

Microstructure Control and Correlation to Creep Properties in Grade 91 Steel Weldment After Thermo-Mechanical Treatments and an Fe-30Cr-3Al Alloy Strengthened by Fe₂Nb Laves Phase

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Dedication

To my loving wife, Brittany P. K. Shassere

For all your patience and encouragement

Forever and Always,

Acknowledgement

I would like to thank my advisor Dr. Suresh Babu. Suresh has mentored me to succeed and stayed encouraging throughout this time. The experiences and stories from Suresh will always remain close to me and will always give me inspiration in difficult times in the future. Thank you Suresh for all your hard work and providing a great graduate school family.

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I would like to thank all the members of Suresh's group at The Ohio State University for a great year of graduate school. Also all the students of the Advanced Manufacturing and Materials Group at The University of Tennessee. All the students were a great family during my graduate studies, and hope to remain colleagues for many years to come. I had great discussions with all of you and allowed great context for this research. I would especially like to thank Niyanth Sridharan for your help and walking along myself in our graduate studies.

Abstract

Type IV cracking in weldments of steel pipes after creep deformation is a concern in modern fossil-fueled power plants. Two possible methods for minimizing or eliminating Type IV cracking will be discussed. The first method alters the initial microstructure of typical Grade 91 steel base metal before welding, while the second provides baseline microstructure characteristics and creep performance of a new alloy that is strengthened by the intermetallic Fe₂Nb Laves phase. The initial microstructure of the Grade 91 steel can be controlled by Thermo-Mechanical Treatments, which aids in precipitation of fine (5-10 nm) MX particles in austenite before transformation to martensite on cooling. Results also reveal that MX is shown to have a reduced volume percent and size of M₂₃C₆ carbide formation upon tempering. A strain rate model has been created based on particle sizes and interparticle spacing to predict creep deformation strain rates from the microstructure. The model reveals that the minimum creep rate can be altered with a change in precipitate distribution, and may have competing creep mechanisms in the heterogeneous microstructure of weldments. The model indicates that Type IV cracking may not have a solution based only on precipitation control. Based on this idea a new alloy is being developed which precipitates a thermally stable Fe₂Nb Laves phase with the average size between 80-150 nm. The alloy has a ferritic matrix and general composition of Fe-30Cr-3Al-.2Si-xNb. The initial base metal creep results indicate the new alloy has similar creep properties to the Grade 92 steel at 700 °C. The microstructure characterization has revealed that a precipitate free zone (PFZ) forms parallel to all the grain boundaries with larger (200-300 nm) Laves phase decorating the grain boundary. Utilizing the strain rate model, a Grain Boundary Sliding type mechanism was identified as the deformation mechanism. In these alloys, it will be discussed how the areal fraction of grain boundary Laves phase and the width of the PFZ

controls the cavitation nucleation and eventual grain boundary ductile failure. This reveals the competition between the intragranular creep resistance of the Laves phase and the intergranular deformation along the grain boundaries.

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List of Acronyms

P91	Designation Grade 91 steel for pipes
FGHAZ	Fine Grain Heat Affected Zone
CGHAZ	Coarse Grain Heat Affected Zone
CSEF	Creep Strength Enhanced Ferritic
HAZ	Heat Affect Zone
N&T	Normalized and Tempered
TMT	Thermo-Mechanical Treatment
FCA	Fe-Cr-Al alloy
OM	Optical Microscopy
SEM	Scanning Electron Microscope
EBSD	Electron Backscatter Diffraction
EDS	Electron Diffraction Spectroscopy
TEM	Transmission Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
PWHT	Post Weld Heat Treatment
GBZ SF	Grain Boundary Zone Strength Factor
BMD Eq.	Bird Mukherjee Dorn Equation
PAGB	Prior Austenite Grain Boundary
LTR	Low Temperature Rolling
HTR	High Temperature Rolling

Chapter 1. Introduction

1.1 Introduction

The first few generations of the new millennium will have to deal with global environmental concerns. Climate change is one of these concerns that are now at the forefront of policymaking. Greenhouse gasses, mainly carbon dioxide (CO_2), cause a warming phenomenon. The U.S. produces over 6.5 billion metric tons of CO_2 annually, and globally 36 billion metric tons is produced [1]. The main source of CO_2 is electricity generation due to the burning of fossil fuels. Power plants have the ability to reduce emissions by improving efficiency through increasing steam temperature and pressure. Abe (2008) has demonstrated that increasing the steam temperature and pressure from 538 °C and 24.1 Mpa to 650 °C and 34.3 MPa can increase the efficiency by 6.5%, which translates to a significant reduction in CO_2 production [2]. With the relatively high temperature and pressure, a variety of steels have been developed for different components of fossil-fueled power plants. One such set of steels is the Creep Strength Enhanced Ferritic (CSEF) Steels. This group of the 9% Chromium steels such as the A335 P91 (seamless pipes), A213 T91 (seamless tubes), and A387 Grade 91 (plates) are most widely used as steam piping for the fossil-fueled power plants [3].

The base metal performance of the Grade 91 steel has been optimized with an extensive amount of research and development [2]. The optimum performance has been achieved by producing a fully tempered martensitic structure from a detailed normalization in austenite phase field and tempering heat treatment. While the base alloy performs well under long-term creep conditions (100,000 hrs at 550-600 °C and 15-20 MPa), the weldments, necessary for power plant construction, fail prematurely (30,000-50,000 hrs) [4]. The premature failure is due to a

weakened microstructure in the Fine Grain Heat Affected Zone (FGHAZ), known as Type IV cracking [5]. During welding and subsequent Post Weld Heat Treatment (PWHT), the microstructure of the once optimized base metal is degraded. These welded joints contain several different microstructural complexities including compositional variations as well as microstructure inhomogeneities from the different heat affected zones such as the Coarse Grain and Fine Grain Heat Affect Zone (CGHAZ, FGHAZ respectively). The microstructure variations cause severe degradation in the creep-rupture life of Grade 91 steel [6, 7]. The metallurgical effects and the triaxial stress state of a weldment itself both contribute to the acceleration of creep and lead to Type IV cracking [8, 9]. These failures are detrimental in many aspects of society. Failures in power plants can affect electricity generation, local economics, and health and safety of those involved [10]. Therefore, it is imperative to minimize or eliminate Type IV cracking. This dissertation will discuss two distinct pathways in the attempt to minimize or even eliminate Type IV cracking with the control of the initial microstructure with thermo-mechanical treatments and development of a new base alloy, through a fundamental understanding of creep mechanisms and microstructure characterization.

Chapter 2. Background

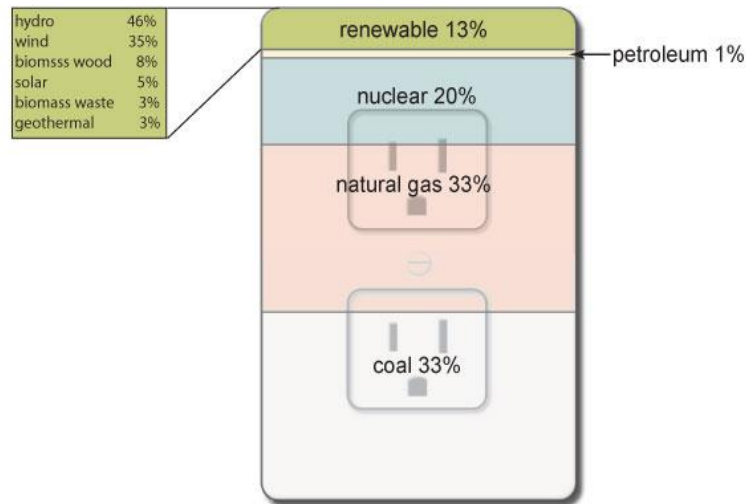
2.1 Considerations for Energy and Environmental Concerns

According to the Energy Information Administration of the U.S. and the Energy International Agency, fossil fuels are a majority source of the electrical generation [11, 12]. About 66% of the electricity generated in the U.S. comes from fossil fuels; this can be seen in the infographic in Figure 2.1. However, about 85% of the world's energy is supplied by fossil fuels [13]. From the burning of fossil fuels such as coal and natural gas, CO_2 is created and emitted into the atmosphere. In 2015 the U.S. emitted 1,925 million metric tons of CO_2 into the atmosphere, courtesy Energy Information Administration, eia.gov/tools/faqs. However controversial, the emission of CO_2 is widely understood to be a dominant factor of climate change. With this, there are several types of environmental and economic concerns. To alleviate climate change by reducing CO_2 emission, it is imperative to increase the efficiency 5-10% of fossil fueled power plants reaching close to 50% total efficiency. It is documented in every undergraduate thermodynamics class how to increase the efficiency of a thermal power plant, which is based on the Rankine cycle. Increasing the temperature of the steam, which also increases the pressure of the steam, can improve the overall efficiency of the thermal power plant based on the ratio of temperatures of the steam before and after the turbine. The larger the difference, the more work ($\dot{w}$) can be done by the turbine. With the improvements in efficiency, the power plant can produce more electricity with less energy input. This energy input comes from coal, which when burned produces CO_2 and other harmful gases such as NO_x , SO_x , CO, methane, and etc. Figure 2.2 shows the reduction of emissions with the increase in power plant efficiency. From where power plants are today, small percentage increases in power plant efficiency can lead to major reductions in emissions. There is however a limit to which power plant efficiency can reduce

emissions. After that, there are options for further reduction in emission, such as carbon capture and sequestration. This effectively captures the emission coming off the stream stack and is “pumped into the ground or other means that can hold CO₂ [13].

It is helpful to understand the layout of a power plant and location of the steels in the current research. Figure 2.3 is an illustration of a coal-fired power plant. In these power plants, water is pumped into the boiler. The boiler is where the coal is burned producing temperatures from 600-800 °C which rapidly converts the water into high-pressure steam (30 MPa). The steam then travels from the boiler to the turbine in the steam lines. The location of the materials used in the research would be located here. The temperatures and pressures are reduced from the boiler section to 500-600 °C and 20MPa due to heat loss. From here the steam is released into the turbine which will spin from the oncoming steam. The turning of the turbine rotates large magnets which will produce electricity in coils of wire. The steam is then cooled to a liquid and is pumped back to the boiler to start the cycle again. For steam generating power plants specific materials are required to provide long life (40-50 years) of the power plant. These materials need to stand up to temperatures and pressures for each given section of the power plant. Grade 91 steel are used in the steam lines running from the boiler to the turbine. The Grade 91 steel has a 9% Cr 1% Mo and minor additions of other elements to be discussed later in greater detail. This material has to withstand temperatures of 550 °C and 24 MPa of pressure. This material also has to withstand these conditions for the lifetime of the power plant (40-50 years). Under these conditions, the material will deform by creep. It is necessary to understand the how the material is behaving under these conditions to ensure the material survives over the lifetime of the power plant.

Sources of U.S. electricity generation, 2015



Source: U.S. Energy Information Administration, *Electric Power Monthly* (February 2016). Preliminary data for 2015

Note: Sum of components may not equal 100% due to independent rounding.



Figure 2.1 Electricity generation by source. Fossil Fuels are by far the majority of the total generation. Courtesy Energy Information Administration.

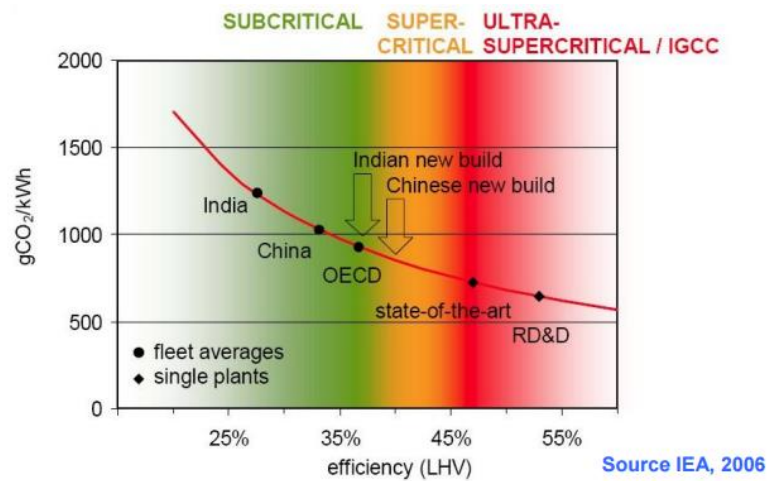


Figure 2.2 The Reduction in carbon emissions with the increase in power plant efficiencies. Courtesy International Energy Agency.

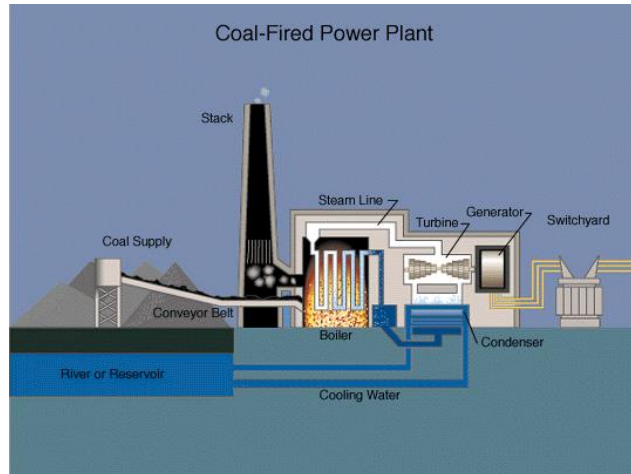


Figure 2.3 Illustration of a coal-fired thermal power plant. Courtesy of Electrical Engineering Tutorials, <http://www.powerelectricalblog.com/2007/03/thermal-power-plant-layout-and.html>.

2.2 Creep Strength Enhanced Ferritic (CSEF) Steels

2.2.1 History of CSEF Steels

Since the mid-20th century, fossil energy demands have led to decades of research to develop high (greater than 2 wt%) chromium steels to meet the ever-evolving temperature and pressure requirements. The first generation of Cr steels began with a 2.25Cr-1Mo steel. Then the need for improved creep properties led to the development of the first 9%Cr steel in the Center for Metallurgical Research of Liege in Belgium in the 1960s [14]. In the 1970s, several countries around the world began to develop different modifications of the base 9Cr-1Mo steel. In France, a 9Cr-2Mo with the addition of V and Nb was developed. However, the presence of delta ferrite in the matrix led to poor Charpy impact toughness. At the same time, Germany was developing a 12Cr-1Mo which was designated HT91. There were also difficulties with this steel. Because of the high carbon content (0.2%), the steel was difficult to weld.

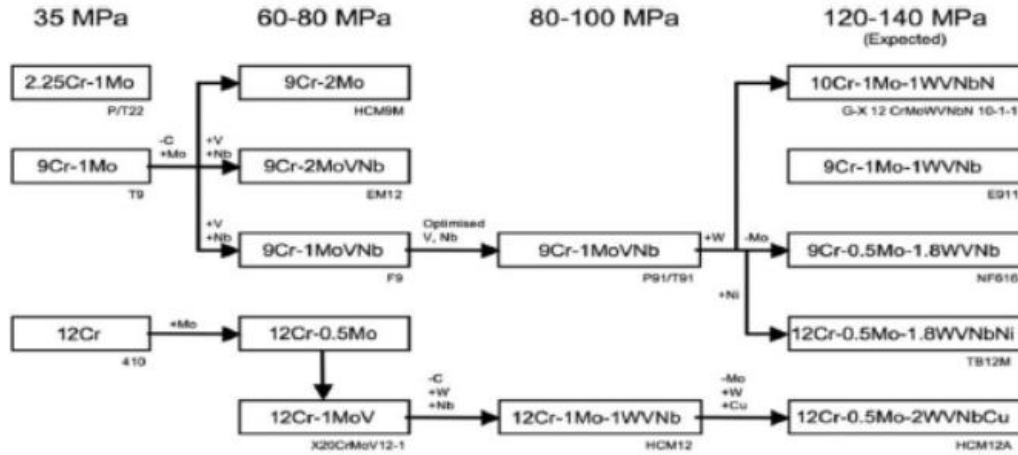


Figure 2.4 The evolution of creep strength enhanced ferritic steels with different allowing additions. The stresses shown above each column represents the rupture strength for 105 hours at 600 °C [16].

Further improvements of this steel were made with lower carbon contents to improve weldability [15]. Also in the 1970s, the Oak Ridge National Laboratory (ORNL) developed a modified 9Cr-1Mo steel, now referred to as Grade 91. This modified version of the 9Cr-1Mo steel also had additions of V and Nb with the extra addition of N. Later, the tempering stage of the process was optimized to allow good room temperature impact toughness. The steel was standardized for power plant operation as ASTM SA-335 P91 for pipes and ASTM SA-213 T91 for tubes. The overall development of the high Cr steels can be seen in Figure 2.4 [16].

2.2.2 Grade 91 Steel

Grade 91 steel is a 9Cr-1Mo base steel with a low carbon content (.08 wt%). This steel is primarily used in as-welded pipelines to transport steam from the hot section of boilers to the steam turbines of electric generation fossil fueled power plants. The base steel used for discussion will be the modified Grade 91 steel developed by ORNL (discussed above). The base microstructure is typically tempered lath martensite after traditional austenization, quenching, and tempering treatments [4]. Kitahara et al. (2006) have performed extensive characterization on several low carbon steels to demonstrate the crystallographic features of lath martensite, essentially the crystallographic relationship between a martensite lath to the parent austenite grain and its relation to surrounding laths. [17]. Figure 2.5, represents a typical morphology of lath martensite. Although (Figure 2.5 does not show a 9Cr steel) similar morphologies and the same crystallographic information can be observed in both steels. Within a Prior Austenite Grain Boundary (PAGB), the martensite is broken up into packets, which contain blocks with specific high angle boundaries between them (10° - 60°). The typical size of the block can range from 2-10 μm . Each block then contains two specific lath variants that maintain the phenomenological martensite crystallography.

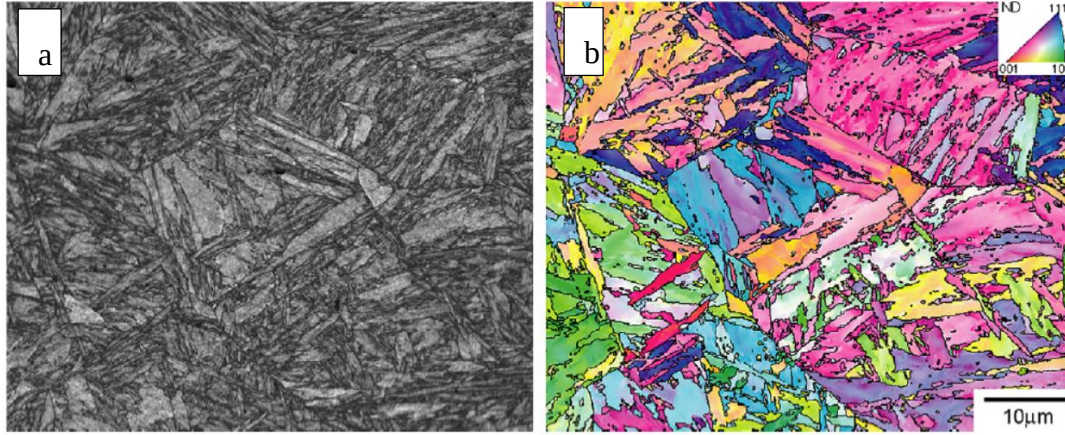


Figure 2.5 Typical orientation imaging maps obtained from the FE-SEM/EBSD measurement of the lath martensite structure in the 0.20 wt.% C steel. Black lines in (b) show the boundaries with misorientation angles larger than 10° [17].

Also, the Grade 91 steel also contains two sets of precipitates, $M_{23}C_6$ and MX. $M_{23}C_6$ (M: Fe, Cr, or Mo) is usually Cr-enriched and has a simple cubic structure with atoms sitting nearly on the face of the cube which appears most like a face-centered cubic structure [18]. The $M_{23}C_6$ carbide is precipitated initially on the grain boundary or transforms from an M_3C carbide during the tempering process [19]. The size range of $M_{23}C_6$ is relatively larger than MX, where $M_{23}C_6$ is generally between 80-200 nm and MX is less than 20 nm. The $M_{23}C_6$ carbide is found on the PAGBs (Prior Austenite Grain Boundary) and the martensite block boundaries [20, 21]. Figure 2.6 illustrates $M_{23}C_6$ and MX on the PAGBs and within the matrix. Because of where $M_{23}C_6$ lies, it pins grain boundaries and creates dislocation pile-ups during creep, which makes it a good contributor to creep strength.

MX (where M: V, Nb X: C, N) is a face centered cubic carbonitride, and also precipitated during tempering. However, a few very large (200-500nm) residual MX particles can be observed after tempering, which forms during the normalization process [19].

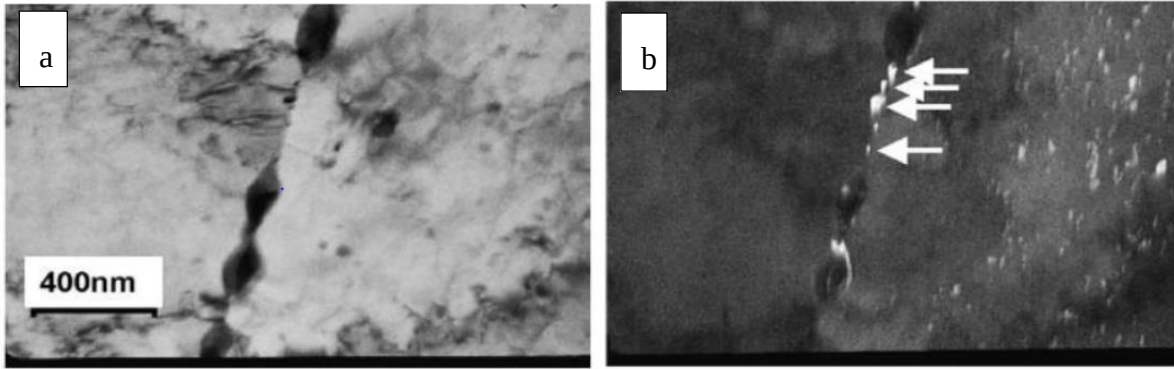


Figure 2.6 (a) Bright field TEM image showing $M_{23}C_6$ on PAGBs and (b) showing MX also on the PAGBs and within the matrix [20].

Unlike $M_{23}C_6$, MX is mainly precipitated within the martensite blocks, but can also be found on PAGBs and martensite block boundaries [22]. MX is smaller and does not have as much competition between the surface energy and volumetric free energy of nucleation compared to $M_{23}C_6$. Therefore, the MX can form more easily within the matrix on dislocations. The size of the MX carbonitrides is generally smaller than 20nm. MX is more stable at high temperature shown by a coarsening rate ($10^{-32} \text{ m}^3\text{s}^{-1}$) that is 1-2 orders of magnitude smaller than that of $M_{23}C_6$ ($10^{-30} \text{ m}^3\text{s}^{-1}$) [23]. This stability also makes MX a good contributor to creep strength since it pins dislocations in the interior of the matrix and does not coarsen, maintaining its creep resistance properties for a longer time.

2.3 Weldments and Type IV cracking

From above, Grade 91 steels have a long history of being a strong, creep resistant material for power plants. Modern fossil-fueled power plants are often large complexes with an extensive network of piping. To build a power plant with such a network, the pipelines have to be welded in the field. The size of the power plants limit the post processing of the welds and pipelines.

Thus, welding needs to be an important aspect of the development of Grade 91 steels. The welding procedure of Grade 91 steels generally follows the thermal history seen in Figure 2.7 (note the actual welding cycles are not shown). Before welding, a preheat temperature (200 °C) is used to help avoid cold cracking. Then during welding, an interpass temperature up to 300 °C is used. A slow cooling rate below 100 °C will still allow for the formation of a fully martensitic microstructure without cracking. After the completion of welding, it is necessary to provide a post-weld heat treatment (PWHT) to achieve the tempered martensitic state and to relieve residual stresses. The PWHT is the standard tempering treatment as the pre-weld tempering (i.e. 760 °C for 2-4 hours) [24].

Choosing the appropriate welding technique is important to provide suitable properties for the steel in service conditions. In the case of Grade 91 steels, all the arc welding processes can be used [14, 16, 25]. These include gas tungsten arc welding (GTAW), Flux core arc welding (FCAW), and submerged arc welding (SAW). In addition to the arc welding processes, laser, and electron beam welding have also been reported to be used for welding Grade 91 steels [25]. The main welding technique for industrial use is the GTAW for complex joints, and for deep welds, FCAW or SAW is used. As a note, the welding technique used in the current research is GTAW with a matching filler metal. In addition to the welding techniques, a matching filler metal for Grade 91 steel is also necessary. A matching filler metal (example weld consumable, ER90S-B9) provides the same strength and high-temperature properties of the parent material. This also prevents dilution problems from the weld to base metal.

Welding is a locally high heat input process (1-3 kJ/mm) that melts the filler metal and part of the base metal to provide a metallurgical bond. As a consequence of the heat input, a Heat Affected Zone (HAZ) is formed adjacent to the newly solidified weld metal. There are many

distinct regions in the heat affect zone. These are represented in Figure 2.8 with a 9Cr steel pseudo-binary phase diagram predicted from ThermoCalc [26].

The main regions of the HAZ that are the coarse grain zone (CGHAZ), fine grain zone (FGHAZ), and the inter or subcritical zones (ICHAZ or SCHAZ). The CGHAZ is immediately adjacent to the weld metal and experiences extensive heating to peak temperatures greater than 1100 °C. This peak temperature causes the martensitic microstructure to transform back into a fully austenitic state. With the high temperature, the austenite grain will grow much larger than the base PAGB. The FGHAZ is the next region after the CGHAZ and is between 0.5-3 mm away from the weld metal and ranges in sizes of 0.25-1 mm across the zone depending on the welding process and heat input. This zone experiences a peak temperature (900-1000 °C) in which the martensite can fully or partially transform back into austenite, and then fresh martensite will form upon cooling. The last zone is the inter and subcritical heat affected zone. Here the peak temperature stays below the A_1 temperature and no detectable transformation to austenite occurs (less than 900 °C). For CSEF steels, premature failures are often reported in the FGHAZ [27-29]. There are four classification modes of failure in a weld or HAZ. Type I is cracking directly in the weld metal. Type II occurs if the failure starts at the fusion line between the weld metal and the HAZ. Type III occurs in the CGHAZ. The last, Type IV, is cracking in the FGHAZ or the I/SCHAZ. Figure 2.9 shows a schematic of the location of the four failure types [30]. It is most noted that failure of CSEF steels is can mostly be seen by Type IV cracking [14, 25, 31]. These failures have been credited to the non-equilibrium microstructures in FGHAZ regions [27].

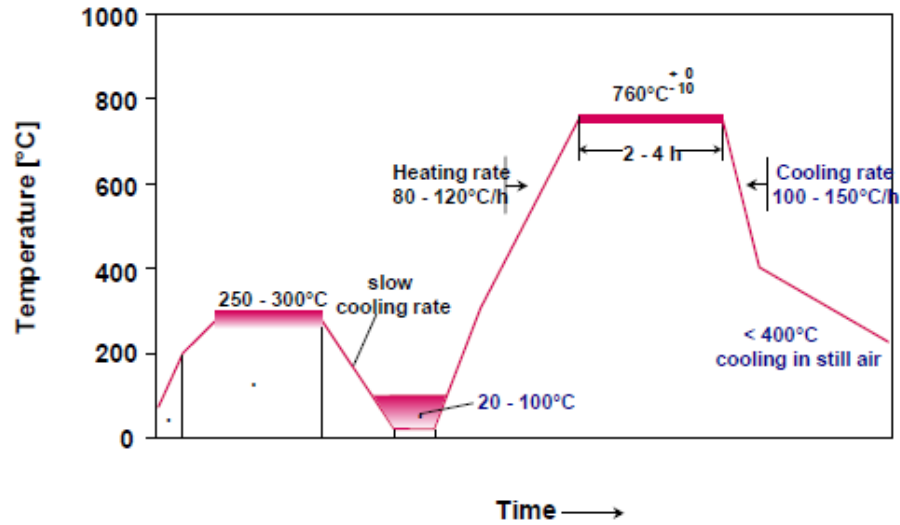


Figure 2.7 Temperature cycle and heat control during welding and PWHT [24].

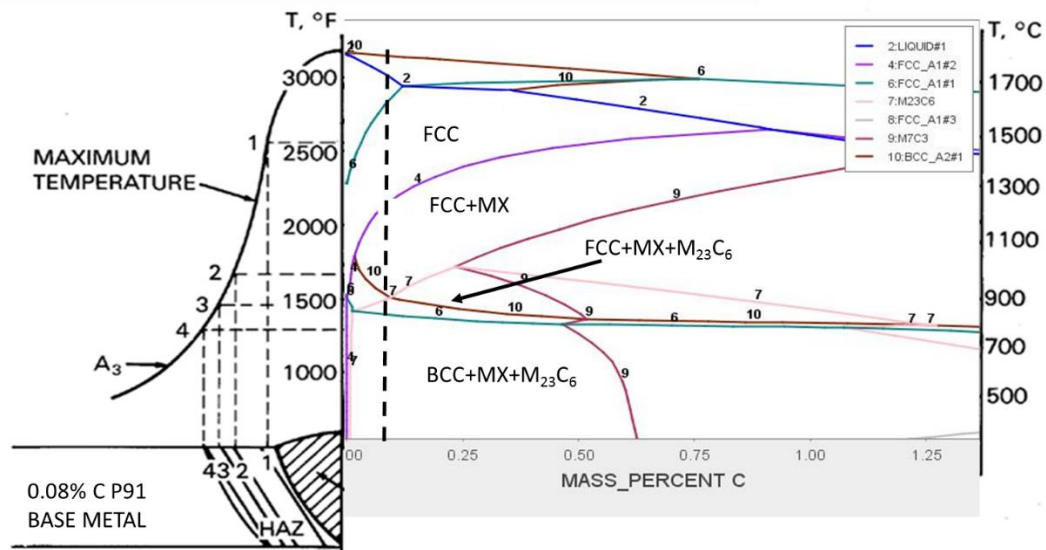


Figure 2.8 Temperature ranges and classification of the different regions of a steel weldment. Overlaid is a pseudo-binary phase diagram of the Grade 91 steel. Phase diagram is overlaid on welding peak temperature schematic from [29]

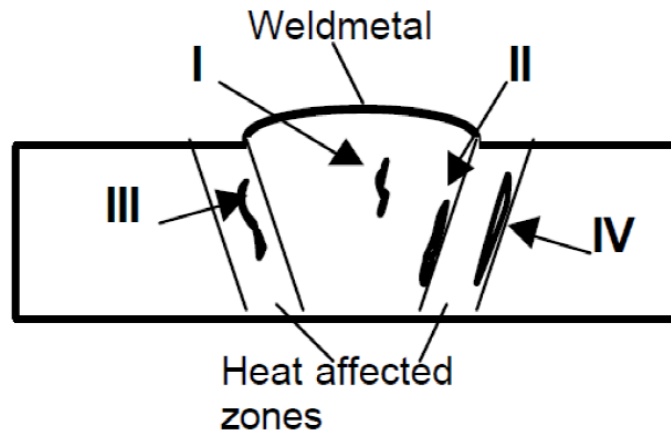


Figure 2.9 Classification of the failure location in CSEF steel welds [30].

2.4 Type IV Failure Mechanisms

The mechanisms for Type IV failure are not entirely understood. However, there have been studies to understand the main aspects of this failure. These studies have focused on the microstructural evolution in the FGHAZ during welding and subsequent PWHT. For an initial study, the effect of the PWHT on a high Cr steel was studied. Albert et al. (2003) studied the effect of varying the time length of the PWHT from 1-4 hours [7]. Understanding the fact that the FGHAZ had poor properties, the PWHT may result in beneficial changes in the carbide precipitation and growth. However, the findings from this study revealed that varying the time length of the PWHT did not have large effects on the creep strength. This result reveals the potential that carbide evolution during welding may be key to understanding the failure mechanisms.

Hirata and Ogawa (2005) studied a simulated HAZ using induction heating and TEM (transmission electron microscopy) carbon replicas [32, 33]. The authors analyzed the

microstructures of the simulated HAZ, which experienced peak temperatures of 830 °C, 1000 °C, and 1200 °C. These temperatures represent the untransformed base metal, FGHAZ, and CGHAZ respectively. Then all the samples were PWHT at 740 °C for 0.5 hours and subjected to creep conditions. The microstructure of the simulated peak temperature of 830 °C was relatively unchanged with slight coarsening. Since this peak temperature is lower compared to the CGHAZ, the $M_{23}C_6$ does not dissolve during welding. In contrast, when the simulation's peak temperature is 1200 °C, full dissolution of $M_{23}C_6$ is observed. This leads to an expected precipitation of $M_{23}C_6$ on fresh PAGBs and martensite boundaries. The sample with the lowest creep strength, however, occurred in the simulation with the peak temperature of 1000 °C. Using TEM, it was found that $M_{23}C_6$ had only partially dissolved. Based on diffusivities, they concluded that a Cr-rich region was left surrounding the residual $M_{23}C_6$. They reported that Cr diffusion led to fast coarsening of $M_{23}C_6$ and MX. It was concluded that the partial dissolution of $M_{23}C_6$ leads to accelerated coarsening of carbides. Figure 2.10 shows a schematic of the carbide evolution during welding.

Recently the location of $M_{23}C_6$ on PAGBs was investigated. Tsukamoto et al. (2012) and later confirmed by Yu et al. (2013), proposed undissolved $M_{23}C_6$ carbides would remain at their original pre-weld locations then over coarsen during PWHT [34, 35]. Tsukamoto et al. suggested that the undissolved carbides remain at ghost PAGBs after PWHT and is the reason for type IV failure. Ghost PAGBs are defined as locations where the PAGBs were in the steel before welding, before fresh austenite is formed. During welding, the carbides on the PAGBs will partially dissolve, and then will be surrounded by a supersaturation of carbon. During the PWHT, the carbon will diffuse to the residual carbides instead of nucleating fresh $M_{23}C_6$. Yu et al. confirmed the undissolved $M_{23}C_6$ during welding.

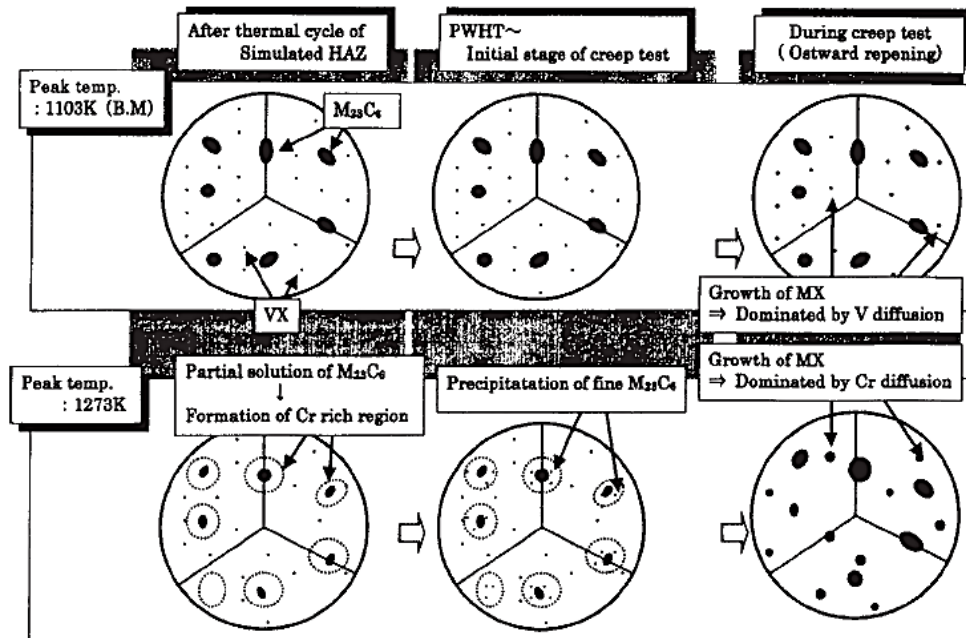


Figure 2.10 Schematic of the carbide evolution during welding from Hirata.

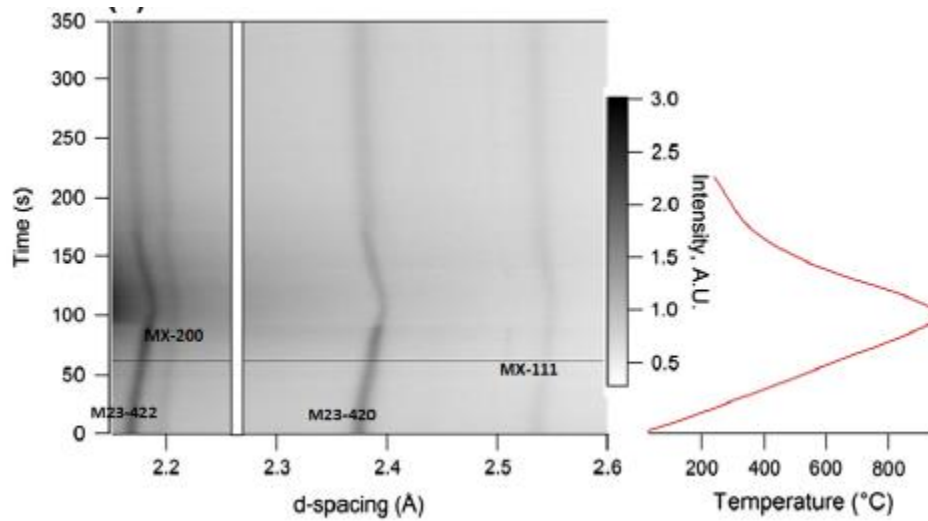


Figure 2.11 In-situ diffraction of m23c6 peaks during the FGHAZ simulation [35].

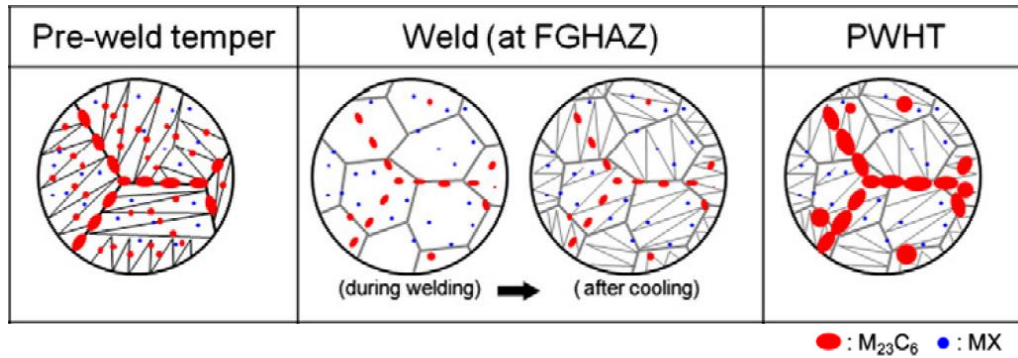


Figure 2.12 Schematic representation of the carbide evolution during tempering, welding, and PWHT [35].

The authors reported using an in-situ high-energy X-ray diffraction technique to investigate simulated HAZ. During welding, the sample exhibited residual $M_{23}C_6$ particles due to incomplete dissolution. Consequently, during PWHT these $M_{23}C_6$ precipitates undergo coarsening at the FGHAZ, which leads to a premature creep failure at these locations. The results of the $M_{23}C_6$ incomplete dissolution is shown in Figure 2.11. Yu et al. (2013) illustrated a schematic representation of the carbide evolution during tempering, welding, and subsequent PWHT (seen in Figure 2.12). The large red spots are $M_{23}C_6$. It can be seen that after the PWHT the $M_{23}C_6$ have coarsened and remained on the initial PAGB.

With the mechanism of the Type IV cracking and the knowledge that Type IV cracking is an issue for power plants, it is imperative to eliminate this type of failure. For power plants, eliminating the Type IV cracking would aid in lowering CO_2 emissions, along with saving money in preventing costly maintenance. The mechanism for Type IV cracking was found to closely be related to the evolution of microstructure. It may be possible to eliminate or control Type IV cracking with microstructure control. There is any number of ways to provide

microstructure control in a steel. A few methods that have been proposed in the past will be discussed below, which leads into the research contained in this dissertation.

