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I, Deepthi Tammana, hereby submit this original work as part of the requirements for the degree of Master of Science in Materials Science.

It is entitled:
Microstructure and Damage Evolution During Short Term Creep of Modified 9Cr-1Mo Steel used in Generation IV Nuclear Energy Systems

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Microstructure and Damage Evolution During the Short Term Creep of Modified 9Cr-1Mo Steel used in Generation IV Nuclear Energy Systems

A thesis submitted to the Division of Research and Advanced Studies of the University of Cincinnati in partial fulfillment of the requirements for the degree of

Master of Science

in the program of Material Science and Engineering in the Department of Mechanical and Materials Engineering of the College of Engineering and Applied Science

by

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ABSTRACT

Major applications for high Cr steels include high temperature applications, advanced nuclear core material applications for Generation IV technology. Grade 91, Modified 9Cr-1Mo steel is being considered for the pressure vessels, turbine and core applications (ducts) of very high temperature reactors, supercritical water cooled reactor systems. All of these components undergo high temperature creep while in service, hence detailed study during the creep of these materials is essential. There are two creep regions with different creep characteristics: short-term creep region, where precipitates and sub-grains are thermally stable, and long-term creep region, where thermal coarsening of precipitates and sub-grains appear.

In this study, creep behavior, damage evolution and microstructural changes during the short creep at different stresses varying from 80 to 140MPa were studied. Creep tests to different creep time intervals ranging from 25% to 75% of total creep life to failure at a temperature of 650°C at three of the stress levels in the range mentioned above were conducted and various microstructural parameters including the cavity nucleation, carbide evolution and sub-grain development were characterized in detail, by Scanning electron microscopy (SEM), Electron backscatter diffraction (EBSD) and Transmission electron microscopy (TEM). Micro hardness measurements were also carried out using Vickers and Knoop indenters and related to microstructural evolution. Calculation of stress exponent indicated dislocation creep as the major mechanism of creep deformation at stresses above 100MPa. Minor change in creep mechanism can be noticed at 100MPa, mechanism being
slightly different below and above 100MPa. Stress exponent calculated along with microstructure characterization results confirm dislocation creep is the deformation mechanism. It was observed that though cavity density close to the fracture area remains almost same at stress levels below 100MPa, but is comparatively lower at higher stress levels. The carbide particle diameters at every stage of creep are greater as the stress level decreases. At higher stress levels the damage initiation and failure occurs in the final quarter of life, whereas at lower stress levels damage initiation and evolution can be seen over a large time interval. The contribution of static recovery of sub-grains due to creep deformation causes the breakdown in creep strength in Grade 91 steels. Creep deformation initially proceeds with sub-grain and carbide coarsening until necking is observed. Increasing strain during the creep test after the necking stage, results in formation of more sub-grains and refinement in sub-grain size. Formation and growth of sub-grain boundaries and coarsening of carbides is the main microstructure evolution mechanism. Higher fractions of sub-grains are formed at high stress levels leading to the recrystallization of microstructure. The near fracture areas show highly recrystallized microstructures. The fracture mechanism is formation of voids at the vicinity of the deformed carbides, which are elongated and located at the grain boundaries and are subjected to high strain. These voids grow quickly and coalesce resulting in micro grain boundary cracks and dimples or larger voids. However, the cavity formation, coalescence and propagation occur after 90% of the creep life even at lower levels of stress. Comparison of the results from the present work with the earlier work and literature in this field gave further support for the above damage mechanisms.
ACKNOWLEDGMENTS

I would like to express my sincere gratitude and appreciation to my advisor, Professor Dr. Vijay Vasudevan for his valuable guidance. His in-depth of experience and pool of knowledge in the field has always been a source of motivation throughout. I am very much thankful to Professor Dr. Peter Nagy and his student Seeran Prajapati for their generous help in allowing us to share their experimental facilities, providing the material and performing a few experiments.

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CHAPTER 1. INTRODUCTION

Challenging technology goals for Generation IV nuclear energy systems are defined as sustainability, economics, safety and reliability, and proliferation resistance and physical protection. By meeting these goals, new nuclear systems can achieve a number of long-term benefits that will help nuclear energy play an essential role worldwide [1]. It is thus required to develop and characterize the performance of materials which are likely to be critical in Generation IV technologies.

The first Cr-Mo steels were used for conventional power-generation applications. Modified 9Cr-1Mo steels, also called as the G91 steels, have tremendous applications in nuclear power plants as boiler tubes, steam pipes and reactor pressure vessels. In future, for boiler constructions G91 has advantage over low Cr-Mo ferritic steels and 300 series stainless steels in USA [2]. Klueh [3] has discussed various alloys developed in the past for use in core and out of core components for the generation IV nuclear plants and qualified ferritic-martensitic (F-M) (9-12%Cr) steels to have a good standing in the list because of high corrosion resistance and thermal stability at high temperatures. F-M steels are also known for high ductility after irradiation and reduced activity (RA) property [4]. The major application for G91 steels are considered to be in the generation IV Supercritical-Water-Cooled Reactor System [1]. Microstructure of these F-M steels consists of martensite lath with sub-grain boundaries decorated with Cr rich M$_{23}$C$_6$ and matrix dotted with MX (X = V,Nb) precipitates which gives it high temperature strength [5,6]. Microstructural stability of Modified 9Cr-1Mo steel at high temperatures up to 650°C under static tensile and creep conditions was reported by Jones et al. [7].
Creep is the time-dependent deformation of a material at high temperature under constant load. Deformation occurs as a result of long term exposure to high temperatures and levels of stresses that are below the yield or ultimate strength of the material. The magnitude of this damage is a dependent on the material properties, exposure time, exposure temperature and the stress. Depending on the magnitude and duration of the applied stress, the deformation may become so large that a component can no longer perform its function leading to failure.

Structural properties of Mod. 9Cr-1Mo steels have been extensively studied in the past two decades. Sonderegger et al. [8] reported that creep in these F-M steels proceeds by sub-grain coarsening, but the grains do not coarsen. Maruyama et al. [9] from Tohoku University studied the long term creep of G91 steels. They suggested that sub-grain boundaries are stabilized by carbides and static recovery of sub-grains lead to creep deformation. Recovery of dislocations also is a part of creep deformation. The carbides become unstable at high temperatures and aggregation of carbides occurs. Hence the pinning force of the carbides is decreased and coarsening of sub-grains starts to occur as creep proceeds. Anderson et al. [10] suggested that the carbides along the grain boundaries are $M_{23}C_6$. As creep proceeds in G91 steels, the MC and MX carbides inside the grain dissolve and the carbides along grain boundaries grow at the expense of these carbides. On the other hand, Cerri et al. [11] reported a bimodal carbide distribution and coarsening of both types of carbides during creep. It can be concluded by saying that long term creep in G91 steels proceeds by aggregation of carbides and sub-grain recovery.

The damage evolution during creep can vary at high strain rates and high stress levels. Most work reported is in the domain of long term creep at low stress levels and very less emphasis has been given to microstructural evolution during short term creep at high stresses. It should be
noted that the operating characteristics of Generation IV high temperature structural components involve long service lives (>60 years).

**Objectives**

The main objective of the present study is to evaluate the creep behavior, damage evolution and microstructural changes during the short term creep of Modified 9Cr-1Mo steel at different stresses at a temperature of 650°C. The mechanism of the formation of sub-grains is well established in literature; sub-grain boundaries are formed when dislocations of same sign align vertically to lower their energy. Basically, the dislocations are introduced by deformation and martensitic transformation and the tempering heat-treatment provides sufficient thermal energy to cause recovery of the martensitic structure and form lower energy configurations in the form of sub-grain boundaries. Hence, the steel is initially heat treated using normalization and tempering to produce high dislocation density and enhance the sub-grain boundary density. This will be the as-received microstructure with the composition of the Modified 9Cr-1Mo steel studied herein. In order to understand creep behavior of the as-received steel, first constant load creep tests would be performed under various conditions which include a constant temperature at 650°C and various stress levels ranging from 80MPa to 140MPa for short term creep. Results of the creep testing would indicate the short term creep behavior of the steel at high strain rates and high temperature. For more detailed analysis on the various parameters of microstructural evolution and creep mechanism determination, different creep time intervals at a temperature of 650°C have been employed for these tests and tests were stopped after certain fractions of creep life. Orientation Imaging Microscopy (OIM) would be performed on the as-received steel before and after creep testing. OIM gives the distribution (fraction) of various boundaries in the microstructure. Detailed microstructural characterization of both the as-received and creep tested steel would be performed
and various parameters including the cavity nucleation, carbide evolution and sub-grain development investigated in detail using the SEM imaging and OIM. Sub-grain boundaries induce additional internal stresses, which would lower the effective stress (applied stress – internal stress) and lead to improvements in creep behavior. In Modified 9Cr-1Mo steel, these sub-grains are sites for internal stress. Internal stress in this project will be determined by regression analysis of the creep data obtained. Extrapolation of the creep data to higher and lower stresses using Monkman Grant equation is also discussed. Efforts are made to enhance the understanding of creep degradation mechanisms of this alloy during short term creep. In addition, creep data and microstructural parameters of carbide sizes and densities are compared with previous reports and established statistics.
CHAPTER 2. LITERATURE REVIEW

This chapter covers the literature review for the present work. A brief history and discussion on the development of Modified 9Cr-1Mo steels is included. Some of the previous work and reports of long term creep testing and mechanism in the above mentioned alloy are discussed. Finally, some important theoretical concepts are presented.

2.1: Background on Steels

This section includes the background on steels, their classification and effects of various alloying elements in the formation of these steels.

2.1.1: Classification of steels

Steels can be classified in general into various systems depending on various factors. Below is a very general classification of steels:

2.1.1a Based on the percentage of alloying element

A) Low alloy steels have less than 10% of alloying elements

B) High alloy steels have greater than 10% of alloying elements

2.1.1b Based on composition of various alloying elements

A) Nickel steels

B) Chromium steels

C) Chromium-Nickel steels

D) Chromium-Nickel-Molybdenum steels
2.1.1c Based on microstructure

A) Ferritic steels
B) Martensitic steels
C) Austenitic steels
D) Bainitic steels

2.1.2 Effect of various alloying elements

Various alloying elements are added to steels to improve their properties for different applications. Influence of various alloying elements in general as studied and reported in Key to Metals online database [12] can be seen below

2.12a. Austenite forming elements

Carbon (C), Nickel (Ni) and Manganese (Mn) are the most important austenite forming elements. Large amounts of Mn and Ni can make the steel austenitic even at lower temperatures like room temperature.

2.12b Ferrite forming elements

Chromium (Cr), Silicon (Si), Molybdenum (Mo), Tungsten (W) and Aluminum (Al) are the most important ferrite forming elements. Steels with more than 13% Cr are ferritic at all the temperatures up to incipient melting.

2.12c Carbide forming elements

Many ferrite forming elements can also play the role of carbide forming. The affinity of the elements for C increases as Cr, W, Mo, Vanadium (V), Titanium (Ti), Niobium (Nb), Tantalum
(Ta), and Zirconium (Zr). Carbides can be iron (Fe) containing (FeC) and non-iron containing (M₂₃C₆, MC, M₂C etc.). Complex carbides contain both Fe and carbide forming element.

2.1.2d Carbide stabilizers

Stability of the carbides depends on the other elements present in the steel. Partitioning of the element between the cementite and matrix determines the stability of the carbide. The ratio of the percentage by weight of the element in each of the two phases is called the partition coefficient, K. Cr has a high value of K, i.e. 28, and hence it’s the most common carbide stabilizer.

2.1.2e Nitride forming elements

All carbide formers are also nitride formers. N can also be used for nitriding of the surface to increase the surface hardness.

2.2:9-12% Chromium steels

9-12% chromium steels were developed around 1912 for steam turbine blades by Krupp and Mannesmann in Germany [13] and later it was realized that these steels with 13%Cr are stainless and do not rust. High Cr and high C martensitic steels are hard and were becoming well known for cutlery knives and tableware [2]. The 9Cr–1Mo steel was co-developed by Combustion Engineering and the Oak Ridge National Laboratory (ORNL) in the late 1970s [2].

