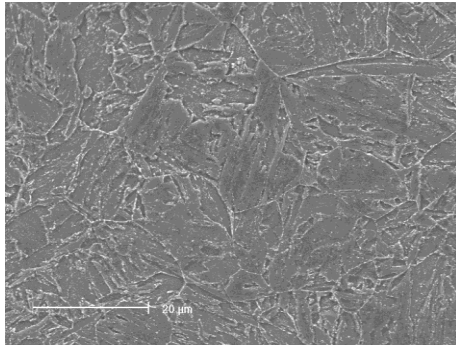


Figure 5.1 Optical micrographs of the as-tempered and crept E911 samples.

5.2. Micrographs by SEM

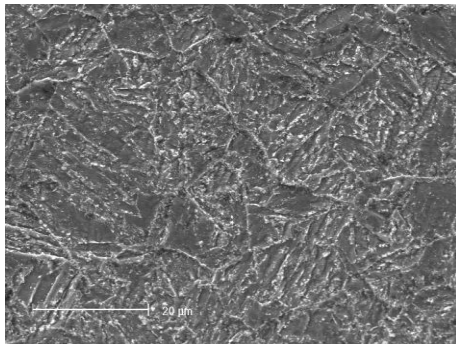
Figure 5.2 (a)-(m) show the microstructure evolution of E911 steel as a result of exposure to high temperature and stress.



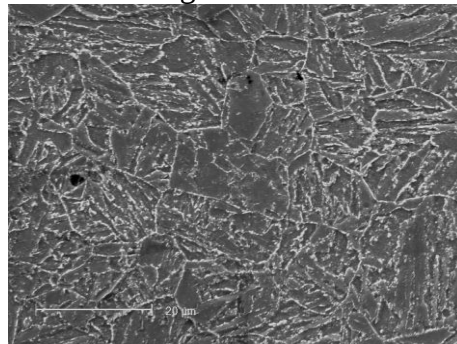
(a) as tempered

20 μm

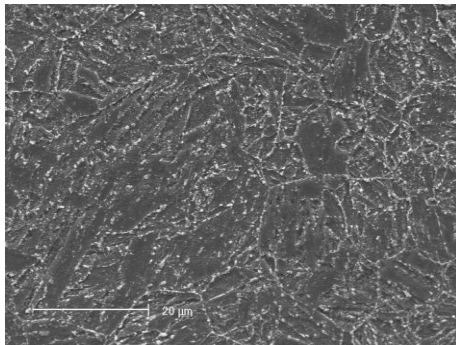
Magnifications on all of micrographs in Figure 5.2 are same.



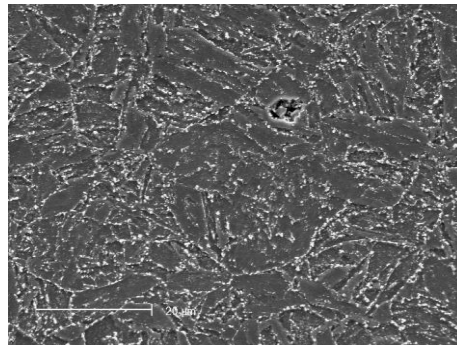
(b) 600°C 1614 hrs head



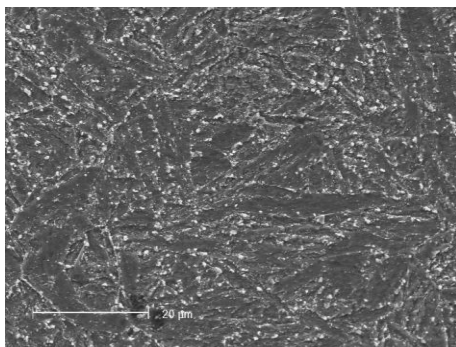
(c) 600°C 1614 hrs gauge



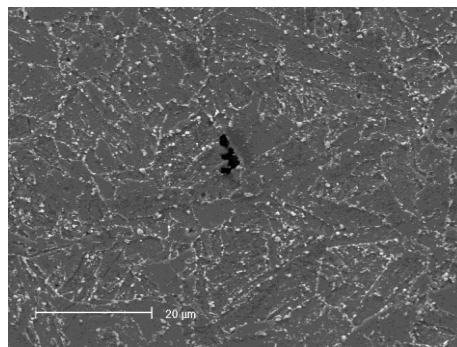
(d) 600°C 13336 hrs head



(e) 600°C 13336 hrs gauge



(f) 600°C 75647 hrs head



(g) 600°C 75647 hrs gauge

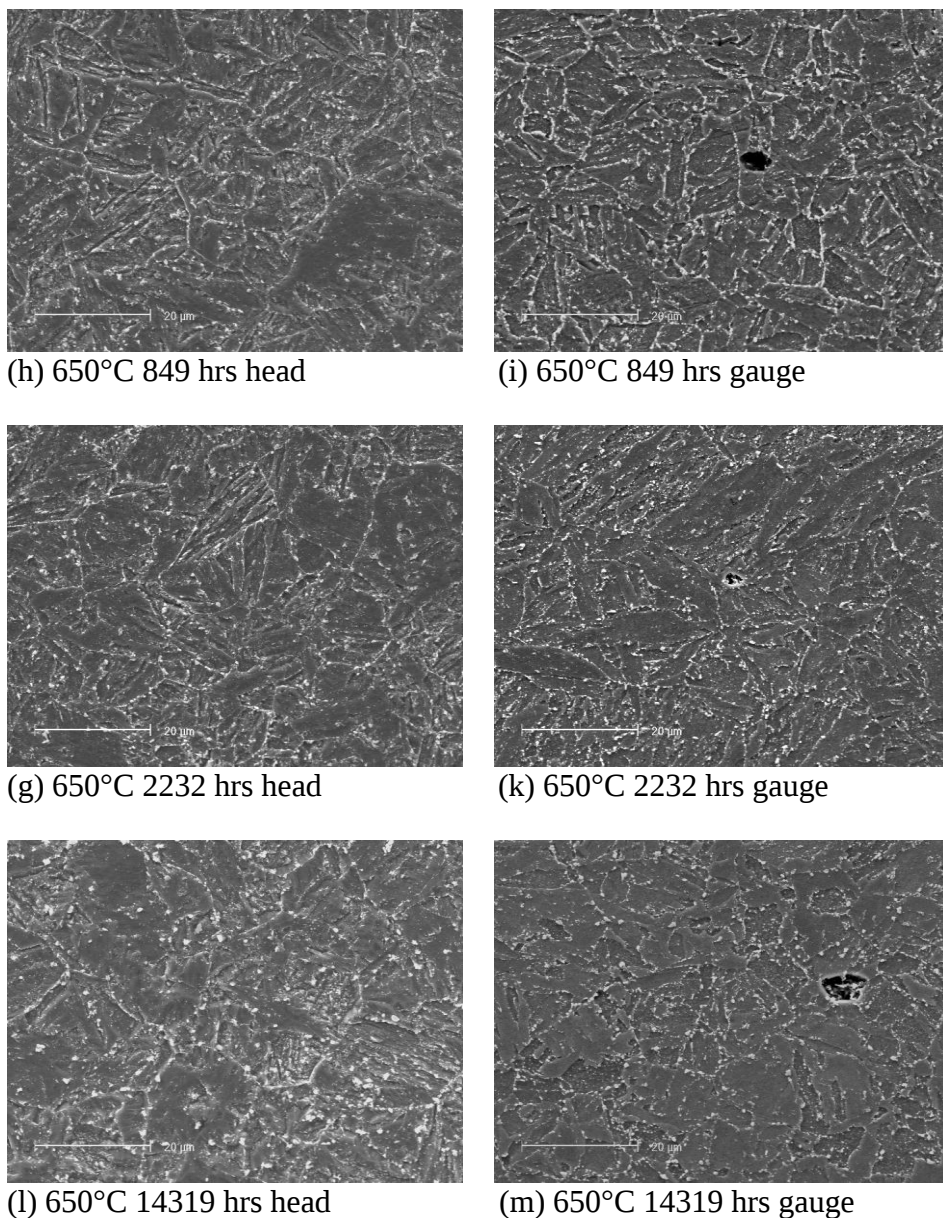


Figure 5.2. Secondary electron images of the as-tempered and crept E911 samples

In the tempered condition, the distinct lines of prior-austenite grain boundaries were observed. The lines are decorated with fine precipitates. These will later be shown to be $M_{23}C_6$ and MX (see section 7.3) the prior austenite grain boundaries separate the larger prior austenite grains well, as shown in Figure 5.2 (a). Inside the prior austenite grain, the array of long martensite laths strengthens the creep resistant properties of the E911 steel. Therefore, this microstructure is desired for high temperature application.

However, this good effect gradually decreases with exposure to the higher temperatures and stresses in long time service. Figure 5.3 shows that the neat array of the long straight martensite laths changes to irregular shapes with longer exposure duration at higher temperature. This will be discussed in Chapter 6 using EBSD.

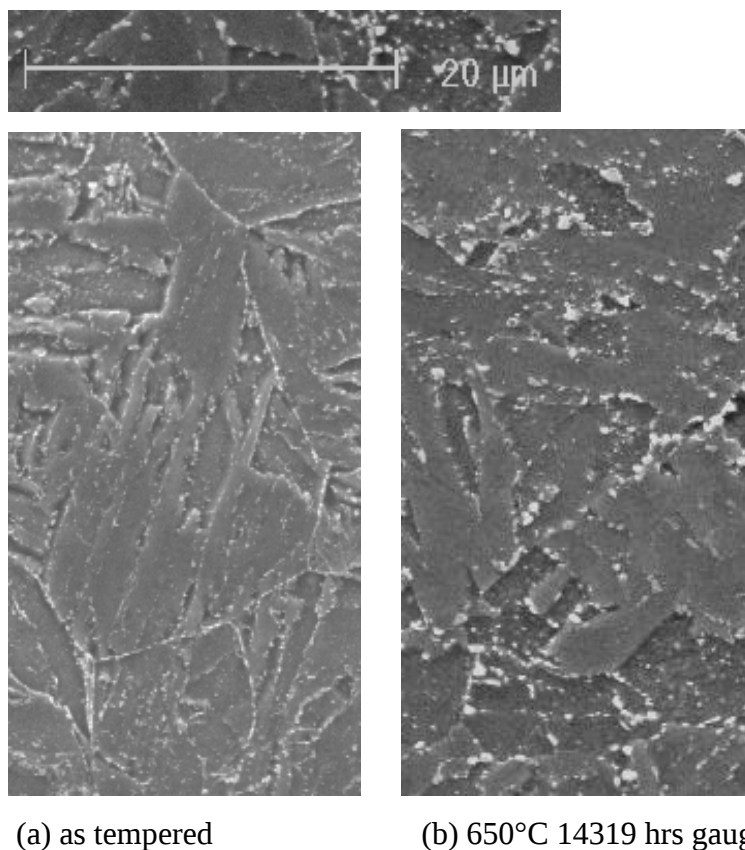


Figure 5.3. The morphology comparison.

Figure 5.2 (f), Figure 5.2 (g), Figure 5.2 (l) and Figure 5.2 (m) clearly show many more larger particles at longer exposure duration than as tempered and shorter duration samples, which will be discussed in Chapter 7.

5.3 Fracture deformation mechanism

Metallographic observations made on gauge areas found cavities, voids, cracks, which is relevant for the fracture mechanism of the E911 steel.

5.3.1 Fracture mechanism

Metallographic observations were made on gauge areas and near rupture areas for all of the E911 samples. Two types of fracture modes were found on the basis of the observation on all of samples, is shown in Figure 5.4. Figure 5.5 shows FEGSEM micrographs of all of these.

Transgranular creep fracture mode: The majority of samples observed were identified as this mode. Voids were found in the sample. These subsequently grow and coalesce by means of plastic deformation processes; coalescence is thus the mode of crack growth for ductile fracture. Void linkup is restricted to the necked region of the tensile sample [2]. Figure 5.4 (a) shows the typical transgranular creep fracture mode.

Intergranular creep fracture mode: The transition from transgranular creep fracture mechanism to intergranular creep fracture results from the growth of cavities generated along the boundaries. On the sample of 625°C 31198 hrs gauge, lots of intergranular cracks were observed, some of which show apparent coalescence. Macroscopic cracks were formed along grain boundaries. Figure 5.4 (b) shows the typical intergranular creep fracture mode; most of the cracks were in grain boundaries normal to the applied load.

5.3.2 Creep fracture mechanism maps

The observations on all of the E911 samples were made by FEGSEM to construct a creep fracture mechanism map.

Figure 5.6 shows the creep fracture mechanism map in terms of applied stress versus time to rupture of E911 steel. In this creep rupture mechanism map, the stress and temperature are commonly used (the stress is not divided by Young's modulus, and the temperature is not homologous temperature). The map was constructed with the stress on the y-axis and time to rupture on the x-axis. Shinya et al. [3] also investigated the 1Cr-1Mo-0.25V steel and proposed a creep fracture mechanism map in terms of commonly used stress and temperature.

Two creep fracture mechanism regions were plotted on Figure 5.6. The different regions are separated by the purple lines on the figure.

(a) A transgranular fracture mechanism field occupies a large area (which is in the left side area of the purple line in Figure 5.6). The samples with transgranular fracture mechanism are marked as black.

(b) A intergranular fracture mechanism field occupies a small patch (which is in the right side area of the purple line in Figure 5.6). The samples with intergranular fracture mechanism are marked as purple.

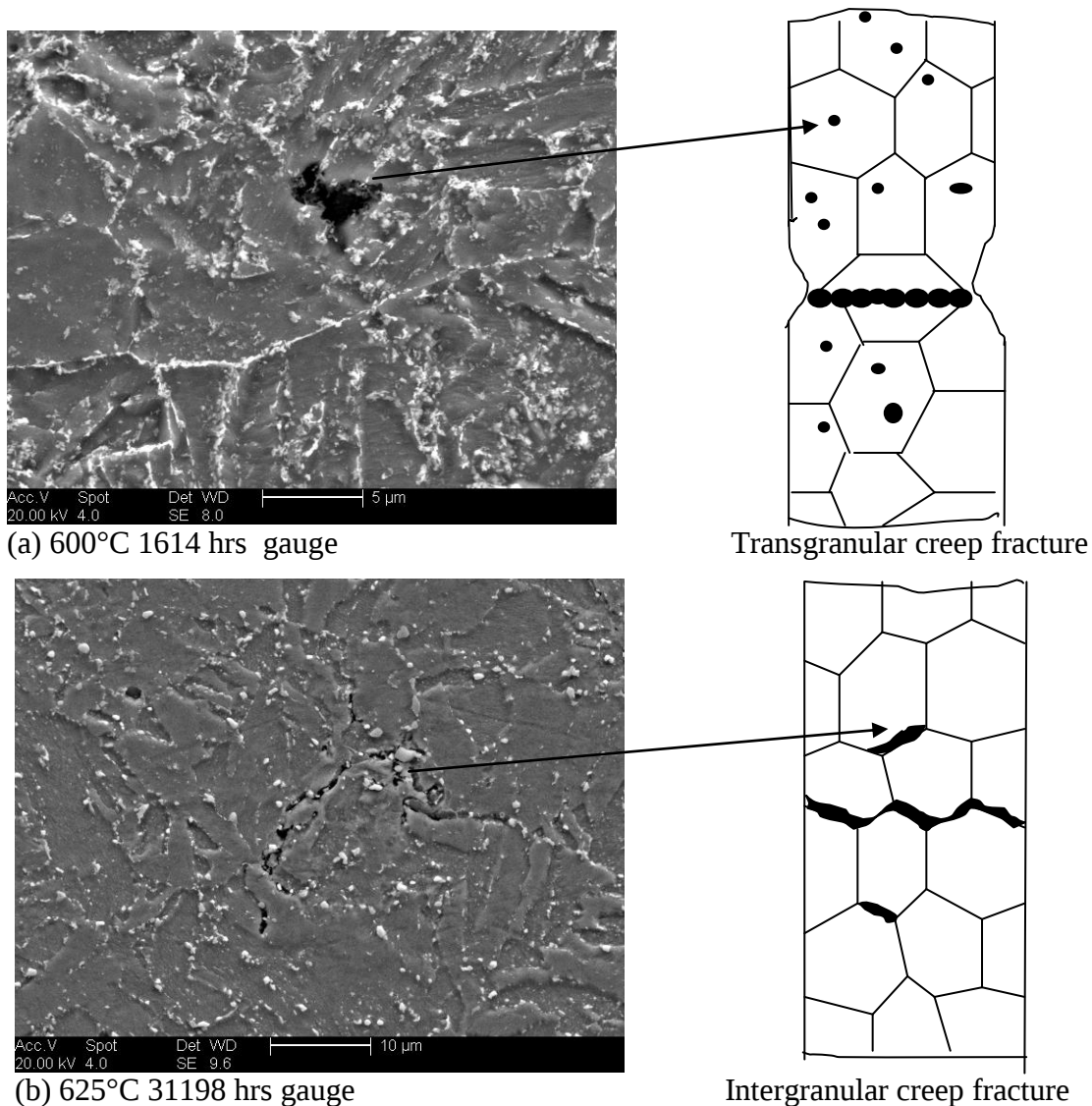
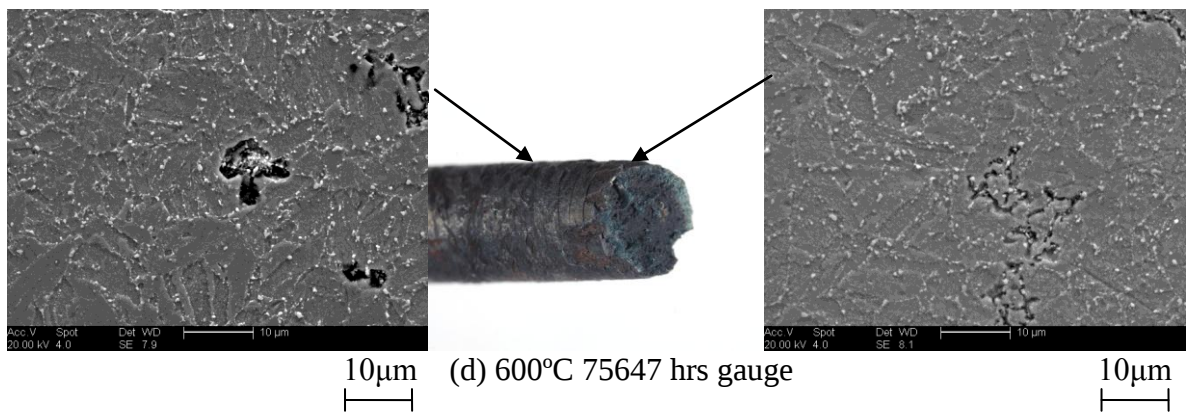
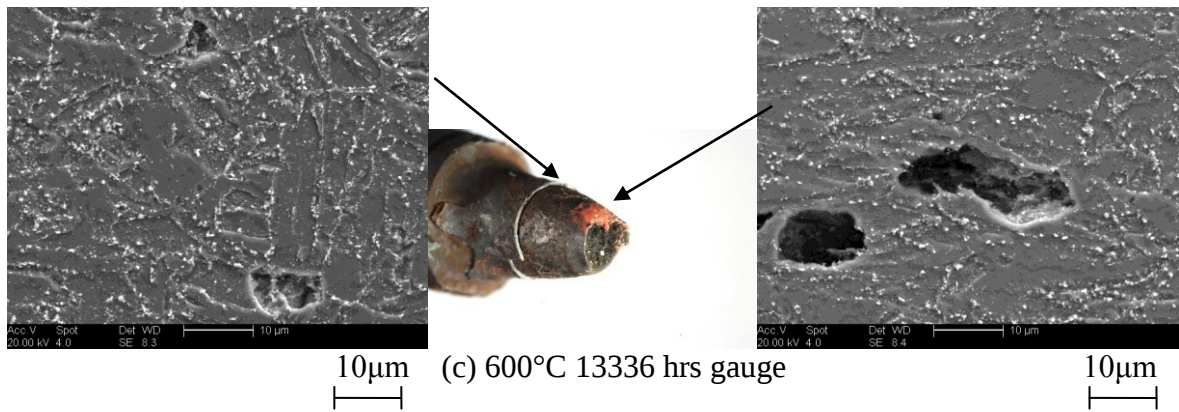
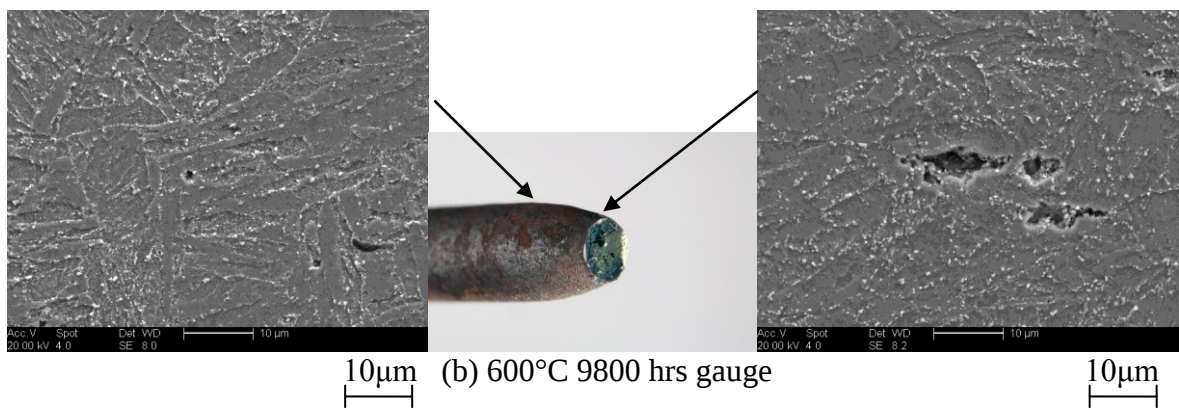
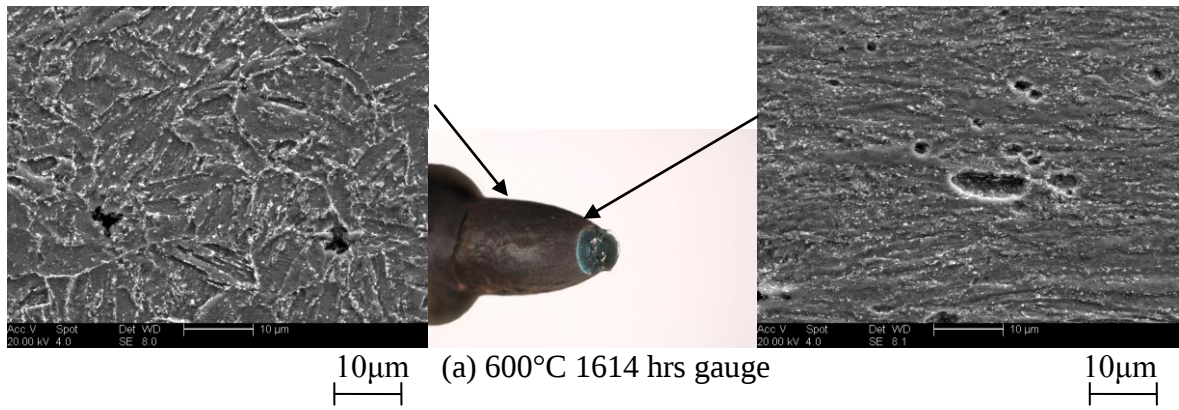
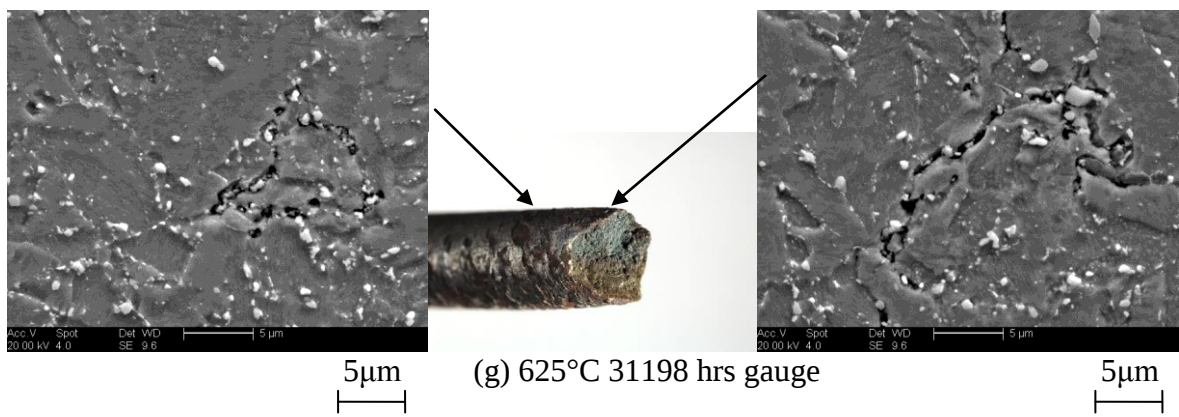
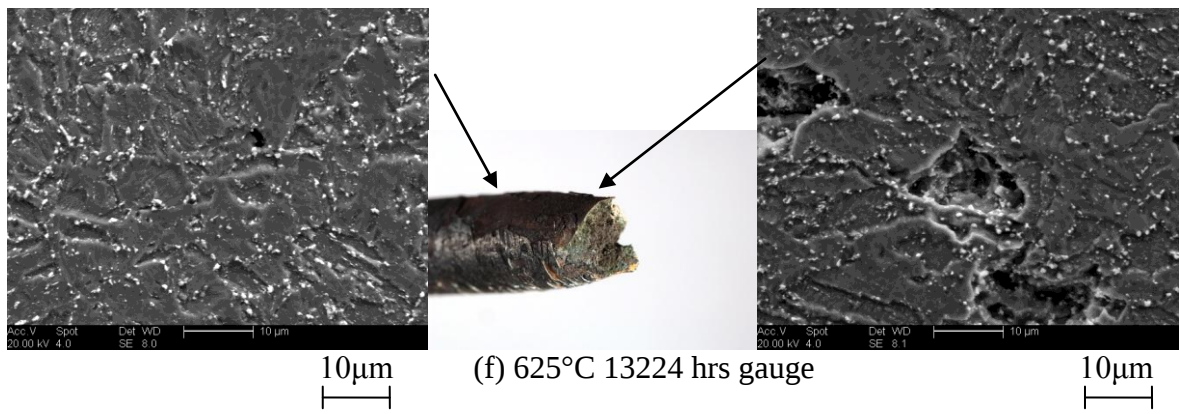
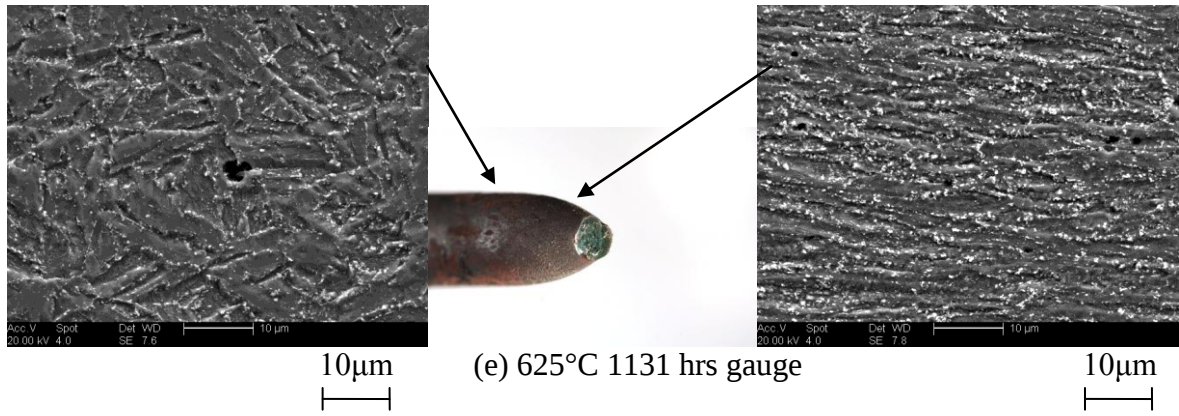


Figure 5.4. Fracture modes in E911 crept samples. The SE images are from FEGSEM in this project while the corresponding schematic drawings are after T.H. Courtney [2] with some modification.