2.5 Microstructure Control with Non-Standard Heat Treatment

To understand the role of welding on the creep strength, the underlying microstructure evolution also needs to be understood. Recently, Yu et al. (2013) demonstrated the effects of peak temperature in the HAZ on the carbides, by performing an in-situ high energy X-ray diffraction to investigate simulated HAZ of different heat-treated Grade 91 samples [35]. The different heat treatments conducted was a standard tempering and a low-temperature tempering (LTT) of 650 °C for 2 hours. In the LTT samples, the carbides did not coarsen as much as the standard heat-treated samples. The results showed that, in the LTT samples, a complete dissolution of the $M_{23}C_6$ carbides occurs at the FGHAZ during welding. This permits re-precipitation of fine $M_{23}C_6$ carbides during the PWHT, which in turn act as strengthening precipitates during creep conditions. In contrast, the standard tempered sample (denoted as HTT) exhibited residual $M_{23}C_6$ particles due to incomplete dissolution of larger $M_{23}C_6$ during the welding thermal cycle. Consequently, during PWHT these $M_{23}C_6$ precipitates over coarsen at the FGHAZ. These coarse carbides have been shown to lead to cavity formations and premature creep failure [6, 36-38]. Yu et al. (2013) also reported more than 2-fold creep-rupture improvement, 2400 hrs, in the steel welds by utilizing the lower temperature tempering, versus 500 hrs after standard tempering. From the previous understanding of creep, and the role precipitates play in dislocation creep, the results can be explained. The interparticle spacing and size of the precipitates are much smaller in FGHAZ of the LTT samples (76 nm versus 164 nm in HTT), which provided more precipitate strengthening. Nonetheless, for Grade 91 steel welds, it can be concluded that a finer size distribution, both an increase in density and decrease in average radius, of $M_{23}C_6$ in the FGHAZ

after PWHT is the key to improving the cross-weld creep properties of the CSEF steels. Even though there was a dramatic increase in the creep rupture properties of the weldments after the LTT, it should be noted that not all the macro level structural properties were maintained. The Charpy Impact toughness of the LTT sample was less than 10 J at room temperature. The standard industrial practice allows the steel to achieve a Charpy Impact toughness of ~150 J at room temperature. This allows the steel to be transported without the risk of fracture. Finally, to solve the Type IV cracking challenge and still be able to be implemented in industry, both the creep properties needs to be improved and the macro level structural properties needs to be maintained. Utilizing other methods of microstructure control may allow for the desired microstructure during the pre-weld temper. In addition, the microstructure control should also be able to maintain all the structural properties required for service, including the toughness.

2.6 Thermo-Mechanical Treatments

Traditionally thermo-mechanical treatments or processing (TMT or TMP) is a manufacturing technique to reduce the austenite grain size, which then reduces the ferrite grain size upon cooling, as opposed to cooling without TMT. The reduction of ferrite grain size is a good method for strengthening steel, which will be discussed later. In TMT, the steel is generally austenitized for some time to completely transform the microstructure into austenite and in some cases to dissolve the precipitates. In the past, the steel was hot worked by rolling or forging at a high temperature, greater than 1000 °C, because the steel is much easier to deform. However, the steel would quickly recrystallize, and the grain size reduction would be minimal. Whereas, when the processing temperature is reduced below a critical temperature, the steel will not recrystallize during manufacturing. This temperature is called the temperature of no recrystallization, T_{nr} . Because the steel cannot recrystallize, the austenite grain sizes remain small and produce an

extra refined ferrite grain structure upon transformation [39]. This process is shown schematically in Figure 2.13 [39].

In recent decades 80s and 90s, the effects of Nb and thermo-mechanical processing on the refinement of grain sizes have been studied. The atomic size of Nb is 25% larger when compared to iron. Thus, Nb creates a good solid solution hardening element. In solid solution, Nb has been shown to slow subgrain boundary migration by the solute drag effect and prevent recrystallization. Therefore, with the addition of Nb recrystallization can be retarded at higher temperatures. Thus the T_{nr} can be adjusted, with an adjustment in Nb content, and can also increase the time before recrystallization at a certain temperature [40]. Small additions of Nb have been beneficial in commercial steels. In Grade 91 steel, Nb is added to precipitate Nb rich carbonitrides for strengthening. Interestingly, with the addition of Nb, the effects of the T_{nr} and TMT can also be utilized to help improve the creep properties of the base metal. Li et al. (2013) have shown that performing TMT of Grade 91 steel before cooling to room temperature, and subsequent tempering can improve the creep-rupture performance of the steel [41]. By performing TMT, the prior austenite grain size and martensite block size is reduced. With this reduction, the amount of grain boundary per unit volume is increased, thus increasing the nucleation sites for $M_{23}C_6$ and carbonitrides. It was shown that with TMT, the sizes of carbides was reduced and the number density is increased. From the knowledge of creep and precipitate strengthening, the interparticle spacing is reduced which improves creep properties.

Recently, the TMT process has been used to control the precipitation of carbonitrides to improve creep strength. Klueh et al. (2003) have reported the TMT concept for improving the creep properties of 9-12Cr CSEF steels through a thermo mechanical treatment (TMT).

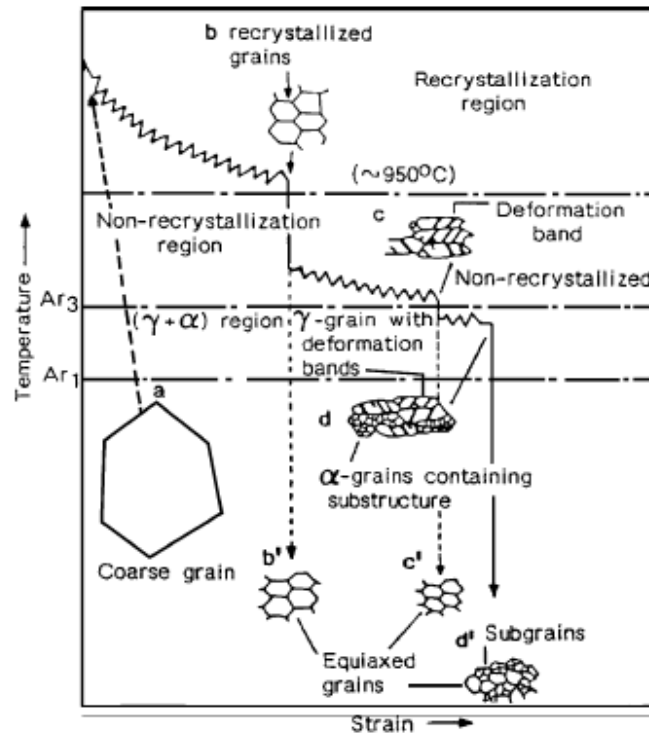


Figure 2.13 Schematic illustration of changes in microstructure with thermo-mechanical processing.

The TMT combines a hot-deformation in a temperature range where austenite is stable (aus-forming) with a subsequent isothermal annealing at the same temperature (aus-aging) [42, 43]. By applying the TMT, the density of dislocations in the austenite matrix is increased which act as nucleation sites for MX (M: mainly Nb and V, X: C, N). Subsequent aus-aging results in dense MX precipitation in the austenite before the matrix transforms to ferrite at high temperature or martensite on cooling to room temperature. The authors reported the material exhibiting almost two to three orders of magnitude longer creep life at 650°C and 138 MPa after deformations of 20-60%. Although the study focused only on the base metal properties, the possibility of this route to improve creep properties of cross-welded samples has never been attempted. It should also be emphasized that the TMT process allows for the added benefit of the improved room-temperature ductility by applying a standard tempering, while benefiting from increased creep strength.

2.7 Fe-Cr Ferritic Alloys

In recent years, there has been a development of a Grade 92 steel with additional strengthening from an intermetallic Laves phase by the addition of W. Abe (2005) has shown the effect of a fine (< 100 nm) precipitation of Fe_2X (X: W, Nb, etc.) Laves phase [44]. While aging during creep, Laves phase would begin to precipitate on the prior austenite grain boundaries and martensite block boundaries, which reduce the creep rate further than traditional Grade 91 steel. However, the effects of welding are not discussed. With traditional M_{23}C_6 carbides still present, Type IV cracking should still be considered an issue. Alongside the development of this Grade 92 steel, there has also been a development of model alloys based on Fe-Cr system with controlled additions of W, Nb, Si, Mo, and Co, all of them with a tendency to form an intermetallic Fe_2X Laves phase. In these alloys, the microstructure remains fully ferritic from

liquid upon cooling. With some aging, Laves phase is precipitated from the ferrite matrix, providing strengthening. Shibuya et al. (2011) have developed a 15Cr-1Mo-2Co-6W-V-Nb which relies on the precipitation of Fe_2Nb intermetallics and M_{23}C_6 carbides [45]. Although the researchers have shown this alloy system based material performs as well as conventional Grade 92 ferritic steels, this alloy contains the M_{23}C_6 carbide, which has been shown to coarsen rapidly during welding and aging ($10^{-25} \text{ m}^3\text{s}^{-1}$). At the same time, Kuhn et al. (2011), has developed a 22Cr-W-Nb alloy system strengthened by only by intermetallics (Fe_2Nb & Fe_2W Laves phase). In this alloy system, the intermetallic compounds do not coarsen rapidly ($10^{-28} \text{ m}^3\text{s}^{-1}$), but the creep strength was insufficient when compared to conventional 9% Cr steels where the 10,000 hrs rupture stress is about 40 MPa while the 22Cr alloy has about 20 MPa rupture stress [46]. Another challenge for these ferritic alloys is the formation of sigma phase. Sigma phase is an intermetallic of Fe and Cr, and is found to be detrimental to the creep rupture properties of these alloys. The current research will focus on the development of a Fe-30Cr-3Al fully ferritic alloy with increased amount of Nb to precipitate the Fe_2Nb Laves phase providing better creep strength. This alloy was also developed to be free of sigma phase at a service temperature of 700 °C.

However, when comparing the fully ferritic alloys to the 9% Cr steels, there is a service temperature difference. When the first generations of the ferritic alloys were being produced the thought was that the alloy would be able to replace the 9% Cr steels and directly eliminate Type IV cracking in all sections of the power plant. The service temperatures for the Grade 91 steels are between 550 and 650 °C, but the service temperature of the Fe-Cr alloys would need to be maintained above the sigma phase solution temperature. In the newly developed Fe-30Cr-3Al fully ferritic alloy, the sigma phase solution temperature is around 650 °C. Therefore, this alloy

would not exactly be considered a direct replacement of Grade 91 steel, but could replace Grade 92 or the austenitic stainless steels in the hotter sections of the power plant. With good creep resistance and excellent steam oxidation resistance this alloy would be a good candidate to be incorporated in modern power plants.

2.8 Creep and Creep Mechanisms

2.8.1 Creep

Creep is a slow time-dependent plastic deformation process that occurs under a constant load. In general, creep is a relatively high-temperature process. By relative, the meaning takes on the form of a homologous temperature of the ratio between the test temperature and the melting temperature T/T_m . Creep most often occurs above $.4T_m$, although creep can take place at all temperatures above absolute zero Kelvin at extremely low rates, mostly not measurable [47]. Creep can be broken up into two to three regions. This is represented in the creep curves of Figure 2.14 (not necessarily to scale). The three regions of the creep curve are the primary creep region, secondary or steady state region, and finally the tertiary creep region. The first region, primary creep, is the region between ϵ_0 and ϵ_1 (Figure 2.14a). This stage is the initial strain upon loading and is, in general, a small fraction of the overall time length of the creep curve. The fast decrease in creep rate can be attributed to the competition between strain hardening and recovery. When this competition gets to a point of equality, the secondary creep regime has started. The secondary or steady state region has the longest time scale. The steady state creep rate is commonly the parameter that is used for determining the creep strength of a creep resistant steel: i.e. the lower the creep minimum creep rate, the better performing material.

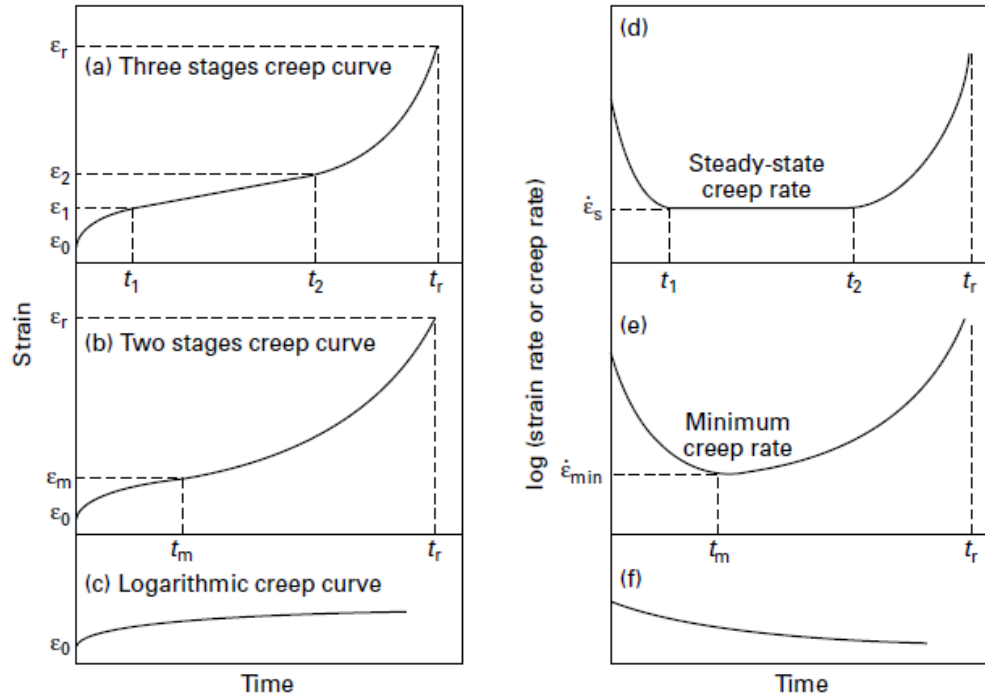


Figure 2.14 (a), (b) and (c) Creep curves of engineering steels under constant tensile load and constant temperature and (d), (e), and (f) their creep rate curves as a function of time [51].

This region is at steady state because of the competition between the rate of recovery and the rate of damage generation. The final creep stage, tertiary creep, is where there is an onset of a runaway creep rate, which leads to final failure. In ductile materials, the beginning of the tertiary region can be seen as the start of necking. When necking starts, the area of the material reduces, thus increasing the stress at the localized region. When the stress increases, the creep rate will increase, and the material will deform more. With more deformation, the stress continually increases, and the cycle continues, thus a runaway feature on the curve. It can also be shown that stress and temperature play an important role in creep and the creep curves. Figure 2.15 shows the stress and temperature dependency on the creep curve. The figure shows that with increasing the stress and/or temperature the creep rates increase, leading to failure faster.

As mentioned briefly above, the minimum creep rate can be used in the comparison of two or more materials. The creep rate of any steel can simply be described as $\dot{\epsilon} = d\epsilon/dt$. Where ϵ is strain and t is time, generally hours. In CSEF steels the minimum creep rate can be modeled using a basic equation.

$$\dot{\epsilon}_m = A\sigma^n \quad (2.1)$$

Where $\dot{\epsilon}_m$ is the minimum creep rate. A is a constant based on material properties and can be predicted from experimental interpolation, and usually has the units of $\text{strain} \cdot \text{h}^{-1} \text{MPa}^{-1}$. n is the stress exponent, which is also determined by experimental interpolation. Further analysis of the factor A reveals the following:

$$A = A' \exp\left(\frac{-Q}{RT}\right) \quad (2.2)$$

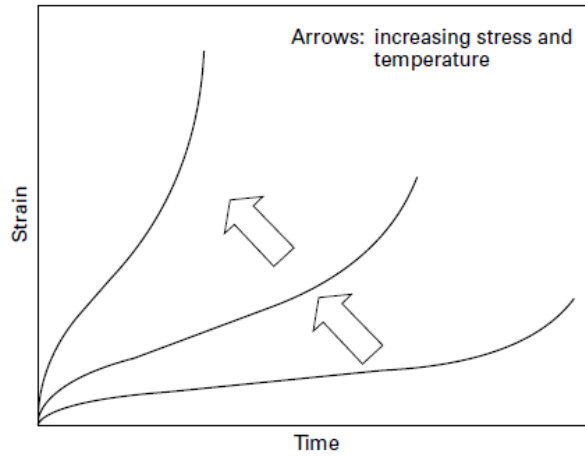


Figure 2.15 Schematic of the creep curves with the dependence of stress and temperature [51].

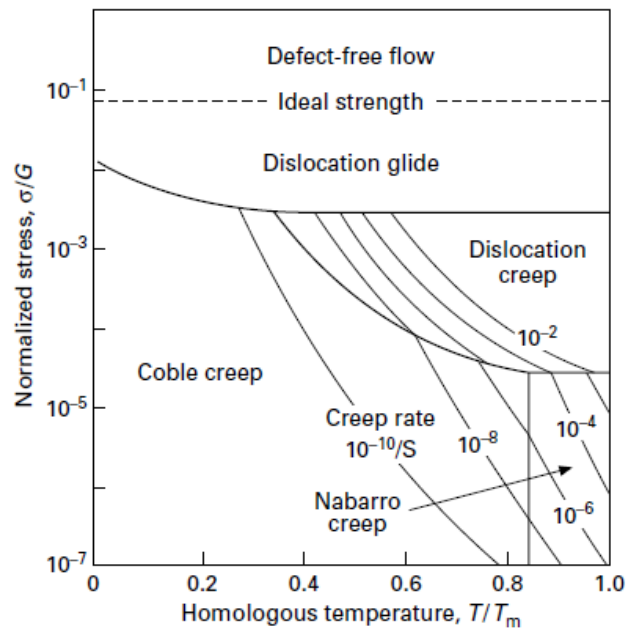


Figure 2.16 Basic deformation mechanism map with contours of constant creep rates [51].

Here Q is the effective creep activation energy. R is the gas constant, and T is the temperature in Kelvin. A' contains detailed material properties. These equations can represent underlying creep mechanisms, which will be discussed in the next section. The stress exponent and creep activation energy are measured experimentally. These two values are then compared with known literature values for a specific creep mechanism and diffusion activation energy. The stress exponent is found by plotting a normalized $\log \dot{\epsilon}$ vs. normalized $\log$ stress. The creep activation energy is found by taking the temperature corrected $\dot{\epsilon}$ vs. normalized stress [48, 49]. After these values are determined then the creep mechanism can be confirmed. An example of mechanism determination is the following: if the experimentally observed stress exponent is 4 and the activation energy was observed to be close to the activation energy for self-diffusion, then the creep mechanism can be confirmed to be dislocation creep.

With understanding the creep equations and mechanisms, it is possible to construct a deformation mechanism map (see Figure 2.16) [50, 51]. Each region of the deformation map shows the creep mechanism that is most dominant. However, this does not mean that it is the only mechanism contributing. For example, during dislocation creep, Coble creep may still play a small role. Thus, the maps can give a general guideline of which creep mechanism that is dominant in the material of interest. The lines separating each region is where the creep rates, determined using the equations, and contribution of each mechanism are equal [50].

Additionally, a map is constructed for a specific material at a particular condition. Grain size, dislocation density, and particle distribution can all change the maps [51, 52]. Therefore, a distinct map for each grain size, dislocation density, or inter-particle spacing must be constructed and can make understanding the creep mechanism of a specific test challenging.

2.8.2 Creep Deformation Mechanisms

Since creep occurs at all temperature values up to the melting point and over a wide range of applied stress ranges below the yield strength, it is understandable that there can be more than one creep mechanism. As shown above, in Figure 2.16, the creep mechanism map shows the mechanisms of creep at different stresses and temperatures. All the creep mechanisms can be modeled by the Bird, Mukherjee, and Dorn equation [53].

$$\dot{\epsilon} = A_{\alpha} D_0 \exp\left(\frac{-Q_0}{RT}\right) \frac{Gb}{kT} \left(\frac{b}{d}\right)^p \left(\frac{\sigma}{G}\right)^n \quad (2.3)$$

Where $\dot{\epsilon}$ is the steady state, or minimum, creep rate. A is a dimensionless constant, which changes based on creep mechanism and α is a placeholder for the mechanism indication. D_0 and Q_0 are the diffusion constant and activation energy for the either grain boundary diffusion or lattice diffusion. G is the shear modulus, b is the burgers vector, k is Boltzmann's constant, T is temperature, d is grain size, and σ is the applied stress. p and n are creep mechanism constants, with p being the grain dependent exponent, and n is the stress exponent, these are often measured experimentally. The subsequent sections will describe the main points of the creep mechanisms.

2.8.2.1 Diffusion Creep

Diffusion creep is dominant at low-stress levels for a particular material. This mechanism is represented by the exchange of vacancies and atoms either on grain boundaries or through the bulk. By these two exchange mechanisms, diffusion creep is easily subdivided into Coble creep and Nabarro-Herring creep. Because of the atom/vacancy transport, smaller grains would mean faster accumulation of vacancies on the grain boundaries. Thus grain size plays an important role in the overall strain accumulation and strain rate.

Coble Creep

Coble creep is the exchange of vacancies along the grain boundaries. Creep cavitation at grain triple points can be found after creep tests indicating vacancy exchange. Although dislocation creep and Grain Boundary Sliding can produce the same cavitation. Thus it is difficult to identify solely on microstructure. The Coble creep mechanism generally occurs at $< .9 T/T_m$ and occurs at all stress levels. However, it is usually dominant where $\frac{\sigma}{G} < 10^{-3}$. The dimensionless constant A_{co} takes a value of 66.8 and the diffusion coefficients are obtained from grain boundary diffusion data [52, 54, 55]. The p and n exponents for Coble creep are 3 and 1 respectively, and are measured experimentally. From the equation, a grain size exponent of 3 shows that this mechanism is highly sensitive to the grain size. Thus, a larger grain size would reduce the creep rate and small grain size would have a faster creep rate. Therefore, the strain rate can be controlled by modifying the grain size. The grain size dependence is based on the available grain boundary area per unit volume. A larger grain would have a reduced amount of grain boundaries per unit volume. Essentially this means the grain boundaries are longer, thus providing a relative larger traveling distance for the total amount of vacancy exchange in the material. If the rate of vacancy exchange is assumed to be the same in a small grained sample and large grained sample, the overall rate at which vacancies can travel and accumulate is faster in the small grained sample.

Nabarro-Herring Creep

Nabarro-Herring creep is the exchange of vacancies within the matrix. In this mechanism, vacancies are emitted from grain boundaries perpendicular to the tensile axis. The vacancies travel through the grain and are adsorbed on grain boundaries parallel to the stress axis.

Elongated voids are observed on parallel grain boundaries, which is an indication of grain separation. This mechanism generally occurs at $> .9 T/T_m$ and occurs at low normalized stress levels. The p and n exponents for Nabarro-Herring creep are 2 and 1 respectively. The dimensionless constant A_{NH} takes a value of 28, and the diffusion coefficients here are taken as the lattice self-diffusion [56, 57]. This creep mechanism is still debated because of the extreme conditions, excessively large grains ($> 1\mu\text{m}$) and temperatures almost to the melting point, needed for this mechanism to become dominate and the evidence provided only shows voids along the grain boundaries parallel to the applied stress. It is however argued that grain boundary diffusion is almost always larger than lattice self-diffusion. For current structural, i.e. precipitate strengthened materials, Nabarro-Herring creep is rarely if never observed.

2.8.2.2 Grain Boundary Sliding

Grain Boundary Sliding (GBS) is a relatively new creep mechanism in its understanding [58]. This means that the mechanism was mistaken as a form of Coble creep in the past. However, since the 1980's GBS has been more thoroughly investigated and recent literature has looked at previous works and shown how the GBS mechanism was mistaken for Coble creep [59]. Researchers have since constructed maps which include GBS, and have demonstrated that GBS is in between the Coble mechanism and dislocation creep [60]. The maps make it evident that GBS can complicate the full understanding of which mechanism is dominant at a given condition. The strain from the GBS mechanism is accommodated by the sliding of grains against each other. There are two types of GBS; the first is called Lifshitz Sliding and the second is called Rachinger Sliding [61]. The Lifshitz mechanism is a diffusion controlled mechanism. This mechanism is most similar to the Coble creep mechanism and thus inherited the confusion. Here the grain rotates under the exchange of atoms along the grain boundary, but this is not stress

dependent. This means that parallel and perpendicular grain boundaries do not get preferential exchange, but the whole grain will slide amongst each other. This mechanism has been traditionally observed by applying a small scratch on the surface across one grain boundary. When sliding occurs the scratch will split at the grain boundary and one half will move away. The Rachinger mechanism occurs more readily at conditions of service and creep testing. The Rachinger process, although GBS, is mechanistically different from Lifshitz. Here the sliding is accommodated by intragranular movement of dislocations immediately adjacent to the grain boundaries. The dislocations travel along the grain boundary and are emitted into the adjacent grain and pile up on subgrain boundaries. This pile up causes a traditional triple point cavity. Because the Rachinger mechanism involves the movement of dislocations, the same metallurgical understanding of impediment can be used. Discrete particles on the grain boundaries can be effective in slowing the dislocation movement [62, 63]. Since the particles are much larger than the dislocations, the dislocations will be stopped as they travel along the slip plane adjacent to the grain boundary. Then the dislocations must climb over the particle before continuing. In a similar fashion, the pile up of dislocations around the particles can produce a cavity. The cavities can eventually link up and produce a crack leading to failure.

2.8.2.3 Dislocation Creep

Dislocation creep is a mechanism that is described by the movement of dislocations by glide through the matrix by a thermal activation. Similarly, to tensile tests, the dislocation movement provides the plastic deformation. In particle-hardened steels, the dislocation movement can be impeded by an array of discrete particles. The dislocation has to then, through diffusional processes, climb over the precipitate before the dislocation can then proceed on its glide plane [64, 65]. Also, other dislocations can slow the movement through the matrix as well. Because

traditional steel strengthening mechanisms slow dislocation creep, this topic will be discussed in the next section with an emphasis in section 2.9.4.

2.9 Strengthening Mechanisms

In order to develop better, longer-lasting steels, it is important to understand the strengthening mechanisms. Knowledgeable and more detailed choices can be made to help improve low and high temperature properties of steel. In general, most of the low temperature improvements can be translated to high temperature properties. For steels, the overall strength can be obtained using multiple mechanisms. The strength equation (Equation 2.5) shows the generic model to understand the contribution of all the strengthening mechanisms, where each mechanism can be defined by its own unique equation.

$$\sigma_{total} = \sigma_0 + \sigma_s + \sigma_\rho + \sigma_g + \sigma_p \quad 2.5$$

The σ_{total} is the total yield stress with all contributions. σ_0 is the contribution due to lattice friction to slow dislocations in pure Fe, σ_s is the solid solution strengthening from large or small atoms, σ_ρ is strengthening from dislocation density (cold working, martensitic transformation), σ_g is the contribution due to grain boundaries, and finally σ_p is strengthening from precipitates.

2.9.1 Solid Solution Strengthening

Solid solution strengthening is a mechanism that is derived from the introduction of different sized solute atoms or substitutional atoms. An example of this is Mo in solid solution with Fe. The Mo atoms are 22% larger than the Fe atoms. Since the Mo atoms will occupy a lattice point in the cubic crystal, a small lattice distortion will occur. When a dislocation approaches the strain field around the substitutional atom, an extra amount of stress will be required for the dislocation

to pass through the strain field [66]. In the case of high temperature and low stress (such as creep), time is then needed for the dislocation to climb, with diffusion, around the atom. In addition, small substitutional atoms will also have a solid solution effect. Instead of an expansive strain field from a large atom, the strain field will be contractive. Although again, an extra stress will be required to move a dislocation through the strain field.

2.9.2 Dislocation Strengthening

Dislocation strengthening is widely used for industrial applications by the process of cold working. It was discussed above that plastic deformation is the result of the movement of dislocations. Therefore, the strength of a steel can be increased by halting the movements of dislocations. Similarly to large solute atoms, dislocations have their own stress or strain field around them. When one dislocation gets close to another dislocation, their stress fields will interact and impede each other's movements. Thus, an increase in dislocation density will lead to an increase in the number of dislocation-dislocation interactions and increase the force required to move dislocations. This relationship can be seen in the following equation [66].

$$\sigma_0 = \sigma_i + \alpha G b \rho^{1/2} \quad 2.6$$

Where σ_0 is the stress required to move dislocations or the yield stress contribution in pascals. σ_i is the stress to move one dislocation in the matrix, α is a constant, G is the shear modulus in pascals, and b is the burgers vector. Finally, ρ is the dislocation density. For Grade 91 steel, cold working is not the mechanism which causes an increase in dislocation density. Here, the martensitic transformation itself introduces a large amount of dislocations. Therefore, in Grade 91 the dislocation density is inherently increased. Maruyama et al. (2001) has shown an improvement in creep strength with the addition of a dislocation substructure. The creep rate for

a bainitic steel with a dislocation substructure is 1/20-1/70, with respect to stress increases, of the creep rate of a ferritic steel without a dislocation substructure. This provides an understanding that the martensitic structure helps to improve the creep strength of the Grade 91 steel over annealed ferritic steels [65].

2.9.3 Grain Boundary and Martensite Strengthening

Another method for strengthening steels is the mechanism of grain boundary strengthening. Unlike other dislocation interactions, the dislocation cannot pass a grain boundary regardless of stress. Therefore, grain boundaries are preferred in strengthening a steel. Since grain boundaries are a good method to stopping dislocations, an increase in grain boundaries per unit area or simply a decrease in grain size is shown to correlate with an increase in yield stress. This relationship is shown in equation 2.7. The relationship is known as the Hall-Petch Relation.

$$\sigma_0 = \sigma_i + kD^{1/2} \quad 2.7$$

Where σ_0 is the yield stress. σ_i is the internal friction stress from the resistance of the lattice to dislocation movement. k is a constant, which measures the hardening due to grain boundaries. Finally, D is the average grain diameter. In most cases, a smaller grain size is desired. However, for alloys that creep under the Coble mechanism, larger grain size is preferred. This slows down the creep rate. As explained in Section 2.8.2.1, larger grain provides a longer traveling distance for the total amount vacancy exchange. For general purpose or dislocation creep, the martensitic transformation provides an easy method of reducing the grain size. Within one prior austenite grain (PAG), martensite can be sub divided into packets, which sub divide into blocks. Then blocks are made up of two of twenty four martensite lath variants [17, 67]. Laths in a given packet have the same plane parallel relationship between close-packed planes. Thus, there are

four crystallographically different packets in an austenite grain. In a packet, there are six variants with different direction parallel relationships on the same coupled parallel close packed plane [67].

With processing and alloying additions, such as carbon, the packet and block sized can change. The packets and blocks can be essentially viewed as effective grain sizes. With these two sizes, it is necessary to find the contribution from both. Since the block boundaries inside a packet act as obstacles to dislocation motion, the slip plane length can be described to a certain extent by block width (d_b) and packet size (d_p). If it is assumed that the block is rectangular, and the length of the block is equivalent to the packet size, the slip plane length can be calculated from the following equation [68].

$$M = \frac{d_b}{\cos \theta} \quad \text{for } \theta \leq \frac{d_b}{d_p} \quad 2.8$$

Then the overall strength contribution of martensite can be calculated from a modified Hall-Petch equation.

$$\sigma_m = K_y M^{1/2} \quad 2.9$$

2.9.4 Precipitate Strengthening

Alongside grain size reduction, the use of precipitates is also a common mechanism for strengthening. There are different types of precipitation, such as soluble solute atoms. For example, copper precipitates in aircraft grade aluminum. Where at high temperatures the atoms are fully soluble in the aluminum matrix. However, at a temperature below the critical temperature, the copper atoms agglomerate and form precipitates, this is called precipitate aging. Another type, which is most common in steels, is the compound type. The compound type

precipitates are the carbides, intermetallics, etc. In general, all the types of precipitates contribute to strengthening the same way. Precipitates impede the motion of dislocation. For low temperature deformation, dislocation motion through discrete obstacles is understood. However, under high temperature creep, describing the way precipitates interact with dislocation and the extent of impediment is more complex and is not easily understood. There are many contributing factors to precipitate strengthening, for example, misfit differences, modulus differences, precipitate cutting, and along with dislocation climb at the interface are a few contributors. These are discussed elsewhere [64, 66, 69, 70]. For this research, the mechanism of Orowan looping and dislocation climb will be discussed as it applies to a threshold stress needed to move dislocations during creep. This threshold stress and relation will be discussed in Chapter 7. When a dislocation approaches an array of precipitates; the dislocation will interact with the stress field around the precipitates. For deformation to proceed, an extra stress is required to bow the dislocation through the array. This motion also increases the stress necessary to continue further bowing. Once enough stress is applied the dislocation will loop around the precipitate and break free while leaving a loop (see Figure 2.17) [66].

During creep, however, the Orowan stress can be used as the stress at which a dislocation can overcome the repulsive interaction between it and the precipitate by thermally activated climb or bypass [64, 71, 72]. Ashby (1966) has described the Orowan shear stress τ in the following equation.

$$\tau = \frac{Gb}{2\pi\lambda} \ln \frac{d}{b} \quad 2.10$$

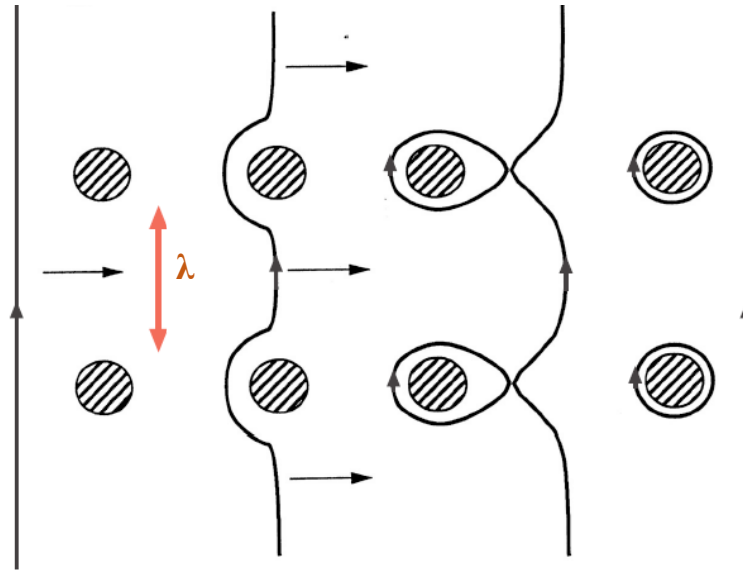


Figure 2.17 Orowan Looping Mechanism with a precipitate spacing of λ , (From Dieter, *Mechanical Metallurgy* [66]).

Where G is the shear modulus, b is the burger's vector. d is the average particle diameter, and λ is the interparticle spacing. The interparticle spacing can be found by the following equation [73].

$$\lambda = r * (.554 * \left(\frac{4*\pi}{3*f}\right)^{\frac{1}{3}} - 2) \quad 2.11$$

Where r is the particle radius and f is the volume fraction of the particles. Based on these equations, the creep rates are found to be sensitive to the interparticle spacing and particle size. With a small change in these parameters, such as alloying additions to increase particle density or processing techniques, the result can have a large effect on the overall creep strength. Coarsening can also change the size and spacing of particle, which can lead to changes in the creep rate during testing or service. The $M_{23}C_6$ carbide is known to coarsen at high temperatures (700-800 °C or below a_c1), leading to an increase in creep rate in Grade 91 steels.

2.10 Characterization Techniques

To further understand how the material responds during creep deformation, characterization of the microstructure is needed. Different length scale (nm to mm) characterization techniques are used to understand the microstructure fully, and can help determine the evolution of the microstructure with time, temperature, and applied stress. The following section is an introduction to different characterization techniques of different length scales.

2.10.1 Light Optical Microscopy

For general characterization, Light Optical Microscopy (LOM) is the first choice and has been widely used since first invented. This technique is used to characterize the surface of materials through a reflective process. Visible light is shown onto the material, usually a metal but can be

polymer or ceramic, and then the light is reflected into optical lens where the image can be magnified several hundred times. In general, the specimen which is being characterized is etched with an acid. Because the differences in phases or grain structures (morphologies and chemistries) the acid will etch away these features at different rates. This will cause these features to reflect light differently causing contrast differences, which can be used to distinguish between certain phases or grain structures. However, with LOM there are some challenges. The LOM does not have depth of field, which means it cannot observe objects in three dimensions' 3D. Although, there are some microscopes which can take several images at different focal lengths and stitch them together to make a false 3D representation of a surface. However, general LOMs do not have this ability, making it difficult to understand microstructure of an etched specimen.

2.10.3 Hardness Mapping

Hardness testing and mapping can give good insight into materials with heterogeneity. While mechanical testing, such as tensile or even creep test, is one of the most important characteristics in understanding material behavior, it cannot be used in microstructures with large heterogeneities such as welds. Weldments have a large microstructural gradient from the weld metal, heat affected zone, and to the base metal, and it may be difficult to understand the properties of each region with a simple mechanical test [74]. However, hardness testing can provide some insight on these microstructures. Traditionally the hardness test is used to evaluate the hardness of a material, but recently can be used to identify the strengths of materials [75, 76]. The mapping capabilities of current machines allow a user to show the hardness distribution of a weldment, which can help identify weak or brittle zones within a weld.

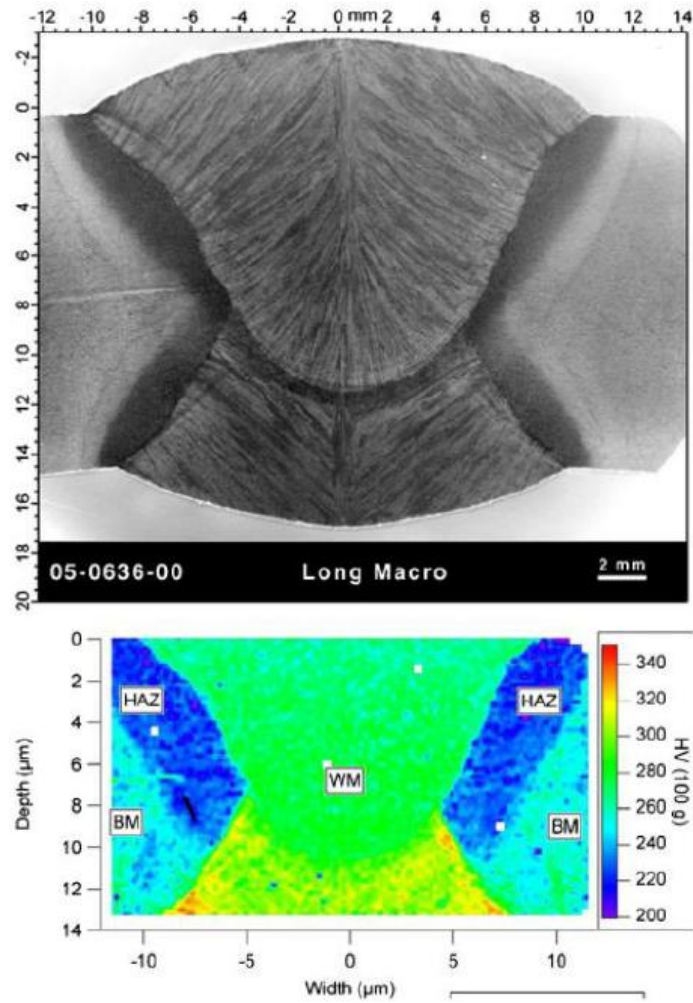


Figure 2.18 Micrograph and hardness map of the X100 steel weld.

Vitek has demonstrated the usefulness of the hardness map. Figure 2.18 illustrates a hardness map of an X100 steel weld. From the figure, the weld metal has an average hardness of 300 VHN, while the base metal has a hardness of 250 VHN. However, the map reveals softening in the HAZ with a hardness of 200-220 VHN. Understanding the hardness can help evaluate that the HAZ is weaker than the weld metal and base metal, and the weldment can be predicted to fail here. Also from the figure, the hardness map can more accurately determine the actual size and location of the HAZ, whereas the optically may not show actual locations. The main advantage of hardness mapping is quickly determining the spatial macro level properties, such as softening via over tempering. For creep, however, the hardness does not always translate into identifying the correct weak point in all conditions. An example is in Grade 91 steel; there is generally a softening effect in the FGHAZ. As described above this HAZ region usually fails first, but at high stress levels (>150 MPa) the failure then moves to the base metal or weld metal. Thus the hardness map does not always accurately determine the failure location for every creep condition.

2.10.4 Electron Microscopy

Unlike the light optical microscopy, electron microscopy uses the interaction of the specimen's surface with an electron beam to form an image, by either a reconstruction or diffraction of electrons. The scanning and transmission electron microscopy, (SEM & TEM) techniques are commonly used for characterization. Because there is no depth of field issue, the electron microscope, mainly SEM, can be used to view 3D features, i.e. differences in height based on etching, on the surface. Also, the resolution of electrons is much smaller than visible light. Thus the SEM can view features at much higher magnification.

2.10.4.1 Scanning Electron Microscopy

The scanning electron microscope (SEM), is one of the most widely used techniques [77-80]. Imaging in the SEM is produced by detecting secondary electrons, using an Everhart-Thornley Detector, emitted from the surface of the sample as a result of electronic interaction from the electron beam. The electron beam is produced from a source by heating up a tungsten filament, or LaB₆ single crystal in high precision models. An electric current between 15-30 kV's is used to heat the filaments. The electrons are focused using magnetic lenses and directed at the specimen where these electrons interact with the surface and subsurface. The lenses use a varying strength magnetic field to focus or change the size of the beam. A weaker magnetic field will produce a blurred image, but increasing the strength of the field, i.e. focusing, the beam will become sharper and so will the image. As mentioned here, the electrons used for imaging are produced from the bombardment of high energy electrons. The electrons excite the atoms on the surface, which makes them go to a higher energy state. The atoms will try to reduce their energy. Therefore, when the atom drops to a lower energy state, a secondary electron is produced alongside X-rays. Simple imaging is not the only way to use the SEM. An SEM can be equipped with many other detectors that can be used alongside the imaging detector. Chemical analysis can be performed using an Electron Dispersive Spectroscopy (EDS) detector. Each element will produce a characteristic X-ray when the atom falls from its excited state. The EDS detector can then match this X-ray with the element. By probing a point, generally a carbide of interest, on the surface of the material, thousands of X-rays can be produced per second. The detector can measure the amounts of X-rays in a given time and calculate the chemical composition of the point. Although, the EDS detector does not produce an image. Therefore, EDS is used in conjunction of other imaging techniques to find the particles.

