Microstructural Evolution in Service Exposed Low Alloy Power Plant Steels

By

Kate Burke

Department of Materials Loughborough University

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Abstract

Abstract

This work forms part of the EPSRC Supergen 2 Lifetime Extension of Conventional Power Plant project. In particular this research investigates the remaining life of a number of different ¹/₂Cr ¹/₂Mo ¹/₄V power plant steels which have been in service for considerable lengths of time and which have subtle differences in chemical composition, microstructure and mechanical properties. The low alloy ferritic steels all operate in the creep regime and therefore resistance to creep is an important microstructural characteristic. There are a number of key questions which this research aims to address: Having endured this extensive time in service how do engineers within the power industry know that the component is still safe to run? Even as the components reach and often exceed their original design life, it is important to safely extend the lives of existing conventional plant in a bid to ensure that the country's electricity supply remains intact.

Twenty two different samples were provided by industrial partners, which had endured a range of times in service from 66,000 hours up to 206,000 hours. All but one of the samples had lost all of the original ferrite/pearlite microstructure present on commencing service. The structure remaining comprised of ferrite grains with large carbides nucleating and growing at the grain boundaries and small carbides within the grains. From an optical microscopy point of view, a number of differences could be observed in the samples; for example, the grain size and the amount of visible large carbides. However, there was no specific relationship observed with service life which could easily be correlated with these features.

Previous works have suggested that the initial microstructure, in some cases, before the steels enter service may be bainite rather than ferrite/pearlite. Therefore two samples of virgin material were used to investigate the effect of the initial heat treatment on the material. Samples were heated to 950°C and cooled at a number of different cooling rates. Bainite was formed during rapid cooling, however, it is difficult to imagine that the cooling of thick section pipes could be sufficiently fast to produce this structure through the wall thickness. The cooling rate most likely to be seen in production was selected for long term aging trials to investigate the long term decomposition of the microstructure.

Thermodynamic modelling was performed to investigate the phase stability in the different compositions of the samples provided. The results suggested that the equilibrium carbide in all of the samples was not necessarily $M_{23}C_6$, which is commonly regarded as the equilibrium carbide for this steel. Steels which contained more carbon were more likely to yield $M_{23}C_6$ at equilibrium than those which contained a lower carbon content. In addition, thought experiments were performed using a thermodynamic modelling package to understand the effect of the different elements within the range of compositions allowed within the British Standard on the phase stability. Carbon affects the microstructure most significantly when all other elements are at the lowest level allowed in the British Standard, whereas molybdenum appears to affect the carbides at higher temperatures much more than other elements do.

The larger carbides nucleating and growing on the grain boundaries were identified using X-ray diffraction (XRD) as $M_{23}C_6$ or Mo_2C . Site specific samples for transmission electron microscopy (TEM) were extracted from the bulk samples using a focused ion beam field emission gun scanning electron microscope (FIB FEG-SEM) in order that diffraction patterns could be obtained from the carbides for a complete characterisation. XRD and EDX results revealed that the $M_{23}C_6$ carbides were not simply chromium carbides, with the level of molybdenum in most samples being sufficient to move the XRD peaks for the particle off the peak position for $M_{23}C_6$ by up to 4°.

A significant amount of work has also been performed on the smaller carbides which are found within the grains of this material. Numerous authors report that they provide the creep resistance of the material as a result of the hindrance to dislocation movement which they provide. Comparing a number of samples from this work, it would appear that any correlation between the small carbides and the amount of life remaining is not clear cut in a particular cast of material.

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A strong link has been identified, however, between the post service microstructure and the post service creep data, using an equation to normalise the creep data for comparison reasons. Thermodynamic modelling has been used to help to predict which of the samples are of particular concern. A number of different relationships were examined; however, it was found that the coverage of the grain boundary carbides showed an excellent correlation with creep life. The result of this research is a product which the power industry can use to identify potentially weak casts of ¹/₂Cr ¹/₂Mo ¹/₄V steels.

Work towards the end of this research has shown that the amount of carbides covering the grain boundaries in this material can be measured from replicas taken from pipes which are in service. These replicas are already taken by the power industry to observe creep damage in these steels which makes the grain boundary carbide measuring a simple additional test to the tests which are undertaken at regular intervals. This means that the methods described for identifying potentially weak materials can be used as an additional tool to the power industry.

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Chapter 1

Introduction

1.1 Overview

This work forms part of the Engineering and Physical Science Research Council (EPSRC) funded SUPERGEN project, entitled 'Lifetime Extension of Conventional Power Plant' which is a consortium of ten industrial partners and four universities with the ultimate goal of producing a 'toolbox' of plant life prediction methods. Phase 1 (2004-2008) of the programme was split into four work packages. The University of Bristol led work package 1 which was associated with the development of in-situ miniaturised condition monitoring tools. Work package 2, led by Cranfield University was concerned with environmental degradation and protection, investigating the potential damage to power plant components as a result of changing service conditions. Work package 3 was led by Loughborough University, concerned with microstructural modelling and characterisation and investigated the microstructural evolution in power plant materials as a function of time, temperature and stress during service. The University of Nottingham have undertaken the modelling of mechanical behaviour, within work package 4. This work aims to improve the understanding of remaining plant life through the mechanical testing and subsequent modelling and verification of power plant components.

The aim of this study, which is part of work package 3, is to understand, and where necessary quantify, the microstucture of $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V power plant steels with slightly differing chemical compositions so that a clearer understanding of their condition as they approach 'end of life' can be established. In particular, the work concentrates on parent materials which have been in service for up to 200,000 hours. Ideally the results from this work will progress forward to be used as a tool for predicting the remanent life of $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V in current power plant applications and facilitate improved decisions as to future applications in retrofits and also in next generation plant.

Introduction

1.2 Background

Over the next two decades 30-35GW of new electricity generating capacity will be required by the UK, see Figure 1.1^[1]. Currently the country has insufficient renewable capital to provide this alone and the ageing fossil fired plants have limited life remaining. Although there are plans to build new fossil fired units, this sharp rise in demand for power will cause a strain. There is, therefore, a need to extend the life of current plant to assist in meeting this potential shortfall.



Figure 1.1: The rise in demand for electricity over the next 12 years, plotted along with the generating capacity if there are no new plants built in the UK^[1].

In 2006, 142,700 TWh of electricity were produced from coal in the United Kingdom ^[2], see Figure 1.2. This indicates that, despite the falling reserves of coal, it still plays a major part in providing power to homes and businesses across the country.

To utilise the energy stored within coal it needs to be burnt. This is achieved in one of the many coal-fired power stations countrywide. A number of these plants have now been in service for up to 30 years, leading to a rise in material related questions. One such question concerns how much longer certain components can remain in service before failure occurs? Indeed, the original design codes were conservative leading to an opportunity to safely extend the lives of particular components, however, this must be based on a quantitative understanding of changes in the materials with reference to the service environment.

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Figure 1.2: Electricity supply by fuel type from 1980 to 2006^[1].

Figure 1.3 is a schematic diagram of a fossil fired power station; the coal is fed into the boiler via the pulveriser where the coal is turned into a fine dust. The heat of the burning coal in the boiler causes the water in the boiler tubes to heat and produce steam. The steam is then fed from the top of the boiler through a system of pipes to drive the turbine, in turn producing electricity.

Most of the coal-fired power stations currently in service in the UK were built in the late 1950's or early 1960's. They are now rapidly reaching (or have exceeded) their original design lives which are generally considered as being conservative. A number of components are of particular concern in these aging plants; these include headers and steam pipe work. This work focuses on the steam pipes. Figure 1.4 is a schematic diagram of a boiler and associated pipe work with the steam pipes under investigation highlighted. Steam from the top of the boiler is transported along these pipes to the turbine. The adverse conditions within the pipe, reaching temperatures of 568°C and internal pressures of 16.5 MPa, are perfect for the initiation and propagation of creep damage within the pipe wall. Previously, failures in these pipes have typically only occurred in the welds via a number of different mechanisms ^[3]. However, concern is now growing over the integrity of the parent, $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steel.



Figure 1.3: A schematic diagram of a fossil fired power station system reproduced from the Didcot Power Stations Guide, RWE group technical publication ^[4].



Figure 1.4: Schematic diagram of a fossil fuel fired boiler and steam turbine with the steam pipe work, which is the subject of this research, highlighted ^[5].

Figure 1.4 gives an indication of the extent to which the steam pipes extend through the power plant. Their main function is to transport the steam from the top of the boiler down to the turbines. The result is a pipe which may extend up to 25 m in length and have numerous changes in direction, with each change resulting in a

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stressed bend corner. Clearly a pipe of this length at high temperatures and under high pressures is a contender for creep damage. To enable the power plant to keep a log of the distance each pipe creeps; each component is fitted with small 'pips'. Two of these pips are attached to the pipe at a set distance apart and with time the distance between them is measured and the amount of creep can be calculated as a function of observed extension ^[6].

Clearly the ideal material would allow the pipes to be placed into service and still be suitable for service at the date when the station is decommissioned. Due to the nature of the environment, one family of steels lend themselves cheaply to the steam environment applications; the low alloy steel ½Cr ½Mo ¼V. Possible alternatives include a number of higher chromium steels i.e. 9% Cr and 12% Cr steel which, despite having superior mechanical properties over the low alloy counterparts, have the major disadvantage of higher costs. The increased alloying element content increases the steel production cost, which must, ultimately be absorbed into the plant building costs. Although these higher chromium steels may have a longer service life and are needed for specific regions of plant which require greater corrosion and oxidation resistance, the increased cost far outweighs the increase in mechanical properties and corrosion resistance for long lengths of standard steam pipework.

Initial testing prior to the installation of these low alloy steel pipes indicated the anticipated safe lifetime of the parent material. As these timescales are now being reached, and in some cases much exceeded, concerns about the parent metal integrity are not without just cause. Plants in Germany have recently seen parent material failures and Figure 1.5 shows the result of such an occurrence; this failure did result in fatalities, which is clearly a situation to be avoided at all costs. Industry partners ^[7] report that failures of ½Cr ½Mo ¼V pipes produced to the German standards, where more carbon is allowed in the composition, are more regularly observed than in the British Standard counterparts.

A comprehensive system of removal of serviced aged material is underway throughout the country and a number of different projects have been involved in the mechanical testing of this material. In particular creep testing and impression creep

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testing have been employed to create a ranking system for cast-to-cast variations. Ideally, the data from these projects will assist in the prediction of remanent life.

With a number of new plant at a planning stage it is important to understand the relationship between creep and microstructure and ideally one would wish to predict the remanent life of a steel by a simple investigative technique, i.e hardness testing, microstructural or elemental investigations, which could easily be carried out in-situ.



Figure 1.5: The result of a parent material steam pipe failure in the German plant, Siempelkamp^[8].

For this research programme, a variety of samples have been provided by RWE npower and E.On. All of the samples had slightly different chemical compositions some within the British Standard and others fall outside the standard boundaries. However, the initial exact composition of the materials prior to service was not known although it is likely that the chemical compositions of the bulk of the samples have not changed significantly during service. In addition all of the samples have been in service for a different number of operating hours. In addition to the post service samples, two examples of virgin material were available, which have been stored within the industry over time and are therefore likely to have similar initial manufacturing conditions to the ex-service material.

Understanding the effect of time in service on the microstructure of the material and ultimately, the effect of the changing microstructure on the creep properties of the pipe is important, both from a financial and health and safety point of view, and is therefore the key aim of this research programme.

Chapter 2 reviews the literature pertaining to steels in general, and low alloy steels in particular. Chapter 3 details the various experimental techniques which have been employed throughout this research, including optical, scanning electron and transmission electron microscopy, image analysis methods and x-ray diffraction. The general microstructure of the steel samples are observed in Chapter 4. Chapter 5 investigates the effect of the initial heat treatment on the microstructure of steels with varying carbon contents. Chapter 6 details the results of thermodynamic modelling of the phase stability which differs from sample to sample as a result of small differences in the composition. The different experimental techniques are utilised to characterise the carbides present. Chapter 8 details how the carbides found in the samples can be linked to the amount of life remaining in a sample with a particular microstructure. Finally, Chapter 9 presents the conculsions and the further work which would progress the understanding of the affect of the carbides on the creep life of $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steels.

Chapter 2

Literature review

2.1 Introduction

This chapter presents an introduction to the physical metallurgy of steel and then reviews the literature concerning the mechanisms of creep failure, current methods of life assessment, typical failure mechanisms and finally the previous research specific to ½Cr ½Mo ¼V steels used in fossil fired power plants which are the subject of this research.

2.2 Physical Metallurgy of Steels

2.2.1 The Fe-C Phase Diagram

The starting point for the likely microstructure to be present in a steel is the Fe-C phase diagram presented in Figure 2.1. Plain carbon steels (those with very low alloying additions) can be referenced to the iron-carbon phase diagram to predict the possible amount of a particular phase at equilibrium.



Figure 2.1: The iron carbon (iron-cementite) equilibrium phase diagram.

The phase diagram provides a method of predicting which phases will be present at a given carbon concentration and temperature. Fe-C alloys with above 2% carbon are termed cast iron. Alloys which contain below 0.8 wt.% C are described as hypoeutectoid and those with between 0.8 and 2% are hyper-eutectoid ^[9]. Ultimately it is possible to establish how much of a phase will be present in a steel of a particular carbon concentration at equilibrium. If the area below 723°C to the left hand side of the diagram is considered, the dominant phase is ferrite, and, the C concentration increases to the right hand side of this section, the pearlite content of microstructure increases. For example, considering two steels of nominally the same composition, one with a high carbon content (1.5 wt.%) and one with a low carbon content (0.25 wt.%), both at room temperature, they would contain quite different quantities of ferrite and pearlite. It is possible to calculate the amount of each phase in a steel of known carbon content at a know temperature through the use of the Lever rule.



Figure 2.2: An explanation of the Lever rule. With the α -phase to the left hand side and liquid to the right, C_{ave} is the point at which the composition is being calculated using eqn. 2.1 at a temperature T. Reproduced from ^[10].

Figure 2.2 and Equation 2.1 describe the Lever rule (or law) which allows the relative amounts of phase to be calculated ^[10] where C_L , C_{av} and $C\alpha$ are the amount of B at the liquid transformation, the average composition of B and the composition at the ferrite transformation line respectively. It is possible to use this method for different phase fields across a phase diagram by adjusting the equation accordingly.

2.2.2 Matrix Phase:Ferrite

The f.c.c. lattice of austenite can undergo a reconstructive transformation to the b.c.c. ferrite if there is little undercooling and diffusion can occur. Diffusional ferrite in steels nucleates heterogeneously and is observed to grow in two forms, allotriomorphic and idiomorphic ferrite. The term allotriomorphic is used when the ferrite has a shape which does not reflect its crystal symmetry. Allotriomorphic ferrite nucleates at prior austenite grain boundaries and then grows preferentially along the grain boundary, where diffusivities are high. Idiomorphic ferrite, however, has a shape which is related to its crystal structure. It nucleates and grows intragranularly, generally taking the form of equiaxed grains.

Widmanstätten Ferrite

If undercooling occurs slightly below the A_{e3} temperature for a particular alloy, the increase in free energy driving force for the reaction and the decrease in atomic mobility result in the formation of Widmanstätten ferrite. (The Ae3 temperature is the temperature at which austenite transforms to ferrite. For pure iron this occurs at 910°C, but transformation occurs at progressively lower temperatures as the carbon content of the steel is increased.) Diffusion of carbon is a thermodynamic necessity and Widmanstaätten ferrite forms with the equilibrium carbon concentration, therefore with carbon partitioning during the transformation. Growth is accompanied by an Invariant-Plane Strain (IPS) shape change, and there is no diffusion of substitutional solute or iron atoms. (A deformation which leaves a plane undistorted and unrotated is called an invariant-plane strain.) At these temperatures the available driving force is much less than the strain energy due to the shape change, and so to accommodate this strain energy, growth involves the simultaneous formation of two plates, appearing under an optical microscope as one, although they have different habit planes with respect to the parent austenite. The growth rate has been shown to be determined by carbon diffusion rates in the austenite at the glissile α_{ω}/γ interface [11]

2.2.3 Bainite

Bainite is a non-lamellar mixture of ferrite and carbides which is formed by the decomposition of austenite at a temperature above the martensite start temperature,

 M_s , but below the temperature at which pearlite can form. It has been shown that during the diffusionless formation of martensite there is a physical change in the shape of the parent phase, whereas a diffusional reaction requires mass transport to produce a change in structure without introducing strains ^[12]. The bainite transformation, being intermediate between the diffusionless martensite and diffusional pearlite reactions has presented difficulties in interpretation in the past ^[13], although these are now beginning to be resolved ^[14,15].

Morphology and carbide precipitation

Bainite consists of non-lamellar aggregates of ferrite and carbides, the ferrite being in the form of thin plates approximately 10 μ m long and 0.2 μ m thick, commonly referred to as sheaves ^[16]. The growth of the sheaves is limited by hard impingement with the austenite grain or twin boundaries, and they have a relatively high dislocation density. Carbides are not an essential feature of bainite, and in fact they are completely absent in many cases. In particular, in alloys containing high concentrations of Si or Al, Fe₃C precipitation is so slow that to all intents and purposes the bainite consists only of bainitic ferrite and retained austenite.

The formation of bainitic ferrite leads to an increase in the carbon concentration of retained austenite. There are two different morphologies associated with bainite formation. Upper bainite forms at the higher temperatures within the range, the cementite precipitating from films of carbon-enriched austenite which separate the plates of bainitic ferrite. The platelets within a sheaf are all in the same orientation in space and the orientation between α_b (bainite) and γ (austenite) is the same as for α_{\Box} (martensite)/ γ . In lower bainite, however, cementite also forms within the platelets of ferrite. In contrast to the cementite obtained after tempering supersaturated martensite, the carbides formed within any given lower bainitic plate usually occur in a single crystallographic orientation. There are therefore two kinds of cementite particles, those growing from carbon-enriched austenite and those precipitating from supersaturated ferrite. The precipitation of cementite generally occurs as a secondary reaction after the growth of bainitic ferrite ^[16]. The precipitation sequences are summarised below.

1. Upper bainite

 $\gamma \longrightarrow \gamma + \alpha_{ub, supersaturated}$

 $\rightarrow \gamma_{\text{enriched}} + \alpha_{\text{ub, supersaturated}}$ $\rightarrow \alpha + \theta + \alpha_{\text{ub, unsaturated}}$

2. Lower Bainite

γ

a. High dislocation density.

- $\gamma \longrightarrow \gamma + \alpha_{lb, supersaturated}$
 - $\rightarrow \theta_{\text{in ferrite}} + \alpha_{\text{lb, unsaturated}} + \gamma_{\text{enriched}}$
 - $\rightarrow \alpha_{lb, \text{ unsaturated}} + \alpha + \theta_{between \text{ ferrite plates}} + \theta_{ferrite}$

b. Low dislocation density

- $\rightarrow \gamma + \alpha_{1b, supersaturated}$
 - $\rightarrow \epsilon \text{ carbide}_{\text{ in ferrite}} + \alpha_{\text{lb, unsaturated}} + \gamma_{\text{enriched}}$
 - $\rightarrow \alpha_{lb, unsaturated} + \epsilon \text{ carbide in ferrite} + \alpha + \theta_{between ferrite plates}$
 - $\rightarrow \alpha_{lb, \ unsaturated} \ + \ \theta_{in \ ferrite} \ + \ \theta_{between \ ferrite \ plates} \ + \ \alpha$

2.2.4 Matrix Phase: Martensite

Martensite forms at the highest undercoolings, when the free energy change for the transformation is very large. Hence, rapid quenching of austenite to room temperature results in martensite, a very hard brittle structure in which carbon, originally in solid solution in austenite, remains in solution. Unlike the formation of ferrite or pearlite, the martensite reaction is a diffusionless shear transformation which is highly crystallographic in character and leads to a characteristic lath or lenticular microstructure.

The addition of alloying elements to a steel can affect the temperature, M_s , at which the martensite reaction can begin on cooling the parent phase. The extent to which the reaction proceeds depends on the undercooling below this temperature. Note that martensite can form at very low temperatures where atomic mobility is almost negligible because the transformation is diffusionless. The growth rate can be very high, limited by the speed of sound in the material concerned.

Tempering of martensite

The presence of martensite in a quenched steel greatly improves the hardness, but it is normally very brittle and so almost all technological steels have to be heat treated to increase their toughness. Tempering is therefore normally carried out in the range 150-700°C. Martensite is a highly supersaturated solid solution of carbon in iron which, on tempering, rejects carbon in the form of finely divided carbide phases. The microstructure after tempering is a fine dispersion of carbides in a ferrite matrix which

often bears no resemblance to the as-quenched martensite. If the martensite reaction does not go to completion on quenching, there will also be some retained austenite which does not remain stable during the tempering process.

2.2.5 Carbides

The carbides most likely to be seen in low alloy steels are described below, the most common carbides identified in previous research likely to be present in $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steels are: M₃C, M₂₃C₆, M₇C₃, M₂C and MC. They are described in greater detail in the following sections.

M_3C

Cementite containing no alloying element additions, Fe_3C , can be thought of as an approximately hexagonal close-packed arrangement of metal atoms with localized distortions to accommodate the carbon atoms. Each carbon atom is surrounded by a triangular prism containing 6 iron atoms.

 M_3C is predominantly an iron-rich carbide with the same orthorhombic structure as Fe₃C, however several alloying elements can partition to this carbide in significant quantities. The unit cell dimensions are affected by partial substitution of alloying elements. Woodhead and Quarrell ^[17] have found that Mn can dissolve in large quantities, as can Cr, with up to one fifth of the Fe atoms being replaced by Cr (specific to low alloy steels). Ni and Co can also dissolve as they form metastable orthorhombic carbides, although they usually partition to ferrite. Mo, W and V have also been found to have limited solubility in M₃C. In general M₃C carbides can be referred to using the general formula (Fe,Cr,Mn,Mo)₃C.

$M_{23}C_{6}$

 $M_{23}C_6$ is a cubic thermodynamically stable carbide with a lattice parameter of 10.621A and typically contains chromium with small additions of iron, vanadium and molybdenum as the metal (M) atoms ^[18]. Vyrostkova *et al.* ^[19] reported that the carbide can contain large quantities of these other elements. It is commonly observed at grain boundaries but it does, on occasion, form as small carbides within the grain.

Hong *et al.* ^[20] studied the effects of $M_{23}C_6$ morphology in an austenitic stainless steel and found that the carbides would precipitate from a grain creating the smallest angle with the grain boundary plane. The carbide then grows into the neighbouring grain adopting the plane with the lowest interfacial energy, the resulting carbide is triangular in morphology. The authors showed, using EBSD, that boundaries where this triangular carbide had grown exhibit more pronounced creep cavitation.

M_7C_3

In addition to $M_{23}C_6$, M_7C_3 is also a chromium rich carbide with an orthorhombic structure and lattice parameters $a = 4.526A_{-}$, $b = 7.010A_{-}$ and $c = 12.142A_{-}^{-}$ ^[21,22] Although not strictly a true equilibrium carbide it is not uncommon that M_7C occurs alongside $M_{23}C_6$ ^[18] and often exhibits a faulted crystal structure, making it easy to identify using electron diffraction due to the presence of streaks within the patterns.

M_2C

 M_2C usually occurs as the hexagonal Mo_2C , which is thermodynamically stable. This carbide contains mainly molybdenum, tungsten and/or chromium ^[22]. If sufficient chromium and molybdenum are present in the alloy it is likely that the more stable $M_{23}C_6$ will form ^[18]. It is possible that this carbide will dissolve some Cr and V but only small amounts of Fe ^[19]. Gingell *et al.*^[23] performed thermodynamic modelling on three steels of the same nominal composition with small chemical variations.

МС

The face centred cubic MC carbide is usually a vanadium rich carbide found commonly as the central section of the H shaped carbides, as shown in Figure 2.9. This carbide has a unit cell parameter of 4.30 A \equiv , a molecular weight of 62.95 ^[24]. During the tempering of $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V the vanadium can be replaced by Mo leaving a predominantly molybdenum rich carbide ^[19]. Carruthers and Collins ^[25] describe how the MC carbide initially present is gradually replaced with M₂C during exposure to 600°C in $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steels. Above this temperature the MC carbide remains thermodynamically preferred.

2.2.6 Nitrides

During the production of steels a number of elements are added for grain refining, niobium, titanium and vanadium are typical grain refiners these are typically strong carbide or nitride formers and as the nitrides are thermodynamically more stable than the carbides these will, where sufficient nitrogen is present, preferentially form. These small carbo-nitrides remain within the grains providing hindrance to dislocation movement. It is also possible for nitrogen to substitute for carbon within 'carbide' structures, such that the MC carbide for example may exist as MX, where X is a combination of carbon and nitrogen.