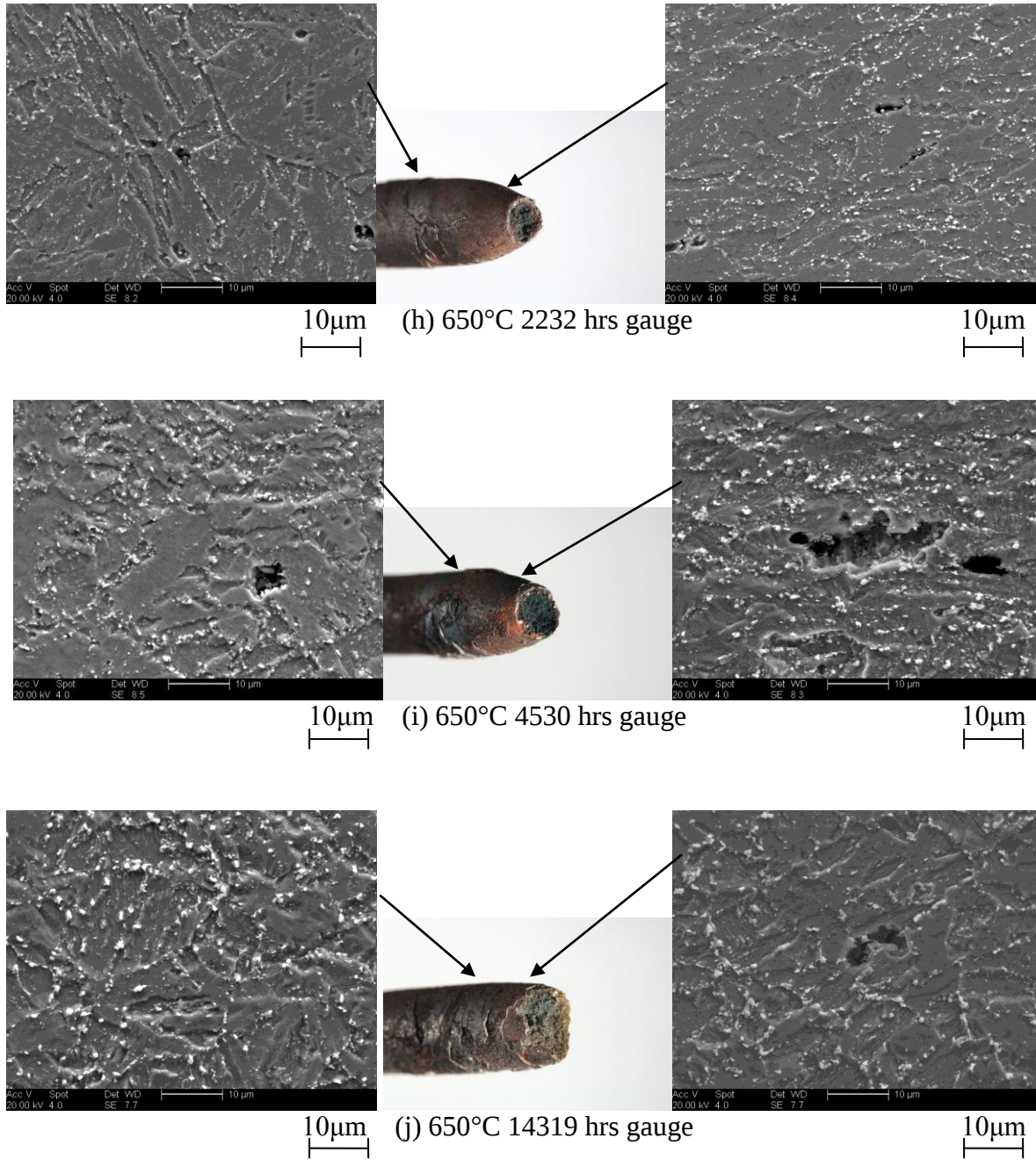


Figure 5.5. Micrographs showing the fracture modes of all of the E911 creep samples.

At the temperature of 600°C, the transition from the transgranular creep mechanism to intergranular fracture mechanism took place on the longest exposure sample of 600°C 75647 hrs. The other samples (600°C 1614 hrs, 600°C 9800 hrs, 600°C 13336 hrs) exhibit the typical transgranular creep fracture mechanism, shown in Figure 5.5 (a), (b), (c). The cavities close to the grain boundaries have a pinning effect on the grain boundary migration when the applied stress is perpendicular with the grain boundary. However, when the stress is parallel

with the grain boundary, this causes the grain boundary migration, which was investigated by Shinya et al. [3]. On ductile fracture samples, micrographs also exhibit the apparent neck down feature on close fracture parts; lots of cavities were found elongated along the direction of stress on the neck down area, which do not lead to intergranular fracture.

When the temperature increased to 625°C, with creep cavity growth, after 31198 hrs exposure at a stress of 93MPa, the transition from transgranular creep fracture to intergranular fracture was completed. The brittle intergranular fracture mechanism was confirmed in this sample with micrographs are shown in Figure 5.5 (g).

At the temperature of 650°C, the fracture mechanism of all of samples was identified as transgranular creep fracture. This type of fracture is associated with a considerable reduction in area [2]. The reduction in area for four crept samples of 650°C is 83, 75, 69, 41 respectively. Lots of voids were found on these four crept samples.

Rupture, characterized by a reduction in area of, or close to, 100% [2], cannot be found on any of the samples observed.

On the basis of SEM micrographs of all of E911 creep samples provided, the creep mechanism map of E911 steel was constructed in which creep damage due to long term service at high temperature working conditions was clarified. This map can be used to estimate the extent of the accumulated damage in service with regard to the various working conditions (stress, temperature and creep duration). However, in order to construct a highly precise creep fracture mechanism map, more crept samples should be collected and analysed in the future.

5.4 Summary

Through microstructure observation by RLM, SEM on all of E911 samples, the changes in the morphology and particles size were observed. These will be further characterised quantitatively by EBSD and TEM in Chapter 6 and Chapter 7.

A creep fracture mechanism map of E911 steel was also constructed on the basis of all of E911 creep samples, which will provide a reference on the life management of components in service.

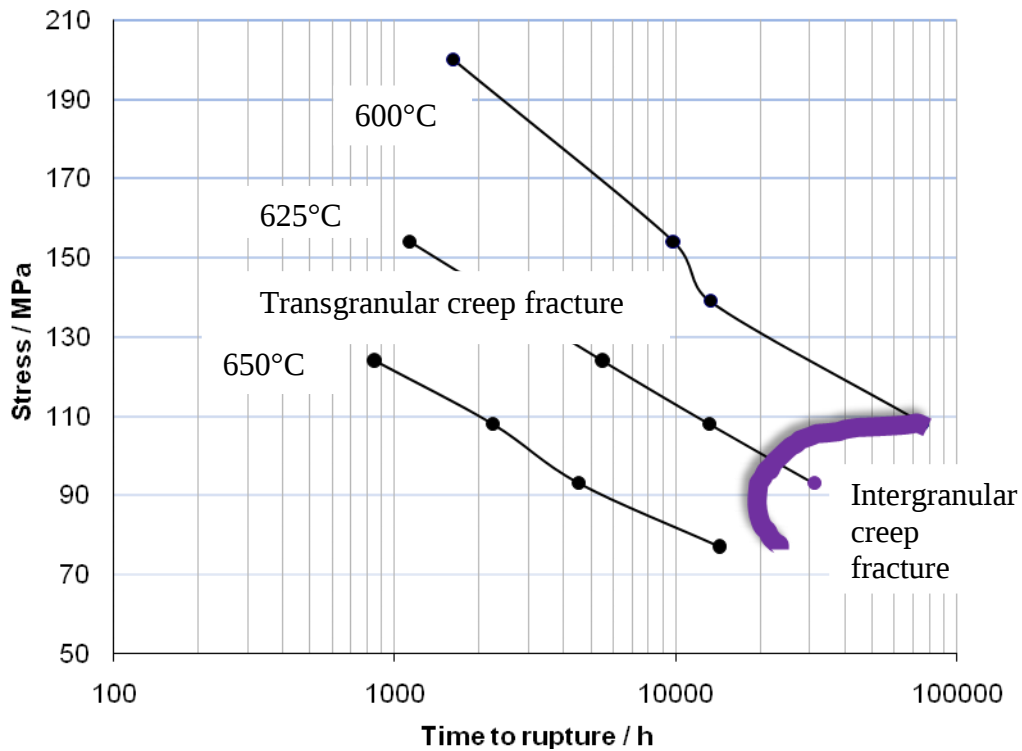


Figure 5.6. Creep fracture mechanism map of E911 steel.

5.5 References

- [1] M. Kimura, K. Yamaguchi, M. Hayakawa, K. Kobayashi, K. Kanazawa, International Journal of Fatigue 28 (2006) 300-308.
- [2] T. H. Courtney, Mechanical behaviour of materials, second edition, McGraw-Hill, Boston, 2000.
- [3] N. Shinya, J. Kyono, H. Kushima, ISIJ Int. 46 (2006), No. 10, pp. 1516-1522.

Chapter 6 EBSD analysis of the grain morphology of E911

The microstructural evolution of E911 steel is complex as has been illustrated in the previous chapters. In this chapter, electron backscattered diffraction (EBSD) has been used to evaluate the changes in grain morphology and crystallography of this tempered martensitic steel that occur as a result of the exposure to temperature and stress.

6.1 Introduction

Whilst there is a good appreciation of how exposure to time and temperature affects the precipitate content and distribution in E911, there have been fewer studies of how creep exposure affects the crystallographic structure of the material. Electron backscattered diffraction is a powerful technique for studying the crystallographic structure of materials [1-3]. Whilst the literature related to EBSD is significant, there have been fewer studies of 9-12Cr steels. Sonderegger *et al* [4] investigated martensite lath width, subgrain size and misorientation in various thermally aged or creep-exposed samples at temperatures of 650°C to rupture times of up to 16,000 hours. They found that martensite lath widths and subgrain sizes could simply be identified by EBSD.

More recently, Sanchez-Hanton and Thomson [5] have used EBSD to study isothermally aged grade 91 (9Cr-1Mo-Nb-V). They showed that gradual subgrain nucleation and growth occurred within tempered martensite laths. The lath structure was stable at aging times up to 10,000 hours; the ratio of low to high angle boundaries and the total grain boundary length increased with increasing ageing times at 650°C.

However, despite these earlier studies, there has been no detailed analysis on how the structure of martensite evolves with temperature and stress. For example, the way in which the prior-austenite grain boundaries, blocks, packets, subgrains etc all evolve is still unclear. This chapter describes the microstructural changes that occurred in creep-exposed E911 by examining the range of E911 samples described in Table 2.2 of Chapter 2.

The advanced high Cr steels generally have extremely fine and complex lath-martensitic microstructures, and the excellent strengths of the steels might be attributed to the combined strengthening mechanisms of the matrix and grain boundaries, as in many other martensitic steels [6]. The lath martensitic structure, which is one of the most important structures in steels, has been investigated widely [7-11]. The lath martensite in low-carbon steels has a three-level hierarchy in its morphology, i.e., laths, blocks, and packets [11], shown as Figure 6.1. The martensitic lath is a single crystal of martensite with a high density of lattice defects. The block is aggregations of laths with the same crystallographic orientation (variant). The packet is aggregations of blocks with the same $\{1\ 1\ 1\}_\gamma$ plane in austenite (parent plane) [11]. The misorientations between different blocks within a packet and between different packets give rise to high angle boundaries [7], the misorientation between the lath boundaries within blocks are low angle boundaries that vary within a few degrees [7]. These different misorientation characteristics of various boundaries in the lath martensite result in effects on the mechanical properties.

The linear relationship between σ_y (yield strength) and $d^{-1/2}$ (d is the spacing of grain boundaries) was plotted by Hall and Petch for ferrite steels [8] to obtain the so-called Hall-Petch relationship. In tempered martensitic steels a unique yield stress does not exist and usually yield stress is expressed in term of 0.2% proof stress. The smaller the width of grain boundary, the better the strength. The block and packet boundaries are high angle boundaries which act as barriers to the movement of dislocations during service [12] and are the most effective boundaries for strengthening. Thus, in order to understand how the strength of the steels changes as a result of microstructural evolution, it is important to investigate the evolution of block sizes and morphology with exposure to temperature and stress.

If the matrix has an equiaxed microstructure, it is relatively straightforward to determine an effective grain size by means of optical micrographs and/or scanning electron microscopy (SEM) images. However, it is not easy to reveal the effective grain size in high Cr steels by optical microscopy and SEM images (as shown in Chapter 5) owing to the complex structure of tempered martensite. EBSD has therefore been used as a tool to define the effective grain boundaries.

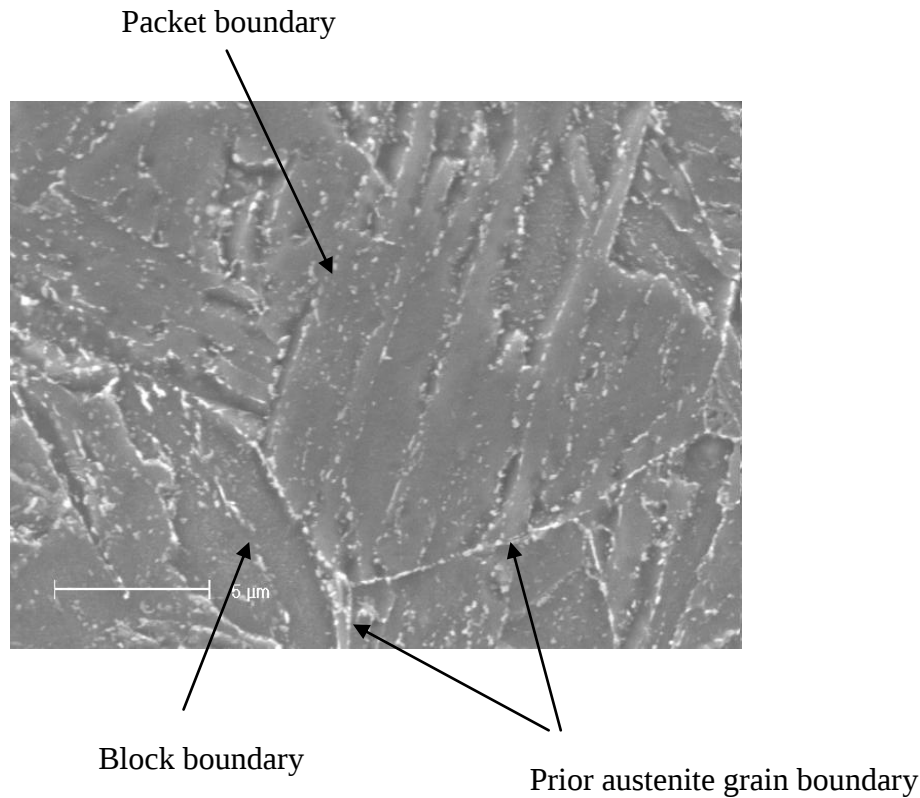


Figure 6.1. Martensitic structure including prior austenite boundaries, precipitate-decorated boundaries inside the block boundary are martensite lath boundaries [11].

6.2 Qualitative analysis of microstructural evolution

This section gives a qualitative analysis of how the microstructure evolves based on a description of the EBSD images obtained from the samples.

The samples investigated covered a full range of time and temperature durations both on the head and the gauge length regions of the E911 creep rupture specimens, examples of which are shown in Figure 6.2, Figure 6.3 and Figure 6.4. The figures show in a) AE+GB15, b) misorientation profiles along a straight line between A and B in (a), (c) BC map, (d) BC+GB2+GB15 maps. The detailed description of each of these is given below.

AE+GB15 maps (Figure 6.2 (a), 6.3 (a), 6.4 (a)) show grains that have been coloured using the “All-Euler” colouring scheme. The different colours correspond to the crystallographic orientation normal to the observed plane. GB15 refers to the fact that boundaries with misorientation angles greater than 15° are labelled in black. This represents the high angle

boundaries (block boundaries, packet boundaries or prior austenite grain boundaries). Thus the images show a map of different grain orientations and high angle boundaries.

Figures 6.2 (b), 6.3 (b), and 6.4 (b) show misorientation profiles taken along a line drawn in the maps shown in the corresponding (a) figures. Figure 6.2 (b) shows that for the as received sample, there are 7 misorientation peaks of $55\text{-}62.5^\circ$ representing the block boundaries across a distance of $12\text{ }\mu\text{m}$. The measured width of the blocks within this area in the region of $1.5\text{-}2\text{ }\mu\text{m}$. Inside the block, there are some discrete changes in the colour of orientation representing subgrain boundaries and martensitic lath boundaries shown in red (Figure 6.2 (d)). By contrast, from Figure 6.3 (b) on the 650°C 14319 hrs head, the measured width of block is in the region of $2\text{-}3\text{ }\mu\text{m}$ along the $12\text{ }\mu\text{m}$ length from point A to B.

It is noticeable that the measured width of blocks in Figure 6.4(b), from the gauge part of the specimen, is considerably larger than for the head part (Figure 6.3(b)), so the block width evolves more rapidly in the part of the specimen experiencing both strain and temperature.

BC maps (Figure 6.2 (c), Figure 6.3 (c), Figure 6.4 (c) are band contrast (image quality) maps, the band contrast map reflects the quality of the Kikuchi patterns for each measurement, so, if the grey-scale is dark, the image quality (Kikuchi line pattern) is poor in this area [13]. At the grain boundaries, it is difficult to obtain clear Kikuchi-line diffraction patterns, therefore, it is not surprising that along the grain boundaries, the grey-scale level is much darker than in other areas.

BC+GB2+GB15 maps (Figure 6.2 (d), Figure 6.3 (d), Figure 6.4 (d)) are band contrast maps with grain boundary information superimposed on the image. Areas with misorientation angles greater than 15° are labelled in black representing the high angle boundaries (as before). Boundaries with misorientation angles greater than 2° are labeled in red which represents low angle boundaries in the microstructure. This map shows that most of the high angle boundaries are completely defined by continuous black outlines, but many of the low angle boundaries appear to terminate in the middle of grains. This is discussed further in section 6.4.

These maps allow the changes in grain morphology and orientation to be determined as a function of stress and temperature. The quantitative evaluation of microstructural evolution is discussed in the following section.

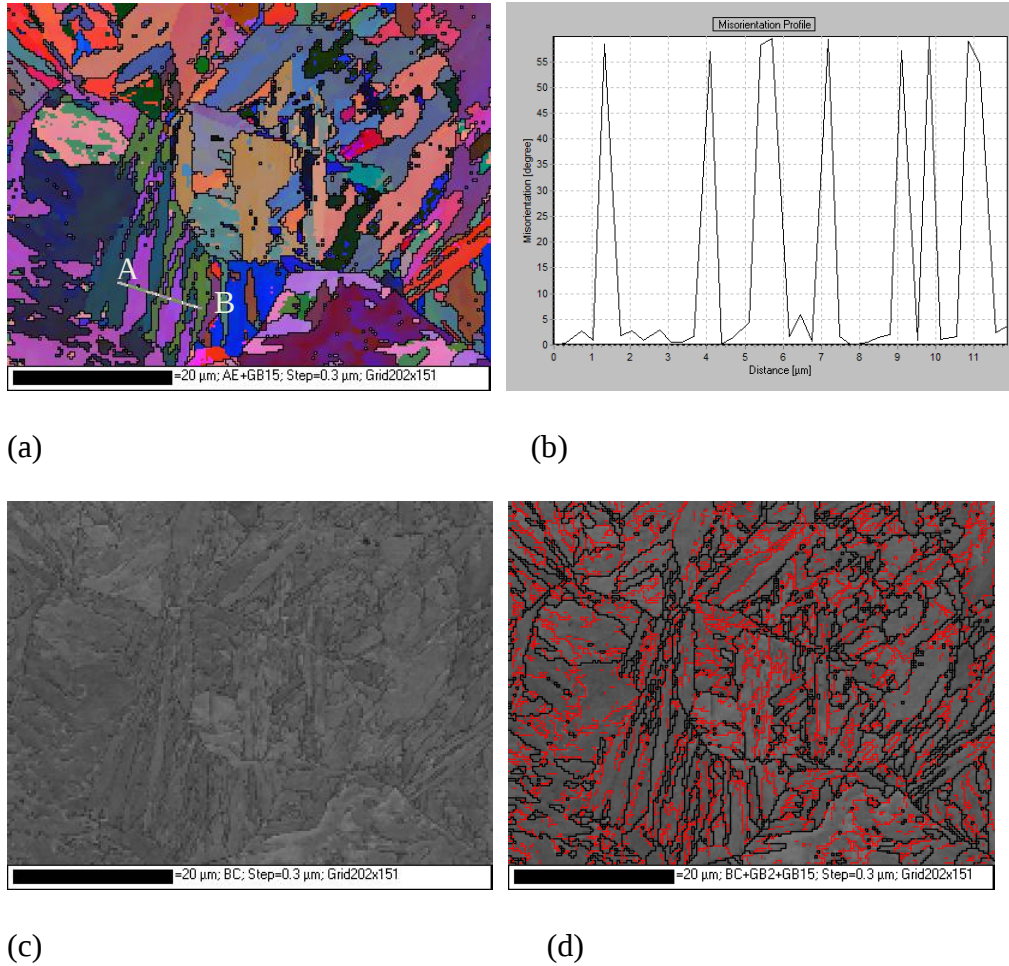
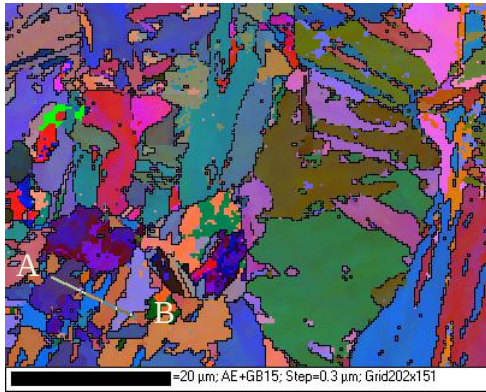
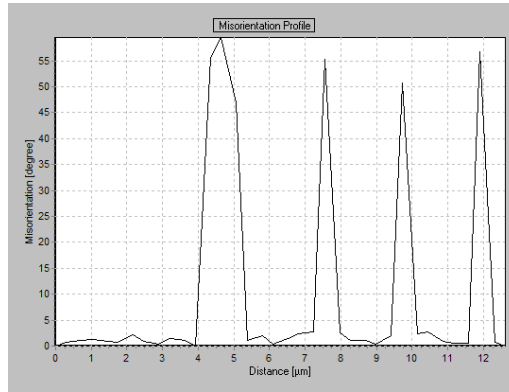


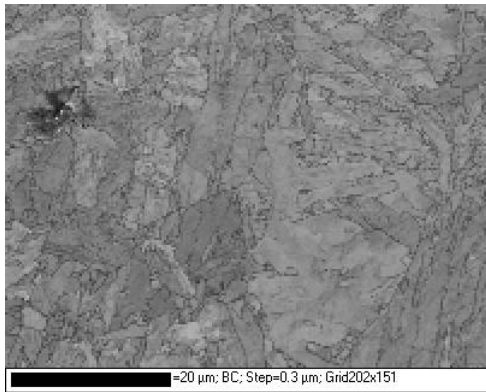
Figure 6.2. The EBSD map of an as received sample: (a) AE+GB15 map, (b) Misorientation profile along the straight line between A and B in (a), (c) BC map, (d) BC+GB2+GB15 map.



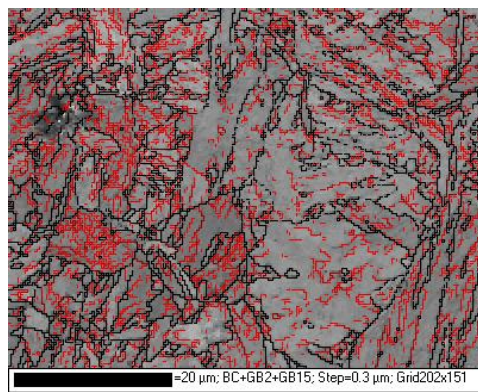
(a)



(b)



(c)



(d)

Figure 6.3. The EBSD map of 650°C 14319 hrs head: (a) AE+GB15 map, (b) Misorientation profile along the straight line between A and B in (a), (c) BC map, (d) BC+GB2+GB15 map.

