CHARACTERISATION OF CREEP AND CREEP CRACK GROWTH PROPERTIES IN A NOVEL HEAT RESISTANT STEEL

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Synopsis

BG12Cr is a novel martensitic heat resistant steel under development by China Baowu Steel Group Corp., Ltd. (Baowu Steel). Comparing to the conventional high chromium heat resistant steel Grade 92, it is aimed to have an improved oxidation resistance and high temperature capacity. Grade 92 is generally used in power plants for structural applications under a temperature of 625°C. BG12Cr is developed for applications up to a temperature of 650°C. With the increase of chromium content, the oxidation resistance is expected to improve. Hence the creep performance is a major concern. However, creep testing such as stress rupture life requires long testing time, often years. It is useful therefore to generate an accelerated testing methodology to understand the creep performance of the material under development. The current study aims to build up a comprehensive understanding about BG12Cr martensitic steel through conducting both microstructural characterisation and creep crack growth testing. The microstructure evaluation of BG12Cr after 10,000 h's stress rupture testing at 650°C has also been investigated. The creep crack growth resistance curves, da/dt versus C*, of BG12Cr have also been characterised at 650°C with a convenient but uncommon geometry, i.e., circumferentially notched tension (ring-notched) test-piece geometry, to compare to the results from compact tension geometry that have been established in a previous study. Additionally, similar microstructural characterisation and mechanic tests have been conducted on Grade 92 martensitic steel as a comparison.

The microstructure of BG12Cr martensitic steel has been characterised in both as-received condition and after 10,000 hours high temperature exposure, using optical microscopy, secondary electron microscopy and transmission electron microscopy techniques. The precipitates strengthening and dislocation hardening mechanisms in as-received BG12Cr have

been studied. $M_{23}C_6$ carbide is the primary strengthening precipitates decorating the boundaries in the as-received BG12Cr steel. Meanwhile, the precipitates coarsening, new phase precipitation (Z-phase) and martensite recovery after long term thermal exposure are confirmed.

Creep crack growth tests were conducted with different stress levels at 650° using ring-notched test-pieces in both high chromium martensitic steels (BG12Cr and P92). It is clearly observed that under the same testing conditions, BG12Cr shows a significantly longer test period compared with P92. The obtained results were compared to the results from CCG tests using compact tension specimens. The linear elastic fracture mechanics parameter, K-the stress intensity factor, and an elastic-plastic fracture mechanics parameter, C*-integral, were applied to correlate the creep crack growth resistance. All the creep crack growth data obtained from different loading conditions, different alloys and different test-piece geometries have been observed to stay in a narrow scatter band indicating a unique linear relationship between C* and creep crack growth rate under log-log scales. This observation indicates that C* is the unique parameter to address creep crack growth resistance.

In addition, the creep crack growth rates were also plotted against ligament stresses for the results obtained from both ring-notch and compact tension test-pieces. Unlike the da/dN vs. C* curves, the influences of alloying, temperature and applied stress become apparent, and there is a general agreement between the two test piece geometries. Another very useful trend can also be seen. At a temperature of 650°C and under a log (da/dt) – linear (stress) axes, the growth curves appear as straight lines with different slopes for the two investigated alloys. Extrapolation of these lines leads to a crossing corresponding to a stress of around 100 MPa, which is consistent to the crossing point obtained from stress rupture results that can only be measured after ~10,000 h's testing. This is encouraging as it might provide an acceleration testing method to evaluate long-term creep properties using relatively short-term creep crack growth testing.

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CHAPTER 1 Introduction

1.1 Summary and background

A novel high Chromium (12%Cr) heat resistant steel, which is proposed and has been developed by Baowu Steel Company, is expected to have a better performance under severe steam service conditions and competitive pricing compared with traditional high Chromium steels (Grade 92). To safely apply this novel martensite heat resistant steel into power plants (mainly for the steaming pipes), an investigation of the creep crack growth mechanism is important for the steel design and construction.

The objective of this study is mainly to investigate the mechanisms and behaviour of creep crack growth in this novel Chromium steel at elevated temperature and microstructure evolution after long period thermal exposure. To gain a better assessment of creep resistance and heat resistance of this novel steel, the creep crack growth behaviour of conventional Grade 92 heat resistant steel (9%Cr) is introduced for comparison. Stress-ruptured samples received from Baowu Steel are analysed to build up a deeper understanding about the failure mechanism of this novel steel compared to Grade 92. The characterisation of crack growth behaviour in creep crack growth tests has been achieved through the application of elastic plastic fracture mechanics. All the testpieces were machined into ring-notched geometry to compare to the results obtained previously on CT testpieces, and to explore the impact of specimen geometry in creep resistance curves with C* as a driving force.

The scope of the study can be concluded as:

- To build up a fundamental understanding about the microstructure of as-received steel compared to the microstructure of Grade 92 steel and understand the strengthening mechanisms (precipitation hardening and dislocation hardening).

- To investigate the microstructure evolution after long period thermal exposure (> 10,000 hours) and understand the loss of strengthening mechanisms in BG12Cr (loss of precipitation hardening and loss of dislocation hardening).
- To explore the creep crack growth behaviour of these two steels at 650°C and understand the mechanism under different loading conditions with ring-notched geometry.
- To acquire the data on the creep crack growth and C* curves with the ring-notched geometry. Then the data will be compared to the C* curves from compact tension (CT) specimens under different testing conditions (temperatures and loads) to verify the path-impedances of C*. Then give an assessment and suggestions for this geometry approach in creep crack growth tests.

1.2 Thesis Outline

After the introduction, Chapter 2 provides a brief introduction about the background of heat resistant steels and their applications in the literature review. Then the development of high chromium steels is introduced and specifically the design of Grade 92 heat resistant martensite steel. After building up a basic understanding of Grade 92, fracture mechanics including both linear-elastic fracture mechanics and elastic-plastic fracture mechanics) are introduced followed by an introduction of creep fundamental knowledge. In the last part of the literature review, some previous work about the prediction of remaining life with C* on high temperature materials is included.

Chapter 3 contains detailed experimental procedures about the creep crack growth testing of ring-notched test pieces including sample preparation, machine operation and direct current potential change technique. Then the analysis technique of the CCGT results is introduced in the following section. In the last sections of Chapter 3, the preparation of as-received (AR) and post-test (PT) TEM samples is also detailed.

Chapter 4 gives the results of: (1) as-received material microstructure characterisation; (2) PT material microstructure characterisation; (3) creep crack growth results and curves (CT specimens and ring-notched specimens); (4) fractography observation and cross-sectional area observation of high temperature stress-ruptured testpieces and creep crack growth tested specimens.

Chapter 5 discusses the microstructure evolution of PT specimens and comparison between these two steels PT microstructure was made to understand the instability of the martensite matrix. Then the explanation about the loss of strengthening mechanism of the novel steel is detailed. In the second part of Chapter 5, the creep crack growth behaviour differences of these two steels are discussed followed by the advantages and disadvantages of ring-notch geometry approach.

Finally, Chapter 6 presents a brief summarization of the discussion followed by with main conclusions and future work.

CHAPTER 2 Literature Review

2.1 Introduction

Electricity, an indispensable form of power globally, is chiefly generated by renewable power stations, ranging from fossil fuel-based to nuclear stations. While the evolution and safety of nuclear power stations have witnessed significant advancements, fossil fuel power stations remain paramount in delivering consistent power for industrial and everyday applications. At the essential component of a coal-fired power station is the boiler, converting the heat from burning fuel into high-pressure, high-temperature steam, which subsequently drives turbines to generate electricity.

Heat resistant steels, renowned for their superior resistance under elevated conditions (typically above a temperature of 500 °C), are extensively used within boiler components, especially in water wall tubes. Grasping the significance of these components necessitates an understanding of boiler mechanisms. Water walls, essentially weld-tubed structures, circulate water, which is then vaporized into steam by the intense heat from coal combustion. Subsequently, this steam undergoes superheating in a superheater. Once superheated, it is channelled into the main steaming pipes, directed towards high-pressure turbines. The low-pressure steam exhaust from these turbines is reprocessed in reheaters before driving lower pressure turbines for electricity production [1]. The picture of a typical header inside power station is presented in Figure 2.1.

The structural integrity of boilers relies heavily on its components, including tubes and thick-walled pipes, all subject to severe service environments. Primarily, these metallic components are crafted to function durably under the rigors of high temperature and pressure. Thick wall pipes, also known as headers, are integral for steam collection and distribution. The core of the power plant incorporates three main types of steam conduit, namely furnace water wall pipes, superheater pipes, and turbine tubes, all pivotal for efficient steam conversion in synergy with

turbines [1]. A typical Ultra Super Critical (USC) steam turbine, a hallmark in modern power plants, is depicted in Figure 2.2 [2].

This thesis delves into two prominent heat-resistant materials, P92 and BG12Cr, employed in fabricating thick wall steam pipes. The motivation for the emergence of the innovative 12Cr material traces back to China's energy landscape. In 2008, China emerged as the world's leading consumer of fossil energy, and coal comprising an astounding 66% of its primary energy consumption by 2015 [3], there arose a compelling need. This need underscored the development of alternative materials to supplant the costlier conventional heat-resistant steels due to higher content of expensive alloying elements, aligning with directives from the Chinese government. These novel steels should not only equal but potentially surpass the resistance of their predecessors, ensuring longevity under extreme temperatures and stresses. Moreover, these materials should offer a competitive edge in terms of cost, especially when juxtaposed against steels like P92.

2.2 Introduction of Grade 91 and its Advanced Successor: Grade 92

To appreciate the evolution of Grade 92, one must first delve into the history and characteristics of its predecessor, Grade 91. Grade 91, a heat-resistant martensitic steel, was a particular offshoot of the 9Cr-1Mo-0.2V-0.05Nb steel formulation and was employed predominantly in seamless pipe components, hence its moniker, P91 [4]. Initially developed by the Oak Ridge National Laboratory in conjunction with Combustion Engineering, the prime intent behind this alloy was its application in steam generators for reactors, specifically those with steam temperature thresholds below 550°C [5]. Currently, with its superior creep strength and thermophysical attributes over the 300 series stainless steels, P91 finds extensive use in fossil fuel power plants (with steaming temperatures below 600°C) and petrochemical industries, predominantly as pressure vessels and steaming tubes [6]. Yet, despite its myriad advantages,

the diminished oxidation resistance of the alloy and susceptibility to type IV cracking (failure occurs in the heat-affected zone of welded joints), especially when utilized as main steam pipes, headers, and tubes in coal-fired power stations, became significant challenges [7].

In response, P92 was conceived and formulated, exhibiting heightened creep strength and extended operational lifespan. It was particularly tailored for components exposed to steam temperatures exceeding 600°C. The advent of P92 coincided with an increasing trend in steam parameters (both pressure and temperature). This uptrend stemmed from an overarching objective to enhance the thermal efficiency of power units, especially in light of tightening restrictions on pollutant emissions, notably CO_2. As a consequence, this ushered in the era of ultra-supercritical (or simply, supercritical) steam parameters. Overcoming these technical constraints demanded two primary approaches:

1. Material innovation and evolution.

2. Introduction of novel steel grades characterized by superior creep strength and oxidation resistance in comparison to contemporary materials.

The adoption by the power industry of these new steel formulations revolved primarily around materials with proven longevity. Consequently, the introduction of Grade 92 was a logical progression, taking cues from the commendable performance of Grade 91 [8,9].

2.3 Chemical Composition and Influence of Metallic Alloy Additions in Grade 92

2.3.1 Chemical composition

The standardized chemical composition of Grade 92 is detailed in Table 2.1. Noteworthy is the stringent cap on phosphorus content, set at a maximum of 0.02% by mass. Similarly, the nickel (Ni) content is confined to remain under 0.04% by mass. For steels with 9Cr, such as P91, a

benchmark for evaluating their composition is the chromium-nickel balance (CNB) formulation, which is elucidated as follows [7]:

$$CNB = Cr + 6Si + 4Mo + 1.5W + 11V + 5Nb + 9Ti + 12Al$$

$$-40C - 30N - 4Ni - 2Mn - 1Cu$$

(equation 2.1)

Where the number before each element is the weight mass percent.

As for 12Cr steels, Cr equivalent value should be considered to restrict the formation of delta ferrite and the calculation of this value is given by:

$$Cr - equivalent\ value = Cr + 6Si + 4Mo + 1.5W + 11V +$$

$$5Nb - 40C - 30N - 4Ni - 2Mn - 2Co(\%)$$

(equation 2.2)

It should be noted here that the value should be controlled relying on the practical applications. It can be decreased by the addition of cobalt then the formation of delta-ferrite can be prevented [7].

2.3.2 Alloy Design of Grade 92

Grade 92, which has the same high Cr content as Grade 91, has a better creep resistance, steam oxidation resistance, and hardenability compared to other creep resistant steels (for example, 300 series steels). The addition of Cr improves oxidation resistance by the formation of a Cr-rich oxide film and decreases the transformation temperature even after tempering, which is because of the introduction of a high density of dislocations into the microstructure. The excess of dislocation plays as a barrier to limit the creep deformation under the primary creep stage [10].

Carbon(C)

Carbon is very necessary and common in steels. It is beneficial for the formation of martensite through the cooling and normalizing transformation process. The formation of a body-centred (BCC) structure in iron depends on the carbon content being low enough to avoid dissolution in the iron matrix. Thus, the addition of carbon will increase material hardenability, which is similar to the effect of addition of chromium. Moreover, the precipitation of carbides occurs during tempering. The majority of carbon precipitates in 9-12%Cr steels are $M_{23}C_6$-type carbides (M is Cr) because of the high chemical affinity between chromium and carbon. There is no significant difference of this type of precipitation behaviour observed compared to the other high Cr content creep resistant steels (for example, Gr:91 steel).

Nitrogen(N)

In Grade 92 steel, Nitrogen was added in an incorporating role compared with its more important part in low alloy steels. Notably, the solubility of nitrogen is significantly influenced by the content of chromium, and it reaches most soluble level in steels with 9%Cr content. The precipitation of nitrides happens not only during tempering but also during creep deformation. Until now, the clear precipitation behaviour of carbonitrides was not classified but it was treated as being beneficial for the increase of creep rupture strength. The primary precipitate of nitrogen is VN, which strengthens the material through increasing creep rupture strength in co-operation with NbC [11].

Molybdenum (Mo) and tungsten(W)

The difference in atomic radius of Mo against the base metal atom (iron) results in solute dragging, which resists dislocation movement inside the martensite matrix. 1% Mo content added to creep-resistant steel is believed to increase the creep strength due to solid solution strengthening of Mo. Compared to Mo, the atomic mass of W is twice that of Mo. 1.8% W

content in P92 was selected based on long period creep rupture data. The precise balance of W and Mo in 9% Cr steel has not been confirmed because the strengthening mechanism of W in this type of steel is not clear so far. However, it can be confirmed that the precipitation hardening due to Laves phase is associated with the balance of W and Mo. A suitable balanced content of Mo and W possibly is effective for finer precipitation of Laves phase in the martensite matrix, which enhanced the creep resistance of the material through precipitation hardening. Current research is focusing on the role of tungsten (W) content in heat-resistant steels, particularly for applications involving temperatures exceeding 650°C (1,202°F).

Niobium (Nb)

The ingot casting and slab-making process result in the formation of Nb-rich carbide precipitates. Normalizing heat treatment normally retains these Nb-rich carbides in 9Cr steels. A Nb content higher than 0.06% in mass is required in 9Cr steel design. However, excess Nb will result in excess precipitations of Nb carbides, which will deteriorate material toughness and machinability.

Vanadium(V)

In low alloy heat resistant steels which are applied for petroleum processing plant, the addition of vanadium is to reduce hydrogen embrittlement. In 9Cr steels, V is expected to precipitate inside the matrix as nitride to block creep deformation under high temperatures. The strengthen mechanism of V and Nb is same and the balance of these two alloy elements should follow the standards.

Boron(B)

In ferritic creep resistant steels, the addition of boron leads to an increase of the hardenability of the material, which increases creep rupture strength and room temperature strength. The addition of suitable boron (10-30 ppm in mass) in 9Cr pct martensite steels was experimentally

verified to increase the creep strength because it promotes the tempered martensite structure (TMS) formation in 9Cr pct steels. Despite numerous studies, the precise strengthening mechanism of boron in heat resistant steels remains uncertain, it was expected to deaccelerate precipitate coarsening during creep deformation [12].

Silicon (Si)

The addition of silicon primarily plays a role in increasing steam oxidation resistance. However, it should be noted here that the addition of Cr dominates the increase of oxidation resistance compared to silicon. Oxidation of pipes and tubes inside power plant reduces the thickness of these essential components, which can be restricted by the addition of Si. Moreover, recent researchers have proven that Si stabilized the Laves phase of high Cr steels at high temperature for long periods.

Manganese (Mn)

Similar to silicon, the addition of Mn also increases the oxidation resistance of ferritic steels by promoting the formation of a thick, protective oxidation layer on the surface of the steels. It should be noticed here that the content of Mn should be controlled below 0.5% in mass for high temperature ferritic steels.

2.3.3 Microstructure of 9Cr pct martensite steels

Heat treatment and tempered martensite microstructure (TMS)

To understand the microstructure of 9-12Cr high temperature steels, the heat treatment process of these alloys must be investigated. For instance, the typical heat treatment process of Gr.91 is normalizing at a temperature range from 1040~1060°C and tempering at a temperature range from 730~800°C. Generally, the temperatures of normalizing and tempering depend on the service component types (e.g., seamless pipe, seamless tube or plate). Heat treatment details and tensile requirements of Gr:91 is listed in table 2.2.

Firstly, the materials are heated above the A_{C3} temperature (higher than 1000°C), and austenite is formed accompanied with dissolution of carbonitrides. Then air cooling leads to the transformation from austenite to martensite, which contains high density of dislocations. Then the tempering process is heating the normalized steels to a certain temperature ($<A_{C1}$) to realize the recovery of excess dislocations and create a fine dispersion of precipitates inside the martensite matrix. A suitable tempering temperature set up can realize the desired toughness-strength balance of the steel.

Figure 2.3 shows the details of tempered martensite structure inside a primary austenite grain and the distribution of precipitates inside the martensite matrix after heat treatments mentioned above; it is suitable for all creep resistant ferritic steels (Gr:91, Gr:92 and Gr:122). Inside the tempered martensite structure (*TMS*), which is commonly referred to as "prior austenite grain (*PAG*)", is composed of some secondary structures (including packet and blocks). Packets are composed of several blocks and martensite laths are finely distributed inside the blocks. Cr-rich $M_{23}C_6$ carbides are primarily located along: prior austenite grain boundaries (*PAGBs*), packet boundaries, block boundaries and lath boundaries, which play the dominant role in stabilizing the dislocations during creep deformation. Whereas some carbonitrides (e.g., MX phase) are expected to precipitate along martensite lath boundaries and be finely distributed inside laths for stabilization effect. The coexistence of subgrain structures (laths and blocks) and fine distribution of precipitates efficiently increased the creep strength of 9-12Cr pct steels.

Figure 2.4 shows a typical optical micrograph of Grade 92 material with tempered martensitic lath structure. Figure 2.5 introduces the TEM micrograph of tempered martensitic structure of Grade 91 steel as a reference. In Grade 92 steels, the retained delta-ferrite have been verified to be detrimental for the creep rupture strength and toughness [13].

2.4 Development of 10-22%Cr steels for advanced steam power plants

The development of higher Cr pct (>10) steels compared to 9Cr pct steels must be associated with the development of advanced power plants, which require higher creep strength and oxidation resistance of materials. Figure 2.6 shows the research projects for the development of creep resistant steels for advanced power plants since 1978 and Figure 2.7 shows the details about the development of high chromium creep resistant steels from 1950 till 1995 [14]. It should be noted here that the development of high temperature steels followed the trial-and-error method over long periods of time.

22Cr pct steel, known as X22CrMoV 12 1, was developed in the 1950s and designed for the application of components to serve in thick-walled power stations. The strength of this super Cr steel relied on the solution hardening and precipitation strengthening ($M_{23}C_6$ carbides). Until now, this steel has been safely applied for decades in power stations.

General Electric Company in USA patented an 11Cr pct rotor steel known as 11%CrMoVNbN, which was developed from Nb alloyed steel [15]. The reduction in the Nb content successfully restricted harmful segregation in the rotor and the formation of δ-ferrite was avoided because of modified alloying elements balance. This steel was already proved to have a creep strength of approximately 90 MPa at high temperature (600°C) over long period (10^6 hours) [16].

Japanese researchers initiated the investigation of a new 12Cr pct steel, which is known as Steel HCM 12, with chemical composition as 0.10%C, 1%Mo, 1%W, 0.25%V, 0.05%Nb, 0.03%N. Compared with other high chromium steels, it shows higher creep strength and weldability. However, δ-ferrite was observed mixed with martensite structures in this new 12Cr steel [17,18]. In the 1950s, The development efforts initially focused on 12CrMoV steel before shifting to TAF steel (12CrMoVNbB) was manufactured as small motor forgings [19,20,21]. During the 1970s, some other modified types of 12Cr steels were developed, such as

TR1100/TMK1 (12CrMoVNb), TR1150/TMK2 (12CrMoVNbWN) [19,20,21,22], TOS 101[23,24] steels and so on. The steels mentioned above were applied for power stations with steam temperature of 593°C and 620°C. Figure 2.8 shows the alloy design philosophy of high Cr ferritic steels which was developed for boilers under 650°C in ultra-supercritical power stations [25]. From the figure, it can be confirmed that the increase of Cr addition will result in the formation of δ-ferrite, which is detrimental for creep strength. Moreover, precipitation of Z-phase was discovered to occur at 15,000 hours after creep stressing at 650°C in high Cr (≥10%) martensite steels [26]. This microstructure evolution was also observed in this research project and will be analysed in detail in Chapters 4&5.

2.5 Strengthening mechanism of creep resistant steels

In this section, the strengthening method for creep resistant steels will be described and all these strengthening methods were mainly for 9-12Cr tempered martensite high temperature steels. To enhance the strength of creep-resistant steels, various methods are applied, including solid solution hardening, precipitation hardening, dislocation hardening, and boundary hardening. [27-30].

2.5.1 Solute hardening

Some solute atoms with larger atomic size compared to parent iron, such as Mo and W, have been proved to be effective in solid solution strengthening both of ferritic martensite and austenite creep steels. It should be noted here that Mo and W also contribute to precipitation strengthening for creep resistant steels, which will be introduced in following sections. Balanced content of W and Mo will result in precipitation of Laves phase (Fe_2(Mo, W)) and enhance a finer distribution of $M_{23}C_6$ carbides decorating along boundaries at high temperature for long periods. Nitrogen, an interstitial solute atom, is widely acknowledged to be beneficial for enhancing the creep strength of both ferritic and austenite creep resistant steels. The strengthening mechanisms of Nitrogen are composed of solution hardening and precipitation

hardening (precipitation of fine MX nitrides). Ir [31] and Re [32], are also good solution strengtheners because of their high solid solubility and Hume-Rothery size effect.