2.3 Continuous Cooling Transformation (CCT) and Time Temperature

Transformation Diagrams (TTT)

Continuous cooling transformation diagrams (CCT) and time temperature transformation diagrams (TTT) allow the microstructure of the steel to be predicted as a function of the cooling rate, for example, Figure 2.3 is a CCT diagram describing the relative speeds at which steels must be cooled to reach a particular microstructure. Each steel has a CCT diagram of its own due to the effect of alloying elements which alter the speeds at which the steel must be cooled to reach a particular structure. The diagram shows that martensite requires the fastest cooling rate of all the phases, followed by bainite which must have a cooling rate which falls within the correct segment of the diagram. Pearlite, which forms along with ferrite has the slowest cooling rate of all. In industrial applications, different methods of quenching the steel would be used to allow the steel to cool into the correct segment of the CCT diagram and thus produce the desired microstructure. Figure 2.4 is a TTT diagram which shows the effect of different carbon contents on the transformation curves. The addition of alloying elements can greatly affect this diagram and Figure 2.4 shows clearly the effect of different carbon contents on the curves of the diagram, effectively opening up the ferritic region with increasing carbon content. Alloying elements delay the transformation from austenite, therefore shifting the pearlite and bainite start times to the right. Chromium and molybdenum delay the austenite to pearlite transformation more than the bainite transformation. The martensite start (M_s) and martensite finish

 (M_f) temperatures are also lowered with increasing carbon and alloying content $_{[10,26,27]}$



Figure 2.3: Continuous Cooling Transition (CCT) graph for ½Cr ½Mo ¼V steel of composition: 0.12 wt. % Cr, 0.25 wt. % Si, 0.55 wt. % Mn, 0.02 wt. % P, 0.02 wt.% S, 0.40 wt. % Cr, 0.6 wt. % Mo, 0.15 wt.% Ni, 0.25 wt. % V. ^[28].



Figure 2.4: A TTT diagram describing the effects on transformation rates of differing carbon contents in steels ^[27].

2.4 Strengthening Mechanisms

The major constituent of steels is iron. In its simplest form iron exists as two different crystal structures, body centred cubic (bcc) (α -iron) (Figure 2.5) or at temperatures above 910°C it exists as face centred cubic (fcc) (Figure 2.6) or γ -iron. γ -iron will remain stable up to a temperature of 1390°C, where the structure reverts back to the bcc structure until the liquidus temperature of 1536°C is reached ^[9].





Figure 2.5: The bcc structure

Figure 2.6: The fcc structure

Elements are added to iron to allow it to be useful in day to day applications. In the case of ¹/₂Cr ¹/₂Mo ¹/₄V steel the additions include, chromium, to impart strength, molybdenum to improve strength and machinability, vanadium to resist high temperature softening and carbon to increase the strength of the material. However, care must be taken when the steel is to be welded as an excess of carbon (above 0.2 wt. %) can cause cracks to initiate easily within the weld zone.

There are a number of methods which can be used to strengthen steels, these include:

- Work hardening
- Solid solution strengthening by interstitial atoms
- Solid solution strengthening by substitutional atoms
- Refinement of grain size
- Dispersion strengthening.

2.4.1 Work Hardening

During this process, steel is worked at room temperature. Working increases the number of defects within the material, which reduce the motion of the dislocations, and ultimately an increase in strength is obtained at the cost of ductility. There are limited uses for this type of strengthening for power plant pipes due to the vast quantity of material to be displaced in a pipe application. Other strengthening methods prove more cost efficient and appropriate/effective.

2.4.2 Solid Solution Strengthening by Interstitial Atoms

The simple addition of carbon to iron is sufficient to create steel. The process of carbon addition dates back over 2500 years when blacksmiths would effectively carburise iron whilst heating the iron in a charcoal fire. Today the process is more refined and the science better understood. Carbon is often accompanied by nitrogen as an alloying element and both elements are small enough to reside as interstitial solute atoms within the fcc or bcc iron lattice creating a strengthening effect ^[9,26].

2.4.3 Solid Solution Strengthening by Substitutional Atoms

Larger alloying elements, such as, molybdenum or chromium are too large to reside in interstitial sites so they exist as substitutional atoms, i.e, they replace the iron atoms in the lattice ^[9]. Figure 2.7 shows how the substitutional atoms affect the crystal lattice at the site of a dislocation. The result from a mechanical properties point of view is that a greater stress must be applied to the lattice to move the dislocation, i.e. the yield strength of the material is raised.



Figure 2.7: The effect of substituting atoms at a dislocation site. (following Higgins ^[29]).

2.4.4 Refinement of Grain Size

In the 1950's Hall and Petch changed the fundamental way in which steel was designed, by suggesting that by reducing the size of the ferrite grain size the yield strength and toughness of the ferrite-pearlite steels could be increased, suggesting the equation

$$\sigma_{\rm v} = \sigma_0 + k_{\rm v} d^{-1/2}$$
 [Eqn. 2.2.]

where σ_0 and k_y are constants, with σ_y being the yield stress and d the grain diameter ^[9,26,29]. In practice, industrial grain refinement is performed through working the material or through heat treatment i.e. a set process of normalising and re-normalising until the required grain size is obtained.

2.4.5 Dispersion Strengthening

In most steels it is possible to identify more than one phase within the microstructure. These two phases will themselves be strengthened by the mechanisms described above but it is possible to control the dispersion of further phases. In most cases the addition of a dispersion will increase the strength of the material, however, there are some cases in which the addition of a dispersion can have undesirable effects on the toughness and the ductility. The most common phase to undergo this controlled dispersion is Fe₃C (cementite), which can occur as a lamellar form, as fine rods or as spheroidal precipitates. In some cases these iron carbides may be replaced by thermodynamically more stable dispersed phases, i.e. nitrides, borides, and intermetallic compounds. All of these dispersed compounds act to hinder the motion of dislocations and the yield strength of the material to the inter-particle spacing Λ ,

$$\tau_0 = \tau_s + \frac{T_d}{b\Lambda/2} \dots [Eqn \ 2.3]$$

where τ_s is the yield strength of the matrix, T_d is the line of tension of dislocation and b is the Burger's vector ^[9]. This equation can be used to identify whether a dispersion will have a favourable or adverse effect on the properties of the material.

In the case of small precipitates within the matrix which can be described as a group of segregated solute atoms particle cutting may occur (during which the dislocation cuts the particle in two), if, however, the interface between the particle and the matrix is too great then particle bypass will occur. During particle bypass the dislocation bends round the particle ^[30].

2.5 The Microstructure of ½Cr ½Mo ¼V Steels

2.5.1 British Standard

¹/₂Cr ¹/₂Mo ¹/₄V steam pipework is covered by British Standard 3604-1 1990. The British Standard requires a particular material composition ^[31]. The composition can be seen in Table 2.1. The standard is for a seamless pipe with the composition as taken from the ladle. According to the standard, production should be followed with a normalisation treatment between 930°C and 980°C with a subsequent air cool, followed by a temper at a temperature between 680°C and 720°C.

 Table 2.1: British Standard composition (wt. %) for ½Cr ½Mo ¼V steel, from BS3604-1:1990 [31]

 amounts of Ni and N are not specified for this steel within this standard.

Element	0	Cr	S	Si	M	ĺn	Р	S	(Cr	M	lo	N	Ji	١	V
Limit	Min	max	Min	max	min	max	max	max	min	max	Min	max	Min	max	min	max
Concentration	0.10	0.15	0.10	0.35	0.40	0.70	0.030	0.030	0.30	0.60	0.50	0.70	-	-	0.22	0.28

The composition in Table 2.1 and these heat treatments should yield a room temperature 0.2% proof stress of 297 N/mm² and a near service temperature (550°C) proof stress of 197 N/mm². The steel under investigation can have a composition which falls anywhere within the maximum and minimum ranges in Table 2.1.

2.5.2 Initial Microstructure

The microstructure observed in virgin pipe material after initial heat treatment is typically described as one of a ferrite and lamellar pearlite structure by some authors ^[32]. However, some others suggest that the initial microstructure may be one consisting of a mixture of ferrite, martensite, bainite and retained austenite ^[33].

Dunlop and Honeycombe ^[34] investigated $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V under a number of conditions and they found, through dilatometry, that after an initial autenitization at 1150°C during the tempering heat treatment the ferrite grain size increased linearly with transformation temperature between 650 - 750°C, and above this temperature there was a substantial increase in grain size up to 775°C.

2.5.3 Post Service Microstructure

With time in service the ¹/₂Cr ¹/₂Mo ¹/₄V can be seen to 'degrade'; this can be observed not only in the hardness but as a change in the microstructure. The initial ferrite/ pearlite structure is seen to change; it eventually becomes a much simpler ferrite structure containing a number of different sized carbides. Some of these carbides precipitate at the grain boundaries and can be observed using light microscopy, others are smaller, typically within the grains, and require scanning or transmission electron microscopy.

The European Creep Collaborative Committee (ECCC)^[35] studied the various stages of post service microstructure. They identified a structure of both large and small carbides with the larger carbides generally being observed at the grain boundaries and the smaller carbides evolving within the grains.

The evolutionary process of this microstructure was studied by the Italian Institute Siperiore per la Prevenzione e la Sciurezza del Lavaro, who produced a scale to which microstructure can be compared to establish how far through it's service life a $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V material is. Figure 2.8 is a reproduction of this scale.



Figure 2.8: Classification of $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V microstructure evolution. The structure begins with ferrite and lamellar pearlite then there is some initial spheroidization along with the beginning of carbides forming at the grain boundaries. An intermediate stage of spherodization is followed by complete loss of the lamellar structure in favour of carbides within the grains and at the grain boundaries. The final two stages involve the carbides becoming homogeneously distributed over the microstructure and the eventual coarsening of these carbides. Reproduced from ref^[35].

From Figure 2.8 it is possible to see how the microstructure changes from that of the initial ferrite and lamellar pearlite structure. This lamellar structure begins to break up before the pearlite becomes completely spherodized and homogeneously distributed

through the grains. Finally the coalescence and coarsening of these carbides leads to an overall growth in carbide size. This scale was created as part of the creep collaborative to identify steels which are susceptible to failure.

Pigrova ^[36] studied a 1Cr steel with the composition shown in Table 2.2 and ranked the carbides in the steel as a function of time and temperature in service.

Tuble 222 Chemiear composition of the steel stadied by Figiova , clements in we /o											
Element	С	Cr	Мо	V	Mi	Si	Mn				
Wt %	0.20	1.0	0.6	0.25	-	0.8	0.3				

Table 2.2: Chemical composition of the steel studied by Pigrova ^[36], elements in wt %

This steel was investigated after both 147,000 hours and 210,000 hours at low (250-300°C) and high service temperatures (520-560°C). X-ray diffraction was then used to establish a ranking of carbides by amount, Table 2.3 shows the carbides which were observed after the different service times and temperatures.

Service time	Low Temperature (250-300°C)	High Temperature (520-560°C)
147,000	M ₃ C, M ₂₃ C ₆ , MC	M ₃ C, M ₂₃ C ₆ , MC
210,000	Material unavailable	M ₂₃ C ₆ , M ₃ C, MC

Table 2.3: Carbides observed in the steel in Table 2.2 in decreasing amounts ^[36].

Pigrova ^[36] described the large carbides remaining after this process as one of three species; cementite, $M_{23}C_6$ and M_6C .

Du *et al.* ^[37,38], used equilibrium calculations to predict the phases which would be present in $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steel after various heat treatments. Their work concentrated on the compositional, morphological and size changes in carbides with increasing tempering time at temperatures typical of service temperatures. They showed that the large M₂₃C₆ and M₆C carbides precipitated at the expense of the cementite with time. They went on to show that the higher the tempering temperature, the shorter the time required for complete transformation to the equilibrium carbides. For example, M₂₃C₆ is typically seen after 5,850 hours at 640°C, however, at experimentally determined 565°C the same transformation requires 9,381 hours. The compositions of the carbides found in the $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V studied are shown in the Table 2.4.

Carbide	v	Cr	Mn	Мо	C .
M ₃ C	0.7-1.1	2.0-7.6	2.0-10.0	0.6-1.0	25.0
M ₂₃ C ₆	0.3-0.6	9.0-15.0	6.0-8.0	3.0-5.0	20.7
M ₆ C	2.0-3.0	5.5-8.0	6.0-8.0	1.0-20.0	14.3

Table 2.4: Composition of the carbides as found by Du *et al.* ^[38] in a $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steel amounts in at $\frac{9}{4}$

Work undertaken by Du^[37] showed that there are also small carbides which are precipitated directly from the matrix, these include:

- H-type carbides: seen to exist with a vanadium rich central bar onto which molybdenum and chromium rich plates nucleate and grow from the central carbides ends, as illustrated in Figure 2.9.
- Thin plate carbides: usually molybdenum rich, sometimes containing in excess of 95 wt.% Mo.
- Other small carbides which took the form of rounded carbides or in some cases cubic morphologies.



Figure 2.9: H-carbide with the vanadium rich centre and the molybdenum rich 'wings', nucleating with approximately 70° between the pair of wings ^[37].

2.6 Large Second Phase Particles in ¹/₂Cr ¹/₂Mo ¹/₄V

Carruthers and Collins ^[25] observed that carbides could be seen to coarsen with time in service. As a result, the authors concluded that the observation of these coarsening carbides can be used as a means of predicting creep damage accumulation and ultimately, remanant life prediction. In their work, creep rupture testing and short term, unstressed ageing trials were used as a method of microstructural investigation. The authors concluded that repeatability of their carbide coarsening measurements was difficult, and therefore that creep life prediction models based on such an approach should be treated with caution.

2.7 The Effect of Chemical Composition in ¹/₂Cr ¹/₂Mo ¹/₄V

It has been reported by various authors that small changes in the quantity of elements can have a profound effect on material properties and more importantly the affect of these small differences can have an effect on the service life of the material. Sanchez-Hanton ^[39] reported that in 9Cr steels used in power plants a small difference in aluminium content can cause a large change in the service life of a material. The results of this author's work have caused the power industry to re-assess their 9Cr pipework and monitor steel compositions of particular concern.

As its name suggests, ¹/₂Cr ¹/₂Mo ¹/₄V is alloyed mainly with chromium, molybdenum and vanadium along with a number of other additional elements; the four main elements and the effect the have on the steel are discussed in the following sections.

2.7.1 Chromium

It is often assumed that the addition of chromium to a steel will automatically increase the strength, however, this effect is only seen if there is sufficient carbon to form hard carbides, usually Cr_7C_3 or $Cr_{23}C_6$. These carbides are harder and thermodynamically more stable than cementite, with $Cr_{23}C_6$ being the most stable ^[29].

2.7.2 Molybdenum

When added to chromium containing steels, the molybdenum acts to improve the machinability. It provides material strength by forming stable, hard carbides, namely Mo_2C , Fe_4Mo_2C and $Fe_{21}Mo_2C_6$. Overall the molybdenum increases the high temperature strength and creep resistance of alloys exposed to harsh environments ^[29] In addition to the properties described by Higgins, Vyrostkova *et al.* ^[19] describe molybdenum as acting to stabilize M_6C and $M_{23}C_6$ carbides in Cr steels.

2.7.3 Vanadium

Vanadium acts as a strong carbide former and is usually present as the VC carbide. The main mechanical advantage of using vanadium is it's ability to resist softening at high temperatures, however, the steel must be heat-treated correctly to ensure that the VC is taken into solid solution ^[29].

2.7.4 Carbon

Increasing the amount of carbon present in steel allows an increasing number of carbides to form due to the excess carbon available for carbide formation. Whether this is detrimental to ¹/₂Cr ¹/₂Mo ¹/₄V steels is yet to be established, however, one author has studied the effects of the German material standard and compared the results with failures seen in German plants ^[40], the results suggest that where there is an increased amount of carbon the susceptibility for failure is much increased.

2.8 Failure Modes

2.8.1 Fatigue

Fatigue failure generally occurs in rotating plant equipment but can also be seen in static components, such as pipelines, where vibration causes fatigue to become an issue. Fatigue occurs when a material is under a repeated impact, twist, tension or compression. The mean stress may be zero or some definite value. There may well be additional steady loads imposed. Under these conditions fatigue failure may occur and the upper stress value may be much below the ultimate tensile stress of the material ^[41,42].

In addition to fatigue both thermal fatigue and corrosion fatigue are phenomena observed in pipework steels. Thermal fatigue is observed as a function of thermal cycling while corrosion in addition to fatigue causes the mean stress of the magnitude of the cyclic stress to be much reduced to cause a failure. A typical fatigue failure has distinctive 'beach marks' across the fracture face. Often a portion of the fracture face will show brittle tendencies where the fatigue crack has grown sufficiently that the stress on the component is sufficient to fail the remaining attached ligament.

2.8.2 Brittle Fracture

Brittle failure generally only occurs in power plant steels when a material has been treated incorrectly prior to going into service, for example if a component has not undergone sufficient softening during the initial heat treatment. The fracture face includes cracking which easily traverses the grains of the microstructure.

2.8.3 Creep

Creep is the most typical type of failure mechanism seen in power plant steel pipelines, this is due to the perfect conditions produced to initiate and propagate creep failures. The constant stress produced as a result of the structures own weight whilst combined with the temperature of 568°C place the materials well within the creep regime.

2.8.4 How Creep Can be Used for Life Prediction

Creep is a failure mechanism, which occurs well below the tensile strength at a particular temperature. Creep occurs when a steady stress is applied to a material and is held at that stress, the gradual deformation of the metal occurs with time in service. As the grains attempt to travel or elongate small voids form along the grain boundaries. The boundaries act as initiators for this cavitation ^[29].

Figure 2.10 shows a typical creep curve for a relatively brittle (line B) and a relatively ductile material (line A). During the initial primary creep the creep rate decreases until it reaches a constant or steady state (secondary creep). Finally tertiary creep represents an increase in creep rate, and this stage usually directly precedes failure ^[43]. Cavitation is usually observed in failing materials only once they are well within the tertiary creep regime. The primary stage is also a relatively quick process, occurring when a material is exposed to service conditions. It is therefore important that materials are managed in service in the secondary creep state. Progression to the tertiary state is likely to result in a failure. Prior knowledge of the materials reaction to service conditions in line with careful monitoring is required to ensure the health of the material.




Creep is first visible in power plant steels as microvoids which usually occur at the grain boundaries. With increased time in service these can be seen to increase in number and density and can eventually coalesce to form microcracks. As more cracks are formed, the risk of rupture becomes greater and eventually failure occurs when the cracks link to create a potentially catastrophic macrocrack.



Figure 2.11: Early stage creep fracture in silver, in which the particles are rounded and dispersed along a grain boundary ^[43].



Figure 2.12: Isolated slightly angular cavities in Nimonic 90 initiating at the grain boundaries [43].



Figure 2.13: A wedge crack in Al-20%Zn.travelling in the plane of the grain boundary [43].

Figures 2.11 to 2.13 present a number of possible cavity formation shapes. The cavities in Figure 2.11 are rounded in shape and distributed along the grain boundary. These are much rounder in shape that those seen in Figure 2.12, where the cavities in Nimonic 90 are more angular. These angular cavities are likely to initiate at triple points where three grain boundaries meet or at corners of grain boundaries. The third shape of cavity in Figure 2.13 are the wedge-like cavities, again originating at areas where grain boundaries converge. Increasing time in service can result in the growth and coalescence of these cavities, and with further increasing time in service this coalescence can result in cracks forming, before ultimately the cracks propagate through the pipe wall and failure occurs. Figure 2.14 is an example of these cracks coalescing to form widespread faceted cracking.



Figure 2.14: Interlinking cracks in a 20 % Cr -35 % Ni steel creep tested at 973K [43].

The Neubauer classification scale can be used to recognise the degree of creep damage which has been experienced by the material. The scale begins at zero and progresses up to 5 with zero being new material and 5 describing the most severe damage with grains becoming loosened and macrocracks growing in the range of millimetres ^[35].

Bhadeshia *et al.*^[44] reported that pipes under high pressure at high temperatures are one of the leading components, along with headers (the main steam collection area, situated in the dead space at the top of the boiler) in power stations that are susceptible to creep damage. It has been seen that creep damage in header components is directly related to the pressure and the thermal stresses while pipework systems can also be subject to variable and unquantifiable external forces, suggesting that the life predictions and site management of both parent material and welds becomes a difficult area.

Despite creep being the dominant failure mechanism within pipework it can be used constructively to identify the remaining life. A number of techniques are used to acquire creep data, mostly centred on strain gauges, measurement during shutdown, measurement grids plated in a noble metal and studs fitted with extensometers are used to track deformation.

The ability of a material to tolerate strain is an important consideration in determining whether a failure will occur gradually with warning, or suddenly. Bhadeshia ^[44] identify that in practice, ductility can vary between 2 and 30% in situations where conditions are almost identical. They showed that factors influencing this creep ductility include residual elements, grain size, inclusions, solution treatment and tempering times. They also observed that in materials with low ductility, creep cavitation was seen for strains as low as 0.5% while in the most ductile materials the onset of cavitation may be delayed until strains of up to 5% are reached.

Creep cavitation occurs at points of stress concentration and it is therefore common to see cavitation occurring at grain boundaries. These provide easy initiation sites as cavities can easily form on either a) ledges or steps created between the two grains or b) a non-deformable particle or hard inclusion. In either form of cavitation the stress causes the particle-grain or grain-grain interface to decohere ^[43].

Bolton *et al.* ^[45] described the use of strain rate as an indicator of residual creep life in $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steels using the formula:

$$\dot{\varepsilon}_{\min} = A(\sigma - \sigma_0)^p \exp\left(-\frac{Q_{SD}}{kT}\right) \dots \left[equ. 2.4\right]$$

where $\dot{\varepsilon}$ is the creep rate of the material, p is a constant (approximately equal to 4), σ is the stress, σ_0 the initial stress, A is Avogadro's constant, k is a constant, T temperature and Q_{SD} is the self-diffusion activation energy. Ageing of the material causes changes in the creep rate (ε) due to the coarsening of fine vanadium carbides to coarse Mo₂C, ultimately altering σ_0 . Figure 2.15 shows how the value of σ_0 decays with time and how the measurement can be extrapolated to predict the remanent life of the component.



Figure 2.15: Variation in σ_0 with time during $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V creep testing at 250 MPa and 565°C (reproduced from Bolton et al. ^[45])

Evans ^[43] also explained that considerable changes in the carbide morphology in ¹/₂Cr ¹/₂Mo ¹/₄V ferritic steels can occur during high temperature creep and that failures occur in an intergranular fashion. The rate of acceleration of creep damage in the tertiary stage (see Figure 2.15) is therefore affected by microstructural instability and also by intergranular damage development. Extensive localised crack formation and link up was seen to occur in the necked region of their creep tests, and these processes occurred late into the tertiary stage before fracture occurred. They concluded that the relative importance of microstructural instability and intergranular damage accumulation would be expected to differ at different stresses and temperatures because the effects of changes in carbides, type, size and distribution should be

negligible at short testing durations due to insufficient time available for transformation to the thermodynamically stable carbides.

The results indicate that the creep of ½Cr ½Mo ¼V steels occurs by a diffusion controlled generation and movement of dislocations in the ferrite matrix. The tertiary stage is increasingly affected by the coarsening of the carbide particles as the creep testing time increases, despite the failure mechanism being intergranular.

Cane *et al.* ^[46] described the two factors which are most likely to cause failure by creep in ½Cr ½Mo ¼V steels as 1) structural coarsening leading to a continuous reduction in creep strength during service exposure and 2) intergranular creep cavitation. Importantly the authors described the difficulties in examining the materials in question suggesting that there are two practical examination methods, namely; monitoring of the operating conditions, therefore allowing stress calculations to be performed and data to be compared with lower bound material data to estimate a possible remaining life and access to the components during routine inspection intervals allows metallographic inspection, micro-sampling, strain measurement, postexposure creep-testing and stress analysis to be performed. However, the authors described their pessimism over the former of these methods suggesting that the material data from which the lower bounds are established was obtained from small test pieces, upon which significant oxidation occurred, and in addition, questions of reliability arose from the extrapolation and scatter of the data.

To overcome these problems, Cane *et al.* ^[46] established a mechanistic approach to predict service life, which takes into account both microstructural coarsening and creep cavitation. They established that the best way to measure the interparticle spacing and its rate of change was via a change in hardness method. However, in order for these hardness measurements to be of any use they must be 'calibrated' to the actual interparticle spacing and Cane *et al.*^[46] described in their publication that due to the variability during replica production and particle measuring, the process of physically measuring the spacing is "yet to demonstrate that measurements are not subjective". As a result confirming that the hardness is a true measurement of the interparticle spacing is also distinctly open to error.

Zhao *et al.* ^[47] have linked creep data and microstructural features of a 12Cr1MoVsteel via a Z-parameter, suggesting that it could also be used as a tool for $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V life assessment. These authors linked the microstructural degradation to tensile strength data by classifying the microstructure into one of five categories with level one being the least degraded and level 5 the most degraded (Figure 2.16) according to the equation:

 $\sigma_b = 608.04 - 28.13E.....[Equ. 2.5]$

where σ_b is the tensile strength of the material. If this equation is then combined with the Z-parameter method, the equation results;

Using this equation a graph of spheroidization level against creep rupture strength a straight line, Figure 2.17, is obtained allowing assessment with respect to microstructural degradation. This work was performed for 12Cr1MoV steel and the paper does not suggest that the same classification system for ¹/₂Cr ¹/₂Mo ¹/₄V steel will yield the same straight line degradation graph.



Figure 2.16: The levels of microstructural spheroidization, E in a 12Cr1MoV steel [47].



Figure 2.17: The speroidization v's Z-parameter graph in a 12Cr1MoV steel^[47].

2.9 Failure Modes In and Around Weldments

Most failures observed in the past have been seen in the welds and heat affected zones (HAZ). It is only recently that failures in the parent material have become a real concern due to the extensive service time of a number of components. This section reviews the failure mechanisms which have been previously observed in the weld and associated zones.

An overview of failure modes was written by Brett (2003)^[3] and the report suggests that there are a number of common failure modes. The failure modes can be seen to change with advancing service life. Cracking mechanisms have been observed in the following order:

- Reheat cracking
- Type IV cracking
- Type IIIa cracking
- Faceted bore cracking
- Smooth bore cracking

Figure 2.18 details the different classification of weld failures which are explained throughout this section.