In particle hardened structural steels, it is important to obtain good imaging and quantification of the particles. One method of doing such is electron backscatter detection. Here a detector is placed, it appears like a donut, around the electron gun. Instead of secondary electrons, the electrons penetrate into the surface of the sample and interact elastically with the atoms and backscattered into the detector, hence Backscatter Electron Detection (BSE). The backscatter phenomenon, elastic electronic interactions, is based on the size of the atom. Thus the heavier atoms will produce more backscattered electrons by being able to send back more electrons directly to the detector. The detector will show a bright spot where it is detecting more electrons. Some particles are enriched in heavy elements, i.e. larger Z number than the matrix (41 for Nb versus 26 for Fe). Thus, these particles will produce more backscattered electrons, and the particle locations can be identified by the bright to dark contrast produced in the image. The disadvantage of this technique is that it cannot be used for carbides or other particles with similar Z numbers to the matrix (25 for Cr versus 26 for Fe). Dimmler has shown the backscatter technique can be used to quantify Laves phase in 9-12% Cr steels, Figure 2.19 [78]. The figure shows good contrast between the Laves phase and the surrounding matrix. Although other particles can be identified the low contrast difference makes it more difficult for software to differentiate and analyze. Here, the author showed that in this steel, particles down to 400nm deep from the surface could be used to calculate the volume density and fraction of Laves phase. This information was used to determine the evolution of Laves phase in the steel during creep. A disadvantage of using the SEM is the poor resolution which makes quantifying smaller particles, < 10 nm difficult. Therefore, an accurate size cannot readily be determined.

Another technique utilized in the SEM is electron backscatter diffraction (EBSD). This technique provides grain orientation data. This is most important when understanding martensite.

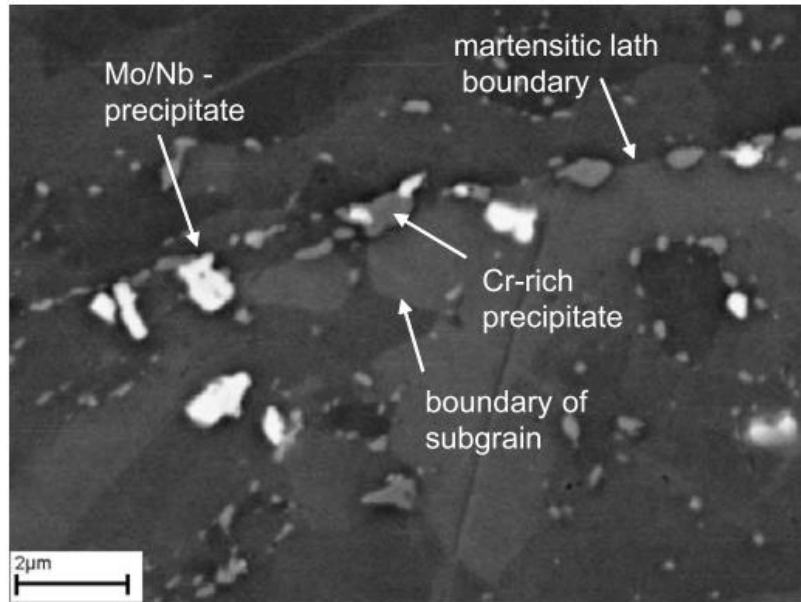


Figure 2.19 SEM image using the BSE detector in the alloy CB8 after creep [78].

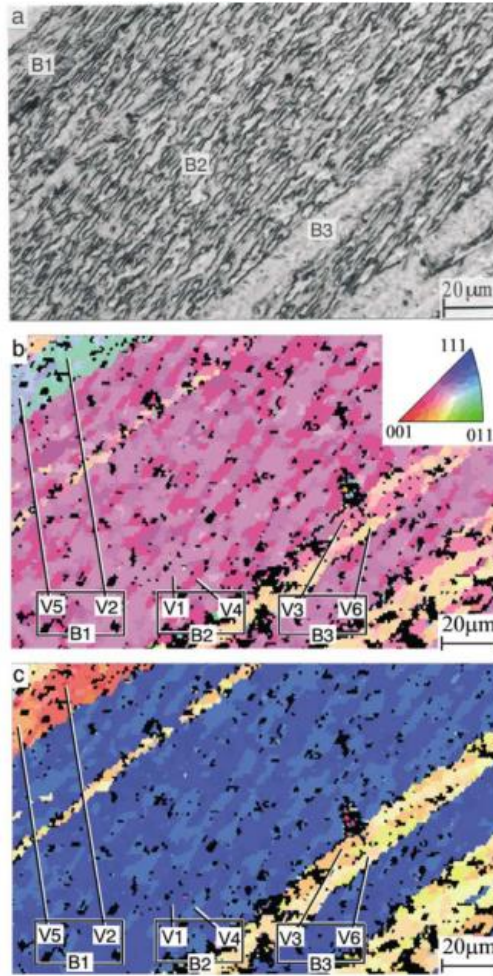


Figure 2.20 (a) Optical micrograph of lath martensite in Fe-0.0026C alloy, and (b), (c) the corresponding crystal-orientation maps obtained by EBSD analysis for the directions of perpendicular and parallel to the polished surface, respectively [81].

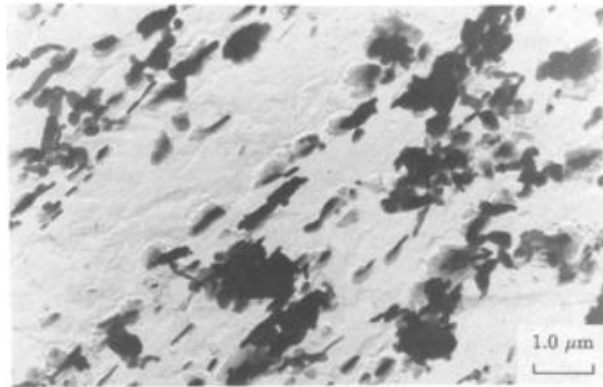
Prior austenite grain size and martensite substructure can be determined, as well as the orientation relationship between parent austenite and martensite. When martensite is formed from austenite, the orientation relationship is fixed ($[111]_{\gamma}/[110]_{\alpha}$). In order to minimize the strain energy during formation, martensite will form on the habit plane of the parent austenite. The habit plane for low carbon steels is the $[111]$ plane of austenite [81]. Then the closest close-packed plane in ferrite is then parallel to the habit plane. The orientation relationship of austenite to martensite is generally seen to be near Kurdjumov-Sachs (KS) relationship. There are 24 variants from four crystallographic plane relations, then four different packets could be seen in a given austenite grain, this was discussed in more detail in Section 2.9.2. This complex crystal orientation family can be imaged and studied using the EBSD technique. An example of this is shown in Figure 2.20. The color map shows the orientation of the martensite laths and relative rotations to each other. Multiple martensite blocks are discernable and within each block, slight color variations show two variants per block. Using this technique, effects of process on the grain sizes can easily be observed.

2.10.4.2 Transmission Electron Microscopy

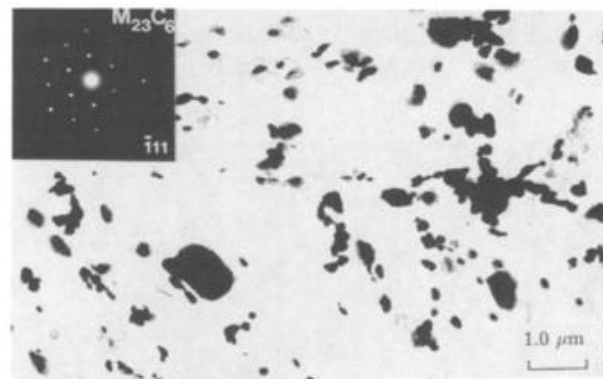
Transmission electron microscopy (TEM) is another microscopy technique of using electrons for imaging. However, in this technique, the electron beam is not diffracted or causes secondary electron emissions. The TEM uses an even higher energy electron beam, ~ 200 kV, to where the electrons pass through a very thin (<100 nm) sample. Some electrons will be slightly refracted as they pass through the sample, and using knowledge of ray physics, an image will be formed below the specimen on a phosphor screen, and nowadays can be captured using a CCD camera. Here too, the TEM also has a range of detectors for additional characterization: Scanning TEM (STEM) with EDS, Electron Energy Loss Spectroscopy (EELS), High Angle Annular Dark Field

(HAADF). STEM detection can be very useful in characterizing precipitates because STEM creates high Z-contrast similar to the backscatter detection in the SEM [82]. Generally, precipitates form with at least one element with a high Z number from the periodic table, for example, Nb in MX has a Z number of 46 as opposed to 26 for Fe. These elements will produce more counts on the STEM detector making them easier to see and then analyze. EELS detectors are able to detect the minute energy losses from incoming electrons. Each element will absorb a different amount of energy from the incoming beam. The detector will then be able to give a more accurate quantification of chemical makeup of the sample or particles. Also, unlike the EDS in SEM the EELS detector can more accurately determine the amounts of the lighter elements, C, O, and N. The HAADF imaging technique is mostly used in conjunction with the STEM mode in the TEM. Because both have excellent Z contrast, and the physics behind the high angle incoherently scattered electrons, imaging to lattice planes can be achieved. This technique allows users to view the coherency of particles in a matrix or grain boundary effects of solute atoms.

The TEM is widely used to characterize the precipitates in steels [2, 36, 83]. Because the TEM has a rather small resolution (which can approach 0.2 nm), precipitates can be imaged with ease. This is especially beneficial for power plant steels which may have multiple types of carbides. Thomson investigated the precipitation evolution in a 12Cr1MoV steel [38]. The author studied the difference in precipitation of an ex-service steel pipe and compared it to a laboratory aged specimen and correlated the carbides to failure. Figure 2.21 shows the comparison between ex-service pipe and laboratory aged specimen in the TEM. Small specimens were taken, and the carbides were extracted using the carbon replica technique.



(a)



(b)

Figure 2.21 Comparison between the distribution of carbides in ex-service material and laboratory aged at 700 C and 1173 hours.

The author correlated failure to the size distribution of carbides and not to the chemical composition of the carbides. In the figure, a black box containing a diffraction pattern can be seen.

An electron diffraction experiment is beneficial in many ways. One is that carbides and phases can be identified by the distance between diffraction spots and angles between two spots with the center. A second beneficial use of electron diffraction is to determine the orientation relationship of a precipitate with the matrix [84, 85]. Yamamoto et al. used this diffraction technique to find the orientation relationship between Laves phase and the matrix, as well as intermediate precipitates in high Cr heat resistant alloys. The orientation relationship of α -Fe to Fe₂Nb Laves phase was found to be $[\bar{1}11]_{\alpha\text{-Fe}}//[01\bar{1}0]_{\text{Fe}_2\text{Nb}}$. This information can aid in understanding the strength of the matrix/particle interface or how the particle may react with stress. This is valuable information when understanding how a precipitate will aid in reducing creep strain in the matrix or when the precipitate is on the grain boundary.

2.11 Relevance of Literature and Unanswered Questions

The previous sections gave a background of relevant knowledge relating to Creep Strength Enhanced Ferritic (CSEF) steels and the Fine Grain Heat Affected Zone cracking observed in modern fossil fueled power plants. The previous section discussed the creep mechanisms, which allows these steels to provide structural integrity, other than the weld, of the power plant's steam lines. Because of the premature failure (40,000 hours) of the weldments, it is necessary to understand everything about the CSEF steels, and thus a multiscale characterization method can be utilized. Characterization techniques such as SEMs and TEMs can be utilized to understand the underlying microstructures of the steels. Then by applying the knowledge of strengthening

mechanisms and further research, the steel microstructure can be altered to provide maximum integrity for as long as possible. For the 9% Cr CSEF steel, much is known about the base metal strengthening. However, there has not been as much research in understanding how to effectively strengthen the Fine Grain Heat Affected Zone (FGHAZ) of the weldments. It was briefly discussed how microstructure control can be used to increase the creep strength of the steels. However, there are a few unanswered questions that can be asked from what was learned in this chapter and that can be applied to direct the current research.

1. Can the FGHAZ be strengthened solely by precipitation strengthening from MX and $M_{23}C_6$?
2. Can we control the precipitation of MX and $M_{23}C_6$ in a way to strengthen the material?
3. Is it possible to understand the nature of the creep of the 9% Cr steels based on the precipitates size and distribution through the matrix?
4. Is there even a solution to the Type IV cracking in 9% Cr steels, and if not what can then be done?

It is known that there are many possible solutions to scientific challenges. It can then be natural to expand a research scope and tackle the problem from a different angle. One such expansion is to try to produce an alloy with similar or exceeding creep strength without having the same challenge. In the recent decade, researchers have started to tackle this challenge by producing an alloy of Fe and Cr without carbon. Since carbon is not used another element must be used to create precipitates for strengthening. The element that is most chosen is Nb which forms a strong Fe_2Nb Laves phase precipitate. Although with any new endeavor comes numerous questions.

1. What composition of the alloy is needed to provide the necessary requirements, ductility, creep strength, and even oxidation resistance?

2. What is the optimum amount precipitate forming elements is needed to provide good creep resistance without adding cost to the alloy?
3. What is the actual creep resistance of the new alloy and how does it compare to the traditional 9% Cr steel?
4. What are the mechanisms that provide this new alloy its strength?
5. Lastly, with the mechanism understood, how can the alloy even be improved?

Chapter 3. Objectives

Type IV cracking is a problem in modern models of fossil-fueled power plants. Type IV cracking and failure is the weakening of the microstructure in the FGHAZ of Grade 91 steels. The microstructure evolution in the weld zone has recently been identified and linked to the challenges of Type IV cracking, but previous research has not been able solve all the challenges in Type IV cracking. The research efforts contained in this dissertation identifies two methods for either minimizing or even eliminating Type IV cracking and failure in steel welds. The overall goal of this research is to answer the questions presented above through the understanding of the microstructure and then correlating the microstructure to the creep properties.

Objectives for Controlling the Microstructure in Grade 91 Steel Weldments:

As described above, Grade 91 steel has a problem with a weakened microstructure in the FGHAZ. Controlling the microstructure evolution during tempering is key to minimizing Type IV cracking. Utilizing a low pre-weld temper will obtain the appropriate size of $M_{23}C_6$ such that they will dissolve during welding. However, further investigation of this technique in service reveals that the overall toughness of the base metal is insufficient, where the toughness was found to only absorb 10 J at room temperature. The industrial standard absorbs roughly 150 J at room temperature. Therefore, there is a need to maintain sufficient toughness in addition to controlling the microstructure during tempering. The method of thermo-mechanical treatments (TMT) was chosen to precipitate the stable MX carbonitrides while reducing $M_{23}C_6$. The TMT method was also chosen to maintain sufficient toughness of the steel for service. The objectives

of the microstructural characterization are to understand the evolution of the microstructure during TMT processing, tempering, welding, PWHT, and creep deformation.

Objectives for Microstructure Control in the Development of the Fe-Cr-Al Alloy:

Current research on TMT of Grade 91 steel reveals that Type IV cracking is unavoidable in these carbon-containing steels. Recently there have been efforts to develop a fully ferritic (BCC) alloy strengthened by only intermetallics. Most of the research on these steels is to produce good creep strength for Solid Oxide Fuel Cells [46, 86, 87]. However, it seems reasonable that with some extra development, this zero-carbon ferritic alloy could have the potential to replace Grade 91 steel and eliminate Type IV failure. The current goal of this research is to obtain a baseline understanding of the microstructure before and after creep. This will allow for the understanding of creep mechanisms in the alloy, as well as understand how the alloy is failing. The objective of the microstructural characterization is to understand the base metal and the precipitation of Laves phase during creep. After understanding microstructure control for the alloys, it would then become easier to develop additional generations of this alloy system with better microstructures, which can account for the deficiencies in Grade 91 steel.

Correlation of Microstructures to Creep Resistance Through Phenomenological Model:

While characterizing the microstructure is beneficial, without understanding the microstructural relationship to creep resistance, it is not possible to provide materials that will withstand the requirements of the future. Above describes the objectives of understanding the evolution of the microstructure of two materials. However, it is necessary to provide a correlation of these results

with the creep resistance and provide guidance in moving forward. The final objective of this research is to use phenomenological numeric modeling to correlate the microstructures to the creep properties of the steel and alloys. It is necessary to understand how the distribution, both size and spatial variation, of precipitates affect the creep properties and how microstructure control through processing can provide improvements to the creep resistance. In addition, it may be necessary to adjust the model for other creep mechanisms. Here, the model can then correlate the microstructures of grain boundaries to the observed creep properties. For the Fe-Cr-Al fully ferritic alloy, another objective is to provide a formula that would allow the prediction of failure in the alloys based on microstructural evidence. Furthermore, this formula could then be used in service to understand when it is necessary to replace sections of piping.

Chapter 4. Experimental Procedures

4.1 Materials

4.1.1 Grade 91 Steel

The chemical composition of the Grade 91 steel and matching filler metal is shown in Table 4.1 below. The steel came in an as received condition in a 25mm thick hot-rolled plate. The as received microstructure was in the normalized and tempered condition. The steels would then be subjected to another normalization at 1050 °C for 2 hours then air cooled. For the thermo-mechanical treatments, the steel was processing using one of two techniques, hot forging or hot rolling. In general, the samples were heated to 1050°C and held for 1h in Ar gas atmosphere to austenitize and solutionize the $M_{23}C_6$ and most of the MX. Immediately following the austenization the samples were cooled by air-cooling to an intermediate temperature of one of three 700°C, 800°C, or 900°C [to achieve below Ae_1 (820°C) or above the Ae_3 (860°C), respectively]. Then either the forging or rolling was performed with varying strain amount, 7-17%. After the TMT the material is allowed to air cool. After this, GTAW was used with the matching filler metal followed by a PWHT at 760 °C for 2 hours. A more detailed explanation of the TMT will be discussed in Chapter 5.

Table 4.1: Chemical compositions (wt %) of the Grade 91 base metal and filler metal (balanced Fe).

(wt %)	C	Mn	Si	Cr	Mo	Ni	V	Nb	N	B
Base metal	0.08	0.27	0.11	8.61	0.89	0.09	0.21	0.07	0.06	<0.001
Filler metal	0.08	0.41	0.31	8.62	0.92	0.15	0.24	0.08	0.04	<0.001

4.1.2 Fe-Cr-Al Alloy

The chemical compositions of the Fe-Cr-Al fully ferritic alloy (FCA) are shown in Table 4.2 below. Four model alloys were made with the base alloy consisting of Fe, Cr, Al, and a small addition of Si. Carbon was not added to the alloy because carbides were not desired. The first model alloy does not contain Nb as to have a control sample with no precipitates. Nb was added to three of the alloys to understand the effects of Laves phase in strengthening and creep strength. Zr was added to the fourth alloy to help promote additional Laves phase and aid in reducing BCC grain size. The alloys were fabricated at the Oak Ridge National Laboratory via arc melting. The alloys were then solution heat treated at various temperatures above 1100 °C. Each alloy required different processing due to varying levels of Nb; this will be expanded on in section 4.2.3 and Chapter 6. After a solution heat treatment, the alloys were rolled to a thickness of less than 2 mm. Creep test specimens were then machined by wire Electro Discharge Machining (EDM).

Table 4.2: Nominal chemical compositions (wt %) of the first generation of FeCrAl alloys.

(wt %)	Fe	Cr	Al	Si	Nb	Zr	C	B
FCA-0Nb	Bal.	30.0	3.0	0.2	0.0	0.0	<0.004	<0.001
FCA-1Nb	Bal.	30.0	3.0	0.2	1.0	0.0	<0.004	<0.001
FCA-2Nb	Bal.	30.0	3.0	0.2	2.0	0.0	<0.004	<0.001
FCA-2Nb-.1Zr	Bal.	30.0	3.0	0.2	2.0	0.1	<0.004	<0.001

4.2 Experimental Procedure

4.2.1 Welding of Grade 91 Steel

After the forging TMT process and tempering, a manual Gas Tungsten Arc Weld (GTAW) was used to make cross weld samples from these samples with or without the matching filler metal. They were machined to make a bevel single U-shape groove. The samples were reheated to 180 °C before welding. In the samples with matching filler metal, welding was performed with one root pass and multiple fill passes; a schematic is provided in Figure 4.1. The welding current, voltage, and speed are 260A, 10V, and 3.4mm/s respectively. The interpass temperature was maintained below 120 °C. The filler wire was 1.6mm in diameter and had a matching composition. After welding the samples were PWHT'ed in a furnace at 760 °C for 2 hours. Cross-weld creep test samples were machined from these welds and leftover materials, after machining, were used for the microstructure characterization as well as hardness mapping.

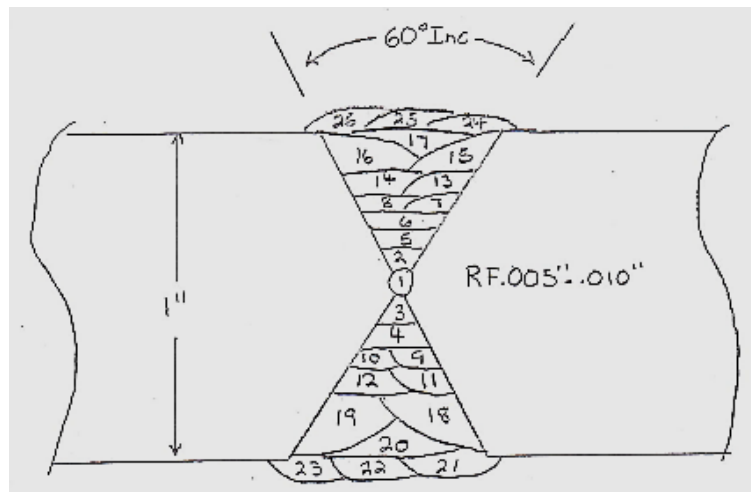


Figure 4.1 Schematic of the multiple fill weldment.

4.2.2 Arc Melting and Heat Treatments of Fe-Cr-Al Alloy

The model alloys were vacuumed arc melted at the Oak Ridge National Laboratory. Based on thermodynamic simulation in the JMatPro software, the four different model alloys were heat treated differently based on the solution temperature of the Laves phase. After arc melting the alloys were drop cast. For FCA-0Nb and FCA-1Nb alloys was homogenized at 1300 °C for 1 hour then cooled to room temperature. Then a hot rolling process of a 60% reduction at 1200 °C, then cooled to 300 °C for a warm rolling reduction of 75%. A solution heat treatment was performed with one step of 30 minutes at 1100 °C and a final step of five minutes at 1200 °C. This was done to dissolve any Laves phase present and limit BCC grain growth. The last two alloys have a different heat treatment. Because of the increased Nb content and higher solutionizing temperature, all heat treatment steps had to be conducted at 1300 °C to dissolve the precipitates. The heat treatment for the FCA-2Nb and FCA-2Nb-.1Zr follows as such. After arc melting and drop casting, the alloys were homogenized at 1300 °C for 1 hour. Then the alloys were hot forged at 1300 °C for a 67% thickness reduction, then a hot rolling at 1300 °C for a 70% thickness reduction. Finally, the samples were given a solutionization for ten minutes at 1300 °C. The intent for both of these heat treatments is dissolve all the precipitates in the BCC matrix, which then would precipitate Laves phase during creep testing. Since Laves phase is known to embrittle the microstructure, having a solid solution or 100% BCC microstructure is thought to regain some ductility before creep testing [88]. However, the heat treatment allows large BCC grains to grow, which in turn then reduces the ductility. Thus, there will need to be a balance between the amount of Laves phase and grain growth. In addition to the solutionizing treatment and alongside the creep test, two samples were using in an aging study. In the solution heat treated state the FCA-1Nb and FCA-2Nb alloys were aged at 700, 800, and 900 °C for two time

lengths, 168 hours and 1008 hours. This study compares the crept microstructure and unstressed aging to better understand the kinetics of the Laves phase growth.

4.2.3 Creep Tests

4.2.3.1 Grade 91 Steel

Creep testing was performed at the Oak Ridge National Laboratory. The creep tests were performed on the TMT 8, TMT 9, and N&T samples after welded and PWHT. An illustration of the creep specimens is shown in Figure 4.2. The tests were conducted according to ASTM E139-06. The creep frames used were lever-arm and calibrated to a load accuracy of $\pm 0.5\%$. The temperature was measured by three K-type thermocouples wired to the gauge section. The creep tests were performed at 600 °C and a load 100 MPa. A proportional temperature controller was used to control the temperature. The sample length change was measured by an averaging extensometer attached by set screws to a small groove in sample grip section. The measurements were converted to strains by dividing by the reduced section length. The strain was recorded every 36 seconds for the first 37 minutes. Then it was recorded every 360 seconds for the remainder of the test.

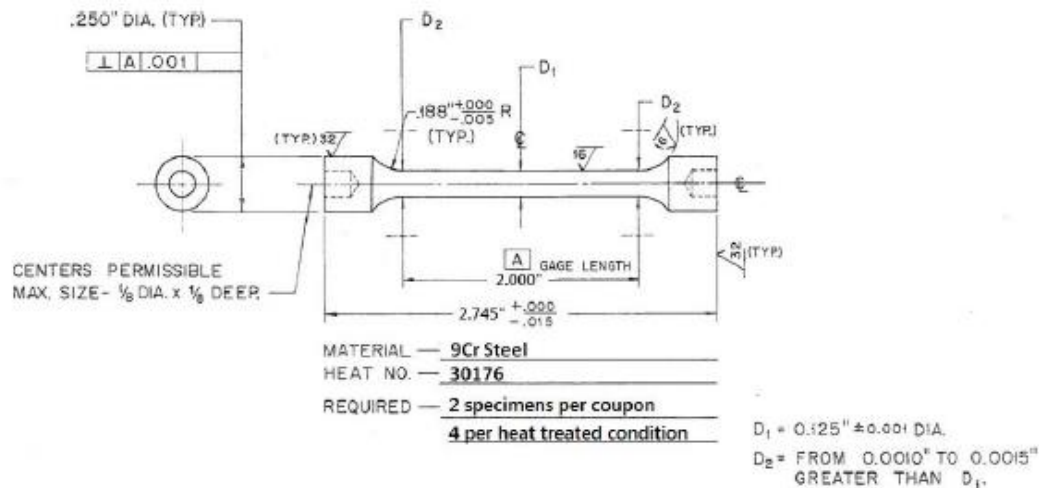


Figure 4.2 Illustration of the Grade 91 creep specimens.

4.2.3.2 Fe-Cr-Al Alloys

The creep testing of these alloys was also performed at the Oak Ridge National Laboratory. However, here the creep tests were performed using sub-sized samples, compared to ASTM standards, due to limitation of materials. It should be noted that there is possibility of a size effect on the creep properties due to size of the specimens and large grain sizes. This will be reiterated in Chapter 6. The hot rolled plates were too small to extract round creep specimens. The specimens were flat dog bone creep specimens and were cut from the solution treated materials using wire EDM. Figure 4.3 shows the creep ruptured specimen of FCA-1Nb. The length of the specimens was ~35mm in length, roughly 5mm across the gauge section and less than 1mm thickness. The creep tests were performed in specially designed direct load creep frames. The entire sample and holder were held at the temperature in a furnace. A proportional temperature controller controlled the furnace.

CC01, 700C/70MPa, 134h, 14.0%



Figure 4.3 Fe-Cr-Al creep rupture specimen.

The temperature was measured by four type K thermocouples. The samples were crept to failure at 700 °C and 70 MPa. The sample length change was measured by an averaging extensometer attached to a plate affixed to the bottom sample holder rod. The measurements were converted to strains by dividing by the reduced section length. After failure, the part of the specimen that contained most of the gauge section was used for characterization.

4.3 Microstructure Characterization

4.3.1 Metallographic Preparation

For both the Grade 91 steel and the Fe-Cr-Al alloys, not TEM sample, were metallographically polished using the same method. The samples were sectioned from the bulk using an Allied High Tech TechCut 5® to the desired size. The sectioned samples were then mounted in a 1-1/4" mount using Konductomet® conductive powder using a Buehler® hot mounting press. Then the samples were polished using fine sand paper grits of 600, 800, and 1200. After the sandpaper, the samples were finely polished using diamond suspension of 9µm, 6µm, and 1µm. A final polish to

a mirror finish was done using 0.05 μ m colloidal silica on a Buehler Vibromet II® for more than 6 hours. EBSD characterization required a final polishing for 15 hours. After final polishing, optical micrographs were taken of the as-TMT samples after etching with an aqueous solution of water, nitric acid, and hydrofluoric acid, “H₂O:HNO₃:HF = 50:5:1”. For SEM characterization of the Grade 91 steel, the samples were etched after a final polishing with an aqueous solution of water, hydrochloric acid, and nitric acid, “H₂O:HCl:HNO₃ = 30:2.3:1”.

4.3.2 Scanning Electron Microscopy and Electron Backscatter Diffraction

SEM was used for the majority of the characterization. General SEM images were taken to compare microstructure as it evolved during all the processing steps to final creep failure in the Grade 91 steel. The prior austenite grain/martensite block size of the as-TMT, TMT + Tempered samples were characterized on a JEOL 6500 FEG-SEM at 20 kV, using a Bruker Quantax EBSD detector. The working distance was 18mm, and the sample was tilted to an angle of 75°. The diffraction pattern was acquired and indexed with TSL OIM Data Collection 7. Prior austenite grains were mapped by highlighting grain orientations between 20-45°. The martensite blocks were mapped by highlighting grain orientations between 15-180°. The Fe-Cr-Al alloys were characterized using the same microscope. However, the creep fracture surface was imaged on a Hitachi S3400 SEM. The alloys were not etched because of the high Cr content, but the Laves phase could be characterized using a backscatter detector inserted below the pole piece. The alloys were imaged on a polished surface. Both grain size and Laves phase distribution could be analyzed from these images.

4.3.3 Transmission Electron Microscopy

4.3.3.1 Extraction Replica and FE-STEM

The as-TMT second-phase (MX) size, density, and volume percent were characterized by traditional carbon-extracted replica technique. The TMT + temper samples were characterized for the second-phase (MX and $M_{23}C_6$) distribution by the same technique. A polished surface of the samples is required. After a final polishing, the samples were etched using an aqueous solution of water, hydrochloric acid, and nitric acid, " $H_2O:HCl:HNO_3 = 30:2.3:1$ ". Immediately after etching a thin layer, ~ 100 nm, of carbon was deposited on the surface. Approximately 2.5×2.5 mm² squares were cut from the carbon layer with a razor blade. The coated sample was then soaked in the same etchant solution for three minutes to remove the carbon replica. Following the soak, the samples were immersed in water, and the replicas released and floated to the surface. A 3-mm Ni grid was used to hold the carbon replicas for subsequent TEM examination. The high magnification observation was conducted by using a Zeiss Libra 200 HT FE transmission electron microscope (TEM) equipped with a scanning transmission electron microscope (STEM) mode with an accelerating voltage of 200kV and a spot size of 5nm. Using the STEM mode, the carbides were identified by composition achieved by Energy-dispersive X-ray spectroscopy (EDS). The small particles (< 60 nm) in the as-TMT and TMT + temper samples were assumed to be MX as they were enriched in Nb and V. The larger particles (> 60 nm) in TMT + temper were assumed to be $M_{23}C_6$ as they were enriched in Cr, which is consistent with literature [22, 89, 90].

4.3.3.2 Diffraction and Dislocation Imaging in Fe-Cr-Al Alloy

TEM specimens of the Fe-Cr-Al alloys were made using the failed creep specimen. The gauge section was sectioned away from the grip section using a low speed diamond blade on the TechCut 5®. The grip and gauge sections were polished to less than 100 μm using very fine sandpaper with grits of 600, 800, and 1200. After the samples had reached the required thickness, 3mm round disks were punched out of the gauge and grip sections. The disks were then twinjet electro-polished using a solution of 10% nitric acid and 90% methanol at -15 °C, 15 volts, and a flow rate of 5 ml/s. This method reduces the thickness at the center of the disk, which allows a small region to become electron transparent. The disks were characterized on a ZEISS LIBRA 200 HT FE MC TEM operating at 200 kV. In order to identify dislocations, the samples were tilted to the [100] zone axis. Using the diffraction mode, a diffraction pattern was produced which can then be indexed. Then using Bright Field imaging conditions, the dislocations can be imaged [91]. Due to the distortion of the atomic planes near the dislocations, a dark contrast is created. This contrast difference against a light background allows for visual identification of the dislocations. The dislocations must be oriented properly relative to the incident electron beam to be visible. Therefore, the dislocations were identified by their disappearance with slight tilts of the sample off of the [100] zone axis.

4.3.4 Atom Probe Tomography

Atom Probe Tomography was used to analyze the chemistries of the Laves phase on the grain boundaries in the Fe-Cr-Al alloys after solutionization heat treatments. Using the Focused Ion Beam (FIB) technique in the SEM, a small needle (300nm x 50nm diameter) is extracted from a region of interest on the sample. In this case, a needle was extracted where a grain boundary

would be captured in the needle. The needle was then inserted into the LEAP® (local-electrode atom-probe) instrument at the Oak Ridge National Laboratory. The atom probe concept is based on field evaporation. An electric pulse (up to 20 kV and between 1-200 kHz) is applied to the needle, and an electric field is generated at the tip. When this electric field is large enough, the surface atoms are ionized and projected away from the specimen. The ions are then directed to a detector. Based on the mass to charge ratio (m/n) of the ions, they will have a distinct time-of-flight before being intercepted on the imaging detector. The detector then identifies the atoms based on the time-of-flight and can match the atoms location on the detector with the original position on the specimen.

4.3.5 Quantification of Particles

4.3.5.1 Carbides in Grade 91 Steel

The carbides in Grade 91 steel could be quantified using images from TEM-STEM from carbon replica technique. The following is a description on the quantification using ImageJ®. An image is opened in ImageJ® and the scale is set, then the contrast and brightness are adjusted for best visual aid. The image is then thresholded to highlight the carbides. The image is converted to black and white; then the image is treated with the watershed macro. The watershed macro breaks up carbides that are too close together for thresholding to resolve. The analyze particle macro is used to quantify the particles. The size was ranged to pick up particle in the size range of 0-60 nm and then rerun with size range 60nm-infinity, about 3-pixel units were ignored to filter noise. The size between 0-60 nm is assumed to be MX and above 60 nm is assumed to be $M_{23}C_6$. The circularity was chosen to be between .3-1 to filter out any of the bright carbon matrix that passed thresholding. The calculated error for the size calculations was found to be 3.26 nm.

The program then gave the results with an area and the major and minor axis of the particles. This information was then used to calculate density and volume percent, as well as the plot the size distribution. Since the images are in 2D, an estimated volume is needed to calculate a volume density. The volume of particles was estimated from the etching time during the extraction process.

4.3.5.2 Laves Phase in Fe-Cr-Al Alloys

The Laves phase could be analyzed using the same quantification method. However, a different method is used to image the particles. Utilizing the backscatter detector in the SEM, the particles could be imaged. For volume calculation, the depth of particle imaging used the same technique as Dimmler et al. [78]. Here since one particle existed, the size constraint was not restricted nor was the circularity. For the SEM, the error was slightly larger and was calculated to be 9.43 nm.

In addition to matrix Laves phase, the Laves phase on the grain boundaries and precipitate free zone (PFZ) was also quantified. The grain boundary Laves phase were selected and cut from the parent image. The Laves phase could then be thresholded and analyzed in the same manner as above. Since all the particles were elongated on the grain boundary, the major axis was used in calculating the areal fraction of Laves phase on the grain boundary. The PFZ was marked off with segmented lines where the matrix Laves phase appeared, and on either side of the grain boundary. Then several lines were measured perpendicular to the two segmented lines. All the perpendicular line lengths were averages and halved to find the Half Width PFZ.

Chapter 5. Thermo-Mechanical Treatments of Grade 91 Steel

Type IV failure in Grade 91 steel has existed since its creation in the 1970's. Performing a multi-scale characterization technique will help to understand the mechanisms of failure and provide some insight into the evolution of precipitates. However, only understanding the microstructure in industrial practices does not provide some way of moving forward in improving the Type IV failure resistance. The path improving the Type IV failure resistance should be by controlling the microstructure by precipitation or either grain structure. The question of how the microstructure can be controlled, and what benefit does this have, needs to be answered. One way to control the microstructure of the Grade 91 steel is through Thermo-Mechanical Treatments.

Either a forging or a rolling action was used to control the precipitation in the Grade 91 steel. This chapter will describe how the deformation process of the forging or rolling will aid in nucleated MX carbonitrides. With an increased number nucleation sites, the number density rises, and the interparticle spacing decreases. The creep mechanism in the Fine Grain HAZ of Grade 91 weldments is most generally thought to be dislocation based. To improve the creep properties of a material in the dislocation creep regime, the dislocations should be impeded. The rationale in the increase in density of the MX is to further impede dislocation movement. After welding, the creep results indicate that the TMT process does improve the creep resistance. The creep test conducted at 600 °C and 100 MPa show an improvement of the cross weld creep strength. This chapter will explain the microstructure after each stage of the process from TMT to final failure.

5.1 Hot Forging of Grade 91 Steel

The hot forming or Thermo-Mechanical Treatment (TMT) of the Grade 91 steel was broken up into two techniques, hot forging and hot rolling. The hot forging was to get a baseline understanding of the effects of deformation on precipitation of MX carbonitrides. The hot rolling was a demonstration of the same effect but to align processing techniques with industrial standards. For ease of communication, the two experiments will be broken up into selected sections. The TMT processing will be discussed below.

For the hot forging treatment, several small pieces (50-100 mm x 150-250mm x 25mm) were sectioned from a 25mm-thickness hot-rolled plate. The samples were heated to 1050°C and held for 1h in Ar gas atmosphere to austenitize and dissolve the $M_{23}C_6$ and most of the MX. Immediately following the austenization the samples were air-cooled (1-3 °C/sec) to an intermediate temperature of either 700°C, 800°C, or 900°C [to achieve below A_{e1} (820°C), achieve intermediate, or above the A_{e3} (860°C), respectively]. These heat treatments were to maintain an austenite structure. Upon cooling to an intermediate temperature, a 7% thickness reduction was achieved by forging with only one press-stroke action. After the thickness reduction, the plates were subsequently placed in a furnace for 1 hour at the same temperature as that of the hot-working, and then air-cooled to RT. A schematic of the temperature profile is shown in Figure 5.1. An illustration of the microstructure evolution is shown in Figure 5.1. After the forging TMT process, a tempering step was performed. The samples were placed in a furnace at 760 °C for 2 hours before proceeding to welding. The naming convention for these samples is as follow TMT7, TMT8, or TMT9 representing forging TMT and the forging temperature.

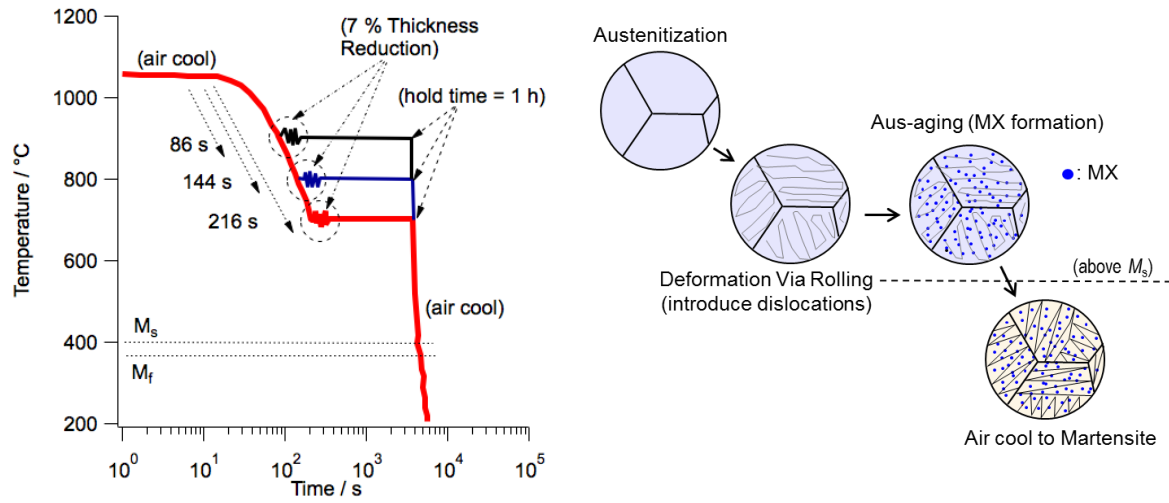


Figure 5.1 Schematic of the temperature profile of the hot forging process and illustration of microstructure evolution during TMT.