2.5.2 Precipitation (dispersion) hardening

Precipitation hardening is the primary strengthening mechanism in creep resistant steels under high temperatures. Several kinds of precipitate particles are contained inside the matrix and decorated along boundaries. Carbides can precipitate along the boundaries (PAGBs, packet boundaries, block boundaries and lath boundaries). The types of carbides in martensite steels are $M_{23}C_6$, M_6C and M_7C_3. Carbonitrides are expected to precipitate along boundaries and finely distribute inside martensite laths. Typical carbonitrides in martensite steels are MX and M_2X. As well as these metallic compounds, some intermetallic compounds are found in creep resistant steels: Laves phase (Fe_2(Mo, W)), μ-phase (Fe_7W_6), χ-phase and so on. Fine dispersion of alloys oxides (e.g., Y_2O_3) are found to have a strengthening effect in some oxide strengthened steels (ODS). Free dislocations inside the matrix and secondary structures (packet and block) will be stabilized by a fine dispersion of precipitates, which simultaneously improves dislocation hardening and the stability of subgrain structures.

2.5.3 Dislocation hardening

High density of dislocations with a range from 1×10^{14} to 10×10^{14} m^{-2} are usually expected to be contained in the matrix of tempered martensite steels [29]. The dislocation hardening can be calculated by the equation shown below [33]:

$$\sigma_\rho = 0.5MGb(\rho_f)^{\frac{1}{2}}$$

(Equation 2.2)

Where ρ_f is free dislocation density in the martensite matrix. In previous studies, the density of dislocations has been controlled by the accommodation of tempering temperatures. For

short-term applications, the dislocation hardening did give higher creep strength [33]. Different components (e.g., boilers or turbines) requires different tempering temperatures. For steels used in turbines, the tempering temperature should be controlled below 700°C to enhance tensile strength at service temperature. For steels used in boilers, the tempering temperature should be controlled in a range from 750°C to 800°C.

2.5.4 Subgrain boundary hardening

As illustrated in previous sections, the martensite matrix is composed of some secondary grain structures such as packet, block and martensite laths. The block and martensite laths inside the block can be considered as elongated sub-grains, which play a role in subgrain boundary hardening and it can be calculated by the equation shown as below [34]:

$$\sigma_{sg} = \frac{10Gb}{\lambda_{sg}}$$

(Equation 2.3)

In this equation, λ_{sg} is the short width of block and laths, which is approximately 300-500 nm in 9-12Cr tempered martensite creep resistant steels [29]. In most of cases, Subgrain boundary hardening was enhanced by the precipitation hardening in high Cr tempered martensite steels because of fine distributions of carbides and MX carbonitrides decorating along sub-grain boundaries [34].

2.6 Creep

2.6.1 Creep curves

The definition of creep can be given as an inelastic deformation when the material (single or polycrystalline solids) is applied with a constant load or stress under high temperature for long periods. Generally, creep tests of engineering steels are conducted at a constant tensile load at

a certain temperature for experimental convenience. The curves from creep tests results are defined as creep curve, which reflect the time dependence of strain. The measurement of creep strain generally applies to gauge length as a reference. Figure 2.9 shows a typical uniaxial creep curve. A creep curve can be divided into three different regions (or stages): primary creep stage, secondary creep stage and tertiary creep stage. These regions can be easily understood with the variations of creep rate.

In the primary creep stage, also known as transient creep, rapid, thermally activated plastic strain occurs, the dislocation was restricted mainly by the work hardening and then shows a deceleration of creep rate. When some metals were exposed to high stresses or temperatures, the primary stage is not easily observed. In some cases, the tertiary stage follows immediately after loading. In the secondary creep stage, the creep rate keeps a constant value (known as steady-stage creep rate), and this stage is the longest one in a creep period. It can be described as a balance state in the competition between strain hardening and recovery. In the tertiary creep stage, there is a drastic acceleration of creep rate and the material is extended to fracture (creep rupture). Weaking metallurgical instabilities (such as localized necking, corrosion and micro-voids formation) dominates the creep tertiary stage. Additionally, recrystallization of strain-hardened grains in this stage is detrimental for the strength of materials. Although the three creep regions can be easily observed in most of materials under certain temperature and stress ranges, the secondary stage of creep period were mostly selected for scientific researching due to its stability. However, the tertial creep stage of creep period was selected for C* application in some cases and this will be discussed in following sections.

2.6.2 Creep mechanisms

The primary creep mechanisms are: dislocation dominated at lower temperatures under higher stresses; diffusion dominated at higher temperatures under lower stresses.

Dislocation creep:

Dislocation creep can be described as the result of dislocations which are simultaneously accompanied with vacancies and thermal activation. The motion of climb over obstacles will be resisted due to low temperature. The slip system will be activated by the increase of temperature and leads to dislocation glide. When those dislocation were restricted by obstacles, it will be stored around the obstacles. At high temperatures, dislocations show the potentiality to climb to a parallel slip plane and repeat this progress until they are blocked by more resistant obstacles. This progress is defined as “climb-glide creep” and it relies more strongly on applied stress than diffusion creep. Precipitation (or dispersion) hardening is applied to prevent dislocation creep in some heat resistant steels.

Diffusion creep:

This differs from dislocation creep, in that diffusion creep dominates at higher temperatures and lower stresses. Diffusion creep can be divided into two types: Nabarro-Herring creep and Coble creep. Figure 2.10 (b) shows the manner of diffusion creep, the grain boundary diffusion and lattice diffusion are presented. Inside a grain, the atoms diffuse towards the top and bottom of the grain, which is initiated and driven by the applied stress. With the effect of high temperature, more vacancies accelerate the elongation of the grains. Nabarro-Herring creep normally exists when the metal is applied with lower stress and higher temperatures. The vacancies diffuse inside the grain perpendicular to the direction of the tensile stress and leads to deformation along the direction of the tensile stresses. Compared to Nabarro-Herring creep, Coble creep occurs at lower temperature. The absence of the influence of higher temperature, diffusions (flow, vacancies and atoms) occurs along the grain boundaries rather than inside the grains. Because of the high sensitivity to temperature of diffusion, the grain boundaries will be

the main diffusion path because of lower activation energy. However, the activation is much higher for bulk diffusion.

Grain boundary sliding:

Grain-boundary sliding is frequently observed before creep to rupture. The deformation of a grain results in the movement of that grain. The centre of the grain will move relatively to make sure the grain boundary is still maintained continuously. Following applied loading direction, rotation and elongation of grain is initiated.

Figure 2.11 shows the histograms of creep deformation mechanism and *Tm* is the melting temperature of the case materials.

2.6.3 Effect of temperature variation

The temperature of creep tests normally is controlled in the range of 0.3 *Tm* to 0.5 *Tm* of the selected materials. The magnitude of creep strains and the duration of creep test vary depending on the specific temperature applied during the experiment [35]. The change of testing temperature will lead to the significant change of creep test results.

2.6.4 Minimum creep strain rate (MSR) and average creep strain rate (Ave.SR)

Two creep strain rates are applied to illustrate the creep curves (see Figure 2.9): minimum creep strain rate ($\dot{\varepsilon}_{min}$), which is used for characterising the secondary creep stage; average creep strain rate (($\dot{\varepsilon}_{Ave}$), which is applied for characterising all three creep regions. The average creep strain rate is related with failure time (t_f) and strain at failure (ε_f) in a creep rupture test. Creep resistant materials are characterised as materials which have relatively lower minimum average creep strain rates.

2.6.5 Creep rupture and creep fracture (elevated-temperature fracture)

Creep failure is defined as a significant change in the dimensions of creep bodies due to creep deformation. Creep failure can be divided into two types: creep brittle and creep ductile. The propagation and growth of micro-voids within the matrix is creep brittle failure while the creep ductile failure is always accompanied with the high deformation of creep regime (e.g., necking). Figure 2.12. shows three creep fracture mechanisms: intergranular creep (voids or wedge crack), transgranular and intergranular mixed fracture mechanisms (growth of voids by power-law creep) and rupture fracture (dynamic recovery and recrystallization).

2.7 Fracture Mechanics Parameters Applied in Creep Crack Growth Prediction

2.7.1 Introduction to C* parameter

When the creep crack growth occurs in a crack body under Mode I loading condition, a fracture mechanics contour integral, C*, can be applied to correlate with the creep crack growth using the equation showing below [36]: -

$$\dot{a} = D(C^*)^q$$

(Equation 2.4)

Where a is the rate of creep crack growth and the others are material constants.

The determination of these materials constants D and q can be done through calculating the gradient q and intercept (log (D)) from Log (a) versus Log(C*) plots. After determining these constants, the a of a specific C* value is possible to be calculated and the remaining life of the cracked bodies can be predicted.

2.7.2 C* parameter derivation background

The stresses and strains ahead of a crack in a cracked body can be characterised with several parameters. The stress intensity factor, *K*, only applies for linear elastic material. Based on the linear elastic fracture mechanics (LEFM), near tip fields including stress and displacement can be divided into three basic cracking modes (Mode I "opening", Mode II "In-plane shear" and Mode III "out-of-plane shear"). Figure 2.13 shows all the three modes of loading a cracking body. Most fracture in metallic materials follows the mode I and the crack surface is separated with $x - y$ and $x - z$ planes. The stresses and displacements in the region around the crack tip in mode I can be calculated with the equations shown as below:

$$\sigma_x = \frac{K_I}{\sqrt{2\pi r}} \cos\frac{\theta}{2}\left(1 - \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right)$$

(Equation 2.5)

$$\sigma_y = \frac{K_I}{\sqrt{2\pi r}} \cos\frac{\theta}{2}\left(1 + \sin\frac{\theta}{2}\sin\frac{3\theta}{2}\right)$$

(Equation 2.6)

Where σ is the applied stress and K_I is the stress intensity factor of mode I. The calculation of K_I is given as below:

$$K_I = \sigma\sqrt{\pi a}$$

(Equation 2.7)

Where a presents the crack length. The equation to calculate K_I when the testpiece geometry is compact tension (CT) is shown below:

$$K = \frac{YP}{BW^{\frac{1}{2}}}$$

(Equation 2.8)

Where P is the applied load, Y is the compliance, B presents the thickness of specimen and W presents the width of specimen [37]. Table 2.3 details the calculations of K on different specimen geometries based on decades' experimental work.

In order to characterize the elastic plastic material, Rice [38] firstly proposed a contour integral, *J,* in 1968. The schematic about the definition of *J* is shown in Figure 2.14. It is defined as a line integral along a contour encompassing the crack tip, starting from the lower surface of the crack and ends at the upper surface. Anderson [39] proved its path-independence and the equation is given by:

$$J = \int_{\Gamma} \left(wdy - \mathrm{T}_i \frac{\partial u_i}{dx} ds \right)$$

(Equation 2.9)

$$\mathrm{T}_i = \sigma_{ij} n_j$$

(Equation 2.10)

$$w = \int_0^{\varepsilon_{ij}} \sigma_{ij} d\, \varepsilon_{ij}$$

(Equation 2.11)

Where T_i is traction vector, u_i is the displacement vector, w presents the strain energy density. The definitions of T_i and w are given separately in equation (2.10) and equation (2.11).

Similar to the J integral, which characterizes the crack tip fields in an elastic or elastic–plastic material, the stress and strain rate distribution in front of a crack tip under steady-state creep conditions can be characterized by a path-independent energy rate line integral called the *C** integral [40,41]. The *C** integral is defined by analogy to the *J* integral [42]. The definition of the *C** integral is the following line integral on a contour Γ surrounding a crack tip (see Fig. 2.15), starting from the lower surface of the crack and ending at the upper surface of the crack.

Slow and stable extension of microscopic cracks leads to the failure of a material when the component is operating under elevated temperatures [43]. Halighongde has proved that C* is also path independent in 2009 [44]. Considering that creep is a time-dependent process, the strains and displacements in the definition of the *J* integral are replaced by their corresponding rates (strain rate and displacement rate) to obtain the equation for the *C** integral:

$$C^* = \int_{\Gamma} \left(\dot{w} dy - \mathrm{T}_i \frac{\partial \dot{u}_\iota}{dx} ds \right)$$

(Equation 2.12)

$$\dot{w} = \int_0^{\varepsilon_{ij}} \sigma_{ij} d\, \dot{\varepsilon_{ij}}$$

(Equation 2.13)

where $\dot{w}$ is strain energy rate density, σ_{ij} and ε_{ij} are the stress and strain rate tensors respectively, T_i is the outward traction vector, $\dot{u}_\iota$ is the displacement rate vector and ds is the arc length along contour path Γ. C* can be determined from a load–displacement rate diagram for a creeping material and it can also be defined from the shaded area of Fig. 2.16.

The calculation of C* parameter has been detailed in Standard ASTM E 1457 and compact tension (CT) specimen geometry is the most widely used approach for *C** calculation work

[36]. Also, the standard introduces some calculation techniques for other geometries, such as circumferential cracked round bar and thumbnail specimens. Some researchers like Tabuchi applied and verified the C* parameter method on a different specimen geometry, circular notched testpiece (ring-notched testpiece). The concept will be explained further in the upcoming section.

2.7.3 Parameters to correlate creep crack growth (*C**, *C(t)* and *K*)

Three parameters have been used to correlate creep crack growth rates in crack bodies: a) C*-stead state contour integral for extensive creep (ductile creep); b) C(t)-the contour integral small-scale creep (ductile creep); c) K-the stress intensity factor for creep brittle material.

Stress intensity factor, K, has been briefly introduced in last section. In this section, how C* and C(t) parameters used to correlate the creep crack growth will be introduced. C* values can be calculated from test results obtained from different testpiece geometries such as compact tension (CT), circumferential cracked round bar and thumbnail specimens. Some researchers like Tabuchi applied and verified the C* parameter method on a different specimen geometry, circular notched testpiece (ring-notched testpiece). The concept will be explained further in the upcoming section.

The distinction between creep ductile and creep brittle behaviour can be told by analysing creep crack growth tests results. In creep ductile materials, the creep crack grows in the region near the crack tip simultaneously with the substantial time-dependent creep strain [45]. Figure 2.15 (t/tr is the ratio about the actual time versus reference time in creep crack growth curves) shows different creep crack growth behaviour from a creep ductile material (Cr-Mo-V) and a creep brittle material (IN 100) from Yokobori's work in 2009. Yokobori found that the acceleration stage of creep crack growth in creep ductile material began earlier than the same stage in creep brittle material, which constituted the most of the total fracture life. C* and C(t) can be used to

correlate the creep crack growth in creep ductile material. Differing to creep ductile materials, creep crack growth occurs with low creep strain around the crack tip in creep brittle material. This is a result from low creep strain around the crack tip in creep brittle materials and it is dominated by the elastic strains local to the crack tip. So, the accelerated stage started later, which happened around 90% of the fracture life (See Figure.2.17). In other words, the steady stage occupied the majority part of total fracture life. When the requirements of steady stage in creep brittle materials are met, *K* becomes a better parameter referring to ASTM E 1457-00 standard. Figure 2.18 shows a schematic of three creep deformation regimes with a crack defect and these are introduced in next sections.

2.7.4 Small scale creep

As shown in Figure 2.18 (a), creep deformation occurs in a very small, uncracked ligament region adjacent to the crack tip. C(t) contour integral is used in this condition to correlate the creep crack growth occurred in small scale creep zone, where was under significant creep deformation. The equation of C(t) in the standard method for compact tension testpiece is given by:

$$C(t) = \frac{P\dot{V}_c}{(BB_N)^{\frac{1}{2}}W}\left(\frac{\acute{F}}{F}\right)$$

(Equation 2.14)

$$\frac{\acute{F}}{F} = \left[\frac{1}{2\left(1 + {}^{a}/_{W}\right)} + \frac{3}{2\left(1 - {}^{a}/_{W}\right)}\right] + \frac{\acute{f}\left({}^{a}/_{W}\right)}{f\left({}^{a}/_{W}\right)}$$

(Equation 2.15)

$$\acute{f}\left({}^{a}/_{W}\right) = 4.64 - 26.64\left({}^{a}/_{W}\right) + 44.64\left({}^{a}/_{W}\right)^{2} - 22.4\left({}^{a}/_{W}\right)^{3}$$

(Equation 2.26)

$$f(a/W) = 0.886 + 4.64(a/W) - 13.32(a/W)^2 + 14.72(a/W)^3 - 5.6(a/W)^4$$

(Equation 2.17)

Where P is the applied load, a is the crack length and $\dot{V}_c$ is the rate of load-line displacement. W and B separately represent the width and thickness of selected specimen (CT). B_N is the thickness of net section.

2.7.5 Transition creep

Transition creep regime is defined as a regime primarily dominated by creep deformation compared to small scale creep regime (See Figure 2.18 (b)). Whereas the whole uncracked ligament of the body is not dominated by creep deformation [46]. In this regime, the instantaneous field of a stationary crack tip can be characterized by a fracture mechanics parameter, C(t). After a long creep period, C(t) reaches a constant value which is normally higher than C* [47]. The calculation of C(t) is shown as below:

$$C(t) = \frac{K^2(1-v^2)}{E(n+1)t}$$

(Equation 2.18)

where K is the stress intensity factor, v is Poisson's ratio, E is the modulus of elasticity, n is the creep exponent in Norton's law and t is the time.

In equation (2.18), the transition time from small scale creep to steady state creep can be defined as the time when C(t) is equal to C*. Its calibration is give by:

$$t'_T = \frac{K^2(1-v^2)}{E(n+1)C^*}$$

(Equation 2.19)

This equation is used to calculate t'_T for each C* value, then t_T is the maximum value of t'_T.

2.7.6 Extensive creep

Figure 2.18 (c) shows the extensive creep regime and creep deformation dominates the whole uncracked ligament. Compared to the size of crack and uncracked ligament, the creep deformation dominant region becomes more significant in size [48]. Under this condition, the extension of the creep zone is much faster than the growth of the crack and the crack tip is surrounded by an extensive creep region. In this case, C* integral is found usually to correlate with creep crack growth rates and calculation of compact tension testpiece C* values referring to standard method given by: -

$$C^* = \frac{n}{n+1}\frac{P\dot{V}}{B_N(W-a)}(2 + 0.522(1 - \frac{a}{W}))$$

(Equation 2.20)

Where a is the crack length, W is the width of compact tension specimen, B_N is the net section thickness of side-grooved compact tension testpiece, $\dot{V}$ is the loadline displacement rate, P is the applied load and n is the creep exponent.

2.7.7 C* approach in the prediction of creep crack growth

The studies about the approach of C* to predict the creep crack growth in different materials at elevated temperatures have been conducted for decades. In 2001, Dogan and Petrovski [49] used C* and K parameters on the creep crack growth calculation of P91 at 600°C. They found that K showed more scatter and potentially C* was a more suitable parameter with less scatter and more accuracy. This conclusion is the same as the studies done by Xia *et al.* [50] in 1998.

The unique relationship between creep crack growth rate and C* has been found based on the pioneering works in previous decades. Tabuchi *et al.* [51] found the similar unique relationship based on the analysis of creep crack growth tests on P92 pipe materials (PM) and CT weld testpieces with different testing conditions (temperature and loading). Figure 2.19 shows the

creep crack growth rates against C* values in different temperatures and loads from Tabuchi's studies. It can be found that all these C* curves with different testing conditions overlapped inside a narrow band area. C* can be confirmed to be a path independent mechanics parameter to correlate the creep crack growth rate and predict the creep crack growth of the high chromium heat resistant steels.

In 2003, Tabuchi and Takeshi [52] pioneered the approach of C* in correlating the creep crack growth in a circular notched bar sample of 1CrMoV steel and 12CrWCoB steel. The dimensions of circular notched bar specimens are shown in Figure 2.20. In their study, the results of the circular notched bar geometry were compared to the results from compact tension geometry. Figure 2.21 shows the C* plots of ring-notched geometry and the unique relationship between creep crack growth rate with C* values was proved in this novel geometry. This relationship was established by comparing the creep crack growth rates obtained from the ring-notched geometry with CT geometry, which is one of well-established specimens' geometries. All the C* curves stayed inside a narrow band which is lower than the data band of CT testpieces. The CT specimen had a higher creep crack growth rate and loadline displacement rate compared to a circular notched testpiece with the same t/t_f value. This can be explained by the stationary stage occupying the most part of the entire creep crack growth life, which is approximately higher than 80% (Figure 2.22). The circular notched testpiece has different creep crack growth behaviour compared to that from CT testpiece, which results from stress multiaxiality in circular notched bar specimens. The correlation between creep crack growth rate against C* was better in a steady creep crack growth stage rather than the early stage of cracking.

2.8 The loss of strengthening mechanism in 9-12Cr steels during long term periods

There has been a lot of effort to figure out the mechanisms of creep strength loss in high chromium tempered martensite heat resistant steels during creep exposure at elevated

temperature higher than 550°C. At present, it can be divided into two mechanisms: (a) loss of precipitation hardening by the formation of carbonitrides during long term high temperature exposure; (2) loss of dislocation hardening due to the recovery of martensite lath structure during long term high temperature exposure. Microstructure evolution such as the lath to block transformation, results in the loss of sub-boundary (lath boundaries and block boundaries) hardening [53].

2.8.1 Loss of precipitation hardening

The precipitation hardening primarily comes from the pinning effect of $M_{23}C_6$ carbides along boundaries (prior austenite grain boundaries, block boundaries and lath boundaries). This kind of precipitate will coarsen to several times its original size after a long period of high temperature exposure. Moreover, the precipitation of some new secondary phases such as carbonitrides (MX), Fe_2(W,Mo) Laves phase and Z-phase is detrimental for the martensite matrix. These phases precipitated during thermal exposure will consume the fine precipitates ($M_{23}C_6$ carbides) adjacent to them.

It has been found that the precipitation of Z-phase and coarsening of M_6X is accompanied by the dissolution of fine MX precipitates and coarsening of $M_{23}C_6$ carbides in 12CrMo(W)VNbN steels. Figure 2.21 shows the Z-phase precipitation in NF12, a 12Cr steels [54].

2.8.2 Loss of dislocation hardening

The creep strength of tempered martensite steels relies significantly on the tempered martensite laths structure. However, progressive coarsening of carbide precipitates results in the loss of pinning effect to block the martensite lath recovery. This results in the progression of laths to blocks transformation in high chromium martensite steels under long time high temperature exposure. The applied stress will accelerate this progress. Once the matrix has lost its tempered

martensite structure, there is no dislocation hardening effect in the material, which results in the loss of creep strength in the matrix [55].

2.8.3 Effect of δ-ferrite

Kimura *et al.* [56] analysed the microstructure evolution of a dual phase 12Cr steel under temperatures ranging from 600 to 650°C for long period creep rupture. They found that the inhomogeneous deformation around δ-ferrite was the primary reason for the degradation of the steel. The large concentration gap between the interface of δ-ferrite and martensite promotes the diffusion of carbon and nitrogen. The promoted diffusion of carbon and nitrogen leads to the precipitates coarsening and tempered martensite structure recovery. Moreover, the non-uniform precipitation of MX-phase in δ-ferrite is detrimental for the martensite matrix strength because the heterogeneous creep deformation is promoted [57].