Figure 2.18: The classification of weld defects (after Brett ^[48]). Type I cracking is that characterised occurring within the weld, type II cracking occurs in parallel to the pipe inner wall but is rarely observed in steam pipes, type III cracking is observed within the HAZ, type IIIa would usually be observed at the HAZ parent metal interface, with type IV presenting itself on the parent material/HAZ interface.

2.9.1 Reheat Cracking

Reheat or stress relief cracking occurs when the strain accumulated during stress relief becomes greater than the local ductility of the Heat Affected Zone (HAZ) or weld. Creep cavitation initiating at the prior austenite grain boundaries (Figure 2.19a) will lead to crack initiation and eventual failure. Figure 2.19b shows the coarse grained microstructure associated with the HAZ.

In 1986 the first catastrophic failure within a power plant was observed at Drakelow C power station, where a steam chest weld failed. Subsequent investigations by the then Central Electricity Generating Board (CEGB) indicated that reheat cracking would be significantly increased if there was sufficient heat applied during welding to coarsen the surrounding microstructure. In addition to the weld temperature, the post weld heat treatment requires careful control to ensure that stress relief occurs at the optimum temperature and not during service. Finally the investigation revealed that impurity levels in the ¹/₂Cr ¹/₂Mo ¹/₂V steel had contributed to the failure. Reheat cracking was observed in pipework during post weld heat treatment or during the first 20,000 hours of service.

An investigation by Brett (2003) ^[3] indicated that radiographic Non Destructive Testing (NDT) was ineffective in identifying this type of cracking. As a result

ultrasonic testing techniques were developed and employed. The CEGB found that these methods of NDT combined with improved welding techniques and well controlled post weld heat treatments, lead to near elimination of reheat cracks leading to failures.



Figure 2.19: Creep cavitation (a) and crack propagation (b):, cavitation occurs initially at grain boundaries at a normal to the direction of the stress in a ¹/₂ Cr ¹/₂ Mo ¹/₄ V steel (from Brett) ^[3]

2.9.2 Type IV Cracking

Type IV cracking became evident with the decline of reheat cracking and is found to occur on the parent side of the HAZ, see Figure 2.20. Unlike reheat cracking, Type IV cracking still occurs today. The cause of Type IV cracking is the result of system stress acting on creep weak regions at the edge of the HAZ. There are three factors which may affect the creep strength:

- Small grain sizes, as a result of insufficient heat input during welding to allow the grains time at temperature to grow;
- The very short time available for transformations to occur which leads to a mixed structure of ferrite and bainite;
- Precipitate overageing occurs as there is insufficient heat input during welding to completely dissolve and reprecipitate the carbides.

Type IV cracking has been observed from 1970 onwards with cases present in $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{2}$ V pipework in both coal and oil fired power stations operating for over 40,000 hours.



Figure 2.20: Type IV cracking on the parent side of the weld HAZ (reproduced from Brett)^[3] this type of failure occurs as a result of stress acting on the creep weak regions at the edge of the HAZ in $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steel.

2.9.3 Type IIIa Cracking

Figure 2.21 shows a Type IIIa crack, found in the HAZ directly adjacent to the fusion line. This type of cracking is seen in most, if not all, power stations employing ½Cr ½Mo ¼V pipework with 2CrMo welds. Failures are usually recorded at operating times above 80,000 hours. Again, as in Type IV cracking, the long range pipe stresses placed on the welds increase the likelihood of failures. However, the factors which encourage a crack to initiate in the Type IIIa mode in favour to that of the Type IV mode include, situations where the HAZ retains a fine grained microstructure in the region of the fusion line. This can result in carbon diffusion preferentially from the ½Cr ½Mo ¼V to the 2CrMo weld material, creating a difference in creep strengths and causing subsequent cracking.



Figure 2.21: Type IIIa cracking adjacent to the fusion line, seen to occur in ½ Cr ½ Mo ¼ V pipework with over 80,000 hours in service. (reproduced from Brett)^[3]

It is important to note that in many cases both types IIIa and IV cracking have been found occurring simultaneously ^[3].

2.9.4 Faceted Bore Cracking

Faceted bore cracking occurs during thermal upshock, i.e. when hot steam is allowed to enter pipework. The temperature gradient across the pipe wall is large as a result of the internal wall being subject to high temperatures. This type of cracking is found in relatively few power stations and there have been no catastrophic failures as a result of faceted bore cracking. Once the crack has been initiated it will continue to creep during service until the next thermal upshock, i.e. start up, where the crack will be energised and encouraged to continue its growth.



Figure 2.22: Faceted bore cracking in ½ Cr ½ Mo ¼ V steel, (reproduced from Brett (2003)) ^[3] a result of thermal upshock occurring as a result of the internal wall being subjected to high temperatures, with every upshock the crack is provided with more energy to grow through the pipe wall.

Figure 2.22 shows a faceted bore crack following a weld fusion line initiating at the pipe bore; these cracks are found to be fully circumferential. Rapid advances in NDT have been established to ensure that this type of cracking can be identified and rectified as rapidly as possible.

2.9.5 Smooth Bore Cracking



Figure 2.23: Smooth bore cracking in ½Cr ½Mo ¼V steel, (reproduced from Brett (2003))^[3] these initiate from the root of the weld and due to their narrow, straight shape are difficult to identify using NDT methods.

It can be clearly seen from Figure 2.23 that smooth bore cracking differs from faceted bore cracking by the shape of the crack. Smooth bore cracking initiates in the root of the weld travelling straight up through the weld itself in a straight manner. The inherent shape of the smooth bore crack makes identification through NDT extremely difficult. Smooth bore cracking occurs as a result of thermal down shocking, i.e. the opposite of upshock. During downshock the bore of the pipe is cooled much more quickly than the outer wall, and the stress created as a result of this temperature gradient is sufficient to cause this type of cracking. Almost half of the power stations in the UK have seen smooth bore cracking in their plants.

2.10 Current Techniques for Remaining Life Assessment

Apart from using creep data as a method of assessing remaining life, there are a number of other methods which can be used. These are split into two main categories: post service methods and operational condition monitoring for use with standard materials data and the life fraction rule. As the names suggest the post service methods are performed once the material has been taken out of service while the operational condition monitoring is performed in-situ, usually during a plant shutdown. The focus of this research is on the post service methods as all of the samples provided have been removed from service.

2.10.1 Post Service Methods

2.10.1.1 Estimation of remanant life using mechanical testing methods

A number of authors have collated information from a wide range of sources in an effort to extrapolate information about remaining life of power plant steels. In particular two groups of work have studied data produced from mechanical testing of virgin and post service material to establish the remaining life. The Plant life Assessment Network (PLAN) is a group of 65 projects covering plant life assessment related subjects. The projects are grouped into 4 categories; inspection, instrumentation/ monitoring, structural mechanics and maintenance. The main aim of the working group was to generate and collect material property data, so that those who may wish to use the information for further work have access to a) the owner of the data and b) the opportunity for further exploitation of data and an indication of existing data availability. The PLAN project is concerned with a number of different steels however, ¹/₂Cr ¹/₂Mo ¹/₄V was not taken into account and 1 Cr steels were the lowest alloy steels studied. The data collated includes fracture and impact toughness, fatigue and creep. Additionally the European Creep Collaborative Committee (ECCC)^[35] have, since their formation in 1992, focussed on accumulation and production of uniaxial creep rupture data for power plant steels and nickel-based super alloys. Again ¹/₂Cr ¹/₂Mo ¹/₄V steels are not specifically targeted, however, life prediction methods produced for higher chromium steels can be used in a similar fashion for the low alloy steels. A number of potentially transferable equations are recognised in ^[49]. An equation of interest in this work is the one that 'normalises' the creep data produced from a number of different test parameters, therefore allowing all data to be compared on equal terms.

The European Collaborative Creep Committee ^[35] (ECCC) was established in 1991 with a number of common targets; 1. Collate, exchange and jointly assess creep data; 2. Support European standardisation; 3. Co-ordinate European creep data exchange; 4. Develop common research and testing programs; 5. Mutually exchange information on high temperature material development and 6. Define common procedures for data generation and assessment. The voluntary project involved industrial and academic partners from across Europe with the sole goal being to share and understand the effects of creep on components in service. Split into work groups, WG1.1 was titled

[•]Post exposure material creep data generation and assessment procedures' and WG3, [•]A specialised in creep behaviour of ferritic steels.' These two groups are of particular interest to the present work.

During the ECCC WG1.1, an investigation was made into the different types of creep testing available, in which three small scale testing techniques were identified; small scale conventional creep where the sample is a scaled down standard test piece; impression creep where an indent is made at high temperatures to produce a constant deformation rate, a creep strain rate can then be identified, and small punch creep testing using a punch arrangement to deform a flat disk to failure at high temperatures, which produces a creep curve similar to that of a conventional creep test. However, as with most of the results accumulated by this working group it was found that various test houses, industrial partners and academic institutions did not work to one standard or adopt one particular test condition as a standard. As a result the group established equations that could be used to standardise the creep data from different test conditions, i.e. different stress and test temperatures.

2.10.1.2 Metallographic methods

Metallographic investigations of the materials can be performed at a number of different points in the life of the material. Small samples of material or replicas can be removed from materials in service via a non-destructive method, which allows areas of particular concern to be targeted, and additionally the time to testing is relatively short when compared to long term creep testing. Resulting micrographs of replicas can be used to identify carbide spacing, size, and cavity distribution.

Cavitation damage replicated from plant can be used for cavity volume fraction, mean cavity size and fraction of cavitated grain boundaries. However, all of these methods are determined by the quality of the replica, which are inherently difficult to repeat. The German code TRD 508 suggests that these methods of cavitation measurement should not be used directly for assessment of remaining life but instead should be used to establish a required inspection period ^[47].

¹/₂Cr ¹/₂Mo ¹/₄V steels rely on small carbides to provide creep resistance, and it is therefore reasonable to suggest that the creep rate is dependent on the interparticle spacing. Assuming that the particle coarsening is diffusion controlled, Kirchner ^[51], Liftshitz and Slyozov ^[52] the interparticle spacing λ , can be assessed with time, *t*, when expressed as

where λ_0 is the initial spacing and *k* is a kinetic constant. The creep rate can then be related to the structure via a modified Nortons law

where A_1 and n are the material parameters and T is the temperature. σ_0 is the threshold stress which has a value close to the Orowan stress. There is a relationship between the interpaticle spacing λ and the creep strength, however the authors note that when the particle spacing is greater than 100-200 nm the results no longer follow the above criteria as solute drag processes become the determining factor ^[50].

2.10.1.3 Hardness testing

Bhadeshia *et al.*^[44] explained how hardness testing has been used to identify life predictions in 1Cr-Mo-V rotor steels in association with an Avrami equation. A number of parameters are required for this type of prediction, namely the hardness of the material when it was put into service, and equally without actually testing the material at longer service times it is difficult to truly validate the model. The work uses equ. 2.10 the life fraction rule to calculate the remaining life of the material:

$$(t_{os}/t_{rs}) + (t_{ra}/t_{o}) = 1.....$$

In its simplest form this related t_{os} , time in service, t_{rs} , rupture time under service conditions, t_{ra} , time to rupture in accelerated tests, t_{ro} rupture time of the new material under accelerated condition. Hart ^[53] suggested that there is a visible difference between tests performed under accelerated temperature and stresses, with results

showing that when using accelerated temperatures the life fraction is obeyed. Further observations stated that this is not the case for stress.

In contrast, the work performed by Carruthers and Collins and Cane ^[25,50] suggest that the use of elevated accelerated temperature testing should be used with caution as they saw changes in the microstructure at temperatures above 575°C, at which the M₂C carbides are more stable, effectively replacing the MC, which is present from the heat treatment stage. They did not, however, go on to relate the microstructural features with the mechanical properties.

2.10.1.4 Strain measurement

Methods of strain measurement can be separated into two different categories; those performed during inspections and those used during operation. Thermally stable pips are welded or peened onto a component surface so that the area of interest is between the pips. During routine outages the distance between the pips can be measured using micrometer bow gauges. This method allows measurements of strain rates as low as 10^{-8} /h over 20,000 hours.

A number of techniques have been developed to help improve off-line condition monitoring, which include stereo photography and laser holography. These methods both use calibrated images to compare the changes of microstructure over time. Additionally suggestions of radiographic methods of condition monitoring have been developed.

Continuous strain measuring is an ideal method for condition monitoring; however, there are a number of factors which affect the materials and the methods employed to measure the strain during service. Most notably the temperature which the gauges must be exposed causes the biggest problem. Conventional strain gauges would easily endure 300° C but the temperatures may be much above this. Improvements in gauge design have led to the development of capacitance strain gauges, some of which have, in laboratory conditions, been used at temperatures up to 600° C ^[50].

2.10.1.5 Acoustic dampening

In addition to the rather conventional methods of life assessment Ohitani *et al.*^[54] used acoustic dampening as a tool for predictions. They found that they could associate acoustic dampening with changes in the microstructure, however, the attenuation curves obtained seemed to peak at roughly 30% life and drop to a minimum at 50% life before increasing towards reduced remaining life. Figure 2.24 is the graph of life fraction against attenuation coefficient. The authors note this reduction in attenuation at 50% life fraction and associate it with changes of the materials ultrasonic properties which is uniquely caused by creep.



Figure 2.24: The effect of attenuation coefficient as a result of creep testing, reproduced from Ohitani^[54].

2.10.1.6 Small scale creep testing

A number of authors have identified ^[55,56] that small scale impression creep testing can be successfully used as a ranking tool on aged parent material. Small scale scoop sampling involves removing a 5 mm diameter semi-circle shape which can then be machined to a parallel sided impression creep test specimen, Figure 2.25.



Figure 2.25: Schematic diagram of impression creep testing on a round and square sample (after Hyde $et al.^{[56]}$).

The authors performed the impression creep tests at 2.248 kN and 600°C to enable direct comparison with a conventional creep test program during which samples were tested at 90 MPa and 600°C. The test programme revealed that the creep testing was capable of ranking the materials in the same order as the conventional creep testing did.

2.10.2 Mechanistic methods of remaining life assessment

2.10.2.1 Crack growth

Fracture mechanics provides a method of estimating the remaining life ^[57], and describes the three separate parts of the creep crack growth; the initial crack which decreases in growth speed as the initial stress relaxes; the secondary constant speed crack and the third growth which involves nucleation and growth of grain boundary cavities. Liaw and Saxena ^[58] used the C*-intergral method of fracture mechanics. This method has been successful in correlating the rate of creep crack growth in structural alloys regardless of applied stress levels and specimen geometry. Neate ^[59,60,61] described the growth rate form to take the general form of:

<u>da</u> =	<u>γC*β</u>	•••••	•••••	 	•••••	 	[Equ.	2.11]
d <i>t</i>	ϵ_{c}							

where da/dt is the growth rate, γ and β are constants and C_c is the material ductility under the same conditions of stress state as existing at the crack tip. The author performed creep testing on compact tension specimens to confirm that the material behaved according to the equation above. In Ref ^[62] Neate concluded that the controlling parameter for creep crack growth in $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steel at 565°C is dependent on the material ductility and matrix creep strength. The author performed testing on two types of materials, those which have been quenched to produce a "creep brittle" condition and those which were described as "creep ductile". For the brittle samples the author reported that the crack propagation data were adequately correlated by the stress intensity factor (as seen in equation 2.12 where K is the stress intensity and A and n are constants). In the ductile samples the failure times were characterised by the initial equivalent stress.

 $\underline{da} = AK^{n} \dots [Equ. 2.12]$ dt

2.11 Summary

This chapter has reviewed the work previously performed on low alloy steels for power plant applications, including the microstructural changes which are likely to be seen in these steels, failure mechanisms and possible methods of predicting when the component will reach the end of its life. The British Standard for this material gives guidance on the elemental content present in ¹/₂Cr ¹/₂Mo ¹/₄V steels, in addition it gives information on the strength of the material which will be obtained as a result of various heat treatments. The initial microstructure is generally accepted to be ferrite and pearlite, which evolves with increasing time at temperature to form a degenerate array of various types and sizes of carbides uniformly dispersed within a ferrite matrix.

Experimental procedure

3.1 Introduction

This chapter details the experimental methods employed throughout this work to characterize the microstructure of ¹/₂Cr ¹/₂Mo ¹/₄V steel. Methods used include optical microscopy along with image analysis methods, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) for characterization and particles sizing of the carbides. Other methods include X-ray diffraction for identification of the larger carbides within the material and Focused Ion Beam Field Emission Gun Scanning Electron Microscopy (FIB FEGSEM) for site specific removal of TEM samples.

3.2 Materials

3.2.1 Ex-service materials

22 samples, 20 post service and 2 virgin, were provided by E.On and RWE npower; all of the samples were nominally ½Cr ½Mo ¼V steel with slightly different compositions. Table 3.1 details the compositions with the first column giving details of the BS 3604 British Standard ^[31] maximum and minimum values for the composition. All of the samples have seen different lengths of time in service prior to removal, these service times are detailed in Table 3.2 along with the service temperature for each sample.

Samples KA86, KA387, KA457, KA727 and KA1490 do not have cobalt, niobium, lead, titanium, tungsten or antimony values. This is due to them not being tested for during compositional analysis. All analyses were made via a spark OES method and all compositions are in wt %.

Table 3.3 details the reason that the material was taken from service and the column to the right describes the observations of the material on its removal, and in particular, notes on cavitation density.

Additionally, post service creep data were provided for the samples, however, not all of the creep tests were performed at the same temperature and stress. Table 3.4 presents all of the creep data provided for the samples supplied.

3.2.2 Virgin material

In addition to the post service samples, two virgin materials were supplied. These have been given the sample names V1 and V2. The compositions of these two samples are shown in Table 3.5. Neither of these samples had seen any service life.

The microstructure of the virgin materials was in the as-produced state in which all of the post-service samples are expected to have been in upon commencing service.

Element (wt%)	BS3604	TLA3	DCAU1B2	KA1706	KA1358	KA1781	MSC9	АТВ	EGG	MSC5Z	TLB20	DCAU1B1	DCAB	MSBI3/I3Z	KA82	КА86	KA387	KA457	КЛ727	KA245	KA1490
С	0.10-0.15	0.120	0.174	0.100	0.120	0.160	0.160	0.125	0.085	0.126	0.100	0.174	0.133	0.160	0.160	0.120	0.090	0.100	0.120		0.130
Si	0.10-0.35	0.150	0.360	0.120	0.260	0.260	0.260	0.170	0.210	0.230	0.150	0.360	0.290	0.310	0.240	0.120	0.200	0.040	0.160		0.190
Mn	0.40-0.70	0.480	0.490	0.500	0.470	0.510	0.540	0.500	0.570	0.570	0.420	0.500	0.500	0.530	0.520	0.600	0.440	0.480	0.500		0.470
Р	0.03 MAX	0.027	0.017	0.017	0.017	0.010	0.015	0.021	0.010	0.021	0.020	0.018	0.016	0.017	0.240	0.033	0.013	0.019	0.015		0.020
S	0.10-0.35	0.020	0.017	0.023	0.025	0.012	0.011	0.040	0.019	0.150	0.260	0.018	0.011	0.018	0.025	0.460	0.029	0.0280	0.016		0.013
Cr	0.30-0.60	0.380	0.420	0.270	0.370	0.320	0.400	0.400	0.320	0.390	0.400	0.420	0.420	0.370	0.410	0.400	0.320	0.460	0.390		0.290
Mo	0.50-0.70	0.560	0.650	0.580	0.540	0.620	0.510	0.540	0.660	0.580	0.560	0.660	0.680	0.560	0.550	0.620	0.590	0.580	0.500		0.480
Ni	0.30 MAX	0.110	0.080	0.140	0.180	0.230	0.080	0.120	0.070	0.090	0.160	0.080	0.070	0.070	0.070	0.160	0.110	0.150	0.130		0.080
	-	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.010	< 0.005	< 0.005	< 0.005	< 0.005	0.005	< 0.005	< 0.005	0.005	<0.010	<0.010	< 0.010	<0.010		<0.007
As		0.024	0.036	0.023	0.031	0.033	0.037	0.027	0.035	0.043	0.026	0.038	< 0.005	0.038	0.030	0.020	0.050	0.050	0.010	A)	
Co		0.014	0.018	0.011	0.018	0.014	0.017	0.013	0.014	0.015	0.016	0.018	0.036	0.016	0.009					Ż	
Cu	0.25 MAX	0.130	0.140	0.140	0.190	0.130	0.030	0.170	0.120	0.040	0.150	0.140	0.016	0.030	0.031	0.110	0.090	0.120	0.080		0.120
Nb		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.130	< 0.005	< 0.005						
Pb		<0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.011	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005						
Sn		0.014	< 0.005	0.022	0.020	0.018	< 0.005	0.026	< 0.005	< 0.005	0.018	< 0.005	< 0.005	< 0.005	< 0.005	0.030	< 0.010	0.010	<0.010		
Ti		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005						
V	0.22-0.28	0.220	0.260	0.240	0.260	0.280	0.250	0.250	0.230	0.250	0.230	0.260	0.260	0.250	0.260	0.230	0.290	0.150	0.260		0.220
W		< 0.010	< 0.010	0.014	0.010	0.010	0.010	< 0.010	< 0.010	< 0.010	< 0.010	0.010	< 0.010	< 0.01	0.010						
Sb		< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005						
N				0.011	0.008	0.100									0.008						

Table 3.1: The compositions of the 20 ex-service ½Cr ½Mo ¼V samples, provided by E.On and RWE npower. The balance element is iron and the units wt. %

Sample	Time in service(hours)	Service temperature (°C)
TLA3	137,900	568
DCAU1B2	131,600	568
KA1706	206,309	568
KA1358	217,921	568
KA1781	201,800	568
MSC9	198,000	568
АТВ	146,000	568
EGG	193,700	568
КА82	174,800	568
KA86	164,000	568
KA387	191,000	568
KA457	176,000	568
KA727	132,000	538
КА245	66,979	568
DCAU1B1	131,600	568
MSC5Z	198,000	568
TLB20	137,900	568
DCAB	128,500	568
MSB13/13Z	171,500	568

 Table 3.2: Sample time and temperature in service.

Sample	Position in service	Reason for removal	Degree of cavitation on removal
TLA3		Weld cracking	No cavitation recorded
DCAU1B2		Weld cracking	No cavitation recorded
KA1706	Main steam bend		Significant creep cracking present
KA1358	Main steam bend		No cavitation recorded
KA1781	Straight section		High cavity density throughout
MSC9	Straight section		High strains recorded by creep pips, no significant cavitation found
АТВ	Straight section		Cavitation on replicas, none found on sectioning
EGG		Weld cracking	No cavitation recorded
MSC5Z		Weld cracking	No cavitation recorded
TLB20		Weld cracking	No cavitation recorded
DCAU1B1		Weld cracking	No cavitation recorded
DCAB	Bend		Interligament cracking at thermocouple pocket on the extrados
MSB13/13Z	Bend		Significant cavitation on replicas but none were found on sectioning
KA82	Main steam pipework		No cavitation recorded
KA86			
KA387	Straight section		No cavitation recorded
KA457	Straight section		No cavitation recorded
KA727	Hot reheat pipework		No cavitation recorded
KA245			
KA1490			

Table 3.3: The reason for removal of the various materials from service and the observations made by industry on removal.

	TLA3	DCAU1B2	KA1490		KA1358	KA1781	MSC9	ATB	EGG	KA82							KA86	
Stress (MPa)	90	90	40	55	40		90	90	90	35	40	54	70	90	100	106	35	54
568°C																823		
600°C	4007	263	17300*]	257	3214	1456									33954
610°C			10392	2004	14013							8591						
620°C						ata	~											
630°C			3540*	765	6529	not				17100		3414					23155	
640°C	· · · · ·					ava					9560	1704	382	36	158		9953	
650°C			1624		2293	uilat				5239		1066					4520	
660°C						ble											4000	
670°C						1											2709	
680°C										1218	797	139						

	KA387			KA457			KA727		KA245	DCAU1B1	MSC5Z	TLB20	DCAB	MSB13/13Z
Stress	35	54	54	35	54	100	35	54		90	90	90	90	90
(MPa)														
568°C						1008								
600°C		12188								308	252	1702	440	660
610°C		4806			7880			17896						
620°C		11226							ata					
630°C	34805	1727		16648	3507		23015	8306	not					
640°C	8840	674							ava					
650°C	3246	723		4670	754		5903	4902	uilal					
660°C	3810	211							ble					
670°C	3091	74	71											
680°C				1142	63		1367	313						

 Table 3.4: Time (in hours) to rupture during post-service creep testing of the samples provided. (Samples annotated with * indicate samples which are still on test.)

Sample	V1	V2					
С	0.11	0.16					
Si	0.18	0.37					
Mn	0.51	0.56					
Р	0.032	0.015					
S	0.029	0.006					
Cr	0.42	0.47					
Мо	0.55	0.57					
Ni	0.12	0.11					
Al	0.009	0.008					
As	0.017	0.006					
Co	0.009	0.008					
Cu	0.12	0.11					
Nb	<0.005	< 0.005					
Pb	< 0.005	<0.005					
Sn	0.014	0.006					
Ti	< 0.005	<0.005					
V	0.25	0.25					
W	< 0.01	<0.01					
Sb	< 0.005	< 0.005					
N	0.008	0.008					

Table 3.5: The compositions of the two supplied virgin materials in wt. %.

3.3 Hardness testing

Hardness testing is a quick, widely used, relatively easy method of evaluating the mechanical properties of materials, whether in service or post service. All samples were

hardness tested using a Mititoyo AVK-C2 micro hardness tester with a load of 10 kg, five hardness indents were made in each sample and the average taken.