5.2 Microstructure After Thermo-Mechanical Treatment (Forging)

Optical micrographs of the samples can give a quick understanding of how the microstructure may have transformed during the TMT process. Figure 5.2 shows the optical micrographs of as-TMT and TMT + tempered samples. Again, these conditions will be called as “TMT9,” “TMT8,” and “TMT7,” respectively. The martensitic microstructure was observed in the as-TMT9 and as-TMT8 samples (see Fig 5.2a and 5.2b), and they are macroscopically very similar to each other. The microstructures after tempering (see Fig. 5.2d and 5.2e) exhibited a typical tempered martensite of Grade 91 steels and appeared very similar.

On the other hand, instead of martensite, only mixed microstructure (ferrite + pearlite) was observed in the as-TMT7 sample (see Fig, 5.2c) and, as a result, no changes in microstructure was observed even after tempering (see Fig. 5.2f). These results indicate that to obtain martensitic microstructure the TMT process (i.e. with an isothermal hold of 1 hour) needs to be conducted at or above 800°C. Therefore, the sample from TMT7 was excluded from further analysis. The reason for TMT7 producing a mixed microstructure may be from the following. A Time Temperature Transformation (TTT) diagram can illustrate the time required during isothermal holding at a temperature below the A_{e3} . These diagrams are often used in generating bainite in steels [92, 93]. In general, the transformation lines on the diagram will form a C curve. It is possible that the nose of this C curve is close to 700 °C allowing for the transformation after TMT7 and not the other samples.

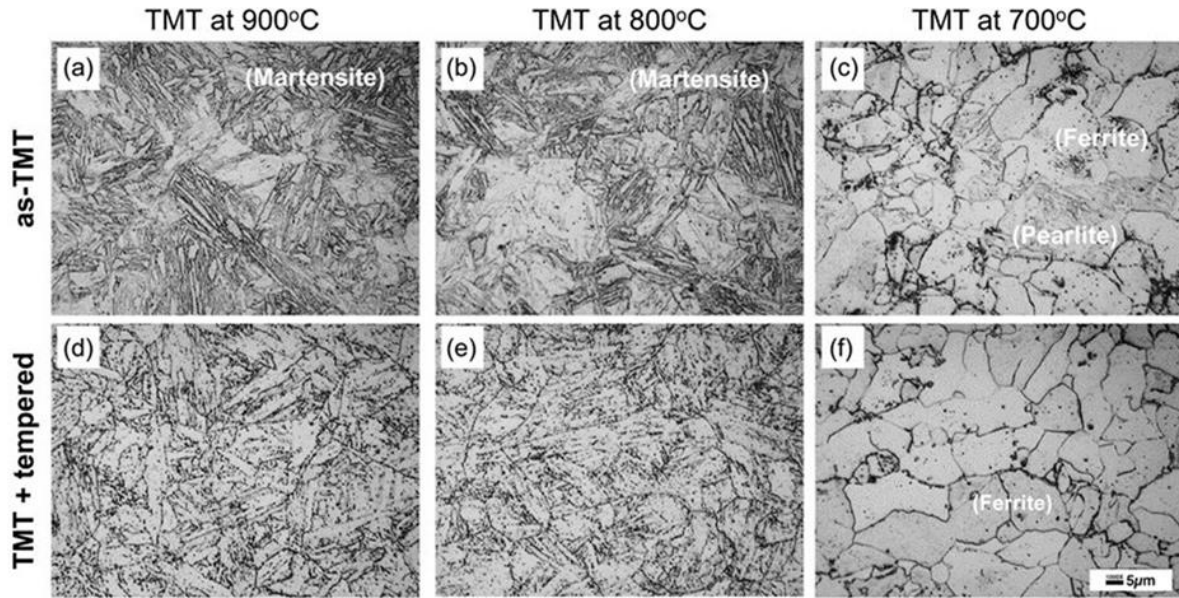


Figure 5.2 Optical micrographs of the as-TMT and TMT + Temper conditions. (a,d) are after TMT at 900C, (b,e) are after TMT at 800C, (c,f) are after TMT at 700C.

The macroscopic investigation provides a fast analysis, which is used to exclude TMT7 from further testing. Detailed microstructure evaluation is needed to identify any differences in the prior austenite/martensite grain size after TMT. Figure 5.3 shows EBSD (electron backscatter detection) micrographs of TMT9, TMT8, and a control (standard heat treatment, normalization and tempering at 760 °C/2hours). The control is the traditional as-normalized condition and the standard 760 °C tempering condition from industry. The control will be denoted at N&T (normalized and tempered), where the as processed condition is the normalization, and the as-tempered is self-explained. Because of the plastic deformation involved during TMT, there may be differences in the microstructure other than the expected precipitation. The EBSD micrographs can be analyzed for PAGBs (prior austenite grain boundary) size and martensite block size. The PAGB can be highlighted with the OIM software. Any grain boundary between two adjacent grains with a misorientation between 20-45° was highlighted [15]. From martensite

crystallography, this misorientation range is absent between martensite packets and blocks. Thus, a grain boundary with this range can be assumed to be a prior austenite grain boundary. The PAGB in the N&T sample after normalization was found to be 30 μm and both the TMT samples was roughly 20 μm . After tempering the size was found to about 25 μm for the N&T sample and was 19 μm in the TMT samples. The PAGBs are highlighted with black lines in Figure 5.3. The apparent drop in size can be attributed to sampling. Since the measured values are an average over a number of images, some regions in the sample may have larger or smaller grain sizes and produce a “drop” in average grain size. The importance of knowing the size of the PAGBs is because the grain boundaries act as nucleation sites for M_{23}C_6 , which was discussed in Chapter 2. Smaller PAGs may allow for the precipitation of a fine distribution of smaller M_{23}C_6 carbides. A finer distribution of carbides may lead to the complete dissolution of carbides during welding. However, fine grain size could increase the creep rate due to grain boundary sliding.

In addition, the martensite block size can also play a strengthening role. It is also known that smaller PAG sizes will produce smaller the martensite block sizes [94]. The PAGB and martensite block sizes are presented in Table 5.1. The trend illustrates that the TMT samples have finer PAGBs after processing. However, the spread of the grain sizes (represented by the standard deviation) of the PAGBs was found to be 5-9 μm , which leads to the conclusion that the PAGBs have no significant differences. The martensite block size spread was found to be between 2-2.5 μm for all the samples, which also can conclude no significant differences here. This observation can be concluded by the fact that the deformation percentage was only 7%, and the expected size reduction would be minimal. Since the grain microstructure is similar in the forgings, the conclusion can be made that the enhancement of creep-rupture properties is due mostly to the precipitation sequence during TMT and subsequent processing steps.

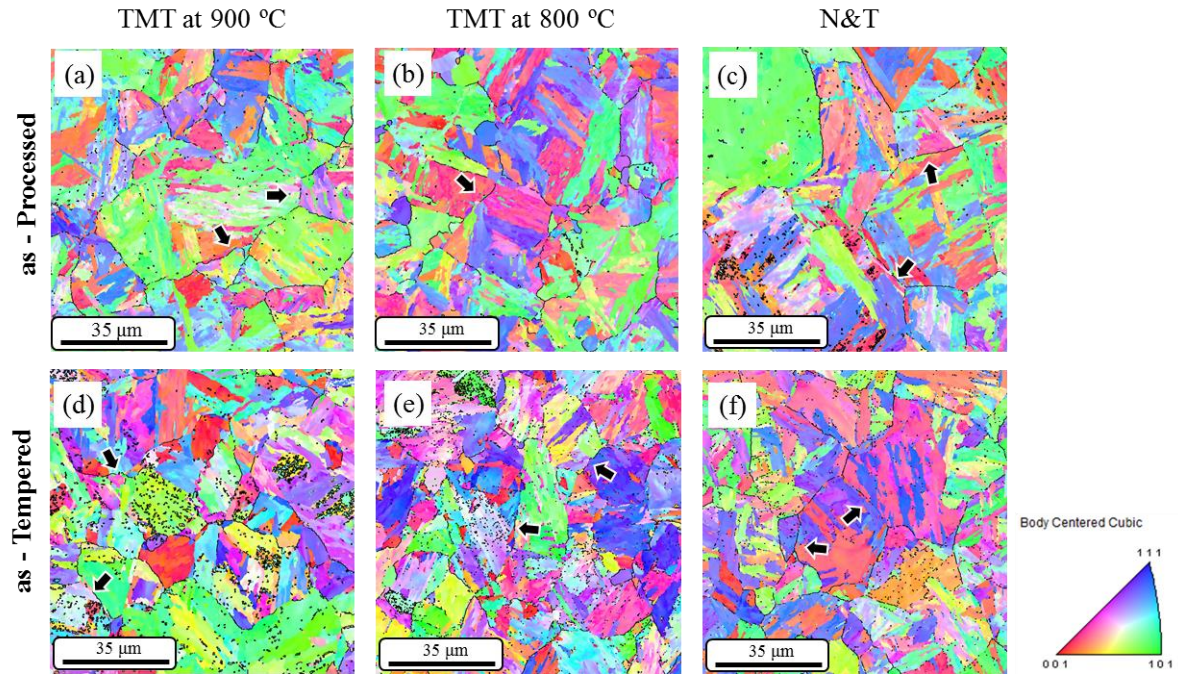


Figure 5.3 EBSD images showing microstructure of as-processed (a-c) and as-tempered (d-f) samples. The aus-forging and aging temperatures are shown above. Here TMT 900 and TMT 800 are compared to standard N&T treatments.

Table 5.1 Average size of PAGBs and martensite blocks after processing and subsequent pre-weld temper (with standard deviations).

	as-Processed PAGBs (μm)	as-Tempered PAGBs (μm)	as-Processed Martensite Block (μm)	as-Tempered Martensite Block (μm)
Normalized	31.2 $\pm$ 9	24.5 $\pm$ 9	4.5 $\pm$ 2.5	4.3 $\pm$ 2.1
TMT 9	21.3 $\pm$ 5	19.7 $\pm$ 6.7	4.4 $\pm$ 2.3	5.2 $\pm$ 2.3
TMT 8	20.1 $\pm$ 5.5	19.1 $\pm$ 3.8	5.0 $\pm$ 2.5	6.0 $\pm$ 2.5

5.3 Hot Rolling of Grade 91 Steels

For the hot rolling treatment, similar small pieces (50-100 mm x 150-250mm x 25mm) were sectioned from another 25mm-thickness hot-rolled plate from the same heat. The samples were heated to 1050°C and held for 1h in an Ar gas atmosphere. Two samples were then subsequently rolled with a single pass at 1050°C and certain amounts of thickness reduction in the range from 10 to 17%. Three other samples were allowed to air cool from 1050°C to 900°C then a subsequent rolling was applied with a single pass. This can be seen in Figure 4.2. The aim of this investigation is to align processing parameters closer to industry practices. Therefore, the relatively low thickness reduction was used. After the samples had been hot-rolled, the plates were placed in a furnace for one h at the 800°C, followed by air-cooling to RT. The samples were then tempered at 760°C for 2h. The samples that were rolled at 1050°C will hence be labeled HTR 17 and HTR 10 for thickness reductions of 17% and 10% respectively (HTR represents High Temperature Rolling). The samples that were rolled at 900°C will hence be labeled LTR 17, LTR 14, and LTR 10 for reductions of 17%, 14%, and 10% respectively (LTR represents Low Temperature Rolling).

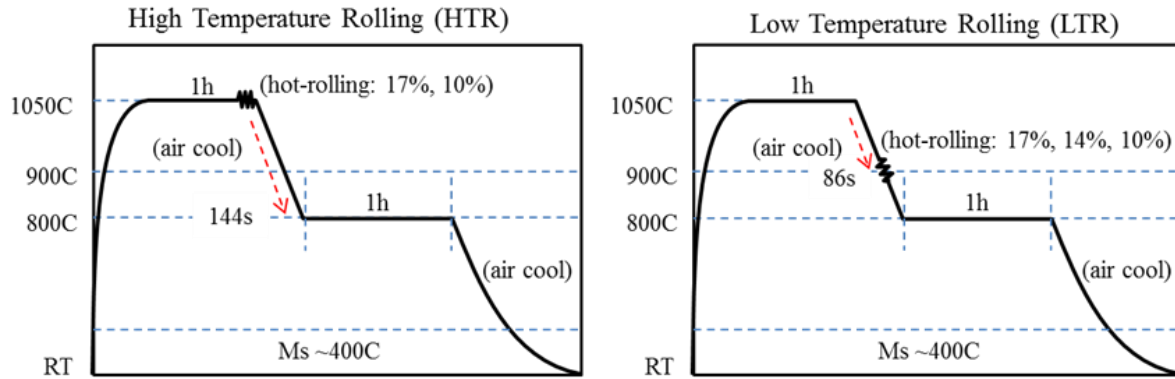


Figure 5.4 Schematic of the temperature profiles of the hot rolling process.

5.4 Microstructure after Thermo-Mechanical Treatment (Hot Rolling)

Some samples from the original steel plate were hot rolled to compare the microstructures with the forging and N&T samples. Figure 5.5 shows EBSD micrographs of the LTR. With rolling always above 800 °C a mixed microstructure was not observed. Although the deformation percentages are a little higher than with the forging samples, the PAG and martensite block sizes are roughly similar to the forging samples. It is thought that the rolling action may have led to differences in microstructure based on some texturing of the austenite grains. However, this does not appear to be the case. All the PAGBs were found to be between 20-24 μm with the smaller sizes being from the 17% deformation samples. The martensite block sizes range from 3-5 μm . The sizes of the PAGBs and martensite blocks is shown graphically in Figure 5.6. Again the differences here between the as-processed and tempered sizes is most likely due to the tempering of the microstructure.

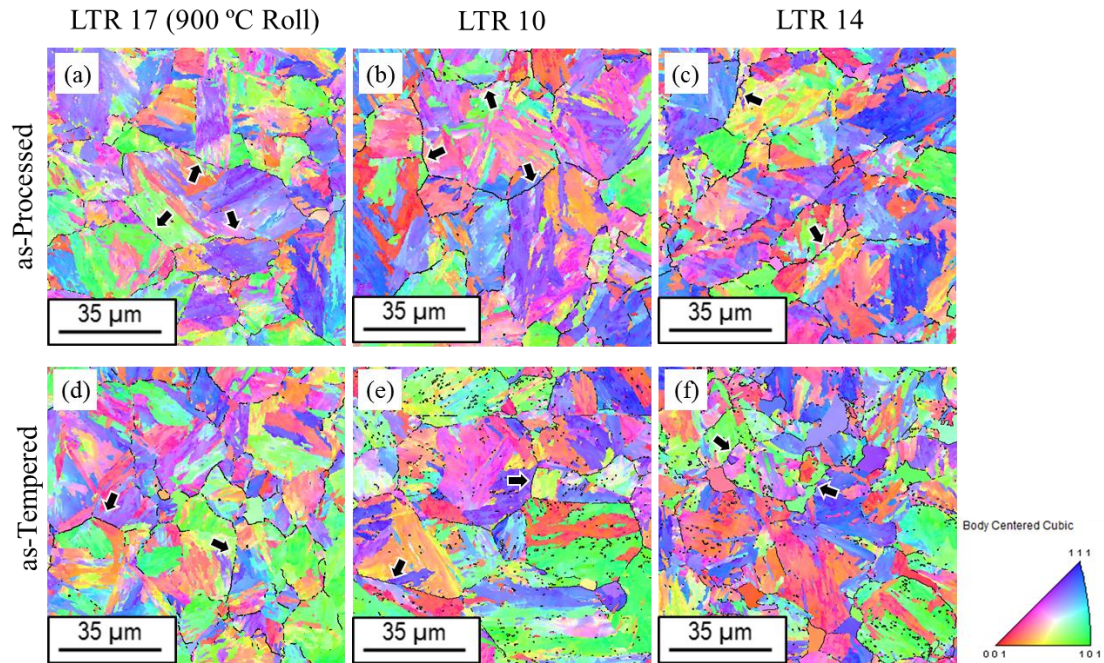


Figure 5.5 EBSD images showing microstructure of as-processed (a-c) and as-tempered (d-f) samples. The aus-forging and aging temperatures are shown above. Here TMT 900 and TMT 800 are compared to standard N&T treatments.

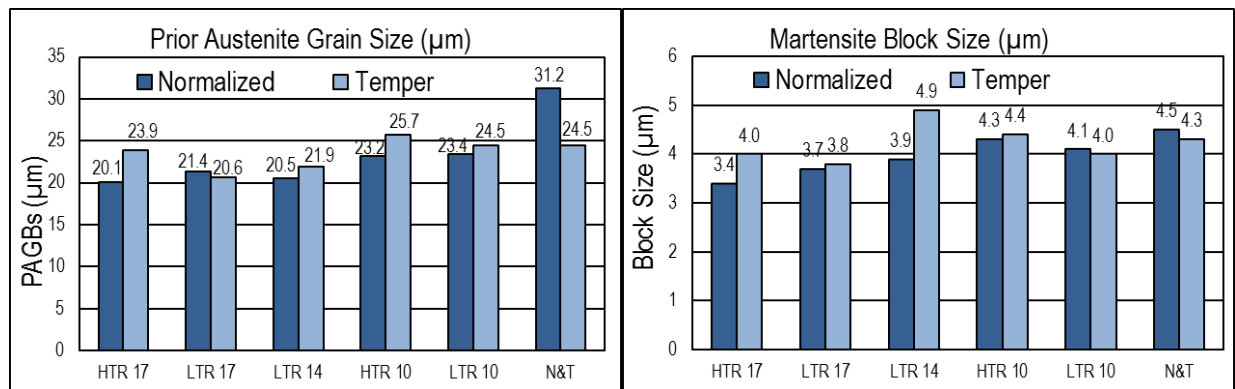


Figure 5.6 Size comparison of Prior Austenite Grain Size and martensite block sizes after hot rolling and tempering.

5.5 Carbide Evolution

5.5.1 Carbide Precipitation After TMT and Tempering (Forging)

The rationale for the TMT is to produce a fine dispersion of small MX carbonitrides in austenite and before tempering. This rationale has two mechanisms for improving the cross weld creep strength of the Grade 91 weldments. The first is the reduced precipitation and growth of $M_{23}C_6$ during the pre-weld temper. From the work of Yu (2013), it was found that smaller $M_{23}C_6$ particles present before tempering would completely dissolve during welding. Because of the smaller size, less time at the same peak temperature (950 °C) is required to dissolve the carbides. Then could re-precipitate on fresh PAGBs and martensite block boundaries [35]. By performing TMT in the austenite phase and then held at temperature for the aus-aging, carbon and possibly some C from the matrix would have been tied up during the precipitation of MX. As a result, during tempering, the quantity and size of $M_{23}C_6$ carbides would be reduced. This could be due to either reduction of available alloying elements (e.g. carbon and/or Cr) or due to sluggish dissolution of small MX during tempering. Instead of coarsening, the alloying elements from the dissolving MX would then be available for $M_{23}C_6$. Since Cr and Fe are strong carbide formers, the $M_{23}C_6$ would have a stronger availability of forming than contributing to the ripening of MX. This mechanism would limit the nucleation and growth of $M_{23}C_6$ during tempering and post-weld heat treatment [42, 43].

Another possibility for a decrease in $M_{23}C_6$ could be the available nucleation sites for nucleating $M_{23}C_6$. After TMT and during aus-aging, the MX will precipitate. The reason for TMT is to generate dislocations which act as the nucleation sites for MX [83]. However, MX also can nucleate at the austenite grain boundaries [40, 95, 96]. During tempering, it can be assumed that

the PAGBs are free of carbides at time zero. However, after TMT there would be MX nucleated on the PAGB. Then when the sample is tempered, the available sites on the PAGBs would be reduced, thus reducing the density of $M_{23}C_6$. However, the size of an individual $M_{23}C_6$ would be larger than the nominal size. There is a likely chance that both of these play a role in the reduction of $M_{23}C_6$. However, the first possibility is more likely based on observation of the micrographs. If TMT8 is examined, there is a decrease in MX after tempering with a reduction of $M_{23}C_6$ and without individual particles growing larger than the N&T sample. This gives the conclusion the first possibility is more likely.

The second mechanism in improving the cross-weld creep strength is producing a fine distribution of MX that would remain stable during tempering and welding. It was discussed in Chapter 2 that decreasing the interparticle spacing would provide extra resistance to dislocation creep. Therefore, the copious precipitation of MX during the TMT process would remain during creep, even after welding. This mechanism would then be inherently independent of the $M_{23}C_6$ size and distribution along the PAGBs. The $M_{23}C_6$ could be large and not dissolved during welding, and the creep rupture results would not change. Nevertheless, during creep, the dislocation motion would be impeded by the increase of MX and would take longer for them to pile up at the large $M_{23}C_6$ particles. This would then delay creep cavitation nucleation and linkage, thus improving the creep strength. The microstructural evolution during TMT, welding, and creep is however very complex. The mechanism for strengthening is not independent and is a combination of multiple mechanisms. This makes it difficult to say which mechanism is most dominate. The rationale for utilizing TMT is to increase the creep resistance of Grade 91 steel and strengthening mechanism is a combination of all discussed here and others not discussed here.

Figure 5.7 are STEM micrographs of carbon extracted replica specimens taken from the as-TMT9 (see 5.7a), as-TMT8 (see 5.7b), and as normalized (see 5.7c) samples. The TMT9 and TMT8 samples illustrate the dispersions of nanoscale particles within the matrix after TMT. The particles were identified as MX from STEM-EDS, indicating enrichment of V and Nb. Higher magnification micrographs show dense particles with the size of 5-10 nm dispersed in the as-TMT8 sample, which is qualitatively similar to the report by Klueh et al. [42]. On the other hand, a relatively smaller number of the particles can be seen in as-TMT9 sample. The average particle size, number density, and volume percentage are described in Table 5.2. In both TMT conditions, the average sizes are statistically very similar, but the number density and volume percent of TMT8 are more than 4 times higher than TMT9 and N&T samples. In addition, the size of the MX in TMT8 is about 2 times smaller than the MX that precipitates during standard N&T after tempering. It should be noted in Figure 5.7b, an inhomogeneous distribution of MX can be seen forming “cloud” like conglomerates, highlighted by red circles. This is hypothesized to be the result of the inhomogeneous dislocation substructure after the TMT deformations [42]. Since dislocations act as nucleation sites, locally higher density regions of dislocations would be expected to precipitate increased quantities of MX. Additionally, it must be noted that in the as-normalized N&T sample only large MX particles can be found. This is due to precipitation, non-dissolution, and coarsening of MX during manufacturing and normalization processes since the absolute solutionizing temperature for MX is roughly 1460 °C.

Figure 5.7d, 5.7e, and 5.7f shows the tempered conditions for TMT 9, TMT 8, and N&T samples respectively. Large particles and small particles can be visualized. The large particles (> 60 nm) were identified as $M_{23}C_6$, and the small particles (< 60 nm) were identified as MX. The particles were identified as their carbide type based on EDS using the TEM-STEM technique. The

tempered conditions of TMT9 and N&T show similar $M_{23}C_6$ carbide size and number density. The size of the $M_{23}C_6$ carbide in these conditions is nominally 140 nm and the number density is nominally $\sim 10^{20}$ particles/m³. It was concluded that the number density of MX in the as-processed condition of TMT9 did not successfully reduce the number of $M_{23}C_6$, although the number density of MX in TMT9 is still higher than that of the N&T sample. In this condition, the volume percent of $M_{23}C_6$ in TMT9 and N&T are very close to the equilibrium value. Utilizing the thermodynamic simulation software, JMatPro, the equilibrium value of $M_{23}C_6$ at the tempering temperature (760°C) is calculated to be roughly 1.7%, and the values measured in this work are, 1.5% for TMT9 and 1.4% for N&T. In contrast, the volume percent in TMT8 was 0.31%, which is almost 5 times smaller. In addition to the $M_{23}C_6$ volume percent reduction, the MX density was much higher than TMT9 and N&T samples. Although the size of the MX is very similar to TMT9, the MX density is almost 2 times higher than TMT9 and 3 times higher than N&T. Because of the amount of MX precipitated in the as-processed condition, it is expected that MX particles may be carbon rich, and would prevent $M_{23}C_6$ formation. This reduction in size and density of the $M_{23}C_6$ would lead to a complete dissolution of the $M_{23}C_6$ on heating to a peak temperature during welding and subsequently, fresh $M_{23}C_6$ will re-precipitate along the fresh martensite/ferrite grain boundaries in the FGHAZ during PWHT, which is expected to improve the creep strength [35].

Figure 5.8 represents the particle size distribution in the as processed and as tempered conditions. Because the N&T sample only contains residual particles and does not contain precipitated MX particles, thus this sample was not included 5.8c. Overall, there is not much deviation in the distributions of MX or $M_{23}C_6$. However, a few points can be made.

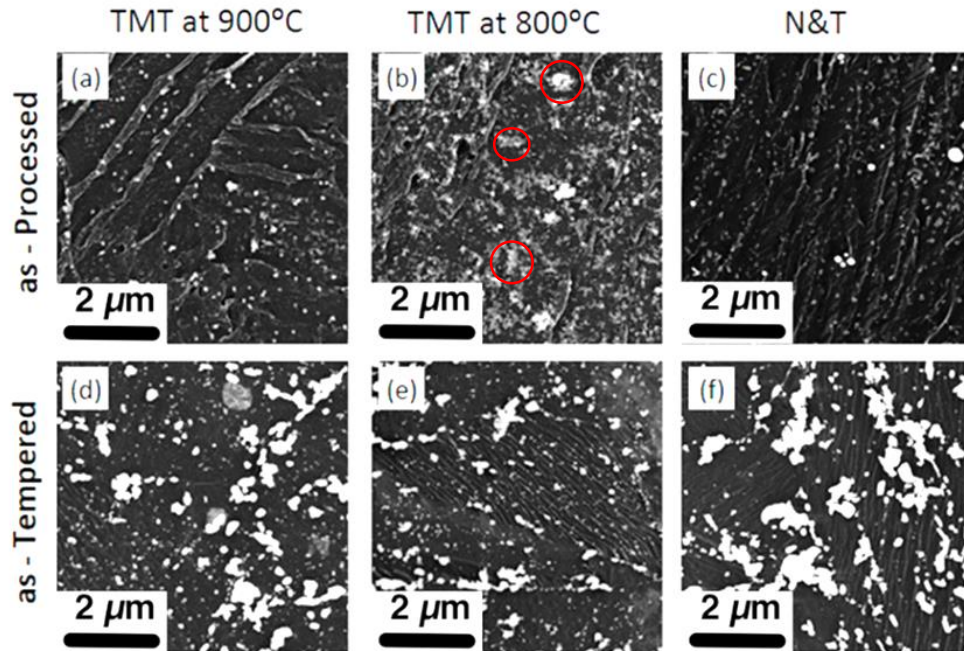


Figure 5.7 Dark field STEM images of carbon extracted replica specimens taken from the Grade 91 steel applied (a, d) TMT at 900°C, (b, e) at 800°C, and (c, f) N&T. In the as-processed condition of TMT specimens, a fine dispersion of MX can be found only in TMT 8 (white spots are carbide/carbonitrides, the black background is carbon support). Agglomerations in TMT 8 are highlighted with red circles, indicating possible inhomogeneous dislocation substructure.

Table 5.2: Average diameter, number density, and volume percentage of carbides in N&T, TMT9 + temper, and TMT8 + temper conditions. *As normalized only contains large undissolved MX from austenization.

	Carbide Type	Diameter (nm $\pm$ 3.26)	Number Density (m ⁻³ $\pm$ 1.12 x 10 ¹⁷)	Volume Percentage (%)
Normalized	MX	110.0	.0093 x 10 ²⁰	0.069 $\pm$.008*
	M23C6	N/A	N/A	N/A
N&T (HTT)	MX	21.8	1.9 x 10 ¹⁹	0.010 $\pm$.002
	M23C6	140.1	10.6 x 10 ¹⁸	1.530 $\pm$.039
TMT9	MX	7.9	1.75 x 10 ²⁰	0.005 $\pm$.002
	M23C6	N/A	N/A	N/A
TMT9 + T	MX	13.9	2.81 x 10 ¹⁹	0.004 $\pm$.001
	M23C6	147.2	9.7 x 10 ¹⁸	1.620 $\pm$.040
TMT8	MX	8.7	7.28 x 10 ²⁰	0.025 $\pm$.009
	M23C6	N/A	N/A	N/A
TMT8 + T	MX	15.4	5.69 x 10 ¹⁹	0.011 $\pm$.002
	M23C6	128.8	3.42 x 10 ¹⁸	0.383 $\pm$.016

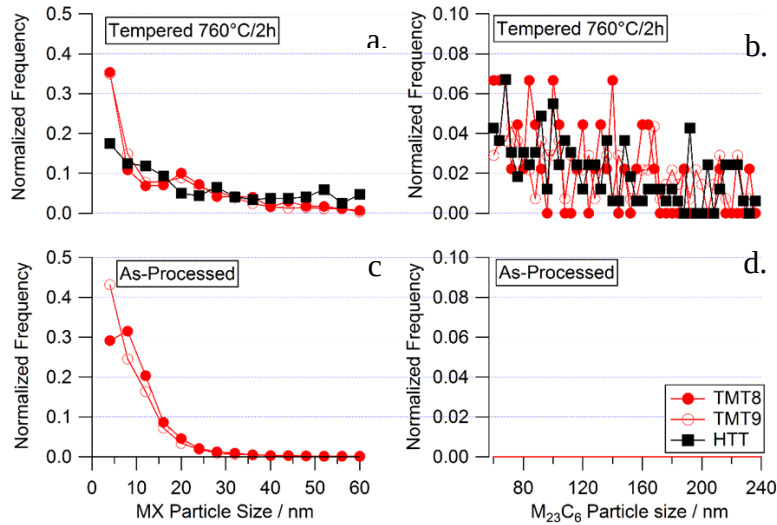


Figure 5.8 Particle size distributions of $M_{23}C_6$ and MX precipitates in the as processed and the as tempered conditions.

The TMT 8 condition does show a larger percentage of small $<10\text{nm}$ MX particles. In addition, it can also be seen that in TMT8, the percentage of $M_{23}C_6$ particles larger than 180nm is rather small. Therefore, it can then be suggested that most of the $M_{23}C_6$ carbides will dissolve during welding and re-precipitate during PWHT, whereas the large carbides in TMT9 and N&T would not dissolve. Therefore, the creep-rupture life is expected to increase in TMT8 with the decoration of ferrite grains by carbides and by preventing large carbide particles within the ferrite matrix [2, 35, 37]. This result shows that the size distribution is less important but the mechanisms discussed above are more important to the increase in creep strength.

5.5.2 Carbide Precipitation After TMT and Tempering (Rolling)

Figure 5.9 represents STEM images of the carbon extracted replica specimens from the as-rolled condition showing a differing degree of dispersions of nanoscale MX from the effect of rolling.

The large particles ($\sim 100\text{nm}$) are again undissolved MX from manufacturing and normalization

[35, 97]. The particles were identified as MX from EDS, using the same method as above, indicated from the enrichment of V and Nb. Klueh et al. reported that dislocations from plastic strain were chosen to act as nucleation sites for MX during the aus-aging process [42]. In Figure 5.9, the number density and volume percentage for each of the samples are labeled at the top of each image. It was found that the average size of MX, which precipitated in austenite during aus-aging, is close to a diameter of 10 nm. It must be noted that the small densities in the HTR (High Temperature Rolling) samples are most likely because the MX may be too small for extraction techniques and thus being undetectable. However, the mechanism of this result is not known. Nonetheless, this result is something of interest and should be studied further using thin films produced by Focus Ion Beam (FIB) techniques in the SEM.

Figure 5.10 represents the STEM images of the carbon extracted replica specimens from the as-temper condition. Here dispersions of MX and $M_{23}C_6$ can be seen, labeled in Figure 5.10e. The large particles (above 60nm) were identified as $M_{23}C_6$, and the small particles (< 60nm) were identified as MX. The identity of these particles was confirmed by STEM-EDS techniques. The large particles were enriched in Cr and the small particles were enriched in V and Nb. From the table, it can be seen that the HTR samples have the lowest $M_{23}C_6$ density, but still lowest densities of MX. From the characterization of the forged samples, it was found that the MX density before tempering has a correlation to $M_{23}C_6$ after tempering. From these results, it can be postulated that the density of MX in the HTR sample may be larger than indicated, but not visible. Very small MX particles were discussed by Klueh et al. 2005 [42]. The authors found that after heavy deformation, particles could not be seen in thin films using the FIB technique, but could be found after tempering.

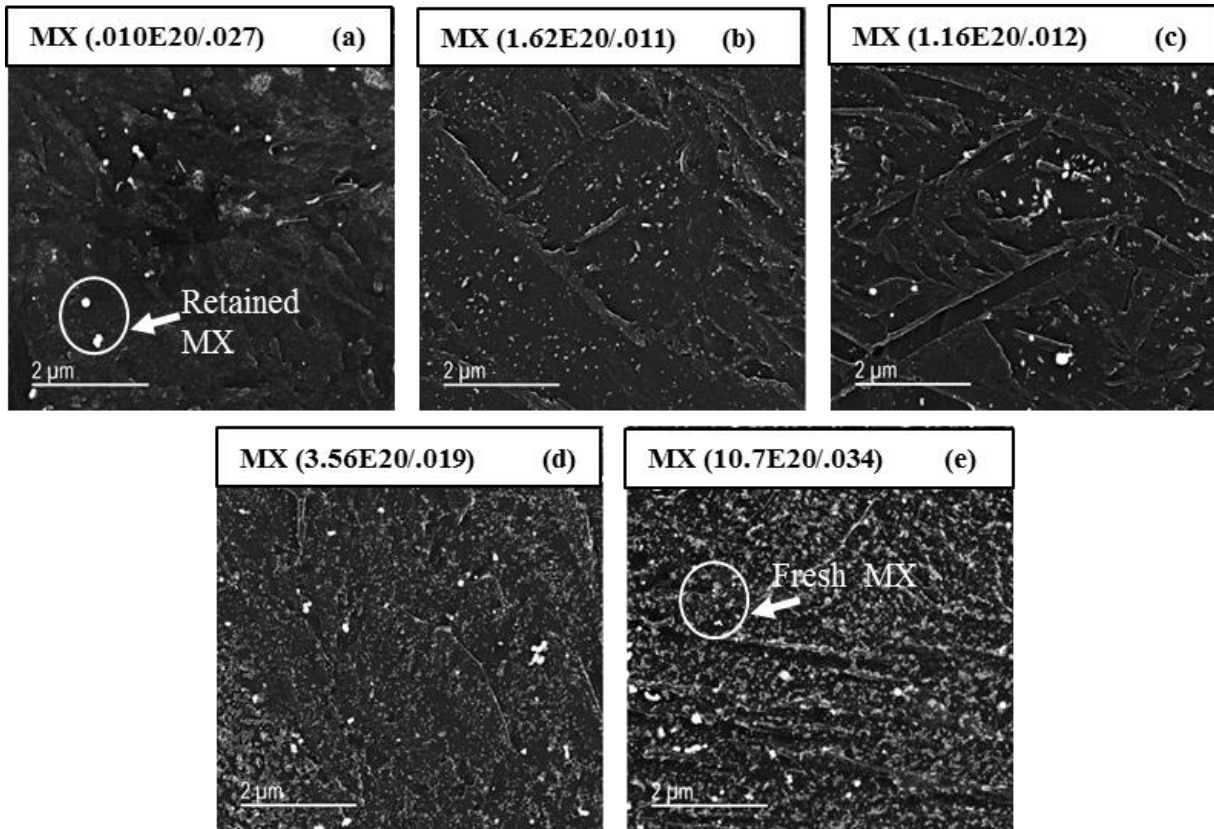


Figure 5.9 STEM images in the as-rolled condition; a. HTR 17 b. LTR 17 c. HTR 10 d. LTR 10 e. LTR 14. Particle density/volume percentages are shown respectively. Large retained MX particles from austenization are visible.

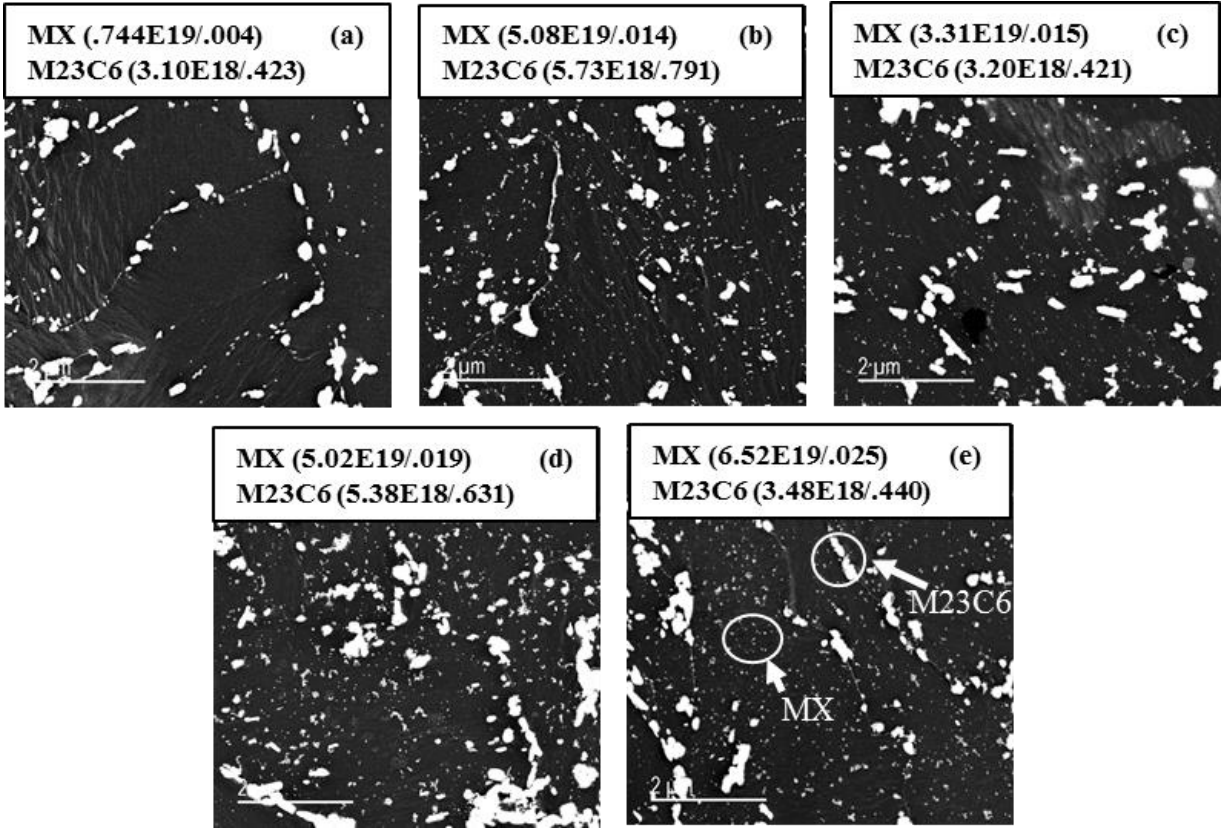


Figure 5.10 STEM images in the as-temper condition; a. HTR 17 b. LTR 17 c. HTR 10 d. LTR 10 e. LTR 14. Particle density/volume percentages are shown respectively.

The significance of obtaining a lower $M_{23}C_6$ density is related to the complete dissolution of $M_{23}C_6$ during welding. As a result, new wave of $M_{23}C_6$ precipitation on fresh prior austenite grain boundaries, and martensite sub-grain boundaries during PWHT. From the results obtained with varying plastic strain, it can be hypothesized that with increasing plastic strain, the amount of MX precipitated will also increase, which in turn leads to reduced amounts of $M_{23}C_6$. Thus, a higher deformation percentage can be used to lead to better cross-weld creep resistances.