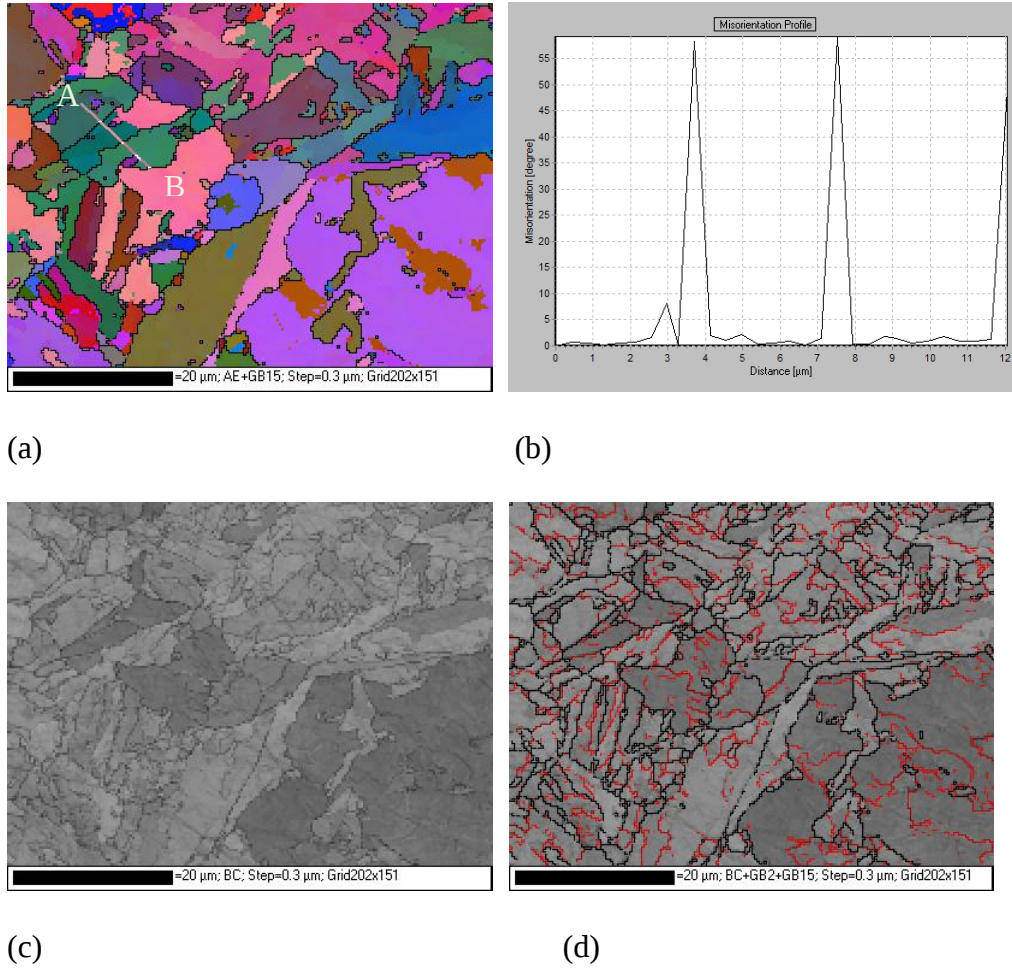


Figure 6.4. The EBSD map of 650°C 14319 hrs gauge: (a) AE+GB15 map, (b) Misorientation profile along the straight line between A and B in (a), (c) BC map, (d) BC+GB2+GB15 map.

6.3 Quantitative analysis of microstructure

EBSD has powerful advantages over optical micrographs and SEM images to quantify evolution of grain morphology in that the grains can be clearly distinguished and the software is amenable to easy quantification of the grain sizes.

In describing microstructure, conventionally, the equivalent circular diameter d_c has been used to quantify grain sizes [14]. However, the question for this research is how to measure the irregular block size of tempered martensitic steel since a circle does not adequately define a martensitic lath. The problem is illustrated schematically in Figure 6.5, which shows that a fitted ellipse shape resembles the irregular block much more successfully than the equivalent circular shape. From equation 6.1, the degree of elongation of the fitted ellipse shape was

characterised by the aspect ratio (major axis of fitted ellipse/minor axis of fitted ellipse); d_{mi} was regarded as a modified effective width of a block (high angle boundary grain) in this work.

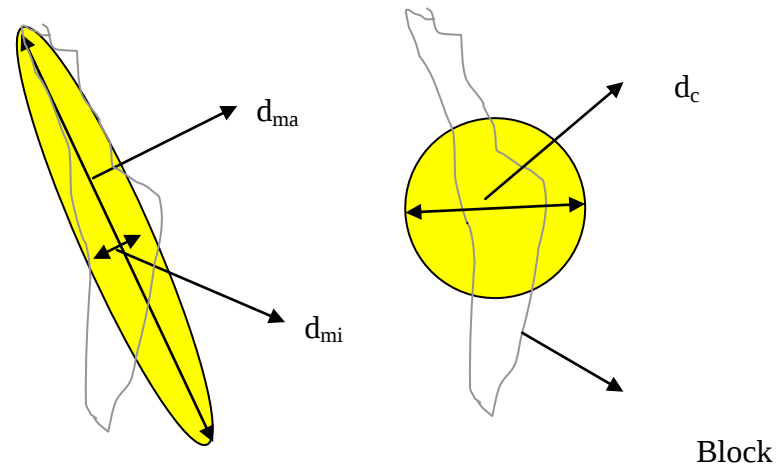


Figure 6.5. Block size measurement

$$k = d_{ma}/d_{mi} \quad (6.1)$$

k : Aspect ratio

d_{ma} : Major axis length of fitted ellipse

d_{mi} : Minor axis width of fitted ellipse

For practical purposes, when the block area $< 2 \mu\text{m}^2$, errors may arise from poor-quality EBSD patterns as a result of precipitates (such as M_{23}C_6 , Laves phase, Z phase or M_2X phase) or other inhomogeneities, which because they are so numerous, tend to bias the results. Thus, it was necessary to exclude the block areas with an area below $2 \mu\text{m}^2$ from calculation. High angle grains with just 0, 1 or 2 neighbouring grains can be regarded as artefacts and therefore these high angle grains were also excluded from calculation. After automatic grain detection through the proprietary HKL CHANEL 5 and EXCEL software packages and the elimination of artefacts, the distribution of the width of the minor axis of blocks and the aspect ratio of blocks against the grid position (labelled as distance (grid) as it represents the distance across the EBSD map as a function of step size) are shown as Figures

6.6-6.9. Each of the graphs below typically represents the analysis of 100 to 300 blocks for each sample. This gave reasonable statistics for each sample. It would have been possible to refine the counting statistics with additional maps but the results are a compromise between accuracy and available time for analysing the large number of samples studied in this thesis as EBSD mapping is time consuming.

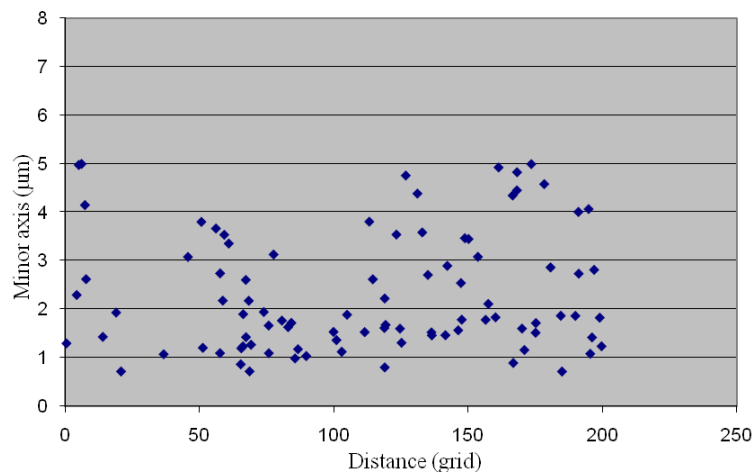


Figure 6.6. Minor axis of blocks along scanned distance of the as-received sample.

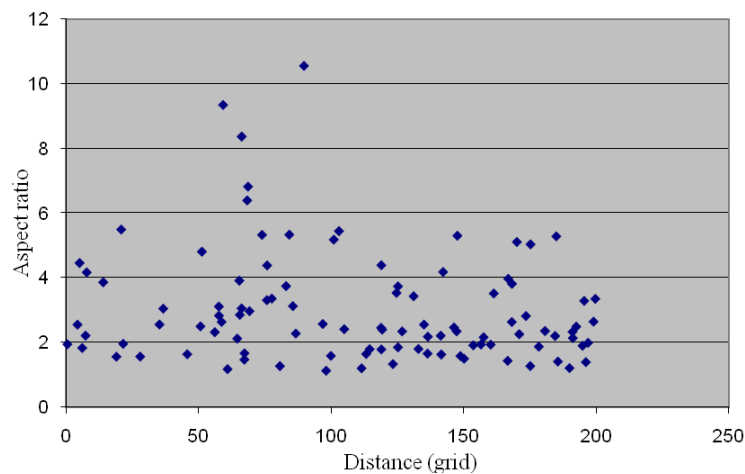


Figure 6.7. Aspect ratio of blocks along scanned distance of the as-received sample.

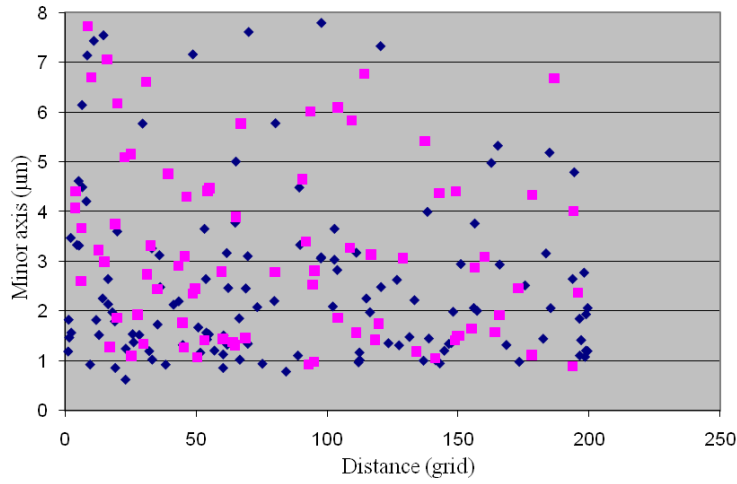


Figure 6.8. Minor axis of blocks along scanned distance on the sample of 650°C 14319 hrs: blue represents the minor axis width in the head part of the sample and red represents minor axis width in the gauge part of the sample.

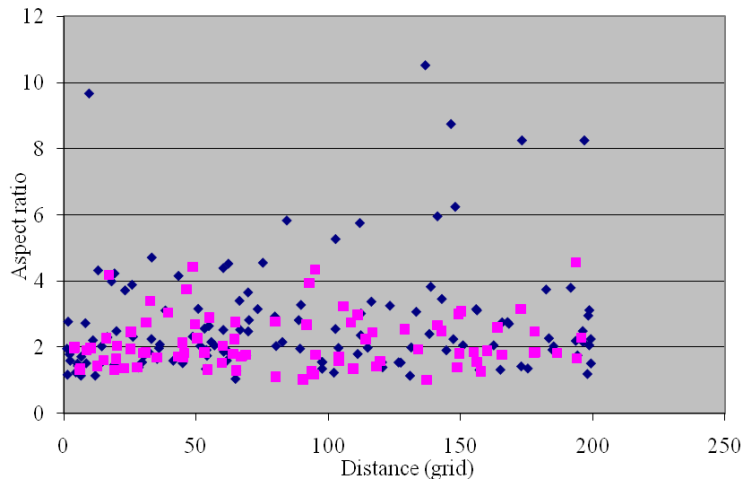


Figure 6.9 Aspect ratio of blocks along scanned distance on the sample of 650°C 14319 hrs: blue represents the minor axis width in the head part of the sample and red represents minor axis width in the gauge part of the sample.

The average value of the minor axis of the blocks of as-received, 650°C 14319 hrs head and 650°C 14319 hrs gauge are $2.3 \pm 1.2 \mu\text{m}$, $2.7 \pm 1.7 \mu\text{m}$, $3.2 \pm 1.8 \mu\text{m}$ respectively, although a large scatter was observed in the block size. The average aspect ratio of the blocks also were calculated to be $3.0 \pm 1.7 \mu\text{m}$, $2.8 \pm 1.9 \mu\text{m}$, $2.1 \pm 0.8 \mu\text{m}$ respectively, indicating that the degree of elongation of fitted ellipse shape gradually decreased due to exposure to temperature and stress.

The width of the minor axis of the fitted ellipse was regarded as representative of the block width. In order to represent how block width changes as a function of stress and temperature, the block width has been plotted as a function of Larson-Miller parameter (see Figure 6.10). These appear to be a general trend for an increase in block width with increase in LMP but the standard deviations are large. The block width increases slowly for the head part of the samples where there are thermal effects only. By contrast, for the gauge part the block widening is greater when both temperature and creep strain are acting on the sample.

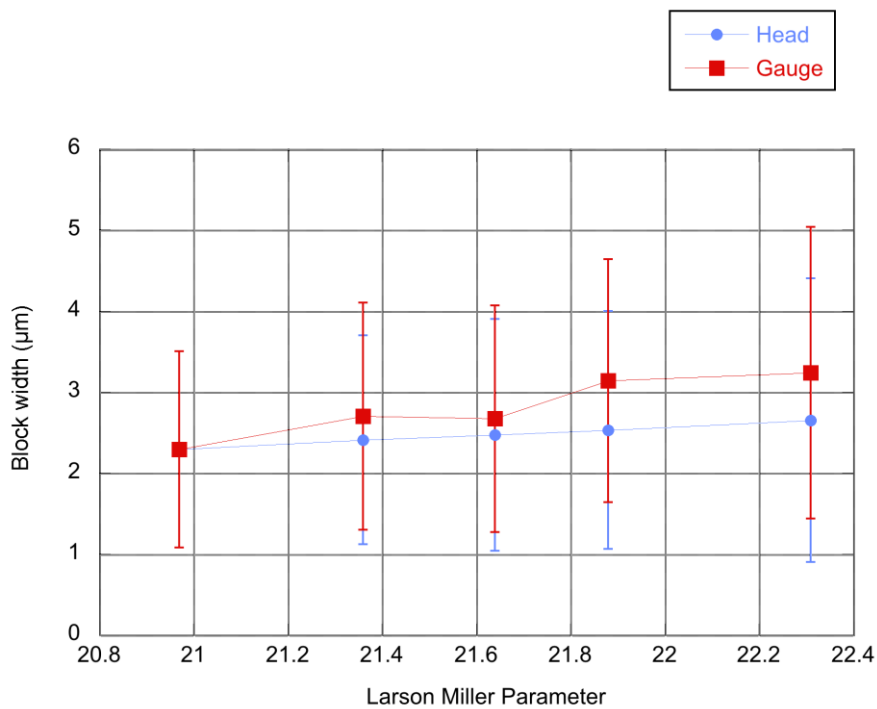


Figure 6.10. The width of the block versus Larson-Miller parameter

6.4 Subgrain nucleation and growth

Initially, martensite laths formed after quenching within a prior austenite grain boundary are elongated single crystals with a high density of dislocations. After tempering, and then exposure to temperature and strain, the defined texture has been changed, and more and more subgrains were formed in a block within the matrix.

In order to view the subgrain evolution in detail, a higher magnification EBSD map of 6000x magnification with step size of 0.05 μm was obtained. The results are shown in Figure 6.11.

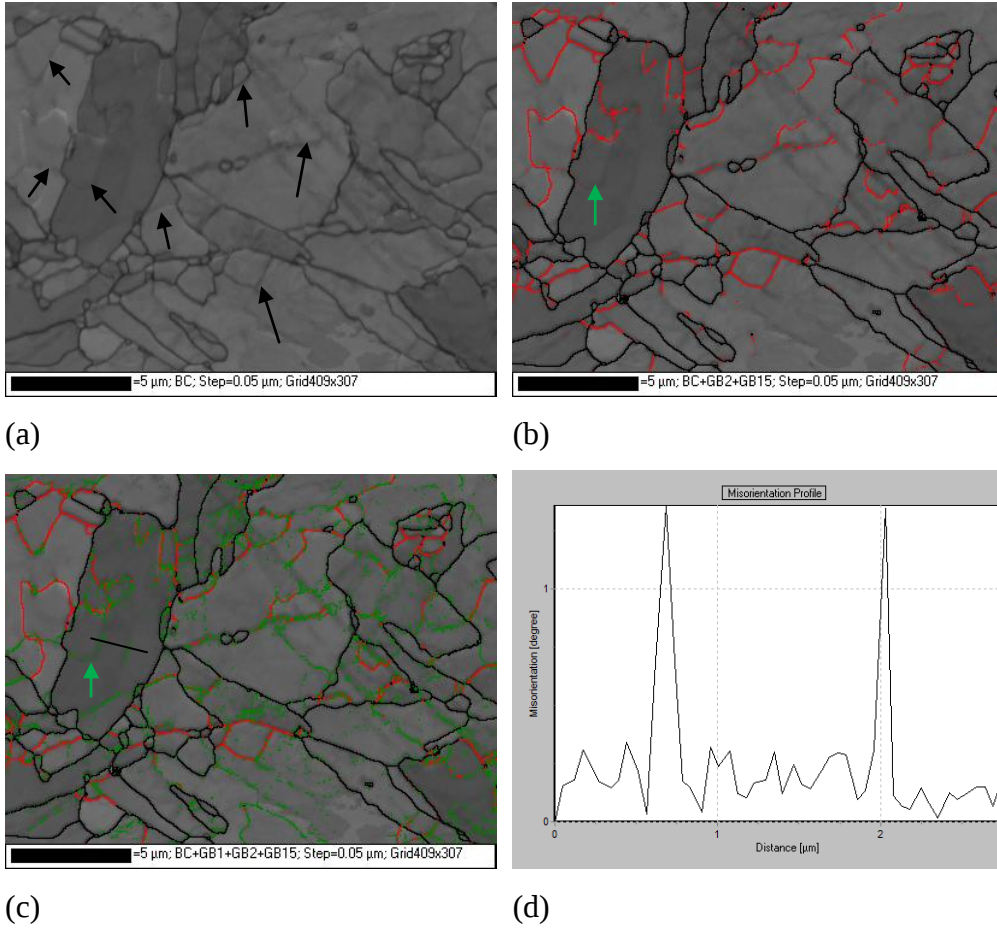


Figure 6.11. Higher magnification EBSD map of 650°C 849 hrs gauge: (a) BC map, (b) BC+GB2+GB15 map, (c) BC+GB1+GB2+GB15 map, (d) Misorientation profile along the straight line in (C).

The band contrast (BC) map of Figure 6.11 (a) was used to view image quality of EBSD, the poorer image quality arises from the grain boundaries, which means that the higher the misorientation angle, the darker the grey-scale degree. Some subgrains (shown by several arrows) seemed to have nucleated and grown along block boundaries. The boundaries in Figure 6.11 (b) were drawn to show high/low angle boundaries, while some subgrain (red line) boundaries are enclosed, others are discontinued or terminated in the matrix which indicated that they are possibly not visible on the plane that was sectioned for these samples, for example, a green arrow indicates a discontinued subgrain in Figure 6.11 (b). In Figure 6.11 (c), a misorientation angle greater than 1° (green lines) was added in the boundary classification process, the subgrain indicated by a green arrow would be enclosed. Therefore, the cut off angle criterion has a significant impact on the subgrain characterization, especially in the process of formation of subgrains.

In order to observe subgrain growth, the sample of 650°C 14319 hrs gauge length at 10,000 magnification was imaged using a step size of 0.1 μm (see Figure 6.12). This magnification allows the subgrain shape and size to be clearly seen but has the disadvantage that not many subgrains are analysed (as compared to lower magnification). However, EBSD analysis of subgrain size has the advantage that it does not rely on TEM thin foil preparation. The subgrain sizes in Figure 6.12 are typically 2-4 μm but some grains are < 1 μm .

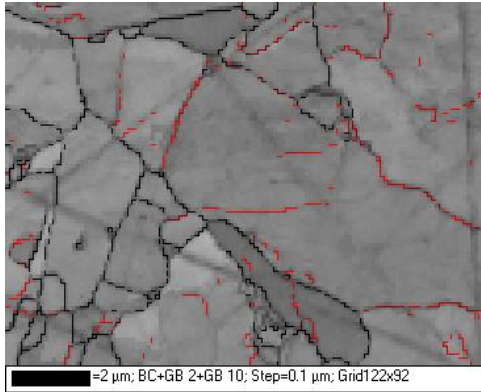


Figure 6.12. EBSD map of sample exposed at 650°C for 14319 hrs (gauge part).

For the 650°C samples, after 10,000 hours, all of the martensitic laths have been completely transformed to subgrains. This change has previously been demonstrated by TEM examinations on thin foils [15].

Since the size of a subgrain is not a constant value, the fluctuation of subgrain size on the samples should be taken into account. In order to minimise the influence of data scattering, a moving average approach has been used following the methodology of Mingard *et al* [14]. The moving average has been calculated using 12 subgrains (which was chosen based on the scan size and the subgrain size) and is used to show the variation in subgrain size between the head samples and the gauge samples across the width of the grid i.e. 202 grid positions which is equivalent to a distance of 60 μm across the sample. The results are shown in Figure 6.13 which shows a comparison between the head (pink) and gauge (blue) of the sample exposed at 650°C 14319 hrs. For this plot, the subgrain diameter was obtained using the circle equivalent diameter method which is justified since the subgrains are almost equiaxed at this exposure time (rather than the previous approach at lower magnifications for investigating changes in lath morphology). The average subgrain diameter was 0.96 μm for the head and

for the gauge length it was 1.31 μm . The subgrain size is therefore greater following exposure to strain and temperature rather than temperature alone.

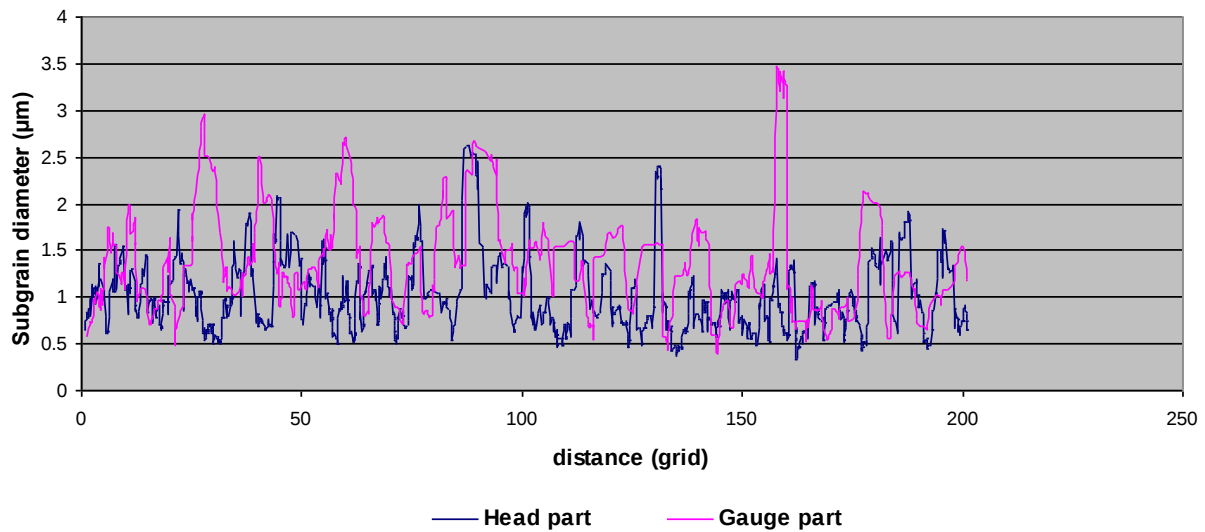


Figure 6.13. Subgrain size measurement across a length of 202 grids on the sample exposed to 650°C for 14319 hrs.

6.5 The evolution of high angle boundaries and low angle boundaries

In order to calculate the changes of high angle boundaries and low angle boundaries, the misorientation distribution data was obtained on all of the EBSD maps. The plots were initially obtained in the form shown in Figure 6.14 which shows the relative frequency against the misorientation angle.

These plots show that there were changes in the low angle (defined as less than 15°) to high angle ratios. For the sample analyzed in Figure 6.14, which had been exposed to a temperature of 650°C and failed after 4530 hours, it can be seen that there are a high proportion of low angle boundaries at up to 5° degrees misorientation followed by a smaller significant peak centred at 57.5°. All the plots obtained show distinct peaks at low angles and high angles but the relative ratios of these peaks changed as a function of creep exposure time and temperature. Figure 6.15, Figure 6.16 and Figure 6.17 show the low angle to high angle ratio as a function of Larson-Miller parameter at three levels of temperature.

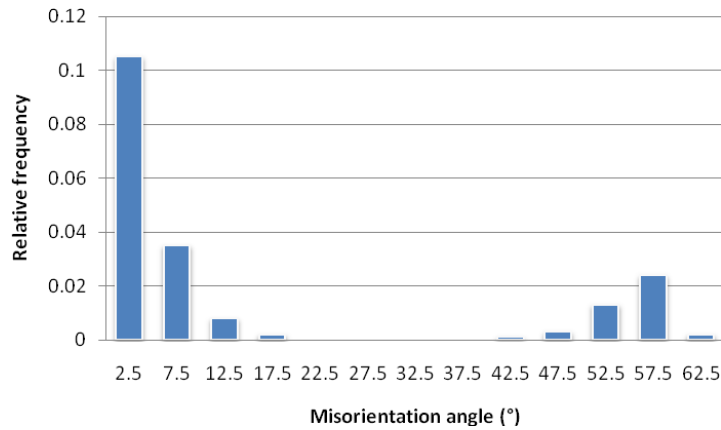


Figure 6.14. The Relative Frequency versus misorientation angle on the sample of 650°C 4530 hrs head.