Hardness is a common method of monitoring the state of a material in service, by following a materials natural softening it is possible to extrapolate the end of its life. Singh and Singh ^[63] explain that ¹/₂Cr ¹/₂Mo ¹/₄V steels can lose as little as 12 HV over a period of 15 years; such small losses are difficult to observe due to the experimental error related to the method. Perhaps regular testing of the material in question allows for the tracking of this softening but certainly these results suggest that it may not be possible to compare different casts of pipe work to accurately predict end of life. Nevertheless, the hardness data for the various steel samples are compared with chemical composition and service data to investigate trends.

3.4 Optical Microscopy

3.4.1 Sample Preparation

Samples were taken from all the materials detailed in Table 3.1 and prepared metallographically, where possible the samples were taken axially along the pipe length, however, some samples were provided to the project already mounted for which the orientation can only be determined from the microstructure, Figure 3.1.



Figure 3.1: Schematic of the direction of sample extraction, the red square representing the surface mounted and polished. This method was used where samples were not provided already sectioned or mounted.

Small 10 mm³ samples were taken from the bulk materials using a Struers Accutom. The samples were mounted in a conductive Bakelite so that the microstructure could be viewed along the axis of the pipe. Samples were ground down using a Struers Tegrapol-25 and Struers 'piano' grinding wheels starting with a 600 grit and finishing with a 1200 grit. The samples were then polished with a 9 μ m, 3 μ m, 1 μ m followed by a 5 minute 0.02 μ m Struers colloidal silica polish. Samples were then swab etched with a 5% Nital solution, where Nital is nitric acid in methanol.

3.4.2 Technique

Samples were observed under a Reichert MEF-3 microscope using bright field illumination. Micrographs of all the samples were taken at the same magnification. These micrographs were used to calculate the grain sizes. This information was later used to investigate whether the grain size and carbide size alters with service or composition. The limiting factor in the use of optical microscopy is the resolution. With the maximum magnification being 1000 times and the limiting factor being the wavelength of light, the smallest of the carbides in these materials cannot be resolved.

3.4.3 Grain size measurements

Grain sizes were measured using a linear intercept method on micrographs at 100 times magnification. Five horizontal lines were superimposed onto the fields and the number of grain boundary intersecting the line was recorded. This was repeated on five separate randomly selected micrographs for each sample. The length of the line was divided by the number of intersections and the average grain size determined from the five micrographs for each sample. Finally the standard deviation of these results was calculated.

3.5 Scanning Electron Microscopy (SEM)

3.5.1 Sample Preparation

Samples were prepared for SEM analysis in the same way as they were prepared for optical microscopy, described in Section 3.4.1.

3.5.2 Technique

A LEO 1530 VP FEGSEM was used in both secondary imaging (SE) and the backscatter mode. The two detection methods can provide subtly different but equally important information. During secondary imaging the primary, high-energy electrons are absorbed by the sample creating an overall negative charge; this can be described as a inelastic or electron-electron collisions. For the sample to regain its ground potential, it releases secondary electrons of lower energy. During backscatter imaging the original electron collides with a nucleus of the sample and rebounds with very little loss of energy and a slight angular deflection as a result of Rutherford scattering. Backscatter detection is given its name due to the fact that the initial electron enters and exits the sample. This type of reaction is called an elastic collision with the primary electron colliding with a nucleus in the material.

3.5.3 Elemental Analysis

Energy dispersive X-ray analysis was used to evaluate the chemical composition of points in the microstructure. The system used was an EDAX Pegasus Energy Dispersive X-ray analysis system. EDX works by quantifying the characteristic X-rays which are released by an element when a sample is irradiated by an electron beam causing the excitation to a higher energy level which subsequently results in the emission of a characteristic X-ray when the electron drops back down to a lower energy level. These X-rays can be collected and identified to produce a spectrum which can be quantified to provide a measure of the chemical composition of point under investigation ^[64]. A second function of the EDX software allows the production of elemental maps; these identify the areas rich in predetermined elements and were particularly useful in this work.

3.5.4 Quantification

In order to quantify the amount of grain boundary carbides in the various different samples, SEM backscatter images were taken of each sample and from these images the grain boundary carbides were traced through onto tracing paper. These tracings were then scanned using the Uthesca image analysis program. A threshold was applied to the image

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and the carbide size was measured via two methods; the Feret diameter method and the carbide length diameter. Figure 3.2 shows the difference in measurement techniques; Figure 3.2a is the maximum length technique and Figure 3.2b the Feret statistical diameter technique. The Feret diameter technique uses the distance between two parallel lines placed at the extremities of the particle, the same measurement is taken at 90° to establish the maximum particle diameter. Figure 3.3 shows that there is a small difference in the two measurement techniques with the length method producing slightly higher values particularly at the longer lengths. The Feret method has therefore been used throughout this project as the results from this method allows for a more cautious approach, and is thought to produce more representative values from the various different shaped carbides encountered in these samples.



Figure 3.2: A schematic diagram illustrating the differences between a) the carbide length method and b) the Feret diameter method. Used to establish which is the most appropriate to use for this work.

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Figure 3.3: A comparison of the Feret diameter method with the carbide length method defining the differences in the two measurement methods.

3.6 Transmission Electron Microscopy (TEM)

3.6.1 Sample Preparation

3.6.1.1 Carbon Extraction Replicas

Carbon extraction replicas were extracted from each sample via the process shown in Figure 3.4. The extraction of particles using this method ensures that there is no iron matrix within the sample, therefore energy dispersive X-ray analysis of the particles will have no iron contribution from the matrix, which would otherwise dominate the X-ray results and the analysis of a non-magnetic sample is easier within the TEM. Initially each sample was deep etched using 5 % Nital. Carbon coating was then performed in an Edwards carbon evaporator during which an amorphous layer of carbon is deposited onto the surface of the sample before the final extraction stage took place using the three stage process shown in Figure 3.5. The three stages include an electrolytic etch in 10% HCl in methanol with an applied voltage of 5 volts, followed by a methanol wash before finally gently floating off the carbon layer in deionised water before catching the small squares of carbon onto a 3.05mm 200 mesh centre marked copper grid.



Experimental Procedure



Figure 3.4: The carbon extraction replica production process. Initially a polished sample is lightly etched to reveal the carbides, a thin layer of carbon is deposited on the sample surface, once this is removed using the process in figure 3.4 the completed extraction is placed in the TEM for analysis.



Figure 3.5: Extraction of the carbon replicas from step 3 in Figure 3.4.

3.6.1.2 Selected Area TEM Sample Preparation

Site specific TEM samples were removed from metallographically prepared samples using an FEI Nova 600 Nanolab focused ion beam field emission scanning electron microscope (FIB-FEG SEM). Figure 3.6 is a schematic diagram of the electron beam and ion beam set up. The area of interest was selected using the electron beam. The sample must then be tilted to 52° so that it is normal to the ion beam. A protective platinum layer was deposited over the selected area and the ion beam was used to gradually remove the material either side of the selected area, a small amount at a time. (Figure 3.7)

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Once the material has been removed from around the selected area the section can be removed from the bulk material and attached to a micro manipulator and moved onto a TEM grid. A platinum deposit was again used to attach the sample onto the grid. The ion beam is once again employed to thin the sample from both sides. The samples were carefully thinned from each side to ensure that the sample did not become distorted during this thinning process. The sample was thinned to electron transparency ~100nm in thickness. Figures 3.8 and 3.9 show a sample fixed to the TEM grid undergoing thinning.



Figure 3.6: A schematic of the electron and ion columns in the Nova nanolab 600 FIB- FEGSEM, samples must be tilted to 52° for use with the ion beam.

Experimental Procedure



Figure 3.7: The selected area of a CrMoV sample with a platinum layer deposited on top and material extracted either side using the ion beam.



Figure 3.8: The extracted sample attached to the TEM holder

Figure 3.9: Partially thinned FIB sample

3.6.2 Transmission Electron Microscopy

Replicas were imaged using a Jeol JEM 2000 FX Transmission Electron Microscope (TEM) allowing high magnification images to be recorded. An image is formed when an electron beam passes through a thinned sample (<300 nm), and the beam then produces an image on a fluorescent screen. Images were typically recorded onto film. Images were all taken using an accelerating voltage of 200 kV in bright field mode. The areas which appear lighter on the negative are the areas where electrons have travelled through without any significant deflection from the sample, and the darker areas represent areas where the deflection from the sample is greater or the thickness of the sample is greater. In addition to imaging, the TEM was used to determine energy dispersive X-ray spectra of carbide compositions and diffraction patterns were produced for investigation of crystal structures.

Selected Area Diffraction (SAD) patterns were taken from particles. These allow the crystal structure of the particle to be established to help confirm the identity of the particular type of carbide together with the chemical composition. Measurement of the interplanar spacing and camera length were used along with the Crystal software package to identify the precipitate.

3.6.3 Analysis of diffraction patterns

The TEM can be used to produce patterns which represent the crystallographic structure of the particle which the electron beam is penetrating. These patterns are produced as the electron beam is diffracted as it passes through crystallographic planes. The pattern of spots produced on the fluorescent screen is called the diffraction pattern. The distances and angles between the spots in these patterns can be used to determine the crystallographic structure of the particle. The distance between these spots can be related to the interplanar spacing within the crystallographic matrix, named d. The distance between the camera and the phosphor screen must be known and this camera length is denoted by the letter L (Figure 3.10). Assuming that the electrons diffract through an
angle of 2θ by the crystal planes, the diffracted beam is displaced a distance 'r' from the undiffracted beam resulting in the equation:

For small angles of θ it can be assumed that tan $2\theta \sim \tan \theta$, therefore:

If these two relationships are combined with Bragg's law the following equation results:

$$rd = L\lambda = camera \ constant \dots [equ. 3.3]$$

Where λ is the wavelength of the electrons, *d* is the spacing of the diffraction planes and *r* is the distance between the spots on the diffraction pattern.



Figure 3.10: Schematic diagram of the geometry relating to a diffraction pattern

Once these diffraction patterns were collected they were used to identify the crystallographic structure and when used alongside chemical composition of particles the type of particle was identified. Selected area diffraction was used to produce these diffraction patterns, it can only be used on areas greater than 1 μ m in diameter. The

sample was placed at eucentric height so that there was no movement laterally during tilting.

To determine the actual crystallographic structure, the diffraction pattern had to be measured to establish the distance between the spots (r) to calculate the distance between the diffraction planes (d).

To establish the crystallographic structure the following steps were followed:

- The distances between the three spots closest to the centre of the pattern were measured. Each distance was averaged over a number of spots.
- The acute angles between the 3 vectors from the origin to the spots were measured.
- d_1 , d_2 , and d_3 were determined from equation 3.3.
- The lattice parameters for the three most common carbides are presented in Tables 3.6 to 3.8. The calculated d values and angles were entered into the Crystal software version 1.6. This programme then determines possible matches between the measured *r* values and the *d* spacing in the lattices of the selected carbide.



Figure 3.11: Schematic of a diffraction pattern with the distances and angles identified which are used to calculate the phase.

3.6.4 Energy Dispersive X-ray (EDX) analysis

Energy dispersive X-ray analysis (EDX) was also used within the TEM using an AN10-25S Oxford instruments Energy Dispersive X-ray microanalyser. EDX of carbide particles benefits in the TEM from the use of a thin specimen and therefore problems with the interaction volume of the SEM were avoided, and also using carbon extraction replicas allows for accurate carbide composition determination without overlap from the ferrous matrix. From these data the weight percentage of elements in a particle can be calculated. 20 to 30 particles were examined in each sample, all selected randomly. A live time (collection time) of 60 seconds was used for each.

3.7 Dilatometry

Dilatometry samples were made from both virgin materials in order to apply controlled heat treatments to investigate the possible starting conditions of the ex-service material. These consisted of 10 mm x 5 mm cylinders. Experimentation was performed on a Bahr DIL805A/D quenching and deformation dilatometer. A small thermocouple was spot welded onto the sample prior to loading into the chamber. A vacuum is produced in the chamber to ensure that there is little or no oxidation occurring during the heating and cooling cycle. Quenching was produced by the controlled flooding of the heat treatment chamber with helium gas. This allows different rates of cooling to be easily achieved.

Samples from both steels were heated to 950°C (the mid point of the British Standard heat treatment for austenitisation) at a rate of 200°C per second and held there for one hour. The samples were then cooled at the following rates: 1, 10, 25, 50, 100 and 200°C per second. Heating of the sample into the austenitic phase region before cooling allows a variety of microstructures to be produced as a result of cooling the samples through different regions of the TTT or CCT diagram. The temperature and the expansion and contraction of the sample during the cycle were tabulated by the software. The cylinders were sectioned, mounted, polished and etched to reveal the microstructure. Optical and SEM images were taken and the hardness of the microstructure associated with each cooling rate recorded.

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3.8 X-ray Diffraction

3.8.1 Sample Preparation

All samples were prepared for X-ray diffraction using a matrix dissolution method in order to quantify the carbide population: 1 cm^3 sections of each sample were ground to a 1200 grit finish. The cubes were cleaned in an ultrasonic bath for 3 minutes. A solution of 10% HCl in methanol was used to dissolve the matrix of the material away under 20-30 V DC applied to the sample for 45 minutes in an electrolytic cell so that the sample was the anode with respect to a stainless steel cathode. During this process some of the solution evaporated due to the heat generated, and therefore periodic topping up with methanol was required. As the time in solution increased the liquid became increasingly 'cloudy' due to the increased number of carbides in the solution. The solution was then filtered through a 0.02 µm Whatman Anodic membrane filter, which ensured that all particles greater than 20 nm were retained. The residue was dried flat on a glass slide ready for X-ray diffraction.

3.8.2 X-ray Diffraction Parameters

X-ray diffraction was performed between 20° and 100°, 2 theta, using a Bruker D8 X-ray diffractometer. The data were then plotted against scattering angle to allow for comparison with the data available through the ICDD database. The three main carbides which were matched against the traces were $M_{23}C_6$, M_2C and MC. The main peaks for these carbides ($Cr_{23}C_6$, M_0C and VC) are presented in Tables 3.6 to 3.8

20	Intensity	Н	k	L
44.121	999	5	1	1
37.745	286	4	2	0
41.506	286	4	2	2
48.303	183	4	4	0
33.634	74	4	0	0
14.393	18	1	1	1
16.635	14	2	0	0

Table 3.6: Cr₂₃C₆, cubic structure, a=10.65Å, 89-2724 in ICDD-JCPDS ^[65]catalogue.

Table 3.7: Mo2C, orthorhombic structure, a=4.724Å, b=6.004nm, c=5.199nm, 89-2669 in ICDD-JPDS [65]catalogue.

20	Intensity	Н	k	L
39.535	999	1	2	1
34.471	208	0	0	2
52.288	152	2	2	1
29.542	6	1	1	1
23.950	2	1	1	0
58.751	1	2	0	2
46.156	1	0	2	2

Table 3.8: VC, cubic structure, a = 4.30 Å, 74-1220 in the ICDD-JPDE ^[65] catalogue.

20	Intensity	h	k	L
43.418	999	2	0	0
37.367	991	1	1	1
63.082	449	2	2	0
75.671	216	3	1	1
79.684	115	2	2	2

3.9 Thermodynamic calculations

MTDATA is a software package developed by the National Physical Laboratory; the program contains a number of functions, but throughout this work the main functions used are the equilibrium phase calculations in a multi component system, isopleth calculations and the calculation of the order of phase stability. Equilibrium calculations use a Gibbs energy minimisation procedure which involves solving equation 3.4 for given temperatures and pressures ^[66].

where

G is the Gibbs energy which is to be minimised by varying the values of n_j , j=1,2,...N, n_j is the amount in moles of species *j* present in the system; each chemical substance with a different phase designation being considered as a distinct chemical species,

N is the number of species in the system,

 μ_j is the chemical potential of species *j*, which may be a function of some or all of the species amounts in the same phase; it also depends on temperature and pressure (the form of μ_j depends on the model of the phase under consideration and is constructued such that $dG/dn_j = \mu_j$),

 a_{ij} is the number of units of component *i* per species *j*,

M is the number of components in the system,

 r_i is the number of moles of component *i* in the system.

Steel composition, temperature range and pressure are inputted into the MTDATA interface and the programme then uses a 9Cr TCFE database for Fe alloys database ^[67] to calculate the stable phases at predefined temperature steps. The elements which could be considered in the programme were iron, carbon, silicon, aluminium, chromium, molybdenum, nickel, manganese, tungsten, vanadium and nickel and the phases allowed were the ferrite matrix, MX, M₂X, sigma, aluminium nitride, cementite, M₃C, M₇C₃,

 $M_{23}C_6$ and M_5C_2 . This ensures that all of the carbides which might occur in this low alloy steel are considered during the calculations. The results are typically presented as a graph of temperature against mass fraction of phase or as a dataset which can be imported into Excel for further detailed analysis.

General microstructure

Chapter 4

General Microstructure

4.1 Introduction

This chapter presents an investigation of the overall microstructure of all 20 exservice samples. An overview is given of the microstructure of each sample using only optical and scanning electron microscopy, allowing a basic comparison of all of the materials from different length service lives. Later chapters further investigate the carbides in greater detail and at higher resolution. Details of simple testing, including grain size measurements and hardness, are also presented in this chapter. Optical and Scanning Electron Microscope (SEM) images provide both low and higher magnification images, which can be used for comparison of the features within the different materials.



Figure 4.1: A schematic illustration of the main features observed within the microstructure of ¹/₂Cr ¹/₂Mo ¹/₄V steels a) an micrograph showing the overall ferritic microstructure at low nagnification; b) an SEM micrograph showing the larger carbides which are present at the grain boundaries, c) is a STEM image of a carbon replica where the small dark shapes are very fine carbides within the ferrite grain.

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Figure 4.1 is an example of a typical ¹/₂Cr ¹/₂Mo ¹/₄V steel having endured a considerable length of time (in excess of 11 years) in service. The image in the centre (a) is from optical microscopy, the material consists of large ferrite grains with major carbides primarily at the grain boundaries which can be seen more clearly in the SEM image on the left (b); the image on the right, (c), is a Scanning Transmission Electron Micrograph (STEM) illustrating the very fine smaller carbides which form within the grains.

4.2 Optical Microscopy Overview of all Samples

Optical images of all samples were taken using an MEF-3 light microscope. Figures 4.2 and 4.3 are micrographs of the two virgin materials, V.1 and V.2, supplied. It can be seen that the pre-service structure is dominated by a ferrite/pearlite structure typical of low alloy steels. It can be seen that there is a difference in grain size between the two different virgin materials and possibly a difference in the amount of pearlite, consistent with the significant difference in carbon concentration. 0.11 in material V.1 and 0.16 wt. % in V.2 respectively. These differences are further investigated in Chapter 5.

All ex-service samples were found to have a ferritic microstructure with larger carbides present at the grain boundaries (only just visible optically at higher magnifications), as shown in Figures 4.4 –4.21. Figure 4.4 is a micrograph of sample KA245, which has been in service for 66,979 hours, a relatively short time compared to the rest of the samples studied. It is clear that there is a difference in the microstructure of this sample with the lamellar pearlite structure still visible in a number of the grains (one area is identified by a white circle). This microstructure is non-equilibrium and with further exposure to service temperature, would degrade to a state similar to that of the samples enduring 100,000 hours and above.

There is very little visible difference in the samples between 100,000 and 200,000 hours service at this magnification, (Figures 4.5 - 4.21, presented in order of increasing time in service), other than differing grain sizes, which will be discussed in Section 4.3. Figure 4.10 from sample ATB has a number of long dark string-like

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particles which can be seen traversing this micrograph. These particles are formed during steel production as a result of impurities. These particles were common in almost all of the samples investigated. More detailed studies of the microstructure require microscopy with higher resolution.

From these optical micrographs, grain size measurements were made for each sample and can be seen later in Figure 4.65.



Figure 4.2: Sample V.1 with the pre-service ferrite, pearlite microstructure, chemically etched with 5% Nital.



Figure 4.3: Sample V.2, the pre-service ferrite, pearlite microstructure, chemically etched with 5% Nital.



Figure 4.4: KA245, 66,979 service hours, an intermediate microstucture with some remaining pearlite (one area observed in the white circle). 5% Nital etched.



Figure 4.5: Optical image of sample DCAB, after 128,500 hours in service chemically etched with 5% Nital.



Figure 4.6: DCAU1B2 131,600 service hours, chemically etched with 5%Nital.



Figure 4.7: KA727, after 132,000 service hours, chemically etched with 5% Nital.



Figure 4.8: TLB20, after 137,900 service hours, chemically etched with 5% Nital.



Figure 4.9: TLA3, after 137,900 service hours, chemically etched with 5% Nital.



Figure 4.10: ATB, after 146,000 service hours, manganese sulphide particles identified by the white circle chemically etched with 5% Nital.



Figure 4.11: KA86, after 164,000 service hours, chemically etched with 5% Nital.



Figure 4.12: MSB13/13Z, after 171,500 service hours, etched with 5% Nital.



Figure 4.13: KA457, after 176,000 service hours, chemically etched with 5% Nital.



Figure 4.14: KA82, after 174,000 service hours, chemically etched with 5% Nital.



Figure 4.15: KA387, after 191,000 service hours, chemically etched with 5% Nital.



Figure 4.16: EGG, after 193,000 service hours, chemically etched with 5% Nital



Figure 4.17: MSC5Z, after 198,000 service hours, chemically etched with 5% Nital.



Figure 4.18: MSC9, after 198,000 service hours, chemically etched with 5% Nital.



Figure 4.19: KA1781, after 201,800 service hours, chemically etched with 5% Nital.



Figure 4.20: KA1706, after 206,309 service hours, chemically etched with 5% Nital.



Figure 4.21: KA1358, after 217,921 service hours, chemically etched with 5% Nital



Figure 4.22: KA1490, provided by industry with an unknown number of hours in service, chemically etched with 5% Nital

4.3 Scanning Electron Microscopy Overview of Samples

A Scanning Electron Microscope (SEM) was used to image all of the samples. Images were taken using secondary and backscatter electron modes, at the same magnification to allow for comparison of all the samples. This section reports on the differences in microstructure observed using these techniques. Secondary electron images show the topographical features of the microstructure whereas backscatter electron images are better for illustrating the compositional differences. The SEM images presented in Figures 4.23 - 4.42 show both the secondary and backscatter electron images for each sample in the study.

With the exception of the pre-service samples (Figures 4.23 and 4.24) and sample KA245 (Figure 4.25), all samples have undergone extensive time in service and none of them contain the original ferrite/pearlite structure, although some samples appear to retain features from it after considerable time in service. From the SEM images the grain boundary carbides can be quite easily differentiated from the matrix although the contrast between the two phases is only very subtle.



Figure 4.23: V.1, Secondary electron image pre-service sample containing 0.11 wt.% carbon.



Figure 4.24: V.1, backscatter image of pre-service sample containing 0.11 wt.% carbon



Figure 4.25: V.2, Secondary electron image pre-service sample containing 0.16 wt.% carbon.



Figure 4.26: V.2, backscatter image of pre-service sample containing 0.16 wt % carbon



Figure 4.27: Secondary electron image of sample KA245 after 66,000 hours in service.



Figure 4.28: Backscatter image of sample KA245 and after 66,000 hours in service.



Figure 4.29: Secondary electron image of sample DCAB.



Figure 4.30: Backscatter image of Sample DCAB.



Figure 4.31: Secondary electron image of sample DCAU1B2.



Figure 4.32: Backscatter image of sample DCAU1B2.



Figure 4.33: Secondary electron image of sample KA727



Figure 4.34: Backscatter image of Sample KA727.



Figure 4.35: Secondary electron image of sample TLB20.



Figure 4.36: Backscatter image of sample TLB20.

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Figure 4.37: Secondary electron image of sample TLA3



Figure 4.38: Backscattered image of sample TLA3



Figure 4.39: Secondary electron image of sample ATB



Figure 4.40: Backscatter image of sample ATB



Figure 4.41: Secondary electron image of sample KA86



Figure 4.42: Backscatter image of sample KA86.



Figure 4.43: Secondary electron image of sample MSB13/13Z, the white circle highlights an area with small carbides visible in within the grain.



Figure 4.44: Backscatter image of sample MSB13/13Z.



Figure 4.45: Secondary electron image of sample KA457.



Figure 4.46: Backscatter image of sample KA457.



Figure 4.47: Secondary electron image of sample KA82.



Figure 4.48: Backscatter image of sample KA82.



Figure 4.49: Secondary electron image of sample KA387.



Figure 4.50: Backscatter image of sample KA387.







Figure 4.52: Backscatter image of sample EGG.


Figure 4.53: Secondary electron image of sample MSC5Z.



Figure 4.54: Backscatter image of sample MSC5Z.



Figure 4.56: Secondary electron image of sample MSC9



Figure 4.57: Backscatter electron image of sample MSC9.

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Figure 4.58: Secondary electron image of sample KA1781



Figure 4.59: Backscatter electron image of sample KA1781.



Figure 4.60: Secondary electron image of sample KA1706 areas of Fe₃C, in the white ellipse, can still be seen in the sample after 206,309 hours.



Figure 4.61: Backscatter electron image of sample KA1706.

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Figure 4.62: Secondary electron image of sample KA1358.



Figure 4.63: Backscatter electron image of sample KA1358.



Figure 4.64: Secondary electron image of sample KA1490.



Figure 4.65: Backscatter electron image of sample KA1490.