The 9-12% Cr low carbon steels with additions of Mo, W, V, Nb and N possess higher creep-rupture strengths along with high oxidation resistance at high temperatures. These steels are being used and are in consideration for use in chemical plants, aerospace industries, power plants and nuclear reactors components like boilers etc. [2]. High chromium ferritic-martensitic steels were first considered for elevated temperature in-core applications (cladding, wrappers and ducts).
for fast reactors in the 1970s, because of their excellent thermal properties and irradiation resistance [3]. 9-12% Cr steels as well as the 7-12% Cr steels for the applications in core components of fast breeder reactors were analyzed and studied by Klueh and Harries [13].

The typical compositions of commercially developed 9Cr steels discussed by Klueh in [3] for the applications of these steels in future nuclear reactors can be seen in Table 2.1 below:

**Table 2.1: Nominal compositions of Commercial and experimental steels [3]**

<table>
<thead>
<tr>
<th>Steel</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>V</th>
<th>Nb</th>
<th>B</th>
<th>N</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>A533 Grade B</td>
<td>0.25 max</td>
<td>0.20</td>
<td>1.30</td>
<td>0.50</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.07 Ti</td>
<td></td>
</tr>
<tr>
<td>2%Cr-1Mo (T22)</td>
<td>0.15 max</td>
<td>0.3</td>
<td>0.45</td>
<td>2.25</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.07 Ti</td>
<td></td>
</tr>
<tr>
<td>2.25Cr-1.6WVNb (T23)</td>
<td>0.06</td>
<td>0.2</td>
<td>0.45</td>
<td>2.25</td>
<td>0.1</td>
<td>1.6</td>
<td>0.25</td>
<td>0.05</td>
<td>0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.25Cr-1MoVTi (T24)</td>
<td>0.08</td>
<td>0.3</td>
<td>0.50</td>
<td>2.25</td>
<td>1.0</td>
<td>0.25</td>
<td>0.04</td>
<td>0.03</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ORNL 3Cr-3WV</td>
<td>0.10</td>
<td>0.14</td>
<td>0.50</td>
<td>3.0</td>
<td>3.0</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td>0.10 Ta</td>
<td></td>
</tr>
<tr>
<td>ORNL 3Cr-3WVTa</td>
<td>0.10</td>
<td>0.14</td>
<td>0.50</td>
<td>3.0</td>
<td>3.0</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
<td>0.10 Ta</td>
<td></td>
</tr>
<tr>
<td>9Cr-1Mo (T9)</td>
<td>0.12</td>
<td>0.6</td>
<td>0.45</td>
<td>9.0</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.10 Ta</td>
<td></td>
</tr>
<tr>
<td>Mod 9Cr-1Mo (T91)</td>
<td>0.10</td>
<td>0.4</td>
<td>0.40</td>
<td>9.0</td>
<td>1.0</td>
<td>0.2</td>
<td>0.08</td>
<td>0.05</td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>E911</td>
<td>0.11</td>
<td>0.4</td>
<td>0.40</td>
<td>9.0</td>
<td>1.0</td>
<td>1.0</td>
<td>0.20</td>
<td>0.08</td>
<td>0.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NF616 (T92)</td>
<td>0.07</td>
<td>0.6</td>
<td>0.45</td>
<td>9.0</td>
<td>0.50</td>
<td>1.8</td>
<td>0.20</td>
<td>0.05</td>
<td>0.04</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>W Nr. 1.4914</td>
<td>0.15</td>
<td>0.45</td>
<td>0.35</td>
<td>11.0</td>
<td>0.50</td>
<td>0.30</td>
<td>0.25</td>
<td>0.008</td>
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Microstructure of ferritic-martensitic steels, which have about 9-12% of Cr, consists of ferrite and austenite stabilizing alloying elements so that 100% austenite forms upon austenization and 100% martensite is formed when quenched or normalized. Upon tempering of these steels at
760°C, most of the martensite transforms into ferrite resulting in a tempered martensite structure. Initially, these steels were developed as materials for fossil fuel power plants. Klueh [3] has summarized various F–M steels that were developed in the last sixty years or so. Continuous development of these steels and microstructural modifications has made their likely use in some Generation IV reactors as they tend to have better corrosion/oxidation resistance than the low-Cr ones. [4]

Some desirable characteristics for the Gen-IV structural materials are noted below [4]:

1. Excellent dimensional stability against thermal and irradiation creep, void swelling, etc.
2. Favorable mechanical properties such as strength, ductility, creep rupture, fatigue, creep–fatigue interactions, etc.
3. Acceptable resistance to radiation damage under high neutron doses, helium embrittlement, etc.
4. High degree of chemical compatibility between the structural materials and the coolant as well as with the fuel. In this regard, stress corrosion cracking, irradiation assisted stress corrosion cracking and many other issues are important.

Further, the out-of-core components (pressure-vessel, piping, etc.) may need to be made from materials other than the low alloy ferritic steels currently employed primarily because similar components in Gen-IV reactors are expected to withstand much higher temperatures [3] and neutron doses. Some of the fabrication difficulty involved in the very high temperature reactors (VHTR) construction demands heavy component forgings [4].
Austenitic stainless steels have good creep resistance to higher temperatures coupled with reasonable corrosion/oxidation resistance. Tempered lath martensite structure is the most important strengthening mechanism in high Cr ferritic steels and its thermal stability is crucial to maintain long-term creep strength of such steels. The tempered lath martensite structures of high Cr steels are not thermally stable, and their static recovery starts after an incubation period. The static recovery is caused by the loss of particle strengthening mainly due to $M_{23}C_6$ precipitates, which is controlled by their thermal stability. The stability of $M_{23}C_6$ precipitates is significantly affected by a change of chemical composition in $M_{23}C_6$ particles during high temperature exposure.

2.2.1: Grade 91 - Modified 9Cr-1Mo steel

Grade 91 is a modification of 9Cr–1Mo steel. The modification consists of additions of vanadium, niobium, and nitrogen and the narrowing of the maximum compositional ranges for carbon, chromium, silicon, molybdenum, phosphorous, and sulphur. Maximum contents are set for nickel and aluminum [2]. Grade 91 is 9Cr-1MoVNb low carbon steel that has a two phase, ferritic-martensitic (F-M) structure. The standard heat treatment consists of a solution annealing in the temperature range of 950-1100°C to completely austenitize the microstructure and dissolve the carbides, and then a tempering treatment in the temperature range of 700-800°C to obtain a good combination of strength, ductility and toughness. When heat-treated to meet the requirements of the specifications for Grade 91, the as-tempered microstructure consists of a fine prior austenite grains that have transformed to a lath-like tempered martensite structure with a high dislocation density that is stabilized by $M_{23}C_6$ carbides and MX carbo-nitrides [2-5]. The sub-grain structure produced by the martensitic transformation and the precipitation of carbides are the primary microstructure features responsible for high temperature creep strength.
While making this steel, the chemical composition should be balanced according to a formulation on the Chromium–Nickel Balance (CNB) as suggested by Swindeman [2] where the elemental contents are in weight percent. If the CNB is less than 10, delta ferrite is not usually present. For CNB between 10 and 12, the presence of delta ferrite is not readily predicted. For CNB above 12, significant quantities of delta ferrite are present. The CNB can be expressed as:

$$CNB = Cr + 6Si + 4Mo + 1.5W + 11V + 5Nb + 9Ti + 12Al - 40C - 30n - 4Ni - 2Mn - Cu$$

2.2.1a Tempered Martensite

Martensite is formed in carbon steels and has a body centered tetragonal (BCT) crystal structure. It is formed by a diffusionless transformation while rapid cooling (quenching) of austenite. Carbon atoms do not have time to diffuse out of the crystal structure to form cementite (Fe₃C). As a result, the face centered cubic austenite transforms to a highly strained body centered cubic form of ferrite that is supersaturated with carbon. Tempering is a heat treatment process, which is used to increase the toughness and reduce the excess in hardened alloys. In low carbon alloys steels, tempering can be used to alter the sizes and distribution of carbides in the hard martensite lath and boundaries to form a microstructure called tempered martensite. Tiny micro-grains and a high density of free dislocations are key features of the microstructure of tempered martensite ferritic steels. The microstructure of tempered martensite ferritic steels is complex [15] and consists of a high density of internal interfaces, carbides and free dislocations in body centered cubic (bcc) ferrite [14, 15, and 16].

2.2.1b Initial Microstructure

Precipitation of carbides in the Mod 9cr-1Mo alloy is similar to that in standard 9Cr-1Mo alloys although during the tempering of these modified alloys, fine precipitation of VC along the
lath interfaces improve the stability of these steels up to 650°C even under static tensile and creep conditions [7]. Jones et al [7] also suggest that the lath morphology in this alloy remains intact for long periods at temperatures as high as 650°C owing to the interfacial pinning by VC precipitates which do not coarsen much. While this leads to the expectation of improved high-temperature fatigue and creep resistance, the potential advantages are limited by the apparent tendency for microstructural changes to occur more rapidly under conditions of strain cycling.

The matrix microstructure of the 9Cr-1Mo-V-Nb alloy is very sensitive to cooling rate. The precipitation reactions during tempering after a normalizing treatment were followed as a function of tempering treatment. In the 9Cr-1Mo-V-Nb alloy, a combination of chromium-rich M23C6 and vanadium-niobium-rich MC carbides were found [6].

Critical strain required for the onset of serrated flow during the tensile testing of these steels increased with the increase in the strength of steel which ultimately depends on the microstructure. Higher strain and higher strength decreases the inter-barrier distance to dislocation motion and also increase in density of precipitate sinks for removal of carbon/nitrogen atoms from the dislocations in the steel [6].

The distribution of precipitates in the alloy after creep is bimodal, including MX carbides and nitrides inside the lath and M23C6 on the sub-grain boundaries. All the precipitates coarsen during creep [11]. Sub-grain size depends linearly on the inverse of the modulus compensated stress in tests to failure and the particles depend on the ratio (stress/modulus) and hence relating the sub-grain size to particle size [11].
2.3. Microstructure Design of High Cr Ferritic Steel

In steels like G91, modified 9Cr-1Mo steel with tempered martensite structure, recovery of dislocation substructure controls creep deformation and further creep failure. Presence of fine sub-grain structure in the material improves its creep deformation resistance. Resistance to recovery of dislocation structure is the main factor essential to have high creep resistance. The microstructure in high Cr steels that help in creep resistance can be described with the following aspects.

2.3.1 Dislocation Substructure

Free dislocation density along with the fine sub-grain structure plays an important role in determining the creep deformation of these steels. The strain to minimum creep rate, known as the primary creep strain depends on the free dislocation density present in the sub-grains. It is easy to control the free dislocation density within sub-grains by changing tempering temperature. Sub-grain size is determined by the dislocation density introduced during the martensitic transformation.

Singh and Bhadeshia [17] have proposed that a large driving force for martensitic transformation and a large deformation resistance of the austenitic phase surrounding martensite domains are required for making a fine sub-grain structure. Low transformation temperature of martensite is also good to produce fine sub-grains. [18]

The presence of high dislocation density should be supported by prevention of recovery of dislocation substructure to improve creep resistance. The recovery of dislocation structures occurs by annihilation of the dislocations from the sub-grain interiors with the dislocations on the sub-grain boundaries. Illustration of dislocation annihilation is depicted in Figure 2.1.
2.3.2 Pinning Particles

Recovery of the sub-grain structure can occur in two ways [19]: (a) Annihilation of dislocations constituting the sub-grain boundaries leading to their disappearance as shown in Figure 2.1 and (b) annihilation of two sub-grain boundaries with each other. The first process occurs during all the stages of recovery, whereas the second process occurs during the final stages of recovery. Dislocations present in the sub-boundaries are stable after tempering and they do not climb. If the dislocations from the matrix glide into the sub-grain boundaries, they disturb the stability and lead to annihilation of dislocations in the sub-grain boundaries. This high driving force of the particles can be counteracted using high pinning force of particles, which is also related to interparticle spacing. Fine interparticle spacing of M$_{23}$C$_6$ particles will maintain the fine sub-grain structure to longer times.