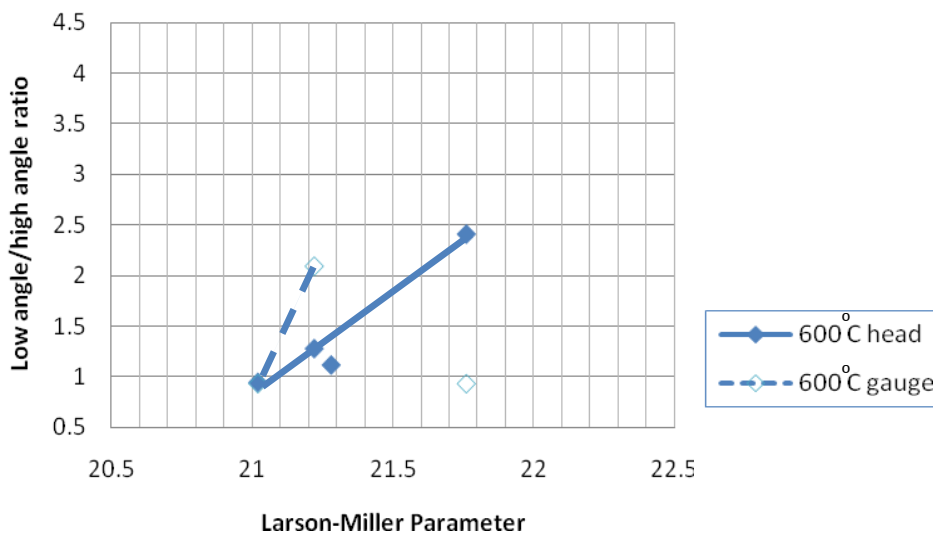


Figure 6.15. Low angle/high angle ratio versus LMP at a service temperature of 600°C (the gauge part of 600°C 13336 hrs sample is too short and therefore the data was eliminated from the analysis).

Figure 6.15 shows that at the temperature of 600°C, the low angle/ high angle ratio for the head increased whilst that for the gauge remained constant with some fluctuation.

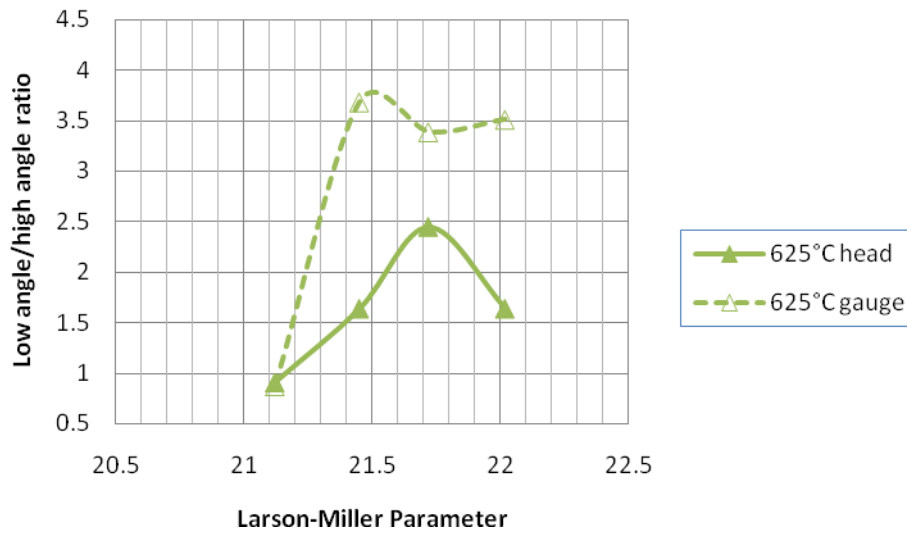


Figure 6.16. Low angle/high angle ratio versus LMP at a service temperature of 625°C.

Figure 6.16 shows that at 625°C, the ratio increases significantly for the gauge, whilst the head rises and then falls for the longest exposure duration.

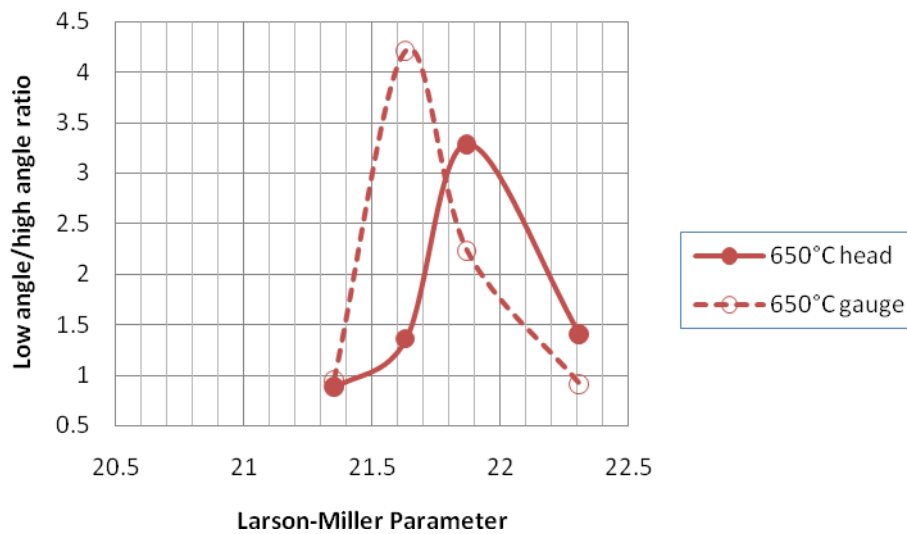


Figure 6.17. Low angle/high angle ratio versus LMP at a service temperature of 650°C.

At 650°C, there is a marked increase in the low angle/high angle ratio in the gauge and a significant increase in the head. However, due to the rapid growth of subgrains, at 650°C, a sharp drop in the low angle/high angle ratio was found on the sample of 650°C 14319 hrs

head and gauge. This is associated with softening of the tempered martensitic matrix under the influence of temperature and creep strain.

6.6 Summary

EBSID has been used to characterise the grain morphology evolution and crystallography changes of this steel. The fitted Ellipse shape was employed to describe the irregular block morphology. The qualitative and quantitative analysis shows that the width of the block (with a high angle boundary) inside a prior austenite grain increases more rapidly in the gauge length than in the head although there is some overlap in the error bars. The aspect ratio decreased with exposure to stress and temperature. The nucleation site of subgrains (low angle boundaries) during service was along the block boundary; the subgrain growth process has been accelerated at the gauge part. These morphology changes contribute to the degradation of the mechanical properties in service.

6.7 References

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Chapter 7 Analysis of precipitates in E911 steel by TEM

E911 steel was developed in the European COST programme [1, 2] for power generation plant boiler, pipe and tube applications in steam driven power generation plant [3]. The creep strength is attributed to the long term stability of the precipitates in the structure. There have been a number of reports on the precipitation behaviour of 9-12% Cr steels but there has not been a systematic study of precipitate evolution in creep exposed E911 at 600, 625 and 650°C which are the temperatures particularly relevant to power plant operation. This chapter reports on the distribution, chemical composition and size evolution of Laves phase, $M_{23}C_6$ phase, M_2X phase and Z phase in E911 samples creep exposed to temperatures of 600, 625 and 650°C.

7.1 Introduction to the analysis of precipitates in 9-12% Cr steel

E911 steel is strengthened by both solid solution and precipitation strengthening mechanisms with Cr, Mo and W primarily contributing to solid solution strengthening and other elements Nb, V and N contributing to the formation of precipitates which act to improve strength and limit grain size. In the normalised and tempered condition, $M_{23}C_6$ precipitates occur on the prior austenite and martensite lath boundaries together with finer V and Nb rich carbonitrides precipitated within the grains (M_2X and MX type precipitates). At the lath boundaries, the $M_{23}C_6$ particles are typically 0.10-0.17 μm in size and the precipitates pin the grain boundaries and help to maintain a high dislocation density and stabilise the microstructure. At high temperatures, the $M_{23}C_6$ precipitates coarsen due to Oswald ripening thus reducing grain boundary pinning which leads to recovery and grain growth with corresponding reductions in dislocation densities. The other main precipitates, which have the greatest effect on precipitation strengthening, are typically fine (<0.1 μm) VN and NbC (MX) type particles. The strength is maximised by ensuring that V and N are stoichiometrically balanced; this balancing is influenced by the presence of secondary chromium, iron and niobium in the precipitates. The VN precipitates have been found to be stable in size over long periods at 600°C and 650°C although over time Laves phase forms between 600 and 700°C which removes W and Mo from the solid solution. When Laves phase grows in service, it evolves to large particles (0.5-1 μm) and gives no additional strength and can decrease ductility [4, 5].

The presence of Z phase precipitates in a number of different 9% Cr steels at 600°C has been investigated by Sawada et al. [6]. Danielsen and Hald [7] showed that Cr has a strong influence on the precipitation of Z phase with higher Cr contents allowing Z phase to be formed more rapidly while the work by Vodarek and Strang [8] has shown that Ni contents have a role in the precipitation of Z-phase. Vodarek and Strang [8] also showed that Z-phase was precipitated on primary NbC precipitates suggesting that niobium is important for Z-phase nucleation. This has been further confirmed more recently by Golpayegani et al. [9]. Z phase is a large particle which does not contribute to precipitation strengthening. The formation of Z phase in E911 is low. In E911 steel, when the Laves phase is precipitated at shorter creep durations, the initial effect is to provide higher creep resistance since the total volume fraction of the secondary phase rises and this can contribute to precipitation strengthening. At longer creep durations, the beneficial effect of Laves phase is reduced by particle coarsening.

The role of M_2X phase evolution was investigated by Chilukuru et al. [10] who found that M_2X phase coarsens much faster than VX, forming large M_2X precipitates at subgrain boundaries at the expense of the M_2X precipitates in the subgrain interior. This reduces the effect of precipitation hardening of the subgrain interior.

7.2 Phase Identification in E911 Steel

The typical chemical compositions of the phases that are responsible for strengthening in E911 are discussed below. It should be noted that EDX only provides a chemical signature which can be used to confirm the phase is present after it has been identified by electron diffraction.

7.2.1 $M_{23}C_6$

A typical EDX spectrum of a particle of $M_{23}C_6$ is shown in Figure 7.1. $M_{23}C_6$ is a Cr rich phase. In high Cr steels, the Cr content of this phase is in the region 60-80 % by weight while Fe content is around 20%, W, Mo and V have also been found in $M_{23}C_6$ particles in E911. The composition of $M_{23}C_6$ in 9-10%Cr steels changes as a function of time and

temperature of exposure. This provides a useful means of estimating average service temperatures for these steels given knowledge of the actual exposure time.

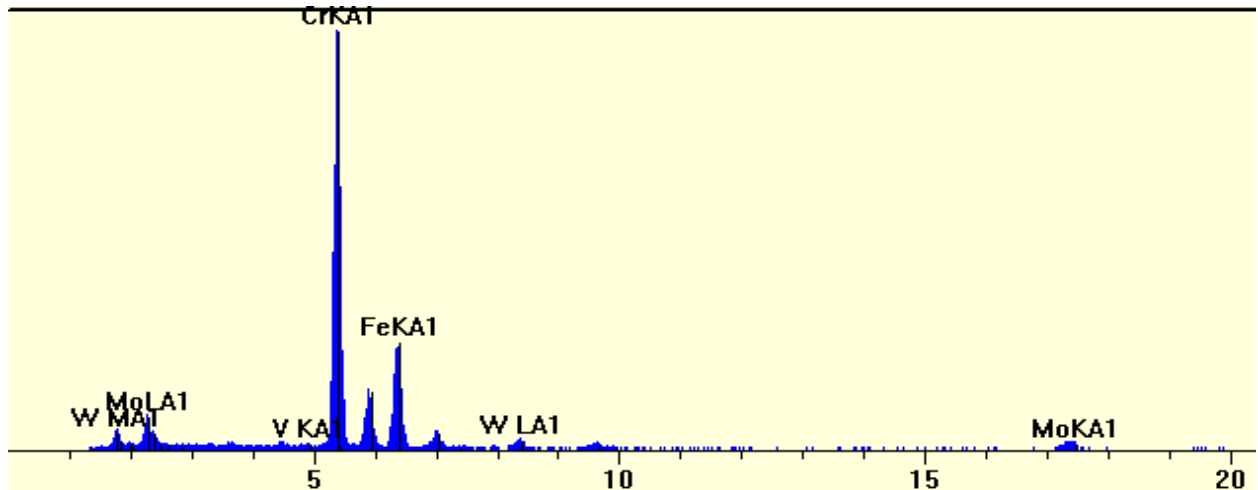


Figure 7.1. EDX spectrum of $M_{23}C_6$ phase

7.2.2 Laves phase

In E911 steel, Laves phase particles usually have the composition $(Fe, Cr)_2(W, Mo)$ [11]. The combined content of Fe and Cr should be 66 at%, and W and Mo should be 33 at%. In practice, a 5 at% deviation from these values is acceptable because of variations in particle thickness and EDX system calibrations. Figure 7.2 shows a typical EDX spectrum of a Laves phase particle in E911 steel.

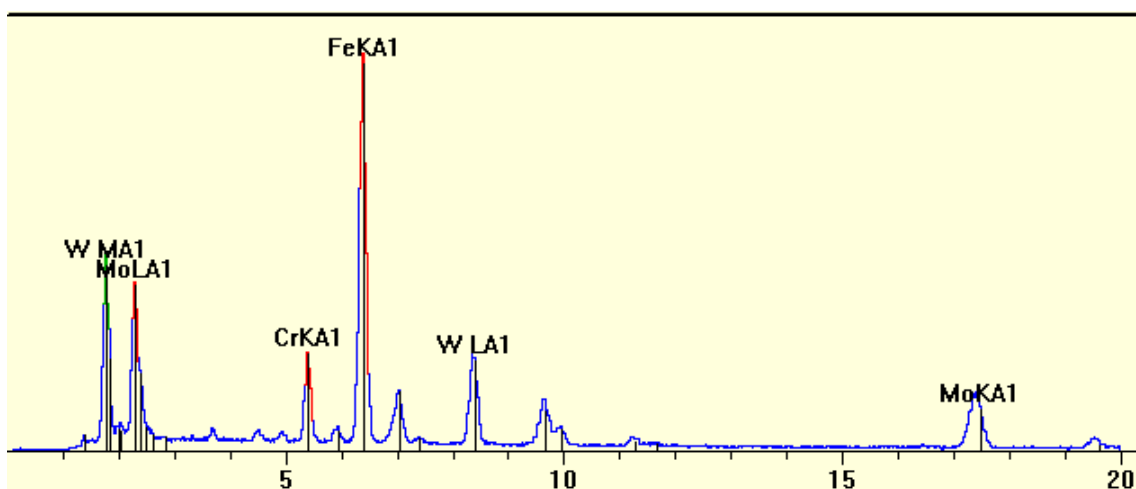


Figure 7.2. EDX spectrum of Laves phase

Table 7.1 shows that for this particle, the combined content of Cr and Fe is 68.09 at%, the content of Mo and W are 31.90 at% and therefore we can correctly identify this particle as Laves phase.

Table 7.1. Element analysis of Laves phase

Element	Line	KeV	CL Ratio	Wt%	At%
Cr	KA1	5.414	1.2000	7.24	10.72
Fe	KA1	6.403	1.3500	41.60	57.37
Mo	LA1	2.293	2.6330	27.28	21.90
W	MA1	1.774	2.3800	23.88	10.00
Total			0.0000	100.00	100.00

7.2.3 MX phase

Primary MX (PMX) is a particulate phase that does not completely dissolve in the austenisation process and is usually spheroidal in appearance. The MX particles persist in the microstructure after solution treatment and tempering. Primary MX is a Nb rich phase with a Nb content of more than 60% by weight. A typical EDX spectrum of a primary MX particle is shown as Figure 7.3.

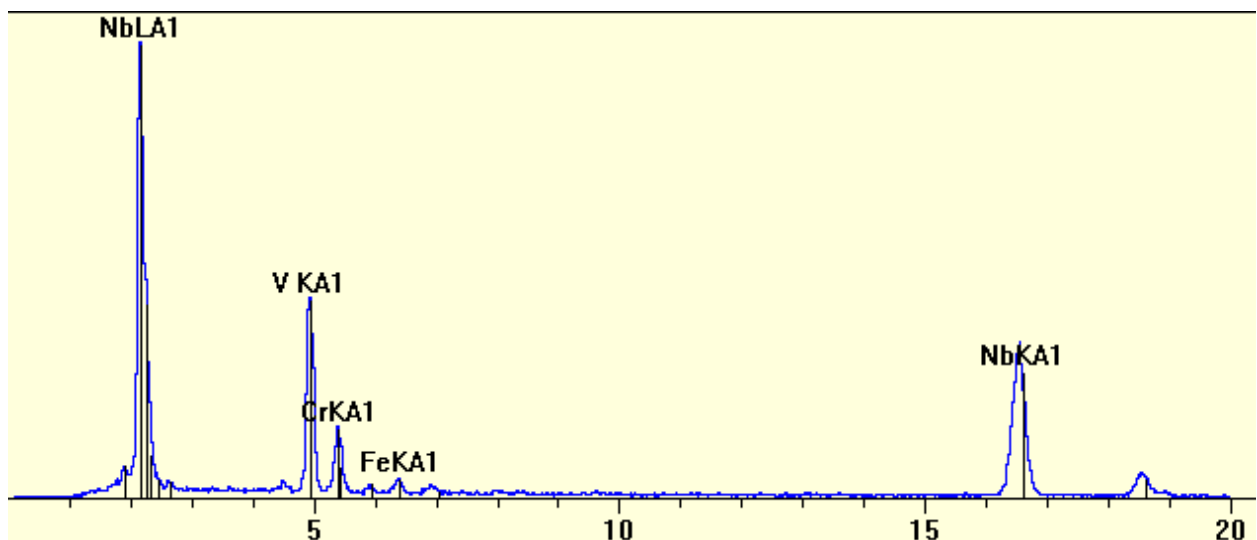


Figure 7.3. EDX spectrum of primary MX phase

Secondary MX phase particles appear after solution treatment and tempering. Secondary MX phase particles are V rich (usually the V content by weight is more than 60%) and can have the composition (V,Nb)(C,N). The Cr content is typically greater than 10 wt %. A typical EDX spectrum is shown in Figure 7.4.

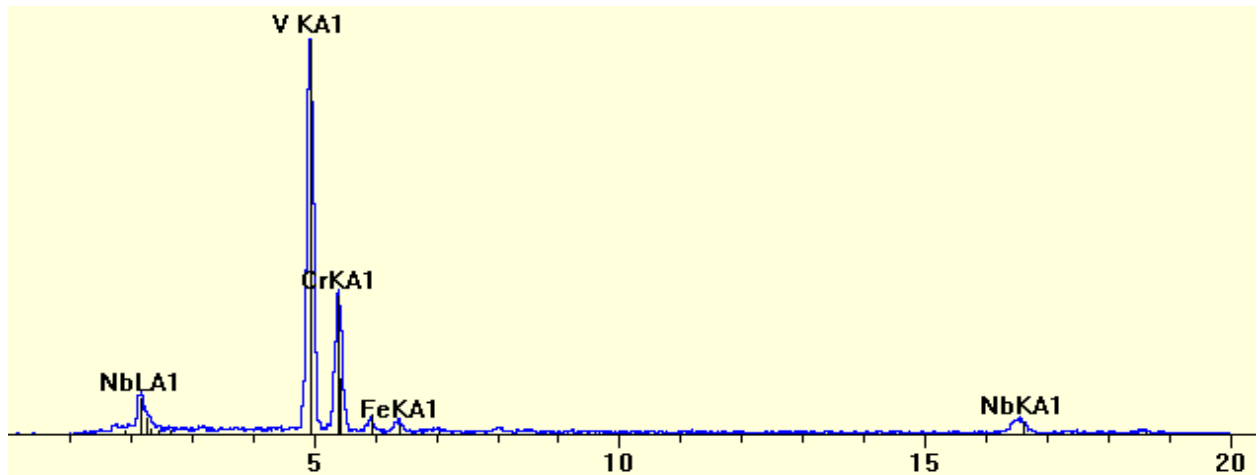


Figure7.4. EDX spectrum of MX phase

7.2.4 M_2X phase

M_2X phase particles are distinctly different from the $M_{23}C_6$ phase particles as can be seen from the EDX spectrum (Figure 7.5). The composition can be Cr_2N or $(Cr,V,Nb)_2(N,C)$. Both $M_{23}C_6$ particles and M_2X particles are Cr rich but M_2X particles have a much higher V content (~ 20 wt % in M_2X phase) than $M_{23}C_6$ particles.

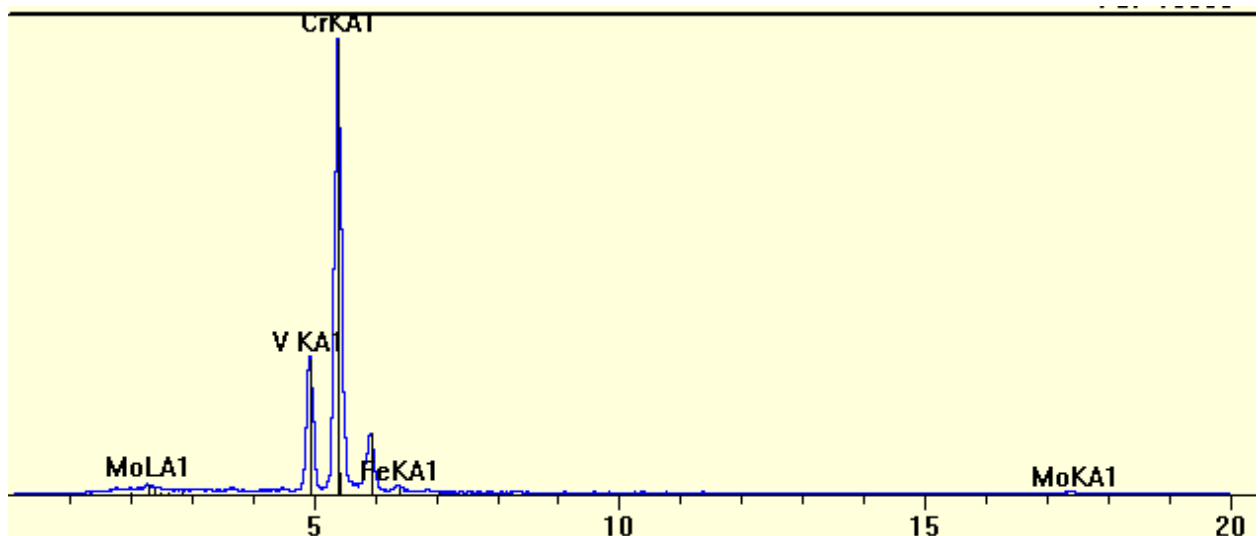


Figure 7.5. EDX spectrum of M_2X phase

7.2.5 Z phase

Z phase is a nitride phase and is usually scarce within E911 samples. The formula of Z phase is (Cr,Fe,V,Nb) N as shown in Chapter 1. If the content of Cr and Fe is 50 at% and the percentage of V and Nb is 50 at%, the particles can be correctly identified as Z phase. The spectrum is given in Figure 7.14 (b).

The following sections use this understanding of the composition of the different phase particles to identify the precipitates in as-received, solution treated and creep exposed E911 samples.

7.3 As received sample

The as-received E911 sample showed a characteristic tempered martensitic microstructure with a dispersion of $M_{23}C_6$ precipitates at prior austenite and martensite lath boundaries. Fine M_2X and MX carbonitride precipitates (e.g. NbC and VN type) were also observed within the laths by TEM. The hardness of the as-received sample was measured to be $269 \text{ VHN} \pm 2.4 \text{ VHN}$. The average size of the prior-austenite grains was found to be $20.2 \mu\text{m}$. Figure 7.6 (a) shows the typical precipitate distribution for the as-received sample and Figure 7.6 (b) shows a corresponding selected area diffraction pattern for one of the $M_{23}C_6$ particles.

For the ‘as-received’ sample, the majority of the precipitates observed are $M_{23}C_6$, MX and M_2X phase. Occasionally, primary MX phase particles were identified. No Laves phase was present. The mean size of M_2X particles is $166 \pm 10 \text{ nm}$ in length, $60 \pm 6 \text{ nm}$ in width. The MX particles are $< 100 \text{ nm}$ in size.

7.4 Solution treated E911 sample

In order to see which particles are present in the sample after solution treatment but before tempering, a sample was heated to 1100°C for 0.5 hour and then cooled in air. A carbon extraction replica was then examined to see which particles were present. A typical TEM micrograph of the structure is shown in Figure 7.7. All of the precipitates were dissolved in the austenisation process except for the primary MX phase which demonstrates that the

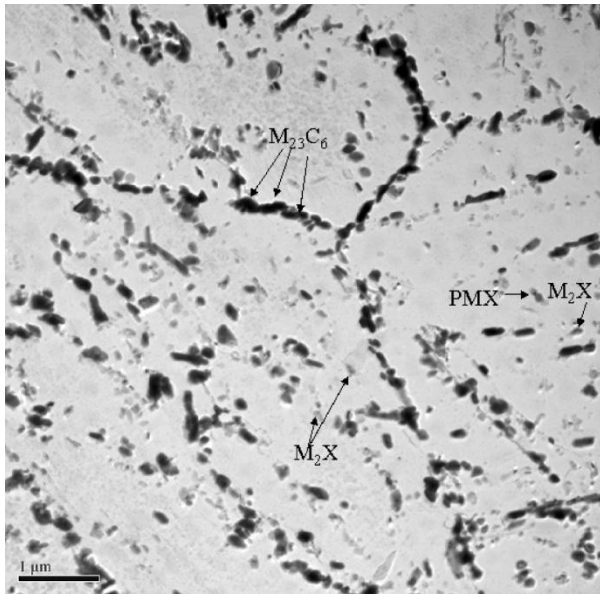


Figure 7.6 (a): TEM micrograph of the precipitate distribution in the ‘as-received’ solution treated and tempered E911.