4.3.1 Pre-service microstructure

Figures 4.2 and 4.3 are the optical images and Figures 4.23 to 4.26 are the SEM images from samples V.1 and V.2. These two samples are the pre-service samples, which have never been part of a functional plant and were, in fact, off-cuts from pipes being installed in plant. The microstructure in both of these samples is that of the initial ferrite-pearlite. In the optical images (Figures 4.2 and 4.3) the darker grains are those which contain the lamellar pearlite while the lighter grains are those of the ferrite. The iron rich Fe₃C, or cementite, does, with time at service temperature decompose in favour of the thermodynamically stable MC or $M_{23}C_6$ carbide. How long this decomposition will take is dependent on a number of factors, including; the initial alloy composition, initial heat treatment, service temperature and service stress. This initial microstructure, and how the cooling rate from the initial heat treatment affects it, will be discussed in greater detail in Chapter 5.

4.3.2 Short service exposure

Sample KA245 (Figures 4.4 and 4.25) is the sample with the shortest service exposure time under investigation during this work. It is clear that even after 7 years (66,979 hours) at service temperature the microstructure still contains a large amount of the initial Fe₃C from the virgin state. It is possible that there is an indication that the microstructure of this sample did not begin its service life as a 'normal' ferrite/pearlite microstructure. There is evidence in Figure 4.27 of a 'lath' structure, possibly bainite and there are fine acicular particles, presumably cementite, which have precipitated within the laths. The range of possible initial pre-service microstructures will be discussed further in chapter 5.

Figures 4.66 and 4.67 are higher magnification images from the same sample and the latter clearly shows the difference between grains which have originally contained the Fe₃C, and those that did not. In Figure 4.67 the major carbides, precipitating at the grain boundaries are clearly visible and some are identified by a white arrow. These are the stable $M_{23}C_6$ which will be discussed in greater detail in Chapter 6.

If this particular sample had endured much longer service times the microstructure would be much more homogenised, with the larger carbides within the grains precipitating preferentially at the grain boundaries as equilibrium carbides. The

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microstructure would be expected to be more similar to that of the longer service time samples, for example, KA86 in Figure 4.42.



Figure 4.66: Secondary electron micrograph from sample KA245, the sample has endured a short interval in service, 66,979 hours and the degrading microstructure is still visible within a number of grains.



Figure 4.67: Higher magnification SEM secondary electron micrograph from sample KA245 showing the difference between the ferrite grains and the ferrite grains with the acicular Fe₃C clearly visible within the grains. The white arrow identifies the large carbides beginning to precipitate at the grain boundaries in favour of the less stable Fe₃C.

4.3.3 Extended service exposure

From the SEM images in Figures 4.22 through to 4.64 it can be clearly seen that there is a difference in both the grain size and the size of the larger carbides which form on the grain boundaries (Figure 4.1). Du ^[38] et al. describes how these major carbides cannot be seen using optical microscopy techniques, however, it is possible that during their work, the carbides under investigation had not coarsened sufficiently during the relatively short ageing times used (up to 66,000 hours). However, this work suggests that the larger carbides can be seen using higher magnification optical microscopy, and the large carbide size around the grain boundaries does make differentiation between these two components of the microstructure because the difference in contrast between the two phases is only very slight. The larger carbides are visible in most of the longer aged samples under investigation during this work to greater or lesser extents.

Figures 4.32 and 4.60 are of samples DCAU1B2 and KA1706 respectively; both of these samples have a large number of carbides on the grain boundaries, considerably more than any of the other samples. However, sample KA727 (Figure 4.28) appears to have very few, if any, of these larger carbides visible at the grain boundaries in comparison to the rest of the samples.

Figures 4.43 and 4.44 are images of sample MSB13/13Z, which contains a more of the larger grain boundary carbides in addition a number of smaller carbides which can be seen within the grains, identified by an arrow in Figure 4.43. These smaller carbides appear to be acicular in shape and relatively 'sharp' compared to the larger carbides at the grain boundaries. Sample DCAU1B2 (Figure 4.32) also contains a number of these carbides within the grains. The only other sample which shows evidence of these larger carbides within the grains is sample KA1706 and in Figure 4.60 these carbides have been identified within the white circle. These carbides seem a little different to the acicular ones found in MSB13/13Z and DCAU1B2, in that they appear to have a 'network'-like structure and may well be interlinked in a third dimension. These carbides have retained a cementite-like structure.

A number of these post service samples were reported by the industrial partners to contain large amounts of grain boundary cavitation. None of these cavities have been observed during this study, however, it is possible that the samples under investigation here have been removed further from the cavity damaged region.

Figure 4.68 presents a plot of all of the grain sizes, measured using a linear intersection method. Five images from random locations were used for each sample to allow for statistical significance. Sample MSC9 has the smallest grains at just over 15 μ m in diameter, samples DCAU1B2 and KA245 have the largest at just over 35 μ m.

Figure 4.69 shows the grain sizes from Figure 4.68 plotted against the service life of the materials. The relationship between grain size and service life is clearly not one which could be used to accurately predict the remaining life. It is not known if the grain size has changed as a result of time in service as the pre-service data are not available, however, as the material has not been heated sufficiently to reach the austenite phase region it would not be anticipated that the ferrite grain size would change significantly during extended exposure at the service temperature.



Figure 4.68: Grain size of all the samples measured via a linear intersection method.



Figure 4.69: Service life in hours plotted against the grain size in microns, shows that there is little, if any, relationship between service life and ferrite grain size.

4.4 Hardness testing

Hardness testing is a quick, widely used, relatively easy method of evaluating materials, whether in service or post service. All samples were Vickers hardness tested using a 10 kg load. Five indentations were made and the average of these values are shown in Figure 4.70. A number of industrial partners use the hardness of pipes to indicate remaining life, however, this method of working requires the pipe to be regularly tested to record any reduction in hardness over time.



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Figure 4.70: Hardness values of all the samples provided, each point is the average of five hardness indents.







Figure 4.72: Hardness on the X-axis versus wt % element on the Y-axis.

From Figures 4.70 and 4.71 it is can be observed that there is a difference in hardness between the samples, with the hardest sample reaching 152 HV and the lowest being 113 HV. When hardness is plotted against hours in service, there is an overall reduction in hardness with increasing time in service, however, the technique is thought to be insufficiently accurate to use alone as a remaining life assessment tool.

Figure 4.72 is a plot of hardness against the weight percent element within each composition; there appears to be no obvious trend to link the hardness of the samples to a particular element.

4.5 Effect of Service Time on the Composition

The compositions of each of the samples have been plotted against time in service to investigate if there is a relationship between time in service and sample composition. Figures 4.73 to 4.78 are the plots of major elements against the hours which each sample has endured in service. In addition to the plots of chromium, molybdenum, vanadium and carbon against the hours in service, plots of Cr:C, Mo:C, V:C and (Cr+Mo+V):C were produced and presented in Figures 4.76 to 4.80. Once again there

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does not appear to be a pattern which associates these ratios with the amount of hours a sample has spent in service.



Figure 4.73: Hours in service plotted against the chromium content (wt. %) of each of the samples, compositions were taken using a OES technique on bulk material.



Figure 4.74: Hours in service plotted against the molybdenum content (wt. %) of each of the samples, compositions were taken using an OES technique on bulk material.

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Figure 4.75: Hours in service plotted against vanadium content (wt. %) of each of the samples, compositions were taken using an OES technique.



Figure 4.76: Hours in service plotted against chromium and molybdenum wt. % divided by the vanadium wt. % for each of the samples.

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Figure 4.77: Chromium to carbon (wt. %) ratio plotted against hours in service.



Figure 4.78: Molybdenum to carbon (wt.%) ratio plotted against hours in service.

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Figure 4.79: Vanadium to carbon (wt. %) ratio plotted against hours in service.



Figure 4.80: Ratio of chromium, molybdenum and vanadium to carbon (wt.%) plotted against time in service.

4.6 Summary

This chapter has presented images taken using optical and scanning electron microscopy from all of the different ex-service samples provided by industry, in addition to two pre-service virgin materials to provide an overview of the general microstructure of these types of steels. In general, it has been seen that the microstructure is dominated by a degenerate ferrite/pearlite microstructure, consistent with that expected from low alloy steels of these compositions.

The dominant primary grain structure is ferritic, with evidence, to varying degrees, of a degenerate pearlite structure also present. This original ferrite/pearlite microstructure appears to take many, many hours in service for complete degeneration and pearlitic regions are visible in samples which have over 100,000 hours of service life. In a number of the samples, the SEM images were able to resolve large carbides which typically had precipitated along the ferrite grain boundaries. In some cases, these were also visible using higher magnification optical microscopy. On first observation, there seemed to be a greater density of carbides within samples DCAU1B2 and KA1706 compared to samples KA727 and EGG, for example. In some of the steels, individual smaller carbides were also observed, typically within the grains, although these were hard to resolve. The carbide populations are investigated in further detail in Chapters 6 and 7.

It was also noted that the microstructure of sample KA245, which had only been in service for 66,979 hours, may not have originated as a fully ferrite/pearlite structure, with some evidence for phases such as bainite being possibly present. However, the two steels which were in the virgin condition did indeed exhibit a 'typical' ferrite/pearlite structure. The different initial microstructures which could be present in these steels are investigated further in Chapter 5.

In many of the steels, large stringers of manganese sulphide particles were visible in the matrix. Three of the samples (DCAU1B2, KA727 and TLA3) were noted as having a particularly high density of these particles.

The mean ferrite grain sizes of all of the samples have been measured using a linear intercept method. It has been found that there is a significant difference in the grain sizes of the ex-service samples, which ranged from \sim 15-35 µm in size. This is perhaps not surprising, given that a significant variation was also observed between the two virgin materials (V1 and V2) which were examined in this research. Attempts to correlate the grain size with the length of time in service did not reveal any specific trends. This is perhaps not surprising because at the service temperatures of interest it is unlikely that the ferrite grains have coarsened significantly and therefore the variation is probably representative of the pre-service variation manifested in the two virgin materials.

Hardness measurements have also been made for all of the samples. Once again, a variation was observed between the samples which ranged from ~110-150 HV. When plotted, against the service life of the samples, it was observed that there was a general trend for the microstructures to become softer with increasing ageing time at the service temperatures, however, there was significant scatter in the data, which, it is thought, rules this out as an isolated methodology for remanent life prediction.

The chemical compositions with respect to the main elements of all of the samples were also plotted as a function of hardness, grain size and service life. No significant patterns emerged in the data, and therefore it is clear that the microstructural degradation is not only a complex function of these various parameters but also may be dependent on parameters such as the carbide type and volume fraction. Therefore, further detailed and higher resolution investigations are necessary to determine accurate methods of identifying components which may be nearing the end of their design life, as discussed in later Chapters.

Chapter 5

The effects of the initial heat treatment on the starting microstructure

5.1 Introduction

The initial heat treatment of ¹/₂ Cr ¹/₂ Mo ¹/₄ V steel prior to service could have a potentially large effect on the resulting post service structure. The conventional starting microstructure is ferrite/pearlite, however, a number of authors ^[33,36] have recognised that the pre-service microstructure may also be partially bainitic. The work in this chapter describes the various phases produced by different cooling rates of the virgin material from an austenitising temperature of 950°C. A sample of the bainitic material produced was then subject to an extended heat treatment at a typical service temperature (586°C) to investigate the decomposition of the bainitic structure and its effect on the equilibrium microstructure.

5.2 Methodology

A dilatometer was used to provide the varying cooling rates of the two virgin steels provided by industry. The composition of the two steels varied across the British Standard with one (Virgin 1) having the lowest amout (0.11 wt.%) of carbon permissible to comply with the British Standard and one (Virgin 2) the highest possible amount of carbon (0.16 wt. %). Other elements in the two steel materials were very similar; the chromium contents for samples Virgin 1 and 2 are 0.42 and 0.47 wt. % respectively. The molybdenum contents were also similar, with Virgin 1 containing 0.55 wt. % and Virgin 2, 0.57 wt. % and finally the vanadium content in both of these samples was exactly the same at 0.25 wt. %, (see section 3.5).

Samples from the two steels were heated to 950°C, the typical normalising temperature, and held for 2 hours before cooling at various rates to enable a number of different microstructures to be produced. To create a complete view of the effects of cooling rate the samples were cooled at 1, 10, 25, 50, 100 and 200°Cs⁻¹ which results in samples being cooled into the various sections of the time temperature

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transformation diagram (Figure 5.1). In addition to these cooling rates, the Virgin 1 sample was also cooled at 150° Cs⁻¹ to confirm that the hardness results from the 100 and 200° Cs⁻¹ rates were accurate.

The slower the cooling, the greater the ferrite/pearlite content of the material. Increasing the carbon content in a system moves the phase fields to the right hand side of the TTT diagram, effectively reducing the cooling rate required to produce the bainite microstructure and increasing the likelihood of martensite production, i.e. increasing the hardenability of the steel.





5.3 Microstructure and mechanical properties

For each of the cooling rates described in Section 5.2, the samples were sectioned and five hardness indents were made, and the results are presented in Figure 5.2. The samples were then prepared metallographically to allow for optical and electron microscopy.

The hardness results in Figure 5.2 show that the hardness of Virgin 1 increases rapidly from 200 HV₁₀ up to the 25°Cs⁻¹ rate at which it begins to plateau at 265 HV₁₀. This plateau remains until the 100°Cs⁻¹ cooling rate, at which the hardness again begins to increase until it reaches a maximum hardness of 350HV₁₀ at 200°Cs⁻¹.

The second sample (Virgin 2) has a slightly higher starting hardness of $243HV_{10}$ which then increases rapidly until the $25^{\circ}Cs^{-1}$ cooling rate where the increase in hardness becomes less rapid. At $100^{\circ}Cs^{-1}$ a maximum hardness of 414 HV₁₀ is reached before the hardness begins to decrease slightly. The final hardness of this second sample eventually reaches 370 HV₁₀ at a cooling rate of $200^{\circ}Cs^{-1}$. An additional data point is shown at a cooling rate of $150^{\circ}Cs^{-1}$ for virgin 2. This is because an additional heat treatment was performed to confirm the reduction in hardness at the fastest cooling rate.



Figure 5.2: Results of hardness testing on two virgin materials of slightly varying composition and cooling rates, after normalising at 950°C for 2 hours in a dilatometer and cooling to room temperature.



Figure 5.3: Optical micrograph of Virgin 1, heated to 950°C and cooled at a rate of 1° Cs⁻¹



Figure 5.5: Optical micrograph of Virgin 1, heated to 950°C and cooled at a rate of 10°Cs⁻¹



Figure 5.7: Optical micrograph of Virgin 1, heated to 950°C and cooled at a rate of 25°Cs⁻¹



Figure 5.4: Optical micrograph of Virgin 2 heated to 950° C and cooled at a rate of 1° Cs⁻¹



Figure 5.6: Optical micrograph of Virgin 2, heated to 950° C and cooled at a rate of 10° Cs⁻¹



Figure 5.8: Optical micrograph of Virgin 2, heated to 950°C and cooled at a rate of 25°Cs⁻¹



Figure 5.9: Optical micrograph of Virgin 1, heated to 950°C and cooled at a rate of 50°Cs⁻¹



Figure 5.11: Optical micrograph of Virgin 1, heated to 950°C and cooled at a rate of 100°Cs⁻¹



Figure 5.10: Optical micrograph of Virgin 2, heated to 950° C and cooled at a rate of 50° Cs⁻¹





Figure 5.13: Optical micrograph of Virgin 1, heated to 950°C and cooled at a rate of 200°Cs⁻¹

Figure 5.12: Optical micrograph of Virgin 2, heated to 950°C and cooled at a rate of 100°Cs⁻¹



Figure 5.14: Optical micrograph of Virgin 2, heated to 950°C and cooled at a rate of 200°Cs⁻¹

Optical micrographs are presented from all the sets of samples in Figures 5.3 to 5.14 which show a clear progression of the microstructure from ferrite/pearlite to martensite. Figures 5.3 and 5.4 are the slowest cooling rates tested, and the microstructure is one of ferrite and pearlite. If Figure 5.3 taken from the Virgin 1

sample is compared with Virgin 2 (Figure 5.4) there is a significant difference in grain sizes, with Virgin 1 having grains that are almost twice the size of those in Virgin 2. In addition, the pearlite regions are much more abundant in Virgin 2 than 1. The amount of carbon in virgin 2 would account for this difference. Using the lever rule for the binary Fe-C diagram to calculate the amounts of pearlite, results in virgin 1 being predicted to contain 11% and virgin 2 18% of pearlite respectively.

After cooling at 10° Cs⁻¹, the samples both appear to look quite similar. However, the amount of displacive phase transformation product is greatly increased compared to the 10° Cs⁻¹ samples with only a few entirely ferrite grains visible. The size difference in the ferrite grains is still noticeable between the two samples.

By the 25°Cs⁻¹ cooling rate the ferrite-pearlite structure is no longer present; instead the lower temperature displacive martensite and bainite regimes have dominated. Differentiation between these phases using optical microscopy is insufficiently accurate enough to make positive identifications. Information from both hardness testing and electron microscopy are required to ensure that the temperature at which the bainite–martensite transformation takes place can be identified.

In addition to the optical micrographs, the samples were examined at higher magnification in the SEM and the images are presented in Figures 5.15 to 5.36.

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Figure 5.15: Virgin steel 1 cooled at 1°Cs⁻¹



Figure 5.17: Virgin steel 1 cooled at 10°Cs⁻¹



Figure 5.16: Virgin steel 2 cooled at 1°Cs⁻¹



Figure 5.18: Virgin steel 2 cooled at 10°Cs⁻¹





5µm

Figure 5.21: Virgin steel 1 cooled at 50°Cs⁻¹





Figure 5.22: Virgin steel 2 cooled at 50°Cs⁻¹



Figure 5.23: Virgin steel 1 cooled at 100°Cs⁻¹



Figure 5.25: Virgin steel 1 cooled at 200°Cs⁻¹



Figure 5.24: Virgin steel 2 cooled at 100°Cs⁻¹



Figure 5.26: Virgin steel 2 cooled at 200°Cs⁻¹

Figures 5.15 through to 5.26 are a series of scanning electron microscope images illustrating the microstructure of Virgin steels 1 and 2 with differing cooling rates from 950°C. Figures 5.15 and 5.16 are the slowest cooling rates at 1°C s⁻¹. The structure is one of ferrite and pearlite. Figure 5.16 is from Virgin 2; this steel contains the most amount of carbon and appears to contain more cementite (Fe₃C) than Virgin 1, with its lower carbon content. As the cooling rates increase, the microstructures change through the bainitic regime into the martensitic structure, and at the 100°C cooling rate, the ferrite grains can no longer be seen and instead the bainitic and martensitic structure dominates. Cooling at 200° Cs⁻¹ produces an extremely fine martensitic structure with laths which are much narrower than the structure of the 100° Cs⁻¹ sample.

It is expected that the martensite lath structure would become increasingly finer with increasing cooling rates due to the nature of the displacive transformation mechanism. Careful examination of the microstructures from optical and particularly scanning electron microscopy indicates that cooling rates of 10-100°Cs⁻¹ in Virgin 1 and only 10-25°Cs⁻¹ in Virgin 2 produce a bainitic microstructure; and cooling rates of 200°Cs⁻¹ in Virgin 1 and 50°Cs⁻¹ and above in Virgin 2 will produce a martensitic microstructure. These results are consistent with the hardness data presented in Figure 5.2, which has been labelled with the probable microstructural constituents in each region taking hardness data, optical and scanning electron microscopy information into account.

5.4 Phase transformation during cooling

Differentiating between martensite and bainite by optical microscopy is typically a difficult task, and therefore to ensure that the phase transformations could be discriminated, the dilatometer was used to collect data relating to the expansion and contraction of the steel samples. In turn, these data can be used to establish the start and finish temperatures of the phase transformation and ultimately which phases are being produced by the different cooling rates.

The dilatometer measures the change of sample length as a function of temperature. These curves can be differentiated so that the rate of change of transformation can be obtained; this clearly shows what temperature the transformation from austenite begins and ends and allows identification of the temp at which the peak transformation rate occurs. Through the use of the transformation start temperatures it is possible to identify the phase which is being formed. For example, the martensite transformation occurs at a much lower temperature due to the larger amount of under cooling required to initiate the change, however the transformation is much quicker than that for the ferrite.

Figures 5.27 through to 5.38 are the dilation curves for each of the heat treatments performed. The blue line represents the change in sample length with temperature as a result of the cooling and the black line is the rate of change of transformation from austenite.

The transformation start temperatures can be determined from each of the graphs; the general trend shows a decrease in transformation start (T_s) temperature with increasing cooling rate due to the increasing undercooling required to create the higher temperature phases. The slow cooling rates yield a larger range between the T_s and T_F (transformation finish). The phases created as a result of the slow cooling rates (1°Cs⁻¹ and to an extent 10°Cs⁻¹) are formed via a diffusional mechanism while the phases created as a result of the rapid cooling (martensite and bainite) are created as a result of predominantly displacive mechanisms.

Figure 5.89 shows the transition start temperatures of samples from both Virgin 1 and Virgin 2 at various cooling rates. In all cases the transition start temperatures in Virgin 2 are lower than those in Virgin 1. This is due to the small differences in alloying additions, i.e. molybdenum and vanadium combined with the more significant effect of the carbon content.

The dilatometery data are consistent with the microstructural information and are summarised in Table 5.1 below. The phases in bold typeface indicate the dominant phase under particular cooling conditions.

Cooling	Virgin 1			Virgin 2		
Rate	Transformation	Transformation		Transformation	Transformation	
°Cs	start	finish	Microstructure	start	finish	Microstructure
1	880	660	Ferrite/Pearlite	800	600	Ferrite/Pearlite
10	650	500	Ferrite/Bainite	640	420	Ferrite/Bainite
25	630	470	Ferrite/ Bainite	520	300	Bainite/Martensite
50	600	400	Ferrite/Bainite	550	280	Bainite/Martensite
100	550	380	Bainite/Martensite	430	280	Bainite/Martensite
200	420	300	Bainite/Martensite	420	300	Bainite/Martensite

 Table 5.1: Transformation start and finish temperatures for samples Virgin 1 and Virgin 2 cooled after normalising at 950°C for 2 hours in a dilatometer and cooling to room temperature.



Figure 5.27: Virgin 1 heated to 950°C, held for two hours and cooled at 1°Cs⁻¹

Figure 5.28: Virgin 2 heated to 950°C, held for two hours and cooled at 1°Cs⁻¹



Figure 5.29: Virgin 1 heated to 950°C, held for two hours and cooled at 10°Cs⁻¹

Figure 5.30: Virgin 2 heated to 950°C, held for two hours and cooled at 10° Cs⁻¹

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Figure 5.31: Virgin 1 heated to 950°C, held for two hours and cooled at 25°Cs⁻¹

Figure 5.32: Virgin 2 heated to 950°C, held for two hours and cooled at 25°Cs⁻¹

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Figure 5.33: Virgin 1 heated to 950°C, held for two hours and cooled at 50°Cs⁻¹

Figure 5.34: Virgin 2 heated to 950°C, held for two hours and cooled at 50°Cs⁻¹

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Figure 5.35: Virgin 1 heated to 950°C, held for two hours and cooled at 100°Cs⁻¹

Figure 5.36: Virgin 2 heated to 950°C, held for two hours and cooled at 100°Cs⁻¹


Figure 5.37: Virgin 1 heated to 950°C, held for two hours and cooled at 200°Cs⁻¹

Figure 5.38: Virgin 2 heated to 950°C, held for two hours and cooled at 200°Cs⁻¹



Figure 5.39: Comparison of the transition start temperatures for samples from steels V1 and V2 cooled at varying cooling rates.

5.5 Long term aging of the microstructure

The 10° Cs⁻¹ samples were selected for long term aging as they represent the most extreme microstructures that are likely to be seen during the production of the large sections which are used in industrial applications. Optical micrographs from the sample microstructures are presented in Figures 5.40 to 5.43 which show that Virgin 1 steel is likely to have a mixed ferrite/bainite structure, with more bainite dominating in Virgin 2. It is difficult to believe that a cooling rate in excess of 10° Cs⁻¹ could be obtained in pipes with wall thicknesses sometimes in excess of 50 mm, and ultimately the full microstructure variation may never be realised throughout the wall thickness of these pipes. The purpose of this short investigation was to examine whether the bainitic microstructure was likely to persist during long term service at operating temperatures of ~565°C. Samples from both Virgin 1 and Virgin 2 materials were prepared and heat treated at 900°C for one hour before cooling at 10° Cs⁻¹, the samples did not receive a conventional temper at 700°C. The samples were then aged in a furnace in laboratory air at a temperature of 568°C for 238 days (5172 hours). They

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were then removed and metallographically prepared and etched before light microscopy and scanning electron microscopy were performed on them, taking care to eliminate any edge effects from decarburisation or oxidation by concentrating on the bulk of the sample.



Figure 5.40: Optical micrograph of Virgin 1 sample after 9 months at 568°C.



Figure 5.41: High magnification optical micrograph of Virgin 1 sample after 9 months at 568°C.



Figure 5.42: Optical micrograph of Virgin 2 sample after 9 months at 568°C.



Figure 5.43: High magnification optical micrograph of Virgin 2 sample after 9 months at 568°C.