5.5.3 Precipitate Evolution During Welding

Although it is known that the base metal has excellent creep resistance, shown by Abe (2008) and Shrestha et al. (2012), where it was indicated the base metal can reach 10,000 hrs at 600 °C and 100 MPa [2, 49]. However, the steel weldment (Fine Grain Heat Affect Zone) has poor creep resistance shown by Yu et al. (2013) [35]. Outside of research, in industry, the steels have multiple welds made in the manufacture of the power plants. Many of the research articles being published focus on improving the base metal, whereas there are fewer focused on the weldments. It does not matter if the base metal has good creep resistance, if the FGHAZ is not improved then the creep response of service pipelines will remain poor. As described in Chapter 3, the goal of this research is to minimize Type IV cracking. In order to minimize Type IV cracking, the welded and PWHT microstructures need to be understood in addition to the pre-weld temper base metal. Figure 5.11 illustrates the microstructures of the FGHAZ in the as-welded and PWHT conditions after GTAW with a single bead, and without filler metal. Note, this is not the microstructure of the through-thickness weld with a filler metal (multipass weld) that was used for the creep specimens. Although the microstructures should be similar, but there could be slight differences because of the thermal cycles experienced in multipass welding. A FGHAZ region in a weld with several passes will experience two or more thermal cycles. In Figure 5.11a, 5.11b,

and 5.11c the as-welded microstructure resembles the martensitic substructure. Some large undissolved carbides can be distinguished. In all the samples, the carbides are all less than 1 μm . The larger particles are assumed to be the undissolved M_{23}C_6 carbides because of the similar sizes reported in the literature [35, 97, 98]. The smaller particles are assumed to be some of the larger dispersion of MX particles, which can be seen in the TMT samples. Furthermore, fewer MX particles can be seen in the N&T sample. This demonstrates the larger volume percentage of MX in the TMT samples. Due to the nature of the welded sample, extraction replicas could not be made as a function of spatial coordinates. Therefore, only a qualitative analysis is made for the M_{23}C_6 particles of the as-welded condition in the SEM images. In the as-welded condition for all the samples, the carbide structures are similar in size and distribution. However, after the PWHT, different microstructures are now discernible. In all the samples, a fine equiaxed ferrite grain structure is observed. The large undissolved M_{23}C_6 particles observed in a straight line in the TMT9 and N&T samples are assumed to be possible “ghost” PAGBs. Yu et al. described ghost PAGBs as the line of carbides that had precipitated on the pre-weld PAGBs [35]. Since PAGBs tend to be straight, a straight arrangement of large M_{23}C_6 particles was identified as the “ghost” PAGBs. During the welding cycle, new austenite grains form on heating and then form martensite creating new PAGBs on cooling. The M_{23}C_6 carbides that do not dissolve stay in the original position of the pre-weld PAGB. In Figure 5.11d and 5.11f, possible ghost PAGBs are shown with white arrows. TMT8 exhibits very few ghost PAGBs after the PWHT. The few ghost PAGBs that are still visible in TMT8, are smaller in length and size. Furthermore, as seen in Figure 5.11e that the ferrite grain boundaries are more decorated than TMT9 and N&T. The average size of the M_{23}C_6 in TMT8 is also smaller (147nm), while the sizes of TMT9 and N&T are both roughly 165nm. In TMT8, the carbides decorating the ferrite grains could help mitigate

grain boundary sliding for longer periods of time, possibly delaying grain boundary void nucleation and growth [5, 6, 37]. The carbide formations and free ferrite grain boundaries of TMT 9 and N&T may allow excess grain boundary sliding. This creates increased stress at the carbide/matrix boundary, which has been shown to produce creep cavitation on this boundary [8, 36, 99]. In addition, the free grain boundaries are effective sinks for defects like dislocations and vacancies. This will also contribute to an increase in strain rate and earlier rupture times. Along with the re-distribution of $M_{23}C_6$, the effects of the TMT process on enhancing MX should also be stressed. As discussed above, the TMT process will enhance the precipitation of MX during processing. With the assumption that MX is more thermally stable, the MX should remain undissolved or only slightly coarsen during welding and post-weld heat treatment. This increased amount of MX will act as inhibitors to dislocation deformation during creep. Therefore, there will be a decrease in strain rate due to multiple creep mechanisms, dislocation creep, Coble creep, or grain boundary sliding.

Since the underlying microstructure has been observed, it is necessary to look at macro level responses in the HAZ. Hardness has been shown to correlate with the creep strength in the cross weld specimens. Figure 5.12 illustrates cross-sectional micrographs of sample plates [N&T see Fig. 5.12a, TMT 9 + temper see Fig. 5.12b, and TMT8 + temper see Fig 5.12c)] with a single pass GTAW, then a standard heat treatment (tempering at 760 for 2 hours) was applied. The cross-sectional microstructures consist of the weld metal, the heat affected zone, and the base metal, and there are no significant differences in the configurations among the samples. Overlaid onto the samples are corresponding micro-Vickers hardness maps. The standard N&T sample shows a high hardness weld metal with moderate hardness in the base metal. This is due to fresh martensite in the weld metal and unaffected, precipitation hardened base metal. However, there

is a distinct soft zone, which corresponds to the FGHAZ. Previously Yu et al. described this region to correspond to coarse $M_{23}C_6$ formation on “ghost” PAGBs resulting in ferrite grain boundaries being devoid of carbides [35, 98]. The TMT9 + tempered sample also exhibited a similar distinct softening zone (<185VHN). The creep-rupture of the cross-welded specimens is typically expected in this area. The hardness profiles observed here correspond to the locations from the microstructure characterization from above, this helps validates the results presented by Yu et al. (2013). However, in the TMT 9 sample, the soft zone in the FGHAZ indicates that TMT at 900 °C is not beneficial from the mechanical properties perspective. Conversely, the TMT8 + tempered shows only a soft zone. Higher hardness (> 230 VHN) is evident in the base metal whereas the other samples show lower hardness (<210VHN) in the base metal. This high hardness in TMT8 sample is attributed to the precipitation hardening due to the dense MX formation [42, 43]. In addition, the TMT8 + tempered samples do also show a lower softening effect in FGHAZ, but with less magnitude (<210VHN). This is attributed to the possible differences in carbide precipitations. Previous studies revealed that the RT hardness profile could reflect, but not predict, the high temperature creep resistances. Based on this empirical correlations, it could be expected that improved creep properties would also be expected in the TMT8 + tempered sample [98, 100].

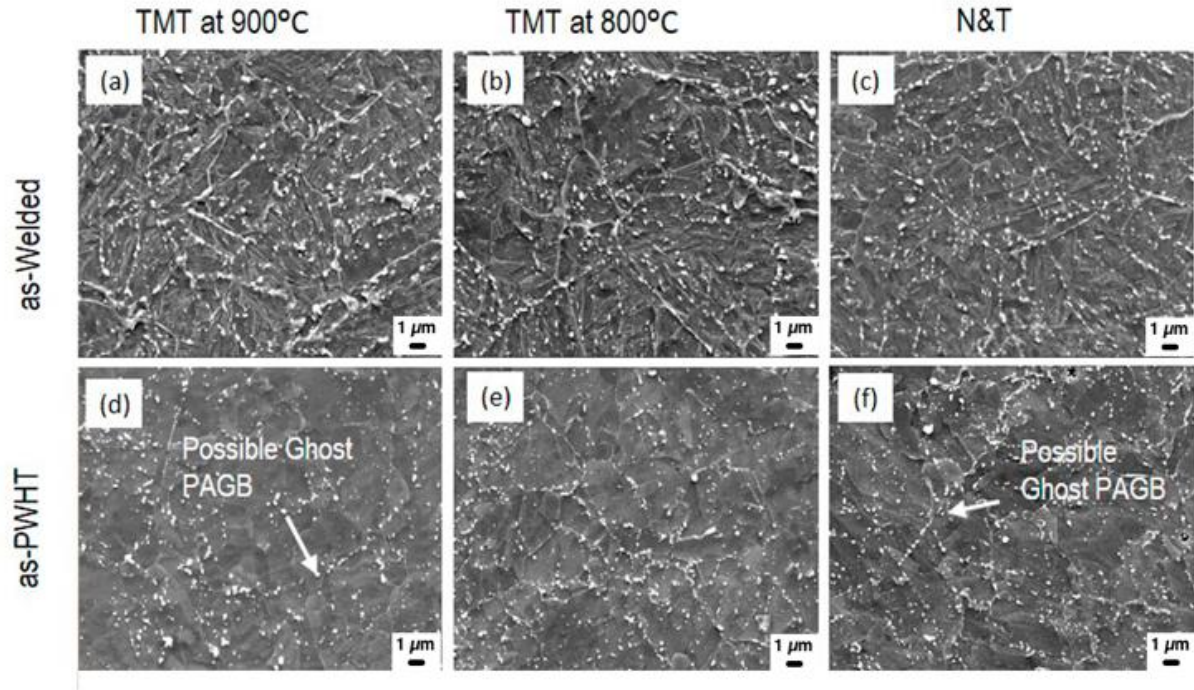


Figure 5.11 SEM images of the single bead as welded and as PWHT sample specimens, (a,d) TMT at 900°C, (b,e) at 800°C, and (c,f) N&T. In the as-processed condition of TMT specimens, a fine dispersion of MX can be found, in N&T only MX remaining after austenization. In as tempered conditions possible ghost PAGBs can be delineated.

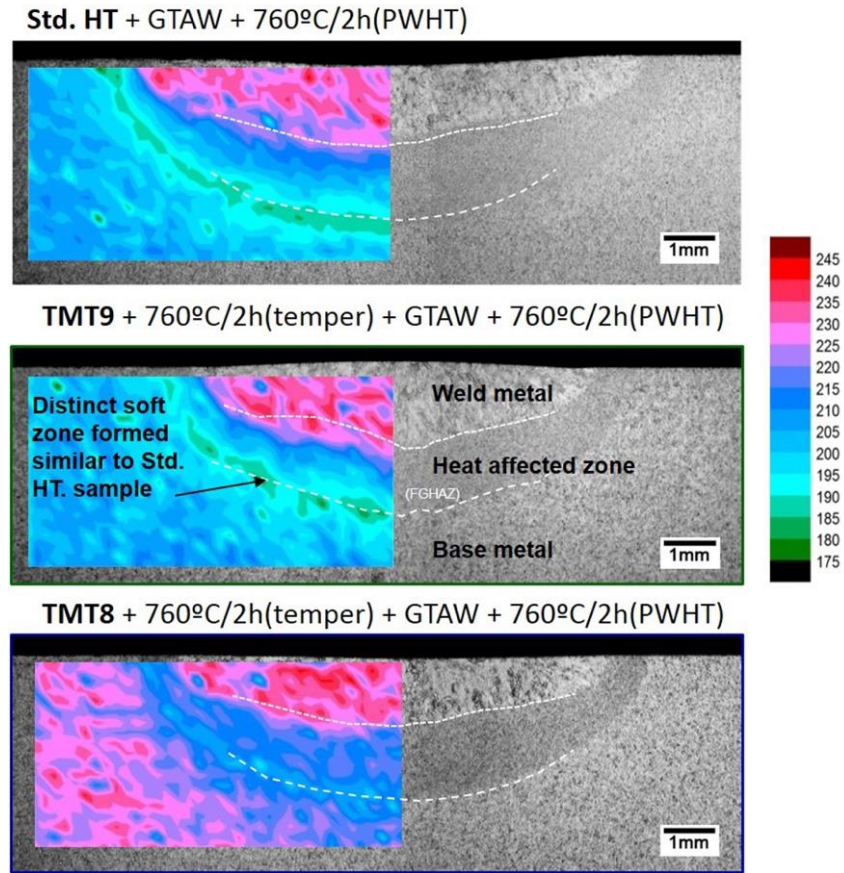


Figure 5.12 Cross sectional microstructure and hardness maps of the Grade 91 steel after (a) standard N&T, (b) TMT at 900°C + PWHT, or (c) TMT at 800°C + PWHT, followed by a single pass GTAW (no filler metal) + PWHT.

5.6 Microstructure After Creep Failure

Again here the carbon replica technique was not used because of the close spatial proximity of FGHAZ to the other regions of the weldment. However, it is still important to understand the microstructural evolution during creep. The failed samples can give some insight into this evolution. Figure 5.13 is a SEM image of the FGHAZ for TMT8 (Fig 5.13a) and TMT9 (Fig 5.13b). Figure 5.14 is the image quality map of an EBSD scan in the FGHAZ for TMT8 (Fig 5.14a) and TMT 9 (Fig 5.14b). The MX carbonitrides could not be evaluated using SEM, but the $M_{23}C_6$ was quantified for size and interparticle spacing. The sizes of the $M_{23}C_6$ carbides for both cases was $\sim 213\text{nm}$, which is significantly larger than that after PWHT. This size change can be attributed to coarsening. It is interesting that the sizes of both particles are the same, while TMT 8 crept for almost 1000 hours more than TMT9. Even though both particle sizes are the same here, the size of the $M_{23}C_6$ after PWHT in TMT8 was somewhat smaller than TMT9. Assuming the particles coarsened at similar rates, the extended time at temperature allowed the $M_{23}C_6$ particle to grow to the same size as TMT9. Thomson (1992) has shown that there is a certain size distribution of $M_{23}C_6$ particles that will lead to creep cavitation nucleation [101]. However, the size of the particles could not be determined at the start of the nucleation of the voids. Figure 5.13 does show extensive creep cavitation. Some of smaller voids can be seen around large $M_{23}C_6$ particles which had been said by Thomson.

Figure 5.14 shows the grain structure of the FGHAZ for both samples. The grain structure consists of equiaxed ferrite grains with most being roughly $3\text{-}5\text{ }\mu\text{m}$ in diameter. Creep cavitation can also be seen here, where some smaller voids not resolved in Figure 5.13 are visible. Although not shown here, the grain structure of the rest of the sample has retained some martensite lath resemblance.

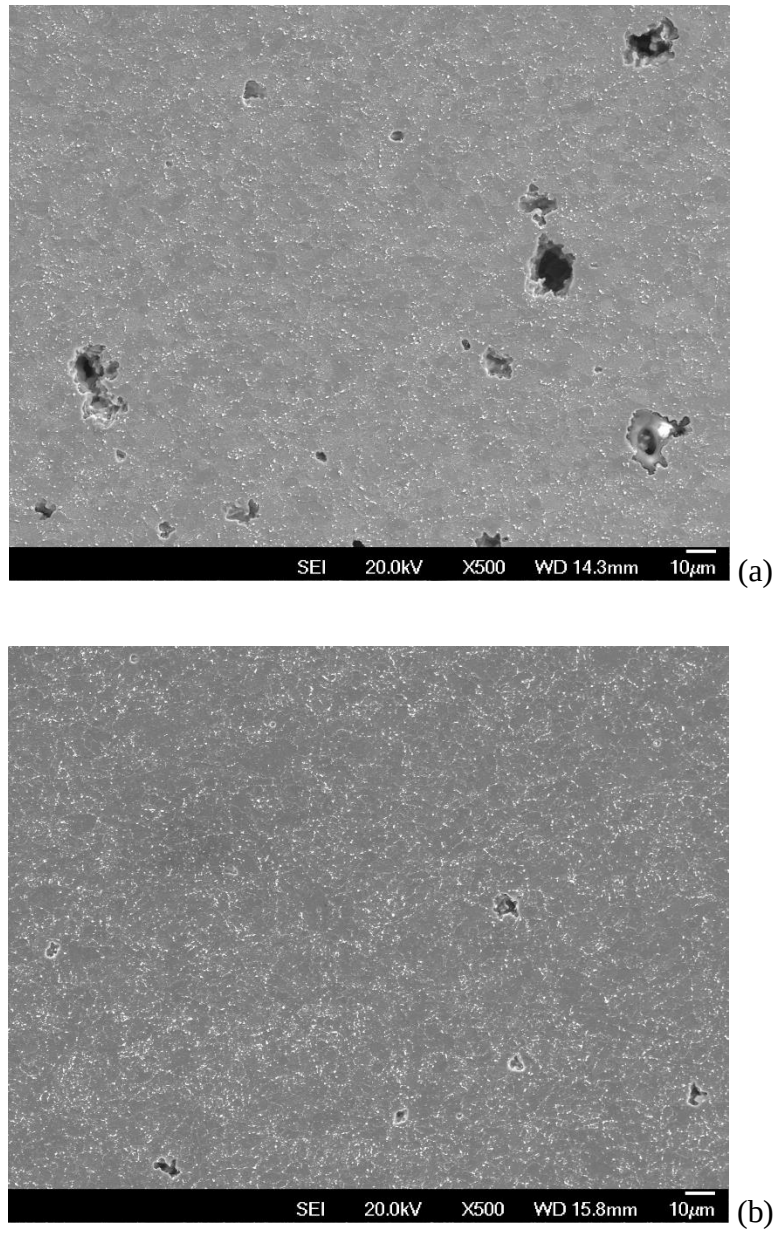


Figure 5.13 Fine Grain Heat Affected Zone after creep test, creep voids can be seen in a and b. (a) the FGHAZ of the TMT8 sample with larger and higher density creep voids. (b) The FGHAZ of the TMT9 sample with smaller and less dense creep voids.

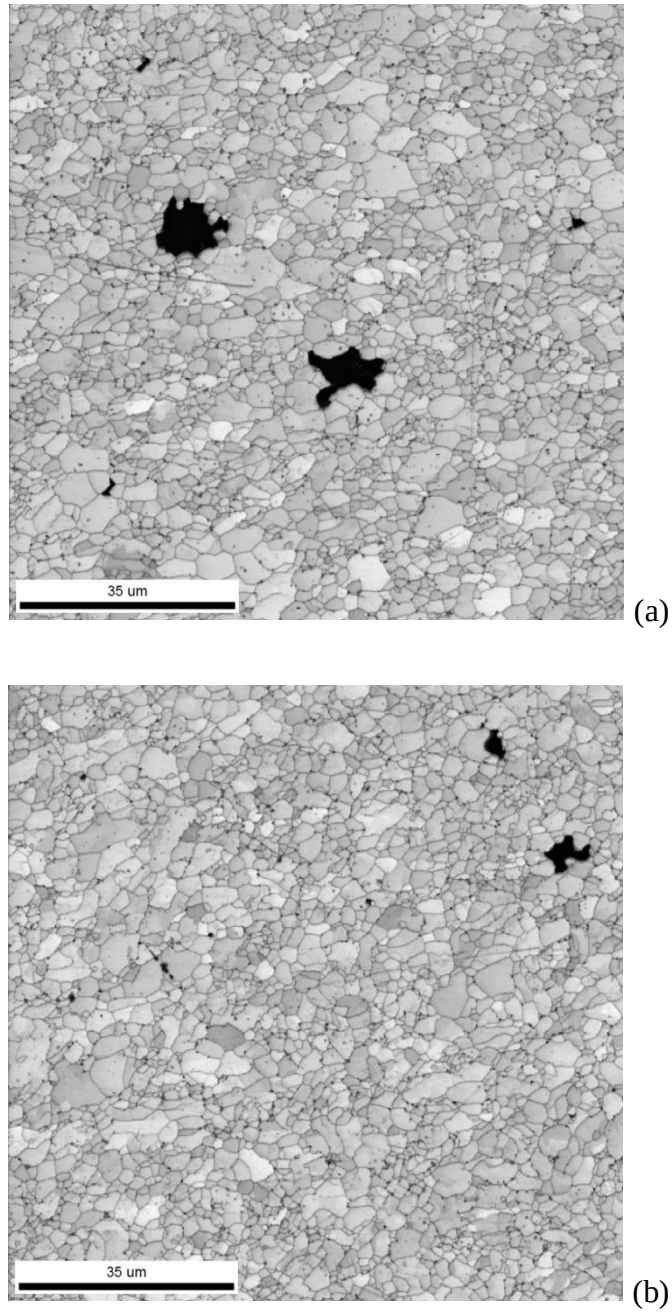


Figure 5.14 Image quality map of an EBSD scan. The images show fine equiaxed ferrite grains. Large and small creep cavities can be seen in both images. (a) IQ map of TMT8 after creep. (b) IQ map of TMT9 after creep.

Equiaxed ferrite is a comparably softer than martensite and would deform more easily. Therefore, the combination of the soft ferrite grain structure and the large $M_{23}C_6$ particles with an increased interparticle spacing can be linked to being the mechanism for final failure in the FGHAZ.

5.7 Mechanical Responses of the Grade 91 steel

5.7.1 Creep Curves

Figure 5.15 illustrates the creep-rupture curves of both TMT + tempered samples after GTAW and PWHT, together with those of the standard (N&T) and non-standard heat-treated (N&T 650 °C) samples [35, 97, 98]. The samples were crept at 600°C and 100 MPa. The observed time to failure of TMT9 + tempered is 1859 hours. This exhibits little improvement over the standard N&T sample. The slight increase in creep life can be attributed to the increase particle density of MX observed in TMT9 although the $M_{23}C_6$ size is similar to the N&T sample. Hence, a slight increase in MX density would lead to a slight increase in creep life. Conversely, the TMT8 + tempered sample exhibits significant improvement of the cross-weld creep properties. The sample failed at 2831 hours, which is almost double the creep life of N&T sample. The instantaneous creep rates (see Fig. 5.15b) were calculated by using the data from Figure 5.15a using a moving linear slope fitting methodology. The plots show that in all samples, at the early stages of testing (< 100 h), the creep rate decreases, which is consistent with primary creep stage. As expected, the N&T sample reaches a minimum creep rate of $2 \times 10^{-7} \text{ s}^{-1}$ within 466 hours and quickly transitions to tertiary creep and failure within 1000 hours. The minimum creep rate decreases by an order of magnitude to a minimum value of $2 \times 10^{-8} \text{ s}^{-1}$ with different processing conditions in the order of TMT9, TMT8, and lastly N&T650.

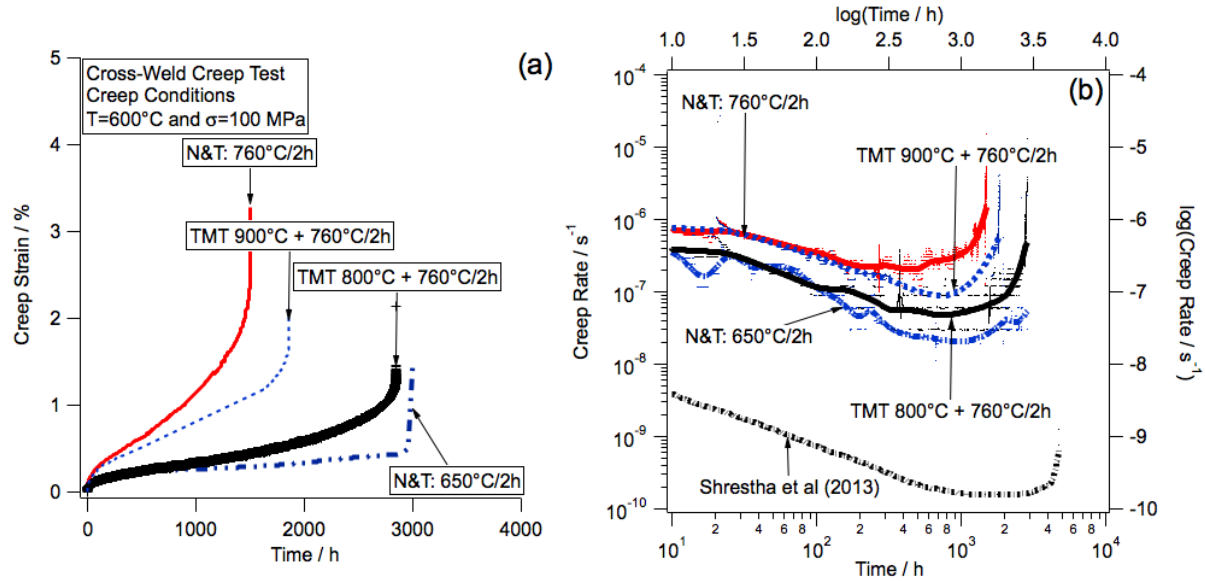


Figure 5.15 Measured (a) cross weld creep strain and (b) creep rate curves of samples tested at 600°C at a stress level 100MPa. The plots compare the data from TMT samples with the published data from standard and non-standard pre-weld tempering. The creep rate data is also compared with published creep rate of base metal grade 91 steel.

Interestingly, all the cross-weld samples show two to three orders of magnitude higher creep rate (10^{-7} and $10^{-8} s^{-1}$) than that of a base metal ($10^{-10} s^{-1}$) reference sample [102]. Even with processing and increasing the density of MX, the creep strength of the weldment still does not meet base metal creep strength. This result suggests that the weldment will never approach the creep strength of the base metal. In order to reach the base metal creep strength, the particles and the grain structure both have to match the base metal. It is shown here that this seems all but impossible for Grade 91 steel. The non-standard heat treatment (650 °C/2 hours) was shown to mostly dissolve the $M_{23}C_6$, but the size and density still do not match the base metal [35]. The microstructure inhomogeneities observed in the FGHAZ are such that the Type IV cracking problem cannot be resolved in the Grade 91 steels but only minimized to a certain extent. With a creep model that can be adjusted for particle size and volume fraction can explain the

discrepancies in creep strength between the FGHAZ and the base metal. A creep model has been developed for the Grade 91 steel and will be discussed in detail in Chapter 7.

5.7.2 Charpy Impact Toughness

Although it has been shown that the creep strength has been enhanced, good room temperature toughness was also a mechanical response necessary for service. As mentioned before, the non-standard heat treatment (N&T 650°C) greatly improved the creep strength of 9Cr steel. However, the toughness of the base metal was insufficient for deployment [35]. The DBTT for the non-standard N&T sample is about 80 °C, which is well above transportation temperatures. This means the pipe would be susceptible to cracking during transportation and power plant manufacturing. The TMT process is intended to enhance the creep-rupture properties as well as maintaining sufficient RT toughness required for service. By providing a standard industrial tempering step, the toughness is expected to be similar to the N&T samples. Figure 5.16 illustrates the RT toughness of TMT8 + tempering compared to standard N&T and the non-standard N&T samples. Here, it must be noted that the sample used in the Charpy impact test was the LTR 17 sample, aus-rolled at 900 °C with 17% thickness reduction, followed by aus-aged at 800 °C for 1h. The average Charpy Impact absorbed energy of the TMT8 + tempered sample was more than 150J, and would be expected to show a similar DBTT of -40 °C of the N&T sample. Although the deformation was greater than that of the sample described in the current study, the toughness is expected to be similar for all TMT samples because of the application of the standard tempering (760°C/2hours) and similar microstructure. Therefore, the TMT process combined with a standard tempering can be said to achieve improved cross-weld creep properties together with sufficient room-temperature toughness of the base metal.

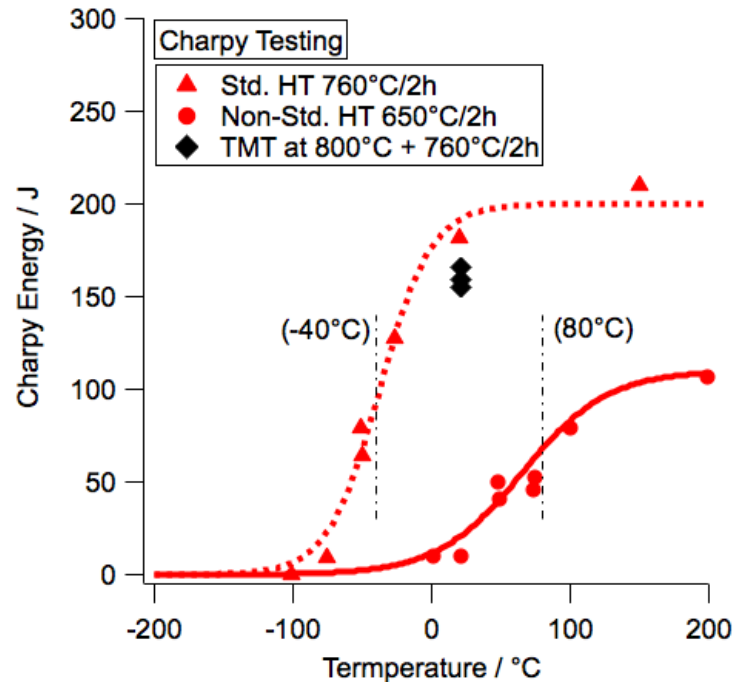


Figure 5.16 Charpy impact test results of the Grade 91 steel applied TMT at 800°C + tempering, together with those of the standard and non-standard heat-treated samples.

5.8 Summary

1. The temperature range for the TMT to produce a martensitic microstructure is greater than 700 °C.
2. The PAGs and martensite grain structure after TMT is remarkably similar in all cases, both forging and rolling do not differ much from the N&T sample. The conclusion from such similar microstructures is that the improvement in the cross-weld creep rate should be attributed to the evolution of the precipitates from TMT to PWHT.
3. The TMT process shows an enhanced precipitation of MX particles. The $M_{23}C_6$ precipitation correlates with an increased density of MX after TMT. The greater density of MX leads to smaller and less dense $M_{23}C_6$ formation during tempering. It is hypothesized that the MX takes up alloying elements needed for the precipitation and growth of $M_{23}C_6$, which slows the process and generating less $M_{23}C_6$ of large size.
4. The carbide evolution in TMT9 is similar to that of the N&T sample during welding. During welding, the large $M_{23}C_6$ do not dissolve and remain on their “ghost” prior austenite grain boundaries. The $M_{23}C_6$ particles grow excessively large compared to TMT8 during the PWHT. These have been shown to lead to creep cavitation and failure in the FGHAZ of the Grade 91 weldments
5. The creep curves of the TMT sample show improvement of the cross-weld creep strength. The TMT 8 sample had the greatest improvement. However, all the samples including the non-standard N&T sample did not get close to approaching the creep strength of Grade 91 base metal. This leads to the conclusion that the Type IV failure mechanism cannot be solved in Grade 91 steel and possibly a new alloy system is needed to provide this resistance.

6. Toughness is also a necessary constraint in the Grade 91 steel. Even though the non-standard N&T sample showed the best creep resistance, the toughness was extraordinarily poor. However, with the application of TMT and the standard tempering process, the toughness is very similar to that of the N&T sample. This shows that performing TMT is a good approach to improving the cross-weld creep strength and maintain industrial standards of tempering and toughness.

7. From the creep rupture results, it can be said that the Type IV failure mechanism in Grade 91 does not appear to have a solution. Even though it was shown that the $M_{23}C_6$ carbides could be prevented from excess growth during the PWHT, the creep rupture did not approach the base metal creep rupture properties. In addition, the increase in MX also did not make such a large improvement to prevent Type IV failure.

Chapter 6. Microstructure of Creep Resistant Fe-Cr-Al Ferritic Alloy

In the previous chapter, we concluded that Type IV failure mechanism cannot be avoided in grade 91 steels. Therefore, the community needs a new path way for improving the high temperature creep resistance for both the base metal and weldment. One possibility is to utilize an alloy (e.g. Fe-Cr-Al) in the hotter sections of the power plant that would not be susceptible to the Type IV failure. However, the operating temperature for the Grade 91 steel is between 550-650 °C. As it will be discussed in this chapter, the operating temperature for the new Fe-Cr-Al alloys must be above the sigma phase solvus temperature. In this alloy, this temperature is around 650 °C. Thus the operating temperature should be above 700 °C. Therefore, in this case, the Fe-Cr-Al alloy should not be considered a direct replacement for Grade 91 steel. It could be viewed to replace other steel grades such as the austenitic stainless steels or even Ni based alloys. The need for the development of new alloy system based on Fe, Cr, and Al, alloy chemistries were discussed in Chapter 4.1.2. Instead of using carbon for a precipitate former, the alloy design strategy relies on Niobium (Nb) as a precipitate former. The Nb forms an Fe₂Nb Laves phase throughout the matrix and along the grain boundaries. Early results also suggest that this Laves phase is more thermally stable than the large M₂₃C₆ carbides in Grade 91 steel [103-105]. Nevertheless, microstructure control is needed to provide creep resistance through precipitation strengthening. Along with the good precipitation strengthening, this alloy is also expected to have good oxidation resistance. Cr and Al are added to provide the oxidation resistance at high temperature. The addition of 3 wt% Al also suppresses the formation of Sigma phase at the expected service temperatures and creep test temperatures. Using thermodynamic software ThermoCalc®, the Al addition was found to stabilize the BCC matrix at creep testing temperatures.

The next microstructural design strategy is to eliminate the precipitates in the as processed condition before service or creep testing. Therefore, this alloy was solutionized to arrive at single phase microstructure. Lack of pre-existing precipitates and their coarsening improves the creep resistance. However, the precipitates will nucleate and grow during the first few hours of creep testing to provide the creep resistance. The above microstructural evolution is expected to be a good replacement for the steels that are sensitive to Type IV cracking. Worldwide research has started to characterize the creep resistance of Fe-Cr alloys at temperatures and compared to the reference data from Grade 91 steel at the same temperature. Initial creep testing was performed at 700 °C and 70 MPa. At this temperature and stress, creep properties of the first generation of the Fe-Cr-Al alloy was comparable to Grade 92, an existing higher creep resistance 9%Cr steel grade. With any new alloy development, there are many difficulties to overcome before deployment in service. The following chapter will provide results of the microstructure control in this alloy system and correlates the same to creep results.

6.1 Microstructure After Solution Heat Treatment

The initial microstructure, before creep, is important to understand because the initial condition can affect creep damage evolution in the FCA (Fe-Cr-Al) alloy system. Ferrite grain size and initial amounts of Laves phase may change the time to failure of the samples. In addition, different initial conditions may be desired based on end goal. Here a fully solutionized microstructure is desired to prevent precipitates being present during welding. Figure 6.1 shows the microstructure of the as solution heat-treated samples as well as a higher magnification image of a grain boundary for each (see Fig. 6.1 e-f). The 0Nb containing alloy (FCA-0NB, see Figure 6.1 a&e) did not contain Laves phase within the microstructure, which is expected because there are no precipitate forming alloying additions.

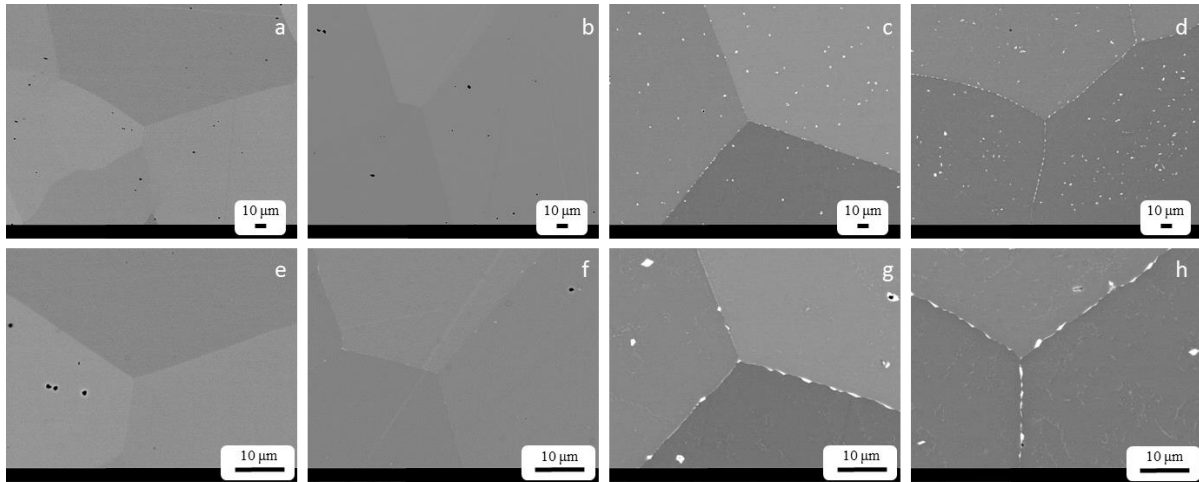


Figure 6.1 As solution heat-treated microstructures. The corresponding alloys are as follows, (a&e) FCA-0Nb, (b&f) FCA-1Nb, (c&g) FCA-2Nb, and (d&h) FCA-2Nb-.1Zr. It is observed that 1300 C for 10 minutes was not successful in solutionizing the Laves phase.

This sample only contained large ferritic BCC grains. In addition, no σ or Alpha Cr phase was detected with visual inspection, which forms at ~ 600 °C for this alloy according JMatPro® a thermodynamic software, this is also the case for all the alloys in the study. The FCA-1Nb alloy (see Figure 6.1 b&f), which has a lower solution temperature (~ 1000 °C), contains a few small Laves phase particles on the grain boundaries. Therefore, it can be concluded that the solution heat treatment was successful in dissolving the Laves phase in BCC. On the other hand, there are observable amounts of Laves phase present in the FCA-2Nb and FCA-2Nb-.1Zr samples (see Fig 6.1 c&g and d&h, respectively). These samples both contain grain boundary Laves phase, large Laves phase particles, and small string like arrays of particles. The large particles were also observed after the creep and were identified by EDS to be Laves phase. These are particles that have remained in the matrix from solidification and did not dissolve during heat treatments. It is also peculiar that the grain boundaries are also decorated with Laves phase. The solutionizing heat treatment for the alloys were chosen based on the information provided by JMatPro®. The

solutionization temperature predicted was found to be 1140 °C. In order to understand the validity of the calculation, the solutionizing temperature was recalculated using the software ThermoCalc®. Interestingly, the solutionizing temperature for FCA-2Nb and FCA-2Nb-.1Zr was found to be ~1225 °C. Figure 6.2 shows the equilibrium weight percent of Laves phase in the alloy as a function of temperature. The two dashed lines are the JMatPro® calculated curves. The solid line is the calculation from ThermoCalc®. Comparing the two 2Nb containing curves shows the differences in the calculated results. This difference can also provide the reason that the Laves phase in the 2Nb containing alloys did not go into solution. Because the particles are still observed after heat treatments, the actual temperature may be closer to 1300 °C.

The ferrite grain size can also be important. If the creep mechanism is Grain Boundary Sliding or Coble creep, then, for example halving the grain size (for example 100 to 50 µm) would produce an order of magnitude faster creep rate. Here, the creep mechanism will be discussed later.

However, to fully understand the initial microstructure, grain size needs to be quantified. Table 6.1 shows the grain size in the solution heat treated samples, measured from images in Figure 6.1. It should also be noted that the standard deviation can be quite large. This means that there is a large spread of grain sizes in a sample. The FCA-2Nb sample did contain a few very large grains. With the creep samples being small, the grain size in a creep specimen may be larger or smaller depending on the local size where it was cut. It should be noted that the ferrite grain sizes differ because of the difference in heat treatment temperatures. The 2 Nb containing alloys were both treated at 1300 °C while the other alloys were treated at 1200 °C. The higher temperature treatment for the 2 Nb contain alloys allowed for faster grain growth than the FCA-1Nb sample.

Table 6.1: BCC grain sizes prior to creep in microns.

FCA-0Nb	FCA-1Nb	FCA-2Nb	FCA-2Nb-.1Zr
152.7±25 μm	305±64 μm	467±188 μm	374±81 μm

Using Atom Probe Tomography (APT), the Laves phase present after solutionizing heat treatments was characterized. Figure 6.3 shows one reconstructed needle from the FCA-2Nb sample. On the right hand of the figure, the Nb atoms are highlighted showing the Laves phase on a grain boundary. Figure 6.4 is a graph showing the atomic concentration profile along a proxigram traversing from the matrix and into the Laves phase. The concentration profile shows a low distance gradient of elements from the matrix to the Laves phase. In addition to the concentration profile the analysis software was able to determine the bulk composition of the matrix and Laves phase. The bulk composition for the matrix was found to be in atomic percent: 61.8% Fe, 31.6% Cr, 5.7% Al, 0.27% Si, and 0.13%Nb. The bulk composition for the Laves phase was found to be in atomic percent: 53.5% Fe, 26.9% Cr, 2.85% Al, 4.5% Si, and 26.9%Nb. The bulk compositions of the matrix and Laves phase shows almost all the Nb has been used up to precipitate Laves phase along the grain boundary. In addition, the composition of the Laves phase is close to equilibrium conditions. The implications of these findings is that simple coarsening models can be used to model the evolution of grain boundary Laves precipitate size distribution. This information can then be used to help optimize the alloy for better creep resistance.

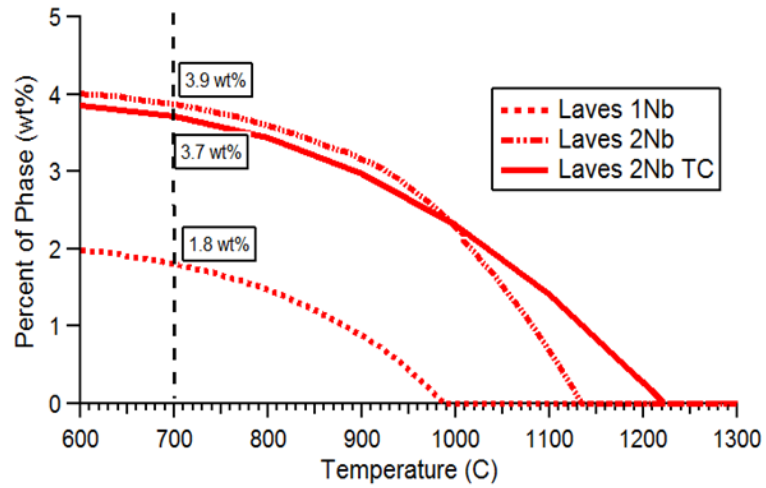


Figure 6.2 Calculation of the equilibrium amounts of Laves phase in the Fe-Cr-Al alloy. The figure shows an increase in solutionizing temperature of the FCA-2Nb alloy, which indicates problems with calculating equilibrium of the alloy.

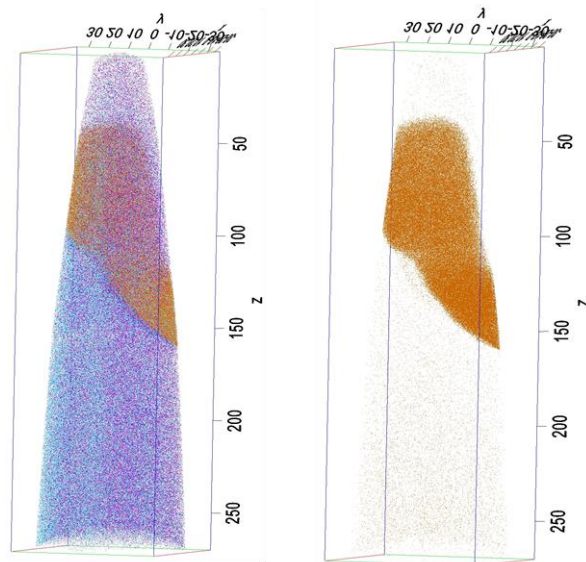


Figure 6.3 Left, all ions collected from the FCA-2Nb sample. Right Nb atoms highlighted showing the location of Laves phase along a grain boundary.