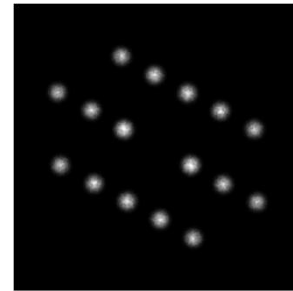


Figure 7.6 (b): Selected area diffraction pattern of an $M_{23}C_6$ particle (inverted image). Zone axis $[112]$

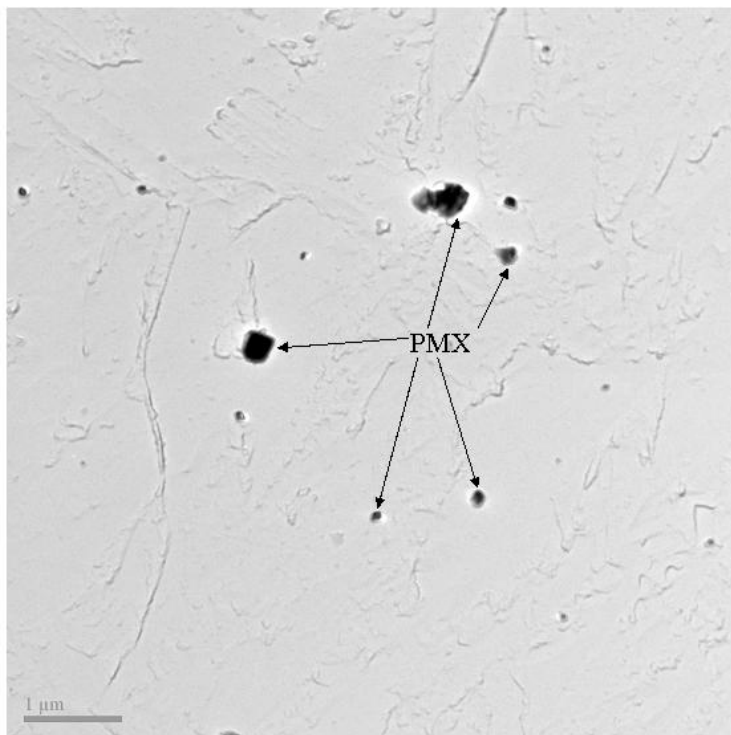


Figure 7.7. A carbon replica on re-solution treated sample

tempering treatment is responsible for developing the precipitates of $M_{23}C_6$ and secondary MX phase.

The following sections show the results of the analysis of precipitates in the creep exposed samples.

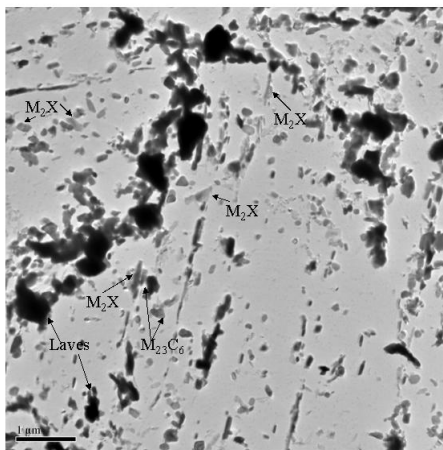
7.5 Creep exposed microstructures

The size and morphology of the precipitates forming in the creep exposed samples have been investigated using transmission electron microscopy on carbon extraction replicas.

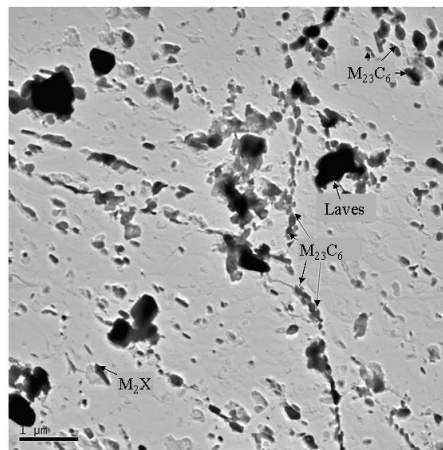
7.5.1 Precipitate distribution

Figure 7.8 shows bright field TEM carbon extraction replicas from the head parts of the specimens that were creep exposed to differing durations at 600, 625 and 650°C. Figure 7.8 (a) shows Laves phase particles distributed along prior austenite grain boundaries and packet boundaries. M_2X and $M_{23}C_6$ particles were distributed along the lath boundaries, packet boundaries and prior austenite grain boundaries. This specimen was exposed to the lowest temperature for a short duration and Laves phase has appeared even after this short time. Figure 7.8 (b) shows a replica from a specimen exposed at 600°C for 75647 hours. The Laves phase particles have coarsened from the particles seen in Figure 7.8 (a). Figures 7.8 (c) and (d) show specimens exposed at 625°C. Again Laves phase is present in both the short duration and longer duration samples. Figures 7.8 (e) and 7.8 (f) show TEM micrographs of the specimens exposed at 650°C. It is noticeable that the density of small particles in the replicas is much reduced as compared to Figures 7.8 (a)-(d) and this accounts for the reduction in hardness that was seen in Figure 4.1 as the precipitates no longer pin dislocations in the structure.

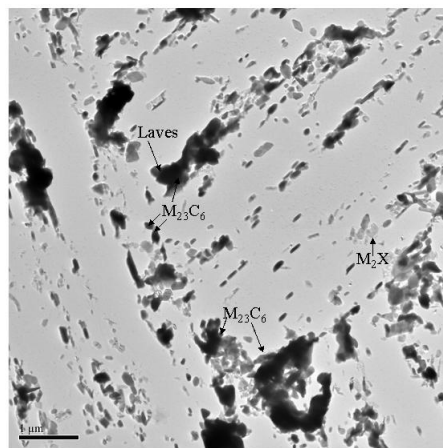
TEM micrographs of the typical precipitate evolution in the gauge are shown in Figure 7.9 (a)-(f). Similar particle distributions were found in the gauges to the heads but particle sizes were larger and coarsening occurred to a greater extent.



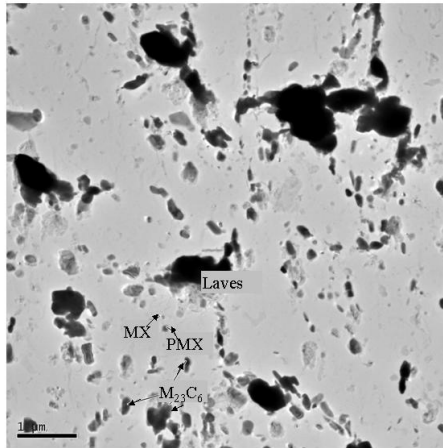
(a) 600°C 9800 hrs head



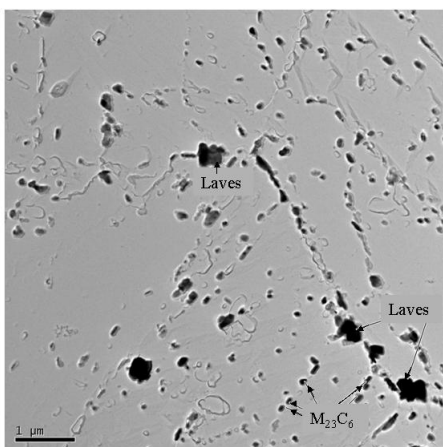
(b) 600°C 75647 hrs head



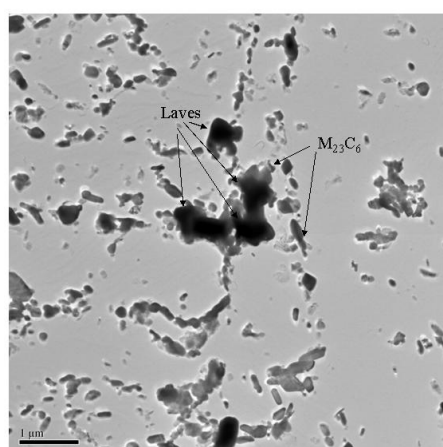
(c) 625°C 1132 hrs head



(d) 625°C 31198 hrs head

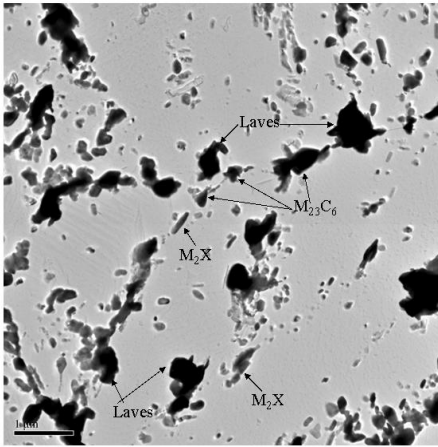


(e) 650°C 849 hrs head

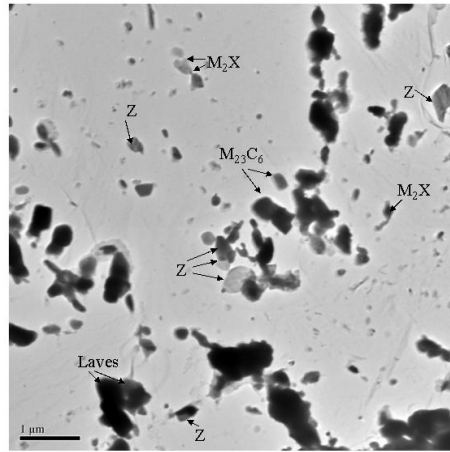


(f) 650°C 14319 hrs head

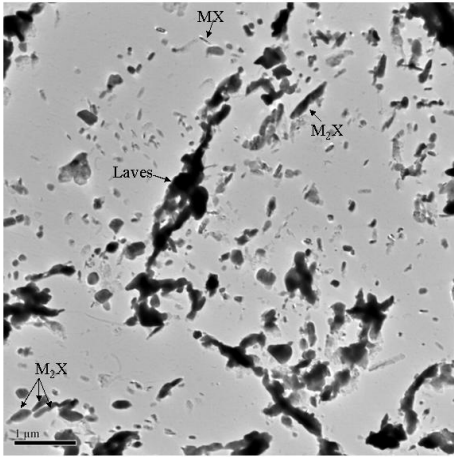
Figure 7.8 TEM micrographs showing the precipitate distribution in the head part of the various creep exposed samples.



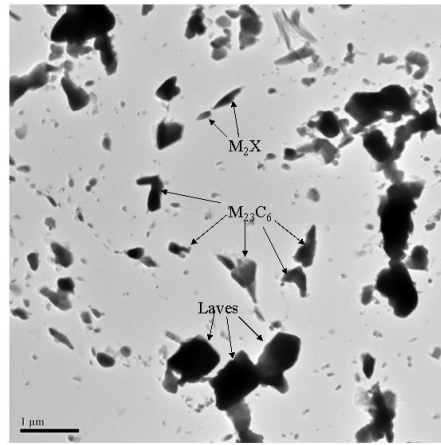
(a) 600°C 9800 hrs gauge



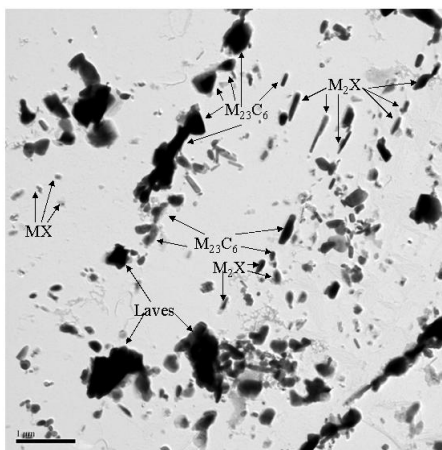
(b) 600°C 75647 hrs gauge



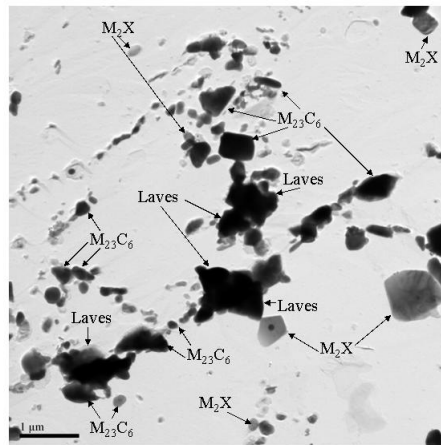
(c) 625°C 1132 hrs gauge



(d) 625°C 31198 hrs gauge



(e) 650°C 849 hrs gauge

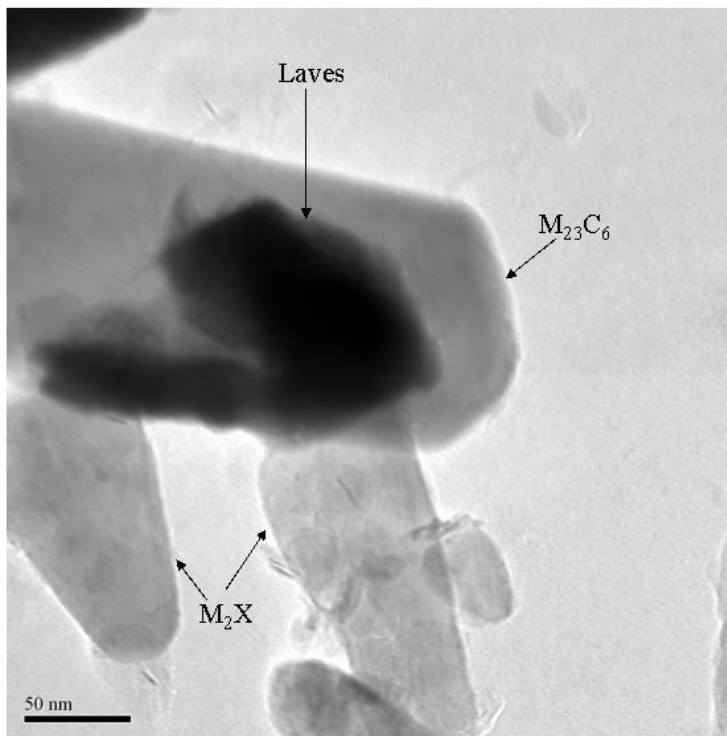


(f) 650°C 14319 hrs gauge

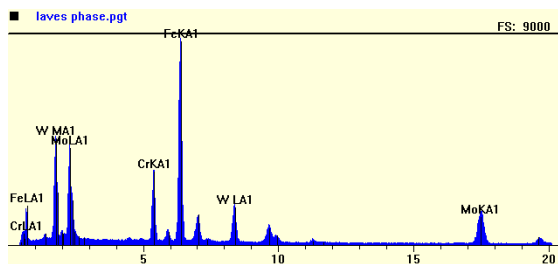
Figure 7.9 TEM micrographs showing the precipitate distribution in the gauge part of the various creep exposed samples.

7.5.2 Laves phase

In the as received condition, no Laves phase (Figure 7.7) was present. However, Laves phase was found in the head part of the shortest exposure duration sample exposed for 1614 hours at 600°C. Laves phase has grown on the site of $M_{23}C_6$ particles as shown in Figure 7.10. TEM images of samples taken from the head part of the sample exposed at 625°C for 1131 hrs show the same effect (see Figure 7.11). The Laves phase particles at these creep exposures are small in size and the degradation in hardness seen for these samples is not too great (the hardness of the two samples are 264 and 250 VHN as compared to 269VHN for the as-received sample).



(a)



(b)

Figure 7.10. (a) TEM micrograph showing nucleation of Laves phase on the site of an $M_{23}C_6$ particle (600°C for 1614 hrs head sample) (b) corresponding EDX spectrum.

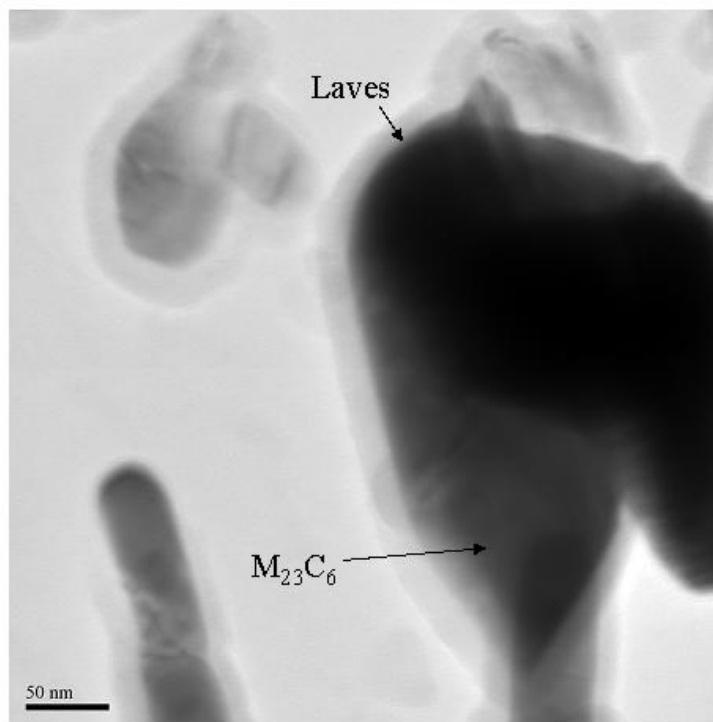
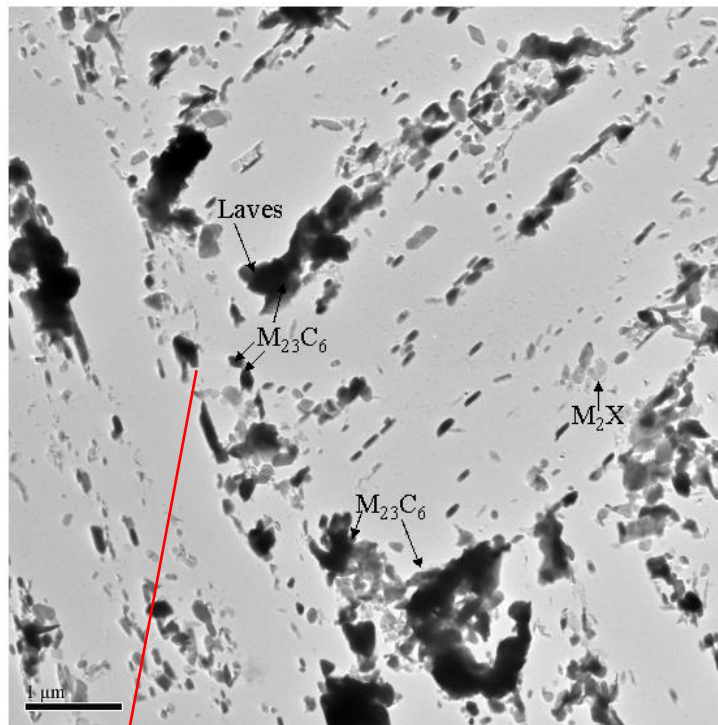
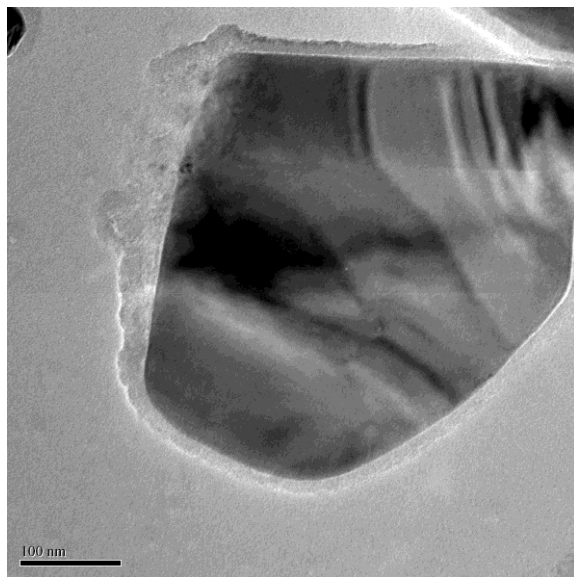


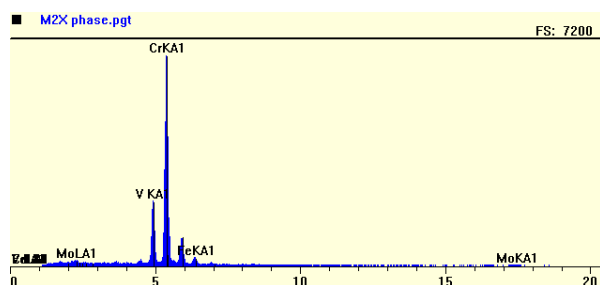
Figure 7.11. TEM micrographs showing nucleation of Laves phase on the site of an $M_{23}C_6$ particle (625°C for 1131 hrs head sample) (a) low magnification (b) higher magnification

7.5.3 M₂X phase

M₂X phase was found for all samples including the ‘as-received’ sample. M₂X has a hexagonal close packed crystal structure [12]. The chemical composition of M₂X phase is distinctly different from that of Z phase so that both phases can be clearly separated by EDX spectrum analysis [13]. Figure 7.12 shows that a M₂X phase micrograph and the corresponding EDX spectrum. The morphology of the M₂X phase was found to change with exposure to stress and temperature. Figure 7.13 shows the way in which the M₂X particles evolved with strain and temperature. In service, the shape of the M₂X precipitates gradually changed from needle-like (coherent) precipitates to more equiaxed morphologies (incoherent). The decrease in coherency increase the interfacial energy and therefore increase the coarsening rate [10]. After long time exposures, the M₂X particles were particularly coarse (see Figure 7.13).



(a)



(b)

Figure 7.12. (a) An example of an M₂X particle (TEM micrograph of sample exposed to 625°C for 31198 hours (gauge)) (b) corresponding EDX spectrum

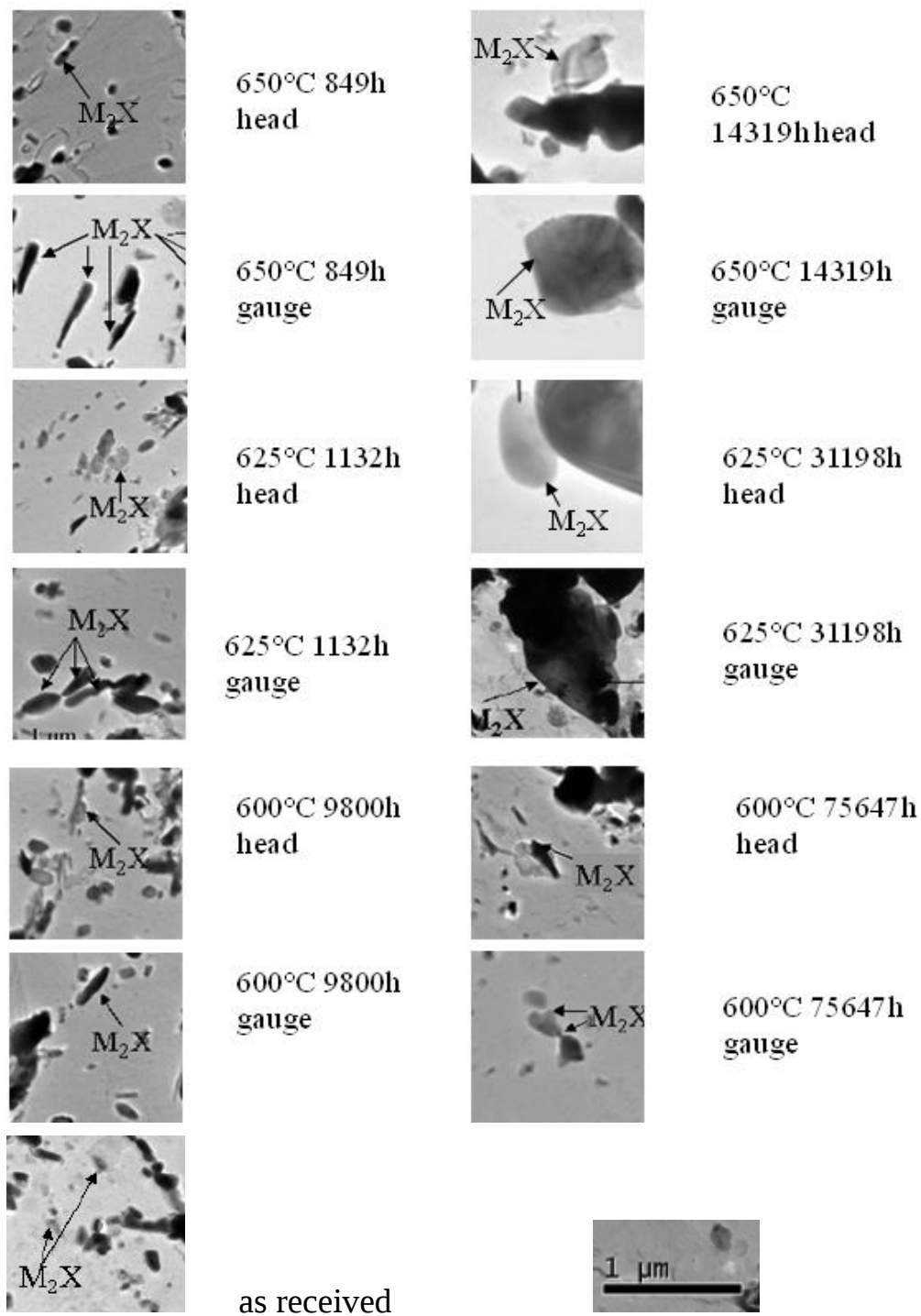
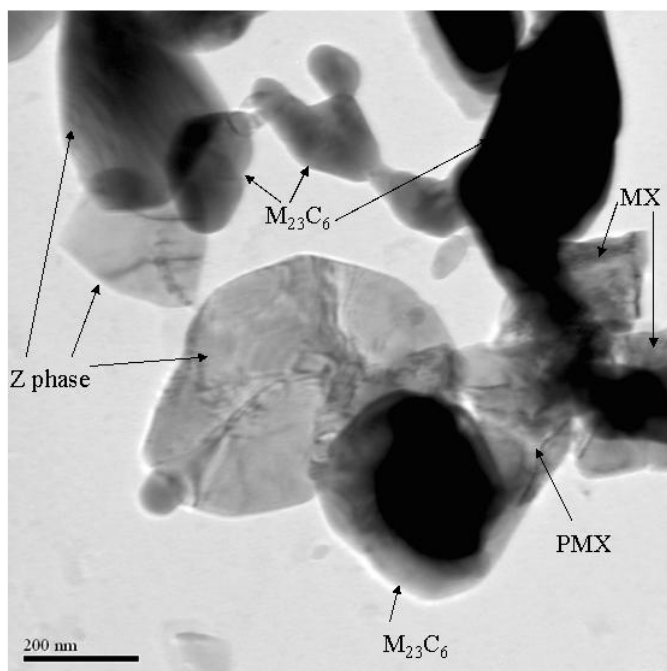


Figure 7.13. The effect of temperature and creep duration on the morphology and size of M_2X particles. After exposure to temperature and strain the particles evolve from an initially needle-like coherent morphology to a more equiaxed incoherent morphologies.