CHAPTER 3 Experimental

3.1 Materials

3.1.1 Materials, test-pieces and heat treatments

P92 and BG12Cr materials used in this research project were supplied as cylindrical bar blanks by Baowu Steel. The nominal chemical compositions of these two alloys are shown in Table 3.1. The as-received BG12Cr steel had been normalized at 1060°C for 90 minutes, followed by air cooling. It was then tempered at 780°C for 1.5 h and air cooled. It should be noted here that the heat treatment of P92 was not supplied by Baowu Steel. The as-received blanks for both alloys were machined into ring-notched testpieces for creep crack growth testing.

3.2 Microstructure characterisation

To develop a comprehensive understanding of the microstructure both in the as-received (AR) state and post testing (PT), microstructural characterisation was performed on specimens before and after the tests.

3.2.1 As received specimens

An as-received slice with a thickness around 15 mm, which was used for the microstructure characterisation for as-received materials, was cut from the cylindrical bar blanks using a cutting machine (Struers Accutom-5) with an alumina disc. Then the slice was mounted in Bakelite. The mounted samples were ground and polished using a LaboPol5 polishing machine. For grinding 120, 240, 400, 800, 1200 and 2500 grit size SiC grinding papers were used with water. Then the samples were polished on cloth with diamond suspensions. The sequence of diamond suspensions was: 6μm, 3μm and OPS for approximately 20 minutes in each step. For the specimens used for EBSD observation, which will be mentioned in the following section, OPS was not required and the last polishing with 3 μm was for approximately 30 minutes. After

this the samples were washed first with water then followed by acetone. Clean samples were dried immediately by air-dusters or blower.

The polished specimens (not etched) were then investigated with an optical microscope (OM, Keyence VHX-6000) to have a basic understanding about the tempered martensite structure. Then they were investigated under a secondary electron microscope (SEM, JOEL 7000F) with a 20kV accelerating voltage and 10mm working distance to establish a deeper understanding about the as-received tempered martensite structure. Energy Dispersive X-ray Spectroscope analysis (EDS) and Electron Backscatter Diffraction (EBSD) investigations were also conducted on the JOEL 7000F. The working distance for EDS analysis was set to 10 mm and the accelerating voltage was set to 15 kV. The step size of EBSD was set to 1 μm. Spot point detection and EDS mapping were conducted to understand the chemical composition of precipitates and distribution of these particles in materials. The micrograph mapping of EBSD was exported in Channel 5 format and analysed using Tango software to generate the distribution of high angle boundaries (HABs) and low angle boundaries (LABs).

To see the structures clearly under OM and SEM, some polished specimens were etched with Kallings' 2 etchant (chemical composition: 40ml HCl, 40 ml Ethanal and 2 g Cupric Chloride) for no longer than 5 seconds.

As-received TEM samples were taken from received blanks in the form of thin foils with a diameter of 3 mm. These thin foils were prepared by grinding down to a thickness of ~ 50 μm, and then electropolished in a solution of 7% perchloric acid + 93% ethanol at 25V and -20°C, using a twin jet electropolisher. Then the observations were conducted under transmission electron microscope (TEM, FEI Talos F200X).

3.2.2 Post testing specimens

After testing, half of the testpiece was kept for fracture surface observation and another half of the testpiece was sectioned along the centre line perpendicular to the fracture surface using a Struers Accutom-5 cutting machine with a diamond cutting disc. Then the cross-section was mounted in Bakelite. The polishing procedures of cross-sectioned testpieces was the same as as-received specimens, which was detailed illustrated in previous section.

1) After creep crack growth testing

To establish a basic understanding of fracture mechanism, after testing, the fracture surface of specimens was observed firstly under the optical microscope (Keyence) and then under secondary electron microscope (Philips XL-30 FEG ESEM). Some fractography work was conducted under an advanced electron microscope (Zeiss EVO15 VP ESEM) with a larger chamber.

Then the cross-sectioned specimens were investigated under a secondary electron microscope (JOEL 7000F) with a 20kV accelerating voltage and 10mm working distance, accompanied with Energy Dispersive X-ray Spectroscope analysis (EDS) with a 15kV accelerating voltage, to have a deeper understanding about the fracture mechanism of the testpieces.

2) After stress-ruptured testing

To understand the fracture mechanism of these stress-ruptured testpieces received after testing from Baowu Steel, the fractography work was firstly conducted on the stress-ruptured specimens under optical microscope and secondary electron microscope (Philips XL-30 FEG ESEM). The matrix of these specimens is listed in Table 3.2. Meanwhile, the specimens without thread parts were cross-sectioned, mounted, and polished. Then the microstructure characterisation was conducted on these specimens with optical microscope and secondary

electron microscope to figure out the failure mechanism of tempered martensite matrix with different testing conditions.

To understand the microstructural evolution of these testpieces with the minimum strain influence, the thread parts of the testpieces were cut, polished, and etched following the similar procedures that are mentioned in previous section. Then the microstructure characterisation was conducted on these polished specimens with optical microscope (OM) and secondary electron microscope (SEM). To understand the microstructural evolution of these two alloys after 10,000 hours, EBSD was also conducted on these two testpieces (BG12Cr after 10380 hours and P92 after 12234 hours) to compare with the EBSD scanning results from the as-received materials. Thin foils with a thickness of approximately 1 mm were taken from the thread part of these two specimens. These thin foils were prepared by grinding down to a thickness of ~ 300 μm, and then electropolished in a solution of 7% perchloric acid + 93% ethanol at 25V and -20°C, using a twin jet electropolisher. Then TEM samples were kept in alcohol solution for storage to avoid deformation caused by magnetic field. The microscopy was conducted on a different TEM microscope (Philips Tecnai F20) compared to the observations on as-received alloys.

3.3 Creep crack growth testing (CCG)

3.3.1 Ring-notched testpiece preparation

Figure 3.1 shows a schematic drawing of a ring-notched specimen, and the spot weld positions for the d.c.p.d crack length monitoring technique. All the ring-notched testpieces were manufactured with a notch root angle of 60° and a notch depth of 1.2 mm. Initially specimens had a diameter of 8 mm (labelled as “S(small)” series). Later specimens had a diameter of 9.525 mm (labelled as “L(large)” series) which allows a larger creep crack growth region.

3.3.2 Crack length monitoring technique

The direct current potential drop technique was used for the measurement of crack length. As this was the first trail of creep crack growth testing with the ring-notched geometry in this research group, three Brightray wires (a Ni-Cr alloy) labelled as "1,2,3", were spot welded at different locations in the vicinity of the notch (see Figure 3.1). The wires 1-3 and wires 1-2 were connected separately to different voltmeters to determine which spot-welding position is the most sensitive to the crack growth. The opposite corner spot-welding position (1-3) was expected to have a higher sensitivity on the creep crack growth compared to the spot-welding position on the same side (1-2) for the first trail test. This will be discussed in detail in Chapter 4. After spot-welding, another pair of wires was connected to the test machine to let the current pass through the grips to supply constant direct current to the testpiece. As the crack extends, the path between potential wires increases and then the measured potential difference (voltage) increases. The recorded potential values were later converted into crack length using a calibration function described below.

3.3.3 Testing procedures

All the testpieces were cleaned with acetone in an ultrasonic cleaner to make sure all contamination was removed. Potential wires were spot-welded before testing and current wires were connected before loading on the testpiece. The wires inside the furnace were covered with ceramic sleeves to prevent short circuits.

All the creep crack growth testing of ring-notched testpieces followed the instructions of ASTM standard E1457-15. The CCGT tests were performed at 650°C using two screw-driven servo-electric close-loop controlled machines: a Zwick Kappa (6 tests) and a Zwick100 (1 test). Throughout the experiments, the direct current potential drop (DCPD) technique was applied for monitoring the creep crack growth. Loadline displacement was recorded through a clip-on extensometer attached on fixtures holding on the root of the specimen, which will be detailed

later. After each test, the creep crack growth rate was calculated from loadline displacement and creep crack length. Then the creep crack growth rate was used to evaluate C*. There is no pre-cracking procedure for the ring-notched testpiece. After spot-welding, the testpiece was set up on the testing machine and was loaded to a very small load of 500 N. A thermocouple was attached to the shoulder of testpiece to monitor temperature during the whole creep crack growth test period. A pair of fixtures made from high strength nickel alloy were used to hold the extensometer. The extensometer was clipped on to the fixtures (see Figure 3.3) and the fixtures are attached on the shoulder part of the specimen (see Figure 3.2) and held by screws made from nickel alloy.

After the temperature had reached 650°C and allowed to stabilize, a constant direct current of 7 A was applied through the test piece. A static load was applied slowly from 500 N (e.g., 1 kN/s). Target load was determined with the stress level designed for each test. The matrix of the ring-notched CCG tests can be found in Table 3.3. The recording of potential and loadline displacement started simultaneously at the very beginning of each test. Meanwhile, the standard travel was automatically recorded by the test machine computer. The test was interrupted immediately after the test reached the tertiary creep stage, which was indicated by the rapid increase of potential values, accompanied with similar increase of loadline displacement values. After interruption, the load was transferred into a lower load (500N) and the furnace was switched off.

After cooling down to room temperature, the load was transferred into sine waveform fatigue on the same testing machine with a frequency of 0.25 Hz and a stress ratio of 0.1. The maximum load of the fatigue cycle was the same as that used for the static creep crack growth test. After this procedure, the crack propagated and grew faster until the specimen was fatigued to fracture. Then the broken sample was used for fractography observation and cross-section analysis to understand the fracture mechanism.

3.3.4 Crack length calibration

After each test, the fracture surface was imaged under an optical microscope. If there was a cup and cone fracture (for ring-notched testpiece), generally the cone part was be selected for observation. The creep crack length could be easily seen and measured due to different morphologies and colours. In ring-notched specimens, crack propagates from the notch edge and circular creep crack region are formed. Crack lengths (initial and final crack sizes) and corresponding voltage values were measured. Crack growth, which was average width of circular ring, was measured from the fracture surface of testpieces. These data points were then interpolated to create a continuous curve, which was subsequently plotted to visualize the relationship between crack length and voltage (see Figure 3.4).

3.3.5 Calculation of K and C*

With the data collected from last section, K and C* were calculated following the standard method ASTM E1457-15 and Tabuchi's work [54] on ring-notched geometry specimens:

$$\boldsymbol{K_1 = \frac{1}{2}\sigma_{net}\sqrt{\frac{\pi a d}{D}}\left(1+\frac{1}{2}\lambda+\frac{3}{8}\lambda^2-0.363\lambda^3+0.731\lambda^4\right)\times\left\{1+0.1\sqrt{\frac{2a}{D}}\left(1-\frac{2a}{D}\right)\right\}}$$

(Equation 3.1)

$$\boldsymbol{C^* = \frac{2n+1}{2n-1}\sigma_{net}\frac{d\sigma}{dt}}$$

(Equation 3.2)

$$\boldsymbol{d = D - 2a, \lambda = d/D}$$

(Equation 3.3)

Where $\boldsymbol{a}$ is the creep crack length, $\boldsymbol{D}$ is the diameter of the sample gauge section, $\boldsymbol{d}$ is the diameter of the notch section and $\boldsymbol{n}$ is the creep exponent.

3.3.6 Hardness testing

The microhardness values of both as-received specimens and post testing specimens were obtained utilizing a Struers Durascan 40 machine with a 0.1kg load applied for 10 seconds. A total 40 measurements were conducted on each polished metallographic testpiece to minimize uncertainty. The indents, typically ranging between 0.025 mm and 0.030 mm, were strategically positioned within a 2.9 x 1.4 mm rectangular area, maintaining a 0.1mm spacing between each indent.

CHAPTER 4 Results

4.1 Microstructure of P92 and BG12Cr

4.1.1 As-received microstructures and its comparison

The specimens for as-received microstructure characterisation were taken from the original blank bars supplied by Baowu Steel. Optical micrographs of the as-received microstructure of both alloys at different magnifications are shown in Figure 4.1.a and Figure 4.1.c. Low magnification views of secondary electron micrographs are given in Figure 4.1.b and Figure 4.1.d.

From Figure 4.1.a, the tempered martensite structure can be clearly identified. However, prior austenite grain boundaries were difficult to see from optical observations in P92. In Figure 4.1.b, the tempered martensite lath structure can be easily observed, and the boundaries can be seen. Compared with P92, the optical observation of BG12Cr comes to a similar conclusion, the tempered martensite structure can be seen. Prior austenite grain boundaries and martensite laths are easily observed in BG12Cr, and it seems to have a relatively large grain size compared to P92 (see Figure 4.1.d).

To understand the difference between these two alloys grain size, the PAGB size distribution histograms of both alloys are shown in Figure 4.2. P92 has an average grain size of approximately 17.3 μm (see Figure 4.2.a). Compared to P92, BG12Cr has a relatively large average grain size, which is approximately 37.5 μm (see Figure 4.2.b). The histogram of BG12Cr reveals a relatively broad distribution.

To have a better understanding about the microstructure and tempered martensite structure differences of both alloys, the EBSD scanning results are shown in Figure 4.3 indicating the results of P92 and Figure 4.4 indicating the results of BG12Cr. The magnification of 5000 with a step size of 0.1 μm was chosen to involve a complete prior austenite grain inside the

micrograph to evaluate the tempered martensite laths structure inside a single grain in both alloys.

Figure 4.3 shows EBSD scanning mapping micrographs of the P92 as-received alloy. Tempered martensite laths can be clearly and easily distinguished. Meanwhile, the prior austenite grain boundary of the grain in the central area can also be clearly observed. Variations in colour grades inside a lath (red arrow in Figure 4.3.c) indicate distinct orientations within the lath. Referring to Figure 4.3.d, the majority of grain boundaries are identified as LABs (lath boundaries) and HABs (prior austenite grain boundaries). The misorientation histogram in Figure 4.3.d demonstrates a high degree of orientation (>55º) between two adjacent laths.

Figure 4.4 shows the EBSD scanning mapping micrographs of BG12Cr as-received material. Compared to P92, a higher density of martensite laths in a single prior austenite grain are clearly observable. Most grain boundaries are LABs (2~15°) (lath boundaries) and HABs (≥15º) (prior austenite grain boundaries) as per Figure 4.4.d. The misorientation histogram in Figure 4.4.d reveals a high misorientation (>55º) between two adjacent laths. The martensite laths in BG12Cr seems to have relative smaller width compared to the laths in P92.

Figure 4.5 shows the microhardness values of both alloys in as-received condition. The microhardness of as-received BG12Cr is measured to be 284 HV_5, which is higher than P92.

4.1.2 Precipitates in as-received P92 and BG12Cr steels

In order to figure out the types of precipitates and their difference in both alloys, some TEM work has been conducted by Dr. Renggeng Ding on both as-received specimens.

As-received P92

General microstructure

Figure 4.6 shows the STEM micrographs of as-received P92 base material. Martensite laths can be easily distinguished with a width of approximately 400nm. Very fine distribution of particles along prior austenite grain boundary and sub-grain boundary are observed (see Figure 4.6.a to 4.6.c. A number of spherical particles, which have an average dimension smaller than 100 nm, are found decorating the prior austenite grain boundaries in Figure 4.6.b and Figure 4.6.c (see white arrows). Some disc-like particles, with an average width of ~10 nm, are found along the lath boundaries in Figure 4.6.c. Moreover, some tiny needle-like particles are found inside the laths and perpendicularly to the lath boundary in Figure 4.6.f. (see white arrow).

To characterise the basic chemical composition of these precipitates, STEM EDS work has been conducted on as-received P92. Figure 4.7 shows the High-angle annular dark-field imaging (HAADF) micrograph and EDS mapping micrographs of precipitates populated area in P92 as-received material. The disc-like precipitates along the prior austenite grain boundary are the (Cr,Mo,W)-rich carbides with an average dimension of approximately 50 nm (see white arrows and yellow arrows in Cr, Mo and W map). (W,Mo)-rich intemetallics (see yellow arrows in W and Mo maps), needle like V-rich carbonitrides (see blue arrows in V and N maps) were founded. V-rich carbides were found decorating the interior of the grain or along the interior grain boundary in Figure 4.7. Beside these precipitates mentioned above, Ti-rich carbonitrides (see arrow in Ti map) with dimension around 50 nm were found inside the matrix area which were located possibly inside the martensite lath. Moreover, (Nb, V)-rich carbonitrides are observed (see red arrows in Nb, V and N maps). The EDS spectra of precipitates show that they are (Nb,V)(CN) and V(CN) precipitations according to Figure 4.8. Clear differences can be seen from the peak of Nb and V.

To characterise the primary types of these precipitates, TEM diffraction was undertaken, as illustrated in Figures 4.9-4.11, with detailed illustration in following sections.

$M_{23}C_6$ carbide

The EDS spectrum of the selected particle is depicted in Figure 4.9.a, which reveals a high concentration of Cr, W, and Mo. Figures 4.9.b and 4.9.c display SAD diffraction patterns of the selected particle and the combination of the particle and matrix, respectively. In Figure 4.9.c, the larger spots originate from the matrix while the smaller spots are derived from the carbide. The SAD patterns captured in Figure 4.9.b align well with the electron diffraction patterns from Cr carbide ($Cr_{23}C_6$, f.c.c, lattice parameter a=10.62 Å). Consequently, the precipitate is identified as the Cr-rich $M_{23}C_6$ f.c.c phase, exhibiting a lattice parameter a= 1.06 nm. The composite SADs in Figure 4.9.c suggest a cube-to-cube orientation relationship between the $M_{23}C_6$ carbide and the matrix.

Laves phases

Figure 4.10.a-b present a High-angle annular dark-field image (HAADF) of the (W, Mo)-rich phase identified in as-received P92, along with its corresponding EDS line scanning histograms. The latter reveals that the phase is rich in W and Mo. This particle can be clearly observed to have a needle-like feature and precipitating nearby a Cr-rich carbides. Figure 4.11 displays the EDS spectrum, Convergent beam electron diffraction (CBED) and SADs work to identify the selected phase. Figure 4.7 (d) illustrates the EDS spectrum of this phase, indicating its atomic composition: 51.7% Fe, 13.4% Cr, 20.2% W, 13.1% Mo, 0.8% Mn, and 0.8% Co. All SAD patterns align effectively with the electron diffraction patterns from the Cr-rich M_2X phase (Laves phase with a hexagonal crystal structure). This phase, thus, is identified as a Laves phase with a lattice parameter a=0.47 nm and c= 0.77 nm, forming along the grain boundary. Furthermore, an enrichment of Cr at the grain boundary is evident from Figure 4.12.

In summary, two major precipitates are found in P92 as-received material: f.c.c $M_{23}C_6$ carbide and Laves phases. (V,Nb)-rich carbonitrides, which should be MX phase and Ti-carbonitride are also observed in P92 as-received material.

As-received BG12Cr

General microstructure

The TEM work to characterise the microstructure of BG12Cr parent metal has been conducted and shown in Figure 4.13. Compared to P92, relatively large nano-sized particles precipitated mainly on lath boundaries (see Figure 4.13.b). Figure 4.13.c1-c2 is the magnified view of the martensite lath and numerous particles are observed inside the laths with a dimension of ~20 nm. TEM results also showed there were high density of dislocations and these precipitates pinned dislocations (see Figure 4.13.b to d2). EDS micrographs show that these particles are primary Cu-rich particles (see Figure 4.14).

Figures 4.15 and 4.16 showcase EDS mapping micrographs of two selected areas to investigate the types of precipitates in BG12Cr decorating the prior austenite grain boundaries and lath boundaries. In Figure 4.15, (Cr, Mo, W)-rich carbides, primarily decorating a prior austenite grain boundary, are observed to have a disc-like feature (see white arrows in Cr, Mo, and W maps). (Mo, W)-rich carbides are found adjacent to (Cr, Mo, W)-rich carbides (see blue arrows in W and Mo maps). Numerous small spherical Cu-rich particles are found in the interior of grains (see red arrows in Cu map). Additionally, tiny spherical (Nb, V) (C, N)-rich precipitates are located along the lath boundary (see yellow arrows in Nb and V maps). Figure 4.16 displays the EDS mapping micrographs along a prior austenite grain boundary, identifying the same types of precipitates as in Figure 4.15. (Cr, Mo, W)-rich carbides are clearly observed with a disc-like feature (see white arrows in Cr, W, and Mo maps). Importantly, it seems that the (Cr, Mo, W)-rich precipitates, with an average size close to 70 nm (see white arrows), are the

primary precipitates decorating prior austenite grain boundary, as compared to (Nb,V)(C,N) precipitates (see yellow arrows in C, N, Nb, and V maps). The (Cr, Mo, W)-rich particles exhibit a disk-like feature, unlike the spherical feature of (Nb, V) (C, N) precipitates. The Cu-rich particles, approximately 50 nm in length, appear to form along a lath boundary (see red arrow in Cu map). Moreover, (Nb,V)-rich carbonitride with ~30 nm are observed precipitating along lath boundaries in BG12Cr.

The types of precipitates of BG12Cr in as-received condition can be summarized as below:

$M_{23}C_6$ carbide

Figure 4.17 presents the EDS spectrum from a selected Cr-rich carbide along a boundary and its SAD diffraction pattern. This can be identified as a f.c.c $M_{23}C_6$ carbide with a lattice parameter a=1.06 nm and an average dimension smaller than 70 nm. The distribution of $M_{23}C_6$ can be observed from the EDS mapping in Figures 4.15 and 4.16 (see arrows in C and Cr maps), primarily decorating the prior grain boundaries and interior grain boundaries (e.g., lath boundaries).

Laves phases

Compared to P92, Laves phases were only occasionally observed in as-received BG12Cr material. Figure 4.18 shows a typical spot EDS spectrum from a (W,Mo)-rich particle and its convergent beam electron diffraction (CBED), indicating that (W,Mo)-rich particle is hexagonal $(Fe,Cr)_2(W,Mo)$ Laves phase with lattice parameters of a = 0.47 nm and c = 0.77 nm.

MX phases

From Figure 4.15 (see yellow arrows in N, V, and Nb maps) and Figure 4.16 (see yellow arrows in N, V, and Nb maps), some small spherical (Nb,V)-rich carbonitrides with a dimension

ranging from 5 to 30 nm are observed, decorating the interior grain boundary and prior austenite grain boundary. These (Nb, V) (C, N) precipitates can be classified as MX phases in as-received BG12Cr steel.

Cu-rich particles

As mentioned above, a fine dispersion of Cu-rich particles inside the martensite laths, pinning the dislocations, with a size of approximately 20 nm is clearly observed (see Figure 4.13, 4.14). Large Cu-rich particles with a size of approximately 50 nm in length were observed precipitating along a lath boundary (see Figure 4.16).

In summary, the primary particles are Cu-rich particles with a size of ~20 nm inside the laths and along lath boundaries, (Cr, W)-rich $M_{23}C_6$ carbides with dimensions of approximately 70 nm along boundaries and (V, Nb)-rich carbonitrides, ranging from 5-30 nm in size. $(Fe, Cr)_2(W, Mo)$ Laves phases were occasionally observed in BG12Cr parent metal.

Phase Constituents of BG12Cr in As-received condition

In the as-received condition, the BG12Cr martensitic steel exhibits a complex and intricate microstructure, which was named “tempered martensitic lath structure (TMLS)”. This section provides a detailed analysis of the precipitates observed in pervious part.