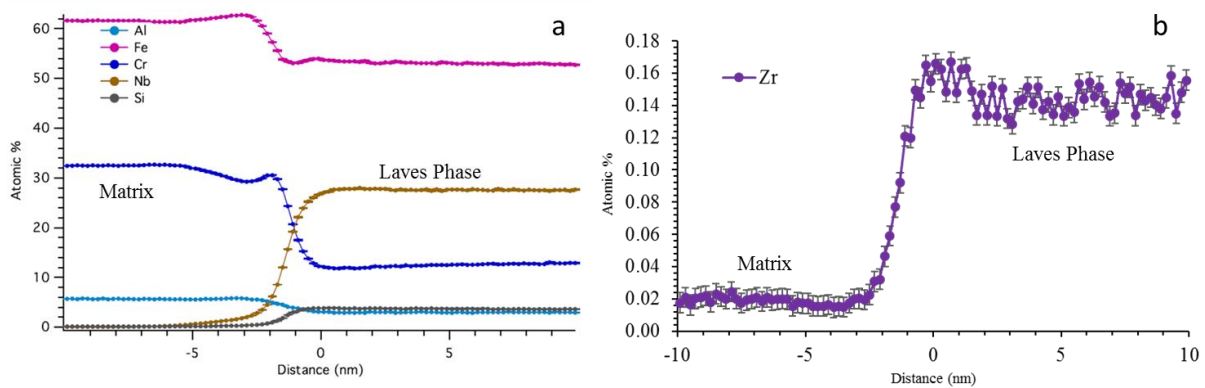


Figure 6.4 (a) Atomic concentrations of element in a proxigram from the matrix to the Laves phase in FCA-2Nb. The laves phase is enriched in Nb and show stoichiometric equilibrium concentrations. (b) Atomic concentrations of Zr from the matrix to the Laves phase. Laves phase is seen to enrich in the Laves phase along the grain boundary. Note the magnitudes in atomic concentrations for FCA-2Nb-.1Zr are the same at (a).

From the grain size comparison, it is interesting that alloy that contains Zr has almost a 100- μm reduction in ferrite grain size. The role of Zr in the sample is not completely understood. The Atom Probe Tomography experiment revealed Zr within the Laves phase at the grain boundary. Figure 6.4b shows the atomic concentration of Zr at the grain boundaries. The figure shows almost zero concentration of Zr in the matrix. Possible mechanisms for the effect of Zr on the alloys is hypothesized as following. The first Zr segregates to the ferrite grain boundaries during solidification or during heat treatments. The Fe-Zr phase diagram shows almost no solubility for Zr in Fe-BCC even at 1300 °C. On the other hand, Nb does have solubility (~ 3 wt%) in Fe-BCC at 1300 °C (according to the Fe-Nb phase diagram). Therefore, during heat treatments the grain growth could be slowed, before the presence of Laves phase, by the solute segregation of Zr. Secondly, the high concentration of Zr at grain boundary could have nucleated Fe_2Zr Laves phase before the on-set of Fe_2Nb Laves phase. Third, during subsequent slow cooling and low temperature heat treatment Nb could have diffused into the Zr-rich Laves phase to form the equilibrium Laves phase with both Nb and Zr, i.e. $\text{Fe}_2(\text{Zr}, \text{Nb})$, as well as, independent Fe_2Nb laves. Although the above microstructure evolution is not proven, the presence of grain boundary precipitates might have slowed down the grain growth from the FCA-2Nb sample.

6.2 Microstructure After Aging

In the present research, two alloys (FCA-1Nb & FCA-2Nb) were chosen for aging studies. The microstructures after aging 168 hours at three different temperatures (700, 800, and 900 °C) for both alloys is shown in Figure 6.5. The size and density of the Laves phase is shown in the respective image. The density shown in the images does not take into account the Laves phase on the grain boundary. The density and sizes were calculated with higher magnification images from the center of a few BCC grains chosen at random. These results demonstrate that as the

temperature increases the coarsening rate also increases, as the size of the Laves phase increases while the density decreases. It is interesting to note that between the FCA-1Nb and FCA-2 Nb samples, the sizes remain similar at all three temperatures. This shows the coarsening rate of Laves phase is similar in both alloys ($\sim 5 \times 10^{-26}$ m/s) and is not affected by additional Nb. However, the density is larger in the FCA-2Nb sample, which can be explained by the alloy containing more Nb. The same trend can also be seen after aging 1008 hours. This is shown in Figure 6.6. Here again the size of Laves phase between the two alloys are similar at each temperature, where the sizes were found to be ~ 100 nm, 150-200 nm, and ~ 200 nm for 700, 800, and 900 °C. However, the density of the FCA-2Nb alloy remains slightly larger, but is within the same order of magnitude. To compare with the temperature of the creep testing (700 °C), the 700 °C aging can be used to model the coarsening of the Laves phase. At 700 °C the size of the Laves phase in both alloys coarsens roughly 20-30 nm while the density also remains fairly stable. The results show that the Laves phase in the Fe-Cr-Al alloy system has a low coarsening rate at 700 °C to a possible few thousand hours. However, to fully understand the coarsening of the Laves phase at longer time intervals, such as 5,000 or 10,000 hours, extra experiments would be needed. The aging studies indicate Laves phase is a good candidate for the creep resistance in the Fe-Cr-Al alloy system. However, welding on the Fe-Cr-Al is yet to be performed and the stability of Laves phase at temperatures higher than 1000 °C is not known. Therefore, it cannot yet be compared to Grade 91 steel weldments.

An important aspect of the ageing studies is the evolution of the grain boundary region. The region involves the grain boundary, which contains Laves phase, and a precipitate free zone directly adjacent to the grain boundary. First, it is clear, for all temperature values and 168 hours of aging, the grain boundary Laves phase is larger in the FCA-2Nb sample than the FCA-1Nb.

For example, the measured value of the grain boundary Laves phase at 700 °C in the FCA-2Nb sample is about 200 nm, while the value is 140-150 nm for FCA-1Nb. The same trend occurs for 800 and 900 °C. Again after 1008 hours of aging the trend continues. The size of the grain boundary Laves phase at 700 °C for FCA-2Nb was found to be 280-300 nm, while the Laves phase for FCA-1Nb was found to be 220-230 nm. In addition to the size differences, the fraction of Laves phase on the grain boundaries also differs. For the 700 °C condition and 168 hours the FCA-1Nb has an aerial fraction of Laves phase on the grain boundary of 0.56, while the fraction for FCA-2Nb is significantly higher at 0.95. After aging to 1008 hours, the FCA-1Nb fraction had increased to 0.72 and the FCA-2Nb fraction decreased to 0.77. The possible reason for these changes is due to coarsening. The Laves phase in the FCA-1Nb sample has less Nb for the formation of Laves phase. Therefore, the coarsening kinetics at the grain boundary will be different than FCA-2Nb. For FCA-1Nb the Laves phase was still growing, so with the growth to 220-230 nm the measured fraction of Laves phase on the grain boundary increases. However, the FCA-2Nb sample contained large Laves phase at 168 hours. Then aging to 1008 hours caused coarsening along the grain boundary. The coarsening caused the measured value of the Laves phase on the grain boundary to decrease with the increase in particle size.

Along with the fraction of Laves phase, the precipitate free zone (PFZ) is also an important aspect in the Fe-Cr-Al alloys. Initially the PFZ forms by taking all the Nb from the immediately surrounding matrix, this is called solute depletion [106, 107]. Then with aging the PFZ will increase in size as a result of Oswald Ripening between the smaller Laves phase within the BCC matrix and the larger Laves phase at grain boundaries. The sizes of the PFZ for FCA-1Nb and FCA-2Nb samples at 700 °C and 168 hours was found to be 0.93 and 0.84 μm respectively.

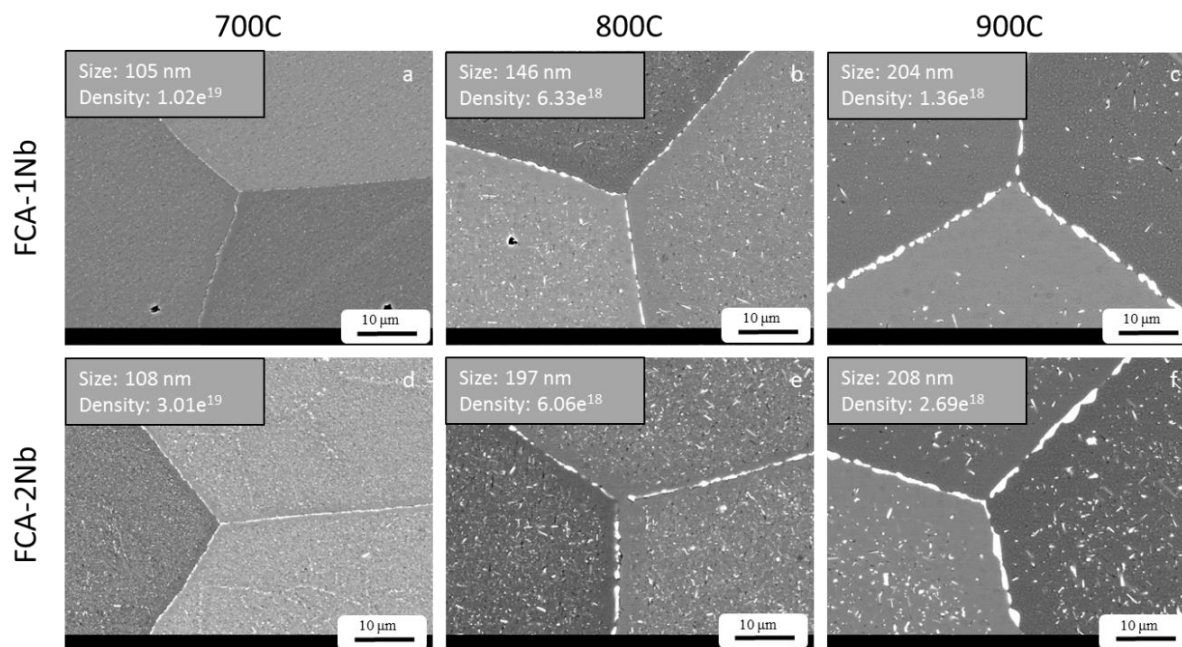


Figure 6.5 Microstructures from aging 168 hours at three different temperatures.

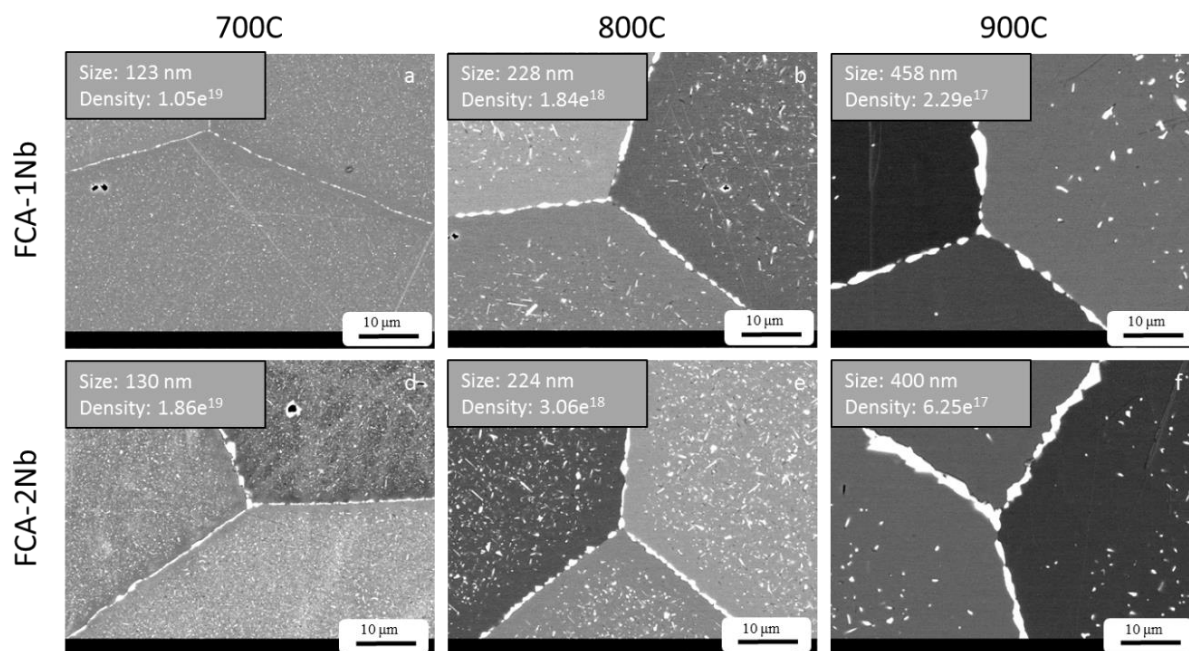


Figure 6.6 Microstructures from aging 1008 hours at three different temperatures.

The size of the PFZ is the average distance from the grain boundary to the beginning of the matrix Laves phase on one side of the grain boundary. After aging to 1008 hours, the sizes of the PFZ for FCA-1Nb and FCA-2Nb was found to be 1.13 and 1.04 μm respectively. The reason for the reduced size of the PFZ in the FCA-2Nb sample is that this sample contains more Nb. This means that more Laves phase can form closer to the grain boundary during nucleation. More of the matrix will be depleted of Nb in the FCA-1Nb sample than the FCA-2Nb sample on the same time scale. The significance of the grain boundary Laves phase and the precipitate free zone directly relates to creep deformation and creep mechanisms. A smaller fraction of Laves phase on the grain boundary allows for enhanced creep cavitation over a larger fraction of particles on the grain boundary. In addition, a larger PFZ allows more deformation during creep, which in turn can be related to the strain rate. The significance of these two parameters on their correlation to the creep rupture properties, fraction of Laves phase and width of the PFZ, will be discussed in Chapter 7.

6.3 Crept Microstructure and Fractography

6.3.1 Transverse SEM

The microstructures [obtained via backscatter imaging] of the three Nb containing alloys after creep failure are shown in Figure 6.7. The microstructures shown are from top of the failed specimen after mounting and polishing. Because the FCA-0Nb did not contain Laves phase and had poor creep properties, only the Nb containing alloys will be discussed here. Figure 6.7 (a-c) shows the top face of the creep failure tip. The FCA-1Nb and FCA-2Nb samples have observable ductility at the fracture tip. From the images, it appears that these two samples failed via a grain boundary failure mechanism (will be discussed in later sections), but were held together with a

few large grains. This can be observed in the FCA-2Nb sample. From Figure 6.7b, there is a recessed region of the sample at the bottom of the micrograph. Here the grain boundary had failed, leaving the large grain at the top of the image to hold the load. With the middle grain boundary failure, the area holding the load was reduced, thus increasing the stress in the remaining grains. With an increase in stress, the sample would start to generate more dislocations and they would start moving more rapidly, causing rapid deformation which will accumulate and stretch the material. This event further reduces the area and then increases stress more. This accumulation of stress and reduction in area will cause a runaway event, which is evident in the tertiary creep regime with a rapid elongation to failure. There are also voids accumulating on the grain boundary in both the FCA-1Nb and FCA-2Nb samples. Creep voids are observed both near large Laves phase and on triple points. This can help to identify the creep mechanism. The mechanism will be discussed later, but the microstructure indicates a Grain Boundary Sliding (GBS) or Coble mechanism. More voids can be observed in the FCA-2Nb sample because it had crept for longer time and thus can accumulate more voids.

The Zr containing alloy (FCA-2Nb-.1Zr) shows little ductility at the tip. From the as-solutionized condition, internal grain boundary cracking was observed and may have been present in creep specimen before testing. The gauge section also contained full grain boundary separation after the creep test (see Figure 6.7f). In addition, the subgrain formation is also reduced in the sample. This indicates that the sample did not stretch like the other alloys. The creep curve indicates that the steady state creep rate is the lowest of the alloys. However, there is a more abrupt transition to tertiary creep, which can indicate a brittle fracture. In traditional creep curves in precipitate strengthened steel, the transition to tertiary creep can occur over 1000 hours. However, this sample transitioned to tertiary creep in less than 100 hours. This could be a

weakening of the interface between the coherent side of Laves phase and the BCC matrix with the addition of Zr. The grain boundaries with cracking do not show Laves phase because they have fallen out of the crack during polishing. From atom probe tomography experiments, Zr was found in the Laves phase along the grain boundaries. As discussed earlier, it is yet unclear the mechanisms that Zr plays in the strength of the grain boundary. Therefore, with the observed abrupt failure, and the microstructure features, it can be assumed that this sample failed via brittle grain boundary fracture instead of a ductile grain boundary failure.

The gauge section in all the samples reveals little creep deformation when observed with the backscatter detector. The grains are still large with unobservable elongation and the strain contrast is limited. The FCA-1Nb alloy appears similar to the aged condition in particle size and distribution with little observed creep voids. Although the FCA-2Nb is also similar to aging conditions, grain boundary voids on boundaries perpendicular to the tensile direction are observed. There are also voids around the excessively large Laves phase particles within the grain interior. The excessively large Laves phase was shown to be present in the matrix prior to creep, and as explained in past section larger particles tend to form voids during creep from an increased amount of dislocation pile up. The voids along the grain boundaries can indicate of either grain boundary creep or Grain Boundary Sliding. From the matrix of the gauge section, the two alloys are very similar. The grain boundary zone will be discussed later in this section along with a quantitative analysis.

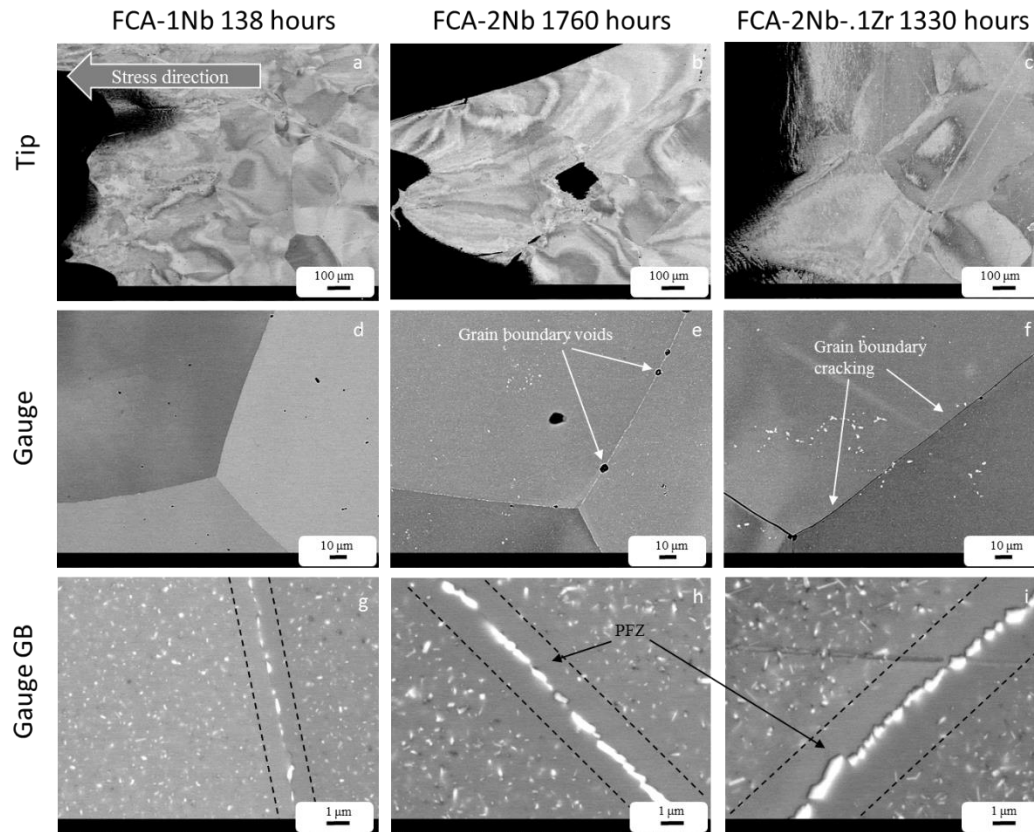


Figure 6.7 SEM micrographs of the creep specimens from the top surface. (a-c) fracture tip, (d-f) low magnification of the gauge section, and (g-i) higher magnification of the gauge section at a grain boundary.

Lastly, in Figure 6.7 (g-i), a higher magnification of the grain boundaries (without cracks) can be seen. The amount and size of the Laves phase in the matrix of the FCA-2Nb alloy 138 nm is drastically larger than the FCA-1Nb alloy 95 nm. However, it should be stressed this observation can be related to aging heat treatment, i.e., the FCA-2Nb alloys were held at temperature for a longer period of time, thus it would be expected that the matrix Laves phase would have coarsened. Another difference in the alloys is the area fraction of Laves phase on the grain boundary. The area fraction of Laves phase on the grain boundaries, in the gauge section, of the 2Nb containing alloys, is 0.79, while the 1Nb containing alloy only has a fraction of 0.48. In addition, a precipitate free zone (PFZ) along the grain boundaries can be observed in all the alloys. The zone forms from the precipitation and growth of large Laves phase on the grain boundaries. Because the Laves phase grows faster on the grain boundary, the particles take up more elements from the surrounding matrix. Thus, Laves phase cannot form in this region [46]. Consequently, with larger grain boundary particles, it would be expected to observe a larger PFZ. The FCA-1Nb alloy has a PFZ that is .8-.9 μm from either side of the grain boundary. While the FCA-2Nb alloy have PFZs are 1.4-1.5 μm from either side of the grain boundary. The significance of this difference will be discussed in Chapter 7 as it pertains to the creep mechanism and failure.

A numerical analysis of the Laves phase in the grip, gauge, and fracture tip sections from the BCC grain interiors of the three alloys is presented in Figure 6.8. The alloys with a higher wt% of Nb contains larger particles and a higher volume percent. However, in comparison with the ageing study (overlaid onto the gauge section), it can be observed that these features are more or less a result of being at temperature (700 °C) for a longer time. The sizes of both the aging specimens after 168 hours are within the calculation error of the FCA-1Nb creep

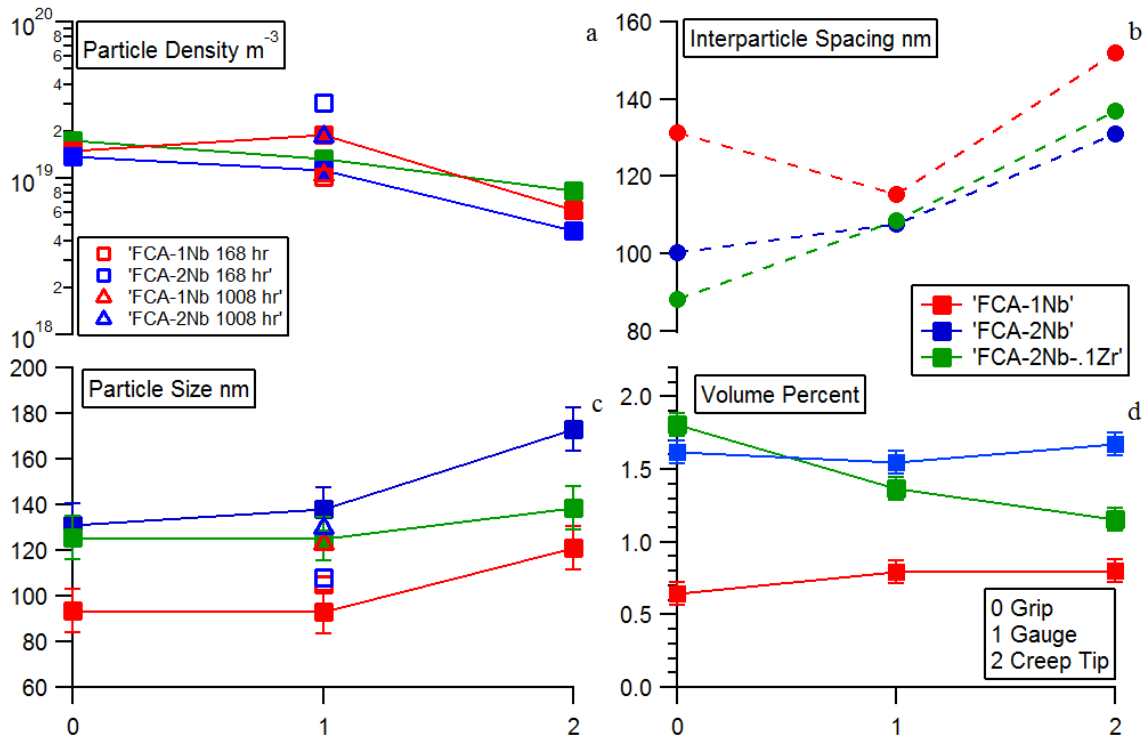


Figure 6.8 Particle analysis of the creep specimens with (a) particle density, (b) interparticle spacing, (c) particle size, and (d) volume percent (from the grain interior) as a function of location. 0 is the grip section, 1 is the gauge section, 2 is the fracture tip. Overlaid on the particle density and size charts are the numerical results from the ageing study.

specimen, which failed at 134 hours. The sizes after aging 1008 hours are observed to increase, with the FCA-2Nb sample with slightly larger sizes from the 168 hours ageing samples. This occurs because the FCA-2Nb sample contains more Nb, and thus would coarsen faster than the FCA-1Nb sample. Furthermore, the FCA-2Nb sample failed after 1760 hours, which shows further coarsening over the 1008-hour aging samples. Thus the conclusion can be made is that the creep failure was not a function of the Laves phase in the grain interior and another mechanism should be dominating. The impact of these results can be taken into context with the creep model and hypothesize the failure mechanism is within the grain boundary zone.

6.3.2 TEM Imaging and Diffraction

In order to further characterize the Laves phase particles, transmission electron microscopy was used. An example of the Laves phase in the grain interior can be seen in Figure 6.9a. It should be noted that all the samples appeared to have very similar densities and sizes of particles. This qualitatively confirms the quantitative analysis performed in the SEM with backscatter detection. Because of the low contrast between the matrix and the particles quantifying the particles was very difficult, thus only SEM analysis was performed. From the figure, a low interparticle spacing can be observed this will aid in pinning dislocations from moving. There are multiple morphologies of the particles. There are some rounder particles and some lenticular plate particles. The round particles are pointed out with yellow arrows and the lenticular plate particles are pointed out with red arrows (see Figure 6.9a). It is not yet known why there are two different morphologies observed. One possibility is based on crystallography of these precipitates, that the smaller round shaped particles are simply being viewed down axis and is, in fact, lenticular particles. In Figure 6.9b, a dislocation can be seen pinned by a Laves phase particle. From creep theory discussed in Chapter 2, it is known that a dispersion of particles can pin dislocations and

an extra shear stress is then required to bow the dislocation through an array of particles. The figure is a magnified image on one particle in the [100] zone axis to image the dislocation (see Figure 6.10), however, from Figure 6.9a, it can be seen that there is a large array of particles with a small interparticle spacing between 100-140 nm. From the grain interior, it can be seen that this array of particles can effectively pin dislocations. Conversely, the grain boundary region is not similar to the grain interior. From SEM images a PFZ is observed. By definition, the PFZ is region without precipitates and thus this region would not have any way of pinning dislocations. Figure 6.9c shows the PFZ next to the grain boundary.

The image shows large Laves phase on the grain boundary, a region without particles, then continues to where the particles begin and appear like the grain interior. Because there are no particles in the PFZ, the dislocation would be free to move and pile up. This is observed in Figure 6.9c. The dislocations can be seen piling up on the grain boundary Laves but the pile ends at a small particle or a free region of the grain boundary. Eventually, a back stress from the dislocation pile up will be accumulated at this point and nucleate a cavity. Therefore, grain boundaries with less Laves phase and thus more free grain boundary area, can form more cavities. From the previous section, the differences in the PFZ and area particle fraction in the grain boundary region. The FCA-1Nb alloy had less areal fraction on the grain boundary. Furthermore, this fraction would allow the dislocations moving within a PFZ to nucleate cavities more easily and thus would fail earlier. This deformation accumulation is illustrated here. The images and information collected from SEM and TEM would support the conclusion of grain boundary ductile failure.

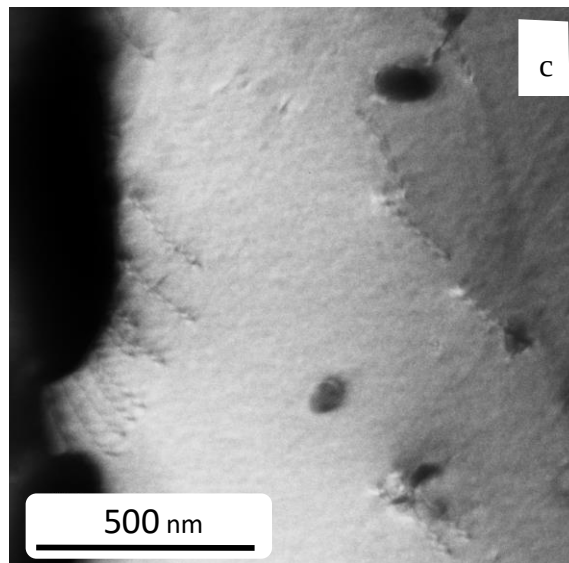
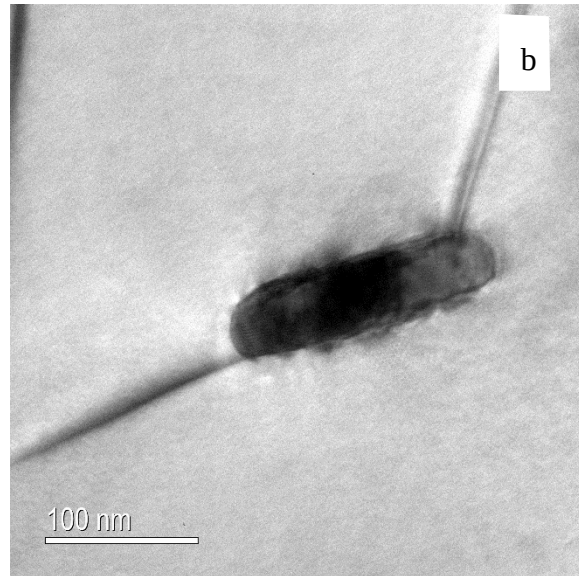
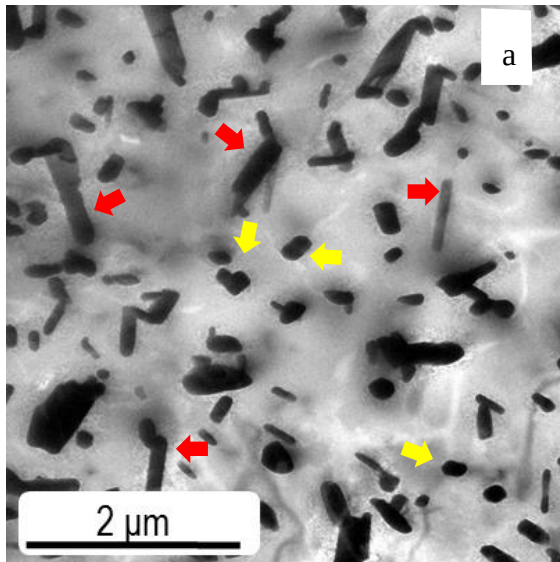


Figure 6.9 (a). TEM micrograph of Laves phase imaged in grain interior, strain contrast can be seen as the white lines, from sample FCA-2Nb. (b) Example of dislocation being pinned by a matrix Laves phase particle in the grain interior, from sample FCA-2Nb. (c) Dislocations imaged on the 100 zone axis seen piling up on a grain boundary Laves phase, indicating deformation in the PFZ, from sample FCA-1Nb.

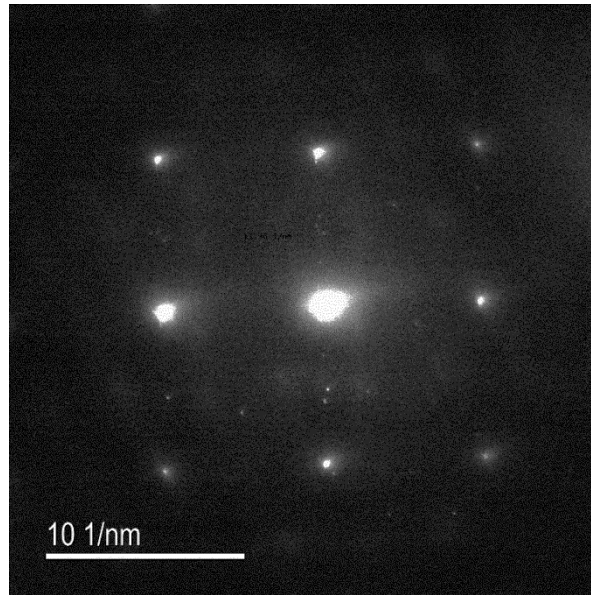


Figure 6.10 Electron diffraction pattern of BCC grain with the [100] zone axis to image the dislocations in Figure 6.7b&c.

6.3.3 Fractography

The SEM and TEM images support the conclusion of grain boundary ductile failure.

Furthermore, fractography of the creep rupture specimens also indicate grain boundary failure as the primary failure mechanism. Figure 6.11 shows the fractography from the FCA-2Nb and FCA-1Nb samples respectively. In Figure 6.11a the grain boundary failure and shear from final fracture can be observed. The figure represents half of the specimen with the other half appearing similar to the image. To better explain the image, a hypothesized failure timeline is as follows.

The grain boundary in the perpendicular position to the applied stress, accumulated creep voids from dislocation pile up. Along with these voids and a ductile PFZ, the grain boundary can separate. When this occurs the remaining material or grains, which did not have grain boundaries in this region, then carry the load. With the local reduced area from the grain boundary separation, the local stress rises. The local stress is much higher than the applied stress for creep. This means the creep rate will become much faster and subsequently pull apart the remaining material causing the shear fracture on the edges. Not only does the fractography show grain boundary failure, it also shows examples of particles in ductile cups (see Figure 6.11b). The significance of the particles being in the ductile cups is that this illustrates the cavity formations around these particles. Even in the flat grain boundary failure region, ductile cups with particles can be observed. The SEM and TEM images of the two different alloys show some differences in the microstructure. However, the fractography shows similar morphologies between the two alloys. Figure 6.11c is the fractography of the FCA-1Nb sample. Here, the distinctive grain boundary ductile failure can also be observed. From all the samples, grain boundary ductile failure can be concluded. The mechanisms for this failure will be discussed in Chapter 7.

Figure 6.11 Selected fractography from creep rupture samples FCA-2Nb (a&b) and FCA-1Nb (c). (a) Macrographs showing grain boundary failure and some local shear from final fracture. (b) A magnified image showing particles inside ductile cups. (c) Grain boundary failure in sample FCA-1Nb.

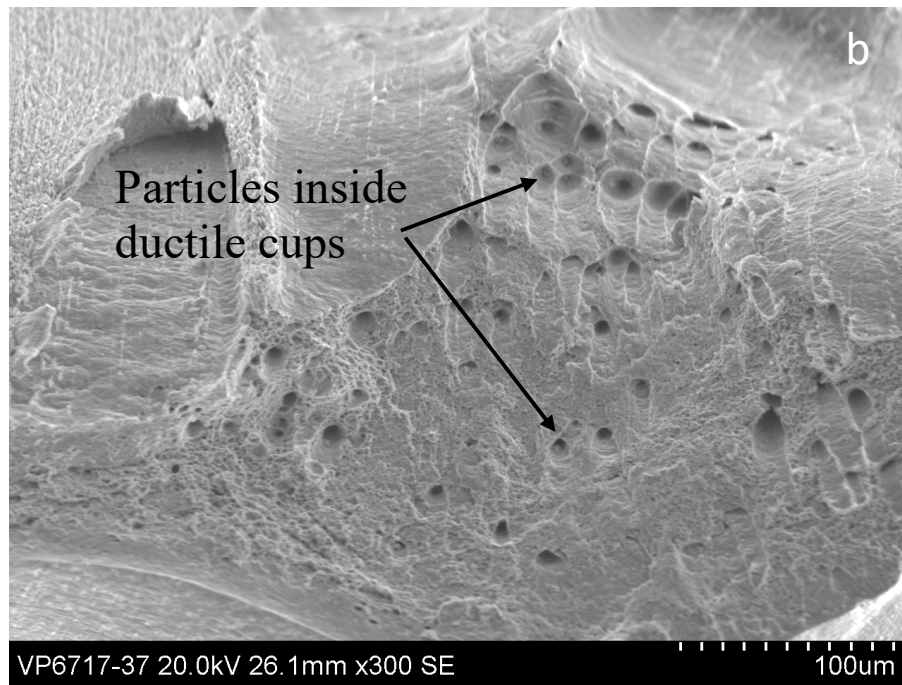
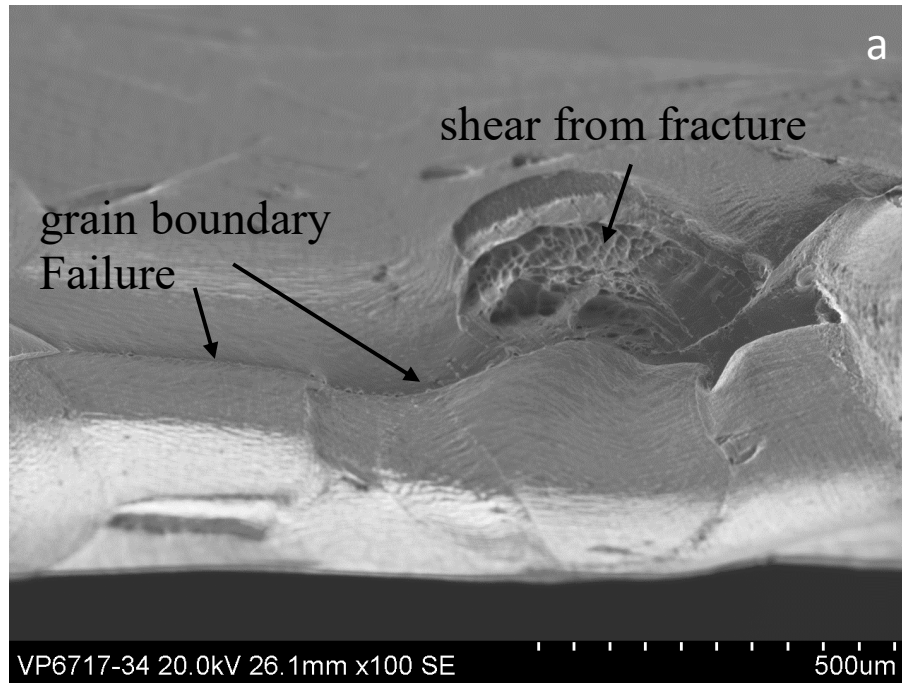


Figure 6.11 continued

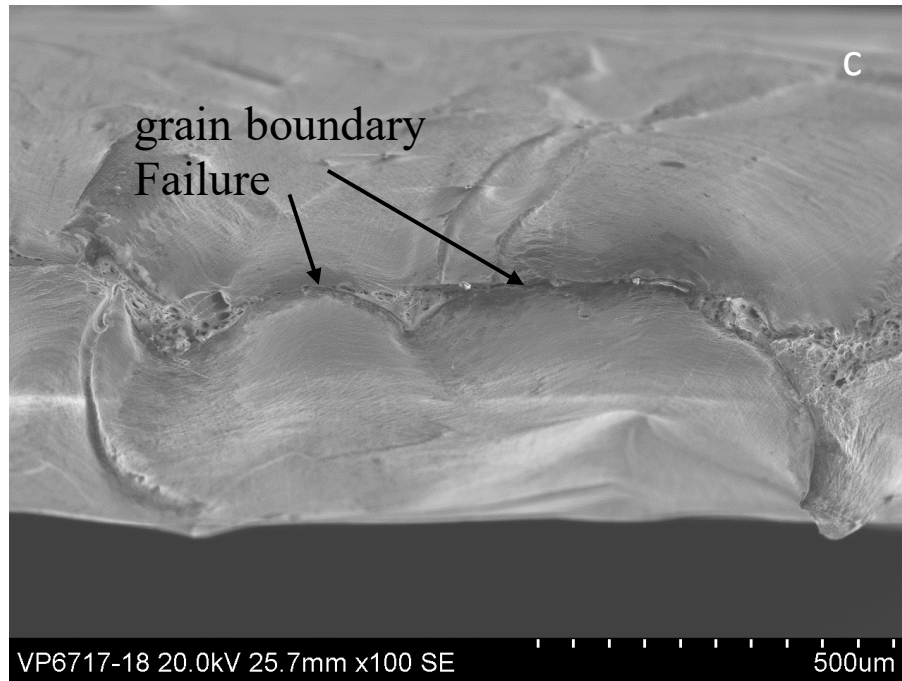


Figure 6.11 continued

6.4 Creep Response of the Fe-Cr-Al Alloy

The creep curves of the FCA alloys are shown in Figure 6.12. As expected, the alloy that does not contain Nb fails quickly, only 1.4 hours. This shows the extent of strengthening effects that precipitates can provide. Unlike many other alloys including steels, this alloy has the ability to show the effects of only the precipitate characteristics on the creep strength at high stresses. Therefore, this result shows how the strengthening of the precipitates can overwhelm the other strengthening mechanisms. The alloy that does not contain Nb does not provide good creep resistance. It does, however, provide some conceptual understanding of the impact of precipitates on creep resistance. In addition, this alloy may also give some understanding of the deformation before the Laves phase precipitates in the other alloys. It could appear as though the 0Nb sample would be operating in a different creep mechanism. With the large grain size and fast failure, it can be assumed that dislocation mechanism is playing a big role. However, the dominate mechanism of the other alloys may be a Grain Boundary Sliding mechanism with the grain boundary ductile failure being predominate. On the other hand, the other curves appear more or less as typical creep curves. The FCA-1Nb failed after 138 hours (minimum creep rate, $1.75 \times 10^{-6} \text{ s}^{-1}$), while the FCA-2Nb-.1Zr failed after 1330 hours ($9.23 \times 10^{-8} \text{ s}^{-1}$) and FCA-2Nb alloy failed after 1760 hours ($1.47 \times 10^{-7} \text{ s}^{-1}$). It is interesting to note that the FCA-1Nb alloy starts to contract at 2×10^{-1} hours (see Figure 6.13). If the as solutionized microstructures are taken into consideration, the FCA-1Nb alloy did not contain Laves phase except for a very few laying on the grain boundaries. Therefore, it can be hypothesized that at this point (2×10^{-1} hours) the Laves phase has starting to precipitate during the creep test. In addition, it would appear that the precipitation and coarsening achieve a steady state around 3 hours, and then the sample continues to the steady state creep region. If this hypothesis is true, then it would be a reasonable assumption that in the

early stages of creep (<3 hours) the FCA-1Nb sample may have had some strain localization at a point. As seen with the FCA-0Nb sample, the creep rates are fast from the very beginning. Therefore, during the short time, while FCA-1Nb only contained the BCC matrix, strain localization could have occurred. If this is the case, it may be possible that the internal stress at the localized area would be greater than the remaining gauge section. This hypothesis is based on the microstructure characterization and the shape of the creep curve. It is also interesting to note that the other two alloys also have a small dip in the creep curve. As shown above, these alloys both contain Laves phase in the “as-solutionized” condition. However, the precipitation in the as-solutionized condition would not yet be in the steady state of precipitation and growth. Therefore, the remaining Nb in solid solution with BCC will precipitate during testing. To further comment on the contraction and precipitation of Laves phase, it is necessary to understand the contraction due to Laves phase. It can be hypothesized that the contraction is due to the precipitation of the Laves phase, but it is needed to know how. The precipitation of a denser particle would lead to a contraction. According to the International Crystal Structure Database, the density of Laves phase is roughly 8.51 and density of BCC Fe is 7.36 [108]. Out of the entire volume of the creep sample, the precipitation of Laves phase would lead to a contraction of 600 μm . Over the entire length of the sample, this may be insignificant. However, comparing to the contraction seen in Figure 6.13, FCA-1Nb contracted 0.5%. This contraction is calculated to be close to 400 μm . Because the dilation of the sample is measured over the entire length of the sample, it would seem reasonable to conclude the contraction is due to the precipitation of Laves phase. Because of the creep test it may be likely that there is some strain occurring in the sample, possibly the strain concentration. This difference of the precipitation of Laves phase (600 μm) and the contraction would lead to the conclusion that 200 μm of strain had

occurred before steady state creep. Chen et al. (2014) analyzed the effects of pre-aging before creep in Laves phase strengthened austenitic stainless steel [109]. In other words, the effects of initial conditions before creep. The authors reported an aging treatment of 800 °C for 4, 12, and 24 hours prior to creep. After aging the time to rupture increased from 132 hours (4 hours ageing) to 258 hours (12 hours ageing) for a base alloy, but the authors did not report the time to failure of the other aged condition. These results reveal that the initial condition does play a role in the creep strength. This information leads to some inconsistencies when comparing the 1Nb and 2Nb samples. The 1Nb sample did not contain any particles prior to creep and a constriction of the sample was observed. On the other hand, the 2Nb sample did contain some particles and had a less extensive contraction of the sample.