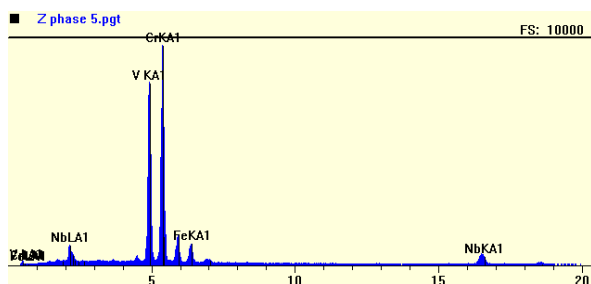
7.5.4 Z phase

Z phase particles were only found in the gauge of the sample exposed to the longest creep duration of 75647 hours. The Z phase particles were small, typically 280-320nm although some particles of around 450nm diameter were found. A TEM micrograph showing a Z phase particle is shown in Figure 7.14 with the corresponding EDX spectrum and selected area diffraction pattern. No Z phase particles were found in any of the other samples. For example, for specimens that were creep exposed at 625°C 31198 hours and 650°C 14319 hours Laves phase, $M_{23}C_6$ and M_2X were all found to coarsen but no Z phase was found. Typically 10 carbon replicas were examined for each sample.

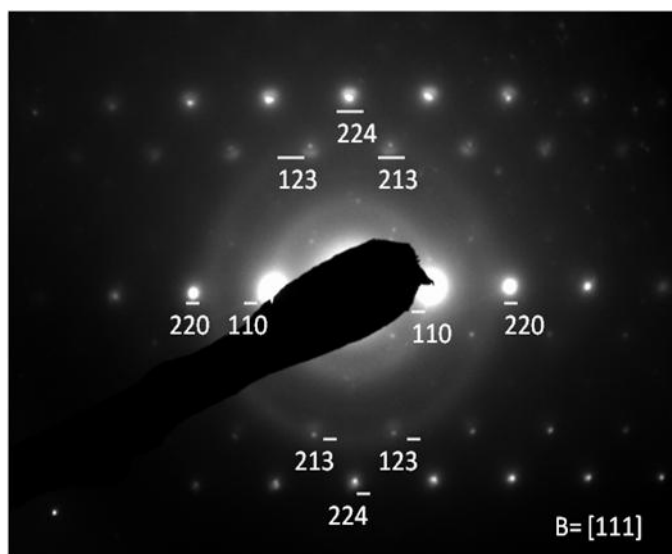
It has been reported by Sawada et al. [14] that if the V and Nb contents increase in the M_2X phase during creep exposure, M_2X phase can change to a Z phase. However, in E911 the Cr content is relatively low and higher Cr content steels (and those with higher Nb contents) are more liable to Z-phase precipitation [15, 16].



(a)



(b)



(c)

Figure 7.14 (a) TEM micrograph of a replica from the specimen exposed at 600°C for 75647 hours (gauge) (b) EDX spectrum from the particle (c) selected area diffraction pattern confirming Z phase structure.

7.6 Phase size evolution

7.6.1 $M_{23}C_6$ and Laves phase

Figure 7.15a-d shows plots of the average particle size against creep duration for $M_{23}C_6$ and Laves phase particles in the head (a and c) and gauge parts (b and d) of the samples. In comparing the two types of particles, the $M_{23}C_6$ phase has the tendency to coarsen after long-term exposure, whilst Laves phase particles coarsen faster. This is shown by the gradual increase in particle size at low creep durations for $M_{23}C_6$ and the more rapid increase in the size of the Laves phase. The coarsening effects are more significant at 625°C and 650°C.

At short creep durations, the fine Laves phase and $M_{23}C_6$ particles act as barriers to prevent grain boundaries sliding and expanding. This pinning effect provides excellent creep strength in service. At higher temperatures, the particles coarsen and lose their effectiveness for pinning the boundaries. To maintain high creep strengths after long durations in E911 it is important to prevent particle coarsening.

7.6.2 M_2X phase

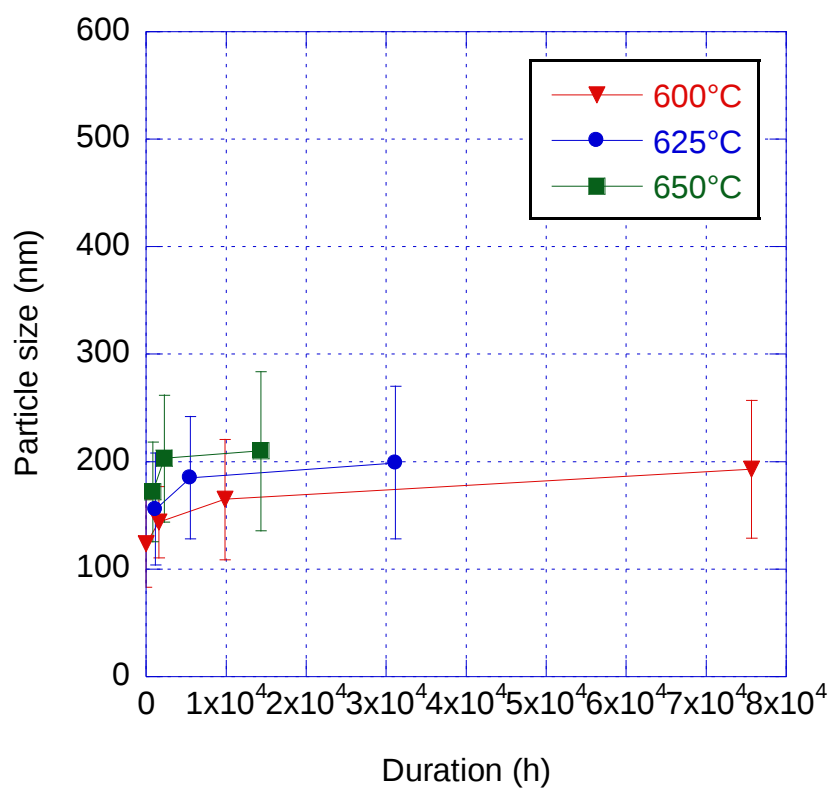
In the as received condition, the mean size of M_2X particles was 166 ± 10 nm in length, 60 ± 6 nm in width. In service, the shape gradually changed from the needle-like (coherent) to the more equiaxed morphologies (incoherent), as shown in Figure 7.13. Coarsening rates were more significant at 625 and 650°C.

7.6.3 MX phase

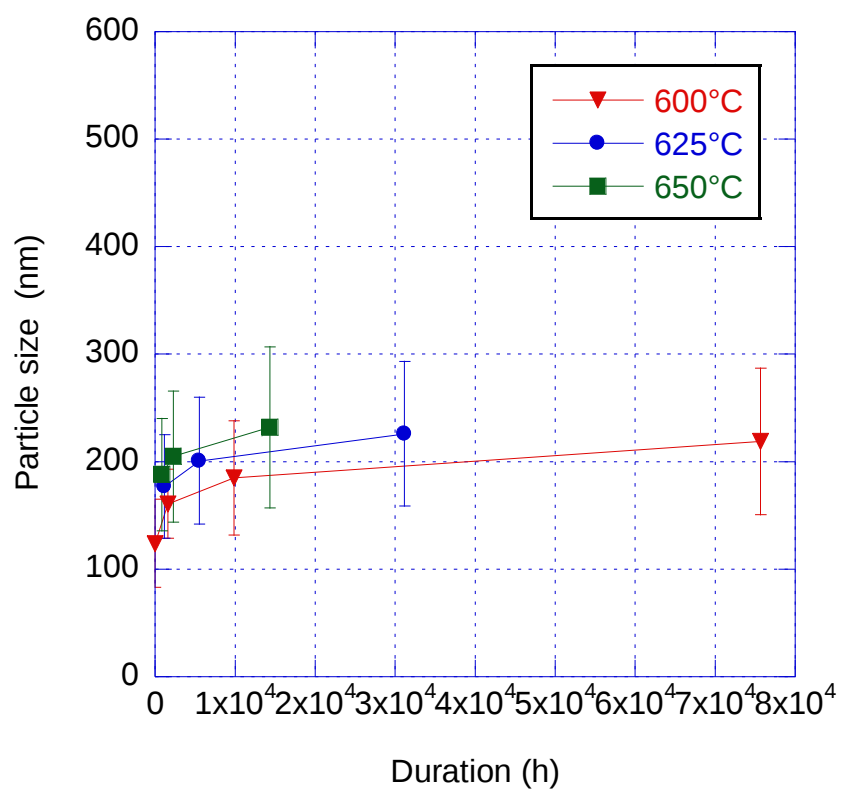
In the as- received condition, the mean size of the MX particles was below 100 nm. Even after the longest exposure, the size was stable. A fine distribution of stable MX precipitates blocks the movement of subgrain boundaries and dislocations, delays degradation process of microstructure, and is a principle factor in retaining high creep strength of this type of steel [17].

7.6.4 Z phase size distribution

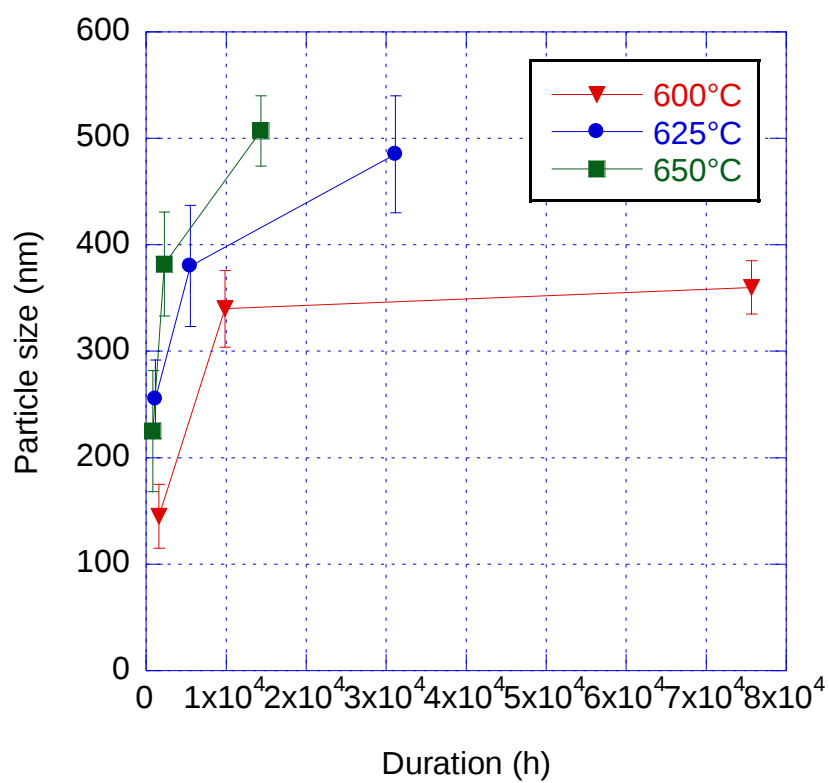
Typical TEM micrographs of Z phase particles are shown in Figure 7.16a-d. The majority of Z phase particles are in the size range of 200-300 nm shown as Figure 7.16 (a), Figure 7.16 (c) and figure 7.16 (d). Figure 7.16 (b) shows a larger ~450nm size particle.



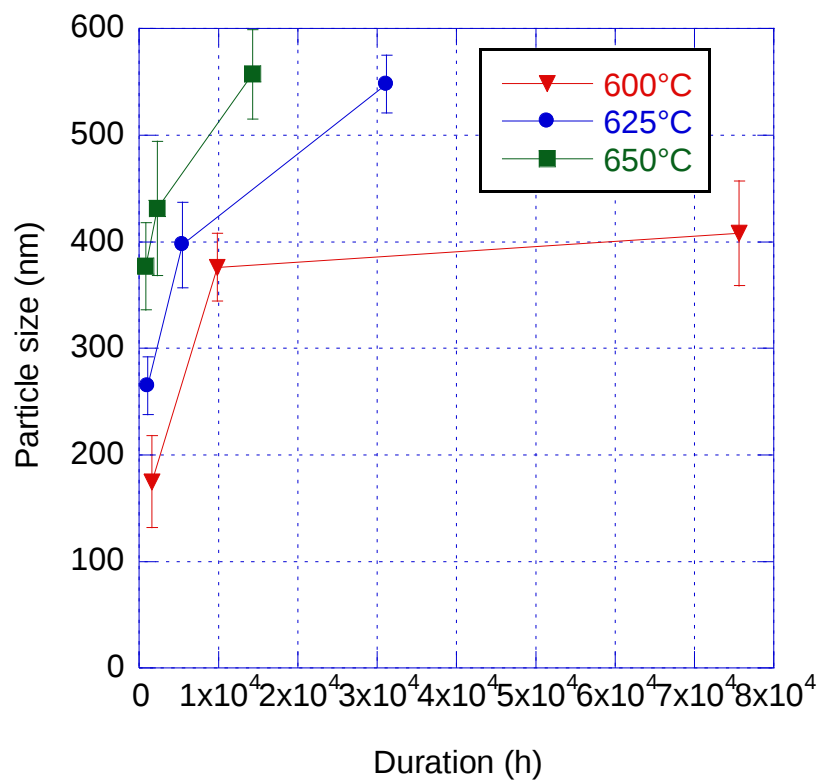
(a) Average $M_{23}C_6$ particle size (sample heads)



(b) Average $M_{23}C_6$ particle size (sample gauges)



(c) Average Laves particle size (sample heads)



(d) Average Laves particle size (sample gauges)

Figure 7.15. The size evolution of Laves phase and $M_{23}C_6$.

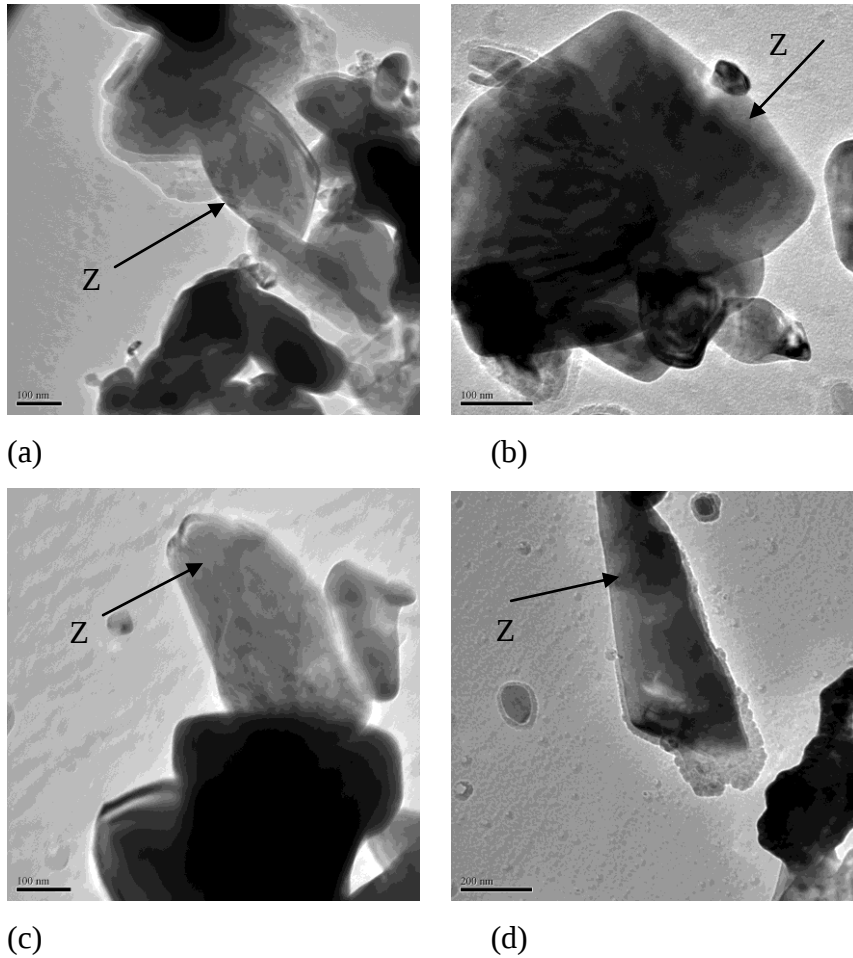


Figure 7.16. Size distribution of Z phase particles on the sample exposed at 600°C for 75647 hours (gauge).

7.7 Chemical composition of phases

The previous section considered how the size and shape of the differing precipitates changed with creep exposure at the different temperatures. In this section, the effect of creep exposure on the chemical composition of the different particles is considered.

Figure 7.17 shows the change of the different alloying elements for the different phases at 625°C.

Figure 7.17 (a) shows that for $M_{23}C_6$ phase, as the creep duration increases the Fe content decreases, and the Cr content increases. The V, Mo and W contents remain broadly similar. Similar results have also been obtained by Výrostková [18].

Figure 7.17 (b) shows the changes in composition of M_2X particles. The composition of M_2X phase is distinctly different from the $M_{23}C_6$. Both phases are Cr rich but the V content by weight is around 17-20% in M_2X phase as compared to approximately 1 wt % for $M_{23}C_6$. The composition of M_2X phase does not change greatly after long term exposure although the particles coarsen as seen earlier.

Figure 7.17 (c) shows the evolution of the chemical composition of the Laves phase particles. Laves phase $(Fe,Cr)_2(Mo, W)$, should have 66 at% of Fe and Cr and 33 at% of W and Mo. 5 at% deviation in these values can be accepted due to the different particle thickness and system calibration.

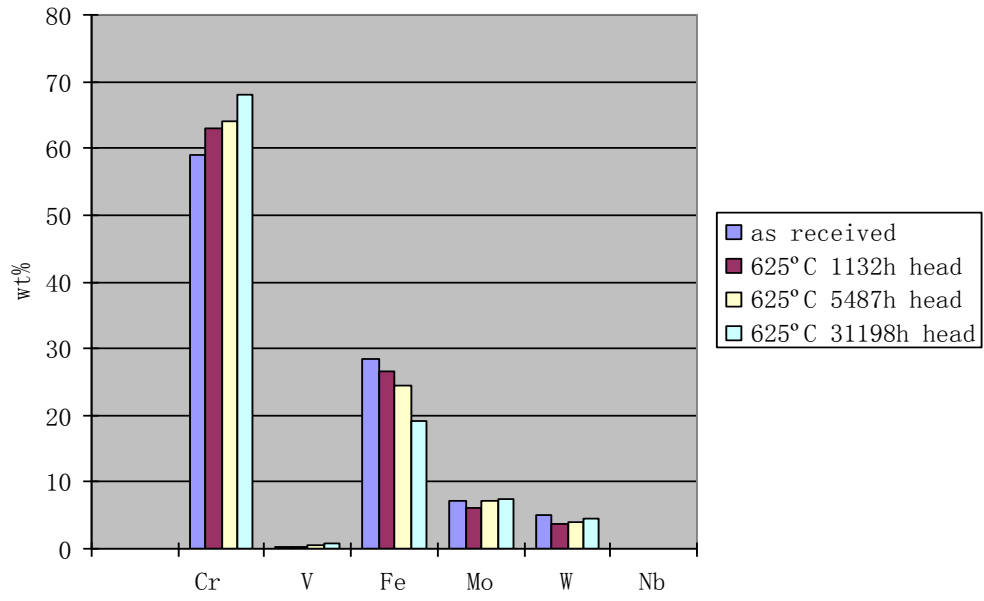
The chemical composition of Z phase is $Cr(V, Nb)N$ shown as Figure 7. 18. On the sample of 600°C for 75647 hours gauge length, Z phase was found. Sawada reported that Z phase formation consumed a large number of MX carbonitrides, Stress and/or strain accelerate Z phase precipitation during creep exposure [14].

No major differences were found between the chemical composition of the different phases between the head and gauge portions. No apparent differences were found between the chemical composition of the different phases for samples that were creep exposed at 600 or 650°C.

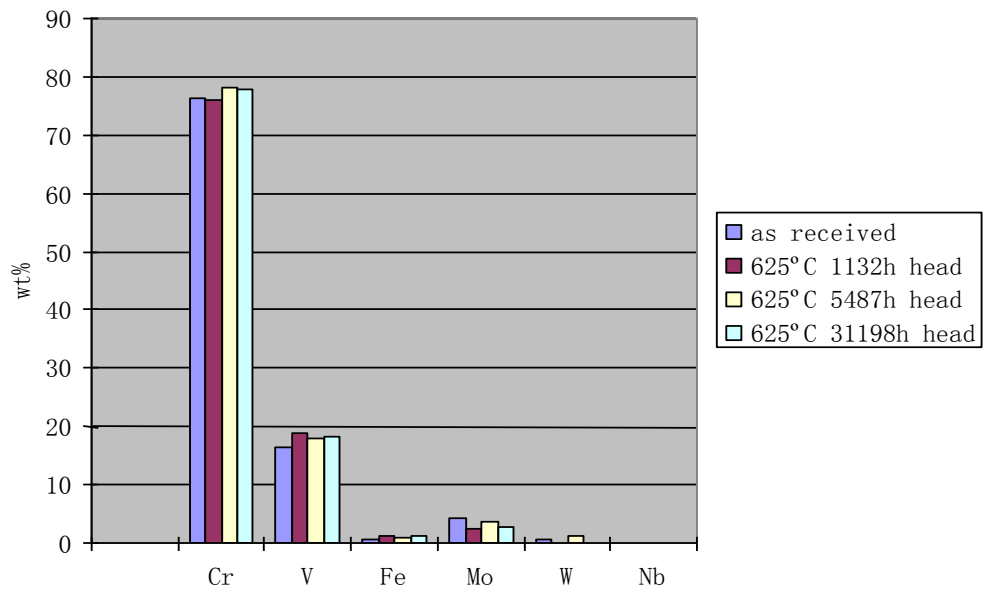
7. 8 Conclusions

The results of the TEM study show that:

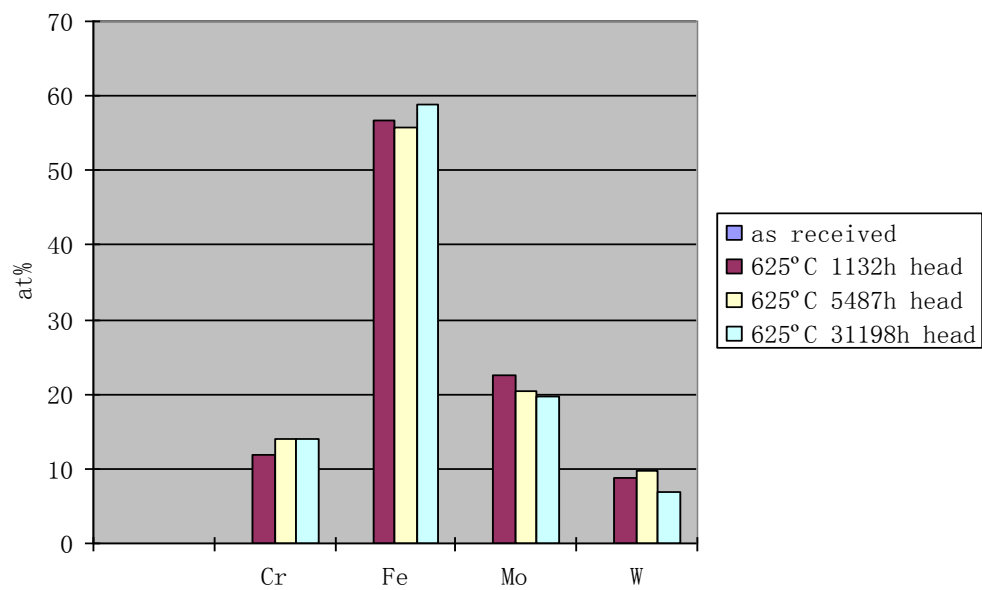
- (1) For samples that were creep exposed at 600°C and at a stress of 108 MPa, the creep strength is retained for long periods due to the relatively small $M_{23}C_6$, Laves phase and M_2X phase particle sizes compared with samples that were creep exposed at 625°C, 650°C. Z phase was found in samples after 75647 hours .
- (2) At higher temperatures (625°C and 650°C), there were greater reductions in creep strength owing to Laves phase and M_2X phase coarsening.



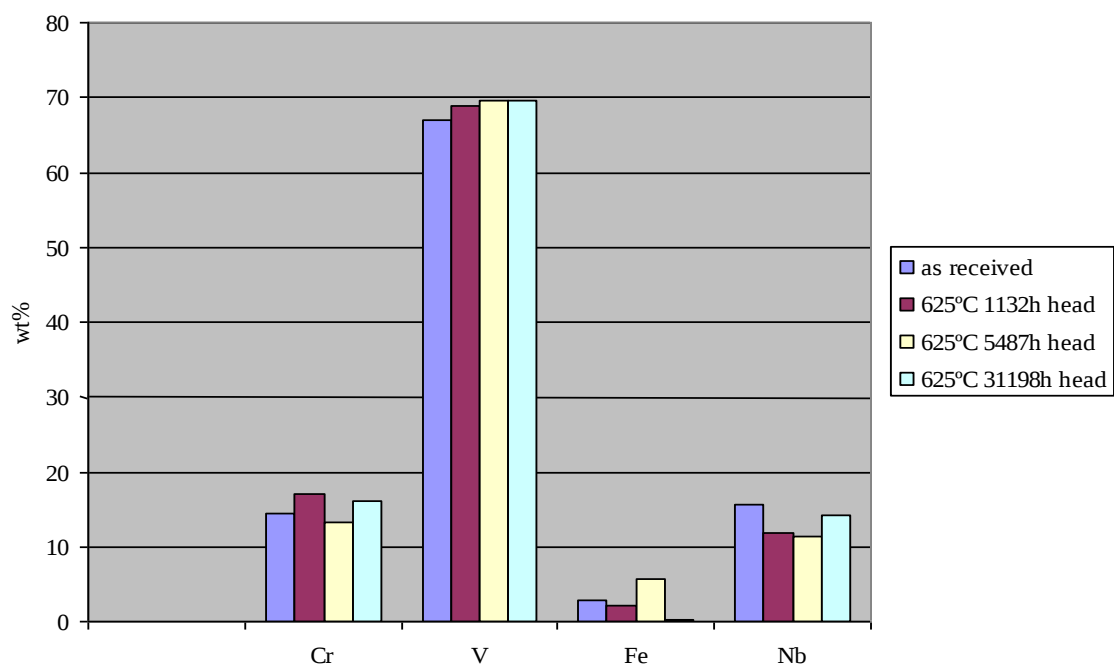
(a) $M_{23}C_6$



(b) M_2X phase



(c) Laves phase



(d) MX phase

Figure 7.17. Chemical composition of the differing phases at 625°C.