Figure 2.2 indicates the typical microstructure of Mod. 9Cr-1Mo steel after the normalization and tempering treatments for high creep strength designed by Jones et al. [7].
2.4: Alloy Design for Stable Dislocation Substructure

2.4.1 Self-diffusion Coefficient

Diffusion coefficient of the material should be as low as possible for creep resistant materials so that they retain fine particles for long duration to slow down the recovery process of dislocation substructure.

2.4.2 Pinning Particles

Dislocation climb is obstructed by the particles present of the sub-grain boundaries, which, in turn, slows down the recovery of sub-grain structure. Higher the density of the pinning particles, slower will be the recovery of the substructure. In high Cr steels, M\textsubscript{23}C\textsubscript{6} particles are the major obstacles to grain boundary movement, since they have the highest density and they decorate the sub-grain boundaries. These particles along with MX particles form during the tempering of steels and they coarsen with creep exposure. In order to make good use of the pinning particles, we have to understand their precipitation and coarsening behavior during high temperature exposure. Figure 2.3 indicates studies by Maruyama et al. [9] to understand the coarsening behavior of
various carbides present in F-M steels under the effect of temperature at 650°C. The M\textsubscript{23}C\textsubscript{6} carbides are stable up to $10^4$ hours whereas the MX particles are stable for longer periods of time when exposed to high temperatures.

![Inter-Particle Spacing vs Aging Time](image)

**Figure 2.3: Inter-particle spacing vs. aging time [9]**

### 2.4.3 Precipitation of Carbide particles

The kinetics of precipitation of carbide particles follows Johnson-Mehl-Avrami equation [20]. Precipitation also proceeds faster when the diffusivity and density of precipitation sites are high.

### 2.4.4 Ostwald Ripening

As pinning particles coarsen, there is agglomeration and reduction in pinning force. For high pinning force, the particles should not coarsen. Coarsening can occur by interface diffusion, volume diffusion, grain boundary diffusion and pipe diffusion. The coarsening of particles in ferritic steels is accelerated by creep deformation, as reported previously [9, 19].
2.4.5 Loss of Creep Strength

Kushima et al. [21] have proposed that the enhanced recovery is the origin of the loss of rupture strength. During long-term tests, the enhanced recovery of sub-grain structure takes place. Strain concentration along the boundary regions forms grain boundary cracks. This results in the low ductility, the premature failure and the loss of rupture strength. In high Cr steel, therefore, the loss of rupture strength accords with the quick coarsening of $\text{M}_2\text{C}_6$. The loss of creep strength can be delayed when the elements that reduce the self-diffusion coefficient of ferrite matrix are removed [19].

2.5: Literature Review on Creep Testing

A material subjected to a constant tensile load at an elevated temperature will creep and undergo time dependent increase in length. Creep becomes of engineering significance at a homologous temperature greater than 0.5. The creep test measures the dimensional changes that occur from elevated temperature exposure and stress rupture test measures the effect of high stresses / temperature in short term load bearing conditions. To determine the creep curve of a metal, a constant load is applied to a tensile specimen maintained at constant temperature and strain of the specimen is calculated as a function of time. [ASTM E139-70]. The slope of this curve is the creep rate. The creep rate initially decreases with time and then reaches a steady state in which creep rate does not change much with time and finally it increases rapidly with time until fracture. The average value of creep rate during the secondary creep stage which is the constant creep rate stage is known as the minimum creep rate. The different types of creep mechanisms are listed below [22]:
1. **Dislocation glide**

   It occurs at high stress and low temperatures, which involves movement of dislocations along the slip places overcoming barriers by thermal activation.

2. **Dislocation creep**

   It occurs by dislocation glide aided by climb through vacancy diffusion. At high temperature if a gliding dislocation is held up by an obstacle, a small amount of climb may permit it to surmount the obstacle, allowing it to glide to the next obstacle where the process is repeated. Since dislocation climb requires diffusion of vacancies or interstitials, the rate controlling step is atomic diffusion.

3. **Diffusion Creep**

   It occurs at high temperatures and low stresses. Creep process here is controlled by stress directed atomic diffusion as suggested by Nabarro and Herring. Flow of vacancies from grain boundaries experiencing tensile stress to those which have compressive stresses and simultaneous flow of atoms in the opposite direction leads to elongation of grain. Nabarro-Herring and Coble creep are two sub-types in this mechanism of creep.

4. **Grain boundary sliding**

   Grain boundary sliding does not contribute significantly to steady-state creep, but it must be present to maintain grain boundary continuity during diffusional flow mechanisms.
2.5.1 Long term creep studies of Mod. 9Cr-1Mo steel

Maruyama et al. [9], Spigarelli et al. [23], Anderson et al. [10] and Ennis et al. [24], conducted creep tests on various 9Cr-1Mo modified steels at several temperature-stress combinations and all observed that these steels exhibit a normal three-stage creep behavior with a primary stage of a decreasing creep rate, a very short secondary region or rather a minimum creep rate followed by the tertiary stage leading to fracture. Creep curves are generally represented strain vs time which gives the time to rupture and the minimum creep rate, both of which are used as design criteria for alloys.

Creep strength of G91, Modified 9Cr-1Mo martensitic heat-resistant steel deteriorates severely when it is exposed at 650°C and higher temperatures under certain stress and corresponding microstructure becomes unstable. The microstructure evolution is accelerated obviously which may be related to enhancing self-diffusion coefficient at 650°C near Curie temperature.

Creep deformation property of 9Cr–1Mo–V–Nb steels was investigated by Kimura et al. [21]. It was discussed that large stress dependence of creep rupture life and minimum creep rate in the high-stress regime, whereas it decreased in the low stress regime. Creep strain at minimum creep rate decreases as the stress decreases [21].

Static recovery of lath martensite is one of the main reasons for the breakdown of the creep strength in these steels when exposed to high temperatures and low stress levels [9]. The sub-grain width is constant in shorter time range during aging and then increases with aging time at temperatures in the range 600 – 650°C. At higher times, the sub-grains are thermally unstable increase in size according to the equation given below [9].
\[ d^3 = d_0^3 + K_1 D t \]  

(2.1)

Where, \( d \) = average sub-grain width

\( d_0 \) = initial value of sub-grain width

\( K_1 \) = material constant

\( D \) = diffusion constant

\( t \) = aging time

The static recovery of sub-grains is controlled only by the aggregation of \( M_{23}C_6 \) precipitates and not MX precipitates [8]. Static recovery of sub-grains can be evaluated by hardness measurement of aged microstructures. Drop in hardness due to loss of sub-grain boundaries which are the main obstacles against movement of dislocations indicates static recovery. Static recovery is caused by loss of pinning ability of MX and \( M_{23}C_6 \) particles [9, 25].

Instability of fine precipitates like MX, \( Cr_2X \) and \( M_{23}C_6 \) are necessary factors to be considered for the creep degradation of steels with 9\% Cr as the alloying element [21, 26]. Another reason for the breakdown of creep strength in such steels is cavity nucleation at coarse Laves phase particles which coarsen during creep on grain boundaries. These cavities trigger brittle inter-granular fracture [26, 27].

Stress exponent values were found to be about 12 at 650°C and at the high stress levels were reported by Kimura et al [11]. An activation energy of ~612 kJ/mol was reported by Choudhary et al [16] in their study of the Modified 9Cr-1Mo steels at IGCAR. It has been suggested that the grain boundary cohesion of 9Cr–1Mo steel is high and the relative strength of
matrix and grain boundaries are similar, which inhibits any stress concentration at the grain boundaries and subsequent development of cavitation damage [28, 29, and 39].

In general, 2.25Cr–1Mo and other low chromium low alloy ferritic steels suffer from loss of creep ductility and typical inter-granular creep damage due to formation of precipitate free zones (PFZs) along the prior austenite grain boundaries [4, 30]. The PFZs facilitate strain concentration resulting from zone shear and grain boundary sliding processes leading to cavitation damage [30].

As suggested by Choudhary et al [28], Modified 9Cr-1Mo steel exhibits negligible instantaneous strain, a small transient creep strain and secondary creep followed by a prolonged tertiary creep regime during long term creep at low stress levels. It was also proposed that the stress dependence of minimum creep rate and rupture life obeyed power law and exhibited high values of the stress exponent. Stress exponents decrease with increasing temperature. Creep of the steel obeys Monkman-Grant relationship. Figure 2.4 shows the strain rate vs. strain curves from various creep tests performed at a temperature of 600°C by Cerri et al. [11].

Figure 2.4: Strain rate vs. strain curve on 9Cr-1Mo steel at 600°C
2.5.2 Creep Mechanism in Mod. 9Cr-1Mo steels

During creep at high temperatures, dynamic recovery of pre-existing dislocation structure happens at a very fast rate and reduces the deformation resistance and the stress dependence of creep. At higher temperatures the precipitates coarsen by diffusion controlled processes and the dislocations have a higher thermal energy to cross over the obstacles (either by climb or by Orowan mechanism). This reduces the effective strength of precipitates as barriers to gliding dislocations and also lowers the stress dependence of creep and the value of stress exponent decreases. [14]

Figure 2.5: Schematic drawing of precipitates in high Cr ferritic steels

High Cr steels like G91, have several obstacles to dislocation motion for improved creep resistance. They include sub-grain boundaries, free dislocations inside the grains and sub-grains, and precipitates which include $M_{23}C_6$ and MX. Figure 2.5 shows a schematic of obstacles to dislocation movement in F-M steels. The strengthening mechanisms can be classified as dislocation hardening, particle hardening and solid solution strengthening. A simple additive rule
does not hold among the three strengthening mechanisms. The most closely spaced obstacles in a material determine the athermal yield stress of the material.

2.5.2a Dislocation Hardening

Strengthening by dislocation hardening arises due to hindering dislocation motion. Because of this, plastic deformation is highly reduced at low stresses. The dislocation substructure will reduce the creep rate in the presence of particles and solute atoms. The dislocation substructure cannot be retained during creep without the presence of obstacles which include particles and solute atoms. Similarly, particles and solute atoms also reduce the creep rate effectively in the presence of dislocation substructure. Hence, dispersed particles and the solute atoms assist the dislocation hardening in addition to their own roles in strengthening.

2.5.2b Particle Hardening

Particle hardening or precipitation hardening depends on the production of fine particles in the matrix or at the grain boundaries, which impede the movement of dislocations and defects in lattice. These precipitates are produced due to changes in solid solubility of the alloy with temperature. These particles play the same role as the particles in particle-reinforced composite materials. The particles decorating the sub-grain boundaries improve the creep resistance by slowing down the recovery of dislocation substructure. In steels having the dislocation substructure typical of tempered martensite, the M_23C_6 particles obviously improve creep resistance, since they slow down the recovery of the dislocation substructure [31]. Tempering of martensite can be categorized into stages. During the first stage, excess carbon in solid solution segregates to defects or forms clusters within the solid solution. Then precipitates form, either as cementite in low-carbon steels, or as transition iron-carbides in high-carbon alloys. In the presence of alloying elements, some of the carbon also forms carbides with the solute atoms. Further annealing leads
to stage 2, in which almost all of the excess carbon is precipitated, and the carbides convert to more stable cementite. Any retained austenite decomposes into ferrite in this stage [31].

Carbides exert Zener forces on sub-grain boundaries. The particles prevent the motion of LAGB and HAGB by exerting pinning pressure, which counteracts the driving force for migration of these boundaries. Zener pinning has a strong influence on recovery, recrystallization and grain growth. When a boundary passes through an incoherent particle then the portion of boundary that would be inside the particle essentially ceases to exist. In order to move past the particle, a new boundary must be created, and this is energetically unfavourable. While the region of the boundary near the particle is pinned, the rest of the boundary continues trying to move forward under its own driving force. This can be seen in Figure 2.6 [32].