The distinctive bainitic structure in Virgin 1 can be seen by comparison of Figures 5.5 and 5.40, however, it is much less well defined after 9 months ageing at 568°C. In the initial as transformed microstructure the bainite is much more defined, with the bainite laths apparently recovering/coarsening to some extent during the long term

ageing at the lower temperature. The darker bainite dominant areas are beginning to reduce, with the lighter ferrite grains becoming much more dominant. Figure 5.44 is the in-lens SEM image of this sample; again this shows that the bainitic regions are beginning to reduce and the ferrite grains are becoming much more dominant. There are also a number of black dots at the grain boundaries (the red circle indicates an area rich in these) which are likely to be the grain boundary carbides which are seen in all of the longer ex-service samples. However, care should be taken when identifying these grain boundary carbides using in-lens techniques as not all of these dots are carbides; some are shadows created by the grain boundary as a result of preferential etching. The green circle in Figure 5.44 is an area which still contains some more obvious remains of the bainitic microstructure. If Figures 5.6 and 5.42 are compared, there is a very obvious difference between the pre- and post-aging microstructures. The initial structure quite clearly contained a large portion of bainite while in the post aging microstructure it is much more difficult to observe the remaining bainite. Figures 5.44 and 5.45 are the SEM in lens images of the samples after their extended heat treatment at service temperature. The Virgin 2 sample still contains a significant amount of the bainitic phase. This suggests that samples with larger amounts of carbon are more likely to yield a higher bainitic portion and the results here also suggest that the sample with the higher carbon content is more likely to retain more of that structure with extended time at service temperatures. The structure of the Virgin 2 sample remains much finer than the Virgin 1 sample with a much higher bainitic fraction, consistent with the smaller grain size particles observed.

Figures 5.46 to 5.49 are the carbon extraction replicas taken from the Virgin materials after a cooling rate of 10° C s⁻¹ followed by a 9 month simulated service temperature of 568°C. There is a distinct difference between the Virgin 1 sample and the Virgin 2 sample with the former having much fewer carbides on the replica, while the latter has a much higher particle density. This is believed to be a genuine result rather than an effect of etching, and is consistent with the higher C concentration in the Virgin 2 material.

Table 5.1 is the average composition of 20 carbides measured using EDX analysis from the carbon replicas from the Virgin 1 sample and the Virgin 2 sample. The results show that in the sample Virgin 1 there are carbides rich in chromium

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containing no vanadium, and also carbides that are chromium rich which do contain vanadium; these have been separated in the table. The Virgin 2 sample did not have any vanadium free carbides and therefore only has one carbide type recorded. Virgin 2 carbides did, however, contain molybdenum. No molybdenum was identified in either of the two types of carbide in Virgin 1.



Figure 5.44: SEM in-lens image of the Virgin 1 sample after 9 months at 568°C, the red circle is an area with black regions at the grain boundaries. These are carbides in some cases, but in others they appear to be shadowing as a result of preferential etching. The green circle denotes an area with some remaining bainitic structure apparent.





Figure 5.45: SEM In-lens image of the Virgin 2 sample after 9 months at 568°C.



Figure 5.46: TEM image taken from a carbon replica of Virgin 1.



Figure 5.47: TEM image taken from a carbon replica of Virgin 1.



Figure 5.48: TEM image taken from a carbon replica of Virgin 2



.Figure 5.49: TEM image taken from a carbon replica of Virgin 2.

Table 5.1: Mean composition of 20 carbides taken from Virgin 1 and Virgin 2, units wt. %analysed using EDX in a TEM

Sample	Carbide Type	V	Cr	Mn	Fe	Mo			
Virgin 1	Vanadium free	0	13.35	12.30	75.36	0			
	Vanadium containing	9.66	10.79	10.16	63.78	0			
Virgin 2		9.33	11.18	9.60	57.90	18.06			

5.6 Summary

The pre-service microstructure in a variety of different conditions has been studied to gain a better understanding of the effect it has on the post service microstructre. The work was performed because reports by other authors suggested that it was possible some bainitic structure remained in longer term service exposed materials.

Two different virgin steels of compositions within the specification for ¹/₂ Cr ¹/₂ Mo ¹/₄ V but with carbon concentrations at the top and bottom of the allowable range have been subjected to normalising heat treatments in a dilatometer to investigate the effects of different cooling rates on the microstructural developments. Both the high and low carbon virgin samples were treated with five cooling rates, and the resulting materials were hardness tested in addition to being examined using optical and scanning electron microscopy.

The sample with the higher carbon content yielded greater hardness at all cooling rates apart from the $1^{\circ}Cs^{-1}$ and $200^{\circ}Cs^{-1}$ where the difference in hardness of the two samples varied only slightly. The microstructures, however, were very different across the range of cooling rates with the slower cooled samples ($1^{\circ}Cs^{-1}$ and $10^{\circ}Cs^{-1}$) producing a ferrite/pearlite structure, those cooled at 25, 50 and $100^{\circ}Cs^{-1}$ producing a bainitic structure, while the sample cooled at $200^{\circ}Cs^{-1}$ produced a predominantly martensitic structure in the Virgin 1 material.

The results suggest that a bainitic structure can be produced at the relatively low cooling rate of 10°Cs⁻¹. After a relatively short exposure to service temperatures, the bainitic structure still remains, in particular the smaller scale structure remains within the grains. Unfortunately, the longer ex-service samples studied within this work have no information concerning their initial microstructure making it difficult to confirm whether or not the structure was initially bainitic. However, some longer service samples have shown signs of almost completely decomposed bainite rather than a more traditional degenerate ferrite and carbide microstructure and the results from this study suggest that this is possible.

Therefore, in summary, it is possible that mixed microstructures of ferrite/pearlite, bainite and martensite exist as starting materials for these steels before entering service. Indeed, thick section pipes may contain mixtures of all three different microstructures. The initial hardnesses and the exact nature of the carbide distribution of the materials may also vary significantly. These factors need to be borne in mind during the examination of the ex-service samples, for which unfortunately the starting microstructures are unavailable.

Chapter 6

Materials Modelling

6.1 Introduction

The modelling in this chapter is centred on thermodynamic equilibrium prediction, which as most of the materials under investigation have endured a significant amount of hours at the service temperature it is reasonable to presume that they are near equilibrium, i.e. they have reached a state where their Gibbs free energy is at a minimum. These modelling methods allow designers to predict the properties of the material after a prolonged amount of time. For example, if the designer is aware that one of the equilibrium phases will be detrimental to the material, they can design to account for such problems or accurately determine the end of life for that component.

The thermodynamic modelling package MTDATA ^[66] has been employed throughout this work, along with an appropriate database for Fe based alloys ^[68]. The inputs are chemical composition, temperature range, pressure and the user is able to select the anticipated phases. The elements used during this work are iron, carbon, silicon, aluminium, chromium, molybdenum, nickel, manganese, tungsten, vanadium and nickel. The phases allowed were; the ferrite matrix, MX, M₂X, sigma, aluminium nitride, cementite M₃C, M₇C₃, M₂₃C₆ M₅C₂. The programme then calculates the thermally stable, equilibrium phases as a function of temperature. The outputs vary from single point data with phase weight fraction and composition to multipoint data over a range of temperatures. This chapter considers the effects of the predicted equilibrium phases and their compositions with variations in sample composition. Section 6.3 considers the effects of varying the composition of the steel to investigate the effects of increasing the concentration of one, and in some cases more than one, element in the system to determine the sensitivity of phase stability to compositional changes in these alloys.

6.2 Predicting the Phases from Actual Material Compositions

Figure 6.1 shows the results of the model for the alloys studied. The carbides are displayed as a weight percentage of the whole system and the balance phase is the ferrite matrix (not shown). From the calculations it can be seen that M₂₃C₆ is the predicted equilibrium carbide in a number of the samples. In particular the samples which have slightly above average carbon values display a higher proportion of this equilibrium carbide. Samples EGG and KA387 are not predicted to contain any M₂₃C₆ at equilibrium; both samples containing less than 0.1 wt % C which is lower than required by the British Standard (Table 3.1). These samples containing the lower amounts of carbon have less available for carbide production compared to those which have large amounts of carbon, for example sample DCAU1B2. In addition to these two samples; KA1490 does not have any predicted M₂₃C₆. This sample has a carbon content of 0.13 wt. %, which is within the British Standard boundaries, however, this sample contains one of the lowest amounts of chromium of the samples provided at 0.29 wt. %. Sample KA1706 has a similar composition to sample KA1490: it has a carbon content of 0.11 wt. % and a chromium content of 0.27 wt. % and this sample has a very low predicted amount of M23C6.



Figure 6.1: Thermodynamic prediction of the equilibrium phases present in each sample at 568°C .

Finally sample TLA3 is also predicted to have very little of the $M_{23}C_6$ equilibrium carbide. This sample, unlike the others discussed here, has carbon and chromium compositions which fall well within the British Standard, however, this sample has a very low molybdenum content when compared to the other samples.

Comparing all of the samples containing high carbon it can be clearly seen that although a number of high carbon containing samples predict higher amounts of the carbide, there are equally some high carbon containing samples where lower amounts of carbide are predicted. Carbon is therefore not the sole controlling element of the $M_{23}C_6$ composition. The results suggest that the factors controlling the composition of the $M_{23}C_6$ carbide are complex with no one element controlling the equilibrium composition. Figure 6.2 shows the composition of the $M_{23}C_6$ in the samples which it was predicted. The chemical composition of the $M_{23}C_6$ particles in some of the alloys are determined experimentally in Chapter 8 (for example, see Table 8.2). It can be seen that the equilibrium thermodynamic predictions are in reasonable agreement with the experimental values, for example Cr is predicted to ~15 wt.% and the measured value is ~12 wt.%. Similar agreement is observed for the Mo concentrations, although it should be noted that some substitution of Mn was measured experimentally in the carbide which is not predicted by the calculations which is probably a result of how the phase is modelled in the thermodynamic database.

The molybdenum content of these samples varies by just 0.01 wt %, implying that although the molybdenum composition does have an effect on the $M_{23}C_6$ it is not the element which controls the carbide composition. The samples do have a difference of 0.04 wt. % carbon. These samples are identified with a red circle in Figure 6.1 which could account for the difference in predictions. XRD results presented in Chapter 7 clearly show that there is a substantial amount of molybdenum in the $M_{23}C_6$, sufficient to cause a shift in the diffraction properties of the carbides. The amount of chromium and carbon in a sample clearly affects the amount of the large $M_{23}C_6$ carbides present and additionally increased amounts of chromium affect the amount within the carbide itself.

Chapter 6

Materials modelling



Figure 6.2: Thermodynamic predictions for the composition of $M_{23}C_6$ in all samples which are predicted to contain it at 568°C.

Figure 6.3 shows the predicted composition of the molybdenum carbide. The dominant element is the molybdenum with some solubility for chromium, manganese, vanadium and tungsten. The additional elements are present in very small amounts and differ from sample to sample. Sample KA387 contains the most molybdenum in it's predicted MoC carbide although differences are extremely small between all samples. This sample falls into the upper levels of the British Standard composition but it is not the sample which contains the most molybdenum and certainly the amount of molybdenum in sample KA387 does not fall outside the British Standard limits. As with the $M_{23}C_6$ it would seem that the predicted amount of molybdenum in the carbide is controlled not only by the molybdenum content but by a complex combination of factors.

Figure 6.4 is the predicted composition of the vanadium carbo-nitride phase. Obviously, vanadium constitutes the largest proportion of this carbide with nitrogen and carbon completing the total composition. Generally the compositions are the same across the samples with DCAU1B1 and DCAU1B2 containing a little more nitrogen than the other samples. The vanadium carbide is predicted in very small quantities in all of the samples.

The M₂C carbide is one which is predicted to exist at equilibrium in all of the samples. Figure 6.5 shows the expected compositions in each sample. The carbide is rich in both molybdenum and vanadium with slightly more molybdenum than vanadium in most samples. The balance consists of carbon and smaller additions from other elements. This mixed carbide is the second most dominant phase behind $M_{23}C_6$. Aluminium nitride was predicted to exist in all of the samples in very small amounts. The composition of the nitride is not predicted to vary from sample to sample with a composition of 0.65 wt % Al and 0.35 wt % N. It is predicted to have no solubility for any other element.



Element

Figure 6.3: Thermodynamic predictions for the composition of MoC in all samples which are predicted to contain it at 568°C.

Figure 6.6 is the predicted composition of the M₇C₃ carbide. This carbide is predicted to exist in only one sample, MSC9, and is a predominantly iron rich carbide with a large chromium constituent. Manganese and molybdenum also appear in smaller quantities. Generally this carbide is not considered to be an equilibrium carbide and instead $M_{23}C_6$ and MoC are anticipated to precipitate from this carbide with increased time at temperature.

From the data shown in Figures 6.1 - 6.6 it is possible to collate a table which represents the phases expected in each sample, Table 4.1. From the table, it can be seen that there are three samples which are anticipated to contain no $M_{23}C_6$. Six samples are expected to contain no MoC at equilibrium. All of the samples contain AlN apart from EGG.



Figure 6.4: Thermodynamic predictions for the composition of V(C,N) in all samples which are predicted to contain it at 568°C.

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Element Figure 6.5: Thermodynamic predictions for the composition of M₂C in all samples which are predicted to contain it at 568°C.



Figure 6.6: Thermodynamic predictions for the composition of M_7C_3 in sample MSC9 predicted at 568°C.

	$M_{23}C_{6}$	MoC	V(C,N)	M_2C	AlN	M_7C_3
ATB	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
DCAU1B1	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
DCAB	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
DCAU1B2	\checkmark	-	\checkmark	\checkmark	\checkmark	-
EGG	-	-	\checkmark	\checkmark	-	-
KA82	\checkmark	-	\checkmark	\checkmark	\checkmark	-
KA86	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
KA387	-	\checkmark	\checkmark	\checkmark	\checkmark	-
KA457	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
KA727	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
KA1358	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
KA1706	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
KA1781	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
MSB13/13Z	\checkmark	-	\checkmark	\checkmark	\checkmark	-
MSC5Z	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
MSC9	\checkmark	-	\checkmark	\checkmark	\checkmark	\checkmark
TLA3	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
TLB20	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	-
KA1490	-	_	\checkmark			-

 Table 6.1: A Summary of the equilibrium carbides predicted by MTDATA thermodynamic modelling for each sample at 568°C.

6.3 Modelling the Effect of Changing One or More Elements in the System

The effect of changing just one or more elements at a time is considered in the next two sections. The mid-point of the British Standard composition has been used as a base line and one element has been changed over the span of it's standard limits. All of the calculations have been performed at 568°C (the service temperature).

Figures 6.7 through to 6.9 are the results of single temperature modelling of the carbides with changing amounts of individual elements. Each column represents a carbide (identified in the key) at a temperature of 568°C.



Figure 6.7: The effect of increasing carbon on the predicted mass of phase with the lowest amount of carbon on the left hand side of the X axis. The most affected carbide is the $M_{23}C_6$ carbide.



Figure 6.8: The effect of changing chromium on the predicted mass of phase with the lowest chromium content to the left hand side of the X axis, the most affected carbide is the M_2C



Figure 6.9: The effect of changing molybdenum on the predicted mass of phase with the lowest molybdenum content to the left hand side of the X axis. In this case the molybdenum carbide is most affected.





From Figure 6.7 reducing the carbon content can be seen to reduce the predicted amount of MoC, at the same time, the $M_{23}C_6$ increases with higher amounts of carbon in the sample. There is also a small increase in the amount of M_2C present at the higher carbon contents. Chromium (Figure 6.8) appears to have the same effect on the $M_{23}C_6$ and the MoC, although to a lesser effect, however, the amount of M_2C reduces with increasing chromium, the opposite to the effect of increasing carbon. When predictions are made at lower molybdenum compositions (Figure 6.9), no MoC is predicted at all and with increasing molybdenum content the amount of the carbide increases. Increasing amounts of molybdenum only affect the $M_{23}C_6$ very slightly with a tiny decrease across the composition range. The M_2C decreases a small amount as a result of increasing amounts of vanadium do not seem to affect the amounts of vanadium carbide but it does effect the $M_{23}C_6$ and to a lesser extent the M_2C . The former reduces in mass with increased vanadium and the latter increases very slightly with increased vanadium.

6.4 Summary of Equilibrium Modelling

 $M_{23}C_6$ is the dominant phase in a number of the samples. In most, but not all cases, those which contain a high carbon composition have higher predictions of $M_{23}C_6$,

although high carbon containing samples do not exclusively produce larger quantities of $M_{23}C_{6}$, as some high carbon samples have yielded average carbide contents. Those which are predicted to contain little or no $M_{23}C_6$ are predicted to have an increased amount of M_2C and MoC.

It would appear that the composition of all of the carbides are controlled by more than one element, suggesting that a more complex system of elemental balance has control over the carbide composition.

The plots of phase mass as a result of increasing elements in the steel show that each element has an effect on one, or more of the phases, with changes in carbon content yielding the greatest changes in the carbide amounts, affecting both $M_{23}C_6$ and MoC to the greatest extent. Vanadium had the least effect on the overall amount of carbides. Molybdenum had a large effect on the molybdenum rich MoC but had very little effect on the other carbides. Finally chromium affected the carbides in a similar fashion to the carbon, however, the effects are much smaller than with carbon.

6.5 Isopleths

Isopleths were plotted using the thermodynamic modelling package MTDATA, to show the effect of changing material composition at equilibrium. The compositions were taken from the upper limit and lower limit of the British Standard. Initially only one element was changed per calculation; to the left hand side of the graph the element being changed is at its minimum British Standard value and to the right the element is at its maximum acceptable British Standard value. All other elements were held constant at their maximum, minimum or mean values as indicated with the Fe changing to balance the composition.

Isopleths were computed between 773 and 1273K (500-1000°C) in steps of 30K. Results were recorded at every 0.01 percent change in composition. Figure 6.7 begins the series of isopleths using the minimum British Standard composition changing the carbon content. At the lower temperatures, increasing the amount of carbon appears to reduce the stability of both the M₂C and the MoC in favour of M₇C₃. At slightly higher temperatures, above 800K, the addition of carbon increases the stability of the,

usually non-equilibrium carbide, cementite (Fe₃C). At temperatures above 1000K the effect of changing C has very little effect on the phases.



Figure 6.7: Isopleth of all elements at the lower bound of the British Standard. Carbon increases from the left hand to the right hand side of the graph.

Figure 6.8 is the lowest band of the British Standard composition with increasing chromium level, and it can be clearly seen that increasing the amount of chromium has little effect on the phases over the temperature range other than lowering the boundary marked 1 with increasing chromium weight percentage.

Figure 6.9 is the lowest limit of the British Standard composition with increasing molybdenum, The stability of the MoC (molybdenum carbide) increases at higher temperatures with increasing molybdenum content. At temperatures above 1000K the increasing molybdenum content has little effect on the stable phases.

Figure 6.10 depicts the effect of changing the vanadium composition. The vanadium appears to have very little effect on any of the carbides with increasing content and doesn't seem to effect the V(C,N), Figure 6.10.



Figure 6.8: Lower British Standard limit, increasing chromium content showing the affect on the carbides present.



Figure 6.9: Lower British Standard limit, increasing molybdenum content showing the affect on the carbides present.



Figure 6.10: Lower British Standard, increasing vanadium content showing the affect on the carbides of the changing composition.The following four isopleths are related to the upper limit of the British Standard with elements changing again from their lowest value on the left to their highest value on the right. In Figure 6.11 the changing carbon content appears to make less difference than in Figure 6.7 where the composition is at its lowest.

Increasing amounts of chromium in this higher limit system causes the M_7C_3 to become increasingly less stable (Figure 6.12). Whereas with the lower limit of the British Standard no $M_{23}C_6$ was predicted, Figure 6.8. In Figure 6.13, where the molybdenum content is changing, it can be seen that the $M_{23}C_6$ and the V(C,N) are becoming increasingly stable at higher temperatures with increasing molybdenum content. Once again changing the vanadium amount appears to have very little effect on the stable phases at different temperatures. (Figure 6.14)



Figure 6.11: Maximum British Standard limit, increasing carbon content showing the affect of the changing composition on the stable carbides.



Figure 6.12: Maximum British Standard, increasing chromium content showing the affect on the stable carbides of the changing composition.



Figure 6.13: Maximum British Standard, increasing molybdenum content showing the affect on the stable carbides of the changing composition.



Figure 6.14: Maximum limit of British Standard, increasing vanadium content showing the affect on the stable carbides of the changing composition.



Figure 6.15: Mean British Standard composition with changing carbon, chromium, molybdenum and vanadium showing the affect on the stable carbides as a result of composition.

Finally Figure 6.15 presents the isopleth produced when the mean British Standard is used with changing carbon, chromium, molybdenum and vanadium. The phase field containing $M_{23}C_6$ appears to increase slightly as the elements increase at higher temperatures. However, at lower temperatures there seems to be little, if any, effect on the carbides predicted.

6.6 Summary of Isopleths

At the lower British Standard limit compositions the carbon appears to have the greatest effect on the phases predicted to be present. In the upper limit isopleths, the carbon has a much smaller effect especially at the lower temperatures.

Increasing the amount of chromium does not have a significant effect on the phases predicted in the lower bound British Standard isopleths but in the upper limit, results in an additional phase field with the M_7C_3 carbide arising at lower carbon contents and lower temperatures.

Both the shape of the plot and the phases predicted appear to be affected by changing molybdenum at the upper and lower boundaries (Figures 6.9 and 6.13), with the

higher composition containing no MoC in the high molybdenum content and lowest temperature sector of the plot. The higher temperature phases appear to be effected by the changing molybdenum content.

In the case of both high and low British Standard compositions the amount of vanadium present does not seem to affect the carbides present, however, if the two cases are compared the carbides which are predicted are slightly different, with the higher British Standard composition predicting $M_{23}C_6$ and MoC to be stable at lower temperatures and the lower composition predicting neither of these phases in this temperature range.

6.7 Summary of microstructural modelling

Thermodynamic modelling has been performed to predict the phases in each sample at 568°C, the service temperature. Not all of the samples of nominally similar $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V power plant steels have the same carbides predicted; some appear to contain large amounts of the equilibrium M₂₃C₆ while others are predicted to contain none or very little. However, those which are predicted to contain none or very small amounts of M₂₃C₆ are expected to contain greater amounts of other carbides so that the overall amount of carbides present in the material is approximately 2.0 wt %.

Increasing the amount of a single element in a system has an effect on various carbides but in the case that an element effects the amount of a certain carbide there is always another carbide which will compensate the loss or increase so that the overall carbide balance is not affected.

The effects of material composition varying across the British Standard has been modelled using isopleths; carbon is predicted as the element to have the largest single effect on the predicted carbides with increasing content. Vanadium appears to have the least effect on the carbides.

The most significant result is the obvious different in carbides which are predicted to exist as a result of very small changes in the materials' composition. In particular the range of compositions allowed within the British Standard has a significant effect on the predicted carbides.

Chapter 7

Major and Minor Carbides

7.1 Introduction

This chapter presents an in depth analysis of the carbide population found in each of the ex-service samples considered in this research. The chapter is divided into two main sections which cover the major and minor carbides respectively. A simple distinction is that the major carbides are visible using optical and scanning electron microscopy whereas the minor carbides require transmission electron microscopy for their examination. Scanning electron microscopy has been used to image the carbides, X-ray diffraction to identify the crystallographic structure of the carbides present and transmission electron microscopy for compositional and structural analysis. Finally, image analysis techniques have been used for a quantitative measure of these carbides.

7.2 Identification of the major carbides

The large carbides observed at the grain boundaries will be described as the major carbides. These have been identified in previous work ^[38] as either $M_{23}C_6$ or MoC. These carbides are not present when the material goes into service but precipitate at the expense of the Fe₃C with increasing time in service. X-ray diffraction has been performed on 15 of the 22 samples. The samples which did not have XRD performed on them were supplied in too small a quantity to allow a full analysis. Samples were prepared via a bulk extraction method which causes the ferrite matrix to be dissolved away from the carbides using a 10% hydrochloric acid solution in methanol; the carbide 'powder' can then be filtered from the acid solution to allow for analysis. X-ray analysis took place over a 20 range in intervals of 0.05° from 20 to 100°. The traces obtained are shown in Figures 7.1 to 7.15. The peaks on the traces were compared with cards from the ICDD-JPDE catalogue ^[24]. In addition to X-ray diffraction, large particles were selectively removed from the bulk material using a Focused Ion Beam Scanning Electron Microscope (FIB FEG-SEM). These samples were removed in the form of a TEM section which was subsequently thinned until

electron transparency was obtained for TEM investigations. The results of the X-ray diffraction are presented here, the ICDD peaks are identified by different coloured dashed lines, there is a discrepancy between some of the results from the card and peaks identified from the samples, this discrepancy will be explained later in this section. The discrepancy between the lines from the cards and the peaks from the experimental work is accounted for by adding molybdenum to the carbide, this is discussed later in this chapter.

The results are presented by hours in service, with those which have served the longest presented first and those which have had the least service last.





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Figure 7.3: X-ray diffraction trace from sample KA1706.

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Figure 7.5: X-ray diffraction from sample KA1781 with the M₂₃C₆ and the VC peaks identified.

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Figure 7.7: X-ray diffraction from sample EGG produced a slightly different trace in which the Fe₃C and VC carbides are the only peaks which can be identified.

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Figure 7.9: X-ray diffraction pattern from sample TLB20 in which both the $M_{23}C_6$ and the VC are identified along with the Fe₃C.

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Figure 7.10: X-ray diffraction from sample DCAB in which the M₂₃C₆ and VC peaks are identifiable.





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Figure 7.12: X-ray diffraction from sample KA82 in which the M₂₃C₆, VC and Fe₃C peaks can be identified.



Figure 7.13: X-ray diffraction from sample KA86 with M23C6 and VC identified.

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The results obtained, show that not all of the samples tested gave the same results despite being nominally the same material. It would be reasonable to anticipate that materials of nominally the same composition would yield similar carbides after a prolonged period in service. In a large proportion of the samples the $M_{23}C_6$ carbide is the dominant phase with the major peak at 44.151 of 20. However, three samples (EGG, KA82 and KA387, Figures 7.7, 7.12, and 7.14) do not appear to contain this major peak and instead a combination of vanadium carbide and manganese sulphides dominates. The samples can be categorised by their carbides into two distinct groups; those that contain the $M_{23}C_6$ carbide and those that do not. In the $M_{23}C_6$ containing group the majority of the XRD peaks can be identified as belonging to $M_{23}C_6$ and VC. In the $M_{23}C_6$ free sample the carbides are a little less well defined.