Martensitic Matrix:

The primary phase in BG12Cr steel is martensite, which forms the matrix of the material. The martensite in the steel exhibits a lath-type morphology, characterized by elongated and parallel laths (see Figure 5.1a). These laths are observed to have an average width of approximately 300 nm efficiently pinning dislocations to maintain the stability of tempered martensitic lath structure. The lath martensite is the dominant phase and provides the steel with its inherent strength and hardness.

Precipitates:

EDS mapping micrographs present the distribution of precipitates in BG12Cr. Correlated with TEM work conducted on the specimen, the majority of precipitates are Cr-rich $M_{23}C_{6,}$ followed by particles like Cu-rich particles of ~20 nm in size and MX phase. Dense Cu-rich particles predominantly form inside the martensite laths pinning dislocations.

Detailed spot EDS and diffraction analysis revealed that the Cr-rich carbide is the f.c.c $M_{23}C_6$ carbide, characterized by a lattice parameter of a=1.06 nm (as shown in Figure 4.17), which primarily precipitated along boundaries (PAGBs and lath boundaries) with an average size of ~70nm. Furthermore, Figure 4.18 showcases a typical spot EDS spectrum from a (W,Mo)-rich particle, accompanied by its convergent beam electron diffraction (CBED). This indicates that the (W,Mo)-rich particle is a hexagonal $(Fe,Cr)_2(W,Mo)$ Laves phase with lattice parameters of a=0.47 nm and c=0.77 nm. Notably, the Laves phase was occasionally observed in as-received BG12Cr and it precipitated adjacent to the $M_{23}C_6$ carbides (Figures 4.16 and 4.18). Laves phase with relatively small size below 100nm is difficult to observe. Thus, there is possible for Laves phase to have a distribution in BG12Cr. However, compared to P92, there is no obvious fine distribution of Laves phase observed in BG12Cr. Moreover, MX carbonitrides were observed decorating along lath boundaries with an average size of ~30 nm.

Delta Ferrite

In addition to the martensitic phases, small amounts of delta ferrite were observed in as-received BG12Cr (Figure 4.1.d). These delta ferrite regions are sporadically distributed and appear as equiaxed tiny grains within the martensitic matrix (inside the PAGs and along PABGs). The presence of delta ferrite is noteworthy, as it may influence the response of the steel to welding and other thermal treatments. Although it has been suggested that a content of δ-ferrite up to 10% could be acceptable in weld materials, which decreases the chance of

propagation of hot cracks, δ-ferrite should be considered a detrimental phase if it exits in a tube wall material.

4.1.3 Microhardness variations after long term thermal exposure in the two alloys

Figure 4.5 presents the microhardness variation of both alloys after long period high temperature exposure. The drop of microhardness should be due to the recovery of tempered martensite structure. Interestingly, there exists a climb in the BG12Cr microhardness, which is possibly due to the new formation of subgrains. After 10000 hours, the microhardness of BG12Cr and P92 dropped to a similar value which possibly indicated that these two alloys had a similar microstructure stability after same period of thermal exposure. To figure out the microstructure evolution in BG12Cr and its comparison to P92, microstructure characterisation has been done and is detailed in the following sections.

4.1.4 Precipitates in the two alloys after long term (>10^4 hours) thermal exposure

One stress-rupture BG12Cr specimen (labelled as "PT BG12Cr") with the longest rupture life of 10380 hours, was selected to build up a deeper understanding about microstructure evolution in this novel 12Cr martensitic steel at 650°C. Another stress-rupture P92 specimen (labelled as "PT P92") with the longest rupture life of 12234 hours, was selected as a comparison to compare the microstructure stability of these two high chromium content martensitic alloys. All observations were taken from the thread part of the specimen to minimise any influence of stressing.

Figure 4.19 presents the optical micrographs of the specimens after etching. The tempered martensite laths can still be clearly observed in PT P92 (Figure 4.19.a1). However, instead of tempered martensite laths, blocks are frequently observed in PT BG12Cr (Figure 4.19.a2), which indicates a higher microstructure instability compared to P92. Referring to a higher magnification of the selected area, the boundaries are relatively easier to observe in PT BG12Cr

compared to PT P92 (see Figure 4.19.b1, b2). Clear observation of boundaries under optical microscope indicating high density of precipitates decorating along the boundaries.

To have a deeper understanding about the microstructure of these two PT specimens, microstructure characterisation under SEM has been conducted and presented in Figure 4.20 and Figure 4.21. Prior austenite grain boundaries can be observed due to populated precipitates decorations in PT P92 (see Figure 4.20.b). After etching, PAGBs are easily found compared to the as-received specimen, indicating the precipitation along PABGs happened after long period at 650°C (see Figure 4.20.c). Blocky areas are occasionally found, indicating relatively less martensite laths recovery happened in this specimen (Figure 4.20.c). A few micro-voids with a size smaller than 10 μm were found along the boundaries and inside grains. Compared to PT P92, significant difference can be found in PT BG12Cr (Figure 4.21.a, c). Prior austenite grain boundaries can be easily distinguished, and tiny grains are found formed along grain boundaries (see arrows in Figure 4.21.b, c). Moreover, tempered martensite lath structure was difficult to be observed and blocks became the primary structure inside the martensite matrix (Figure 4.21.c), which indicates significant recovery of martensitic structure in BG12Cr after long period high temperature exposure. In other words, the instability of microstructure in BG12Cr is relatively much higher than P92. Besides, micro-voids are occasionally observed in PT BG12Cr compared to PT P92.

To have a better understanding of the tempered martensite lath structure evolution in both alloys after long period at 650°C, EBSD scanning results have been detailed in Figure 4.22 and Figure 4.23. Figure 4.22.c introduces the IPF (Inverse Pole Figure) colouring Y map involving an individual grain of P92. Martensitic laths widening are observed but not very significant, which reveals that the tempered martensite structure is maintained after long period high temperature exposure in P92 steel. However, significant martensitic laths widening were clearly observed in PT BG12Cr. Instead of fine martensite laths in as-received condition (Figure 4.c), blocks

have become the main structure in the prior austenite grains. Although the variation in colour grades can still be observed inside the blocks, the previous tempered martensite lath structure seems fully recovered into blocks in PT BG12Cr (see Figure 4.23.c). The grain boundaries and misorientation profile of both alloys are found to have a similar distribution (Figure 4.22.d and Figure 4.23.d). The recovery of the tempered martensite lath structure is tightly associated with the precipitation evolution in PT BG12Cr. To investigate the precipitate evolution of both alloys after 10,000 hours, some TEM work has been conducted and detailed below.

1) BG12Cr-E exposed under 650°C, Tested duration: 10380 Hours. (ID: PT BG12Cr)

General microstructure

TEM bright field (BF) micrographs of this specimen are displayed in Figure 4.24. Most regions are observed with low densities of dislocations (Figure 4.24.a) and a PAGB labelled with a white dashed line. Relatively small grains with a size smaller than 1 μm are observed, which are populated by particles around (see red arrows in Figure 4.24.a). Martensitic lath structure was occasionally seen and appeared to be similar to the width of block boundaries. Moreover, dislocation annihilations followed by low angle grain boundary formations, which indicates recovery, were frequently observed in PT BG12Cr (see yellow arrows).

Some STEM EDS work has been conducted to characterise the precipitates observed in PT BG12Cr and EDS micrographs are shown in Figure 4.25 and Figure 4.26. Three species of precipitates were observed: (1) Cr, W rich-precipitates that are spherical and 100-500 nm in diameter decorating along boundaries (see arrows in Cr map); (2) W and Fe-rich precipitates larger than 200 nm decorating along boundaries (see arrows in W map); (3) N, V, and Nb-rich precipitates larger than 100 nm with various morphologies decorating along boundaries (see arrow in V map).

However, there are no observations of Cu-rich particles from STEM EDS observations. So, some EDS work of this testpiece had been conducted to understand the evolution behaviour and distribution of Cu-rich particles after long period (see arrows in Cu map, Figure 4.27). It was found that Cu-rich particles coarsened to a size of approximately 300 nm, which located inside the grain.

To understand the types of these precipitates in the specimen, the other microstructure characterisation work has been done and the results are summarized as below:

$M_{23}C_6$ carbides

As shown with arrows in Cr maps from Figure 4.25 and Figure 4.26, correlating with previous study in as-received material, these precipitates can be confirmed to be Cr-rich f.c.c $M_{23}C_6$ carbides. After long period high temperature exposure, it tends to be spherical with 100~500 nm in diameter decorating along boundaries.

Laves phase

(W, Mo)-rich particles were found to be coarsened larger than 200 nm in diameter in PT BG12Cr (see arrows in W, Mo maps in Figures 4.25, 4.26, 4.28). To gain a comprehensive understanding of the precipitates, additional TEM analyses were performed, and results are detailed in Figure 4.29. The low magnification view of this particle (see Figure 4.29.a) shows the difficulty to focus due to a magnetic field caused by the sample, indicating the major phase presented in this specimen can be confirmed to be ferrite.

The recorded SAD file (see Figure 4.29.e, f) exhibits electron diffraction patterns indicating beam directions: [0,0,0][1,0,0],[0,1,2] or [$\bar{1}$, 0,0],[0,0,0],[0,1,2](after tilted to 19°), indicating the crystal structure to be an h.c.p structure (lattice parameters a=0.480 and c=0.788 mm). The EDS spectra of this phase and matrix revealed that the precipitate has a composition of 51Fe-15Cr-2Co-17W-14Mo-Res. (V, Mn, Ni) at%. Consequently, the precipitates can be confirmed

to be C14 ($P6_3/mmc$) type Laves phase $(Fe_{0.70}Cr_{0.30})_2(W_{0.55}Mo_{0.45})$ with an average size greater than 200 nm.

Z phase

(Nb,V)-rich carbonitrides were observed adjacent to the Laves phase mentioned above (see red arrow of V, Nb maps in Figure 4.28). The shell part of the particle is observed to be richer in Vanadium than the core part (see red arrow of V map in Figure 4.28). The core of this particle was observed to be enriched in Nb compared to the shell (see white arrows of Nb map in Figure 4.28). The EDS spectra of different parts in this particle are presented in Figure 4.29. It can be concluded that the chemical composition of the core part is 40N-13V-27Cr-5Fe-14Nb-Res. (W, Mo) at%, 40N-21V-28Cr-4Fe-5Nb-Res. (W, Mo) at% in the rim (shell), and 40N-16V-28Cr-5Fe-11Nb-Res. (W, Mo) at% overall. Correlated with SAD profiles of the particle (Figure 4.30), the particle can be confirmed to be Z-phase with a tetragonal structure (a=0.290, b=0.792nm), which coarsened to over 200 nm.

Cu-rich particles

As listed in previous section, the Cu-rich particles were observed to be coarsened over 200 nm in PT BG12Cr (Figure 4.27). The fine dispersion of Cu-rich particles (< 20nm) in as-received BG12Cr was not observed in PT BG12Cr.

In summary, a significant amount of equiaxed ferritic structures, with minimal dislocations, were identified in PT BG12Cr. Four different types of evolved precipitates were identified, summarized as follows:

1. Cr-based $M_{23}C_6$ carbides, which are the predominant precipitate with a size from 100-500 nm.
2. C14 type Laves phase coarsened over 200 nm.

3. Z phase with a stoichiometric ratio of Cr:(Nb, V) =1:1, many of which have coarsened to the size more than 200 nm and undergo chemical evolutions of Nb and V within a particle.
4. Cu-rich particles coarsened over 300 nm.

2) P92-E exposed under 650°C, Tested duration: 12234 Hours. (ID: PT P92)

General microstructure

Similar microstructure characterisation work was also conducted in PT P92 as a comparison to see the microstructure stability difference of these two alloys. Figure 4.31 shows the TEM bright field (BF) micrograph of PT P92. The majority of the microstructure is observed to be martensitic lath structures, where the boundaries are pinned by particles sized less than 1 μm. Compared to PT BG12Cr (Figure 4.24), the microstructure of PT P92 is finer.

Figure 4.32 and Figure 4.33 show the EDS maps of the specimen to build up a basic understanding of the precipitate's evolution in P92. The major particles found from the figures are Cr-rich precipitates and W-rich particles (see Cr, W map in Figure 4.32-33), which locate primarily along boundaries. These Cr-rich coarsened as large as the ones commonly observed in PT BG12Cr. Moreover, fine V-rich carbonitrides with an average size smaller than 100nm were found and it kept a fine distribution inside the martensite matrix (see V maps in Figure 4.32,33). Nb-rich particles were found to have a similar size as V-rich carbonitrides (see arrow in Nb map, Figure 4.32). Figure 4.34 and Figure 4.35 introduces some precipitates with pinning effects on the boundaries. Besides Cr-rich and W-rich particles, multiple number of V-rich carbonitrides are also found pinning lath boundaries (see V map in Figure 4.34). Similar finds are found in Figure 4.35. Interestingly, similar to the finds in PT BG12Cr, V-rich carbonitride can be seen covering Nb-rich particle (see V, Nb maps in Figure 4.35). To figure out the types of these evolved precipitates, some TEM work has been conducted and is given as below:

$M_{23}C_6$ carbides

Figure 4.36 presents the TEM micrographs and SAD pattern profile of the Cr-rich carbides in PT P92. The precipitate was observed to be precipitated along the lath boundary on low magnification (see Figure 4.36.a, b) and with a disc-like feature smaller than 100 nm in width on high magnification (see Figure 4.36.c, d). It can be concluded as $M_{23}C_6$ carbide with a=1.07nm. As mentioned in previous general microstructure in PT P92, the $M_{23}C_6$ carbide is one of the major boundaries pinning precipitates. Moreover, it has a higher number density and a relatively smaller size than that found in PT BG12Cr.

Figure 4.37 presents a potential phase transformation found in $M_{23}C_6$ carbide from PT P92. Apparently two ellipsoidal particles lining top to bottom were observed (see Figure 4.37.a). TEM dark field (DF) suggests the one on the bottom shows two different crystal structures, divided vertically in the middle of the particle (see Figure 4.37.b). To understand what reason leads to the crystal structure difference, STEM EDS micrographs were shown in Figure 4.37.d. The bottom part of the precipitate clearly can be found to be enriched with Vanadium (see red area) and the left part is enriched in Chromium (see green area). Figure 4.38 shows the EDS spectrum of the top and bottom parts from the $M_{23}C_6$ carbide, clear peaks can be seen at 0.39keV (NKα), 2.17keV (NbLα) and 4.95keV (VKα) in the V rich region, which verifies the potential transformation of $M_{23}C_6$ carbide in PT P92.

MX phase

To figure out the specific type of fine V-rich carbonitrides observed in PT P92, some work has been conducted and shown in Figure 4.39 and Figure 4.40. TEM darkfield and SAD pattern reveal that the fine particle, which is sized well below 100nm, has a f.c.c crystal structure with lattice parameter a=0.42nm. Qualitatively analysis by EDS is shown in Figure 4.40, clear peaks

of Nb and V can be seen in the precipitate. Regarding the crystal structure and lattice parameter, this particle can be confirmed to be MX pinning the lath boundaries in PT P92.

Laves phases

Referring to the studies conducted on as-received P92, the (W,Mo)-rich particles found in PT P92 can be confirmed to be Laves phase, which coarsened to an average size of approximately 270 nm.

In summary, the majority of the microstructure in PT P92 is martensitic lath structures. Three different precipitates have been identified in PT P92:

1. Cr-based $M_{23}C_6$ as a major precipitate, which appears to be finer than the one in BG12Cr. A potential evolution of the carbide was observed with V, Nb, and N partitioning.

2. Fine carbonitrides (MX phase), primarily on lath boundaries (<100nm), which are currently concluded to have an f.c.c structure.

3. Laves phase: The majority of which were concluded to be the same type as those found in BG12Cr, i.e., C14, following the chemical analysis results.

4.2 Mechanical Results

This study was based on previous studies in creep crack growth with compact tension (CT) testpieces. The details of previous creep crack growth tests are detailed in Table 3.1 and the creep crack growth resistance curves with different driving force parameters (K and C*) are introduced in Figure 4.41 and Figure 4.42.

Both the linear elastic stress intensity factor K and elastic-plastic parameters were used to characterise crack growth rates in compact tension specimens. It should be noted here that the data before transition to extensive creep are not included following the standard. An obvious

difference can be seen from these two-creep crack resistant curves with CT specimens. Curves in the da/dt-K plot are mostly separated from each other. Whereas the curves in the da/dt-C* appear to distribute within a narrow band compared to the da/dt-K plot. Based on the studies in CT testpieces, C* parameter is a more suitable driving force parameter to characterise the crack growth compared to K parameter. Moreover, it has been confirmed that C* is time-dependent regarding loading and testing temperature difference referring to previous study finished by Ke Liu. This finding will be detailed in next chapter.

Relying on these previous studies, it is of necessity and important to understand whether the testpiece geometry will influence the C* driving force parameter to characterise the crack growth or not. Thus, ring-notched testpiece approach was applied to verify this proposal.

4.2.1 Creep crack growth in ring-notched testpieces at 650°C

Referring to previous work done by Ke Liu, K is not an appropriate parameter to characterize the crack growth which has been confirmed with CT testpieces. Thus, only C* parameter is considered in ring-notched creep crack growth tests and the plot of C* in ring-notched testpieces is presented in Figure 4.43. Compared to the plot with CT specimens (Figure 4.42), it can be obviously seen that all the curves in the da/dt-C* plot with ring-notched testpieces stayed inside a narrow band. When the C* value is larger than 1N/mm/h, it can be seen that all the curves stay along a single line, confirming that a unique linear relationship exists between all these curves with the application of ring-notched geometry.

Figure 4.44 introduces the creep crack growth resistance curves for two different geometries under different loadings at 650°C. Regardless of the plot distribution in CT testpieces is found to be higher than the plots in ring-notched specimens, all the curves are observed to stay inside a narrow band indicating C* is appropriate time-dependent elastic-plastic parameter to characterize the crack growth. The variability of crack growth rates is one of the key criteria

for assessing the appropriateness of using the C* parameter to characterise creep crack growth behaviour. Compared to the results obtained from CT testpieces creep crack growth tests, similar da/dt-C* curves distribution can be obtained from relatively smaller sized ring-notched testpieces. Details about each ring-notched testpiece creep crack growth test is listed in Table 4.2.

4.2.1.1 Trail creep crack growth test at different stress levels at 650°C (C-PS2)

To validate the novel circular notched creep crack growth methodology with these two alloys, the first trial circular notched creep crack growth test was conducted on P92 at 650°C under 3 different load levels. The increase of load levels was intended to shorten the trial test life. This testpiece was labelled C-PS2. Different observation methods were conducted to build up a specimen processing system for future creep crack growth tests ring-notched testpiece. It should be noted here that the extensometer was not attached for this trail test but it was set for all the rest experiments.

1) Fractography and cross-section observation of C-PS2

Figure 4.45.a presents an optical image of the fracture surface of this testpiece, revealing three discernible creep crack growth regions. The first CCG region was not visually obvious, which was continued for 307 hours in total, and no obvious potential difference increased. The second creep crack growth region was grown under a stress level of 170 MPa to accelerate the test, which is the circular grey region near by the notch edge. This region was interrupted after approximately 166 hours. Then the stress level was increased to 250 MPa, which was the inner dark region of the specimen. It can be concluded that three load levels introduce three different circular CCG regions in this specimen. The successful formation of circular CCG zones in these testpieces indicate that the ring-notched geometry can be applied for creep crack growth

tests. Following similar analysis procedures conducted on previous CT testpieces, the fractography observations C-PS2 is detailed in Figure 4.46.

In the beginning stage of CCG zone, some intergranular fracture feature can be observed (Figure 4.46.b, c) due to low loading levels. Then dimples were observed in the middle stage of CCG zone indicating a ductile fracture mechanism (Figure 4.46.d). Shear dimples were frequently observed in the final stage of CCG due to plastic deformation. Figures 4.47 and 4.48 present the optical images and SEM micrographs of cross-sectioned C-PS2 specimen. Micro-voids can be visually seen and primarily distributed below the CCG fracture surface (Figure 4.47.a). In the beginning stage of CCG, micro-voids were found formed along the prior austenite grain boundaries (PAGBs) (Figure 4.47.b2 and Figure 4.48.a1, a2). Compared to the beginning stage, coarsened micro-voids connected through grains were found indicating a ductile fracture mechanism (Figure 4.47.d2 and Figure 4.48.b1, b2). In summary, although the boundaries between the three loading levels were not easy to distinguish, similar intergranular to ductile dimples fracture mechanism transformation was clearly observed in ring-notched fractured testpiece compared to CT fractured testpiece.

4.2.1.2 Creep crack growth test at 100 MPa at 650°C (C-PL1)

1) Creep crack growth plots

Figure 4.49 illustrates plots of creep crack length (mm), loadline displacement (mm), loadline displacement rate (mm/h), and creep crack growth rate (mm/h) versus time (hours), together with the creep crack growth rate versus C* plot for CPL-1. The loadline displacement curve (Figure 4.49.a) reveals three discernible stages of creep crack growth. The crack length increases steadily, while the loadline displacement sees a rapid increase in the initial stage, which can be attributed to the crack tip blunting effect. Referring to Figure 4.49.c, deceleration succeeded by an acceleration is evident in the loadline displacement rate versus time curve.

These stages correlate with the creep crack growth rate versus time curve (Figure 4.49.b). The loadline displacement rate curve indicates that the accelerating stage of crack growth makes up roughly 20% of the test life for CPL-1, whereas the steady growth stage encompasses the remaining 80% of the whole test life.

2) Fractography and cross-section observation

Figure 4.45b shows the fracture surface and the potential wire weld position of the specimen from optical microscope observations. A circular creep crack is clearly observed, albeit somewhat irregular. The creep growth is uneven, as indicated by crack length on one side being significantly larger than the other. A very narrow creep crack area (~364 μm) can be seen between notch edge and light fatigue fracture region. This narrow band, located adjacent to the potential wire position, possibly increase the uncertainties of potential drop measurements in this test.

In order to investigate the fracture mechanism of this test, SEM fractography details are shown in Figure 4.50. From Figure 4.50.a1-a2, clear different zones of creep crack growth region can be obviously observed. The fracture surface nearby the notch edge was found to be covered by films of oxide. For the beginning stage of CCG zone, intergranular features can be found (Figure 4.50.b1, b2) and dense needle-like oxides were clearly observed on a high magnification SEM image (Figure 4.50.b3). Thus, intergranular fracture should be the fracture mechanism for the beginning stage of this test. Figure 4.50.c1-c3 presents the middle stage of CCG, which is also called the transition stage of CCG. Dense dimples can be easily observed (Figure 4.50.c2) and tiny dimples were found decorating the edge of larger dimples (Figure 4.50.c3). Figure 4.50.d1-d3 show the final stage of CCG, dense dimples were clearly observed (Figure 4.50.d2) and dense tiny dimples were found decorating the edge of larger dimples (Figure 4.50.d3). Dimples found in this zone appeared to be more irregular and larger than the

dimples found in the transition stage (Figure 4.50.c2, d2). Ductile fracture mechanism should be the dominant mechanism in the last two stages of this test. In summary, the fracture mechanism of this test should be mixed fracture mechanisms.