![Figure 2.6: Interaction of a boundary and a particle [33]](image-url)
2.5.2c Obstacle-Controlled Creep Rate

At high temperatures, diffusion helps dislocations move past the obstacles and the yield stress decreases. During creep, dislocation substructure is the major obstacle controlling the creep rate, especially when it does not recover during the test. The dislocation density present in the sub-grains decrease and the sub-grain size increases as creep proceeds. These changes are the typical recovery process of the dislocation substructure. Dislocation substructure is the main obstacle that hinders the dislocation motion during creep.

2.5.2d Recovery of Dislocation Substructure

Dislocation substructure of tempered martensite is stable even to 650°C but plastic deformation leads to decrease in this stability and promotes recovery. During creep of tempered martensite structure, the sub-grain width increases and free dislocation density within the sub-grains decreases. The elongated sub-grains typical of the martensitic transformation will become equi-axed sub-grains because of creep deformation. The sub-grain width increases with creep strain and then reaches a stationary value above a critical strain. Similar saturation occurs in the free dislocation density within sub-grains [19].

2.5.2e Effects of Recovery Speed on Creep Deformation Resistance

Slow growth of the sub-grain width reduces the creep rate and consequently extends creep rupture life. The good correlation between the recovery speed and the creep rate from various studies [19] confirms the decisive role of the dislocation substructure in creep.

2.5.3: Internal Stress

Various sources of internal stress in T91 are discussed in the discussion section, Chapter 5 and these internal stresses are affected by the application of stress and temperature. During creep,
internal stress due to the dislocations decreases at a rapid rate, which reduces their effect in contributing to creep strength. The dislocation network acts as a weak obstacle to the gliding dislocations. The carbides in the matrix coarsen with time and their size renders them as weak obstacles. Major strengthening factor in modified 9Cr-1Mo steels is the sub-grain substructure and carbides. The carbides on these boundaries prevent dislocation migration and also the knitting in and out reactions delaying coarsening of the sub-grains. The internal stress due to the sub-grain boundaries is inversely related to the distance between these boundaries.

2.6: Useful theoretical concepts

This section discusses some theoretical concepts required to understand the present thesis effectively.

2.6.1 Grain boundaries

The types of grain boundaries based on the misorientation angle can be categorized as those having misorientation angle greater than a certain angle – high angle grain boundaries (HAGB), and those whose misorientation is less than this angle – low angle grain boundaries (LAGB). The angle at which the transition from low to high angle boundaries occurs is typically taken as between 10 and 15 and is to some extent dependent on what properties of the boundary are of interest. In general, low angle boundaries are those that can be considered to be composed of arrays of dislocations and whose structure and properties vary as a function of misorientation, whilst high angle boundaries are those whose structure and properties are not generally dependent on the misorientation. There are also some special high angle boundaries that do have characteristic structures and properties [34].
2.6.1a Sub-grain boundary structure

The transition crystalline region, where atoms are shifted from their original positions, separating two crystals or grains of different orientations is referred to as the grain boundary. Phase boundary is the interface between grains which differ in chemical composition and structure [35]. The macroscopic structure of grain boundaries is commonly assessed according to the relative orientation between the two neighbouring grains [36].

2.6.2 Dynamic Recrystallization

During the deformation at high temperatures, softening processes of recovery and recrystallization can occur, also called dynamic recovery and recrystallization, which involves static annealing process. Dynamic recovery and dynamic recrystallization occur during metalworking operations such as hot rolling, extrusion and forging and can also occur during creep deformation, the main difference between hot working and creep being the strain rate. Hot working is generally carried out at strain rates in the range of 1–100 s⁻¹, whereas typical creep rates are below 10⁻⁵ s⁻¹. In many cases similar atomistic mechanisms occur during both types of deformation. [34]

Dynamic recovery occurs via dislocation climb, cross slip and glide, which results in formation of low angle grain boundaries. Applied stress provides additional driving force for the movement of LAGBs and those of opposite sign will be driven in opposite directions, and this stress-assisted migration of dislocation boundaries may contribute significantly to the overall strain. Such migration results in some annihilation of dislocations in opposing boundaries and Y-junction boundary interactions and these enable the sub-grains to remain approximately equi-axed
during the deformation. The sub-grains can therefore be considered to be transient microstructural features.

During steady state deformation, the dislocation and sub-grain structure almost remains constant and the original grain boundaries do not migrate much but the grains change shape. Though the flow stress remains constant, microstructural steady state is not achieved when dynamic recovery occurs. This is particularly true if the strain is sufficient to reduce the separation of high angle boundaries to a value comparable with the sub-grain size.

There are two types of dynamic recrystallization: 1) discontinuous and 2) continuous. Discontinuous dynamic recrystallization occurs by nucleation and grain growth. The grains after this stage are coarse and distributed heterogeneously throughout the deformed area. In continuous dynamic recrystallization, progressive accumulation of dislocations occur in low angle grain boundaries, which lead to increase in their misorientation and they progressively form high angle grain boundaries. After continuous dynamic recrystallization, uniform distribution of small grains in the matrix is observed [37, 38].

2.6.2a Discontinuous dynamic recrystallization

During dynamic recrystallization new grains originate at the old grain boundaries, but, as the material continues to deform, the dislocation density in the new grains increases, thus reducing the driving force for further growth, and the recrystallizing grains eventually cease to grow. An additional factor which may limit the growth of the new grains is the nucleation of additional grains at the migrating boundaries. This type of dynamic recrystallization, which has clear nucleation and growth stages, can be classified as a discontinuous process. There are other mechanisms which
produce high angle grain boundaries during high temperature deformation, and which may be considered to be types of dynamic recrystallization.

2.6.2b Continuous dynamic recrystallization

Continuous dynamic recrystallization can be classified into two types which are geometric dynamic recrystallization that occurs during annealing of highly strained alloys and the other being gradual rotation of sub-grains adjacent to high angle boundaries.

2.6.2c Dynamic recrystallization by progressive lattice rotation

There is considerable evidence that in certain materials, new grains with high angle boundaries may be formed during straining, by the progressive rotation of sub-grains with little accompanying boundary migration. This is a strain-induced phenomenon, which involves rotation of sub-grains adjacent to pre-existing grain boundaries as the material is strained. Grains develop a gradient of misorientation from centre to edge with the ones at the edge having comparatively higher misorientation. Hence, towards the grain boundary, the misorientations increase, and at larger strains, high angle boundaries may develop [34].
CHAPTER 3. EXPERIMENTAL METHODOLOGY

This chapter gives the general description of the materials used in the current study, creep testing of the materials and creep parameters, sample preparation techniques and instruments used for characterization like TEM (Transmission Electron Microscopy), SEM (Scanning Electron Microscopy), Electron Back Scattered Diffraction and Hardness measurement.

3.1 As-Received Steel

Two blocks of Modified 9Cr-1Mo steel of dimensions 10in X 5in X 2in were obtained from Idaho National Lab (INL). The blocks were normalized and tempered, as per the usual heat treatment recommended for Mod. 9Cr-1Mo steels for producing an initial microstructure of tempered martensite. The rolled steel plate was normalized at 1035°C for about 33 minutes and tempered at 785°C for about 90 minutes and air cooled after the heat treatment. The heat treatment schedule with temperatures and times of treatment can be seen in the Figure 3.1.

![Heat Treatment graph for Modified 9Cr-1Mo steel](image)

*Figure 3.1: Heat Treatment graph for Modified 9Cr-1Mo steel*
The composition of the Modified 9Cr-1Mo steel used in the present work is given in Table 3.1 below.

**Table 3.1: Composition of Modified 9Cr-1Mo steel**

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Cu</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>V</th>
<th>Ti</th>
<th>Al</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>.09</td>
<td>.46</td>
<td>.012</td>
<td>.002</td>
<td>.13</td>
<td>.27</td>
<td>.22</td>
<td>8.4</td>
<td>.89</td>
<td>.211</td>
<td>.002</td>
<td>.012</td>
<td>.42</td>
<td>Rest</td>
</tr>
</tbody>
</table>

**3.2 Creep Testing of Modified 9Cr-1Mo steel**

The blocks received from INL were then sent to Cincinnati Testing Labs (CTL) for machining of creep samples. Standard creep samples of dimensions shown in the below in Figure 3.2 were machined out by CTL. Creep test were then performed on these samples. To determine the creep curve, a constant load is applied to a tensile specimen maintained at constant temperature and strain, in the specimen is measured using an extensometer is calculated as a function of time as per ASTM E139-70. Creep was carried out at a temperature of 650°C and at different stress levels, namely 140MPa, 120MPa, 100MPa and 80MPa. The creep test was also carried out to different time intervals at the stress values of 120MPa, 100MPa and 80MPa, namely 25% life, 50% life and 75% life. The total fracture life at a stress level was initially established by performing 3 or 4 creep tests up to failure and the total time taken up to fracture was averaged. Then the 25%, 50% and 75% creep life values were calculated and creep tests were again performed this time up to the required quarter of life and not up to fracture.
Figure 3.2: Standard bar specimen for creep testing

3.3: Material Characterization

The various characterization techniques used in present work for microstructural characterization of as-received steel and steel after creep testing at all combinations of stress and temperature are discussed below.

3.3.1: Scanning electron microscopy (SEM)

The SEM is one of the most versatile instruments for investigating the microstructure of materials. Visible light used in optical microscopes has wavelengths from 4,000 - 7,000Å; while electrons accelerated to 10,000 KeV have a wavelength of 0.12Å providing much higher resolution. Under electron bombardment, a variety of different signals are generated (including secondary electrons, backscattered electrons, characteristic x-rays, and long-wave radiation in the ultraviolet and visible region of the spectrum) that can be used for materials characterization. With secondary electrons, SEM expands the resolution range to a few nanometres (under favourable conditions), thus bridging the gap between optical (light) microscopy and transmission electron
microscopy. Electron microscopes work by generating a beam of electrons in vacuum, which on interacting with the sample surface, generate different responses. The most common mode of imaging is using secondary electrons (SE), which are low energy electrons generated by inelastic interaction of beam electrons with the sample atoms, causing ejection of electrons from the outer orbitals of atoms. These secondary electrons are then detected by an Everhart-Thornley Detector (E-T detector), which is a scintillator-photomultiplier system. As the secondary electrons originate from a very shallow distance (in tens of nanometres) from the surface, they provide contrast based on topography of the sample and emission. In addition to the higher lateral resolution, SEM also has a much greater depth of field compared to optical microscopy, due to the small size of the final lens aperture and the small working distance. SEM offers possibilities for image formation that are usually easy to interpret and will reveal clear pictures of as-polished and etched cross sections as well as rough surfaces and particles. Backscattered electron (BSE) imaging mode utilizes backscattered electrons to obtain compositional information from the samples.

To characterize the crept samples at every stage, the SEM was used. The trapezium shaped area starting from the uniform gage section till the fractured area was cut using an Accutex electrical discharge machine (EDM). Small areas from the uniform gage section were also cut using the EDM from the uniformly elongated samples at different life fractions as mentioned above. All the samples were polished to a mirror finish using different grades of SiC papers starting from 600 grit to 1200 grit and then with the Buehler diamond micron pastes of 3µ and 1µ particles. The final polishing was carried out using the Buehler colloidal silica to obtain perfect mirror finish without any scratches. These samples were then etched using the Villella agent to reveal the individual grains, grain boundaries and the particles along the boundaries. Various etchants used in general for alloy steels were tried to reveal all the details. The best one was found to be Villella
etchant, which revealed all the grain boundaries and precipitates very well. The composition of Villella agent is 1gm picric acid in 5ml of HCl and 100ml of ethanol. These etched samples were then observed under the FEI XL-30 FEG ESEM in the SE mode with an accelerating voltage of 15V and spot size 4. Images were captured at magnifications of 3500x and 8000x to record the grains, cavities and precipitates from different areas of the samples. The images were captured from the fractured samples, at a distance of 100µ from the fracture to 600µ at different locations at a distance of 150µ each.