KA387, TLB20, EGG and KA82 (Figures 7.14, 7.9, 7.7 and 7.12, respectively) appear to contain the non-equilibrium carbide Fe₃C. In particular this occurs in samples which are not predicted to contain the M₂₃C₆ equilibrium carbide. Sample TLA3 contains manganese sulphide and vanadium carbide with no M23C6. The major manganese sulphide peaks can be observed in a number of the samples including; KA1781, MSC9, MSB13/13Z, KA86 and KA387 (Figures 7.5, 7.6, 7.11, 7.13 and 7.14). The major peaks of these manganese sulphide particles are at 30° and 50°. In all but sample TLA3 these peaks are very small due to the reasonably small amount of the sulphide found in the steels. The likelihood of all of the extractions used for XRD having manganese sulphide particles in is very small due to the very small amount of the impurity found present in the samples. In Section 5.2 these particles can be seen in a number of the samples under investigation, although the particles are large they are widely dispersed, and the likelihood of one being removed in the 1 cm³ used for bulk extractions is small. Hence the absence of this particle from the traces of the remaining samples, although it could well be present to some extent in all of the samples depending on the cleanliness of the steel.

Two samples show no peaks in the $M_{23}C_6$ positions; TLA3 and EGG. Samples KA387, KA82 and TLB20 (Figures 7.14, 7.12 and 7.9) all show signs of $M_{23}C_6$ in the XRD peaks but they appear to be much smaller than the $M_{23}C_6$ peaks in the samples which the carbide has been positively identified using this method. Of these samples EGG, TLA3 and KA387 are predicted during thermodynamic modelling to contain no

 $M_{23}C_{6}$, Figure 7.1, Sample TLB20 is predicted to contain only a small amount of the equilibrium carbide. However, sample KA82 (Figure 6.12) doesn't appear to contain any $M_{23}C_{6}$ from the XRD results on the other hand the thermodynamic predictions suggest that this sample is relatively rich in the stable carbide.

The $M_{23}C_6$ peaks in all samples are at least 1° too high when compared to the position established from the PDF cards (the red dashed lines on the graphs). This shift is due to the molybdenum content of the carbides. The PDF card presents the information for a $Cr_{23}C_6$ carbide, and the composition of the carbides in this material are not strictly chromium but a mixture of both chromium and molybdenum. The detailed structure and composition of these carbides will be presented in Chapter 8. Ultimately the substitution of molybdenum for chromium atoms affects the structure of the carbide resulting in the lattice parameter for the carbide changing, hence the difference in the results from the powder diffraction files and the results obtained during this work.

Three of the samples under investigation, TLB20, MSB13/13Z and KA82 (Figures 7.9, 7.11 and 7.12) show that they do contain $M_{23}C_6$ however, the counts obtained for the peaks of this carbide are lower than some of the others. KA82 (Figure 7.12) has a particularly low major $M_{23}C_6$ peak. In this case the Fe₃C and vanadium carbo-nitride appear to be the dominant phases in favour of the thermodynamically stable $M_{23}C_6$.

Ten of the tested samples have a peak which appears at 27°. This could be a result of preferred orientation or a compositional effect. Preferred orientation would occur if the carbide settled onto the filter paper in a particular orientation during the filtering process, and therefore if, during the collection of XRD the beam remains at the same angle to the particles the result would be this peak. In addition a peak at this position could be revealed if the amount of molybdenum in the carbide increased and modelling results have shown this effect. However, a simple test was used to establish which of these two phenomenon were causing this peak in a few of the samples. By using a position sensitive detector it is possible to compare the results at one angle to another, therefore establishing if the effect is a preferred orientation one. Figure 7.17 is a graph showing a model of the peaks expected from $M_{23}C_6$ if the carbide is entirely chromium and the results from both a Bruker D8 and a Nonius PDS120. The Bruker D8 remains at the same angle to the sample toroughout its collection while the Nonius

PSD 120 has a controllable position which permits the simultaneous measurement of diffracted X-ray intensities at all angles of 2θ across 120° with a static beam-sampledetector geometry, which is ideal to test for preferred orientation effects exhibited by samples. Figure 7.16 shows the difference between the two collection methods.



Figure 7.16: The difference in detection between the Bruker D8 system with the moving detector and Nomius position sensitive detector.





The results in Figure 7.17 confirm that the peak at 27° is in fact a preferred orientation effect rather than a compositional effect with the position sensitive machine not producing the peak.

In addition to this peak at 27° , the peaks which correspond to the $M_{23}C_6$ do not appear to match the values from the card. This is due to the amount of elements (iron and molybdenum) in addition to chromium which were present in the carbides. It is possible to calculate the effect of the elemental additions from the experimental data. This involves the use of two equations.

where:

 λ is the wavelength of the X-rays

d is the d-spacing of the lattice in the sample

 θ is the acquisition angle

a is the lattice parameter of the phase

N relates to the indices of the plane in question, such that $N=h^2+k^2+l^2$.

By using these equations it is possible to calculate the wavelength from the vanadium carbide for which the peak appears at the same point as the ICDD cards identify. Rearranging the equation allows the d-spacing for the $M_{23}C_6$ to be calculated. The result is that the d-spacing for the $M_{23}C_6$ carbide is 10.8503 Å when determined experimentally from sample DCAU1B2.

The samples can therefore be split into three distinct groups of materials from their XRD results, and these are presented in Table 7.1. Three categories of sample are revealed; those in which $M_{23}C_6$ is the dominant phase, those which contain $M_{23}C_6$ but it is not the dominant phase and those which contain no $M_{23}C_6$.

M. C. dominant	M ₂₃ C ₆ containing but	
samples	another carbide dominates	Contains no M ₂₃ C ₆
DCAU1B2	KA387	EGG
KA1358	KA82	TLA3
KA1781		KA1706
KA86		
MSC5Z		
DCAB		
MSB13/13Z		
KA457		
ATB		
TLB20		
MSC9		

Table 7.1: Classification of samples as a function of carbides observed during X-ray diffraction
analysis.

7.3 Minor Carbides

The smaller carbides which nucleate within the grains have been the subject of numerous studies with the most significant observation being the effect of these smaller carbides on the creep life of the materials.

Within this section a number of steels from the selection supplied by industry have been compared to greater understand the effect of both composition and time in service on these particles, particularly with respect to the minor carbides.

The smaller carbides found within the grains are observed in a number of different morphologies ranging from small rounded particles, separate particles which nucleate on one another, needle-like particles which sometimes nucleate parallel to one another and in some samples, cubic precipitates can be observed. Particles were removed from the samples using a carbon replica technique to allow for transmission electron microscopy to be performed on the samples without interference from the matrix. In addition to imaging, EDX was used to establish the chemical composition of the particles and electron diffraction used to confirm the crystal structure of the particles. High angle annular dark field images were later used within an image analysis technique to calculate the mean particle size and particle size distribution and number of particles.

7.4 Transmission electron microscopy of the minor carbides

Images from the samples were taken and energy dispersive X-ray analysis was performed on a number of carbides. Figure 7.18 and 7.19 are typical carbide morphologies present in all of the samples investigated. The H-type carbides in Figure 7.18 have been observed in previous research ^[38]. These carbides were found to contain a vanadium carbide centre surrounded by molybdenum carbides which have nucleated at the vanadium carbide. The needle-like carbides in Figure 7.19 are molybdenum rich. The scattered orientation can be attributed to the carbon extraction method. These particles are often large enough to view using scanning electron microscopy.

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Eight samples out of 20 post service samples have been investigated using the TEM, and all have shown that they contain a number of small carbides of varying composition and morphology.





Figure 7.18: "H"-shaped carbides



The amount of carbide present in each sample varies with some samples containing a high fraction of carbides while others contain a low fraction. This difference is easy to see in the following images. Sample DCAU1B2 (Figure 7.20) has a high number of particles while sample KA82 (Figure 7.21) has a significantly lower number of carbides. These samples were prepared in a consistent manner using the carbon replica technique and therefore it is felt that these differences are real rather than andartefact of the technique. As well as a difference in the overall number of small carbides in each sample, there is a grain to grain difference with some grains containing many particles and others containing just a few. The images also show a difference in the size of the particles in different samples. Sample KA82 (Figure 7.21) has fewer small carbides and DCAU1B2 (Figure 7.20) appears to have a large proportion of relatively large particles.



Figure 7.20: Low magnification TEM image from a carbon extraction replica sample from DCAU1B2



Figure 7.22: Low magnification TEM image from a carbon extraction replica sample from KA1781



Figure 7.21: Low magnification TEM image from a carbon extraction replica sample from KA82



Figure 7.23: Low magnification TEM image from a carbon extraction replica sample from KA1706



Figure 7.24: Low magnification TEM image from a carbon extraction replica sample from KA387



Figure 7.25: Low magnification TEM image from a carbon extraction replica sample from KA1358

Figures 7.20 to 7.25 illustrate that the carbides are present in a number of different forms. Sample KA1706 (Figure 7.23) contains an extensive number of acicular particles which are mostly uniform in size and orientation, whereas sample DCAU1B2 contains a large number of rounded particles of varying size. Samples KA82 and KA1781 (Figure 7.22) have a reasonably large, rounded, uniformly sized particles. Samples KA387 (Figure 7.24) and KA1358 (Figure 7.25) both contain a range of sizes and particle morphologies, KA387 contains some elongated particles in comparison to the very much rounder carbides in sample KA1358.

All eight samples show a large proportion of fine molybdenum rich carbides. These grow in a number of different morphologies. Most regularly the molybdenum carbides are seen to form as the wing-like ends on "H" shaped carbides. They are also observed as rounded particles and in some cases sharp needle-like carbides.

The central section of the H carbides appear to be vanadium rich, however, in many of the compositions taken using EDX, a large proportion of molybdenum can be seen. This is most probably due to the central particle being sufficiently small that the smallest spot size on the TEM is too large to record EDX data from that carbide alone and some data is collected from the 'wing' ends.



Figure 7.26: High magnification TEM image of 'sharper' H-type carbides found in TLA3.



Figure 7.27:High magnification TEM image of rounded H-type particles found in KA1358

Figures 7.26 and 7.27 present two different types of "H" carbide. Figure 7.26 shows the sharper H found in sample TLA3, with figure 7.27 showing a more rounded morphology in KA1358.

Figure 7.28 appears to show a small grain boundary carbide, which is rich in molybdenum. Unlike the H carbide, the molybdenum carbide has formed in a rounded shape. Figure 7.29 has a number of sharp molybdenum rich needles. Most of the needles are of similar size, and appear to be aligned in a particular direction.



Figure 7.28: High magnification TEM image of a large particle from sample KA1358



Figure 7.29: Plate-like carbide within sample TLA3

7.4.1 Morphology, Chemical Composition and Diffraction Data

Figure 7.30 is a TEM image of a Mo_2C carbide particles, and Table 7.2 details the chemical composition of the particle and Figure 7.31 is the diffraction pattern for the Mo_2C carbide. The Mo_2C carbides appear much darker on the images than the VC carbides. Figure 7.32 is the diffraction pattern related to this particle, identified as VC in Figure 7.30.



Figure 7.30: High magnification TEM image of Mo₂C carbides in sample



Figure 7.31: Diffraction pattern from the Mo₂C particle in Figure 7.30 identified by the solid black circle.

Element	V	Cr	Fe	Mo
Wt. %	18.8	3.1	2.3	77.8

Table 7.2: Composition of Mo₂C particle in Figure 7.30.



Figure 7.32: Diffraction pattern from the VC particle in Figure 7.30 identified by the dashed black circle.

Element	V	Cr	Fe	Мо
Wt. %	64.2	1.56	1.35	27.8

Table 7.3: Chemical composition of the VC particle in Figure 7.32.

7.5 Composition of the Small, Minor Carbides

Initial trials were performed to identify any obvious trend in the composition of the smaller carbides. Three samples were selected for closer examination: KA82, KA387 and TLA3. The composition of vanadium carbides was recorded for each and plotted in ternary graphs with chromium, vanadium and molybdenum forming the axis of the graphs to allow for a direct comparison of the carbide compositions.



Figure 7.33: Composition of vanadium carbide particles in sample KA82.

The compositions of a number of these vanadium rich carbides in sample KA82 can be seen in the ternary diagram, Figure 7.33. It is clear to see that the composition of the vanadium carbide vary from 50 to almost 100 wt.% vanadium and from 3 wt.% molybdenum up to almost 50 wt.% molybdenum. In almost all of the carbides sampled the amount of chromium remains similar at around 7 wt.%. Figure 7.34 shows the compositions of the vanadium rich carbides found in sample KA387 and again the compositions range within the same boundaries as the compositions recorded from sample KA82.



Figure 7.34: Composition of vanadium carbide particles in sample KA387

Figure 7.35 presents the composition of the vanadium carbides in sample TLA3. A small number of them contain a greater quantity of molybdenum, which as described previously, is most likely due to the size of the H particles and the difficulties in completely isolating the vanadium rich carbides form the molybdenum rich carbides during TEM analysis. The amount of molybdenum in the carbides examined in this sample is slightly greater than that of the other samples examined. Most of the vanadium rich carbides are found as the central part of the H carbide.



Figure 7.35: Composition of vanadium carbide particles in sample TLA3.

The initial studies of the vanadium carbide composition reveal that in these three samples there is a relatively large amount of molybdenum in addition to the vanadium within the carbide.

7.6 Summary

The microstructure of ex-service $\frac{1}{2}Cr\frac{1}{2}Mo\frac{1}{4}V$ power plant steels is that of a ferrite structure with two main types of carbide; those within the grains and those which nucleate and grow at the grain boundaries. The carbides at the grain boundaries have been identified as $M_{23}C_6$ in all but 5 samples. In the 5 samples without $M_{23}C_6$, Fe₃C was identified which is a non-equilibrium carbide. In a number of samples manganese

sulphide was identified, present as an impurity which is created during the manufacture of the steel. These sulphides were identified optically in most samples, however, the random, sparse dispersion mean that the likelihood of a particle being within the sample taken for XRD is relatively small, hence the peak was not identified in all samples. The vanadium carbides recognised in most of the samples is the much abundant small strengthening carbide which reside within the grains.

The smaller carbides within the grains were identified as either Mo₂C or VC. TEM images have shown that of the two types of carbide which regularly appear nucleated on one another in H shaped carbides; the vanadium carbide forms the central portion and the molybdenum carbide, the H 'wings'. This type of carbide has been identified in a number of different morphologies from sharp structures to much rounder ones, and in some cases the shapes have been seen to link and make square carbides with 4 molybdenum carbides surrounding the vanadium carbide centre. Chapter 8 will discuss the effect both these major and minor carbides have on the creep life of these steels in more detail.

Chapter 8

Creep Life and Carbides

8.1 Introduction

This chapter investigates possible links between the creep life and the carbides present in the microstructures discussed in Chapter 7. The work presented here allows the power industry to use the microstructure of $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V to identify materials which may be reaching a point at which creep damage has become a pending issue. For many years the use of creep damage evaluation has been the only method of recognizing materials which were potentially at risk of failure. However, by the time creep cavitation is visible the failure mechanism is well advanced. The method presented here can be used long before any creep cavitation is visible and using replicas which can be taken in-situ, to identify possible problematic materials on site.

8.2 ECCC Modeling of Creep Data

The European Creep Collaborative Committee (ECCC) is a group of more than 40 European industries and research institutes who share the same common goal to allow creep rupture data to be available to all so that improvements can be made to testing standards, inspection methods and plant safety ^[49,69]. The part of this ECCC work which is of interest to the current research is the equation which allows creep data from a number of different test conditions, i.e. temperature and stress, to be 'normalised' so that comparisons can be made between the datasets. As there has not been one set of standard testing parameters for these samples of $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steel, it is vital that comparisons between the different testing conditions can be made. Equation 8.1 forms the basis of this normalisation method.

$$P(\sigma) = \ln(tr^*) - a - eT - f/T = b \log \sigma_0 + c \sigma_0 + d \sigma_0^2 \dots \dots \dots \dots \dots \dots \dots \dots [equ. 8.1]$$

where a, b, c, d, e and f are constants, $P(\sigma)$ is the creep rupture parameter, tr* is the predicted rupture time in hours, T is the absolute temperature and σ_0 is the stress in

 N/mm^2 . To enable the equation to be used for this application $P(\sigma)$ must first be calculated:

where b = 8.43513299, c = -0.0018661666 and d = -0.0000291037377. These values have been determined by careful fits to a range of experimental data. The equation can then be rearranged so that ln (tr*) can be calculated.

 $ln(tr^*) = P(\sigma) + a + eT + f/T....[equ 8.3]$

where a = -39.765873, e = 0.00935613085 and f = 49662.4102. It can then be established that:

exp (ln(tr*)) = ECCC calculated time to rupture/hrs......[equ 8.4]

If the observed number of hours to rupture during creep testing is then divided by the ECCC calculated hours to rupture the result is the relative life of each sample. It is then possible to use the log of this relative life value to estimate the amount of life used up.

This method was initially proposed for use on a more highly alloyed virgin material before use in plant. It is important to note, however, that the material under investigation here has endured many hours in service prior to the creep testing which has been normalised here. One school of thought suggests that all of the materials are considered to be virgin material, despite the prior service life and those which have endured the longest service life will of course have the least amount of life remaining. If the log relative life of each sample is plotted against the service life (Figure 8.1) it can be seen that the amount of time in service (service life increasing with distance from the Y-axis) does not appear to be directly related to the predicted amount of life used up during service by the ECCC method. Therefore, the hypothesis that the

sample with the longest service life has the shortest remaining life is not proven. These data can also be plotted against other factors to make comparisons about the features of the microstructure which affect the creep rupture life. A low value for the antilog of log (mean relative life) indicates a material with a small amount of life remaining.



Increasing service life

Figure 8.1: Antilog of log (relative life) as a result of normalising the post service creep data using Equation 8.1, the samples are ordered by length of time in service with the shortest service on the left and the longest to the right.

Plots of the steel carbon, chromium and molybdenum content against the antilog of the log relative life Figures 8.2 - 8.6, all suggest that the amount of life 'used up' in each sample does not correspond simply to one particular element.

In addition to the plots of carbon, chromium and molybdenum against the antilog of log (mean relative life), the grain size and hardness were plotted. Figures 8.5 and 8.6. Again there does not appear to be a relationship between the amount of life 'used up' before creep testing and the antilog of the log (mean relative life).

The results in Figures 8.2 through to 8.6 show that there is no obvious relationship between the ECCC normalised creep value and some of the obvious microstructural and compositional features. If a relationship exists, it is a more complex one than those shown in these figures. Otherwise it is possible that the equation is insufficiently

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accurate for this material, bearing in mind that it was originally established for a more highly alloyed virgin steel.



Carbon wt % Figure 8.2: Antilog of log (mean relative life) plotted against weight percent carbon.



Figure 8.3: Antilog of log (mean relative life) plotted against weight percent chromium.





Figure 8.4: Antilog of log (mean relative life) plotted against weight percent molybdenum.



Figure 8.5: Antilog of log (mean relative life) plotted against hardness.



Figure 8.6: Antilog of log (mean relative life) plotted against grain size.

8.3 The Relationship between Major Carbides and Creep.

The major carbide content of each sample varies quite significantly, Figures 8.7 and 8.8, as described in Section 8.2, show SEM images for samples DCAU1B2 and KA727, which have the most and least amount of carbides respectively. Figure 8.7 is an SEM image of sample DCAU1B2 and in the area identified by the white circle, a large number of grain boundary carbides can be seen. There is very little difference in colour between the large grain boundary particles and the matrix. This is due to the compositions of both phases being similar. These particles can be seen all over this sample (not just inside the white circle), the distribution being reasonably homogeneous with an even distribution across the sample. The same cannot be said for sample KA727, Figure 8.8. This sample appears to have very few carbides within it; the few that are visible in the field in Figure 8.8 have been highlighted by white arrows. The major carbides in this sample are not homogeneously distributed and are difficult to see, even when using high magnification SEM images.

The differences shown in these two samples are the extremes; DCAU1B2 is incredibly rich in these particles while KA727 is extremely sparsely populated by

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them. In between these two extremes, an order of carbide amount can be roughly established just by examining the SEM images. In order to properly quantify these large grain boundary carbides, an image analysis technique was established. Unfortunately the lack of contrast between the carbides and the matrix makes it difficult to differentiate between the two using standard image analysis programmes.

In addition Electron Backscattered Diffraction (EBSD) was used in an effort to automate the matrix/carbide differentiation. Figure 8.9 is the grain orientation map (or inverse pole figure) and Figure 8.9 the grain boundary rotation angle. The purple arrow identifies what could either be a small grain or a large carbide. However, if the EBSD map was to be compared to an SEM images the size and morphology of the feature would in fact suggest that it is a carbide rather than a grain. These grain boundary features can be seen on the grain orientation map but once again differentiation between grains and carbides is the limiting factor in using this technique for quantitative analysis of these large carbides.



Figure 8.7: SEM image of sample DCAU1B2, one of the materials which was most densely populated with the large grain boundary carbides. The area within the white circle contains a high volume of large carbides.



Figure 8.8: SEM image of sample KA727 which is one of the most sparsely populated by the large carbides. The white arrows identify two of the very few grain boundary carbides visible in this image.



Figure 8.9: a) Grain orientation map from sample DCAU1B2 and b) the grain boundary rotation angle map

In order to overcome this problem, a method of quantifying the carbides was developed: Five SEM images from each material were taken at the same magnification from randomly selected areas on each sample. These images were then

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used to trace the carbides onto a 63 grams per square meter tracing paper. These images were scanned into the Uthesca image analysis tool which was used to threshold the images and measure the size of each carbide, as shown in Figure 8.10.

There are limitations to this process, namely, the tracing of the carbides is open to large error due to its inherent human intervention. In addition the use of chemical etching again reduces the repeatability of the work. To alleviate these problems a number of other methods were examined.

Ion beam imaging has proven successful at differentiating the carbides from the matrix in more highly alloyed steels, for example, West ^[70] describes that ion etching reveals different features of a microstructure with increasing etching time, and can allow quantification of both the Laves and $M_{23}C_6$ particles. The author suggests that if this technique is used along with EBSD techniques it is possible to fully characterize the microstructure. Figure 8.11 is an ion beam image of sample KA1706, which, from the SEM images, contains one of the highest amounts of the major, grain boundary carbides on initial inspection. It is, however, almost impossible to identify any of the carbides in this sample. Therefore, ion beam imaging was not pursued as a route quantifying the carbides.



Figure 8.10: The process of identifying, tracing and quantifying the grain boundary carbides. The first image on the left is the SEM image, the second image is the tracing which was scanned into the Uthesca image tool for sizing of the carbides



Figure 8.11: Ion beam image from sample KA1706 showing few, if any, carbide which have been preferentially etched at the grain boundaries due to the very small difference in composition.

Forward scatter detector imaging in the SEM was shown to be significantly more promising than ion beam etching, with both the carbides and the grains being clearly visible with sufficient contrast for differentiation as shown in Figure 8.12. Samples can be investigated in the un-etched condition but require a well prepared and cleaned surface finish prior to imaging. The elimination of the chemical etching process reduced the number of variables but unfortunately the image analysis software was still unable to differentiate the carbides from the grains. Figure 8.12 shows the initial trials of this process on sample DCAU1B2.



Figure 8.12: Initial trials of forward scatter detector imaging in the SEM of sample DCAU1B2 reveal that the method can differentiate the carbides from the grains in the image shown.

If the results from the ECCC 'normalising' equation (Section 8.2) are used to plot the amount of grain boundary covered by carbides, Figure 8.13 is produced. The graph

has a downward trend with reducing amounts of carbide at the grain boundaries yielding a greater amount of remaining potential service life. For example, sample DCAU1B2 has just under 14% of the grain boundary covered in carbides and just a small amount (5.9%) of its life left whereas sample KA727 has very little grain boundary coverage (0.39%) and has 71% of its potential life remaining. Figure 8.13 shows that there is a decreasing amount of life left per sample with increasing carbide coverage of the grain boundaries. This identification of the amount of carbides covering the grain boundary as an indicator of life remaining in low alloy steels is a potentially excellent tool to add to the current techniques available to the power industry in the UK. The method can be used effectively to rank the materials by strength order alongside other techniques currently employed to identify potentially weak materials. This finding reveals a quick and simple method of weak material identification in $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V steels. Chapter 9 describes the processes which industry can inspect these pipes using simple replication from plant.

Effectively this plot is one of susceptibility to creep damage accumulation. The large carbides at the grain boundary act to increase the rate of creep damage (or void formation) at this area therefore increasing the risk of these voids 'linking up' and producing a continuous crack. Figure 8.14 is a schematic diagram illustrating the potential of the technique and illustrates how the grain boundary coverage can be linked to the areas which are most susceptible to creep damage. One might expect that the carbides would 'progress up' the curve as the sample's service life increases and ultimately more carbides form at the grain boundaries. However, the thermodynamic modeling suggests that this is not simply the case because, depending on chemical composition, different carbides are predicted at equilibrium. Samples towards the higher end of the curve are predicted to contain M₂₃C₆ as the equilibrium carbide, while at the other end the predictions suggest that the dominant phase will be the molybdenum rich MoC. Therefore, the curve could be thought of as indicative of how susceptible a certain material will be to creep damage, for example a sample with the most carbides at the grain boundary is the most likely to form voids and ultimately fail while samples which contain fewer carbides are less likely to nucleate voids and therefore the risk of these materials failing is much lower.