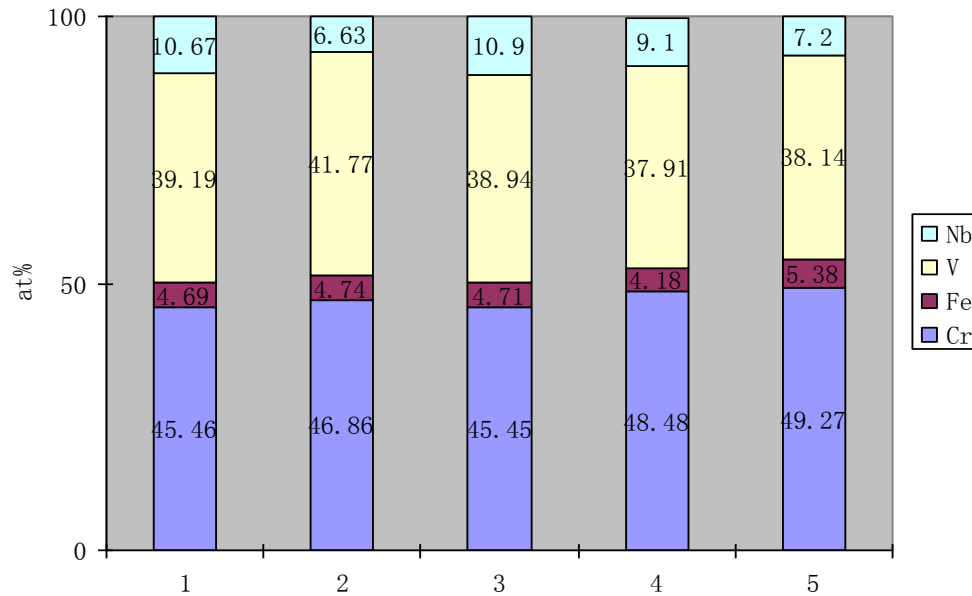


Figure 7.18. Z phase chemical composition for the sample creep exposed at 600°C for 75647 hours (gauge).

7.9 References

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Chapter 8 Analysis of four experimental casts

This chapter focuses on the analysis of mechanical properties and minor phases of the four experimental casts that had been thermally aged to see whether Z phase was present. E911 was also thermally exposed to investigate the effects of thermal exposure alone on the mechanical properties (see Chapter 2 for details of composition and heat treatment etc.). The aim of this study was to determine the effects of Ni and Cr contents on Z-phase precipitation. It should be noted that both W and Mo are also different in the experimental steel from the E911 composition; thus differences will have some effects on the mechanical properties.

8.1 Hardness analysis

The thermal ageing experimental tests were conducted on both four experimental casts and E911 steel. The samples were exposed to four different temperatures for the durations given in Tables 2.4, 2.5, 2.6 and 2.7 in Chapter 2. Vickers hardness tests using a 20kgf load were conducted on all the samples. Plots of hardness versus ageing duration are shown in Figure 8.1, Figure 8.2, Figure 8.3 and Figure 8.4. As temperature and duration of exposure increases, the hardness is expected to decrease, based on data collected previously on steel E911 (see Chapter 4).

Figure 8.1 shows Vickers hardness evolution for thermal exposure at 625°C for durations up to 10,000 hours. In the as tempered condition, the values of hardness of four casts are much higher than that of E911. However, it is noticeable that the hardness of E911 steel is almost constant over the duration of testing but the four experimental casts all decrease in hardness. The decrease in hardness of the four casts is significant with the hardness dropping by 77, 69, 78 and 75 HV20 for Code 28, 29, 30 and 31 respectively. The hardness decrease for E911 is 22HV20.

There are two obvious reasons for the decrease in hardness with ageing:

(a) Tempering temperature: tempering processes give rise to the increased ductility of steel owing to precipitation and a decrease in dislocation density (see Chapter 1). The tempering temperature was 760°C for the E911 steel while the tempering temperature is 700°C for four

experimental casts. Thus, the initial hardness of the four experimental casts is higher but the thermal exposure causes this high initial hardness to be lost rapidly and this effect is accelerated at 650°C, 675°C and 700°C.

(b) Chemical composition: if we compare the chemical composition between E911 and the four casts, shown in Table 2.3 (Chapter 2), the biggest difference is the content of W. The content of W in the four casts and E911 steel is 0.002% and 0.98% respectively. The role of W is explained in Chapter 1 and Chapter 7 in detail but essentially it contributes to the solid solution strengthening and aids in the formation of fine precipitates of Laves phase which pin the grain boundaries. Thus, the lack of W in the experimental casts leads to the more rapid softening of these casts on thermal exposure.

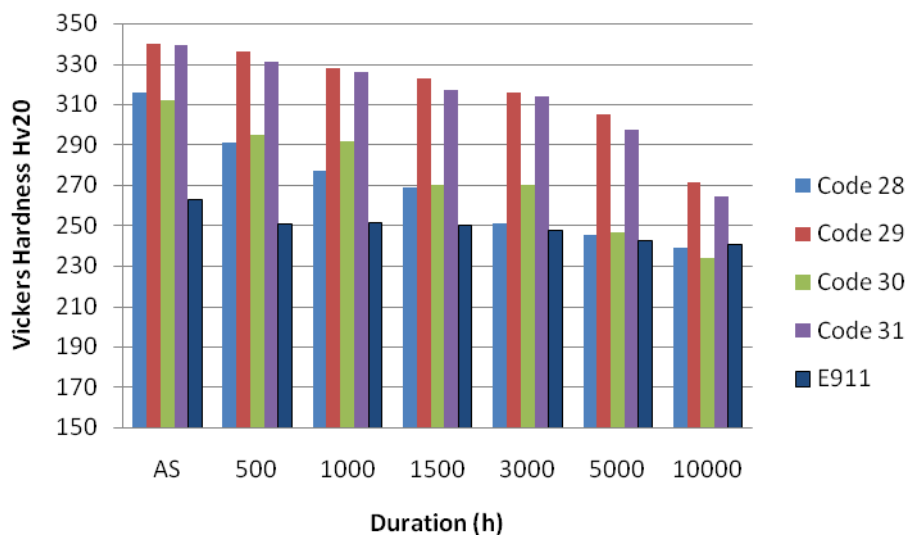


Figure 8.1 Vickers hardness versus thermal ageing duration at a temperature of 625°C (AS represents the hardness of the as tempered samples).

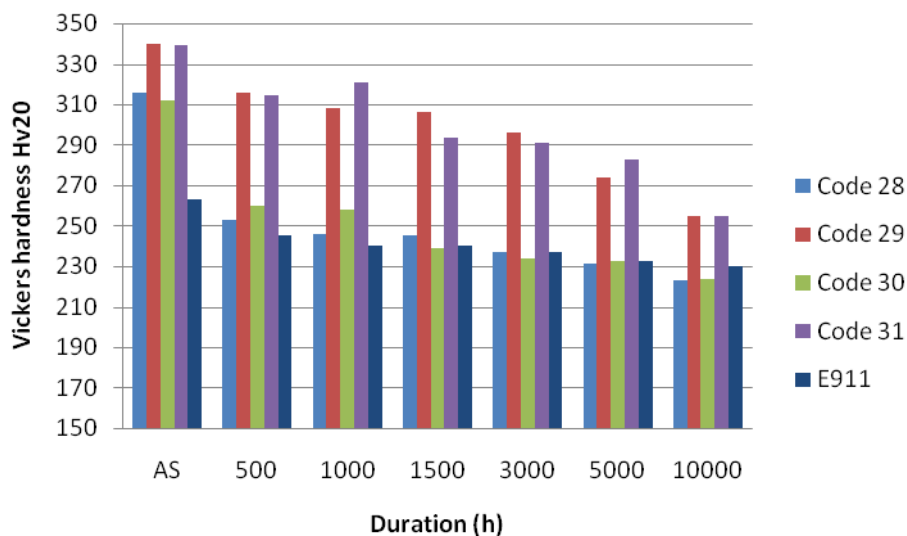


Figure 8.2. Vickers hardness versus thermal ageing duration at a temperature of 650°C (AS represents the hardness of the as tempered samples).

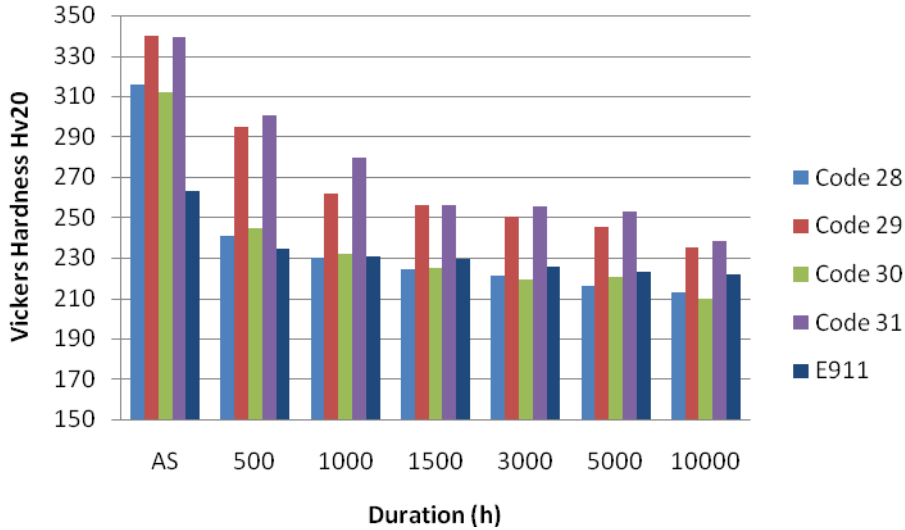


Figure 8.3. Vickers hardness versus thermal ageing duration at a temperture of 675°C (AS represents the hardness of the as tempered samples).

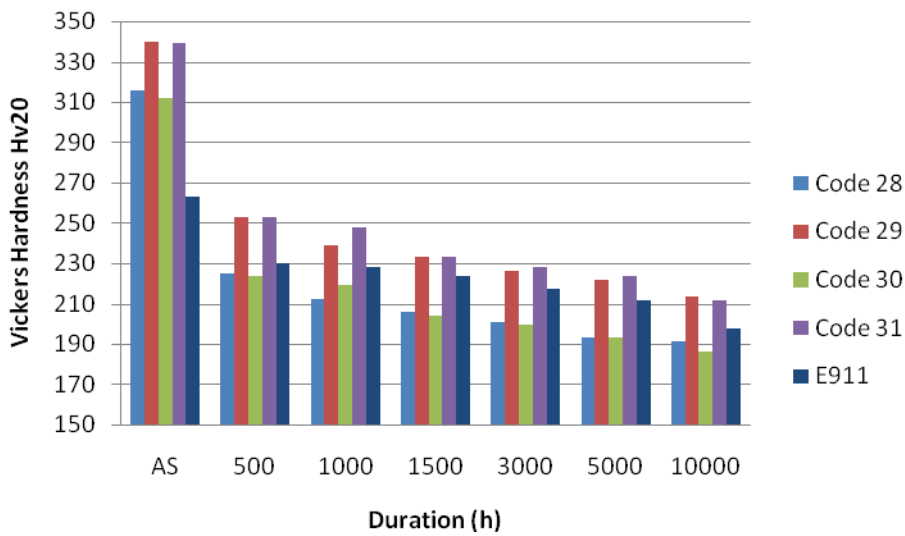


Figure 8.4. Vickers hardness versus thermal ageing duration at a temperture of 700°C (AS represents the hardness of the as tempered samples).

The third possible cause for a decrease in mechanical properties of high Cr steels is the formation of Z phase. In order to see whether Z phase was present, the minor phases in four experimental casts was analysed by TEM and the findings are presented in the following sections.

8.2 Phase analysis for the samples thermally exposed to 5000 hours

The TEM coupled with EDX was used as a tool to investigate the minor phase precipitation behaviour in the four experimental casts. It was found that most of particles in the microstructure were $M_{23}C_6$ and MX. Occasionally, primary MX (Nb rich MX phase) and M_2X phase particles were found. No Z phase or Laves phase was present at the exposure duration of 5000 hours.

Figure 8.5 and Figure 8.6 show representative carbon replica TEM images of 29B4 (3000 hours thermal ageing at 650°C) and 29C5 (5000 hours thermal ageing at 675°C). It is obvious that prior austenite grain boundaries are still visible up to 5000 hours exposure. $M_{23}C_6$ phase decorated the prior austenite grain boundaries and martensite lath boundaries; extremely fine MX phase was dispersed within the matrix.

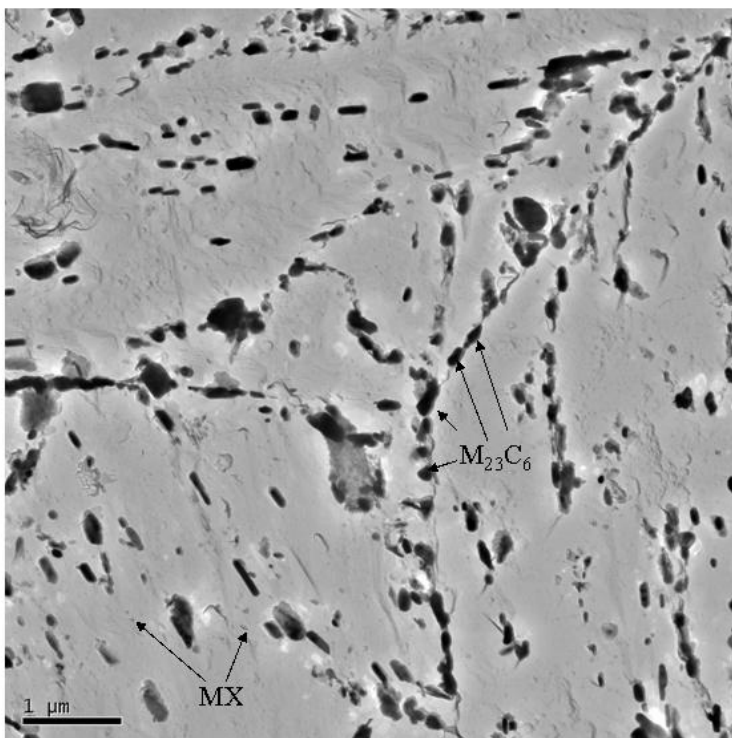


Figure 8.5. TEM image of a carbon replica of 29B4 (650°C/3000 hours).

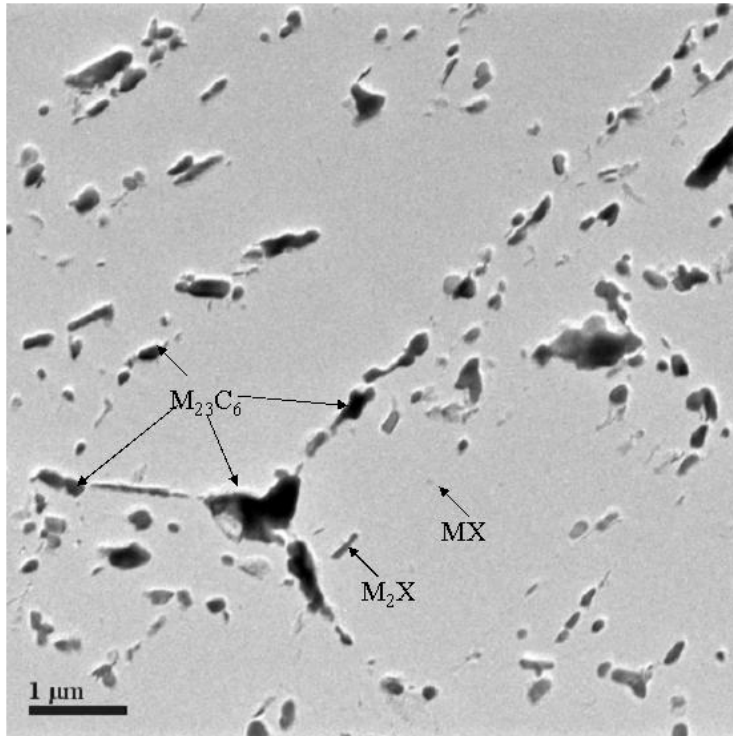


Figure 8.6. TEM image of a carbon replica of 29C5 (675°C/5000 hours).

Figure 8.7 shows that the typical EDX spectrum of $M_{23}C_6$ in the experimental casts. No W was found in the chemical composition of $M_{23}C_6$ phase as would be expected from the low W content in the initial cast composition.

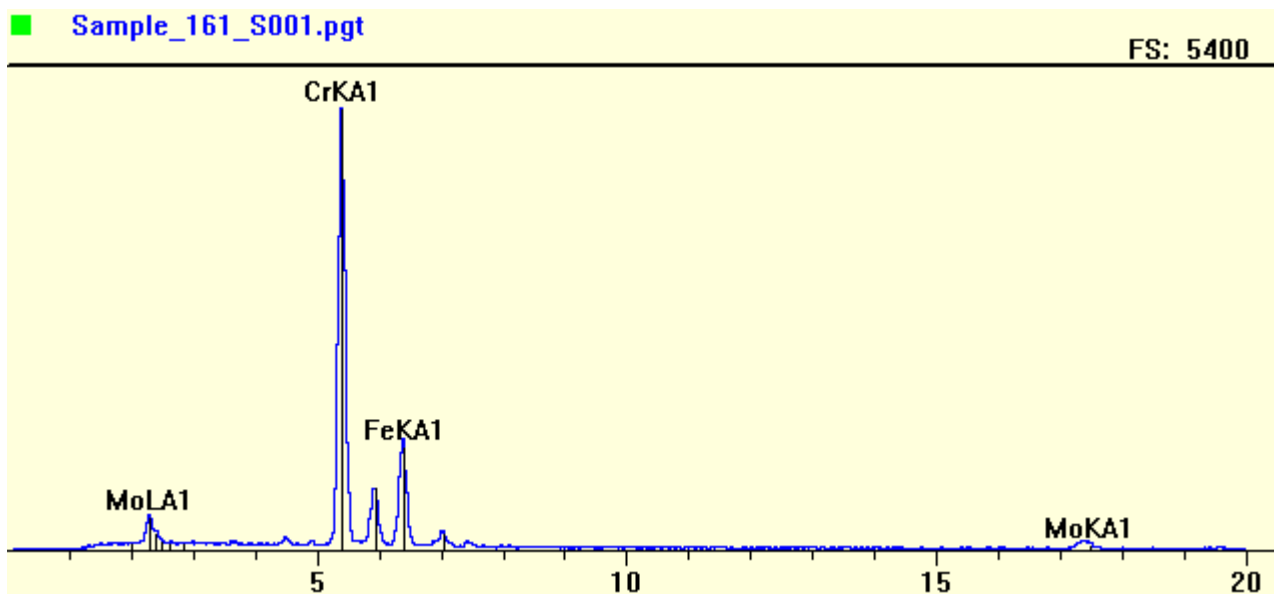


Figure 8.7. Typical EDX spectrum of $M_{23}C_6$ particles.

The secondary MX phase composition was the similar as the E911 steel as shown in Figure 8.8 containing V, Nb and Cr, however, less Nb and more Cr for E911 in Figure 7.4 was noticed.

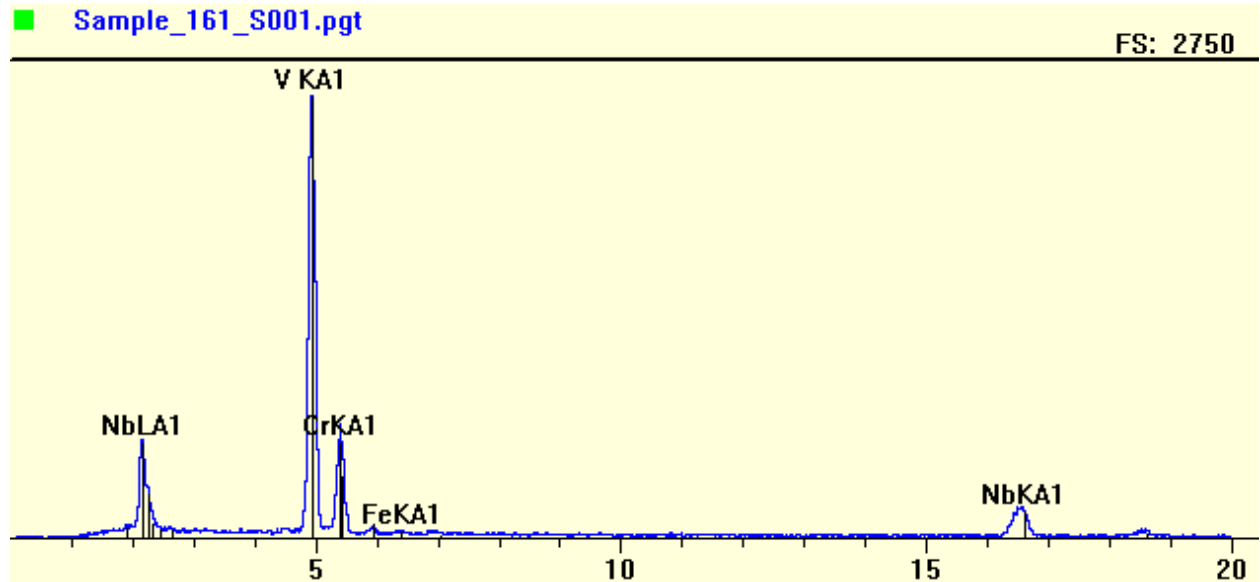


Figure 8.8. Typical EDX spectrum of MX phase particles (sample 29 D4 (700°C/3000hours)).

After 5000 hours exposure duration, no Laves phase was found for any of the four casts. Since the Nb content was low, and Nb is important for the formation of Z phase, no Z phase was found after 5000 hours thermal exposure. Will Z phase will present after longer exposure? The following section discusses the precipitates seen after 10,000 hours thermal exposure.

8.3 Phase analysis for the samples thermally exposed to 10,000 hours

For the samples that had been thermally exposed for durations up to 10,000 hours, it was found that most of particles were $M_{23}C_6$ and MX. $M_{23}C_6$ phase decorated along the prior austenite grain boundaries and martensite lath boundaries, and extremely fine and stable MX phase was dispersed within matrix. Examples are shown in Figure 8.9, Figure 8.10 and Figure 8.11. The size of the precipitates increases with increasing ageing temperature as can be seen from examining the three micrographs. $M_{23}C_6$ tends to spheroidise as shown in Figure 8.11.

No Laves phase was found for all of the observed samples of code 28 and code 29.

Table 8.1 summarizes the minor phase precipitates found for the samples of code 28 and code 29 at the exposure duration of 10,000 hours. While the majority of precipitates are $M_{23}C_6$ and MX, small amount primary MX phase was found for all of samples.

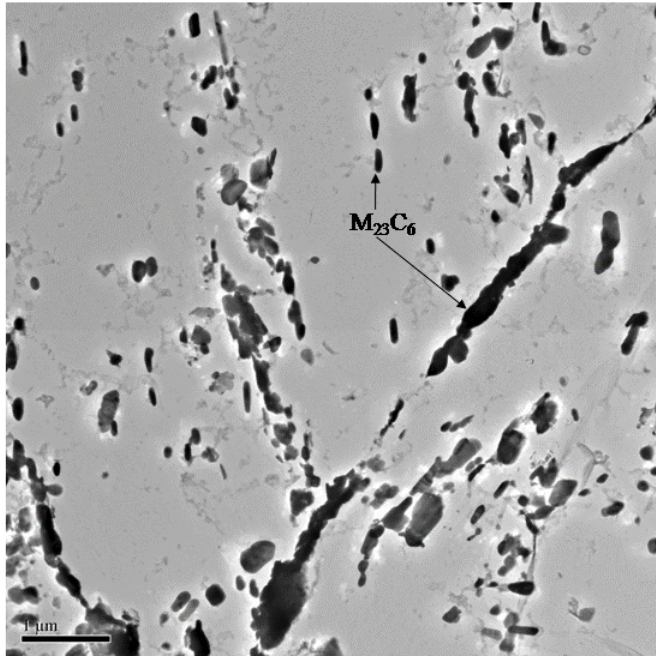


Figure 8.9. TEM image of a carbon replica of 29B6 (650°C/10,000hours).

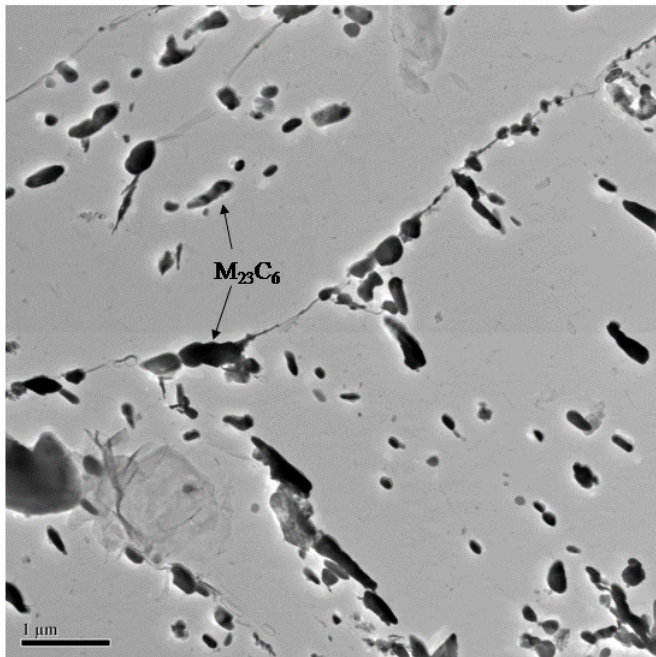


Figure 8.10. TEM image of a carbon replica of 29C6 (675°C/10,000 hours).