In order to fully understand the fracture mechanism and the microstructure evolution in CPL-1, the OM&SEM fractography images taken from longitudinal cross-sectioned testpiece are shown in Figure 4.51. Dense micro-voids were observed distributed across the whole specimen with a depth of approximately 1mm below the fracture surface (Figure 4.51.d). Creep crack growth region can be easily distinguished by the covering of an oxide film (Figure 4.51.a). Micro-voids were observed formed along PAGB (Figure 4.51.c1), which should be the beginning stage of crack growth in this test. After the crack extended longer, coarsened micro-voids can be seen inside the grain and some cracks across prior austenite grains (PAG) are frequently observed. Moreover, a high density of particles was found precipitated primarily along the PAGBs through all the observation areas (Figure 4.51.b1-c1). The mixed fracture mechanism can be confirmed.

3) SEM EDS analysis on the precipitations

EDS point analysis was conducted to better understand the precipitation in this test piece, with the EDS electron images and spectra provided in Figure 4.52. The chemical compositions for the selected particles are listed. Therefore, it can be concluded that the precipitates along the prior austenite grain boundaries close to the fracture surface are (Cr, W, Mo)-rich carbides and Mo, W-rich carbonitrides in this test piece.

4.2.1.3 Creep crack growth test at 170 MPa at 650°C (C-BS3)

1) Creep crack growth plots

Figure 4.53 shows creep crack length (mm) and loadline displacement (mm), loadline displacement rate (mm/h), creep crack growth rate (mm/h) versus time (hours) plots, creep

crack growth rate versus C* plot of C-BS3. The first creep crack growth stage is not obvious from the loadline displacement versus time plot. The crack length grows steadily whereas the loadline displacement increased rapidly in the initial stage (Figure 4.53.a). Referring to Figure 4.53.c, there is first a deceleration and a second acceleration in loadline displacement rate versus time curve (Figure 4.53.c), which correlate with creep crack growth rate versus time curve (Figure 4.53.b). The loadline displacement rate curve shows that the accelerating stage of crack growth occupies less than 20% of the life for C-BS3. The steady state crack growth region occupies a large part of the life, and then the crack grows rapidly in the accelerating stage for sample C-BS3.

2) Fractography and cross-section observation

Figure 4.45.f shows an optical image of C-BS3 fractured sample and a circular creep crack can be clearly observed (dark region between light fatigue region and notch edge).

In order to investigate the fracture mechanism of C-BS3, fractography work has been done and SEM fractography of the fracture surface of C-BS3 is shown in Figure 4.54. For this specimen, two areas were selected for investigation and low magnification micrographs of the CCG zones are shown in Figures 4.54.a1 and a2. High magnification micrographs of area-a1 showing intergranular fracture can be seen before the end of the CCG zone (Figure 4.54.b2, b3). Dimples are clearly observed (Figure 4.54.b4) indicating a ductile fracture mechanism in the final CCG stage. Moreover, ductile fracture was found across the whole CCG region (Figure 4.54.c1, c2) and dimples were found in the end of the CCG region (Figure 4.54.c3). In summary, the fracture mechanism of C-BS3 is a mixed fracture mechanism.

To fully understand the fracture mechanism and microstructure evolution, SEM and OM images taken from longitudinal cross-sectioned creep crack growth C-BS3 testpiece are shown in Figure 4.55. Micro-voids were found primarily below the creep crack fracture surface, which

is different from P92 (Figure 4.55.e). Figure 4.55.a1-a2 show an overall view of the creep crack growth region including the notch edge and a micro-crack was found below the notch. Micro-voids were found along PAGBs and inside the PAGs in the crack growth initiation stage (Figure 4.55.b1, b2). Coarsened micro-voids with a width of ~10μm were found close to the fracture surface. As the crack extended further, micro-voids were found primary inside the grains and some of them were found to have a tendency to merge at grain boundaries to form larger micro-voids (see red arrow in Figure 4.55.c2). Moreover, cracking across PAG was observed in the final CCG stage. All these findings confirm a mixed fracture mechanism driven by microcavities coarsening in this testpiece.

3) SEM EDS analysis on the precipitates

The EDS point analysis and spectra of particles decorating PAGBs from C-BS3 is presented in Figure 4.56. Cu-rich particle was labelled “spectrum 1”, decorating the PAGBs. Coarsened (Cr,V)-rich carbonitrides were found along PAGBs labelled as “spectrum 2”, which should be $M_{23}C_6$ carbides. (W,Mo)-rich particle was labelled as “spectrum 3”, which should be Laves phase.

Figure 4.57 presents the particles decorating the lath boundaries. All these particles were observed to be Cu-rich with Mo and W, which indicates that Cu-particles are possibly the precipitation location of (Mo,W)-rich Laves phase in BG12Cr.

4.2.1.4 Creep crack growth test at 200 MPa at 650°C (C-PS3&C-BS2)

1) Creep crack growth plots

Figure 4.58.a1 and Figure 4.58.b1 display the creep crack length (mm), loadline displacement (mm), and the creep crack growth rate versus C* plots for C-PS3. The extensometer used for recording loadline displacement was firstly attached to the specimen in this test for practice. Due to an interruption in the machine—caused by reaching the testing machine variation

limitation—the data was analysed after the interruption, which explains the disappearance of data points in the plots.

Figure 4.58.a2-d2 illustrate the plots of creep crack length (mm), loadline displacement (mm), loadline displacement rate (mm/h) and creep crack growth rate (mm/h) versus time (hours), as well as the creep crack growth rate versus C* plot for C-BS2. A steady extension in crack length and a similar growth trend in loadline displacement are observed. In Figure 4.58.a2, only two stages of creep crack growth are clearly identified from the loadline displacement curve. Compared to the C* curve of C-PS3 (Figure 4.43) under the same testing conditions, C-BS2 exhibits a lower creep crack growth rate for the same C* value. There is a noticeable deceleration followed by acceleration in the loadline displacement rate over time, as presented in Figure 4.58.d2. For C-BS2, the steady-state crack growth region constitutes a significant portion of its lifespan, after which the crack grows rapidly in the accelerating stage. Figure 4.58.b2 shows the unique relationship (log-log) between the creep crack growth rate and the C* driving force for the C-BS2 specimen. It should be noted here that, under the same testing conditions, the test life of BG12Cr (~1346 hours) was approximately fourteen times than the test life of P92 (~96 hours) (see Table 4.2).

2) Fractography and cross-section observation

Figure 4.45.c Despite the fracture surface being covered by an oxide film, a circular creep crack region can still be observed, situated between the light fatigue region and the notch edge. Compared to C-PS3, Figure 4.45.f shows an optical image of the fractured C-BS2 surface, where a relatively obvious and uniformly circular creep crack is noticeable, starting from the notch edge. The boundaries between the fatigue fracture region and creep crack growth (CCG) zone can be clearly distinguished for both testpieces.

3) SEM EDS analysis on the precipitations

In order to investigate the fracture mechanism of C-PS3, some fractography work was done and SEM fractography of fracture surface of C-PS3 is shown in Figure 4.59. Three regions are easily observed, which are the notch edge covered by severe oxidation, the CCG zone and the fatigue to fracture region (Figure 4.59.a). Figure 4.59.b and Figure 4.59.c present high magnification SEM images of the CCG zone. The specimen was found to be deformed (Figure 4.59.b) and ductile dimples can clearly be observed (Figure 4.59.c). Dense need-like oxide was found covering the fracture surface at the beginning of the CCG zone (Figure 4.59.d, e).

Compared to C-PS3, the SEM fractography of C-BS2 under the same testing conditions is given in Figure 4.60. The relatively flat notch edge can be clearly seen in the specimen and intergranular fracture and ductile fracture were observed in the beginning stage of crack growth (Figure 4.60.c). Ductile fracture was frequently observed in the middle stage and dimples were found in the final stage of CCG zone (Figure 4.60.d, e). Both observations indicating a ductile dominated fracture mechanism in this testpiece, whereas intergranular may dominate the creep crack growth in the very early stage of this test.

To fully understand the fracture mechanism and microstructure evolution, SEM and OM images taken from a longitudinal cross-sectioned creep crack growth testpiece are shown in Figure 4.61 (C-PS3) and Figure 4.62 (C-BS2). A high density of precipitates is observable along the prior austenite grain boundaries, and micro-voids, less than 10 μm in size, have formed on the grain boundaries, as corroborated by Figure 4.61.b1-b2. As the crack extended longer, dense tiny micro-voids (~1μm) were found close to the fracture surface. The grains around these areas were found to be deformed due to plastic deformation and these cavities cannot be easily located. Figure 4.61.e displays a low magnification image of the cross-section area, the microcavities are found primarily formed close to the fracture surface and some areas below the central region.

The OM and SEM micrographs of cross section through C-BS2 are shown in Figure 4.62. Numerous micro-voids are observed near the fracture surface (Figure 4.62.a) within the creep crack growth region. Micro-voids were found along prior austenite grain boundaries away from the fracture surface (Figure 4.62.b1), suggesting that intergranular cracking may be the dominant fracture mechanism in the crack propagation stage. Relatively larger micro-voids sized around 10μm, were observed inside the PAGs close to the fracture surface at the beginning of crack growth (Figure 4.62.b2). As the crack grew longer, it can be found that the micro-voids are formed inside the grains close the fracture surface (Figure 4.62.c2) and some of them have a tendency to connect together to form relatively larger micro-cavities (red arrow in Figure 4.62.c2). In the final stage of creep crack growth before the test was interrupted, micro-voids were found inside the PAG (white arrow in Figure 4.62.d2) and some micro-voids were found coarsened together to form a larger micro-cavity (red arrow in Figure 4.62.d2), indicating micro-voids coarsening ductile fracture mechanism. Moreover, precipitates were found primarily decorated along the boundaries (PAGBs and lath boundaries). Figure 4.62.e displays an optical image of the cross section. Microcavities were found primarily in the CCG region and close to the fracture surface.

3) SEM EDS analysis on the precipitations

Energy-Dispersive X-ray Spectroscopy (EDS) point analysis and spectra from specimen C-PS3 are presented in Figure 4.63. The chemical compositions of particles were presented in Figure 4.63. The findings indicate the presence of Chromium (Cr)-rich carbides adorning the prior austenite grain boundaries (PAGBs) with tungsten content.

Figure 4.64 shows Energy-Dispersive X-ray Spectroscopy (EDS) point analysis and spectra of particles from areas with high particle density in C-BS2. Compared to C-PS3, a high density of particles was found precipitated along boundaries. Three particles were selected for EDS

analysis and exhibited the following chemical composition, the results were listed in Figure 4.64. Particle 1 (labelled as “spectrum 1”) can be concluded as a Cr-rich carbonitride and particle 2 (labelled as “spectrum 2”) can be concluded as a V-rich nitride. Compared to particles found for EDS analysis in C-PS3, the particles were visually larger in C-BS2.

4.2.1.5 Creep crack growth test at 150 MPa at 650°C (CPL-4&CBL-1)

1) Creep crack growth plots

Figure 4.65 displays the plots of creep crack length (mm) and loadline displacement (mm), loadline displacement rate (mm/h) and creep crack growth rate (mm/h) versus time (hours) plots and creep crack growth rate versus C^* plot of CPL-4. Compared with the curve of creep crack length, loadline displacement increased rapidly in the initial stage, then transitions to a steady increase due to crack tip blunting (Figure 4.65.a1). It can be concluded from Figure 4.65.b2 that there is first a deceleration and second an acceleration for loadline displacement rate which correlates with the creep crack growth rate versus time curve. The steady state crack growth region occupies a significant part of the creep crack growth test, and the acceleration only occupies less than 20% of the test for CPL-4. Compared to C-PL4, different creep crack growth behaviour was observed from mechanical result curves from C-BL1 (see Figure 4.65.b2-d2). The total test life of C-BL1 was approximately 3234 hours which is around six times the total test life of C-PL4 (~536 hours), indicating the BG12Cr has a higher creep crack growth resistance compared to P92 under these testing conditions. This is also revealed from the creep crack growth plots. It takes more time (>1000 hours) for BG12Cr to reach a similar creep crack growth value compared to P92 (see Figure 4.65.a1, a2). The crack length extension and loadline displacement both exhibit a similar steady growth trend and accelerate upon entering the extensive creep stage. Interestingly, only two phases of creep crack growth can be observed from the loadline displacement curve (Figure 4.65.b2). Like C-PL4, the steady state

crack growth region accounts for a significant portion of the lifespan (approximately 80%) in C-BL1, after which the crack grows rapidly in the accelerating stage.

2) Fractography and cross-section observation

Figure 4.45.d displays an optical image of the fracture surface of CPL-4, where a uniform circular crack can be observed (the dark region between the notch edge and light fatigue fracture region). To investigate the fracture mechanism of CPL-4, SEM fractography images of this test piece fracture surface was taken and are presented in Figure 4.66. Figures 4.66.b1-b2 present the initial propagation region, where voids approximately the same size as the grain size of P92 can be seen. This suggests that intergranular fracture is likely the dominant fracture mechanism for this stage. Figures 4.66.c1-c2 depict the middle stage of the CCG region, where ductile fracture is observed to dominate the extension of crack growth. Figures 4.66.d1-d2 show the final stage of the CCG region. Micro-voids were observed near the end of the CCG region due to the increase of net section stress and obvious ductile fracture can be clearly observed for the final CCG stage.

An optical micrograph of the fracture surface of C-BL1 is shown in Figure 4.45.e. A circular creep crack can be observed, although it is not very uniform. To understand the fracture mechanism, some fractographic work has been carried out, which is outlined in Figure 4.67. Figure 4.67.a provides an overall image of a partial circular crack. Figures 4.67.b1-b2 show the initial crack propagation stage, coarsened micro-cavities were frequently observed and intergranular fracture possibly existed in this stage. The notch edge was undergoing severe plastic deformation and is like a “shear-lip zone” (see red arrow in Figure 4.67.a1) found in stress-ruptured tests in BG12Cr. This finding indicates that necking deformation possibly happened in this testpiece. Figures 4.67.c1-c2 present the middle stage of the creep crack fracture surface, where ductile fracture is observable. Figures 4.67.d1-d2 depict the final stage

of the creep crack growth, where ductile dimples can be observed. Moreover, the originally regular fracture surface is difficult to observe, replaced instead by the characteristics of a fracture surface covering irregular small particles, which indicates the martensite matrix possibly lost its strength to maintain the martensite matrix structure (Figure 4.67.d2). In summary, compared to C-PL4, more ductile fracture was observed in C-BL1 indicating a ductile fracture mechanism dominated crack growth progress. Intergranular fracture may exist in the very beginning stage.

To fully understand the fracture mechanism and microstructure evolution in CPL-4, SEM images taken from the longitudinal cross-sectioned creep crack growth CPL-4 test piece are presented in Figure 4.68. Figure 4.68.a is an overall secondary electron image that shows the whole CCG region, which was taken from the area shown in OM micrograph (Figure 4.68.e). The machined notch edge is hard to visualize (see Figures 4.68.b1). Figure 4.68.b2 shows a high magnification image of the initial crack growth region, where some micro-voids smaller than 5μm are found inside the PAGs and along the PAGBs. These micro-voids were also found to have the tendency to form micro-crack locating on PAGBs. As the crack extends further, fine micro-voids (~5μm) form closes to the fracture surface (Figure 4.68.c1) with the majority of them forming along PAGBs (see Figure 4.68.c2-c3). Those micro-voids found along the PAGBs tend to form a micro-crack along prior austenite grain boundary. A high-density of precipitates is also found along PAGBs and lath boundaries (4.68.c3). A similar micro-void distribution was also observed in the final CCG stage (Figure 4.68.d1). Figure 4.68.e displays an optical image of the cross-section region. Microcavities were found primarily formed in the CCG region and close to the fracture surface. All these finds confirm that micro-void coarsening ductile fracture should be the dominate fracture mechanism in C-PL4.

Figure 4.69 shows SEM and OM images taken from a longitudinal cross-section through creep crack growth CBL-1 testpiece. Figure 4.69.a-b is an overall image of the notch and crack area.

Corresponding with fractographic observations, the entire CCG fracture surface was covered by a dense layer of oxide. Coarsened micro-cavities were clearly observed close to the fracture surface (see red arrows in Figure 4.69.a, b). Figure 4.69.c displays close-up image of the crack propagation area. There is a high-density distribution of precipitates along the prior austenite grain boundaries and lath boundaries. Micro-voids were observed formed along the PAGBs and inside PAGs, some of them was found connecting to form micro-cavities. Figure 4.69.d displays an optical image of this cross-section region. Microcavities were found primarily in the CCG region and close to the fracture surface. The observations from cross section area of CBL-1 confirmed the micro-voids coarsening ductile fracture mechanism in this test.

3) SEM EDS analysis on the precipitations

The EDS point analysis and spectrum from C-PL4 are shown in Figure 4.70. The chemical composition of different spectrums and matrix were presented. Particle (1) (labelled as "spectrum 1") can be concluded as a (W, Mo)-rich carbide on a PAGB. Particles (2) (labelled as "spectrum 2") can be concluded to be Cr-rich particles along grain boundaries (lath boundaries).

The EDS point analysis and spectra of selected particles from CBL-1 testpiece are shown in Figure 4.71. Particle (1) (labelled as "spectrum 1"), precipitated inside the martensite matrix, can be identified as a (W,Mo)-rich carbide. Particles (2) (labelled as "spectrum 2") is identified as (W,Mo,Co)-rich carbides decorating along the grain boundary.

4.2.1.5 Comparison between CCGT conducted under the same testing conditions with a different geometry

In this section, the group of C-PL4 and C-BL1 was selected to compared with the group of CT testpiece with 6kN under 650°C (Table 4.1-4.2). The OM, SEM fractography and cross section observations of two CT specimens (P92-6kN-650°C and BG12Cr-6kN-650°C) are detailed in

Figures 4.72-4.74. The test life of BG12Cr (886 hours) was around 5 times than the test life of P92 (188 hours).

1) P92 tested at a temperature of 650°C under 6kN loading (CT)

SEM fractography from this test are shown in Figure 4.72. Dimples are the dominant features throughout the whole creep crack growth region, which indicates a ductile fracture failure mechanism. It can be also found from the optical image (Figure 4.72.a) that significant lateral contraction had occurred in this testpiece indicative of significant matrix deformation during the test.

Figure 4.72.c1-c2 show a cross-section of this testpiece. A secondary crack can be found at the start of the creep region, which grew through PAGs. Coarsened micro-voids are found primarily formed in the interior of the PAGs. Some very large voids were found within PAGs around the secondary crack further confirming the ductile fracture failure (microcavities coarsening) mechanism.

2) BG12Cr-E TWT tested at a temperature of 650°C under 6kN loading (CT)

Representative SEM fractography taken at different crack lengths along the creep crack growth path are shown in Figure 4.73. It was found that at the beginning of creep crack growth, the failure mechanism is mainly intergranular along PAGBs (Figure 4.73.a-b). After some crack growth, the failure mechanism was found to gradually turn into a mixture of ductile fracture (Figure 4.73.c-d) and at the final stage of crack growth ductile fracture became dominant in the appearance of equiaxed dimples (Figure 4.73.e-f).

Secondary and backscattered electron images of the cross-section of the initial short crack in this test are shown in Figure 4.74. Micro-voids were found along the PABGs in the early stage of creep crack growth (see Figure 4.74.c). After the crack grew longer, coarsening micro-voids

were found formed mainly in the interior the PAGs and a micro-crack was found formed in the final stage of crack growth below fracture surface (Figure 4.74.d).

It can be concluded that, similar fractography can be obtained by relatively smaller ring-notched testpiece compared to traditional CT testpieces, which reduce the cost of experimental materials. Meanwhile, the test life of CCGT in ring-notched testpieces was longer than CT specimens indicating longer steady creep crack growth stage.

4.2.2 Stress-rupture under 650 ºC test result

4.2.2.1 Stress versus rupture life plots

Variations in applied stress levels with different rupture life at 650ºC are displayed in Figure 4.75. Different stress rupture behaviour is observed between the two alloys. BG12Cr demonstrates a longer rupture life when subjected to a high stress level (>100 MPa) compared to P92. Conversely, P92 shows a longer rupture life when a lower stress level (<100 MPa) is applied. The strength of BG12Cr dropped significantly after approximately 10000 hours compared with P92. This strength loss could be associated with the microstructure evolution that occurs in BG12Cr after 10,000 hours of testing. The variations in micro-hardness of these two types of steels are plotted in Figure 4.5. Interestingly, it appears that BG12Cr steel tends to lose its strength after 3000 hours, as suggested by the hardness histogram. After 10,000 hours of high-temperature thermal exposure, the micro-hardness of BG12Cr drops by around 100 HV_5 compared to the AS condition. In contrast, the micro-hardness of P92 drops by 60 HV_5.

4.2.2.2 Microstructure investigation on the gauge section

Stress-rupture fractography

Seven long term stress-ruptured samples of the two alloys were received from Baowu Steel to investigate the failure mechanism and microstructure evolution. Figure 4.76 displays the optical images of these samples. It should be noted that some images did not cover the grip

regions due to the larger size of the test pieces. Necking deformation is clearly observed from all the BG12Cr stress-ruptured samples, whereas no necking deformation is evident from the P92 stress-ruptured samples. Thus, BG12Cr appears to be more ductile compared to P92 steel under the same testing conditions (stress and temperature).

In order to have a basic understanding of the fracture mechanism for these samples, SEM fractography of fractured samples are shown in Figure 4.77. Compared to P92 ruptured specimens, obvious necking features with elliptical cross-sections are seen in BG12Cr specimens under various stress rupture deformation conditions (see Figure 4.77 (1)-(7)).

1) P92-E-90MPa

Figure 4.77.1-a shows the central region of the stress-ruptured fracture surface, very few micro-voids were found in the central region. Figure 4.77.1-b is taken from the lip zone. Ductile dimples are clearly observed, and tiny ductile dimples were found on the inner walls of large particles (see the arrow), indicating a ductile fracture mechanism. Oxidation was found inside the dimples and the inner walls of shear dimples.

2) P92-E-100MPa

From Figure 4.77.2-a, ductile fracture surface can be clearly observed, with the major feature in the fibre zone being ductile equiaxed dimples. Shear dimples were found in Figure 4.77.2-b, which locates in the shear-lip zone. Additionally, dense tiny dimples decorate the outer walls of large dimples. The dense array of dimples in the central region indicates that the dimple rupture leads to ductile fracture of the specimen under these stress-rupture conditions.

3) BG12Cr-E-65MPa

From Figure 4.77.3, an obvious cone fracture surface is observed, consisting of three regions: the fibre zone in the central region, a radiation zone, and a shear-lip zone at the outer periphery,

indicating ductile fracture. Dimples and micro-voids were observed in the fibre region (see Figure 4.77.3-a). Dense shear dimples are observed in the shear-lip zone (See Figure 4.77.3-b).