An explanation of the steady state and tertiary creep regions will be attempted by understanding the microstructure of the as crept specimens. To understand the impact of the results, the time to failure and creep rates should be compared to existing literature. Chiu and Lin (2012) provided results from the alloy development of Crofer 22H, a .5 Nb and 1.94 W modified 22% Cr fully ferritic steel [86]. The author present creep curves in a range of temperatures from 650 °C to 800 °C. The time to failure from the current creep test result can be compared to the author's results. The time to failure of the literature sample with creep condition (73 MPa and 700 °C) the closely matches current test conditions, failed at 1100 hours. This result is within the same order of magnitude of the current results of the 2Nb containing alloys, indicating that the FCA-2Nb alloys appears to fail as expected for the Laves phase strengthened alloy.

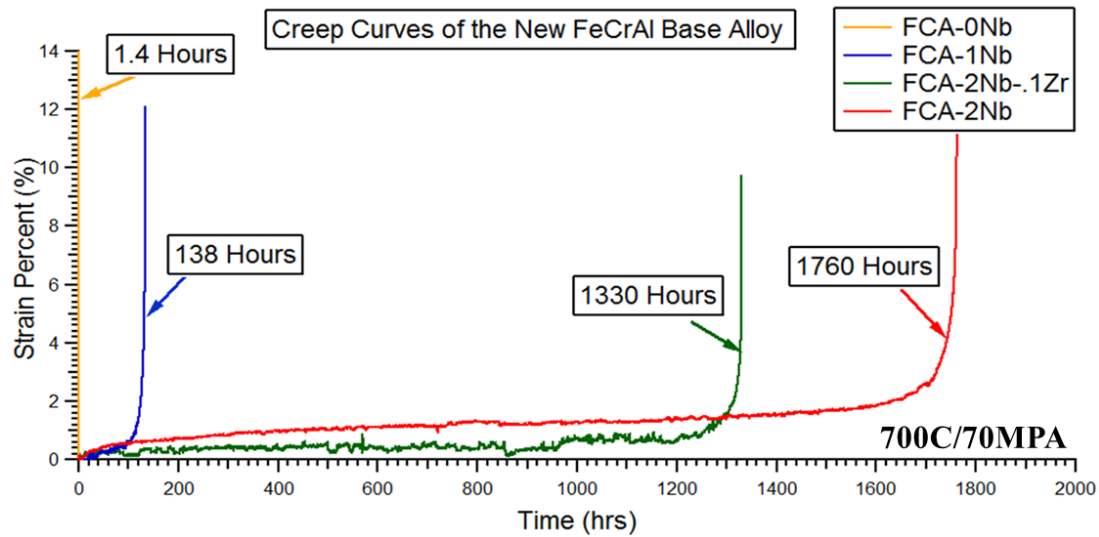


Figure 6.12 Creep rupture curves for the four selected alloys, indicated in the figure. Creep test was performed at 700 °C and 70 MPa.

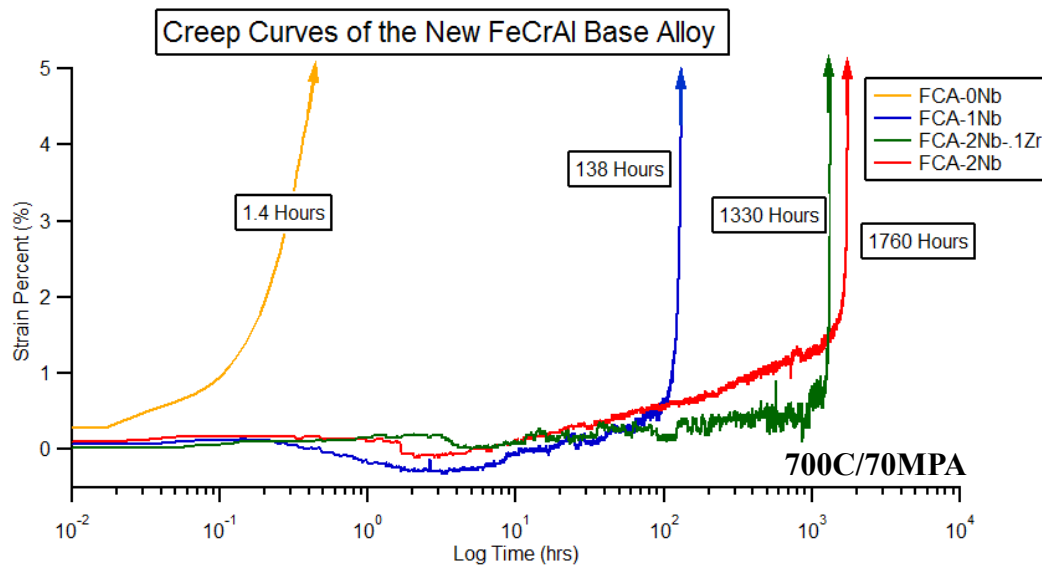


Figure 6.13 Creep rupture curves of the alloys in log time scale and magnified strain to 5%. FCA-1Nb shows ~0.5% contraction in the first 2 hours of creep test. This can be postulated to be from the precipitation of Laves phase.

To fully understand the “steady state” or secondary creep regime, a strain rate with respect to time curve is produced. In general, an instantaneous differential will provide the instantaneous strain rate. The data points produced can then be plotted as the strain rate in the y-axis and log time in the x-axis. This method was first performed in the software IgorPro®. Here, it should be noted that the raw creep curves from Figure 6.12 and 6.13 are rather noisy. Thus the first differential calculated was extremely noisy and the plot of the data did not contain anything of usefulness. To solve this the creep curves were digitized using a macro in IgorPro® that allow the user to manually smooth out curves. The digitized curves are presented in Figure 6.14a. The curves can be seen smoother and without noise. They also appear extremely similar to original curves in Figure 6.12. From the digitized curves, the strain rate can be calculated with less noise. Figure 6.14b shows the calculated strain rates with time. Although this data does not represent raw data, it still can be compared and analyzed. From the figure, the FCA-1Nb curves shows no reduction in creep rate before tertiary creep begins. It should be noted that the curves digitized curves do not contain the contraction seen in Figure 6.13. Therefore, only the secondary regime is captured. The curve essentially indicates that there is almost an acceleration of creep from the beginning. This means that the microstructure did not provide creep resistance at this temperature and stress. The curve may also provide a suggestion that the initial hours of creep in the sample may play a role in the creep test. If there was a strain concentration then the deformation, even after precipitation, would continue at a faster rate and then finally accelerate. On the other hand, the 2Nb contain alloys do show the typical strain rate vs. time curve of precipitate strengthened steels. The creep rate first slows then comes to a minimum creep rate before finally transitioning to the tertiary creep regime.

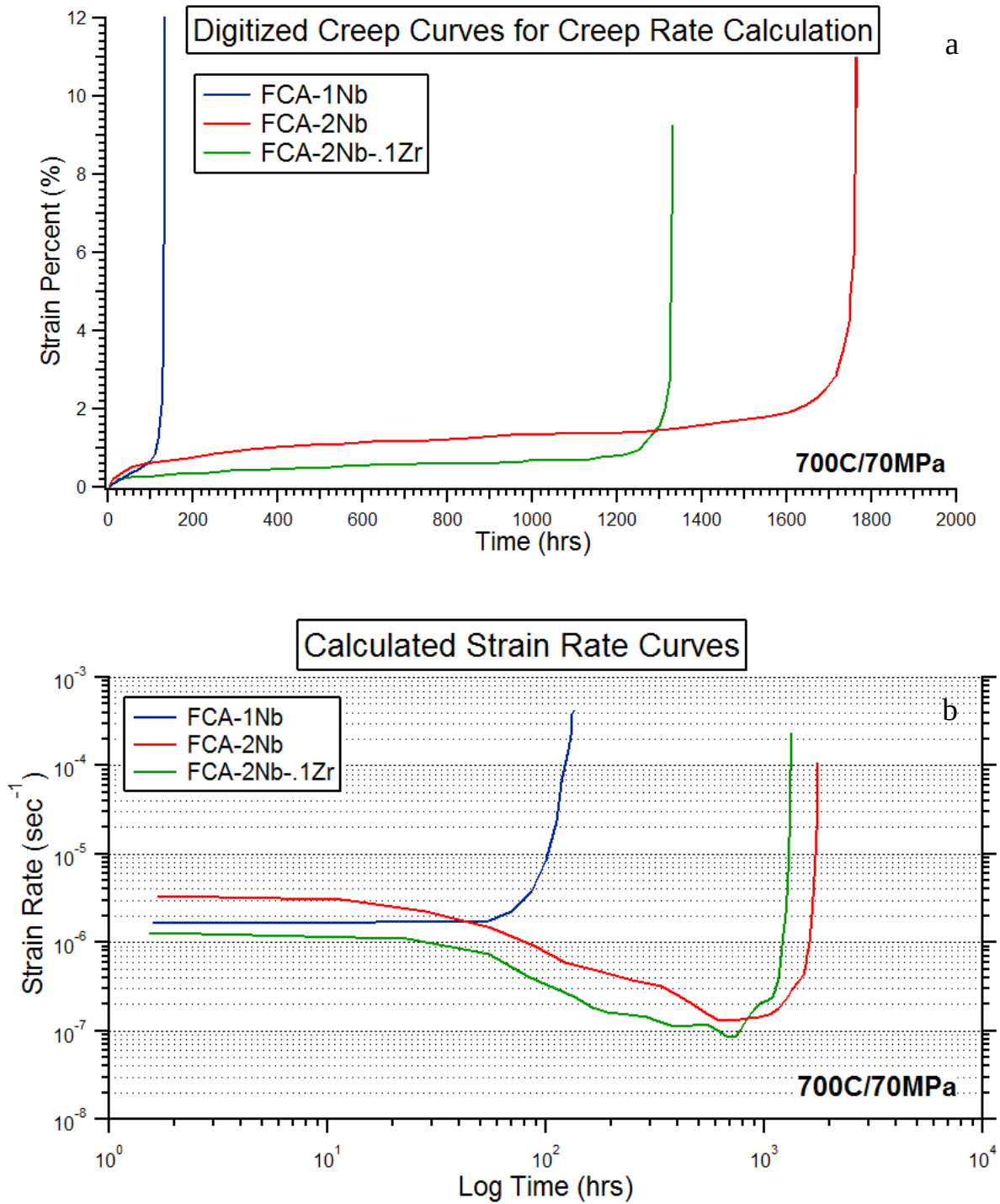


Figure 6.14 (a) Digitized creep curves from original data, the creep curves are smoothed to calculate creep rate. (b) Calculated strain rate curves with time from the digitized data.

The Zr containing alloy starts out with a lower creep rate and approaches the minimum creep rate faster than the FCA-2Nb sample. This would suggest better creep resistance but with earlier failure. This early failure is most likely related to the complete grain boundary cracking shown in Figure 6.7. In addition, the FCA-2Nb sample also has a short tertiary creep regime when compared with other precipitate strengthened steels like Grade 91 [44, 47]. As discussed above, the reason for the short tertiary regime can be explained using the grain boundary ductile failure mechanism. As the creep deformation proceeds, cavities nucleate and grow on the grain boundaries. when the cavities coalesce the grain boundaries will fail leaving a smaller fraction of material to hold the load. The local stress at the failure point increases dramatically and the creep rate will rise drastically. Because the grain boundary failure and local remain material is small, there is heavy localization. Therefore, the material cannot hold itself under increasing strain rate and thus fails quickly after tertiary creep begins. This mechanism does not occur in the Grade 91 steel and thus the Grade 91 steel will show the lengthy tertiary creep regime.

6.5 Summary

1. New base alloys of Fe-Cr-Al-Si-xNb were introduced as a solution to Type IV failure. Four base alloys were introduced, with the 2 wt% Nb containing sample showing comparable creep performance to Grade 92 Steel at 700 °C. Both reaching 1500 hours.
2. In order to prevent precipitates from experiencing the thermal cycles of welding, the alloys were solution heat treated to dissolve all the particles. Even though welding was not performed, the samples were creep tested in the as solutionized condition. The FCA-1Nb sample did not contain particles prior to creep testing, but the FCA-2Nb and FCA-2Nb-.1Zr alloys were shown to contain Laves phase on the grain boundary and within the grain interior.

3. Ageing studies were performed to compare the microstructures with that of the creep rupture specimens. The microstructures of the aging specimens at 700 °C for both the FCA-1Nb and FCA-2Nb samples are similar. The size and density of the Laves phase particles are within the same order of magnitude. From the microstructure, the predicted creep properties should be similar. However, the creep curves indicate an order of magnitude difference between these two samples. Further microstructural investigation leads to a hypothesis that the failure mechanism is most likely due to the grain boundary region.

4. Creep voids and grain boundary cracking can be seen in the microstructure of the creep rupture samples, indicating a grain boundary failure mechanism. The gauge section grain interior Laves phase particles are different in size and density (FCA-1 Nb: 93nm, 1.88×10^{19} FCA-2Nb: 138nm, 1.15×10^{19}). However, this was explained to be a consequence of being at temperature different lengths of time and follow the sequence of the aging experiments. The grain boundaries in the gauge section also showed creep voids on Laves phase and triple points. This further indicates a grain boundary creep mechanism.

5. The fractography indicates the failure occurred at the grain boundaries. The conclusion can then be made that the failure mechanism is a grain boundary ductile failure mechanism from the presence of the grain boundary Laves phase and the Precipitate Free Zone. Laves phase particles were found to be present in the ductile cups indicating cavities forming around them.

6. The creep curves of the alloys were presented. The FCA-1Nb sample failed rather quick, while the 2Nb containing alloys lasted over 1000 hours. It is believed that there could be some strain localization in the first few hours of creep because of the absence of Laves phase particles. This produces an acceleration of creep rate from the beginning of creep ($1.75 \times 10^{-6} \text{ s}^{-1}$) and can be

observed in a strain rate vs. time curve. The strain rate vs. time curves for the 2Nb containing alloys follows similar path as other particle strengthened steels. The small tertiary creep regime was found to be due to the grain boundary failure mechanism which does not allow for a long tertiary regime.

Chapter 7. Correlation of Microstructure to Creep Resistance with Phenomenological Model

7.1 Strain Rate Model

In Chapter two concepts of creep mechanisms were discussed to interpret the data observed in previous chapters. The creep mechanisms are very related to the initial microstructure and the evolution of the microstructure during creep testing or service. It is extremely difficult to model microscopically the evolution of the microstructure, macro and micro-level strains within a sample as a function of time. However, the researchers of the 1960's and 1970's created equations that could be used to model the performance of a metal under creep by calculating the steady state or minimum creep rate. The Bird-Mukherjee-Dorn (BMD) equation is a phenomenological equation that relates several parameters to predict the minimum creep rate [53].

$$\dot{\epsilon}_{min} = AD_0 \exp\left(\frac{-Q}{RT}\right) \frac{Gb}{kT} \left(\frac{b}{d}\right)^p \left(\frac{\sigma}{G}\right)^n \quad 7.1$$

Where A is constant. D_0 is diffusivity, Q is the diffusion activation energy, R is the gas constant, and T is temperature. G is the shear modulus, b is the burgers vector, and k is Boltzmann's constant. d is the grain size and σ is the applied stress. The p and n exponents are the grain size and stress exponent parameters. These parameters are not derived directly from the microstructure observations, rather, extensive data analysis has been conducted over several decades to find the correlation between these parameters and creep mechanisms. The equation also relates diffusion, the modulus of the material, and stress to predict the minimum strain rate. Because these parameters are independent and can cover a large range, researchers have used

these type of equations to generate creep mechanism maps as seen in section 2.8.1 [51, 52].

These maps break up the wide range of stresses and temperatures the material may be exposed base on mechanisms. However, with further examination of the equations, one can notice that many other important factors may also play in determining the minimum strain rate. One such factor is the grain size. The grain size can change the creep rate drastically with an increase or decrease in grain size, the creep rate can even exceed creep rates from dislocation mechanism with smaller grains and a little higher temperature. Grain size is also rather easy to control through heat treatments or thermo-mechanical treatments. Therefore, researchers have also constructed deformation maps to include the change grain size [54]. These maps were constructed for pure metals or solid solution alloys. However, the maps do not directly correlate to the microstructure of the new multi-component precipitate strengthened and complex microstructures of structural steels and alloys. Nor do the maps correlate the relative contribution of multiple creep mechanism operating at a specific condition. There are however modifications to the BMD equation that could closer be related to the microstructure of a particular structural steel.

Shrestha et al. [110] have described the creep deformation mechanisms in the Grade 91 steel utilizing a modified Bird-Mukherjee-Dorn (BMD) equation, which incorporates a threshold stress, seen below [102, 110]. This modification of the equation is used for the dislocation creep mechanism. Here, the grain size does not play a role in dislocation creep. Therefore, the

$\left(\frac{b}{d}\right)^p$ term is not used in the following equation. The following equation is the modified BMD equation for dislocation creep utilizing a threshold stress.

$$\frac{\dot{\epsilon}_m kT}{D G b} = A_{Dis} \left(\frac{\sigma_a - \sigma_{th}}{E} \right)^n \quad 7.2$$

Where $\dot{\epsilon}_m$ is the minimum creep rate in the units of s^{-1} , D is the diffusion coefficient corresponding to self-diffusion of iron calculated using the following relationship.

$$[D = D_0 \exp\{-Q_0/RT\}] \quad 7.3$$

Furthermore, R is the gas constant, G is the shear modulus, b is the burger vector length of Edge dislocation in bcc iron lattice, k is the Boltzmann's constant, and T is temperature in Kelvin. A_{Dis} and stress exponents n are parameters often calibrated through published data. For dislocation creep the A_{Dis} is usually taken as $2.5e^6$ but this value can change depending on the material. The n exponent, which is usually used to determine creep mechanism, is usually taken as a value of 4-5. σ_a is the measured stress value and σ_{th} is the threshold stress required to overcome the particle distribution. The threshold stress then takes into account the interparticle spacing λ and particle size d_{part} by the following equation taken from Ashby [72].

$$\sigma_{th} = \frac{Gb}{2\pi\lambda} \ln \frac{d_{part}}{b} \quad 7.4$$

This analytical model allows the modeling of structural steel strengthened particularly by precipitates. The Grade 91 steel has been extensively studied and the creep mechanisms are widely known. However, the creep mechanisms are for traditional normalized and tempered Grade 91 steel and not after a thermo-mechanical treatment. Nor does the current knowledge correspond to the creep mechanisms in samples that have microstructural heterogeneity, e.g., samples subjected to welding thermal cycle. This model will allow the comparison of the microstructural control from TMT and relate back to generic Grade 91 steel. In addition, the microstructure during all stages of producing including welding and the Post Weld Heat Treatment were presented in this research. The model will take the microstructural information

and allows the prediction of creep properties in every weld location zone. This give the ability to understand further the mechanisms relating to the pre-mature failure of Type IV cracking.

Because the creep strain is calculated over the entire gauge section, which includes the unaffected base metal, HAZ, and the weld metal, the overall creep improvements cannot entirely be described with this model. The above statements lead to two fundamental questions: (i) is it possible to correlate the minimum creep rate to precipitate distributions using published phenomenological models; and (ii) what is the role of strain localization in the FGHAZ? These questions will be answered in Section 7.2

7.2 Creep Deformation Mechanisms in Grade 91 Steel Weldments

It was discussed in Chapter 5 that the precipitation of MX was enhanced after TMT and an ausaging process. As a result, an increased number density of MX remains through pre-weld tempering, weld thermal cycle and post weld heat treatment. Furthermore, in the chapter, there are also marked differences in $M_{23}C_6$ carbide size distribution when compared to the traditional N&T sample. Since the creep deformation mechanism in Cr-Mo steels, at the current creep conditions, have been attributed to dislocation creep, the effects of TMT on creep resistance can be postulated. It is well known that particles impede the motion of dislocations (described above). Therefore, by increasing the density of particles through TMT, it can be expected that the dislocation motion would further be impeded. The minimum creep rate after TMT at 800°C is reduced ($4.8 \times 10^{-8} \text{ s}^{-1}$) when compared to that of the standard N&T sample ($2.8 \times 10^{-7} \text{ s}^{-1}$).

Although, the mechanisms described above may only partially represents the true reduction in minimum creep rates for a welded sample. The BMD model is used to determine minimum strain rates in the base metal, but does not exclusively examine the FGHAZ.

To answer the first question, the phenomenological BMD model will be used to understand how the particle distribution in tempered and the HAZ effects the calculated strain rate based on microstructure. It is possible to evaluate the minimum creep rate in a sample with uniform microstructure defined by precipitate diameter and interparticle spacing. Utilizing TMT and traditional heat treatments, a wide range of particle diameters and spacing can be imagined. Typical parametric calculations using range of precipitate diameters (10 nm to 150 nm) and interparticle spacing (100 nm to 500 nm) are overlaid with experimentally measured minimum creep rates (see Fig. 7.1a). By varying the particle size and spacing, a range of strain rates can be observed. This plot illustrates the sensitivity to these parameters. With the understanding of how the changes in particle size and spacing effect the strain rate, it is helpful to generate a strain rate map with all realistic diameters and spacing. Figure 7.1b is a new type of map that show strain rate for all combinations of particle size and spacing at a given temperature and applied stress. Since the model is analytical, it is easy to change the input temperature and stress to recreate the map. Otherwise, the map would need to be plotted in 3D and would then make it difficult to read. The map shows a rather sensitive band of strain rates that lie within a general size and spacing distribution observed in Grade 91 steel. The outer most region of red indicates that the particles are no longer providing strengthening and the material will deform quickly. On the other hand, the region in purple represents the distribution of particles in which the creep conditions for this calculation would make the threshold stress larger than the applied stress. Therefore, this indicates a transition in creep mechanism from dislocation dominate to Coble mechanism or GBS. This small band shows that through microstructure control the strain rates can be lowered. Even with small amount of TMTs, the creep response of the Grade 91 steel can be improved.

The plots demonstrate that the experimentally measured creep properties and precipitate (both $M_{23}C_6$ and MX precipitates) lie in a very sensitive area. A small change in particle diameter or spacing may lead to large changes in minimum creep rate of bcc ferrite matrix. This is evident in the white dash ovals (see Fig. 7.1b) which represents a theoretical range of MX or $M_{23}C_6$ one could expect after different processing conditions. It should also be noted that the ranges could also be large due to the errors in measuring experimentally from different researchers. In addition, points of experimentally measured precipitate characteristics are plotted (see Table 7.1) for different stages, i.e., as tempered, FGHAZ region after the post-weld heat treatment before creep testing, and at a FGHAZ failure location after creep testing. As expected, the number density of $M_{23}C_6$ reduced with concurrent increase in diameter of the particle, which results in higher interparticle spacing. The above analysis shows that the local creep rate of ferrite matrix is strongly a function of collective and spatial heterogeneity of precipitates (both MX and $M_{23}C_6$) that evolves during each and every step of manufacturing operations, including welding. This evolution of the $M_{23}C_6$ shows how the possibility for faster creep rates in the FGHAZ. The weld metal and CGHAZ precipitate fresh $M_{23}C_6$ and mx particles during the PWHT. Thus, it would be assumed that these particle distributions could be plotted in the same position as the “As-Tempered” location. The unaffected base metal would also lay in this same region. The differences in predicted strain rates become obvious. The location of the FGHAZ would have a much faster creep rate, thus producing a strain localization. This strain localization would lead to failure much earlier than the base metal. This earlier failure is the predicted Type IV failure observed in the Grade 91 steel.

To answer the second question posed in the previous section it is necessary to under the relevance of the BMD models to cross-weld creep samples.

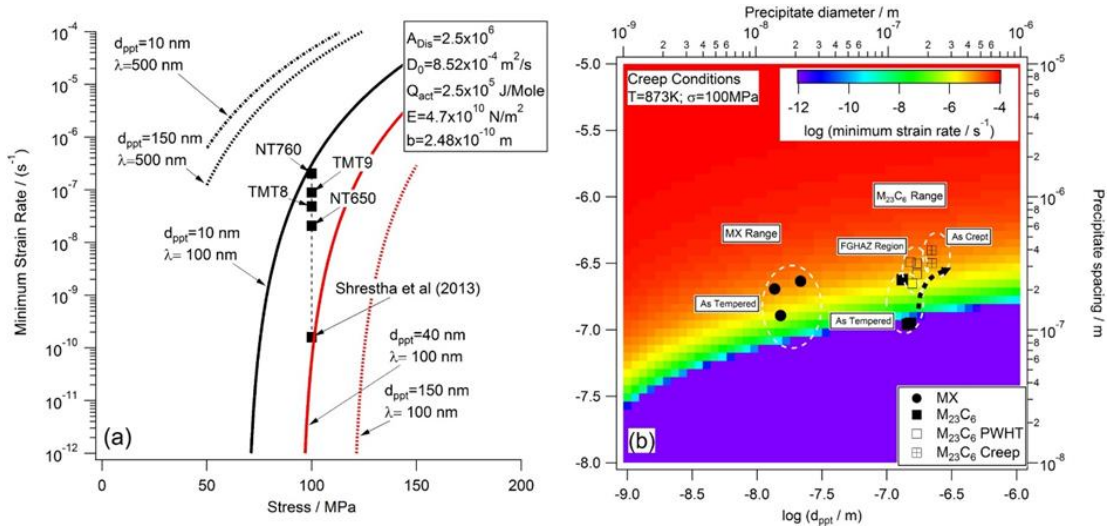


Figure 7.1 Results from parametric calculations of minimum creep rate using BMD phenomenological model as a function of (a) stress and (b) precipitate characteristics.

Table 7.1: Average diameter, number density, and volume percentage of carbides and interparticle spacing of $M_{23}C_6$ in HTT, LTT, TMT8, and TMT9 weld samples at FGHAZ before creep testing. In addition, the precipitate characteristics of TMT8 and TMT9 weld samples after creep testing.

	Diameter (nm $\pm$ 15)	Number Density (m $^{-3}$ $\pm$ 3.93 x 10 15)	Volume Percentage (%)	Interparticle Spacing (nm $\pm$ 37.8)
N&T (HTT)	165.5	2.18 x 10 18	.518	263.0
N&T (LTT)	152.6	3.20 x 10 18	.594	223.7
TMT 9	156.4	2.22 x 10 18	.525	315.2
TMT 9 (Crept)	214.2	1.56 x 10 18	.800	317.2
TMT 8	147.2	2.55 x 10 18	.425	322.7
TMT 8 (Crept)	213.8	1.01 x 10 18	.515	396.7

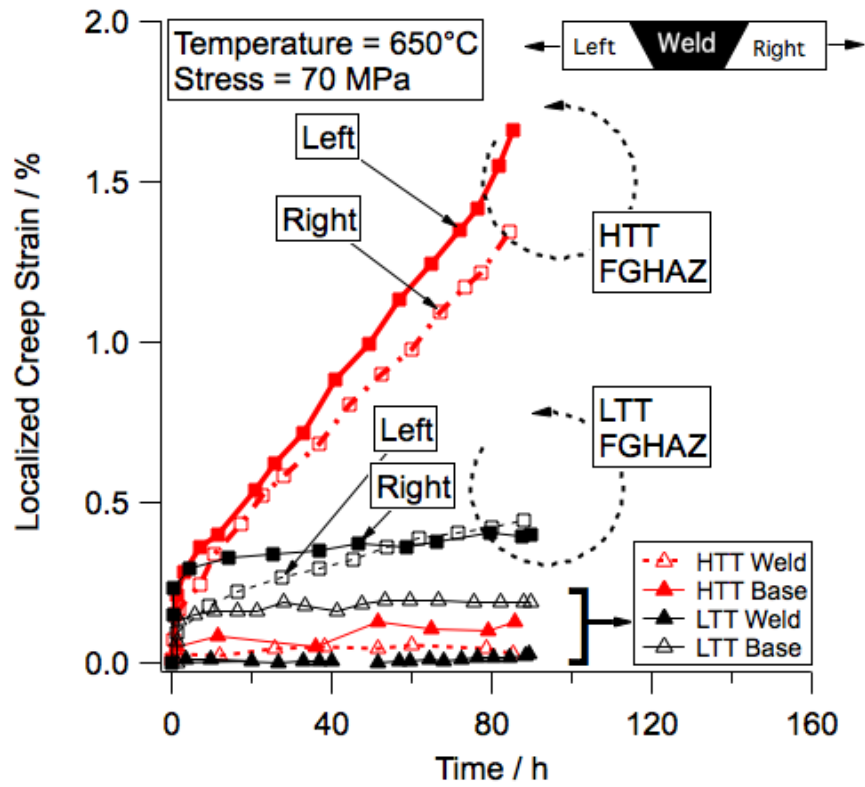


Figure 7.2 Reanalysis of strain localization data published by Yu et al. This shows higher creep rate of HTT and LTT FGHAZ compared to base metal and weld metal region. This demonstrates the need for spatial and temporal measurement of creep strains and microstructures.

It is important to note that the BMD model is developed for creep samples with uniform microstructures without gradients, such as welds. Therefore, the extension of the BMD model to cross weld creep testing requires further discussion. Based on data from Section 5.3.3, it is obvious that there would be a spatial variation of particle size and number density along the length of the cross weld creep testing sample.

As a result, during creep testing, each and every part of the cross weld sample may exhibit different creep response. Unfortunately, the standard creep testing measures only the overall length change and is not sensitive to strain concentrations in the FGHAZ region. This issue was recently addressed by Yu et al (2014) through the use of digital image correlation (DIC) during early stages of creep testing of HTT and LTT samples at 650°C and 70 Mpa [98]. In this work, the strain localization at the early stages of creep testing (< 100 h) was observed in the FGHAZ region on both the left and right sides of the weld metal region. Their data was digitized and local creep rates were calculated from the same data (see Fig. 7.2). The calculations showed that the localized creep rate of the FGHAZ [left side= $3.5 \times 10^{-6} \text{ s}^{-1}$ and right side = $4.3 \times 10^{-6} \text{ s}^{-1}$] of HTT (standard tempering 760 °C/2hours) sample is one order of magnitude greater than base metal and weld metal creep strain rate [$1.6 \times 10^{-7} \text{ s}^{-1}$] in the similar condition. Similarly, for LTT (non-standard tempering 650 °C/2hours), the localized creep rate of the FGHAZ [left side= $8.6 \times 10^{-7} \text{ s}^{-1}$ and right side = $2.7 \times 10^{-7} \text{ s}^{-1}$] is one order of magnitude greater than base metal and weld metal creep strain rate [$7.4 \times 10^{-8} \text{ s}^{-1}$] at the same condition. The above analyses clearly demonstrate that the correlation of observed creep rate and the microstructures in cross weld samples

7.3 Evaluation of Creep Mechanism Model in Fe-Cr-Al Alloy

Above, the BMD equation was used to predict the minimum strain rate based on particle size and distribution with reference to Grade 91 steel. For Grade 91, it was revealed that the particles would coarsen during welding, and could be tracked on a calculated strain rate map. Figure 7.3 is a recalculation of the strain rate map under the creep test conditions used for the Fe-Cr-Al alloys (700 °C, 70 MPa). Overlaid on the map are the numerical results from the Laves phase in the grain interiors of gauge section of Fe-Cr-Al alloys after creep failure. The points on the map show that the Laves phase size and interparticle spacing are not drastically different from each other. The model would suggest that these alloys should show similar strain rates. However, the points lie outside the region for dislocation creep.

A recalculation of the threshold stress showed that the threshold stress is, in fact, larger than the applied stress. This suggests that the creep mechanism operating at these conditions is Coble creep or a Grain Boundary Sliding mechanism. The strain rates predicted from the BMD dislocation model suggest that the strain rates should be in the order of 10^{-12}s^{-1} . However, the measure steady state strain rates for the alloy are as follows: FCA-1Nb $1.75\text{e}^{-6}\text{s}^{-1}$, FCA-2Nb $1.47\text{e}^{-7}\text{s}^{-1}$, and FCA-2Nb-.1Zr $9.23\text{e}^{-8}\text{s}^{-1}$. It makes sense that other creep mechanisms would be operating. From the literature on creep mechanisms and the creep conditions being used the most likely mechanism is a Grain Boundary Sliding type mechanism. Therefore it makes sense to utilize the BMD equation for GBS [60].

Because of the large grain size, microstructural evidence, and still rather quick strain rate, the mechanism most likely operating is the Grain Boundary Sliding mechanism. Grain Boundary Sliding is now a more accepted and is considered a major creep mechanism. Langdon (2006) has

recently shown deformation maps to include grain boundary sliding [58]. The BMD equation can now be used to understand the creep mechanism and relate the microstructure to the creep response of the Fe-Cr-Al alloys. The following is the BMD equation used for modeling of GBS in the Fe-Cr-Al alloys [60].

$$\dot{\epsilon}_{min} = A_{GBS} D_0 \exp\left(\frac{-Q}{RT}\right) \frac{Gb}{kT} \left(\frac{b}{d}\right)^1 \left(\frac{\sigma}{G}\right)^2 \quad 7.5$$

Here all the variables have the same meaning as before. A_{GBS} is the Grain Boundary Sliding constant and was taken as 10 for the model. The p exponent here is 1 and the stress exponent is 2. Even though GBS is a deformation mechanism involving grain boundaries the diffusion expression is taken as the lattice diffusion because the actual deformation is adjacent to the grain boundary and not within the grain boundary itself.

With microstructure observations and literature understanding it seems likely that the creep mechanism may be GBS and thus a strain rate map for GBS should be constructed. Figure 7.4 is a calculation of the BMD model using the GBS equation. Here the color palette was changed to better show the variants in strain rate with varying parameters. The strain rate map follows the concepts for GBS. The smaller the grain size results in faster creep rates. This is because the increased amount of grain boundaries will allow more deformation to occur in a given time. The results from changing stress are obvious. The higher the stress the faster the creep rate. Overlaid on the map is the points representing the grain size from the FCA-1Nb and FC-2Nb samples. Interestingly the calculated strain rate for the FCA-2Nb sample is similar with the calculated strain rate is $1.57 \times 10^{-7} \text{ s}^{-1}$ and the observed strain rate was $1.47 \times 10^{-7} \text{ s}^{-1}$. However, the calculated strain rate for the FCA-1Nb sample is an order of magnitude larger than the observed strain rate.

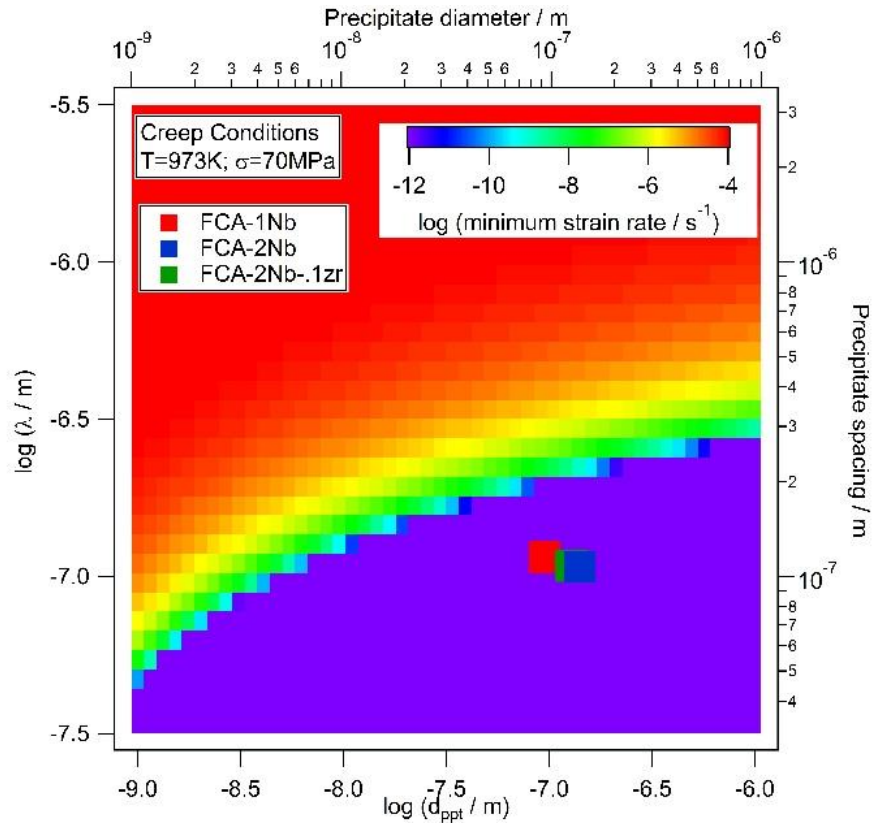


Figure 7.3 Recalculation of the strain rate calculated map under the creep conditions for the FCA alloys. Overlaid are the numerical results of the Laves phase from the gauge section after creep failure.