3.3.2 Electron backscatter diffraction (EBSD)

Electron backscatter diffraction is a SEM based microstructural-crystallographic technique to measure the crystallographic orientations of grains in a crystalline material. The electron beam is scanned in a grid across a polycrystalline material and the crystal orientation is measured at each point. This results into a map that will reveal the constituent grain morphology, orientations, boundaries and the texture present in the material. This map is called the orientation map. EBSD makes use of Kikuchi patterns to determine the crystallographic information. When an electron beam is incident on a crystalline material, electrons diffuse in all directions, forming a point source. Some of these electrons satisfy Bragg’s condition for different sets of planes. These electrons diffract corresponding to each diffracting plane and form a cone corresponding to each set of planes (Kossel cones). These cones upon intersecting with a phosphor screen give the appearance of a band, which is characteristic of the diffracting planes. For EBSD analysis, the sample is tilted 70° from the horizontal as it enhances the fractions of electrons scattered from sample. Since the width of these Kikuchi patterns is related to inter-planar spacing and the angle between the bands relate to angles between the diffracting planes, these Kikuchi patterns can then be indexed to
identify the planes and the zone axis. The Kikuchi patterns can be analysed to get information on texture, grains and grain boundaries and phase discrimination.

Samples for EBSD were polished for about 60 minutes on a micro-cloth with colloidal silica to get better surface finish since electron back scattered diffraction is quite sensitive and picks up even sub-surface deformation due to deeper scratches from prior polishing steps. EBSD mapping and misorientation analysis of grain boundaries of as-received material as well as the crept materials at all stages was carried out using FEI XL-30 FEG ESEM with TSL 4000 system.

3.3.3 Transmission Electron Microscopy (TEM)

Transmission electron microscopy (TEM) is technique in which a beam of highly focused electrons is transmitted through a thin sample (<100 nm). As this beam interacts with the material, some of it transmits directly through the foil while some are diffracted. Information on sample is gathered from both transmitted and diffracted beam. The contrast generated is essentially due to the variation in intensity of diffraction in the sample. A great advantage in TEM is the ability to obtain images as well as diffraction patterns from the same location, enabling study of microstructure and crystal structure simultaneously.

TEM observation of the thin foils were carried out on an analytical Philips CM20 TEM with Gatan CCD, EDAX and nanoprobe mode operating at 200 kV. Thin foils for TEM were sliced using a diamond saw followed by mechanical grinding to 100 microns and then reached to electron transparency using two techniques as described below.
3.3.3a **Twin Jet Electro polishing**

This is the conventional method of preparing TEM thin foils for metallic samples. Thin slices were sectioned from the area of interest and thinned down by mechanical grinding up to a thickness of ~ 100 μm. Disc of 3mm diameter were then punched using a disc punch. The discs were polished on SiC paper to remove burs, formed from the punching and then further thinned down to ~80 μm. The sample was then electrolytically polished using a Fischione Model 110 Twin-Jet Electro polisher. In this electro polisher two jets of electrolyte are incident on the opposite sides of disc, near the centre and appropriate voltage is applied to the sample through a platinum anode to polish the sample till a hole is struck near the centre of sample. The hole is detected by a photo cell which stops the polishing as soon as the hole is struck. The areas around that hole are electron transparent and used for analysis. The advantage of polishing with this method is that no mechanical force is used on the thin sample and hence in a case where plastic deformation is to be studied one can eliminate sample preparation as a source of deformation. The following conditions were used for polishing the samples in this study: Electrolyte- 10% Perchloric acid + 90% Ethanol, Voltage -30V, Temperature of the electrolyte = -40°C.

3.3.3a **Dimpling and Ion milling**

Dimpling and then Ion milling is a mechanical method of preparing TEM foils for analysis. This technique can be used to obtain samples from very specific areas and areas from where only one foil can be made, like near fracture areas. To prepare such a sample, a thin slice was sectioned from the required area. This slice was thinned down to 100μm by mechanical polishing and then 3mm discs were punched out. A dimpling wheel with diamond paste media ranging from 6μ to 1μ was then used to thin the center of this disc to a thickness of ~ 20μm. The disc was then polished
with a polishing wheel using non-crystallizing colloidal silica (0.02 μm) to a mirror finish, till all scratches were removed. This was done to remove any deformation layer introduced due to sample preparation. After this, the 3mm disc was ion-milled using a Fischione instruments Model 1010 ion mill until perforation was detected by a laser beam photo cell device. During ion milling, the centre of sample is thinned by sputtering using inert gas (Ar) ions. As soon as the perforation is achieved, the milling is terminated by detection of a laser light. Two ion sources are used to thin sample faster, from opposing surfaces of the disc. Sample was also cooled using liquid nitrogen to avoid any artefacts and continuously oscillated 60° during ion milling, to have a larger thin area. Following ion milling parameters were used: Current: 5mA, Voltage 5V, Sample rotation = 60°, Beam Incident Angle =14°, stage temperature = -80° C

The techniques of Dimpling and ion milling were used for samples from the gauge area where the sampling area was small and only one or two TEM discs could be made. TEM thin foils were prepared from the gauge areas of the 80MPa and 140MPa crept sample. TEM thin foils were then prepared from the as-received samples, grip areas of 80MPa and 140MPa samples which have undergone only heat treatment at 650°C for different times with twin jet electro-polishing.

3.3.4 Image analysis using Image J

ImageJ is a public domain, Java-based image processing program developed at the National Institutes of Health. ImageJ was designed with an open architecture that provides extensibility via Java plugins and recordable macros. The SEM images captured from the crept samples were analysed using image J for the cavity size & densities and precipitate size. In each case, 5 images were analysed. The images at a distance of 100 microns from the fracture surface were captured at 5 different locations and the cavities were analysed. The cavity density was then calculated by
averaging the total number of cavities over the total area in the images. These cavity density values are reported and compared in the results section. Similarly, sizes of the carbides along the grain boundaries were also calculated for every stage of the crept samples using ImageJ. These values are also reported and compared in the Chapter 4.

To calculate the grain size, ASTM standard for grain size measurement was used.

3.4 Hardness Measurement

Micro hardness measurements on the polished samples were made using knoop indenter on a LECO micro hardness tester at 500 gm load for 15 seconds on the polished surface. Knoop micro hardness tests were conducted on all the samples to observe the hardness variation trends as the creep proceeds at all the stress levels and also as the hardness varies from the fractured area to the non-necked gage area along the variation of strain. The trends are plotted and compared in the Chapter 4.
CHAPTER 4. RESULTS

In this chapter, the results obtained in the present work, from the creep testing of modified 9Cr-1Mo steel and microstructure characterization during the creep at various stress levels and temperature of 650°C are presented in the form of plots, analysis of data and micrographs. The experiments comprise of creep testing, microscopy using SEM, EBSD and TEM and hardness evaluation using Knoop and Vickers indenters.

4.1 Initial Microstructure

A small sample measuring 1cm by 1cm was cut out of the rolled and heat treated block of the Modified 9Cr-1Mo steel received from Idaho national laboratory (INL). The sample was polished and etched as described in the section 3.3 in Chapter 3. An SEM micrograph showing the initial microstructure of the as-received steel can be seen in the Figure 4.1. The initial grain size was calculated to be ~5µm manually using image analysis as described in the E1382-97, Standard test methods for determining average grain size using automatic and semiautomatic image analysis by ASTM.

Figure 4.1: SEM image of as-received Modified 9Cr-1Mo steel
The micrograph in Figure 4.1 shows the typical tempered martensite structure that exists in these kinds of steels after the initial normalization and tempering treatment as mentioned in section 3.1. The microstructure consists of laths of tempered martensite with uniform sub-grain structure within the laths. The sub-grain boundaries are decorated by $M_{23}C_6$ ($M = Cr$) carbides and $MC$ ($M = V, Nb$) carbides are present inside the grains. The EBSD orientation map of the as-received steel is seen in Figure 4.2, which demonstrates the lath structure of the tempered martensite with a uniform sub-grain structure as well. The fractions of low angle grain boundaries ($<15^\circ$ misorientation) and high angle grain boundaries ($>15^\circ$ misorientation) in the as-received material microstructure are 0.43 and 0.57 respectively. On an average each grain consists of 3 sub-grains. The pole figure in Figure 4.2 suggests that the as-received material has a random texture.

![Figure 4.2: EBSD orientation map and pole figure of the as-received Mod. 9Cr-1Mo steel](image)

Figure 4.3 illustrates the images obtained by TEM of the as-received steel after the normalization and tempering treatments. The details of normalization and tempering are described in section 3.1 in Chapter 3, experimental methodology. The tempered martensite laths which are typically ferrite and carbide particles decorating the sub-grain boundary triple points can be seen evidently in the TEM images. TEM micrographs in Figure 4.3 (a) and (b) indicate that the as-
received steel has a microstructure characterized by grains and micron sized uniform sub-grains with carbides at triple points and grain boundaries. Much smaller carbides can also be seen within the grains/laths, which are suggested to MC carbides based on the previous reports [5, 8, 9, 10 and 11]. A high density of dislocations can be observed in the micrographs.

Figure 4.3(a), (b): TEM images of as-received Mod. 9Cr-1Mo steel

4.2 Results from Creep Tests on Modified 9Cr-1Mo Steel

Standard creep samples were machined out of the blocks of the as-received Modified 9Cr-1Mo steel and creep testing was performed as detailed in the section 3.2. Creep testing was performed at various stress levels ranging from 80MPa to 140MPa and at different life intervals ranging from 0.25t_f (t_f = time to fracture) to 0.75t_f and until fracture. All the creep tests were performed at a temperature of 650°C.

Figure 4.4 shows the strain versus time graphs of all the crept samples at stress levels of 140MPa, 120MPa, 100MPa and 80MPa. The rupture strain of all the samples was manually calculated to be ~50% from the dimensions of the fractured samples at all the stress levels.
Table 4.1 indicates the minimum creep rates and creep rupture life at different stress levels derived from the creep curves in Figure 4.4. It can be seen that the rupture life increases exponentially with a decrease of 20MPa of stress at every step. It can also be noticed that the minimum creep rate is much lower at a lower stress levels.

**Table 4.1: Creep data at all the stress levels**

<table>
<thead>
<tr>
<th>Stress (MPa)</th>
<th>Rupture time (Hrs)</th>
<th>Min. Creep Rate (%/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>50.2</td>
<td>0.5</td>
</tr>
<tr>
<td>120</td>
<td>58</td>
<td>0.07</td>
</tr>
<tr>
<td>100</td>
<td>343</td>
<td>0.016</td>
</tr>
<tr>
<td>80</td>
<td>1459.7</td>
<td>0.0078</td>
</tr>
</tbody>
</table>
It can be seen that at all the stress levels in the range of 80-140MPa at 650°C, the primary creep region is very quick similar to those at lower temperatures and stress levels. But, at high temperature-high stress combination, the min creep region which is the secondary region is prolonged and the tertiary region is very quick. At temperatures below 600°C, it was observed that secondary region is quick and the tertiary region is prolonged [11, 40].

Figure 4.6 is a log – log plot of the minimum creep rate versus the stress. Regression analysis of the data gave a good linear fit, from which the stress exponent, n, was determined to be 9.
Dispersion strengthened alloys are characterized by exponents higher than 7 and high activation energies [22]. The slope from the above graph, which is the stress exponent for creep of Modified 9Cr-1Mo steel, $n \sim 9$, indicates that the mechanism of creep at these stress levels is dislocation creep.

Figure 4.7: Stress rupture plot for Modified 9Cr-1Mo Steel at 650°C
The stress rupture plot from the creep data obtained in the present work can be seen in the Figure 4.7. A change of slope on the stress rupture plot indicates a change in creep mechanism and from the present plot we can conclude that there is a slight change in mechanism of creep as stress goes beyond 100MPa at 650°C. The plot in Figure 4.7 can be used to extrapolate and find out the creep rupture life to at lower stress levels.

As also mentioned in the objectives, the creep behavior was also studied at different fractions of creep life i.e. time to fracture, $t_f$ which are 0.25$t_f$, 0.5$t_f$ and 0.75$t_f$ at 120MPa, 100MPa and 80MPa. The creep curves at different fractions of creep life are also plotted and the creep data was analysed.