4) BG12Cr-E-75MPa

From Figure 4.77.4, an obvious cup fracture surface is observed, and three zones are also discernible. Dense dimples were clearly found in the fibre zone of the ruptured surface, and some tiny dimples formed along the outer wall of some larger dimples (see Figure 4.77.4-a). Figure 4.77.4-b shows the shear-lip region of the fracture surface, where shear dimples surrounded by tiny, sheared dimples can be clearly seen.

5) BG12Cr-E-90MPa

From Figure 4.77.5, a cup fracture surface with a relatively larger shear-lip zone is observed. A high magnification image of the fibre zone shows a high density of equiaxed dimples, indicating a dimple-lead ductile fracture mechanism. Notably, some dimples reached a dimension of approximately ~40 μm (Figure 4.77.5-a). Moreover, several small dimples with diameters ranging from 1 to 5 μm were observed on the walls (inner and outer) of large dimples. Shear dimples were found in the shear-lip zone (see Figure 4.77.5-b).

6) BG12Cr-E-100MPa

From Figure 4.77.6, a cup fracture surface is observed. Numerous large dimples with an average dimension of ~15 μm were observed and the outer wall of these large dimples were decorated by several tiny dimples with an average dimension ranging from 1 to 5 μm in the fibre zone. Moreover, shear dimples are observed in the shear-lip zone.

7) BG12Cr-E-110MPa

From Figure 4.77.7, a cup fracture surface is observed. Large uniform dimples with an average dimension of ~20 μm were observed and the outer wall is decorated with numerous small

dimples (~2 μm) in the fibre zone. Serpentine glides were observed on the walls of the dimples (See arrow in Figure 4.77.7-a). Shear dimples were observed on the edge region (see arrow in Figure 4.77.7-b).

In summary, no necking deformation was found from P92 stress-ruptured testpieces. On the contrary, necking deformation exists in all the BG12Cr stress-ruptured testpieces and cup-and-cone fractured surfaces were clearly observed. Ductile dimples were frequently observed in the fibre zone. The size of these dimples were found to increase with the increase of stress levels.

Cross-section SEM observation

To fully understand the fracture mechanism of these high-temperature stress-ruptured samples, metallographic sections cut perpendicular to the loading direction were analysed under SEM, and the BSE images are provided in Figures 4.78-4.84.

1) P92-E-90MPa

Figure 4.78.a provides an overview BSE image of the cross-sectional area of specimen P92-E tested under conditions of 90 MPa and 650°C. Three areas were selected for analysis (see red rectangular areas). Figure 4.78. b illustrates an area close to the edge of this specimen, where some micro-voids have been detected (indicated by the arrow). Figure 4.78.c magnifies the micrographs of area-a, revealing micro-voids with dimensions of approximately 20 μm concurrently, a high density of precipitates is visible at this area. Boundaries were not very easy to distinguish which indicates that no high density of precipitates formed along boundaries. Figure 4.78.d exhibits a close-up micrograph of area-b, where numerous microcavities ranging from 1 to 2 μm in size are seen possibly along the prior austenite grain boundaries. It appears these microcavities have a propensity to form micro-cracks. Figure 4.78.e details area-c, where a micro-crack of approximately 200 μm in length is identified in the central region of the

fracture surface. Figures 4.78.f-g show regions far from the fracture surface, where a density of microcavities has formed along boundaries, particularly lath boundaries.

2) P92-E-100MPa

Figure 4.79.a displays BSE images from the longitudinal cross-section of the P92 stress-ruptured sample at 650ºC and 100 MPa. Figure 4.79.b offers a close-up of area-a. Several micro-cracks are evident below the fracture surface (refer to Figure 4.79.a). Numerous microcavities were observed in the fracture surface frontier compared to last specimen (see Figure 4.79.b), and a micro-crack was found formed close to the fracture surface, vertical to the stress direction. Figure 4.79.c is a high magnification image of area-b, revealing the details of the micro-cracks. Magnified views of areas distanced from the fracture surface are displayed in Figures 4.79.d-e, suggesting that the majority of micro-cavities primarily form within the PAG and along the lath boundaries.

3) BG12Cr-E-65MPa

Figure 4.80.a presents low magnification BSE images of the longitudinal cross-section of the BG12Cr stress-ruptured sample at 650ºC and 65 MPa. Figures 4.80.b-c provide magnified micrographs near the necking edge, clearly showing micro-cavities. Figures 4.80.d-e show high magnification views of regions beneath the fibre zone where dense micro-cavities were observed. A micro-crack, which is perpendicular to the stress direction, is also noticeable. The micro-crack was found formed perpendicular to the micro-cavities (Figure 4.80.e). Figures 4.80.f-g are close-up micrographs of areas distant from the fracture surface, where microcavities have formed along boundaries.

4) BG12Cr-E-75MPa

Figure 4.81.a reveals a low magnification BSE image taken from the longitudinal cross-section of the BG12Cr stress-ruptured sample at 650ºC and 75 MPa. coarsened microcavities are

noticeable near the fracture surface in region a (refer to Figure 4.81.b, c). Dense micro-voids with lengths ranging from a few micrometres to hundreds of micrometres was found beneath the fibre zone of the fracture surface (see Figure 4.81.d, e). Micro-crack approximately longer than 100 μm can be observed far from the necking area in region b (see Figure 4.81.f). Microcavities formed within the grains can be seen in the area far from the necking region (see Figure 4.81.g).

5) BG12Cr-E-90MPa

Figure 4.82.a provides a low magnification BSE image taken from the longitudinal cross-section of the BG12Cr stress-ruptured sample at 650ºC and 90 MPa. Figure 4.82.b displays a high magnification micrograph of area-a, where micro-cavities is clearly evident near the fracture surface, which possibly caused by necking deformation before rupture. When neck occurs, the cross-sectional area in the necked region decreases, leading to a significant increase in stress levels in area-a. Shear deformation exists in the necking edge region. Dense coarsened microcavities are seen in the central area beneath the fracture surface (refer to Figure 4.82.c). The micro-cavities tend to form micro-cracks (see Figure 4.82.d). Figure 4.82.e presents the region beneath area-c, still clearly showing the presence of micro-cavities. Figures 4.82.f-g illustrate magnified views of the region far from the necking area. Microcavities formed within the grains are clearly visible.

6) BG12Cr-E-100MPa

Figure 4.83.a depicts a low magnification BSE image from the longitudinal cross-section of the BG12Cr stress-ruptured sample at 650ºC and 100 MPa. Figures 4.83.b-c illustrate that large instance of micro-cavities close to the fracture surface, and their density tends to increase closer to the central region of the necking area. Smaller micro-cavities can still be clearly seen away from the fracture surface in the central region (see Figure 4.83.d). Figures 4.83.e through 4.83.g

offer magnified views of regions far from the necking deformed area of the specimen. Microcavities with widths ranging from 10 to 20 μm are observed, primarily forming within the PAGs.

7) BG12Cr-E-110MPa

Figure 4.84.a displays a low magnification BSE image from the longitudinal cross-section of the BG12Cr stress-ruptured sample at 625ºC and 110 MPa. Two areas labelled as a and b, have been selected for higher magnification observation. Figure 4.84.b reveals slender micro-cavities close to the necking edge and beneath the fracture surface. A larger area of dense micro-cavities was found in the central region beneath the fracture surface (see Figure 4.84.c). Figures 4.84.d-e show the region below the central area, where slender martensite is apparent. Figures 4.84.f-g present the regions far from the necking areas. The microvoids across two PAGs can be clearly seen, and microcavities are primarily formed within PAGs.

4.2.2.3 Microstructure investigation on the thread section

Figure 4.85 presents optical photographs from the thread section of all the stress-ruptured specimens in the sequence of stress levels. Figures 4.85.a-b are optical micrographs of P92 after 12234 hours and 7756 hours. The martensite lath structures and PAGBs can still be clearly observed in P92 steel after long time high temperature exposure. Several spherical dark voids, indicating there was still creep-strain induced due to very limited specimen received from Baowu lab, can be observed along the PAGBs After long time high temperature thermal exposure, a high density of martensite laths can still be observed in P92 steel. The TEM specimen was then taking from the very bottom of the thread part to avoid the influence of creep. Figures 4.85.c-g introduce the BG12Cr microstructure after 10380, 5723, 3048, 8597 and 7286 hours. Compared to P92 steel after long time high temperature exposure, the PAGBs in BG12Cr steel can be easily observed indicating a high density of particles precipitated along

boundaries. However, some martensite laths structure is replaced by blocky regions (or blocks), which are called “martensitic lath widening” phenomena.

From Figure 4.85.c-g in the sequence of test duration, the occupation of blocky regions increases inside the martensite matrix. Interestingly, the martensite laths to blocks transformation happened from 3048 hours in BG12Cr steel (Figure 4.85.e). Tiny grains, which recrystallized on the PAGBs, are frequently observed on the PAGBs after 5723 hours (Figure 4.85.d). Compared to P92, the microcavities are occasionally seen in BG12Cr steel.

In order to understand the microstructure evolution in the undeformed region of these two types of steels, some BSE micrographs (no etching) and some SE micrograph (etched) were taken from the undeformed regions in Figure 4.86 and Figure 4.87.

1) P92-E after 7756 hours

Figure 4.86.2-a shows a low magnification micrograph of the undeformed region from specimen P92-E 100MPa under 650°C and Figure 4.86.2-b is the magnified view of the selected area. The precipitates are mainly decorated along the boundaries (primarily PAGBs) and lath boundaries.

2) P92-E after 12234 hours

In Figure 4.86.1-a, tempered martensite laths structure can still be clearly observed. A magnified view of the selected area is shown in Figure 4.86.1-b. The precipitates are mainly decorated along the prior austenite grain boundaries and lath boundaries.

3) BG12Cr-E after 3048 hours

Figure 4.86.5-a shows a low magnification image of the undeformed region of specimen BG12Cr-E, 75 MPa under 650°C after 3048 hours. In Figure 4.86.5-b, which is a magnified view, the precipitates are mainly decorated along boundaries, primarily on PAGBs and block

boundaries. Microcavities smaller than 5 μm are found in the interior of the grains. Some tiny grains with different features (spherical, spindle-like, disc-like) are found recrystallized on PAGBs and in the interior of PAGs.

4) BG12Cr-E after 5273 hours

Figure 4.86.4-a shows a low magnification image of the undeformed region of specimen BG12Cr-E under 650°C after 5723 hours. In Figure 4.86.4-a, which is a magnified view, the majority of the precipitates are decorated along the PAGBs and some of them precipitated along boundaries (packet boundaries, block boundaries and lath boundaries). Microcavities are observed to have formed in the interior of grains and tiny grains are found along PAGBs.

5) BG12Cr-E after 7286 hours

In Figure 4.86.7-a, a low magnification micrograph of specimen BG12Cr-E under 650°C after 7286 hours is shown. Microcavities formed inside the martensite matrix and tiny grains recrystallized along PAGBs can be clearly observed (see Figure 4.86.7-b).

6) BG12Cr-E after 8579 hours

In Figure 4.86.6-a, a low magnification micrograph of specimen BG12Cr-E under 650 °C after 8579 hours is shown. Figure 4.86.6-b shows a magnified view of the martensite matrix. Precipitates are found primarily along boundaries. Tiny grains are found recrystallized along the PAGBs and in the interior of PAGs. Microcavities are found in the interior of grains (especially inside blocky areas) and some of them are vertical to the direction of martensite laths.

7) BG12Cr-E after 10380 hours

Figure 4.86.3-a presents a low magnification BSE micrograph of BG12Cr steel under 650 °C after 10380 hours. In Figure 4.86.3-b, which is a magnified view of PAGs including martensite

matrix, the precipitates are primarily decorated along the PAGBs. Martensite laths are occasionally seen in the BSE image inside PAGs. A number of recrystallized tiny grains are clearly observed along the PAGBs (see the red elliptical area).

Figure 4.87 presents SE micrographs of the ruptured specimens after etching to give a clear understanding of the blocky phenomena, which means the transformation from martensite laths to blocks. From Figure 4.87.2-2, the martensite laths can still be clearly seen in P92 steel after 10^4 hours. However, from Figure 4.87.3-7, blocky phenomena seem to appear before 3048 hours in BG12Cr steel and the occupation of blocks inside the martensite matrix increased as the test life increases. Dense recrystallized tiny grains with different features (primarily disc-like in appearance) are clearly observed along PAGBs after 8597 hours. However, the recrystallized grains can be easily observed from 3048 hours. These martensitic laths widening will lead to the loss of strength during long time high temperature testing, which will be discussed and analysed in detail in the next chapter.

CHAPTER 5 Discussion and Analysis

5.1 Initial characterisation of materials

5.1.1 Microstructure of As Received BG12Cr Martensite Steel

This novel 12Cr heat resistant steel, was proposed and manufactured to be applied in more severe conditions such as higher temperature above 650°C and higher stress levels compared to Grade 92 steel in some critical components, e.g., steaming tubes and pipes. The chemical composition of this steel is given in Table 3.1. Addition of Co is expected to enhance thermomechanical properties such as creep [61-63]. A successful case can be found in the design of MARBN steel, which has an addition of 3% Co and higher Cr compared to T/P92 steel [64,65]. The high Cr content introduces a higher oxidation resistance, and this design is widely applied in 11-12 wt.%Cr martensitic steels [66-69]. Another successful case is 12Cr2W grade 122 (T/P122), which was widely used in power plants in Japan [69]. However, the addition of Cr content will also introduce the precipitation of Z-phase (Cr(V,Nb)N) during long term high temperature exposure. In 12 pct Cr martensite steels, the expected precipitation time of Z-phase is around 10,000 hours. The precipitation of Z-phase is detrimental for the stability of martensite laths structures, which leads to the loss of creep strength [70]. The heat treatment of BG12Cr has been detailed in Chapter 2. It can be clearly seen that finer tempered martensite lath structure, with a relatively larger prior austenite grain size compared to Grade 92, have been achieved through this processing procedure. However, the heat treatment procedure details of P92 were not supplied by Baowu Steel.

Correlating with all the microstructure work given in last chapter, a schematic microstructure of as received BG12Cr is given in Figure 5.1.a. In as-received BG12Cr, there is an average size of prior austenite grains of ~ 37.5 μm with little delta ferrite (see Figure 4.1-4.2). The precipitates are mainly decorated along PAGBs and lath boundaries and fine particles are

distributed within the martensite laths pinning dislocations. Figure 4.1.d shows that the precipitates decorating along the delta ferrite boundaries, which are expected to be detrimental for the stability of the martensite matrix. This will be discussed in coming section.

To characterise the microstructure of a martensitic steel, it is important to understand its tempered martensitic structure. A tempered martensite structure (TMLS) is composed of prior austenite grain boundaries (PABGs) and subgrain structure. The blocks and martensite laths are described as sub-grains in tempered martensitic structure. A consistent and uniform single-phase microstructure is essential for attaining superior creep strength, as established in previous research [71]. In addition, the utilization of tempered martensite is beneficial, as it allows for the full exploitation of subgrain hardening. Subgrain boundaries are recognized as significant barriers to the movement of dislocations during creep, a phenomenon that has been extensively documented [71-74]. This subgrain hardening approach is suggested to offer a more potent strengthening effect compared to the Orowan stress resulting from precipitates, thereby contributing to enhanced creep strength [72]. Thus, it is of great importance to understand the microstructure of as-received BG12Cr steel and the strengthening effect from the subgrain of its martensite matrix.

5.1.2 Microstructure of As Received P92 Martensite Steel

P92 steel, which has been studied and applied for decades, has been chosen as a base material for comparison with the BG12Cr. Similar to the microstructure in as-received BG12Cr steel, a tempered martensite lath structure can be clearly observed from optical micrographs (see Figure 4.1.a-b). The prior austenite grains in as-received P92 have an average size of approximately 17.3 mm, which is smaller than the average PAG size in BG12Cr (see Figure 4.2.a).

The chemical composition of P92 has been detailed in Table 3.1. The alloy design of this metal has been described in detail in Chapter 2.

5.1.2.1 Phase Constituents of P92

P92, in the as-received condition, is widely recognized for applications in high temperature power plants and presents a rich and intricate microstructure. This section analyses the various phase constituents identified within this material found in this study, emphasizing on their morphological characteristics, distribution, and explores the potential implications these phases may have on the materials mechanical and thermal properties.

Martensitic Matrix:

The schematic microstructure of P92 is shown in Figure 5.1 (b). The primary phase in P92 steel is tempered martensite, which forms the matrix of the material. This tempered martensite is characterized by a lath-type morphology, with laths appearing as elongated, parallel entities. These laths are observed to have an average width of approximately 400 nm. Compared to P92, it can be confirmed that the BG12Cr has a finer tempered martensitic lath structure in the as-received condition, which indicates possibly better heat-resistance properties.

Precipitates:

The distribution of precipitates is clearly presented in Figure 4.7. Correlating with the TEM work conducted, the primary types of precipitates in as-received P92 can be concluded as: (1) Cr-rich carbides, which can be confirmed to be $M_{23}C_6$ precipitates with an average dimension of ~50nm decorating along boundaries; (2) (W,Mo)-rich intermetallic, which can be confirmed to be the Laves phases (M_2N) precipitated adjacent to $M_{23}C_6$ carbides along boundaries; (3) fine V/Nb-rich carbonitrides, which can be confirmed to be MX phase precipitated primarily intergranular the martensitic laths pinning the dislocations [75].

In summary, it can be concluded that the structural fortitude of the P92 martensite matrix predominantly emanates from the Cr-rich $M_{23}C_6$ precipitates, the Laves phases (M_2N), and a fine dispersion of V/Nb-rich (MX) carbonitrides. The TEM observations indicated that Cr-rich $M_{23}C_6$ precipitates to decorate along the (sub)boundaries of the martensite lath structure, along with the Laves phases which were predominantly localized along the PAG boundaries beside these carbides. The V/Nb-rich carbonitrides were observed primarily distributing intragranularly martensitic laths effectively pinning dislocations. These particles effectively strengthen the tempered martensite lath structure against potential recrystallization during extended thermal exposures.

In summation, P92 was strengthened by fine distribution of precipitates (e.g., $M_{23}C_6$ precipitates, Laves phase, V-rich carbonitrides) along boundaries. Differ from P92, BG12Cr seems to be strengthened with fine distribution of Cu-rich particles inside martensite laths to restrict martensite lath recovery. Moreover, Laves phase was occasionally seen in BG12Cr rather than P92 in as-received condition.

5.2 Comparative Analysis of as-received alloys

5.2.1 Detailed Comparison of Initial Microstructures

In the martensite matrix of BG12Cr, primary precipitates are decorated along the PAGBs and lath boundaries. Empirical observations from optical micrographs of martensitic steels in the as-received state indicate that BG12Cr steel presents a more refined tempered martensitic laths structure and a comparatively larger PAG size than P92 (Figure 4.1). Correlating with the EBSD scanning micrographs and PAG size distribution histograms (see Figure 4.2-4.4), BG12Cr shows a finer width of approximately 300 μm (Figure 4.6.c and Figure 4.13.a) and higher density of martensite laths (from EBSD scanning area) compared with P92, in which the martensite laths have a width of approximately 400 μm. In addition, BG12Cr has an average PAG size of approximately 37.5 μm, which is larger than the size of PAG in P92 (approximately

17.3 μm). A precise classification of the martensite lath density within the PAGs will further improve the understanding of these martensitic steels. The finer TMLS the alloy has, theoretically the better heat resistance this alloy has, which is associated with a higher density of dislocations and nanoprecipitates from TMLS [76,77]. The frequency of LABs (=2°) in P92 (~0.38) is lower than in AS BG12Cr, which is approximately 0.45.

The martensite matrix of BG12Cr is predominantly strengthened by two factors: 1). Precipitates decorating along boundaries (primarily $M_{23}C_6$ carbides) and particles dispersed intergranular martensite laths (primarily Cu-rich particles); 2). dislocation hardening from martensite lath structures. Compared to P92, Laves phase was occasionally observed in the as-received BG12Cr alloy. However, a fine distribution and density of the Laves phase in as-received alloys possibly contributes significantly to the creep resistance of high chromium content martensitic steels.

The major variation in these two steels is the Cu-rich particles in BG12Cr. The carbides can effectively increase the martensite matrix strength, and the recovery during creep deformation will also be effectively retarded by these dispersed carbides [78,79]. Although the creep rupture life should be extended with the increase of fine dispersed carbides, these carbides will result in the decrease in the toughness and oxidation resistance. That is the reason why Cu was added to high chromium martensitic alloy design. Cu particles can precipitate within the martensite laths [80-82] at separate sites from carbides [83]. Also, the addition of Cu is beneficial for the phase balance to restrict the formation of delta ferrite in martensite steels, because Cu tends to broaden the austenite phase region without lowering b.c.c.→f.c.c. reversion temperature so much [84]. A successful example is the 9Cr4Cu martensitic steel. Yuichi and Toshihito found that this had about a seven times longer creep-rupture life than the 9%Cr base steel [85]. In the present study, the principal pinning effect blocking the lath dislocation recovery in BG12Cr can be attributed to the high density of Cu-particles both along the lath boundaries and within

the laths. The concentration of Cu profoundly impacts the ductility of creep-resistant steels. This is because the precipitation of Cu-particles within the martensite laths leads to dislocations tangling with these particles. This tangling results in a substantial pinning effect, acting as a barrier to block the recovery of martensite laths. In essence, the movement of dislocations is inhibited by these Cu particles, ensuring efficient prevention of recovery [86]. Moreover, an optimal concentration of Cu (approximately 4%) not only improves creep strength but also restricts the excessive formation of δ-ferrite in high Cr martensite heat-resistant steels [87]. Although a fine dispersion of Cu-particles was achieved in BG12Cr, delta ferrites were still clearly observed formed along grain boundaries and some of them were found interior the grains. Cu-content should be confirmed with Baowu steel which is beneficial for understanding its effect in BG12Cr.

5.2.2 Summary and comparison of as-received P92 and BG12Cr

In short, compared with as-received P92 alloy, a finer tempered martensite lath structure consisting of high-density smaller martensite laths is observed in as-received BG12Cr alloy. The martensite matrix of both alloys is strengthened by the martensite laths dislocation hardening and precipitation strengthening.

In as-received P92 alloy, the strength of the matrix is increased by precipitation hardening, which includes Cr-rich $M_{23}C_6$ precipitates, (W,Mo)-rich Laves phase and (Nb,V)-rich carbonitrides (MX phase). Ti-rich carbonitrides are also observed inside the grains which perform a role in precipitation hardening. Ti-rich carbonitrides are stable and show a slow coarsening rate under high temperature service, hence providing the precipitation hardening to increase the creep strength [88,89]. All the particles mentioned above play as obstacles for the recovery of dislocations in martensite laths.

In as-received BG12Cr alloy, the strengthening effect of precipitation mainly comes from: Cr-rich $M_{23}C_6$ precipitates, Cu-rich particles and (Nb,V)-rich carbonitrides (MX phase). Considering very few Laves phase particles were observed, the precipitation hardening of BG12Cr should not involve Laves phase. Compared with P92, the high-density dispersion of Cu-rich particles inside the laths plays an essential role as barriers to prevent martensite recovery during long periods of thermal exposure or creep.