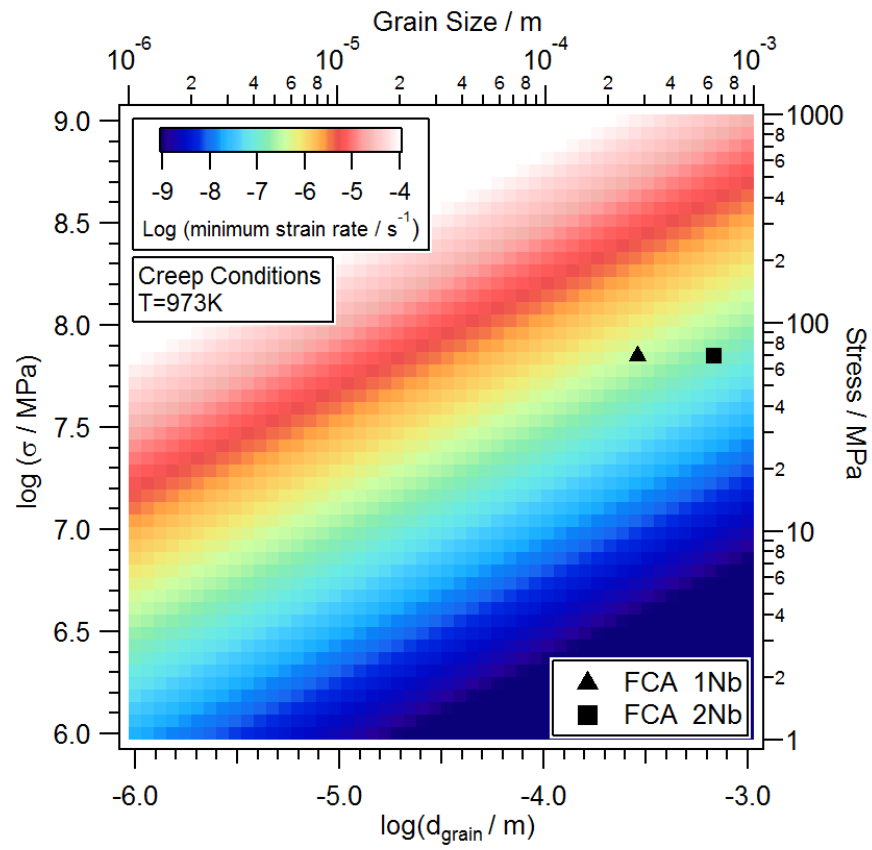


Figure 7.4 Calculations of minimum creep rate using BMD phenomenological model as a function of grain size and stress.

If the hypothesis of the strain concentration for FCA-1Nb, as described in Chapter 6, is used, then this may be an explanation of the inconsistency. If there was a strain concentration in the FCA-1Nb sample, then observed strain rate would be higher than that of a theoretical strain rate. The new model considering the GBS does well to correlate the observed strain rates and calculated strain rates. However, it is necessary to use the microstructural evidence to support GBS as the creep mechanism. The microstructures clearly show grain boundary Laves phase and a PFZ. The question that needs to be answered is how do these microstructural parameters effect the creep and failure of the FCA alloys.

7.4 Grain Boundary Region Microstructure Analysis

Because the GBS mechanism is generally related to the grain boundary, it is necessary to further describe the details of the grain boundary zone and how it relates to the creep mechanism. Figure 7.5 is a SEM micrograph of a grain boundary region in the FCA-2Nb sample after creep testing. The Laves phase on the grain boundary is larger than the Laves phase in the interior of the grain. Immediately adjacent to the grain boundary is the Precipitate Free Zone, marked with dashed lines. From Figure 6.5 it was shown that the PFZ width changes with different samples. In addition, it can be observed that there are points along the grain boundary that are free from Laves phase. Therefore, an area fraction of Laves phase can be calculated along the grain boundary.

Both the area fraction and width of the precipitate free zone can be measured for all conditions, ageing and creep tests. For the Grade 91 steel, the creep failure was related to the size distribution of the $M_{23}C_6$ particles. It was found that only when the particle reached a certain size, failure quickly followed. The same thinking can be used here.

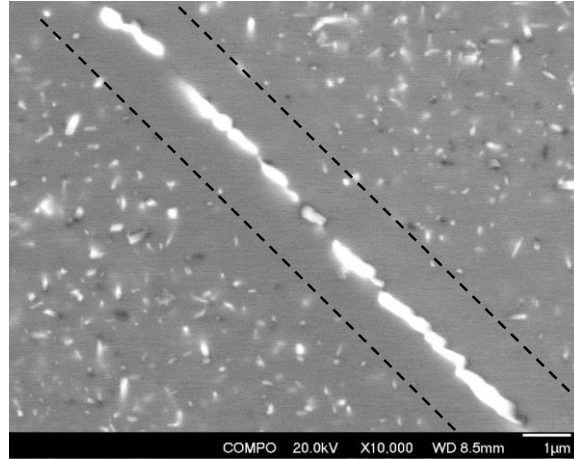


Figure 7.5 Micrograph of a grain boundary in the gauge section of the FCA-2Nb sample. The PFZ is marked with dashed lines.

Table 7.2 Comparison of the area fraction of Laves phase on the grain boundary and width of PFZ after creep test in FCA-1Nb and FCA-2Nb samples.

at Fracture	f_{GB}^{Laves}	δ_{PFZ}^{hw} (um)
FCA-1Nb	0.487	0.813
FCA-2Nb	0.793	1.437

Creep cavities were observed in along the grain boundaries, and thus there must be a point in the microstructure evolution that allows nucleation and growth of the voids. Table 7.2 gives a comparison of the area fraction of Laves phase on the grain boundary and the half width of the PFZ. The half width of the PFZ is simply the width of the PFZ on one side of the grain boundary.

First, it is a reasonable assumption that the smaller the area fraction of Laves phase may lead to higher amount of creep cavity nucleation. It could be plausible that there is some area fraction of Laves that evolves during creep that would start to generate more cavities.

However, the FCA-2Nb sample maintained a large area fraction of Laves phase on the grain boundary after failure. Therefore, is it possible that such a high fraction of Laves phase leads to creep cavities? Although this is not the only parameter within the grain boundary region.

On the other hand, there may be a width of the PFZ that allows more deformation. Here again, there is some inconsistency. The FCA-1Nb failed with a smaller width of the PFZ while the FCA-2Nb last longer with a larger PFZ. This again does not support the hypothesis that only one parameter can be used to predict the failure. It then should be noted that the PFZ should always be deforming after it reaches some minimum width. The matrix within the PFZ can be assumed to be similar to a BCC matrix without precipitates. Therefore, at the applied stress, dislocation creep would be dominating. Thus the dislocation model used in the Grade 91 steel can be applied, where the width of PFZ can be taken as the interparticle spacing. This means that the minimum width of the PFZ would be a “inter particle spacing” that when the threshold stress is calculated, would be equal to the applied stress. In the case of the Fe-Cr-Al alloys the minimum width of the PFZ is ~200 nm. However, the calculated strain rates in this region would not be significant until the width of the PFZ shows a strain rate equal to the observed strain rate. Here,

the width of the PFZ is ~400 nm. Nevertheless, the measured PFZ for all alloys is more than double this value. Therefore, there must be a relationship between the area fraction of Laves phase and the width of the PFZ.

7.5 Correlation of Grain Boundary Region to Creep Properties

The grain boundary region takes into account two parameters, area fraction of Lave phase on the grain boundary and the width of the precipitate free zone. The previous section described the possibility that one parameter could be used to predict creep rupture. However, this was found not to be plausible. It is possible to combine these experimental parameters to create a factor which can be used to predict when failure is most likely to occur. Equation 7.6 describes a Grain Boundary Zone Strength Factor (GBZ SF) by taking the ratio of the area fraction of Laves phase to the width of the PFZ.

$$GBZ\ SF = \frac{f_{GB}^{Laves}}{\delta_{PFZ}^{hw}} \quad 7.6$$

Where f_{GB}^{Laves} is the area fraction of the Laves phase on the grain boundary and δ_{PFZ}^{hw} is the half width of the Precipitate Free Zone. Because this factor is related to both the area fraction of Laves phase and the width of the PFZ, the factor would be expected to change with time. This method would allow an engineer to track the likeliness of failure. Figure 7.6 shows the creep curves of the Fe-Cr-Al alloys and overlaid is the selected GBZ SF for aging and after rupture. It is interesting that all the alloys failed with a GBZ SF below 0.6. The GBZ SF was also calculated from the aging study of the FCA-1Nb and FCA-2Nb alloys. Again an interesting trend emerges. The calculated GBZ SF for the FCA-1Nb aged sample for both 168 & 1008 hours stays close to 0.6. This shows that the creep condition and aging conditions compare well.

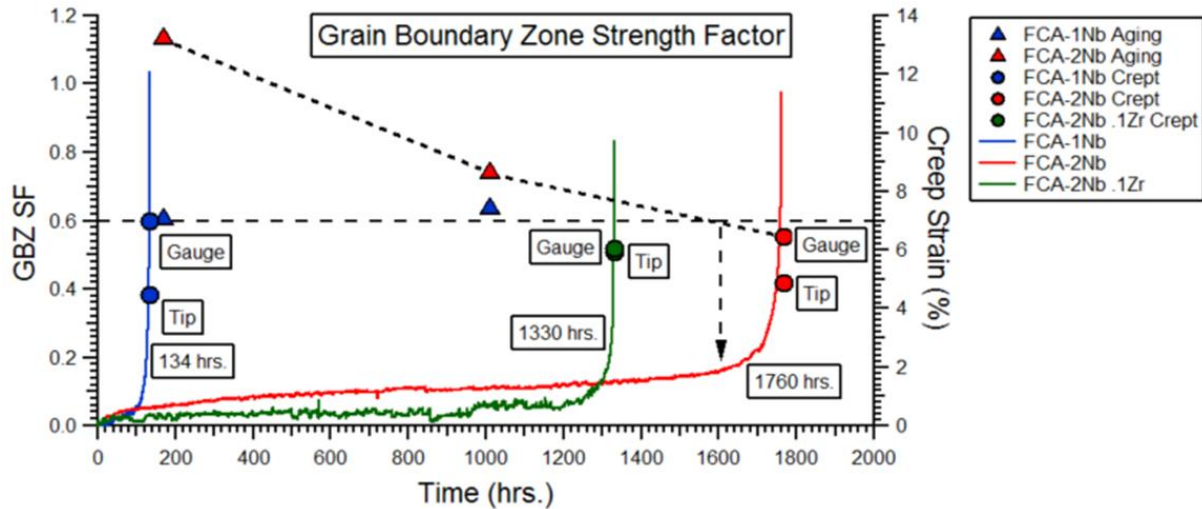


Figure 7.6 Calculation of the GBZ SF over laid onto the creep curves of the Fe-Cr-Al alloys. All the alloys failed when the GBZ SF drops below a value of 0.6.

In this case the FCA-1Nb sample is already in the area which predicts the sample is susceptible to failure and thus no surprise that it failed quickly. On the other hand, the aging conditions for the FCA-2Nb sample show a drastically different result. After aging for 168 hours the GBZ SF was calculated to be between 1.1-1.2.

If the assumed correlation between aging and creep test is accurate, it can be postulated that this value would be similar during creep. Then after aging for 1008 hours the GBZ SF was calculated to be close to 0.8. This means that the fraction of Laves phase and the width of the PFZ is changing and is approaching condition favorable for failure. Then the GBZ SF was calculated for the gauge section after rupture in the FCA-2Nb sample. Here, the value was calculated to be ~0.58, which again is below 0.6. Similarly, if the assumed aging to creep correlation is correct, then the observed values show a change with time and approach a condition favorable for failure.

It should be discussed that the GBZ SF does not necessarily mean there is a direct relationship between the two parameters. Repeating the creep modeling of the PFZ from above, it was shown that dislocations move within the PFZ. It is also known and described in Chapter 2.8.2 that free grain boundaries are excellent sinks for defects. Therefore, any free amount of the grain boundary in the Fe-Cr-Al alloy would also be expected to form creep cavities. Any area fraction of Laves phase on the grain boundary less than 1.0, would have points on the grain boundary that is devoid from particles. Both of the alloys, at failure, had an area fraction less than 0.8. Therefore, it should be concluded that the GBZ SF does not relate any one microstructural parameter to the other, but simply relates both parameter to a condition most favorable for failure.

Finally, it is necessary to know if the deformation accumulated in the PFZ is enough to provide the strain observed in the creep curve. If the amount of PFZ in the entire sample cannot accommodate the deformation, then another mechanism may be involved. However, the calculation does, in fact, show that the PFZ in the samples can give the strain percentages observed in the creep curve. To simplify the calculation, the 2D area of the grains and the PFZ will be used. In addition, for the calculation, the grains are assumed to be circular. The result can then be assumed to correlate with the volume. To calculate the total area of PFZ in the gauge section, the total area of one grain is calculated using its true diameter. Then the area of the grain with a diameter that takes into account for the PFZ is calculated. The area of the PFZ is the area of the true grain diameter subtracted by the area of the grain with PFZ included. For FCA-2Nb, the average grain size was taken from the As-Solutionized sample or 470 μm diameter. The area for one grain is .173 mm^2 . After subtracting the area of a circle to include the PFZ, the area of the PFZ is found. The area of the PFZ for one grain is .002207 mm^2 . Now the total number of

grains in the gauge section should be calculated. The length and width of the creep specimen is roughly 20 mm X 5 mm with an area of 100 mm². Therefore, the estimated number of grains in the gauge section is 420 grains. Now the total area of the PFZ can be calculated, and the value for the FCA-2Nb sample is found to be .927 mm². This calculation was then done for the FCA-1Nb sample with the grain size of 305 μm diameter. The total area of PFZ was calculated to be .795 mm². If the strain percentage taken from the point just before the initiation of tertiary creep, then this should be the amount of deformation that could have been accumulated from the PFZ. Because the total area of the gauge section was found to be 100 mm², then the calculated area of PFZ should be the percentage of strain the sample could accommodate. For the FCA-1Nb sample, the percent strain was found to be 0.5%. Therefore, for this sample, it can be concluded that the PFZ can accommodate the deformation observed in the specimen. However, for the FCA-2Nb sample, the strain percentage observed is ~1.73%. This value shows that only the PFZ would not be able to fully accommodate all of the deformation. However, in contrast to the FCA-1Nb sample, the FCA-2Nb sample has accumulated more creep cavities over time which would allow excess strain not produced directly within the PFZ. Since the calculation is also an area approximation, volume considerations could also lead to differences in these values. From this calculation and the evidence presented in the research, it would be a best approximation that the failure of the Fe-Cr-Al alloys is a grain boundary ductile failure and the deformation can be linked to the PFZ which can mimic the appearance of Grain Boundary Sliding.

The conclusion that should be made after understanding the interaction of grain boundary region during creep is that this alloy creeps under heterogeneous conditions. The alloy is similar to a weldment in that multiple different regions are found within a bulk sample. However, in this case the heterogeneous nature is on a much finer scale, for example, the grain boundary, PFZ,

and grain interior can be on the scale of nanometers. Each region is creeping at its own rate, but all the rates are averaged into the measured strain rate. For example, the matrix strain rate and contribution is low, while the strain rate in the PFZ may be orders of magnitude faster than the observed global strain rate. The true conclusion is that more than one mechanism may be operating at the same time in different regions but overall one mechanism may be observed.

7.5 Summary

1. Using a threshold stress, the minimum creep rate of precipitate strengthened creep resistant materials can be modeled. A strain rate map was produced showing the creep rate produced by a range of precipitate diameters and interparticle spacing. The model was used to predict the strain rate at each major region in a weldment of a Grade 91 steel. The model revealed that the predicted strain rate measured from the $M_{23}C_6$ increases an order of magnitude after welding and Post Weld Heat Treatment. Then after creep, the model shows the strain rates further increase upon coarsening during creep. This illustrates that during creep and at high temperatures, the instantaneous creep properties of the precipitate strengthened alloys can change with the evolution of the precipitate size and interparticle spacing.
2. The model has shown that the particle distribution of $M_{23}C_6$ and MX in Grade 91 steel lay in a sensitive region of a strain rate map. Small changes in precipitate distribution can change the creep properties of the Grade 91 steel. This illustrates how the thermomechanical treatments produced a precipitate distribution that improved the creep properties of the Grade 91 steel weldment. Microstructure control can be improved through the optimization of the thermomechanical treatments, which allows for better creep rupture properties and maintains industrial standards for base metal toughness.

3. A Digital Image Correlation (DIC) was conducted by Yu et al. of a Grade 91 steel weldment after two different pre-weld heat treatments. A reanalysis of the data shows that the FGHAZ of the weldment has an order of magnitude higher creep rate than the base metal. The results from the DIC confirms the strain rate modeling based on the precipitate distribution.

4. The results from the model clearly illustrate the degradation in the FGHAZ of weldments. Results from the literature, and the results from the thermomechanical treatments show that the $M_{23}C_6$ and MX distributions after welding are not favorable for high temperature creep strength, as compared to the base metal. Although it cannot be conclusively said, it seems very likely that the Type IV failure in the weldments of Grade 91 steel cannot be avoided.

5. A new alloy was then introduced that has the potential to not being susceptible to the Type IV failure mechanisms. To correlate the observed Laves phase distribution in the microstructure to the initial creep properties, the same threshold stress model was used. From Chapter 6, the grain interior microstructures of all the alloys had similar particle distributions, which would indicate the alloys should behave similarly during creep. The threshold model also indicates that the minimum creep rates for all the alloys should be very similar. However, this was found to not be the case. Furthermore, the model suggests that the creep mechanism should be a grain boundary type mechanism. The model was reanalyzed using the Grain Boundary Sliding (GBS) mechanism. The model, using GBS, more closely aligned with the observed minimum creep rates of the alloys based on their grain sizes. This illustrates that the creep mechanism follows GBS, but without further evaluation the mechanism cannot be confirmed. Nevertheless, this indicates the creep and final failure was localized to the grain boundary region.

6. Since the creep mechanism was found to follow the GBS mechanism, a more detailed evaluation of the grain boundary region was conducted. The areal fraction and width of the precipitate free zone (PFZ) was determined. It would make sense that one of these parameters could be correlated to the creep rupture properties of the alloys. However, neither parameter shows a strong correlation to the creep rupture. It could be expected that a low areal fraction of Laves phase on the grain boundary could lead to creep cavitation. In addition, a large width of the PFZ could also lead to heavier deformation in the region leading to more creep damage. When comparing the FCA-1Nb to the FCA-2, the two parameters together do not support this idea. The FCA-1Nb sample had a small areal fraction of Laves phase (.487), but had a smaller width of the PFZ (.813 μm). Conversely, the FCA-2Nb sample had a larger areal fraction of Laves phase on the grain boundary (.793), but here also had a larger width of the PFZ (1.437 μm). Therefore, the creep rupture properties could not be correlated to either individual parameter.

7. Since both the areal fraction and width of the precipitate free zone alone could not be correlated to the creep rupture, there must be a correlation with both the parameters. A Grain Boundary Zone Strength Factor was identified by taking the ratio of areal fraction of Laves phase on the grain boundary to the width of the precipitate free zone. Interestingly, the value of the GBZ SF for all the alloys after failure was found to be less than 0.6. However, the change in the factor with time should be investigated to confirm the significance of the GBZ SF. The grain boundary regions of the aged FCA-1Nb and FCA-2Nb samples were analyzed and the GBZ SF was calculated after 168 and 1008 hours of aging. For the FCA-1Nb sample the GBZ SF for both aging times remained close to 0.6, which helps to illustrate the poor grain boundary region from the beginning and would not support longer times for creep. On the other hand, the FCA-2Nb

sample had different results. After 168 hours of aging, the GBZ SF was found to be close to 1.7, which indicates good creep resistance. Then after 1008 hours of aging, the GBZ SF was found to be close to 0.8. This shows an aging effect on the grain boundary region and has an indication of degrading microstructure. If a line is drawn linking the GBZ SF from the aging samples and the creep rupture sample, a clear representation of the evolution of the microstructure can be observed. The Grain Boundary Zone Strength Factor illustrates the effect of these two parameters on the creep rupture properties of the Fe-Cr-AL fully ferritic alloy.

Chapter 8. Conclusion and Future Work

8.1 Conclusion

The research presented here in this dissertation is to understand how the microstructure control of a weldment in a Grade 91 steel and an Fe-Cr-Al fully ferritic alloy and how the microstructures correlates to the creep strength. The following is to summarize and conclude the work presented.

1. Thermo-Mechanical Treatments were conducted on a Grade 91 steel plate with a variety of processing conditions. The purpose of the TMT is to nucleate an increased density of MX carbonitride particles via the dislocations introduced from deformation. The MX particles are thought to be more thermally stable than the Cr enriched $M_{23}C_6$ carbides. The TMT was shown to be effective in producing a large density of MX particles after TMT. A standard tempering was used on the steel. The higher density of MX particles correlated with a reduction of $M_{23}C_6$ carbides.

2. The microstructure of welded TMT plates again showed an effect of the TMT process. With TMT at 800 °C, there was a reduced amount of $M_{23}C_6$ carbides on “ghost” Prior Austenite Grain Boundaries. It was hypothesized by Yu et al. (2013) that the Type IV failure was due to the fact that a large percentage of $M_{23}C_6$ did not dissolve during welding and leads to $M_{23}C_6$ remaining on the “ghost” PAGBs. This was hypothesized as the mechanism of the premature failure.

3. The creep resistance after TMT was observed to increase. The increased time to failure along with the reduction in minimum creep rate showed the improvements in creep resistance.

However, the improvements did not come close to the creep resistance of an un welded base

metal. It was concluded based on the microstructural control before welding that it is not possible to eliminate the Type IV failure in Grade 91 steel.

4. Another purpose of the TMT was to improve the creep strength but maintain industrial standards for toughness. The presented room temperature toughness does approach the toughness of the standard N&T sample and is expected to be sufficient for the industrial standardization.

5. Because the conclusion was made that the Type IV failure could not be eliminated in Grade 91 steel, a new alloy was devised to be another solution for Type IV failure. Four base fully ferritic alloys with a base composition of Fe-30Cr-3Al-.2Si-xNb were created. The alloys are strengthened by Laves phase particles. Because these alloys are being developed, welding was not done, and the creep strength was measured for the base metal. However, because welding would be needed for industrial purposes, a solutionized microstructure was necessary before creep testing. The solutionized microstructure was necessary to prevent particles from experiencing the thermal cycles of welding.

6. The solutionized microstructure in the 1Nb alloy did not contain particles. However, the 2Nb containing alloys did contain grain boundary particles and some particles within the grain interior. Then aging studies were performed to compare with creep rupture specimens and to understand the kinetics of the Laves phase. It was found that for the grain interior, the Laves phase for the FCA-1Nb and FCA-2Nb samples were similar in size and density.

7. The creep rupture results indicated that the addition of 2 Nb aided in improving the creep strength. However, it was found that the failure mechanism was a grain boundary ductile failure, and thus the creep strength within the matrix was not affected by the addition of 1 wt% Nb. The differences in microstructure were found to be linked to the fact that the FCA-2Nb sample was

held at temperature for longer times. The fractography was also used to indicate a grain boundary mode of failure. The differences in the grain boundary region was, however, linked to the differences in Nb content.

8. A General microstructural model was presented to correlate the microstructure with the observed strain rate. For precipitate strengthened steels, the model was developed based on the size and interparticle spacing of the carbides. The creep mechanism for the Fine Grain Heat Affected Zone of the Grade 91 weldment was found to be dislocation creep. In addition, the size and interparticle spacing of the $M_{23}C_6$ carbides were able to be tracked. The model indicated that through welding and Post Weld Heat Treatment, the $M_{23}C_6$ carbide would coarsen to a point that the strain rate for the FGHAZ is much higher than for the base metal. This indicates the observed Type IV failure correlates to the evolution of the carbides in the FGHAZ during welding and PWHT.

9. The same model was used for the Fe-Cr-Al alloys. However, the model indicated that all the alloys were in a region of a grain boundary type creep mechanism. The model was adjusted for Grain Boundary Sliding and was applied to the alloys. Here, the model more closely correlated to the observed strain rates. Therefore, this showed there was more evidence for GBS as the dominant mechanism. The grain boundary zone was further investigated. It was found that when the ratio between the area fraction of Laves phase on the grain boundary and the width of the PFZ, on one side of the grain boundary, dropped below 0.6 the conditions were favorable for failure. In addition, the total volume of PFZ in the gauge section was also found to be a large enough to accommodate the observed strain. Therefore, the creep mechanism observed in the Fe-Cr-Al alloys was found to be most likely related to the deformation due to dislocation movement in the PFZ, and the failure mechanism is grain boundary ductile failure.

8.2 Future Work

From the understanding of microstructure control in the Grade 91 steel, other techniques to increase creep resistance can be used. One such technique is to modify the Prior Austenite Grain size. It was shown how the $M_{23}C_6$ preferentially nucleate and grow on PAGBs. Utilizing the model presented in the research, it is known that a fine distribution of $M_{23}C_6$ is beneficial to creep resistance. In addition, the microstructure in the FGHAZ needs to be similar to the base metal after welding. Therefore, one conclusion is to make the base metal similar to the FGHAZ. One way to accomplish this is conducting a heat treatment to reduce the PAG size. By reducing the grain size, the grain boundary per unit area will increase. This will allow a better distribution of finer $M_{23}C_6$ because of the increased nucleation sites. Because the $M_{23}C_6$ size would be smaller, it would be expected that the particle then would fully dissolve during welding. Then could re-precipitate on the fresh PAGBs, similarly to what was seen after TMT at 800 °C. In addition to this, the fine grain structure would be seen in the FGHAZ and the base metal. Thus the gradient of microstructure would not exist, except for the CGHAZ and weld metal. It is however not known what this effect would play in the creep resistance of the weld. An experiment was conducted to produce refined PAGBs. A cyclical heat treatment was performed, the EBSD micrographs with the measured PAGBs and martensite block boundary sizes are shown in Figure 8.1. The cyclical heat treatment performed was a series of subsequent rapid heating and rapid cooling on a Gleeble thermo-mechanical simulator. Two experiments were completed, one with a rapid heating to 950 °C and cooled to room temperature. This was then repeated 10 times. The second experiment was a repeat of the previous experiment, but the peak temperature was 1100 °C. The figure shows that the PAGB size was reduced to slightly larger than 3 μm . This is a drastic reduction from the 25 μm observed in the N&T sample. Another

technique for the grain modification is to grow the austenite grains to extremely large sizes by a long term, high temperature heat treatment. The excessively large grains would force the $M_{23}C_6$ to then nucleate and grow on the martensite block boundaries. The block boundaries have been shown to produce smaller particles. In addition, the smaller effective grain sizes of martensite maintain an increased number of nucleation sites. With both of these parameters, it would be expected to produce a fine distribution of $M_{23}C_6$ particles. However, another beneficial factor would be that during one or two thermal cycles of welding, the resulting grain reduction would not be on the same scale as in the traditional heat treatments and welding. Consequently, there would still be a microstructure gradient in the weld to the base metal, and it is unknown how this gradient would affect the creep resistance of this microstructure control method.

To further understand the microstructural changes occurring, in-situ measurements can be utilized. One such in-situ experiment is synchrotron X-ray diffraction. In such experiments, the thermal and crystallographic information can be observed. Therefore, the effects of the large or small grain sizes on the precipitation of $M_{23}C_6$ carbides can be observed. An early experiment has been conducted at the Brazilian Synchrotron Light Laboratory. Here a Gleeble® Thermo-Mechanical simulator is positioned in the direct path of the synchrotron X-ray beam. The samples were subjected to the cyclical heat treatments discussed above. 2D diffraction data was taken during the cyclical heat treatments and during tempering. An example of the 2D diffraction data is shown in Figure 8.2. The data can then be converted into a 1D diffraction pattern graph where the diffraction peaks can be identified. Based on the peak intensities, more precise measurements of the volume percentage of $M_{23}C_6$ can be determined. Then the values can be compared with the traditional normalized and tempered conditions. Using this understanding of $M_{23}C_6$ precipitation the cyclical heat treatments can be optimized.

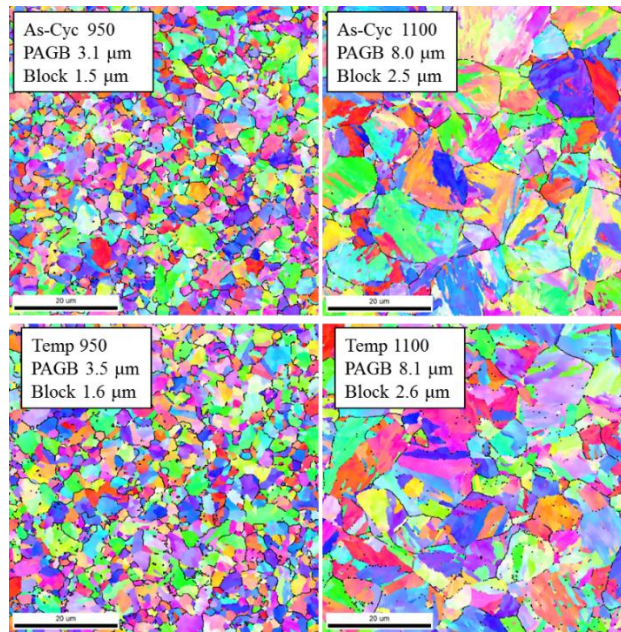


Figure 8.1 EBSD micrographs of a cyclical heat treatment experiment illustrating the reduction of PAGB and martensite block sizes.

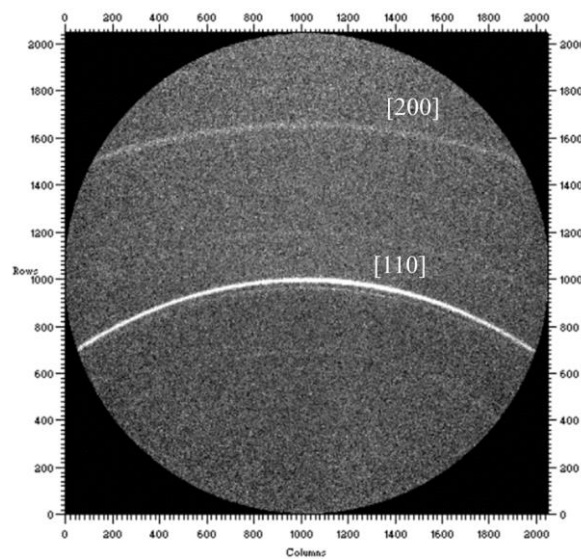


Figure 8.2 2D diffraction pattern of Grade 91 steel after normalization, the $[110]$ and $[200]$ peaks are shown.

Alternative Methods of Determining Creep Damage

The SEM is a good technique to provide a snapshot of one serial sectioned location within a specimen. For creep, this method does not always provide the best representation of cracking throughout the thickness of a specimen, especially grain boundary cracking. However, there is one characterization technique that has the ability to represent the 3D internal defects of a creep rupture specimen. X-ray Tomography is a technique that can be used to analyze the through thickness cracking behavior of creep rupture specimens. It may even be used to analyze the cracking behavior in interrupted creep tests after long (>15,000 hrs) times to show a more comprehensive evolution of crack propagation. X-ray Tomography reconstructs a sample volume by stitching together several serial images along one axis (i.e. X,Z axis). Initial testing of this technique was performed on the FCA-2Nb-.1Zr sample. Figure 8.3 is a reconstruction of the tomography results. The reconstruction shows evidence of grain boundary cracking near the tip of the creep specimen. However, the sectioned and polished sample did not show cracking in tip of the specimen. This method illustrates that only sectioning and polishing one single time does not give a good three dimensional understanding of defects. In addition, the results helped to confirm that cracking only exists along the grain boundaries and that a grain boundary type deformation mechanism is the reason for failure in these alloys. These results show the viability of this technique to be used for future optimization of the Fe-Cr-Al fully ferritic alloys.

Elimination of the Precipitate Free Zone

The results from the Fe-Cr-Al alloys shows that the Precipitate Free Zone is detrimental to the creep resistance. Therefore, it is necessary to reduce or eliminate the PFZ. Another alloy system that contains a detrimental PFZ is the precipitate strengthened Al alloys.

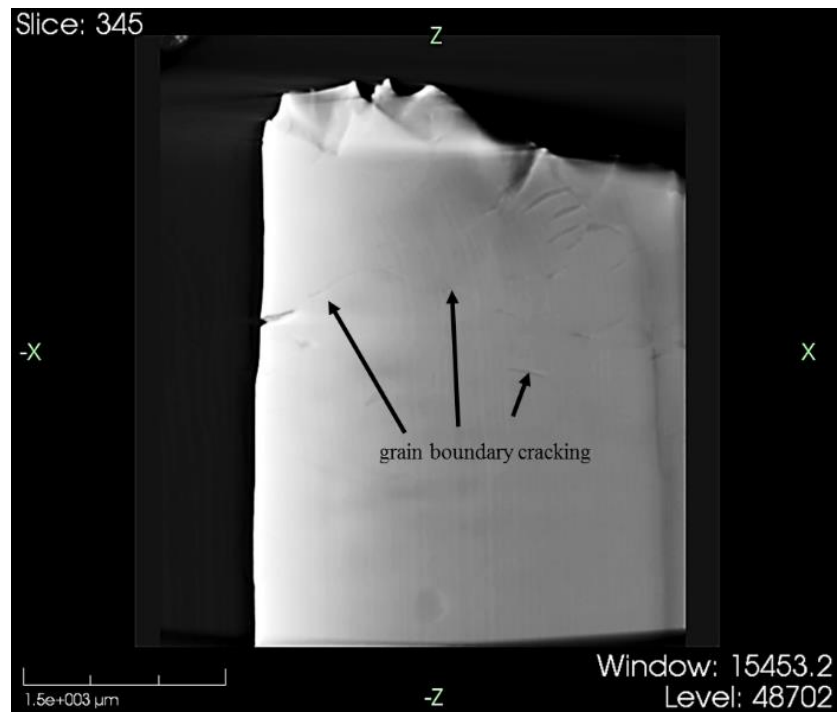


Figure 8.3 X-ray Tomography reconstruction of the FCA-2Nb-.1Zr alloy. The reconstruction shows grain boundary cracking.

Research on a two-step heat treatment has been conducted and has shown a beneficial reduction of the PFZ [111, 112]. In this work a low temperature heat treatment was applied which allowed for nucleation of precipitates even close to the grain boundary. The low temperature heat treatment did not allow the grain boundary precipitates to take all the surrounding solute atoms. Then a normal high temperature heat treatment was applied to grow the precipitates to the desired size. This could be one method to eliminating the PFZ in the Fe-Cr-Al fully ferritic alloys. Figure 8.4 shows preliminary characterization results of an addition of a second precipitate forming element. From figure 8.4b, the addition of 2 wt% Ti shows the elimination of the PFZ. Although, the addition of elements may also affect the microstructure evolution in a negative way. Figure 8.4a shows the coarsening rates of selected alloy compositions. Most of the alloys have a larger coarsening rate than the CC05-3, which represents the FCA-2Nb sample. This would then mean that the particle could grow large enough to produce similar cracking effects to the $M_{23}C_6$ carbides in the Grade 91 steel. The mechanisms of the elimination of the PFZ from this addition of Ti is not yet known. The figure also shows that a 1Nb-1Ti alloying addition did not eliminate the PFZ. Possible hypotheses on this mechanism is discussed here. First, the differences in the nucleation rates of Ti Laves phase over the Nb Laves phase. If one of Laves phase nucleates much faster than the other the grain boundary get decorated with one type of Laves phase. Then the other Laves phase would not have a solute depletion zone near the grain boundary, and would then be able to nucleate and grow in the matrix, even close to the grain boundary. Another possible hypothesis is that the solubility in Fe-BCC of the two elements will be different. In this case, the Fe-Nb and Fe-Ti phase diagrams can be compared for a qualitative understanding. The phase diagrams show that Ti has some solubility in Fe-BCC at higher temperatures, whereas Nb has almost no solubility in Fe-BCC, even at high temperatures.

Note the additional elements, Cr, Al, and Si, will affect the thermodynamics of the system. With the differences in solubility, one element may (mainly Nb) preferentially segregate to the grain boundary. This will again leave one element in the grain interior to nucleate and grow Laves phase even close to the grain boundary.

Finally, with any new modification to microstructure or creation of a new alloy, the creep mechanism with respect to temperature and stress should be investigated. In the literature, there is a more or less standard for providing the creep mechanisms with differing stress levels at a certain temperature. By plotting a log of the normalized minimum strain rate versus the log of the stress, a value for the stress exponent, n , can be determined. The value of the stress exponent has been correlated to a particular creep mechanism, for example, an n value of 4-5 is correlated to the dislocation creep mechanism. This is usually conducted over several temperature values. In addition, the activation energy for creep is also required to correlate to a particular creep mechanism. Here the normalized minimum strain rate is plotted against inverse temperature. The activation energy for creep, Q , is then determined. The measured activation energy for creep is then compared to the activation energy for diffusion for lattice and grain boundary diffusion. For the dislocation creep mechanism example, the activation energy for creep should be comparable to the activation energy for lattice diffusion. When both the stress exponent and activation energy for creep are determined and align with a certain creep mechanism, it can then be stated the creep mechanism for the material at the given stress and temperature. From the current research, it was determined that the creep properties of selected materials could be altered through microstructure control. Therefore, the stress exponent and the activation energy curves should be plotted for the TMT altered Grade 91 steel and Fe-Cr-Al alloys. This would allow for better correlation of the microstructure to the observed creep response.

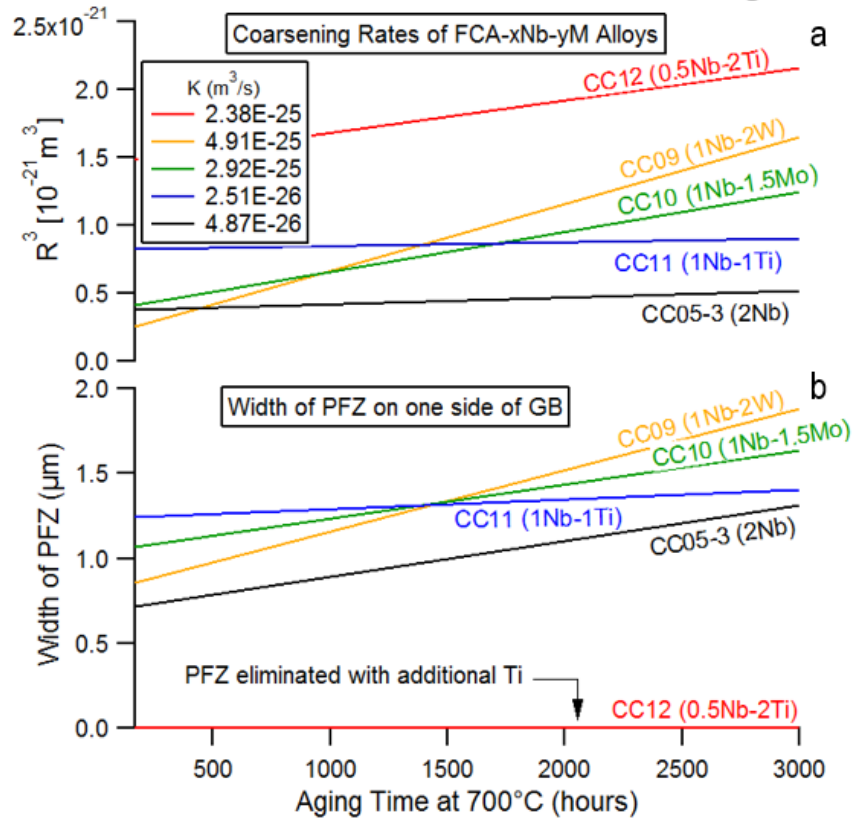


Figure 8.4 (a) Coarsening rates from alloys with addition of a second precipitate forming element. (b) The width of the PFZ of the selected alloy. The addition of 2 wt% Ti shows the elimination of the PFZ.

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Vita

Benjamin Shassere was born in Arlington Texas on February 14, 1989, to the parents of Michael and Kathy Shassere. He attended Oak Ridge High School in Oak Ridge Tennessee. After high school, he attended Tennessee Technological University in Cookeville, Tennessee. He was awarded a varsity NCAA D1 scholarship to run Cross Country. Ben graduated Tennessee Tech. University in 2011 with a Bachelor's of Science degree in Chemical Engineering. After graduation, he accepted a Post Bachelors Internship at the Oak Ridge National Laboratory. There he designed and constructed a Magneto-Caloric Regenerator prototype. This prototype was used to study the effect of several variables on the performance of the regenerator. While at ORNL, he was introduced to Material Science and Engineering. In 2012, he accepted a graduate research assistantship at The Ohio State University in Welding Engineering. In the fall of 2013, he transferred to The University of Tennessee with his advisor. There he continued his graduate studies in The Bredesen Center for Interdisciplinary Education and Research with a focus in Material Science and Engineering. He will obtain his Doctor of Philosophy degree in December 2016.