*Figure 4.8: Creep behavior as it proceeds at 120MPa, 650°C*
Table 4.2: Creep data at different life stages at 120MPa, 650°C

<table>
<thead>
<tr>
<th>Fraction of life at 120MPa</th>
<th>Creep time (hrs)</th>
<th>Creep Strain (%)</th>
<th>Grain size (µ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25% Life</td>
<td>16</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>50% Life</td>
<td>32.3</td>
<td>3.9</td>
<td>5</td>
</tr>
<tr>
<td>75% Life</td>
<td>48.3</td>
<td>4.1</td>
<td>5</td>
</tr>
<tr>
<td>Fracture</td>
<td>58</td>
<td>~50</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Figure 4.8 indicates the creep behavior, i.e. stress versus strain graphs at 120MPa at four life fractions as creep proceeds. Table 4.1 indicates the creep time and strain and the grain size at all the life fractions at this stress level. From the creep curves we can observe that up to 75% of the rupture life, the creep strain is as low as 4% but in the last quarter of the life there is a drastic increase in strain until fracture. Hence, maximum deformation from necking to failure takes place in the final quarter of life, representing a catastrophic failure. The grain sizes at each stage of creep were calculated manually according to the ASTM standards. Uniform grain size of ~5µm was observed until 0.75t. The grain size at fracture could not be calculated as elongation of grains was observed after 75% of life and hence the grain size calculations are not accurate.

Figure 4.9 indicates the creep curves i.e. the stress versus time graph as the creep proceeds at 100MPa for all the four life fractions. Table 4.3 indicates the creep time, strain and the grain size at all the life fractions at this stress level. From the creep behavior it can be observes that up to 75% of rupture life, the creep strain is as low as 2% but in the final quarter of the life there is a drastic increase in strain until fracture. Hence, maximum deformation from necking to failure takes place in the final quarter of life at 100MPa as well.
**Table 4.3: Creep data at different life stages at 100MPa, 650°C**

<table>
<thead>
<tr>
<th>Fraction of life at 100MPa</th>
<th>Creep time (hrs)</th>
<th>Creep Strain (%)</th>
<th>Grain size (µ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25% Life</td>
<td>94</td>
<td>1.2</td>
<td>5</td>
</tr>
<tr>
<td>50% Life</td>
<td>171.2</td>
<td>1.8</td>
<td>5</td>
</tr>
<tr>
<td>75% Life</td>
<td>257.4</td>
<td>1.6</td>
<td>5</td>
</tr>
<tr>
<td>Fracture</td>
<td>343</td>
<td>~50</td>
<td>n/a</td>
</tr>
</tbody>
</table>

**Figure 4.9: Creep behavior as it proceeds at 100MPa, 650°C**
Table 4.4: Creep data at different life fractions at 80MPa, 650°C

<table>
<thead>
<tr>
<th>Fraction of life at 80MPa</th>
<th>Creep time (hrs)</th>
<th>Creep Strain (%)</th>
<th>Grain size (µ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40% Life</td>
<td>595</td>
<td>1.31</td>
<td>5</td>
</tr>
<tr>
<td>50% Life</td>
<td>730</td>
<td>1.23</td>
<td>5</td>
</tr>
<tr>
<td>75% Life</td>
<td>1094</td>
<td>3.1</td>
<td>5</td>
</tr>
<tr>
<td>Fracture</td>
<td>1459.7</td>
<td>~50</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Figure 4.10: Creep behavior as it proceeds at 80MPa, 650°C
Figure 4.10 shows the creep behavior i.e. the stress versus the time graph as the creep proceeds at 80MPa, 650°C to four life fractions. Table 4.4 indicates the creep time and strain and the grain size at all the life fractions at 80MPa. From the creep behavior at 80MPa as well, it can be observed that up to 75% of the lifetime, the creep strain is as low as 3% but in the last quarter of the life there is a drastic increase in strain until fracture. Hence, maximum deformation from necking to failure takes place in the final quarter of life here as well.

4.3 Evolution of Grains, sub-grains, grain boundaries, cavities and particles

Scanning electron microscopy (SEM) and electron backscattered diffraction (EBSD)/orientation imaging microscopy (OIM) techniques were used for characterizing microstructure evolution during creep of modified 9Cr-1Mo steel at various stresses and times. Various SEM images in the SE (secondary electron) mode were captured to analyse the cavities and carbide particles during and after creep. As shown below, in Figure 4.11, all the images were captured at a magnification of 3500X and at a distance of 100µm from the fracture surface. Table 4.5 gives the cavity densities calculated using the image J software and verified manually for all the stress levels.

Figure 4.11 indicates cavities near the fracture area. It can be inferred that the number density of cavities at the vicinity of the fracture area is about 3 times higher when crept at 140MPa as compared with 120MPa.
Figure 4.11: Cavities from fracture area at all stress levels

Table 4.5: Cavity densities near the fracture at all stress levels

<table>
<thead>
<tr>
<th>Stress (MPa)</th>
<th>~Cavity density (number/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>33992</td>
</tr>
<tr>
<td>120</td>
<td>12286</td>
</tr>
<tr>
<td>100</td>
<td>53149</td>
</tr>
<tr>
<td>80</td>
<td>51023</td>
</tr>
</tbody>
</table>
Relating carbide morphology and cavity density, the cavity density depends on the carbide density as the carbide at grain boundary is the preferential site for cavity nucleation. As creep proceeds, the dislocation motion of the dislocations present in the sub-grain matrix leads to accumulation of dislocations at the vicinity of carbides. Accumulation of dislocations proceeds to formation of voids/cavities and further micro-cracks. We can see higher carbide density and hence higher cavity density at 140MPa.

The exposure and rupture time at high temperature and stress is much higher at 80MPa and 100MPa when compared with the above stress levels. Near the fracture areas at both stress levels, the carbide density is very similar. The reason for this can be explained considering exposure time and carbide density. Though the carbide density is lower at 80MPa, the exposure time is exponentially higher when compared to that at 100MPa. Longer the exposure time, greater will the time for the nucleation and formation of voids and cavities. Hence, both the samples fractured at 80MPa and 100MPa have a similar cavity density owing to exposure time and carbide density, respectively.

Figure 4.12 displays the carbides at different stress levels after creep from near fracture at stress levels 80MPa, 100MPa, 120MPa and 140MPa. The carbides decorating the grain boundaries of the ferrite lath after creep from an area which is 100µm from the fracture surface at all the stress levels were compared with the as-received structure of the Modified 9Cr-1Mo steel. The carbide size in each case were measured using the Image J software averaged over 5 images taken from the same distance of 100µm from the fracture surface. The average carbide size in each case is recorded into Table 4.6.
Table 4.6: Average carbide size at all stress levels

<table>
<thead>
<tr>
<th>Average Carbide Size (nm)</th>
<th>Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>200</td>
</tr>
<tr>
<td>193.2</td>
<td>140</td>
</tr>
<tr>
<td>223.6</td>
<td>120</td>
</tr>
<tr>
<td>258.3</td>
<td>100</td>
</tr>
<tr>
<td>324.5</td>
<td>80</td>
</tr>
</tbody>
</table>

Figure 4.12: Carbides along the grain boundaries at all stress levels
To evaluate the growth of carbides as creep proceeds, SEM images at each quarter life of creep were also captured. Figure 4.13 displays the growth of carbides as creep proceeds at 120MPa. Growth of carbides was observed but the growth was very slow due to the very high stress level and lesser time for diffusion of atoms to help grow the carbides.

![SEM images of carbides at different stages of creep](image)

**Figure 4.13: Carbides as the creep proceeds at 120MPa (a) 25% life, (b) 50% life, (c) 75% life and (d) at fracture**

Vickers hardness was measured at the gage area of the creep specimen at all the stages during the creep of the steel at 120MPa and 650°C. The hardness was then plotted as a function of time along with the carbide size. The decrease in hardness and the increase in carbide size as the creep proceeds at 120MPa can be seen clearly from the graph in Figure 4.14.
The above was again repeated at 100MPa and 80MPa as well to look at the trends of carbide size and hardness. Figures 4.15 and 4.16 show the carbides at life fractions of 25%, 50%, 75% and at the uniform gage area after fracture at 100MPa and 80MPa, respectively. All the images are taken at 8000x and analysed for particle size using Image J, image analysis software. Though not very evident, a small increase in the size of the carbides and reduction in the carbide density can be seen from the images. The actual values of carbide sizes calculated by the above mentioned methods are noted in Table 4.7

![Figure 4.14: Change in hardness and carbide size as creep proceeds at 120MPa, 650°C](image)

The above was again repeated at 100MPa and 80MPa as well to look at the trends of carbide size and hardness. Figures 4.15 and 4.16 show the carbides at life fractions of 25%, 50%, 75% and at the uniform gage area after fracture at 100MPa and 80MPa, respectively. All the images are taken at 8000x and analysed for particle size using Image J, image analysis software. Though not very evident, a small increase in the size of the carbides and reduction in the carbide density can be seen from the images. The actual values of carbide sizes calculated by the above mentioned methods are noted in Table 4.7
Figure 4.15: Carbides as the creep proceeds at 100MPa (a) 25% life, (b) 50% life, (c) 75% life and (d) at fracture

Table 4.7: Carbide sizes at different life fractions at 80MPa, 100MPa and 120MPa

<table>
<thead>
<tr>
<th>Life fraction</th>
<th>Carbide Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>80MPa</td>
</tr>
<tr>
<td>25% life/40% life</td>
<td>145</td>
</tr>
<tr>
<td>50% life</td>
<td>156</td>
</tr>
<tr>
<td>75% life</td>
<td>180</td>
</tr>
<tr>
<td>Fracture</td>
<td>276</td>
</tr>
</tbody>
</table>

Table 4.7 displays the diameters of the carbides present on the grain boundaries at all the life fractions of the stress levels 80MPa, 100MPa and 120MPa. The trend of increase in carbide
size as creep proceeds at all these stress levels, can be seen. The values at fracture are from the uniform gage section of the sample after creep and hence the strain at this level is only ~8%. The overall increase in carbide size is not drastic as these are short term creep tests.

Figure 4.16: Carbide evolution as the creep proceeds at 80MPa (a) 40% life, (b) 50% life, (c) 75% life and (d) fracture

EBSD/OIM was used to characterize the grains, sub-grains, grain boundaries and evaluate grain sizes. EBSD/OIM scans were obtained at every stress level and every stage of the crept samples. Figure 4.17 shows the typical EBSD/OIM maps from all stages of creep at 120MPa starting from 25% life to fracture. The pole figure and the OIM map indicate random orientation of grains and no specific alignment of grains. The fractions of low angle grain boundaries (LAGB) and high angle grain boundaries (HAGB) are indicated. It can be seen that the fraction of LAGB increases as the creep proceeds which indicates formation of sub-grain boundaries.
Figure 4.17: OIM map as creep proceeds at 120MPa (a) 25% life, (b) 50% life, (c) 75% life, (d) fracture

Figure 4.18: OIM map as creep proceeds at 80MPa (a) 25% life, (b) 50% life, (c) 75% life, (d) fracture
Figure 4.18 shows the orientation maps as creep proceeds at 80MPa, starting from 25% life to fracture. Same trend as above can be seen here as well. The fraction of LAGB increases as creep proceeds but the increase is much lower compared with that at 120MPa. Elongated grains can be seen near the fracture surface but not before 75% of life, which verifies the fact that most of the damage accumulation and accelerated creep occurs in the final quarter of life. Formation and growth of sub-grain boundaries is the main microstructure evolution mechanism at lower stress levels.