5.3 Microstructural Evolution under Thermal Exposure

The enhancement of creep strength is not a simple outcome of incorporating key alloying elements, such as tungsten (W) and molybdenum (Mo). Researchers, including Kumura and collaborators, extensively examined over 40 heat-resistant steels and alloys to assess creep rupture life, as depicted in Figure 5.2 [90,91]. Their investigation unveiled those steels with high alloy content demonstrated elevated short-term creep strength. However, as rupture life extended within the mid-stress regime, an abrupt decline in creep strength became evident, illustrated schematically in Figure 5.3. Referring to the stress-rupture curves of BG12Cr (Figure 4.75), the strength drop in the mid-stress regime can be clearly observed compared to P92. The shape of the curve in Figure 5.3 is the characterized by a sigmoidal inflection, denoting a rapid decrease within the mid-stress range [92]. Subsequent research has identified microstructural instability as the cause behind this abrupt drop in strength in the mid-stress regime [92]. The similar significant drop in the Regime M was clearly observed in BG12Cr around 3800 hours, which indicates the higher instability of microstructure in BG12Cr compared to P92.

The as-tempered martensite initially present undergoes a transformation under the influence of elevated temperatures and high stress during extended operational periods. This evolution is attributed to the inherent nature of tempered martensite, which exists as a non-equilibrium phase. The process of microstructural evolution in martensitic heat resistant steels can be

characterized by various manifestations, including the widening of laths, the vanishing of PAGBs, the emergence of sub-grains, the precipitates coarsening, and the occurrence of new phase precipitation. The subsequent sections delve into a comprehensive review of how these processes happen in BG12Cr after 10,000 hours.

5.3.1 Evolution in BG12Cr and P92 Steel after 10,000 Hours of Exposure

To assess the microstructural evolution and stability of the novel BG12Cr martensite steel under prolonged high-temperature exposure, specimens were subjected to thermal exposure of >10,000 hours at elevated temperature (650°C in this study). The microstructure evolution of BG12Cr was analysed in detail and compared to the microstructure evolution of P92 in this section.

Martensitic lath widening

In some previous studies on 10%Cr heat resistant steels, the lath widening after creep at 600°C was observed. Following deeper studies have proved that the martensitic lath width increased with the rupture life. The widened laths eventually expanded and evolved into subgrains after long-term creep for 8345 hours at 600°C in 10Cr heat resistant steel. The TEM observations of the progress of martensitic lath widening are shown in Figure 5.4 [92]. In the present study, the as-tempered martensite laths structure was occasionally seen in PT BG12Cr after 10,000 hours of thermal exposure and martensitic lath widening was frequently observed inside the prior austenite grains (Figure 4.23-24). The original fine martensitic lath structure was replaced by dense of blocky regions, which can be explained as expanded martensitic laths or blocky martensitic laths.

It has been noted that a comprehensive study by Sawada and colleagues [93] involved conducting *in situ* transmission electron microscope (TEM) observations on the phenomenon of lath widening. The investigation focused on a thin foil sample of normalized 9Cr2W4Co

steel subjected to tempering at 667°C under an applied load of 98 N, as depicted in Fig. 5.5. The underlying mechanism of lath migration was elucidated, revealing a process wherein localized sections of the lath boundary exhibited protrusions and migration. This cyclic bulging and migration of localized sections culminated in the collective migration of the entire lath boundary. The martensitic lath migration mechanism can be explained as that the beginning of lath migration starts in some local parts then repeats and expands to the migration of the complete lath boundary. Meanwhile, relatively small laths would decrease and disappear as the larger lath widening ongoing. However, there is no martensitic lath widening change during the aging progress due to high thermal stability of the lath structure, compared to the as normalization condition [94-95]. Consequently, the driving force behind the phenomenon of lath widening has been attributed to the accumulation of strain resulting from martensitic transformation or creep deformation [93].

This insight sheds light on the complex interplay between microstructural evolution and mechanical behaviour in high-temperature materials.

Compared to PT BG12Cr, the martensite lath structure can still be clearly observed after a long period of thermal exposure in PT P92 (>10^4 hours) (Figures 4.6,4.31). Compared to PT BG12Cr, clearly the stability of the TMLS in PT P92 is higher. Lath widening happened in P92 but was relatively inconspicuous referring to the EBSD scanning results of -as-received P92 and PT P92 (see Figure 5.1).

In summary, the factors which initiate the martensitic lath widening phenomenon can be summarized as a process in which strain acts as the driving force. Then the widened laths will tend to grow larger, and the small laths will shrink. If the lath migration follows the mechanism in Figure 5.5, this process can be effectively prevented by decorating the lath boundaries with precipitates [93]. As shown in Figure 5.1, the primary precipitate in both steels along the lath

boundaries and PAGBs is $M_{23}C_6$, a relatively larger size particle. So, the lath boundary will be expected to enter into the inside of adjacent laths where the boundaries are decorated with relatively smaller MX precipitates during the bulging out progress. The previously fine dispersed Cu-particles lost their pinning effects after coarsening to larger Cu-particles. This design is efficient for BG12Cr in the short term but not very suitable for long period application. As a result, the lath bulging out progress cannot be easily interrupted until it reaches another lath boundary or grain boundary.

Disappearance of PAGB

In both steels after long term high temperature exposure, PAGBs are found to be invisible and can only be tracked by the precipitates which decorated them in some regions (see redlines in Figure 5.6). PAGBs, can be thought of as walls of dislocations, which trap and eject dislocations in martensitic heat-resistant steels [92]. $M_{23}C_6$ precipitates significantly stabilize the PAGBs and pin the movement of PAGBs even though it coarsened to a certain size after a long period. The reason why this type of precipitate gradually loses its pining effect can be ascribed to the precipitation of Laves phase adjacent to it. In PT BG12Cr, the precipitation of Laves phase during long time thermal exposure is unavoidable. High density of coarsened Laves (>200 nm) phase can be clearly observed decorated along the boundaries in PT BG12Cr (see W, Mo map in Figure 4.26). It is only occasionally observed in AS BG12Cr. The emergence of the Laves phase brings about two notable outcomes. Firstly, it leads to the absorption of $M_{23}C_6$ precipitates by forming and growing on them, which is called the “swallowing behaviour” of Laves phase in high Cr heat resistant steels [96]. Secondly, the larger Laves phase particles tend to gather along the PAGBs. The phenomenon of Laves phase clustering concurrently entails the absorption of other useful particles. Consequently, this clustering behaviour liberates the PAGBs from the pinning effect of other potent precipitates such as $M_{23}C_6$. Ultimately, this leads to the gradual vanishing of the PAGBs through dislocation motion. Referring to Figure

5.6.a, the PAGB where Laves phase with an average size larger than 200 nm had formed, was observed to have totally disappeared in PT BG12Cr. This behaviour is also observed in PT P92 (see Figure 5.6.b), however, the Laves phase coarsened to a relatively smaller size.

Emergence of subgrains in PT BG12Cr

The emergence of subgrains with size less than 1μm, with polygonal shape, can be easily observed from TEM micrographs shown in Figure 5.7. Similar findings were found in 10Cr steel by Yan in 2023 [92]. The predominant method of enhancing the strength in tempered martensitic steels is through the carbide-stabilized substructure hardening mechanism, as extensively documented [97-103]. However, in the context of 9-12% Cr ferritic/martensitic heat-resistant steels, it is notable that subgrain boundaries play a pivotal role in obstructing the movement of dislocations especially in short term applications (<10,000 hours). This underscores the significance of subgrain hardening as a crucial mechanism for bolstering creep resistance [104]. The formation of subgrains can be explained in two aspects: a) the influence of creep deformation and increase of testing temperature; b) the influence of coarsened precipitates [92]. The creep deformation and the increase of temperatures will lead to the acceleration of subgrain formation due to the increase of quantity and mobility of dislocations, which is in agreement with the results of Panait et al. [106] and Cerjak et al [106]. In the present study, the formation of subgrains can be explained as the result of dislocation movement at high temperatures, which leads to the polygonization and the formation of walls of dislocations. The walls of dislocations will eventually become the boundaries of subgrains (see Figure 5.7, marked as yellow arrows). Considering the specimen was taken from an unstrained region, the subgrain coarsening in PT BG12Cr should be controlled by the stability of precipitates [104].

In short, for BG12Cr, the TMLS will eventually evolve into a subgrain structure after a long period of thermal exposure. The mechanism of this evolution can be summarized as shown in Figure 5.8. Hence the loss of strength in BG12Cr after a long period of high temperature exposure should also be related to martensite recovery, which was the formation of new subgrain structure (blocky areas). Whereas the stability of subgrains is tightly associated with the pinning effect from $M_{23}C_6$ carbides in both alloys (see Figure 5.9, red arrows show $M_{23}C_6$ carbides). The pinning force from MX is relatively small compared to $M_{23}C_6$ carbides so it cannot stabilize the subgrain boundaries. Some $M_{23}C_6$ carbides in PT BG12Cr around subgrains were observed to coarsen to greater than 500 nm in diameter which is detrimental. Clearly it has a higher coarsening rate compared to P92 under similar conditions. This can be explained as the reason why PT BG12Cr also loses its subgrain strengthening after 10,000 hours. The loss of the pinning effect of $M_{23}C_6$ carbides will be detailed later. In BG12Cr, once the coarsening and migrating of the subgrain boundaries has started, the loss of creep strength will start simultaneously. The larger the subgrains are, the lower the dislocation density will be inside this structure. The decrease in dislocation density is revealed by the decrease of the microhardness of the material. The hardness of BG12Cr started to show a high decrease due to the drop in dislocation density, which correlates with the hardness histogram of BG12Cr (see Figure 4.5).

Coarsening of precipitates

1) $M_{23}C_6$ carbides

$M_{23}C_6$ carbides, which finely precipitate along grain boundaries with a high density after tempering in the as-received condition, play a significant role in stabilising the boundaries in 9-12%Cr martensitic heat-resistant steels. These carbides will coarsen to a certain size range under the influence of strain and temperature during long periods of high temperature exposure.

Compared with Laves phase and MX type carbonitrides, $M_{23}C_6$ type carbides play a significantly more important role in the stabilization of tempered martensite structures during creep or thermal exposure. Also, it will have a relativly higher coarsening rate in long-term creep [105]. Some studies have proved that the pinning pressure from $M_{23}C_6$ type carbides was approximately 200% to 400% larger than the other two types of precipitates during creep [107]. Coarsened $M_{23}C_6$ carbides are clearly found in PT BG12Cr with a dimension range from 100 to 500 nm (See Cr Map in Figure 4.26). The coarsened $M_{23}C_6$ carbides are also the primary precipitates in PT P92 but they have a relatively small size (100-200 nm), which means a lower coarsening rate compared to PT BG12Cr under the same period of thermal exposure. In 10%Cr heat resistant steels, it has been found that the $M_{23}C_6$ carbides can still be effective GB stabilizers when they have coarsened to a range of 100-200 nm [92]. It was found from the TEM results of PT BG12Cr that coarsened $M_{23}C_6$ carbides with an average size larger than 200 nm, ware frequently observed, which lost the pinning effect to restrict martensite recovery. The rapidly coarsen phenomena of $M_{23}C_6$ carbides in BG12Cr should be the primary reason leading to the loss of strength. However, the addition of Cobalt [108] and Boron [109-111] can effectively reduce the coarsening rate of $M_{23}C_6$ carbides referring to some studies. It seems that the addition of Cobalt and Boron does not deaccelerate the coarsening process of $M_{23}C_6$ carbides in BG12Cr.

2) MX carbonitrides

Compared to $M_{23}C_6$ carbides, MX carbonitrides are much more stable during long periods of thermal exposure and applied as lath boundaries stabilizer. The higher stability of MX phase along boundaries can strengthen the dislocation hardening and prevent the martensite laths from recovery. It is worth nothing that compared with the other particles ($M_{23}C_6$, Laves phase), the pining effect of MX phase is remarkably smaller [107]. Fine MX precipitates (<100 nm) can be clearly observed decorating lath boundaries in PT P92. There are no MX carbonitrides

observed in BG12Cr after 10,000 hours, which is confirmed to be transferred into Z-phase. This will be discussed in the coming sections. MX has a significant higher stability, revealed by size, chemical composition and volume fracture, even under creep conditions with strain induced [112].

Precipitation of new phases

In 9-12%Cr martensitic steels (especially Cr>10%), it is easy for the precipitation of some new phases during long term thermal exposure with or without the creep strain influence. Typically, new precipitations are of two types: 1) Laves phase, 2) Z-phase. In PT BG12Cr, both new precipitates are observed. The precipitation and nucleation mechanism of these phases will be analysed in detail in the following sections. The effect of these precipitates on the loss of strength in BG12Cr will also be discussed.

1) Laves phase

In this section, the Laves phase in PT BG12Cr will be characterized. The precipitation behaviour (nucleation and growth) will also be analysed. Then, the effect of Laves phase on the martensitic matrix of BG12Cr will be analysed and discussed in detail.

The emergence of the Laves phase initially came to light within ternary Mg alloys. This phase was found to materialize under AB2 stoichiometries, facilitated by a specific range of atomic radii ratios spanning from 1.1 to 1.6 [112]. In 9-12%Cr heat-resistant steels, Laves phase, which is rich in tungsten and molybdenum, is usually observed in types as Fe_2W, Fe_2Mo or $(Fe, Cr)_2(W, Mo)$ [105].

Compared to the carbides mentioned above, the precipitation of Laves-phase, which is occasionally observed in as-received BG12Cr, is frequently observed in PT BG12Cr. Even though the Laves phase is occasionally observed in the as-received condition, it cannot be concluded as there is not a fine distribution of Laves phase in as-received material. Small Laves

phase precipitates are difficult to find. Laves phase need to be larger than 200nm in size then it can be clearly observed under SEM or TEM [112]. In PT BG12Cr, C14 type Laves phase is clearly observed with a dimension larger than 200 nm, which verified the similar results mentioned previously. As shown in Figure 5.1.a-b, the locations of Laves phase are along the boundaries and always adjacent to $M_{23}C_6$ carbides. Hence the coarsening behaviour of Laves phase in BG12Cr can be concluded as: (1) in the AR condition, the Laves phase precipitated along lath or gain boundaries in needle-like structures; (2) evolved new precipitation of Laves phase will be present in large black rectangular or spherical particles along boundaries. Similar coarsening behaviour of Laves phase was also observed in studies of 10%Cr heat-resistant steels, where it is also found that one side of coarsened Laves phase particles tends to be closely adhered to lath boundaries or grain boundaries [92]. Figure 5.10.c-d shows a different precipitation behaviour of Laves phase in PT BG12Cr, where it is at the boundaries of possible δ-ferrite or recrystallized ferrite boundaries and block boundaries. It was found that a higher density of Laves phase decorated the grain boundaries and formed closely to $M_{23}C_6$ carbides in the appearance of needle-like or spherical shapes. Laves phase can be easily distinguished from BSE images due to the W and Mo, which have large atomic number, which explains why Laves phase are always bright in BSE images. The appearance of Laves phase have been proved to be different along the δ-ferrite boundaries, where it tends to be irregular spherical in appearance [113,114]. The high density of Laves phase decorating along δ-ferrite boundaries can be explained through different aspects: (1) δ-ferrite is rich in W and Mo, which are the important composition elements to form Laves phase [92]; (2) there are no substructure flaws comparted to martensite matrix. A schematic illustration of Laves phase nucleation and growth is shown in Figure 5.11.

It is necessary to discuss the detrimental effect of the precipitation of Laves phase. A high density of Laves phase is clearly observed in PT BG12Cr, which grows adjacent to and on

$M_{23}C_6$ carbides (See Figure 4.25-27). Similar precipitation behaviour has been found in some other studies by Dimmler et al. [96]. The coarsening of Laves phase will lead to the consumption of fine precipitates nearby [115]. This is also revealed by the Cr element detected from Laves phase in EDS mapping results (Figure 4.25-27). As a result, the process of precipitation of Laves phase and its growth will lead to instability of neighbouring $M_{23}C_6$ carbides and MX carbonitrides. Especially for the $M_{23}C_6$ carbides, it is the primary pinning particles in 9-12%Cr heat-resistant steels. However, the stabilizer effect from it will be significantly influenced by the formation of Laves phase after long period thermal exposure.

It should also be noted here that Cu-rich particles are found inside the laths and along the lath boundaries (See Figure 5.1). In PT BG12Cr, the fine dispersion of Cu-particles inside the laths were not observed. However, the EDS scanning maps show Laves phase containing Cu-rich particles (see Figure 4.27, W and Cu maps). It can be presumed that Cu-rich particles possibly provide a nucleation site for Laves phase to precipitate and grow in PT BG12Cr. Similar studies by Sauthoff et al. also found that Laves phase occasionally grew on Cu-rich particles [116]. It has been found that the dense dispersion of Cu-rich particles pinning the laths in previous sections. However, it can be assumed that Cu-rich particles may be nucleation sites for some detrimental precipitation after long-term high temperature exposure. Meanwhile, previous fine dispersion of Cu-particles will gradually be replaced by coarsened Cu-rich particles, which cannot prevent martensitic lath recovery after long time thermal exposure. These phenomena should be considered into future BG12Cr modification. Also, suitable addition of Si [117] can effectively restrict the growth of Laves phase in high chromium steels. Cobalt can decrease the solubility of W and Mo in the martensitic matrix, which was also verified in the work of Cui et al [119].

2)Z phase

Binder et al. [118] firstly observed Z-phase in 1950 in an Nb alloyed creep resistant austenite steel. It was identified as a tetragonal crystal structure of CrNbN by Jack et al. [122]. The Z-phase observed in PT BG12Cr, can be sorted as modified Z-phase (containing Vanadium), which was initially found in 18Cr-12Ni-VNbN austenite steel by Andren et al. [122] in 1985. This differs from the original Z-phase found by Binder, in that the chemical composition of modified Z-phase is Cr (V, Nb) N and it has a cubic crystal structure. The precipitation of modified Z-phase only occurs after long term high temperature exposure and then coarsens with low density [121, 123-125] and has the highest precipitation rate at 650°C [125].

Based on the TEM results (see Figure 4.30), (Nb,V)-rich carbonitrides (Z-phase) were observed to have coarsened to larger than 100 nm in BG12Cr after 10,000 hours. In the as-received condition, the original (Nb,V)-rich carbonitrides (MX-phase) were measured to have a dimension of ~16 μm in diameter. A gradual transformation from MX phase to Z phase is expected to happen in 12 pct Cr martensite steels after 10,000 to 30,000 hours [126]. The two possible processes of Z-phase nucleation are shown in Figure 5.12 and it seems that Z-phase formation followed the 2nd path in BG12Cr based on the EDS scanning results (Figure 25). In this study, the MX phase was found to have transformed to Z-phase in PT BG12Cr and was found in the location of the original MX phase. It was found that Z-phase always precipitated along martensite lath boundaries and PAGBs, which were originally decorated with MX carbonitrides [127]. This differs from Laves phase, which relies heavily on plastic flow [126]. Cr plays the most significant role as the driving force in Z-phase precipitation and growth. For instance, in 9%Cr heat-resistant steels like P92, the precipitation of Z-phase is very slow and has less influence on the population of MX phase after 10^5 hours at 650°C. When the content of Cr was increased to 10.5%, a strong acceleration of Z-phase precipitation was clearly observed [92]. In the present study, due to the higher Cr content (>12%), the precipitation of Z-phase in BG12Cr occurred much earlier compared to 9%Cr steels, after around 10,000 hours.

Nitrogen is also influential to the formation of Z-phase but not that significant compared to Cr [128]. Co and C will also influence the driving force of Z-phase. Once the Z-phase started to coarsen, the adjacent $M_{23}C_6$ carbides started to become unstable and become unable to tie up Cr. Hence the precipitation of Z-phase not only consumes the most stable MX carbonitrides but also decreases the stability of $M_{23}C_6$ carbides, which is the primary stabilizer for the lath boundaries in BG12Cr. Also, the high content of Cobalt in BG12Cr will result in the reduction of Cr affinity to the ferrite matrix, which also promotes the precipitation of Z-phase. Above all, this can explain why the Z-phase is found to have coarsened in BG12Cr PT after just 10,000 hours.

The precipitation of Z-phase should be one of the primary reasons why BG12Cr loses its strength faster than P92 during long term high temperature exposure. It can be explained by the precipitation of Z-phase consuming fine MX precipitates directly and $M_{23}C_6$ carbides indirectly. Similar studies have proved that Z-phase was the major reason why the creep strength dropped significantly in some 11-12%Cr heat resistant steels after short-term creep (<15,000 hours) [123,130]. Cr content difference therefore can be considered to be the primary reason for the Z-phase precipitation behaviour difference between BG12Cr and P92.

In summary, the progression of microstructural changes in BG12Cr can be categorized across five key areas: (1) expansion of martensitic laths, (2) disappearance of PAGBs, (3) emergence of subgrains, (4) precipitates coarsening, and (5) new precipitation and phase transformation, including Laves-phase and Z-phase.

The first three aspects pertain to substructural evolution, all ascribed to the continuous displacement and annihilation of dislocations. Notably, martensitic lath widening is defined by a specific process propelled by strain or deformation during creep. The vanishing of austenite grain boundaries results from the diminished pinning effect on dislocation movement,

attributed to coarse precipitates like Laves-phase. Subgrains take shape through dislocation movement within laths. Typically, lath widening and subgrain formation correlate with reduced hardness and dislocation density, which eventually result in the strength reduction in BG12Cr.

The latter pair of transformations centres on precipitate coarsening. MX carbonitrides, characterized by remarkable thermal stability, exhibit consistent behaviour under long-term high-temperature creep conditions. In contrast, $M_{23}C_6$ carbides grow at a slightly accelerated rate compared to MX carbonitrides. The precipitation of Laves phase and Z phase, accompanied with the consumption of W and Mo from the ferrite matrix and the consumption of fine particles, leading to the strength reduction of BG12Cr. Additionally, the dense dispersion of Cu particles possibly supports more nucleation sites for Laves phase during long period thermal exposure.

5.4 Stress-rupture behaviour in P92 and BG12Cr at 650ºC

In the following sections, the mechanical performance of BG12Cr in high temperature stress-rupture will be discussed in detail relying on the microstructural analysis.

5.4.1 Stress-rupture behaviour difference of these two alloys

Two different stress rupture behaviours of these two alloys are clearly observed from stress-rupture plots (Figure 4.75). BG12Cr has longer stress-rupture life when a higher stress is applied. Whereas P92 has better performance when a lower stress is applied. The creep strength of BG12Cr falls significantly after approximately 10,000 hours (see the cross-point in Figure 4.75) and the loss of strength is associated with the microstructure evolution happening inside BG12Cr martensite matrix. Interestingly, it is found that the reduction of creep strength in BG12Cr seems to initiate after 3800 hours. The microstructure evolution has been fully illustrated in previous sections and it can be concluded that the precipitation of Z-phase, which is normally expected after 10,000 hours to 30,000 hours, should be the dominant factor in

leading to the loss of strength. More stable microstructure in P92 after 10,000 hours leads to the longer service life presented in applied stress versus rupture life plots. The drop of creep strength is controlled by the microstructure stability and is illustrated in Figure 5.3. A strength drop can be clearly observed from BG12Cr in regime M and it can be prolonged by improvement in microstructure stability.