Creep Life and Carbides



Figure 8.13: The antilog of log mean relative life against the % grain boundary covered by carbide for each sample for which the data were available. Sample DCAU1B2 has the greatest amount of grain boundary covered by the carbides and is the sample which has the least amount of life remaining. Sample KA727 has the least amount of grain boundary covered by carbides and is the sample which has the most amount of service life remaining. The line is a line of best fit trendline.

Figure 8.15 presents the amount of hours that each sample has endured in service plotted against the amount of life predicted to be remaining using the ECCC calculations. Although there is a slightly upward trend across the graph which indicates that the samples which have been in service for the longest are beginning to use up more of their potential life, the results also indicate that there is not a fixed amount of time that all of the samples can endure and some that have been in service for a relatively short time have used up almost all of their potential life. This would suggest that the carbide nucleation and coarsening in some samples is much quicker than other samples. A number of factors could influence this, in particular, service temperature, stress and composition. As all of these samples have come from service it is probable that not all of them have endured similar service conditions. For example, samples which have been removed from a bend in a pipe will have endured greater stresses than those which have come from a straight section of the steam pipe. In addition some areas, such as the bends, may experience slightly higher temperatures. Of course these service factors are in addition to the significant chemical compositional variations.

Figures 8.16 and 8.17 are the ECCC plots with the carbon and chromium compositions respectively highlighted for particular sample compositions. The samples which contain the greatest amounts of these elements are in red, those which fall in the mid-compositional range are green and those which contain the least are blue. A slight trend in the carbon contents of the samples suggests that samples with higher amounts of carbon will reside towards the left hand side of the curve. The chromium results (Figure 8.17) reveal a slightly different trend, the sample which contain the most chromium appear to reside in the central portion of the curve with the samples containing the lower amounts of chromium distributed from the top to the bottom of the curve.

These results suggest that the amount of grain boundary carbide is not solely related to the carbon or the chromium content and as has been observed during thermodynamic modeling (Chapter 6), the equilibrium, grain boundary carbides are controlled by a complex combination of sample compositions.



Increasing potential material damage (testing using post service creep testing)





Figure 8.15: Hours in service plotted against percentage life used up during service as predicted from the ECCC calculations. The figure shows that samples which have endured the longest service life do not necessarily have the least amount of life left and *vice versa*.

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Creep Life and Carbides



Anthog of log mean relative me

Figure 8.16: The ECCC creep curve with the samples colored by the amount of carbon in the material: Red represent the high carbon samples, green the mid-content samples and blue, the low carbon samples.



Creep Life and Carbides



Antilog of log mean relative life

Figure 8.17: The ECCC creep curve with the data points categorised into high, medium and low chromium containing samples.

8.4 Site Specific Sample Examination

In order to investigate the differences in carbides across the curve presented in Figure 8.13 TEM samples were extracted from three samples at the top, middle and bottom of the ECCC curve. The selected samples were DCAU1B2, TLB20 and EGG. Site specific areas were selected to ensure that grain boundary carbides were extracted from each of the samples to allow images to be obtained along with the composition and structural information.

Figure 8.18a is the TEM image of sample DCAU1B2, with the carbide identified by the red arrow, Table 8.1 is the composition of the carbide and matrix, and Figure 8.19 is the resolved diffraction pattern from the carbide. The carbide in this sample is relatively small despite the sample's large carbide density. This is due to the lack of 3-dimensional information available before extracting the particle using the FIB. Figure 8.20 is the image of the TEM sample removed from sample TLB20. The carbide extends through the section of the sample along the grain boundary. Table 8.2 is the composition of the carbide and matrix from this sample and Figure 8.21 completes the identification of the particle with the resolved diffraction pattern. Finally sample EGG is shown in Figure 8.22, it is worth noting that the grain boundary carbides in this sample were particularly sparse and simply finding one in the sample to remove using the FIB was a difficult process. Table 8.3 is the composition of the carbide and the matrix and Figure 8.23 is the diffraction patterns for the matrix and the carbide.



Figure 8.18 a) the area from which the FIB section was removed in sample DCAU1B2 and b) the extracted carbide, identified by the red arrow.



Figure 8.19: Cementite diffraction pattern.

Table 8.1: Composition of the matrix and the carbide in sample DCAU1B2 in wt. %.

	Si	V	Cr	Mn	Fe	Mo
Matrix	-	-	-	-	100.00	-
Carbide	3.56	-	9.78	9.60	76.04	4.58



Figure 8.20: a) the area from which the carbide was removed in sample TLB20 and b) the thinned section with the carbide identified by the red arrow.



Figure 8.21: M₂₃C₆ diffraction pattern, where the M represents a combination of chromium and molybdenum.

Table 8.2: Composition of the matrix and the carbide in sample TLB20 in wt. %.

	Si	V	Cr	Mn	Fe	Mo
Matrix	-		-	-	100.00	-
Carbide	-	-	11.94	6.68	68.75	12.63



Figure 8.22: a) the area from which the carbide was removed in sample EGG and b) the extracted sample and carbide identified by the red arrow.



Figure 8.23: Molybdenum carbide diffraction pattern

	Si	V	Cr	Mn	Fe	Mo
Matrix	-	-	-	-	100.00	-
Carbide	3.56	-	0.98	1.24	37.00	57.21

Table 8.3: Composition	of the matrix and	the carbide in	sample EGG in wt. %
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The TEM sample results show that not all of the samples contain the grain boundary $M_{23}C_6$ carbide, the carbides across the creep curve seem to vary somewhat with sample DCAU1B2 (the sample with the least amount of predicted life remaining) containing $M_{23}C_6$ and the lowest level of molybdenum with 4.58 wt. %. In
comparison to samples TLB20 and EGG which contain 12.63 and 57.21 wt. % molybdenum respectively. In sample EGG the carbide is not identified as $M_{23}C_6$ but as the molybdenum rich MoC.

This site specific extraction of carbides is a relatively long, expensive process. Although the three selected samples represent the top, middle and bottom of the ECCC creep curve (Figure 8.13), ideally a number of carbides from each of these three samples would be removed for comparison and allow averaging of the compositional values. However, the results, supported by those from the XRD work, suggest that there is a difference in the major carbides in samples across the ECCC creep curve. The samples towards the top of the curve represent those which have $M_{23}C_6$ as the dominant phase while those towards the bottom contain fewer of the large grain boundary carbides and are dominated by molybdenum carbide.

8.5 Summary of the Relationship Between Creep Life and Major Carbides.

The ECCC method of normalising the creep data allows all of the samples under investigation to be compared to a factor common to all. Effectively the method allows the data from a number of different creep rupture tests under different conditions to be turned into a single value for a given material.

8.6 The Relationship between the Minor Carbides and Creep.

It has been shown in earlier sections that these low alloy steels contain both large carbides visible in the SEM, typically located at the grain boundaries, and also fine carbides visible only in the TEM and typically located within the grains.

A number of authors have suggested that the fine carbides play a significant role in hindering the mobility of dislocations and therefore potentially have an impact on the creep behavior of the steels. Therefore, this section is concerned with the investigation of the chemical composition, type, shape and size distribution of the fine scale carbides to see if any relationships can be established between these factors and the creep lives of the different material.

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Four samples were selected from different regions of the curve in Figure 8.13 for detailed TEM analysis of particle composition, size and distribution. DCAU1B2, KA1358, KA82 and EGG represent the various extremes of the curve with DCAU1B2 having the least amount of life remaining and the largest amount of grain boundary carbides, while EGG has a large amount of life predicted to be remaining and very few carbides at the grain boundaries. TEM images of these samples have been taken using a Tecnai transmission electron microscope and are presented in Figures 8.24 to 8.27



Figure 8.24: a) DCAU1B2 taken in high angle scanning TEM. b) DCAU1B2



Figure 8.25: a) KA1358 taken in high angle scanning b) KA1358,



Figure 8.26: a) KA82 taken in high angle scanning b) KA82



Figure 8.27: a) EGG taken in high angle scanning b)EGG.

All of the images in Figures 8.22 through to 8.25 are taken at the same magnification to allow for easier comparisons. Sample DCAU11B2, Figure 8.24, is not only very densely populated with the grain boundary carbides (discussed earlier in this chapter) but it is also very rich in the smaller minor carbides as shown in the images in Figure 8.24. This particular sample also contained a number of larger carbides (Figure 8.24 a). The different images illustrate that not only is there a much larger number of very small carbides within sample DCAU1B2, but also that the carbides appear to be much rounder in morphology than in other samples. EGG (Figure 8.27), for example, contains some acicular carbides which are relatively large in size. KA1358 (Figure

8.25) and KA82 (Figure 8.26) which are from a similar area of the grain boundary carbide against antilog of log (creep life) graph, have roughly similar carbide morphologies and densities, with KA82 containing a few more larger carbides than sample KA1358. Sample EGG in Figure 8.27 clearly has the lowest number of carbides present in all of the samples investigated.

Figures 8.28 to 8.32 present the compositions of one hundred particles selected at random in each of the four samples. The compositions were measured in a transmission electron microscope using EDX from carbon extraction replicas.



Figure 8.28: The composition of 100 particles on a carbon replica taken from sample DCAU1B2, measurements in wt. %.



Figure 8.29: The composition of 100 particles on a carbon replica taken from KA1358, measurements in wt. %.



Figure 8.30: The composition of 100 particles on a carbon replica taken from sample KA82, measurements in wt. %.



Figure 8.31: The composition of 100 particles on a carbon replica taken from sample EGG, measurements in wt. %.

The triangular figures in Figures 8.27 to 8.31 show that the four samples all exhibit broadly similar compositions of fine carbides. However, there are certainly differences in the composition of individual particles; but in general, the carbides are rich in molybdenum with increasing amounts of vanadium. Very few of the carbides were rich in chromium, and those which were found are probably small $M_{23}C_6$ particles. These compositions were collected only from the small minor carbides from within the grains; however, it is possible that some larger $M_{23}C_6$ particles have been partially extracted during the replication process producing smaller than usual $M_{23}C_6$ carbides. Samples DCAU1B2 and EGG appear to have more carbides residing towards the left hand side of the triangle in the molybdenum rich, vanadium depleted area.

Figures 8.32 - 8.35 present the distribution of particles sizes measured as the mean Feret diameter from the STEM images for the minor carbides only shown in Figures 8.24 to 8.27. Six images were taken at random from each of the four samples, these were then processed using the Uthesca image analysis software.

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Figure 8.32: Particle Feret size dispersion in sample DCAU1B2, measurements in microns.



Figure 8.33: Particle Feret size dispersion in sample KA1358, measurements in microns.

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Figure 8.34: Particle Feret size distribution in sample KA82, measurements in microns.



Figure 8.35: Particle Feret size distribution in sample EGG, measurements in microns.

The dispersion of particle sizes (Figures 8.32 through to 8.35) show that by far sample DCAU1B2 (Figure 8.32) contains the most particles with the largest number of particles falling within the 0.03 to 0.04 μ m size distribution. 0.04 μ m is the smallest size particle observed for a number of reasons, firstly the smallest particle which the image analysis software can resolve and secondly, the size of the particles which can be extracted via the extraction replica techniques. Sample KA82 contains the second highest number of particles with the largest number of particles falling within the 0.05 to 0.06 μ m size window. It would appear from these results that there is not a simple trend between the minor carbide content within the 4 samples examined in detail using TEM. Therefore, the particle size distributions do not suggest that there is a relationship between the ECCC creep curve and the particle size distribution. In addition to the particle size distribution, a number of other parameters were extracted from these data; these include mean particle size, mean area covered by carbides in each sample, the number of carbides in each sample (in 6 fields of view) and the mean carbide size multiplied by the number of carbides.



Figure 8.36: Mean particle sizes from the carbides measured in Figures 8.32 to 8.35.



Figure 8.37: The total number of particles in 6 fields of view for each sample.



Sample

Figure 8.38: Mean particle size multiplied by the number of particles measured, area covered by the carbides.Figures 8.36 to 8.38 show the samples categorized by the mean particle size, the number of particles in 6 images, the mean particle size multiplied by the number of

particles and the mean particle area multiplied by the number of carbides which effectively gives the area covered by the carbides, Figure 8.38.

Figure 8.36 shows the mean particle size with the samples listed across the x-axis from left to right in ascending remaining life order. The mean sizes suggest that the sample containing the largest particles (0.08 μ m) is sample KA82 which falls towards the lower half of the ECCC creep curve, Figure 8.13. The sample with the next largest mean particle size (0.07 μ m) is sample KA1358 which lies slightly further "up" the creep curve, closer to the materials which have very little life remaining. Sample DCAU1B2 which is predicted to have the shortest amount of life remaining has a relatively small mean particle size of 0.06 μ m. This sample is described earlier in this chapter as the one which contains the most major carbides. Sample EGG falls towards the lower end of the creep curve and, it is anticipated to have a large amount of life remaining, and contains very few major carbides at the grain boundaries.

Figure 8.37 is the number of particles measured from each sample; the results were taken from six fields of view. Sample DCAU1B2 contains the most amount of minor carbides with over 6000 being measured and recorded. This is well above the next most densely populated sample, KA82, from which 4500 particles were recorded. Sample KA1358 has slightly fewer particles, just under 4000 were measured and sample EGG contains the fewest particles; with just over 3000 recorded from the 6 fields of view.

8.7 Summary

The amount of grain boundary covered by the carbides can be plotted against the ECCC creep value (a normalising process which reduces the various creep parameters to a single value) and a curve can be fitted to the data which shows a systematic reduction in the amount of grain boundary covered by carbide with increasing amount of life remaining. This therefore appears to be a promising tool for the ranking of $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V power plant steels. Effectively this curve is a plot of how susceptible to creep failure a particular cast is in comparison to other casts. This relationship represents the potential a material has to accumulate creep damage, based on the

amount of grain boundary covered by the carbides. Large carbides residing on these grain boundaries act to reduce the boundary cohesion and ultimately reduce the creep strength of a material.

The XRD results revealed that there were three categories for the different $\frac{1}{2}$ Cr $\frac{1}{2}$ Mo $\frac{1}{4}$ V compositions; those which contain M₂₃C₆, those which contain M₂₃C₆ but in which it is not the major carbide and those which do not contain M₂₃C₆. Most of the samples with little or no M₂₃C₆ appear to fall towards the bottom right hand side of the ECCC curve, Figure 8.13. The metallographic investigations of materials from this area of the graph show that there are very few, or none, large grain boundary covered by the carbides is plotted against the ECCC creep data the relationship indicates that the fewer large carbides within the material, the greater the remaining creep life.

If the XRD results are compared to the ECCC creep life curve the samples towards the left hand side of the graph with little life remaining contain $M_{23}C_6$, moving across the ECCC graph the XRD results change, the samples which fall in the middle of the graph do contain $M_{23}C_6$ carbides but in smaller quantities, and the equilibrium carbide is no longer the dominant peak/phase. Towards the lower end of the graph, the end with much more remaining, life the XRD results reveal that the samples no longer contain the $M_{23}C_6$ and instead the samples contain a number of different carbides.

The large grain boundary carbides have also been extracted directly from the matrix using a site specific sample preparation technique in a dual beam. Identification of these carbides using EDX for chemical composition and electron diffraction for the crystal structure was consistent with the XRD results in that the $M_{23}C_6$ dominated in samples DCAU1B2 and TLB20 and MoC in sample EGG.

A significant study of the minor carbides present in 4 materials using TEM has not been able to reveal a clear trend between the number, size, size distribution and type of carbides and the creep life remaining of the samples. The minor carbides are generally found to be V-rich, and also contain significant amounts of Mo. In some samples, the presence of Fe_3C was observed and in others, a number of manganese sulphides were identified in addition to the large Cr-rich or Mo-rich particles which dominated along the grain boundaries and the fine Mo/V rich particles which dominated within the grains.

Conclusions and Further Work

This work has shown that there is not a simple relationship between composition and remaining life in ¹/₂Cr ¹/₂Mo ¹/₄V power plant steels. Conventionally, hardness has been used to identify materials which soften significantly and are therefore likely to be reaching the end of their lives. To some extent this is a method which is still employed in the lifeing of ¹/₂Cr ¹/₂Mo ¹/₂V power plant steels. However, this work has shown that there are significant variations in microstructural evolution depending on the chemical composition and starting microstructure. For hardness to be used effectively the material needs to be tested at regular intervals throughout the service life to allow the softening to be monitored. Indeed, in this research hardness testing of all the samples revealed that the samples were of varied hardness ranging from 112 HV to 156 HV. Plotting this hardness against the elemental amounts, revealed that no one element clearly controlled the hardness of the material.

Optical and SEM imaging of the materials revealed that not all of the samples had the same size grains and in addition not all of the samples contained the same number of large grain boundary carbides. A number of samples contained large manganese sulphides which were visible using optical microscopy. The industrial partners were comfortable that this level of inclusion was typical of those seen regularly. Most of the samples involved in the study have a fully ferritic microstructure with almost all of the original pearlitic structure decomposed to produce a combination of large grain boundary carbides which rest within the grains.

Although the initial microstructure of ¹/₂Cr¹/₂Mo¹/₄V steels is typically ferrite/pearlite, previous studies of these materials had suggested that the initial, pre-service microstructure could also be bainitic. Cooling rate experiments during this work have

suggested that to obtain a bainitic microstructure the cooling rate must be extremely high, and are dependant on the carbon concentration. It is very unlikely that cooling rates of this magnitude are seen in the 60 mm through wall sections being studied in this work. However, it is possible that bainitic structures can be realised in areas of materials which have been affected by welding where the heat from the process can be quickly removed from the area due to the large neighbouring area of metal which acts as a heat sink.

Thermodynamic modelling of the materials has revealed that at thermodynamic equilibrium not all of the samples are predicted to contain the same carbides. Most contain the major $M_{23}C_6$, however, some are predicted to contain none of this carbide and instead have an increased amount of other carbides. Samples which contained greater amounts of carbon were predicted to contain more $M_{23}C_6$ than those with less carbon. Thermodynamic modelling experiments to investigate the effects of changing the amount of one element in a steel of mean British Standard composition revealed that increasing the amount of carbon increased the $M_{23}C_6$ content at the expense of the smaller vanadium carbo-nitrides and the molybdenum carbides. Increasing the amount of chromium in the steel caused a slight increase in the $M_{23}C_6$ at the expense of the M_2C carbides. Molybdenum content had a profound affect on the amount of molybdenum carbide present where steels with the minimum British Standard molybdenum content had very little effect on the carbide population.

Creep data was provided by the industrial partners, however, the tests, had been performed under varying test conditions, which led to data which were difficult to compare. The ECCC equation, which was designed for use on 12Cr steels, was utilised to produce a normalised value for each sample which could then be compared to the results from other samples. Simple factors (hardness, carbon and chromium composition) were plotted against the values obtained from the ECCC equation, none of these produced a convincing result which distinguished the samples which were likely to have a short remaining life from those which had a long remaining life.

Investigations of the large grain boundary carbides revealed that not all of the samples contained the same carbides. XRD results revealed that a number of samples did not contain the thermodynamically stable $M_{23}C_6$ carbide and were instead rich in a number of other carbides, including MoC, Fe₃C and VC. These XRD results were consistent with the thermodynamic modelling predictions. Measuring these carbides with respect to the grain boundary length revealed a trend when plotted against the normalised creep values obtained from the ECCC equation. The trend indicated, that in samples where more of the grain boundary was covered by carbides, the material's susceptibility to creep damage was much greater than that of a sample with much less of the grain boundary populated with the large carbides.

A large quantity of transmission electron microscopy has been performed on the smaller carbides which nucleate within the grains. These carbides were identified as typically either a vanadium carbo-nitride or a molybdenum-rich carbide, however, there appears to be very little relations between the amount of life used up during service and the type, size and distribution of small carbides in these samples.

The most significant conclusion from this work is the relationship between the ECCC creep factor and the amount of grain boundary covered by the carbides. This result is the most significant for industry given its ease of use via the onsite replication methods which are already in regular use. The relationship shows a clear trend between an increased amount of grain boundary carbides and susceptibility to accumulate creep damage.

The amount of grain boundary covered by carbides gives a clear trend when plotted against the ECCC normalised creep value for the material. However, the removal of actual material from plant only occurs when the component has reached, or is thought to have reached, it's end of life. Therefore it is important to devise a procedure which can be used to identify potentially weak materials without the need to remove samples of material as a monitoring tool to identify potentially vulnerable components. Currently inspection via replication is used to identify pipes which are revealing signs of creep cavitation. It was therefore important to investigate whether the grain boundary carbide coverage identified in this work as a potentially useful indicator of life could be determined from normal plant procedures. Two approaches were therefore used initially, a replica was made from a polished and etched section of material which has already been qualified using a commercial replication kit commonly used on plant. The optical images from the steel sample were then compared to those from the replica to investigate any differences in measurements of the grain boundary coverage. Additionally, replicas taken from plant during a previous outage were inspected to ensure they revealed the grain boundary carbides. If Figures 9.1 and 9.2 are compared it is possible to see that there is very little difference between the image obtained from a metallographically prepared sample and the image obtained from a replica and therefore this is indeed a very promising tool for use in industry.

The process of plant replication involves the preparation of the component surface using polishing techniques similar to that used in a metallurgy laboratory, however, the tools used are easily transported. After grinding and polishing the surface to an acceptable level it is etched. The replication kits consist of an acetate sheet with a foil backing (called a replica foil) and a transcopy liquid which is dripped onto the replica foil so that the foil's surface can mould to the metal surface. Once the foil is wetted with the transcopy liquid the foil is placed onto the prepared surface and pressure is applied. The foil dries, is gently removed and a copy of the microstructure is revealed on the foil's surface. Unlike a carbon replica this process does not remove the carbides from the surface of the steel; the image obtained is simply a result of the surface topography created during the etch.



Figure 9.1: Optical micrograph of an etched sample surface.



Figure 9.2: An optical micrograph taken from a plant replica

These replicas can be used in a similar way to the samples used in Chapter 8. The grain size can be measured using a linear intersection method, and the carbides can be traced onto tracing paper ready for image analysis. Ideally for statistical relevance it is important that a number of replicas are taken from a steel. The work earlier in Chapter 8 required 5 images taken at random to ensure statistical significance. For plant investigations, the use of at least 5 images is advised. Once the amount of grain boundary covered by the carbide has been established for a particular pipe, the ECCC curve can be used to rank

the material against those which have undergone post service creep testing. Figure 9.3 illustrates how a material with a known grain boundary coverage can be ranked against materials which have undergone a series of creep tests, therefore allowing an estimation of potential remaining life to be made.

In terms of further work to be carried out, additional validation is required in industry. It has been clearly shown that the coverage of the grain boundaries by large carbides can be linked to remaining creep life. It has also been shown that thermodynamic modelling can give a good indication of whether $M_{23}C_6$ is likely to dominate depending on the chemical composition of the steel.

It has also been shown that the grain boundary carbide coverage can be determined using replication methods routinely used on plant.

The application of the process on materials which remain in service would provide the industry with relatively simple method of identifying casts of material which are likely to be those affected most significantly by creep damage. The outcome of this work is therefore a useable tool for industry to predict which components need replacing based on a sound understanding of the microstructural evolution in ½Cr½Mo¼V steels.

Conclusions and Further work





Figure 9.3: The ECCC curve with red arrows representing the way it can be used to rank a material with no creep testing history against those which have been tested using the amount of carbide covering the grain boundary methodology proposed in this work.

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Appendix A Carbide and Grain Size Data

	Ave. Number of carbides	Ave. spherical diameter of carbide (microns)	Ave standard deviation of carbide diameter	Ferrite Grain diameter (microns)	Ferrite grain radius (microns)	area of grain if a hexagon (microns ^2)	Number of grains in an image	total boundary length	Grain boundary covered by carbides (%)	95% confidence index	Antilog of mean log relative life
TLA3	84.00	3.22	1.37	23.97	11.99	373.19	238.77	7869.46	3.44	1.37	0.60
DCAU1B2	267.00	2.68	0.99	35.71	17.86	828.27	107.58	5282.30	13.57	0.89	0.06
KA1706	194.80	2.67	2.60	23.84	11.92	369.15	241.38	7912.37	6.57	2.32	_
KA1358	137.67	3.53	1.39	28.97	14.49	545.12	163.46	6511.25	7.46	1.13	0.25
KA1781	222.00	3.70	1.51	31.00	15.50	624.19	142.75	6084.87	13.51	1.35	0.00
MSC9	196.00	3.98	1.44	15.92	7.96	164.71	540.98	11845.35	6.59	1.44	0.26
ATB	75.20	3.42	1.34	24.65	12.33	394.66	225.78	7652.37	3.36	1.20	0.55
EGG	60.80	1.47	0.69	22.60	11.30	331.75	268.59	8346.50	1.07	0.56	0.36
MSC5	148.00	3.18	1.32	18.16	9.08	214.08	416.21	10390.03	4.52	1.18	0.22
TLB20	64.60	3.50	1.33	22.04	11.02	315.51	282.41	8558.57	2.64	1.19	0.38
DCAB	202.20	2.75	1.04	19.86	9.93	256.08	347.96	9499.99	5.86	0.93	0.22
MSB13/13Z	239.40	3.06	1.44	23.94	11.97	372.28	239.35	7879.09	9.29	1.29	0.15
KA82	139.17	2.74	1.13	18.91	9.45	232.21	383.72	9976.25	3.82	0.92	0.40
KA387	38.00	1.64	0.72	23.12	11.56	347.31	256.55	8157.31	0.76	0.64	0.44
KA457	371.00	1.78	0.59	21.21	10.60	292.16	304.99	8894.03	7.42	0.52	0.37
KA727	12.80	2.52	1.13	22.86	11.43	339.28	262.63	8253.38	0.39	1.01	0.71