Figure 4.19: OIM maps as a function of strain at 140MPa (a) ~8%, (b)~25%, (c)~30% and (d)~50%

Orientation maps as a function of strain which is again as a function of distance from the fracture area varying from 100µ to 6000µ at all the stress levels can be seen in Figure 4.19 to figure 4.22. As the strain varies from ~8% to ~50% and we can see that the fraction of LAGB also increases which indicates formation of more subgrains which can also be evidently seen from the OIM images.
Figure 4.20: OIM maps as a function of strain at 120MPa (a) ~8%, (b)~25%, (c)~30% and (d)~50%

The microstructure and sub-structure at lower stress was characterized by EBSD/OIM to ascertain the grain size, morphology and grain boundary characteristics. Here the GS is grain size and the Sg.S is the sub-grain size. The sub-grain size is about same and around 2.5µm near the fracture surface. It is obvious that by decreasing the level of stress the fraction of the newly formed recrystallized grains near fracture surface is decreased notably. The grains are elongated and contain sub-grains. The degree of elongation is lower than higher stress levels. This is mostly attributed to decrease in strain rate at lower stresses. Formation and growth of sub-grain boundaries is main microstructure evolution mechanism at lower stress levels. The creep mechanism is still dislocation creep at these levels of stress.
Figure 4.21: OIM maps as a function of strain at 100MPa (a) ~8%, (b) ~25%, (c) ~30% and (d) ~50%

Figure 4.22: OIM maps as a function of strain at 80MPa (a) ~8%, (b) ~25%, (c) ~30% and (d) ~50%
Table 4.8: LAGB and HAGB fractions at all stress levels near fracture surface

<table>
<thead>
<tr>
<th>Stress level (near fracture ~50% strain)</th>
<th>LAGB</th>
<th>HAGB</th>
<th>Grain size (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80MPa</td>
<td>0.48</td>
<td>0.52</td>
<td>n/a</td>
</tr>
<tr>
<td>100MPa</td>
<td>0.43</td>
<td>0.57</td>
<td>n/a</td>
</tr>
<tr>
<td>120MPa</td>
<td>0.47</td>
<td>0.53</td>
<td>n/a</td>
</tr>
<tr>
<td>140MPa</td>
<td>0.56</td>
<td>0.44</td>
<td>n/a</td>
</tr>
</tbody>
</table>

Table 4.8 shows the values of the fractions of LAGB and HAGB at ~50% strain level at different stress levels and it can be seen that the LAGB values are almost same at lower stress levels but the increase is somewhat at 140MPa where more sub-grain boundaries form perhaps because of very less time and high strain.

Table 4.9: LAGB, HAGB fractions and grain size values at all stress levels at 6000µ from fracture surface

<table>
<thead>
<tr>
<th>Stress level (6000µ from fracture ~8% strain)</th>
<th>LAGB</th>
<th>HAGB</th>
<th>Grain size (microns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80MPa</td>
<td>0.36</td>
<td>0.64</td>
<td>4.75</td>
</tr>
<tr>
<td>100MPa</td>
<td>0.4</td>
<td>0.6</td>
<td>4</td>
</tr>
<tr>
<td>120MPa</td>
<td>0.4</td>
<td>0.6</td>
<td>4.5</td>
</tr>
<tr>
<td>140MPa</td>
<td>0.4</td>
<td>0.6</td>
<td>5.55</td>
</tr>
</tbody>
</table>
The table 4.9 shows the values of LAGB and HAGB at ~8% strain which is obtained at distance of 6000µm from the fracture surface at all the stress levels. This is the area where the gage section is uniform below the necked area after the fracture. The strain at this area was calculated from the dimensions. The grain size was calculated manually using the ASTM grain size measurement techniques. It can be seen that despite being under different levels of stress and different amount of time at 650°C at each particular stress level, the LAGB fraction almost remains same, around 40% at the strain level of ~8%.

4.4 Observations and Comparison with Transmission Electron Microscopy Results

TEM observations of samples crept were made at the highest and lowest stress levels, namely are 140MPa and 80MPa from the gage section and grip section of each fractured specimen. The grip section is the part of the sample which undergoes only heat treatment at 650°C, which is the temperature at which creep is carried out, whereas the gage section experiences stress and the effect of both stress and temperature can be seen.

Figure 4.23(a, b) illustrate the uniform sub-grain structure of the heat treated material with a huge carbide particle present at the grain boundary. The image (b) in the same figure shows the magnified carbide present exactly at the grain boundary triple point. When the images in Figure 4.23 are compared to those from the as-received, uncrept samples in images in Figure 4.3, it can be confirmed that after heat treatment for almost 1500 hours, the grains and sub-grains increased in size and the carbides along the grain boundaries and sub-grain boundaries also increased in size. Figure 4.23 (c, d) also show the uniform sub-grains with dislocations. The effect of heat treatment is seen in the form of a decrease in dislocation density as compared with the as-received structure.
Figure 4.23 (a), (b), (c), (d): TEM images of Mod. 9cr-1Mo steel heat treated at 650°C for about 1462 hours

Figure 4.24 (a) (b): TEM images of Mod. 9cr-1Mo steel heat treated at 650°C for about 75 hours
Figure 4.24 shows the TEM images from the grip section of the 140MPa sample, which is equivalent to heat treatment at 650°C for about 75 hours. When compared with above images from Figure 4.24, we can see that sub-grains are much smaller here and also the carbides are smaller than those heat treated for about 1500 hours. This proves the fact the carbides and sub-grains both grow enormously under the effect of just temperature. It can be seen that dislocation density in this case is higher compared to those in Figure 4.21, heat treated for about 1500 hours.

Figure 4.25: TEM images from gage after creep at 80MPa

TEM images from the uniformly elongated gauge section of the crept specimen at a stress level of 80MPa can be seen in Figure 4.25. When compared to as-received material, fewer dislocations are observed at this stage and the sub-grains size almost remains the same. The grain boundary pinning by the carbide particle can be clearly seen Figure 4.25 (b).

Figure 4.26 (a, b) shows images from the gage area of sample crept at 80MPa. The images show the interaction of dislocations with the small carbides inside the lath. These carbides also help pin the sub-grain boundaries. Pinning by small carbides in the matrix during the creep is one of the main reasons for high creep strength in these materials.
Figure 4.26 (a) (b): Interaction of dislocations with carbides (80MPa, 650°C)

Figure 4.27 shows images from the uniformly elongated gage area of the sample crept at 140MPa. When compared with Figure 4.26, a higher dislocation density can be seen. The sub-grain size is smaller when compared to those in Figure 4.26 at 80MPa with regard to the longer amount of time. Figure 4.27 (a, d) show elongated grains and sub-grains due to the creep. In Figure 4.27 (e), strain-free, dislocation free, small newly formed recrystallized grains can be seen. This supports the fact that recrystallization occurs under the effect of strain and temperature. Figure 4.27 (f, g) show typical sub-grain boundaries formed by arrays of dislocations and the carbides present on the sub-grain boundaries. Figure 4.27 (f) also shows small carbides and their interaction with dislocations. Figure 4.27 on the whole shows a mixture of sub-grains with free dislocations, dislocation free sub-grains, recrystallized grains, and carbides interacting with sub-grain boundaries and dislocations and hence depicting a clear picture of recovery and recrystallization during the creep.
Figure 4.27(a, b, c, d, e, f, g and h): TEM images from gauge after creep at 140MPa
CHAPTER 5. DISCUSSION

The results of this research presented in the Chapter 4 are discussed in the following section. The results obtained during the present work are analysed and compared with the previous work in this field. The overall mechanism by which creep proceeds during the short term creep at high stress and high temperature combinations is discussed below.

5.1 General Creep Behavior of Modified 9Cr-1Mo steel

The objective of the present thesis is to study the thermo-mechanical properties and microstructural evolution during the creep of Modified 9Cr-1Mo steel after a certain heat treatment. The results from Chapter 4, describe that creep and damage evolution mechanism after extensive creep testing of Modified 9Cr-1Mo at different stress levels at the temperature of 650°C. A stress exponent value of ~9.0 was calculated from the log-log plot of stress vs time, as indicated by Figure 4.6 in Chapter 4. Previous studies on the creep behavior of modified 9Cr-1Mo steel in the range of 600-650°C up to 300MPa by Kloc et al. [40] suggested a regime of viscous creep below the power law regime. The stress exponent was approximately unity in low stress tests up to 100MPa and above this the exponent increased to 10 and higher. The authors conducted uniaxial tensile creep tests above 100MPa and used helical springs below 100MPa. Figure 5.1 identifies the viscous creep regime and power law regime as indicated by Kloc et al [40].

Figure 5.2 is the modified version of Figure 4.6 with the data points at stress levels above 100MPa. The figure indicates the stress exponent of ~10 which is comparable to the value obtained by Kloc et al. The $R^2$ value during the regression analysis is higher in Figure 5.2 when compared to Figure 4.6 hence proving that power law regime starts above 100MPa.
Figure 5.1: Stress dependence of minimum creep rate for P91 steel in power law and viscous creep regimes. [40]

Figure 5.2: Stress dependence for minimum creep rate for Modified 9Cr-1Mo steel in power law regime
Extrapolation of the short term creep data to creep rupture times at lower stress levels is an important aspect for the design of new creep resistant steels. At lower stresses, creep is controlled by diffusion creep and at higher stresses creep is controlled by dislocation creep which can be described by the well-known Norton equation.

$$\dot{\varepsilon}_{\text{min}} = A\sigma^n$$ (5.1)

In the range of constant exponential relationship between the minimum creep rate and the applied stress, an extrapolation of the creep rate to lower stress levels can be carried out. Extrapolation of time to rupture can be based on the Monkman-Grant relationship [22].

$$\dot{\varepsilon}_{\text{min}} t_f = C$$ (5.2)

Where C is the Monkman Grant constant.

From the creep data obtained from the present study, the value of C was calculated to be 7.8 at stresses below 100MPa averaged over 3 data points. For stresses above 100MPa, the constant C was calculated to be 12.5 averaged over 3 data points again. The above constants can be used to extrapolate the fracture life of the modified 9Cr–1Mo steel of the composition mentioned in Table 3.2 to different stress levels below and above 100MPa. The above results also indicate a slight change in mechanism of creep at stress levels below and above 100MPa at 650°C.

5.2 Microstructural characterization

Modified 9Cr-1Mo steel is generally used in normalized and tempered condition for high sub-grain density, which is required for high creep resistance in precipitation hardened alloys. Modified 9Cr -1Mo steel has a typical structure of tempered martensite consisting of parallel
martensite laths arranged inside prior austenite grain. These martensite laths have high density of free dislocations as indicated by Cerri et al. [11], dislocation structure recovers when tempered and the laths become elongated sub-grains with a typical width of 0.25 to 0.5 µm. Depending on the tempering conditions, high dislocation density ($\sim 8 \times 10^{-14} \text{ m}^2$) [24] exist in the laths contained within the prior austenite boundaries. The most dominating precipitates present are $\text{M}_2\text{C}_6$ particles which exist mainly on lath boundaries and prior austenite boundaries. Previous literature indicates the range of particle diameters is around 60-150 nm [3]. The $\text{M}_2\text{C}_6$ size calculated by averaging particle size over 10 TEM images from the present study give an average particle size of $\sim 195$ nm. The particle size calculated from SEM images as reported in table 4.6 is 200nm verifying the above calculated particle size from the TEM images. Also according to the literature [4] the presence of V and Nb, fine distribution of MX particles exist which range from 20 to 80nm. The MX particles sizes calculated in the present study from the same TEM images as above give the average MX particle size to be $\sim 68$nm.

In service, the material is exposed to stress and high temperatures in the range of 550-650°C. This temperature exposure leads to reduction in dislocation density, and this decrease is greater during a creep test when compared with the effect of temperature alone. The hardness of the steel from the grip section was measured to be 250Hv. It can be seen from the data in Chapter 4 that there is a higher reduction in the hardness in the gage section when compared to the unstressed region of the shoulder. The reduction in dislocation density can be clearly seen in Figures 4.24 from the gage area when compared to Figure 4.22 and 4.23 from the grip area addition to the decrease in hardness of the material.

In the present work, the hardness was also evaluated in the regions from the neck to the un-necked part of the gage. The lowest hardness could be seen at the neck which is in the range of
170-200Hv and the hardness increased along the gauge from the neck to the uniform region of the gauge where necking could not be seen. The hardness remained uniform all along the non-necking region which is in the range of 250 to 265Hv at all the stress levels. From this we can conclude that reduction in dislocation density and recrystallization are responsible for the loss of creep strength.