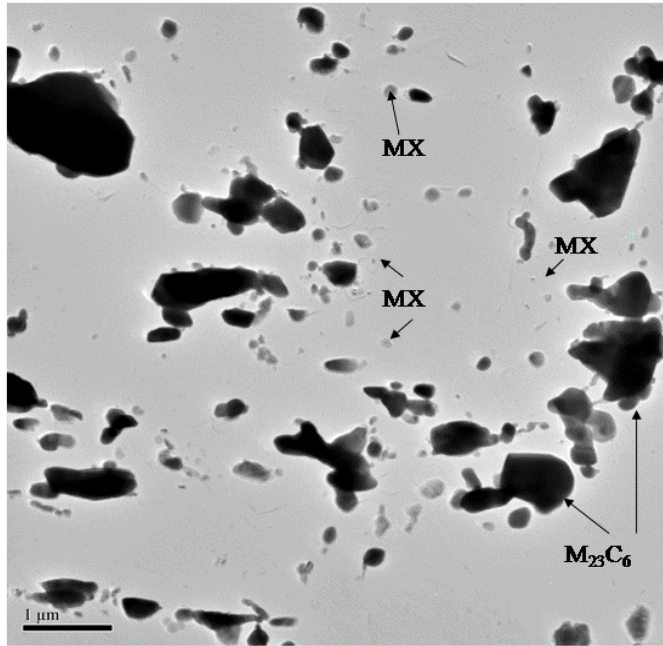


Figure 8.11. TEM image of a carbon replica of 28D6 (700°C/10,000 hours).

Table 8.1 Summary of precipitates found after ageing to 10,000 hours for the samples of Code 28 and 29. (A, B, C and D are 625,650,675 and 700°C respectively. ? denotes identification by EDX alone)

Sample	M ₂₃ C ₆	MX	PMX	Z	M ₂ X	Laves
28 A6	Y	Y	Y (low)	N	N	N
28 B6	Y	Y	Y (low)	N	N	N
28 C6	Y	Y	Y (low)	N	N	N
28 D6	Y	Y	Y((low)	N	N	N
29 A6	Y	Y	Y (low)	2 (?)	Y (low)	N
29 B6	Y	Y	Y (low)	1 (?)	Y (low)	N
29 C6	Y	Y	Y (low)	3 (?)	Y (low)	N
29 D6	Y	Y	Y(low)	1 (?)	Y (low)	N

Extremely low numbers of Z phase particles were found on the samples of code 29A6, 29B6, 29C6 and 29D6. No Z phase was found on samples of 28A6, 28B6, 28C6 and 28D6. Figure 8.12 shows a Z phase image on a carbon replica of 29A6, the EDX measuring area is circled with red, and the EDX spectrum of this phase is shown in Figure 13. Table 8.2 shows clearly the chemical composition of this phase: (Cr+Fe) is 53.4 at% while (V+Nb) is 46.6 at%.

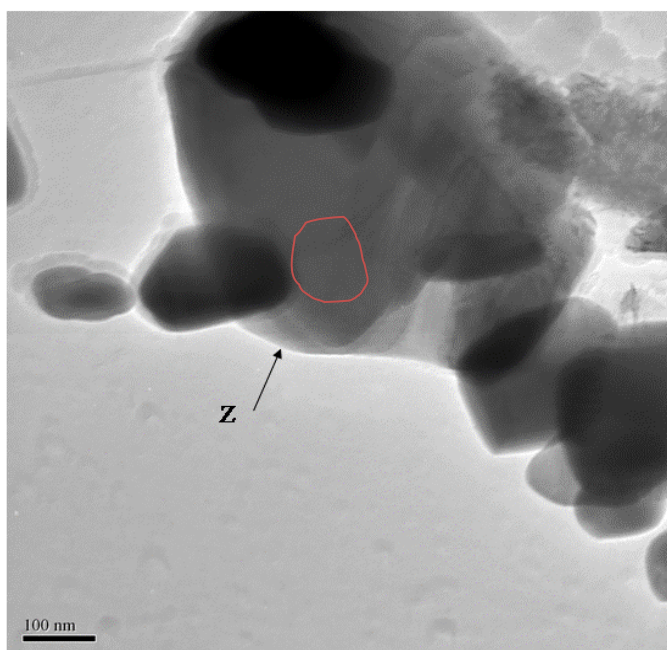


Figure 8.12. TEM image on a carbon replica of 29A6

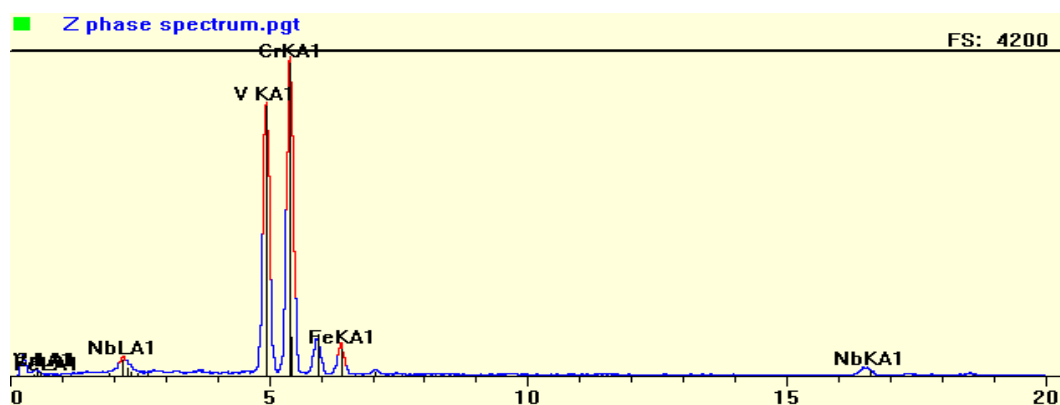


Figure 8.13. The EDX spectrum of Z phase of 29A6

Table 2.3 (Chapter 2) shows that the only difference in chemical composition of code 28 and code 29 is the content of Cr: 8.5% for code 28 and 11.49% for code 29 respectively. It seems that the higher Cr and Ni content (code 29) is likely to cause the precipitation of Z

phase, but due to the extremely low number of particles found on the samples, further evidence will be needed to support this. No Z phase particles were found on the samples with a low Ni content.

Table 8.2 Chemical composition of Z phase

Element	Line	KeV	CL Ratio	Wt%	At%
V	KA1	4.951	1.1600	41.81	43.37
Cr	KA1	5.414	1.2000	48.03	48.81
Fe	KA1	6.403	1.3500	5.40	5.11
Nb	LA1	2.166	2.5430	4.76	2.71
Total			0.0000	100.00	100.00

After thermally ageing the samples to 10,000 hours, Z phase was present in extremely low quantities; this is probably owing to the low Nb content. High Cr steels and Nb containing steels are more liable to Z phase precipitation [1].

8.4 Summary

Vodarek and Strang [2] noted that high Ni contents in samples led to the earlier formation of Z-phase. Danielsen and Hald [3] proposed that high Cr content promoted Z phase formation and that Ni content was not a significant factor in Z phase formation. If low Cr did not favour Z phase formation this would be supported by the results from samples code 28. If Z phase was favoured by high Cr and high Ni contents it would be present in samples of code 29. This was indeed found to be the case.

However, after 10,000 hours duration, there were few Z phase in the samples studied and therefore additional work is required to fully confirm this result. Additionally, future work could be focussed on casts with a higher Nb content and an initial tempering temperature of 760°C to give a better chance of studying Z phase formation at shorter thermal ageing durations. It is possible that the casts studied here will allow better conclusions to be drawn after exposing the samples to longer durations.

8.5 References

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Chapter 9 Discussion, conclusions and further work

9.1 Discussion and conclusions

9.1.1 Mechanical properties of E911 steel

In this study, E911 creep samples exposed to temperatures of 600°C, 625°C, 650°C at differing stress levels were supplied by CORUS. Hardness was measured along longitudinal cross-sections through the creep exposed samples. The hardness of the gauge length that experienced both creep strain and temperature was found to be lower than that of the head where thermal softening only can be assumed. In both cases, the hardness of the samples had decreased substantially from the solution treated and tempered “as-received” sample.

In order to predict the creep rupture life of materials, an equation was developed by Larson Miller to extrapolate experimental data. The Larson-Miller Parameter, which has been widely used usually simply takes into account the temperature of exposure in rupture life and does not account for any effects of the tempering process on mechanical properties. In this work, the LMP values used for the Hardness versus LMP plots (Figure 4.1 in Chapter 4) have been adjusted to take into account the original 2 hours tempering treatment at 760°C given to the material prior to testing. Table 9.1 shows the comparison of LMP with and without taking account of the original tempering process.

9.1.2 Creep mechanism of E911

Through microstructure observation by RLM and SEM on all of the E911 samples, changes in the morphology and particles size of the precipitates were observed qualitatively. A creep fracture mechanism map of E911 steel was also constructed on the basis of optical micrographs of the E911 creep samples. Two modes of creep mechanism were identified, they are: transgranular creep fracture and intergranular creep fracture.

At 600°C, the samples which failed after 1614 hrs, 9800 hrs and 13336 hrs exhibit the typical ductile transgranular creep fracture mechanism. The values of reduction in area are high, in the range between 63% to 81%, significant necking being observed in the gauge length of all three samples. In the sample with the longest exposure at 600°C namely 75647 hrs, a transition from transgranular creep mechanism to intergranular fracture mechanism took

place because both transgranular voids and intergranular cracks were observed on the sample. Therefore, on the creep mechanism map, the purple line (Figure 5.6) was drawn just across the sample of 600°C 75647 hrs.

Table 9.1 The comparison on LMP values

	t(h)	LMP with 2 hrs tempering effect taken in	LMP without 2 hrs tempering effect taken in
600°C	1614	21.03	20.26
	9800	21.22	20.94
	13336	21.28	21.06
	75647	21.77	21.72
625°C	1131	21.13	20.70
	5487	21.45	21.32
	13224	21.72	21.66
	31198	22.02	22.00
650°C	849	21.36	21.16
	2232	21.64	21.55
	4530	21.88	21.83
	14319	22.31	22.30

At 625°C, the samples which failed after 1131 hrs, 5487 hrs, and 13224 hrs) were identified as failing by a ductile transgranular creep fracture mechanism. In the sample that failed after 31198 hrs, lots of intergranular cracks were observed, some of which showed apparent coalescence. Macroscopic cracks were formed along the grain boundaries. Most of the cracks were in grain boundaries normal to the applied load. A brittle intergranular fracture mechanism was confirmed in this sample. Therefore, on the mechanism map (Figure 5.6 in Chapter 5), the purple line was drawn before 31198 hrs across the 625°C line.

At the temperature of 650°C, all of samples were identified as having a ductile transgranular creep fracture mechanism. Therefore, on the mechanism map (Figure 5.6 in Chapter 5), the purple line was drawn above the 650°C line.

It has been reported that the rupture (recrystallization) mode took place on Cr-Mo-V turbine rotor steel [1], with finer grains closer to the fracture surfaces. The fracture surface portions are greatly reduced in area and softened, and they show a type of rupture by recrystallization [2]. When the rupture mode takes place, a reduction in area is, or close to, 100%. The nucleation of internal cavities must be suppressed and, the nucleation of voids is prevented by the process of dynamic recrystallization [3]. However, either voids or cracks were present in all of the observed crept E911 samples. Therefore, the rupture mode (recrystallization) does not exist for any of the observed E911 samples.

9.1.3 EBSD analysis of E911

Electron backscattered diffraction has been used to evaluate the changes in misorientation and grain morphology as a function of creep exposure in E911 samples. The EBSD technique gives powerful insight into the additional quantifiable changes occurring to the microstructure as a result of exposure to strain and temperature. EBSD gives a much more detailed approach to characterizing grain size and morphology than either optical or scanning electron microscopy alone as it does not suffer limitations from etching such as not revealing small grains. In addition, subgrain size and morphology can also be analyzed.

The solution treated and tempered martensite microstructure is highly textured. In the as received condition, the microstructure will exhibit good mechanical properties. However, as a result of creep exposure, the size and morphology of the grains evolves and the strength of the material degrades. The work in Chapter 6 has presented a detailed analysis of the changes in lath size and morphology, subgrain size and morphology and misorientation ratios for a range of creep exposed steels.

Since measurement of equivalent circular diameter does not adequately define a martensite lath, a fitted ellipse shape was used to characterise the irregular block shape of the martensite laths. It was found that the increase width of the block is more significant in the gauge length at higher temperature after longer duration exposure while there is just a slow change in block width on the head part of the samples. The aspect ratio was found to decrease with exposure to creep strain and temperature. According to the Hall-Petch relationship, these changes in block size can account for the decrease of mechanical properties of E911 in service although there are additional complexities from the contribution of the distribution and size of precipitates (as discussed in Chapter 7).

Sub-grain nucleation and growth have been characterised by band contrast maps and three levels of misorientation angle boundary classification (1° , 2° , 15°). The nucleation of sub-grains was found to occur along the block boundaries and the shape is more equiaxed than for the martensite laths. Sub-grain growth was observed after exposure to temperature and creep strain. On samples that were creep exposed at a temperature of 650°C and for long duration, all of the martensite laths were found to have been completely transformed to sub-grains, for example on the samples of 650°C 14319 hrs. The subgrain size fluctuation along the scanned area has also been plotted (Figure 6.13 in Chapter 6). The subgrain size of the gauge length is larger than that of the head section.

At a magnification of 2000 times, good statistics and quantitative data on the morphology of tempered martensitic steel have been obtained with reasonable acquisition times. Although at lower magnification (such as 500 times), the statistics from automatic calculation by EBSD would be more accurate, it was impossible to completely eliminate problems from image drifting due to the longer scan duration. A 2000 magnification is a good compromise, with enough sub-grain boundaries and block boundaries being included within the scanning area to obtain reasonable statistics. For the purpose of detailed investigation of morphology inside the block, a magnification of 6000 and 10000 were applied to obtain the information on sub-grain nucleation and growth.

The approach used to analyze the sub-grain size using the moving average method [4] was found to allow differences between the head and the gauge of the samples to be clearly distinguished.

Previously, researchers investigating the evolution of microstructure in 9% Cr steels have used the misorientation angle or low angle/high angle ratio for characterizing the microstructure evolution of thermally exposed 9%Cr steels [5]. However, for the sample set examined in this thesis, this approach was found to have limitations owing to the growth of sub-grains after longer exposures at both creep strain and temperature. Once sub-grains grow to a significant size, after long term exposure at high temperature and creep strain, the low angle to high angle boundary ratio decreases. Further work would be required with a more extensive sample set to quantify the rate of sub-grain growth. Additionally, 3D EBSD characterisation techniques should be employed to aid volume reconstruction [6].

9.1.4 TEM analysis of E911

EDX in the TEM has been used to investigate the precipitate evolution on all of the creep rupture tested E911 samples. The microstructure of the as tempered sample consists of a tempered martensite structure containing $M_{23}C_6$ on prior austenite and lath boundaries and fine M_2X and MX precipitates in the matrix. After prolonged exposure at high temperature and creep strain, the size of MX phase is found to be extremely stable. The growth of Laves phase, M_2X phase and $M_{23}C_6$ phase was observed during long term exposure. The coarsening of these phases was accelerated at higher test temperatures and on the specimen gauge part. Z phase just was only found on the gauge part of samples of 600°C 75647 hrs at a stress of 77 MPa. The chemical compositions of these phases were also analysed, which will provide a reference for further alloy design.

$M_{23}C_6$

For $M_{23}C_6$, most of the precipitates occur on prior austenite and martensite lath boundaries. The fine $M_{23}C_6$ particles act as barriers to prevent grains expanding. At high temperature, the $M_{23}C_6$ particles coarsen and lose their effectiveness for pinning the boundaries. This means that controlling the size and composition of $M_{23}C_6$ particles is important for controlling the creep strength of E911. An attempt to suppress the growth of $M_{23}C_6$ in 9-12% Cr steel has been carried out by adding in boron into the chemical composition [7, 8, 9]. Abe [7] has shown that the addition of boron retards the Ostwald ripening of $M_{23}C_6$ near prior austenite grain boundaries during creep at elevated temperature (650°C). Abe [7] showed that for a 9Cr-3W-3Co-0.2V-0.05Nb steel with 139 ppm B addition, the creep rupture life was approximately 30,000 hours at a stress of 100 MPa, whereas for this kind of steel without B addition, the creep rupture life dropped down to about 15,000 hours at a stress of 60 MPa [7].

Laves phase

In the as received condition, no Laves phase was present. However, Laves phase was found after the shortest exposure durations (600°C 1614 hrs, 625°C 1131 hrs, 650°C 849 hrs respectively). When the Laves phase is just starting to form, it is small in size. The fine Laves phase also acts as barriers to prevent grain boundaries sliding. After long term exposure at creep strain and temperature, the phenomenon of Laves phase coarsening was observed. Laves phase precipitates grow by extracting Mo, W from the matrix, which causes the solid solution strengthening effect from Mo and W to be lost. Hald indicated that solid solution

strengthening from Mo and W has no significant effect on long-term microstructure stability of 9-12%Cr steel, and precipitate hardening should be regarded as the most significant strengthening mechanism. Thus, the microstructural stability of the 9-12%Cr steels under creep load is controlled by the precipitate stability [10].

Since Laves phase grows by extracting Mo and W from the matrix, reducing the content and Mo and W in the casts would seem to be a sensible solution. However, there is sufficient evidence to suggest that W additions do confer improved stress rupture strength, at least to test durations of around 50,000 hours that have been achieved in creep testing [11]. Comparing the chemical composition (shown in Table 1.1) of P91 (Mo:0.92, W:0), P92 (Mo: 0.46, W: 1.78, B:0.003) and, E911 (Mo: 1.01, W: 1.00), at 600°C, the 100,000 hours creep rupture strengths were 94 MPa, 115MPa, and 110MPa respectively [11], which shows that reduced Mo and increased W gives a good effect on the creep rupture strength. The size of Laves phase after longer exposure (up to 60,000 hours) at elevated temperature in P92 has been analysed by Korcakova [12]. The results in that study were similar to those shown in section 7.6.1 in that the particles initially coarsened rapidly and then coarsened more slowly although there was no correlation between coarsening and the chemical changes occurring. Hald [13] concluded that W produces the fine stable Laves phase in steel P92. The question that arises is whether W alloyed Laves phase $(Cr, Fe)_2W$ or Mo, W alloyed Laves phase $(Cr, Fe)_2(Mo, W)$ are finer after elevated temperature creep and this issue needs to be investigated further.

M₂X phase

M₂X phase was found for all samples. In service, the shape of the M₂X precipitates gradually changed from needle-like (coherent) coarse precipitates to more equiaxed morphologies (incoherent). After long time exposure at 625°C and 650°C, the M₂X particles were particularly coarse (see Figure 7.13 in Chapter 7).

The behaviour of M₂X in E911 is dissimilar to that observed in 12CrMoVNB steels by Vodarek and Strang [14] where the fine M₂X particles gradually dissolved due to precipitation of (V, Nb)X phase. This phase then gradually dissolved due to the precipitation of Z phase during further exposure.

Danielsen and Hald [15] suggested that over-stoichiometric alloying of N with respect to Nb+V will lead to the formation of chromium nitride (M_2X). A low nitrogen content will also stabilise V(N,C). Therefore, decreasing the N content overall will help to suppress M_2X phase coarsening.

MX phase

In the as-received condition, the mean size of the MX particles was below 100 nm. Even after the longest exposure, the size was stable. Therefore, it is the most desirable phase in E911 steel. However, the formation of Z phase consumes a large number of MX phase particles.

Z phase

Z phase particles were only found in the gauge length of the sample exposed to the longest creep duration of 75647 hours at 600°C. No Z phase was found on the samples at exposure temperatures of 625°C and 650°C. In E911 the Cr content is relatively low and higher Cr content steels (and those with higher Nb contents) are more liable to Z phase precipitates [16, 17].

In long term high temperature dynamic straining conditions, such as creep, diffusion rates in the matrix are increased leading to rapid increases in precipitate growth and dissolution rates compared with the thermally exposed unstrained sample heads.

Optimum particle size

With regard to the effect of precipitate size on strengthening of high chromium steel, the particle hardening mechanism should be clarified. For the crystalline materials, the small particle size usually results in dislocations passing through or “cutting” the particle while dislocations tend to bow between large particles [3]. Figure 9.1 shows the interaction between particle size, volume fraction, and “strength” for the cutting and bowing processes [3]. The transition from cutting to bowing and the maximum particle hardening can be obtained. From the view of lines (c) and (d), the smaller the precipitate size, the higher strength is obtained (when particles size $r > r_1$ or r_2). However, when the particles size r equals r_1 or r_2 , the maximum strength is obtained; if the particle size is below r_1 or r_2 , the precipitate strengthening effect is decreased.

Most precipitates in steels are relatively large, so dislocations have to travel between them (bowing) rather than cut through them. This is called Orowan bowing [18]. When the

precipitates grow, the distance between the carbides therefore increases, thus, making the dislocation movement easier. At the same time, the dislocation movement and accumulated strain energy can reach a critical value, and the formerly pinned dislocations can overcome the carbides [19]. Therefore, the fine particles are the most desirable in 9-12% Cr alloy design for the purpose of precipitation strengthening in long time service. On the other hand, by reducing the carbon concentration of 9% Cr steel (9Cr-3W-3Co-0.2V-0.05Nb-0.05N) to a very low level of 0.018%, the creep strength increased significantly; when the carbon concentration is down to 0.002%, the unstable $M_{23}C_6$ phase can be eliminated and the large number of nano-size MX nitrides (<10nm) are found distributed along lath, block, packet and prior austenite boundaries. This was reported by Abe (see Chapter 1). However, there is still a question as to whether nano-size MX nitrides are an optimum particle size or not? This issue needs to be investigated further.

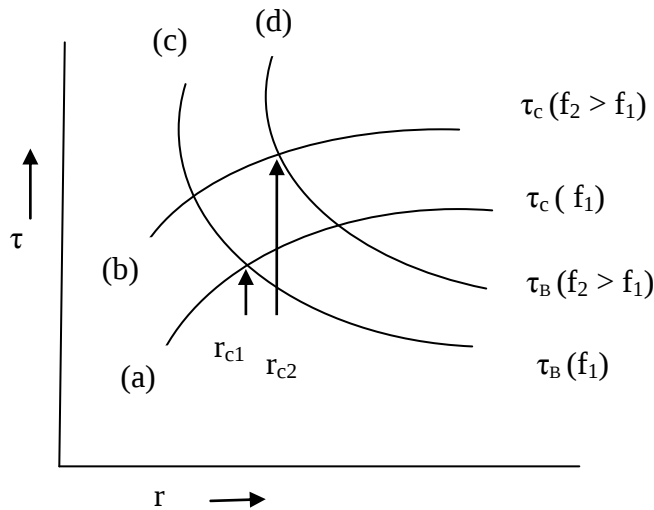


Figure 9.1. The competition between cutting and bowing. After T. H. Courtney with some modifications [3].

τ_c : the shear strength associated with dislocation cutting;

τ_B : the shear strength associated with dislocation bowing;

f_1, f_2 : volume fraction;

r_{c1}, r_{c2} : the optimum particle size with the maximum strength for the volume fraction of f_1, f_2 .

9.1.5 Thermally aged sample analysis

The significance of Z phase Cr(V, Nb)N in 9-12% Cr steels has been realised: the presence of this phase seriously limits the long-term rupture strength of 9-12 % alloys.

Recent work by Danielsen and Hald [20] has shown that Cr has a strong influence on the precipitation of Z-phase with higher Cr contents allowing Z-phase to be formed more rapidly. They suggest that Ni has little influence on the precipitation of Z-phase. However, work by Vodarek and Strang [21] has shown that for three casts, Z phase precipitates were observed earlier in the cast containing more Ni. This is strong evidence that Ni does in fact have a role in the precipitation of Z-phase; the presence of alloying additions of elements such as Ni, which is traditionally added to suppress the formation of delta- ferrite in this class of steels, accelerates its precipitation. The Z phase appears to precipitate with chemical compositions which are close to equilibrium at the service temperature. As a result there is no driving force for changes in Z phase which means that once precipitated the composition of Z phase is stable [21].

Thus, the investigation of the effects of Ni and Cr on the microstructural stability of these steels was the basic aim for studying four thermally aged experimental casts with different levels of Ni and Cr.

The precipitate analysis on the four experimental casts was carried out by TEM coupled with EDX. Previous evidence has suggested that the higher Cr level in 9-12% Cr steel is likely to cause the presence of Z phase. However, due to the influence of the lower tempering temperature and lower Nb content of the four experimental casts, it was hard to find this phase within the exposure duration of 10,000 hours, therefore, the longer exposure running duration is needed for the further investigation. However, the results do show that Z phase was found for the cast with both the highest Cr and highest Ni content (Code 29 in Chapter 8) and thus it would seem that Ni is having an effect on the Z phase precipitation. More definitive conclusions may be possible after studying sample exposed to longer durations.

9.2 Further work

9.2.1 Further work on EBSD

9.2.1.1 Investigation of the microstructure evolution in a single block within a prior austenite grain

A martensite lath is a single orientation crystal in the quenched condition. On the inverse pole figure, this is shown as 1 dot using the subset technique by EBSD. After tempering and long term exposure, this single crystal changes to multiple orientation due to sub-grain formation. In order to express this evolution, the samples should be scanned at high magnification (greater than 5000) to obtain the detailed sub-grain information inside a block by EBSD. The data analysis method will be: enter into the subset, choose one block, plot the orientation and misorientation evolution using inverse pole figures and pole figures.

9.2.1.2 Phase ID by Kikuchi pattern

The precipitate distributions should be plotted on the AE maps at higher magnifications (between 6000-10000). Using phase identification by means of Kikuchi patterns, a 20-50 nm spatial resolution (0.02-0.05 μm step size) can be achieved by improving the parameters in the EBSD software with a highly polished surface. The matching unit selections should be: Fe (BCC), M_{23}C_6 (FCC), Z-phase (Tetragonal) and Laves phase (Hexagonal).

9.2.2 Further work on TEM

Eight samples need to be analysed by TEM. They are: 30A6, 30B6, 30C6, 30D6, 31A6, 31B6, 31C6 and 31D6. Additionally, there are 16 further thermally ageing samples still running (with durations greater than 10,000 hours). When they are due to be taken out of the furnace, precipitate analysis should be carried on these by TEM.

Which element (Cr or Ni) has an accelerating effect on Z phase precipitation should be investigated on the basis of the overall data analysis.

9.2.3 Further work on modelling

Recently, computing based simulation by means of Thermo-Calc and DICTRA has been developed extensively. Thermo-Calc calculates the Gibbs energy for most of the phases in

multi-component alloy system. It is possible to predict the phase presence and growth at certain temperatures and exposure durations.

However, 9-12 % Cr steel is a complex Fe alloy system. due to the demanding of high accuracy of the predictable models, advanced thermodynamic and diffusion database will need to developed further.

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