5.4.2 Microstructure evolution under different testing conditions

1) Martensitic lath widening

The microstructure evolution happens faster in BG12Cr than in P92 under long periods of high-temperature exposure based on the electron microscope images analysis. In BG12Cr, the martensitic lath structures can still be clearly observed after 8597 hours (see Figure 4.85.f) but martensitic lath widening is observed to happen after around 3048 hours (see Figure 4.85. e). Dense recrystallized ferrite grains with a rod-like shape, which formed along the PAGBs, can be clearly observed after 8597 hours thermal exposure in BG12Cr. The disappearance of TMLS in BG12Cr can also be found from secondary electron micrographs (see Figures 4.86-87). It can be found that the area of blocky regions in BG12Cr increased as the time increased. In comparison, the martensitic lath structure is very stable in P92 even after 12234 hours thermal exposure (see Figure 4.86.a). Unlike BG12Cr, no recrystallized tiny grains in P92 were observed from the selected areas. From the optical observations, it can be concluded that TMLS in BG12Cr steel has a higher instability compared with TMLS in P92 steel.

2) Precipitates distribution difference

The density of precipitates inside the martensite matrix in BG12Cr drops when the rupture time increases, and the density of precipitation decorating PAG boundaries significantly increased after 10,000 hours (see Figure 4.86.3-7). Dense small grains (less than 10 μm) can be clearly identified after 7286 hours, which are expected to be recrystallized ferrite grains. A high density

and bright precipitates (Cr-rich $M_{23}C_6$ carbides and (W, Mo)-rich Laves phase) were found decorating the grain boundaries (see Figure 4.27). As discussed previously in last section, the bright particles found in BSE images should be Laves phase, which also play a detrimental effect on the stability of TMLS in BG12Cr steel.

5.4.3 Fracture mechanisms analysis

1) P92-E-90 MPa and P92-E-100 MPa:

Ductile fracture can be clearly observed from the SEM fractography of both specimens indicating a micro-void coarsening ductile fracture mechanism. Compared to BG12Cr, no obvious necking deformation was observed.

2) BG12Cr-E specimens under different stress levels:

A cone-like fracture surface is observed consisting of a fibre zone at the central region, a shear-lip zone at the outer periphery and a radiation zone, indicating a very typical ductile fracture mode for all specimens (e.g., see Figure 4.77.3). Many deep and equiaxed dimples are observed in the fibre zone. Shallow and parabolic shear dimples due to shear stress are clearly observed on the shear-lip zone. All these observations indicate that dimple rupture dominates the whole rupture deformation progress.

A high density of martensite cracking and coarsened microcavities can be clearly observed (Figure 4.80-4.84) from a magnified view of cross-sectional areas close to the fracture surface. Martensite cracking can be characterized as thin cracks formed at the martensite lath boundaries [130]. The formation of martensite cracking in BG12Cr can be explained as the result of lath boundaries sliding. As discussed in the previous section, the precipitates inside the laths and along lath boundaries in BG12Cr lose their pinning effect after long term thermal exposure, which eventually leads to the lath boundaries sliding. The stress is concentrated on the lath boundaries which promotes the nucleation of microcracks. Then the growth of

microcracks eventually leads to the formation of martensite cracking [131]. The formation of coarsened microcavities close to the fracture surface is due to the stress concentration. Precipitates pin the movement of dislocations which will lead to the formation of dislocation pileups. Then stress concentration is initiated near the precipitates and leads to the formation of microcavities. Compared to P92-E, complete PAGs structure was difficult to observe close to the fracture surface in BG12Cr, which is replaced by deformed grains. All these finds reveal a fully ductile fracture mechanism in BG12Cr stress ruptured specimens.

In summary, all the stress ruptured BG12Cr specimens exhibit significant necking with an elliptical shape in a typical cup and cone appearance. A dense array of deep and equiaxed dimples appear at the central region of the fracture surface. Martensite cracking and coarsened microcavities are clearly observed close to the fracture surface from the cross-sectional magnified observations. It can be concluded that ductile fracture is the dominant fracture mechanism in BG12Cr during short-term stress rupture tests. Under similar testing conditions, BG12Cr is more ductile compared to P92.

5.3 Creep crack growth in P92 and BG12Cr at 650ºC

5.3.1 Creep crack growth resistance curves

1) C* approach to creep crack growth in CT testpieces

The creep resistance of CT samples has been plotted with the driving force K and C* separately (see Figures 4.41-4.42). The details about the creep resistance curves are listed in the result sections. Obviously, K (stress intensity factor) is not a suitable driving force to access the creep resistance of these two heat-resistant steels (Figure 4.41). The application of the linear elastic stress intensity factor K assumes small scale yielding (plastic deformation) ahead of the crack tip. For a cracked body, in which the majority of the body has shown time-dependent plastic deformation (creep), the assumption of small-scale yielding is no longer valid.

Compared to the creep crack growth rate against K plots, all the curves in the da/dt-C* plot appear to distribute within a narrow band and show a unique linear relationship (Figure 4.42). The difference is that K is a parameter which is mainly controlled by the local crack tip stress field, while C* is controlled by extensive deformation within the testpiece, this indicates the limitation if applying K to address creep crack growth resistance. The progress of fatigue crack growth is mainly governed by the crack tip damage within a very small region, while creep crack growth is usually associated with a much larger area ahead of the crack tip. When extensive creep is established, creep deformation will spread across the whole body and creep damage is likely over a large region. In conclusion, C* is path-independent parameter to assess the creep resistance of both heat resistant steels using CT geometry in this study.

2) C* approach to creep crack growth in ring-notched testpieces

A similar trend has been found in the C* plots when the tests use a ring-notched geometry (Figure 4.43). The da/dt of circular notched specimens could be characterized by C* except for the data of initial crack growth rate. Similar findings have also been found by Tabuchi et al. in 2003. They firstly used circular notched specimens to investigate this approach on assessing creep resistance of high chromium content heat resistant steels [132]. They also found that the higher the ratio of notch depth to the specimen diameter, the higher the creep crack growth rate with larger C* values. This is because cracking rate is accelerated as multiaxiality increases in ring-notched testpieces. Hence the reason why the the distribution of C-PS3 creep resistance curve is higher than the other two specimens in the C* plots in this study due to higher ratio of notch depth to the specimen diameter (see Figure 4.43). The distribution of these curves with two different geometries stays inside the same C* range from 0.01 to 10 kJ/m^2h (see Figure 4.44). In this study, the extended part of the ring-notched P92 C* curves (see Figure 4.43) stay along a single line and the C* curves of ring-notched BG12Cr stay along a single line when

the creep crack growth rate is higher than 1E-3 mm/h. Compared to the P92, the plots of BG12Cr show relatively less scatter.

5.3.2 Investigation on the geometry influence on C* curves

The relations of creep crack growth rate (da/dt) versus C* of compact tension testpieces and ring notched testpieces are plotted together for comparison to see the influence of testpiece geometry (see Figure 4.44). All these curves stay inside a narrow band, which proves that C* is a more suitable parameter to evaluate the creep crack resistance under 650º, even if the geometry of the testpiece is different. A compact tension testpiece, which has larger dimensions, has a higher creep crack growth rate compared to a ring notch testpiece under the same C* value. This is revealed from the CT data band which stays above the ring notched data band (see Figure 5.14). The circular notched C* results stay within a relatively lower creep crack growth rate region compared with CT band which was expected to be observed. Similar distributions were also observed with a 12CrWMoB alloy in Tabuchi's work in 2003 (Figure 5.15) [132]. Thus C* can be applied to access the creep crack growth resistance in samples machined as ring-notched or circular notched geometry in Cr content heat-resistant steels [130]. Whereas the increase of specimen thickness leads to an increase in da/dt in CT testpieces because of constraint effects [133]. Meanwhile, the increasing of applied stress also seems to play an important part in the increasing of creep crack growth rate, which should also be considered. Creep crack growth rates with specimens of $2a_0/D$=0.4 were about ten times faster than the creep crack growth rates with specimens of $2a_0/D$=0.2 in 12CrWMoB at 650°C. The same tendency of mechanical constraint effect on creep crack growth rate was obtained in small ring-notched testpieces instead of very large CT testpieces [132]. All these findings reveal that da/dt was accelerated due to the increase of stress multiaxiality. Thus, this geometry approach can be considered to be effective in assessing creep crack growth resistance in 12Cr heat-resistant steels compared to CT geometry and close to conditions.

5.3.3 Creep crack growth behaviour of a ring-notched P92 testpiece

1) fracture mechanism analysis

Referring to the fractography and cross-sectional areas observations, it can be concluded that intergranular fracture dominated the propagation of the crack. As the crack extended further, micro-voids coarsening ductile mechanism was the dominant failure mechanism.

Creep cracks were found primarily along grain boundaries with the formation of voids. Coarsened micro-cavities were found close to the final stage of CCG. Similar creep crack growth behaviour was found by Tabuchi [132]. The diffusive void growth was possibly accelerated due to the multiaxial stress conditions. The fracture mode (microcavities coarsening) observed from all these BG12Cr specimens was of great significance because it was similar to the situation of comparable structural components.

5.3.4 Creep crack growth behaviour difference in different geometries

Different creep crack growth behaviour was observed in the CCG tests in the ring-notched testpieces compared to CT specimens. In ring-notched testpieces, the steady crack growth period occupies the most part of the whole test life, which reaches almost 70%-80% of the whole life. On the contrary, the extensive creep crack growth stage occupies the most part of the whole life in the tests with CT geometries. The different creep crack growth behaviour can be characterized by normalizing the test life and plotting against loadline displacement rate & creep crack growth rate (see Figure 5.16). More time is required for the ring-notched testpiece to reach the acceleration stage compared to a CT testpiece despite the constraint effect. A similar difference in behaviour was also found in the studies of 1CrMoV heat resistant steel at 538°C, where the occupation of acceleration stage is 20% in circular specimens whereas it was 70% in CT specimens [133]. This behaviour difference can be explained by the effect of multiaxial stress field [132]. For the samples labelled with “L” in this study, the ratio of notch

depth (a_0) to testpiece diameter (D) is 0.25. This ratio for samples labelled with "S" is 0.3. The relationship between da/dt with C* is related to this ratio rather than the size of the testpiece. Creep crack growth rate increased as the ratio increased [132]. This can be seen from the C* plots of P92, where CPS-3 has a relatively larger creep crack growth rate compared to CPL-1&4.

It can be concluded that the approach of ring-notched test method is very effective to access creep crack growth properties even if it is tested under different conditions compared to a CT testpiece. Also, it is appropriate to use the ring-notched test method to simulate a structural component with a sharp notch or crack under tensile conditions in practice.

In summary, BG12Cr has a better heat-resistance compared to P92 under higher stress levels (>100MPa) under 650°C. Under same higher stress levels, it takes more time for creep crack growth in BG12Cr compared to P92 in creep crack growth tests.

Finer tempered martensitic lath structure with dense precipitates (Cu-rich particles and $M_{23}C_6$ carbides) distribution leads to the higher heat resistance in BG12Cr in short term (<10,000 hours) tests. However, BG12Cr has higher microstructure instability compared to P92 during long term (>10,000 hours) high temperature exposure. Fine dispersion of Cu-particles (<20 nm) effectively pinning dislocations and enhance the creep crack resistance during short term tests. However, it coarsened to a relatively larger size (>300nm) and the pinning effect from coarsened Cu-rich particles significantly dropped. Thus, the lath widening could easily happen in BG12Cr than P92. Meanwhile, the primarily pinning precipiates-$M_{23}C_6$ carbides, were observed to coarsen to as large as 500 nm in size, which indicates a higher coarsening rate for this type of particles in BG12Cr than P92. In BG12Cr, the dense precipitation of Laves phase during long time thermal exposure is detrimental for its microstructure stability. Moreover, the new precipitation of Z-phase due to high chromium content replaces MX phase from as-

received BG12Cr, which is also detrimental to the microstructure stability. Thus, BG12Cr has a higher martensitic lath widening rate compared to P92.

5.4 The application of ligament stress to correlate creep crack growth rate (mm/h)

C* parameter, which has been developed and widely used for decades, especially is applied in heat resistant steels. As discussed in previous section (section 5.3), it is a more suitable parameter than K to correlate with creep crack growth rate in both alloys (BG12Cr and P92) due to a unique linear relationship (compared with K-stress intensity factor). Some previous studies have proved that ligament stress ($\sigma_{ligament}$) possibly be more effective to plot against the creep crack growth rate and have a similar linear relationship compared to C* driving force parameter [134]. In this section, the ligament stress will be plotted again creep crack growth rate in both alloys with different testpiece geometries under different testing conditions (temperature and load). The obtained plots will be discussed with C* plots to investigate its application in this project.

5.4.1 The calculation of ligament stress in different testpiece geometries

For the ring-notched testpiece, ligament stress can be easily obtained through the calculation of net-section stress, which is given by:

$$\sigma_{ligament} = \frac{P}{\pi d^2} = \frac{P}{\pi(\frac{D-2a}{2})^2}$$

(Equation 5.1)

Where $\sigma_{ligament}$ is ligament stress, P is the load, d is the diameter of net section, D is the specimen diameter and a is the crack length.

As for the CT testpiece, the calculation of ligament stress has been summarized in previous study [134] and is given by:

$$\sigma_{ligament} = \sigma_{tensile} + \sigma_{bending}$$

(Equation 5.2)

$$\sigma_{tensile} = \frac{P}{B_n(W-a)}$$

(Equation 5.3)

$$\sigma_{bending} = \frac{6P(a + \frac{W-a}{2})}{B_n(W-a)^2}$$

(Equation 5.4)

Where $\sigma_{ligament}$ is ligament stress, $\sigma_{tensile}$ is the tensile stress, $\sigma_{bending}$ is the bending stress, B_n is the thickness of net section, P is the load, W is the specimen width and a is the crack length.

5.4.2 Plots of creep crack growth rate (mm/h) versus ligament stress (MPa)

5.4.2.1 Plots of creep crack growth rate versus ligament stress with ring-notched testpieces at 650°C

Figure 5.17&5.19 shows the plots with ligament stress obtained from the ring-notched creep crack growth tests at 650°C. Interestingly, all the P92 plots stays along a unique line (see red dotted line) and BG12Cr plots stays along another unique line (see blue dotted line) for the static growth stage, indicating ligament stress can be applied in these alloys with the same geometry at 650°C (see Figure 5.17). The extensions of these two trendlines converge at one point which is approximately around 100 MPa, this value of ligament stress is then confirmed to be 116.97 MPa (see Figure 5.19). This finding corresponds to the intersection found in the stress-rupture plots of these two alloys (Figure 4.75), which ranges from 90 to 110 MPa. The P92 possibly has a better performance than BG12Cr when the stress level is below this intersection point and BG12Cr is better when the stress level is above this intersection point

following the tendency of these lines constructed. However, the intersection (with a ligament stress value of 116.97 MPa) obtained from da/dt vs $\sigma_{ligament}$ plots can serve as a more accurate boundary to distinguish between the performance of the two alloys under 650°C. After the stress level increases above 116.97 MPa, P92 can be more obviously found to have a relatively higher creep crack growth rate compared with BG12Cr in da/dt vs $\sigma_{ligament}$ plots compared to da/dt versus C* plots (see Figure 4.44). In the part where the plot is rapidly approaching its end, there is an upward trend in the curve (Figure 5.17). This can be explained as being due to the crack propagation not following an ideal circular shape but may expand in a somewhat non-uniform manner.

In conclusion, creep crack growth rates can be plotted against ligament stress in all the ring notched creep crack growth tests and linear relationships can be observed at a 650°C. Compared to C* curves, it is much easier to compare these two alloys' performance in the da/dt vs $\sigma_{ligament}$ plots. The da/dt vs $\sigma_{ligament}$ plots support a more precise critical value (116.97 MPa) to distinguish these two alloys compared to the stress-rupture plots under 650°C. At the same time, these finds also indirectly demonstrate the advantages of the ring-notched creep crack growth test method Moreover, the application of $\sigma_{ligament}$ can increase the efficiency of assessing alloys' properties compared to the application of C*, which requires the calculation of loadline displacment rate. Until now, the possibility of $\sigma_{ligament}$ has been verified with these two alloys with ring-notched geometry under the same testing temperature. In the following section, the approach of $\sigma_{ligament}$ will be investigated and discussed with CT testpieces under different testing temperatures.

5.4.2.2 Plots of creep crack growth rate versus ligament stress with CT testpieces at 650°C and 700°C with different loading conditions

Figure 5.18 shows the da/dt vs $\sigma_{ligament}$ plots of creep crack growth tests with CT testpiece under different testing temperatures (650°C and 700°C). Similar to the results of da/dt vs $\sigma_{ligament}$ plots

in ring-notched testpieces, the plots of CT specimens also indicate a specific linear relationship between da/dt with ligament stress, with the intersection point of the two trendlines also occurring at around 116.97 MPa when the testing temperature is at 650°C. Furthermore, it is evident that when the ligament stress exceeds this value, P92 exhibit a faster crack growth rate. Until now, it can be concluded that ligament stress can be applied in plotting against creep crack growth rate with different testpiece geometries. Moreover, as the temperature increases to 700°C, the unique linear relationship was also observed in both alloys (see arrows in Figure 5.18).

5.4.2.3 Plots of creep crack growth rate versus ligament stress with different testpiece geometries at 650°C different loading conditions

Figure 5.19 gives a summary of all the da/dt vs $\sigma_{ligament}$ plots with different testpiece geometries with different testing conditions. It can be concluded that all the P92 plots with different geometries are distributed along a single trendline (see red dotted line) and most of the BG12Cr plots locate along another single trendline (see blue dotted line). The intersection point is located at a ligament stress with a value of approximately 116.97 MPa. Obviously, P92 has a higher creep crack growth rate compared to BG12Cr alloy.

In conclusion, the ligament stress can be applied to assess different alloys' performance under a certain high temperature, and it is possibly to be testpiece geometry, loading conditions and temperature independent, which need to be confirmed in future study. Compared to C*, it presents a more intuitive and concise representation of the performance of these two alloys at high temperatures. Moreover, this method is simpler to implement since it does not require recording or calculating loadline displacement.

CHAPTER 6 Conclusions and Future Research

In this chapter, the conclusions of this PhD project are listed in detail and some suggestions for future research are given for reference.

6.1 Conclusions

1. The as-received BG12Cr alloy has a finer tempered martensitic structure compared to P92. This provides the material with higher hardness and better monotonic strength. The strengthening mechanism of BG12Cr steel arises from two major sources: (1) Precipitation strengthening primarily from $M_{23}C_6$ carbides and Cu-rich nano particles; (2) Dislocation hardening from tempered martensitic matrix.
2. Compared to P92, better stress rupture life is seen with BG12Cr at relatively higher stresses (>116.97 MPa) at 650°C which is attributed to the refined martensitic microstructure. However, at the stresses equivalent to and lower than 116.97 MPa, inferior stress rupture life is obtained. The examinations of the microstructure of the test-pieces after stress rupture testing under lower stresses, hence long-term thermal exposure (>10,000 h) reveal a higher microstructural instability of BG12Cr compared to P92 steel.
3. It is observed that in BG12Cr martensite laths start to transfer into subgrain structures after 3800 h. The microstructural evolution of BG12Cr can be summarized as following: (1) rapid coarsening of $M_{23}C_6$ carbides and Cu-rich particles; (2) martensite lath widening and recovering; (3) precipitation of new harmful phases such as Laves phase and Z-phase.
4. The mechanisms of inferior stress rupture life obtained for BG12Cr under lower stress are deduced to due to: (1) loss of precipitation hardening (primarily from $M_{23}C_6$ carbides, Cu-rich nano particles); (2) loss of dislocation hardening, tempered martensitic structure turns into blocks along with coarsening precipitates; (3)

precipitation of secondary phases (Z-phase, Laves phases) accelerates coarsening of $M_{23}C_6$ carbides, Cu-rich nano particles.

5. A creep crack growth testing methodology using an alternative to common compact tension (CT) test-pieces, i.e., circumferential notched tension (ring-notch tension), has been applied in the current study. The creep crack growth resistance curves, da/dt versus C*, generated from this geometry are similar to those obtained using a CT test-pieces. However, an insignificant influence of test-piece geometry is seen with the results from ring-notch test-pieces appearing slightly higher in the plots. Like results obtained from CT geometry, a relatively single unique da/dt versus C* relationship can be obtained to represent both investigated alloys at a temperature of 650°C. It has been verified that C* is a unique mechanical driving force to address the creep crack growth resistance.
6. In addition to C*, ligament stress has also been proved to be a very useful term to describe creep crack growth rates. Different to the da/dt vs. C* curves, in the da/dt versus $\sigma_{ligament}$ plots it is convenient to comparing creep crack growth resistance between alloys. Interestingly no influence of test-piece geometry can be seen.
7. A superior performance of BG12Cr can be concluded from the da/dt vs. $\sigma_{ligament}$ plots for the investigated stress range. However, extrapolating the lines of the two alloy leads to a crossing at around 116.97 MPa. This implies that beyond this point (with stress lower than 116.97 MPa) the performance of BG12Cr is likely to be inferior to that of P92. This stress value coincides to the cross-over stress found in the stress-rupture results which require more than 10,000 h of testing. It seems that creep crack growth testing can be used as an accelerating method to predict long term creep performance with ligament stress parameter applied.

8. The current study suggests although BG12Cr steel shows better creep crack growth resistance compared to P92 at higher stress conditions, the higher microstructural instability makes it unsuitable for long term (>10,000 hours) applications.

6.2 Future work

1. Additional groups of ring-notched creep crack growth tests should be carried out to complete the building up of a data base of C* plots in BG12Cr. It should be noted here that larger size of ring-notched testpiece should be used to give the crack more space to grow.
2. More TEM work should be done for the rest of PT BG12Cr samples (e.g., PT BG12Cr at 3800 hours). It is of great significance to figure out the precise time when the precipitation of Z-phase happens in BG12Cr and the reason why it precipitates much earlier than in other high chromium content (>9%) steels. All these works are beneficial for the improvement on the manufacturing of this novel steel.
3. The precise addition of Cu should be investigated in BG12Cr. This is because these particles are not observed in the PT BG12Cr specimens used for TEM analysis in this study. However, a fine dispersion of them is frequently observed in as-received material, which pins the dislocations effectively in short-term applications. As the duration of application increases above 10,000 hours, these populated Cu-particles will coarsen from 20 nm to 300 nm in size. The fine dispersion will not exist after long term at 650°C, which leads to the recovery of martensitic laths and eventually leads to the loss of alloys' strength. On the other hand, the introduction of Cu-particles inside the martensitic laths were successful for short-term applications. Compared to fine dispersion of MX phase in martensitic laths, the addition of Cu is much cheaper. However, the balance of these

strengthening alloys element should be investigated carefully in the future to avoid high ductility of BG12Cr.

4. Ligament stress can be applied to assess the high temperature creep crack growth performance instead of comprehensive parameter such as C* if more work is done on this trend.

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