Carbides are formed mostly on grain boundaries, and martensite packet or lath boundaries. The carbide has spherical morphology in the un-deformed samples. Coarsening of M23C6 particles is one main microstructural feature associated with the creep of Modified 9Cr-1Mo steels, which leads to the formation of equi-axed sub-grains from the martensite laths. Coarsening of MX precipitates is also present along with the coarsening of M23C6, but is much slower. [1, 3, 9] In the present work, the coarsening carbides was very carefully analysed and the carbide sizes were measured. It can be seen that at all the stress levels, the carbides grew in size from the initial size of 200nm to a higher size as seen in Table 4.6.

Carbides are refined in the fracture area i.e. highest amount of strain. This could be because of the dissolution of carbides assisted by strain as well as recrystallization of the alpha phase. In the deformed areas carbides are located along grain boundaries and oriented parallel to the stress axis. Interestingly, carbides are deformed and elongated at higher stress levels.

Coarsening of pinning particles follows the Ostwald ripening and it is also associated with agglomeration and reduction of pinning force. Coarsening can be described by the equation 5.3 below [19]

\[ d_p^n - d_o^n = K_d t \]  

(5.3)
where $d_o$ and $d_p$ are the average diameter of the carbides before and after testing at time $t$, and $K_d$ is constant. The exponent $n$ indicates the coarsening mechanism. The mechanisms for different values of $n$ are listed in the table 5.1.

Coarsening of $M_{23}C_6$ particles follows the above equation with exponent $n = 3$, i.e. follows Ostwald ripening with volume diffusion as the coarsening mechanism.

### Table 5.1: Coarsening mechanisms

<table>
<thead>
<tr>
<th>Exponent, $n$</th>
<th>Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>Coarsening by interface diffusion</td>
</tr>
<tr>
<td>3</td>
<td>Volume diffusion</td>
</tr>
<tr>
<td>5</td>
<td>Pipe diffusion</td>
</tr>
</tbody>
</table>

**Figure 5.3: Growth of $M_{23}C_6$ particles during creep at 650°C**

\[ y = 21921x \]
\[ R^2 = 0.9882 \]
Figure 5.3 is plotted with the exponent 3 and the experimental values of carbide sizes calculated. Regression analysis is performed, the $R^2$ value of $\sim0.99$ indicates that the coarsening follows the Equation 5.3 with $K_d = 21921$. This confirms that coarsening of $M_23C_6$ follows Ostwald ripening with volume diffusion as the coarsening mechanism.

Coarsening of MX particles is much slower and it follows the pipe diffusion with $n = 5$. [19] Calculation of MX particle coarsening rates were not carried out in present work.

An empirical expression equation 5.4 can be used to correlate particle size with stress as suggested in [41] to correlate the particle size with stress,

$$d_{M_23C_6} = K''b (\sigma/E)^b$$  \hspace{1cm} (5.4)

where $d$ is the diameter of the $M_23C_6$ particles at the stress level $\sigma$. $E$ is the young’s modulus of the material, which is found experimentally, equals to be GPa.

The constants $K''$ and $b$ have values of 3.6 and 0.68nm respectively. This expression permits extrapolation of the dimensions of particles at all stress levels to give a rough idea of their distributions. Dimensions of particles are function of time of exposure, hence this expression gives an indirect dependence of particle size on stress. Table 5.2 compares the diameters of carbide particles obtained from the above equation and those determined experimentally as presented in Chapter 4.
Table 5.2: Diameters of carbides calculated experimentally and empirically

<table>
<thead>
<tr>
<th>Stress (MPa)</th>
<th>Diameter(experimental) (nm)</th>
<th>Diameter(empirical) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>140</td>
<td>194</td>
<td>234</td>
</tr>
<tr>
<td>120</td>
<td>224</td>
<td>260</td>
</tr>
<tr>
<td>100</td>
<td>258</td>
<td>295</td>
</tr>
<tr>
<td>80</td>
<td>324</td>
<td>344</td>
</tr>
</tbody>
</table>

A difference of 20-40nm in every case can be seen but this equation can be used to roughly estimate the carbide size at required stress levels.

Above calculations suggest that as the creep proceeds, the essential carbides present on the sub-grain boundaries which help pin the sub-grain boundaries and improve the creep resistance of the material coarsen under the effect of temperature coarsen by volume diffusion following Ostwald ripening. The carbide sizes can also be estimated using an empirical expression as mentioned in equation 5.4. As the carbides coarsen the pinning force of the carbides decreases and the sub-grains coarsen as well, leading to creep deformation.

Microstructural study in the present work at all the stress levels and calculations of cavity densities was also presented in the Chapter 4. The cavity densities from areas very close to the fracture surfaces were carefully observed and calculated as mentioned in the Chapter 3. Very high cavity density at areas very close to the fracture areas indicate the formation of cavities due to high strain accumulation. At 650°C there is no evidence of the void formation and presence of any cracks until 75% of fracture time at all the stress levels. Creep curves show that deformation and
most of the damage initiation and accumulation occurs at the very end term of the creep process at this condition. Almost no cavities are present after a distance of 200µm from the fracture area. Cavities nucleated at the grain boundaries next to large carbides. Creep Voids/Cavities are formed at the grain boundaries and coalescence of cavities was observed and tend to orient along the grain boundary parallel to the stress axis and form grain boundary micro cracks. This phenomenon of coalescence is more obvious at higher stress levels above 100MPa because of the presence of higher strain.

Much greater cavity densities were observed at areas very near the fracture surface at stress levels of 100MPa and below. The microstructure study at the necking part of the fractured samples at 100MPa interestingly shows that micro cavities are present after about 25-35% creep deformation. The diffusion creep is more dominant at stress levels below 100MPa as suggested by Kloc et al [40] and as also observed in the present study. The presence of more cavities at lower stress levels can hence be attributed to the availability of longer time for nucleation of cavities at all the carbide sites. Coalescence of the creep voids is not observed at lower stress levels, hence the number density of cavities is much greater here. This occurs near 90% of whole creep life. These results show that by decreasing the level of stress, it is possible to observe the very first steps of void initiation. Also the fracture mechanism is formation of voids at the vicinity of the deformed carbides, which are located at the grain boundaries and subjected to the higher strain. These voids grow very fast and coalesce resulting in grain boundary micro cracks and dimples or larger voids.
The microstructure very close to the fracture surface at a distance on 100µm with the strain of around 40% clearly shows recrystallization. EBSD images very well prove that dislocation creep is the deformation mechanism as also suggested from the log-log plot of minimum creep rate vs stress in Figure 5.1, which gives the stress exponent to be 10.

![Histogram of misorientation angles of as-received 9Cr-1Mo steel](image)

**Figure 5.4: Histogram of misorientation angles of as-received 9Cr-1Mo steel**

Analysis of the misorientation angles in the as-received sample indicates two main groups of matrix boundaries, low angle (below 15°) and high angle (50° – 60°) boundaries. Figure 5.4 shows the results of analysis of the misorientation angles. An analysis of the rotation angles is shown in Figure 5.5 in the form of reduced pole figures. The statistics of low angle boundaries look random, the rotation of low angle boundaries is random, whereas the high angle boundaries
show preferential misorientations. From the literature review, as suggested by Sonderegger [8], low angle martensite lath boundaries do not exist in this case, hence all the boundaries are assigned to sub-grain boundaries because of their low misorientation angles.

Figure 5.5: Rotation axis of low angle misorientation (left) and high angle misorientation (right)

The angles of these sub-grains are tending to increase by increasing the strain further. Figure 5.6 shows the histograms of misorientations at 140MPa comparing the uniform gauge area and the near fracture area, at strain values of ~8% and ~50%. The fraction of misorientations of LAGB is decreased and the fractions of midrange misorientations have increased. The dynamic recrystallization mechanism could be continuous. There are a couple of hypotheses at this time but it is clear that high amount of strain is applied to those regions near fracture surface which overcomes the barrier energy for recrystallization. The recrystallization itself could damp the strain energy of deformation, resulting in higher elongation i.e. higher creep strain.
Figure 5.6: Histogram of misorientations at 140MPa, 650°C, after creep at the uniform gauge section (left) and near the fracture area (right)

Figure 5.7: Histogram of misorientations at 80MPa, 650°C, after creep at the uniform gauge section (left) and near the fracture area (right)

Figure 5.4 indicates the number fractions of boundaries in the as-received material and left image in Figure 5.7 indicates those in the gauge area after creep at 80MPa, 650°C. The fraction of LAGB has decreased in this case, which shows that during uniform elongation in a creep test, there
is growth of sub-grains as suggested in the literature for creep of modified 9Cr-1Mo (G91) steels. [9, 10, 11] Formation and growth of sub-grain boundaries is main microstructure evolution mechanism at lower stress levels.

Figure 5.8: Variation of sub-grain size with stress

Figure 5.6 compares the low and high angle boundaries after creep at 80MPa at different strain levels. The area necked and near fracture has a strain of about 50% and the area from the gauge has experienced a strain of 8%. The number fraction of the low angle boundaries is high at fracture when compared to that at the gage, which indicates that there is formation of sub-grain boundaries during necking and increase in strain. Increase in strain during the creep test during the necking results in formation of more sub-grain boundaries and refinement in sub-grain size as the
grain size remains almost same. The grain size in the gage area and at the fracture area are 5.3µm and 5.4µm respectively. Figure 5.8 shows the variation of sub-grain size with stress, calculated manually from the OIM maps of near fracture areas of all the stressed samples. Higher the stress, smaller is the sub-grain size at fracture indicating heavy deformation.

Figure 5.9 shows the rotation axis of low angle misorientations and high angle misorientations in the form of reduced pole figures at the fracture area after creep at 80MPa, 650°C. This also supports the above, i.e. formation of higher low angle boundaries at fracture when compared to the gage area, as well as in the as-received material without any creep deformation.

![Figure 5.9: Rotation axis of low angle misorientation (left) and high angle misorientation (right) at fracture, 80MPa, 650°C](image)

5.3 **Evaluation of internal stress**

At constant temperature, a semi empirical relationship is applied to describe the stress dependence of the minimum creep rate is given in the form of the Norton equation as seen in equation 5.1
\[ \varepsilon_{\text{min}}^* = A\sigma^n \]

Figure 5.2 shows the log-log plot of minimum creep rate vs applied stress for Modified 9Cr-1Mo steel at 650°C, which is used to evaluate the stress exponent. High values of stress exponent suggest that creep rates can be correlated to an effective stress,

\[ \sigma - \sigma_0 = \sigma^* \]  \hspace{1cm} (5.5)

Where \( \sigma_0 \) is the internal stress and \( \sigma^* \) is the effective stress.

The Norton equation can be incorporated with internal stress and modified to be

\[ \varepsilon_{\text{min}}^* = A' (\sigma - \sigma_0)^{n'} \]  \hspace{1cm} (5.6)

The total internal stress in G91 alloy is due to the contributions from precipitates, lath boundaries, substructure and network dislocations all of which impede dislocation motion. Total internal stress can be written as

\[ \sigma_{\text{OT}} = f (\sigma_{\text{OPP}}, \sigma_{\text{OLaths}}, \sigma_{\text{OSubgrains}}, \sigma_{\text{op}}) \]  \hspace{1cm} (5.7)

Where

\( \sigma_{\text{OT}} \) is internal stress

\( \sigma_{\text{OSubgrains}} \) is the internal stress due to the sub-structure

\( \sigma_{\text{op}} \) is the internal stress due to mobile dislocation density

\( \sigma_{\text{OPP}} \) is the internal stress due to precipitates

\( \sigma_{\text{OLaths}} \) is the internal stress due to laths
Already formed and evolved dislocation structure generates resistance to dislocation motion in the crystal during plastic deformation. Contribution to internal stress from dislocations decreases with time.

The role of precipitates in creep strength is multifold which include slowing down the migration of sub-grain boundaries by pinning, impeding the knitting reactions of mobile dislocations with sub-grain boundaries and acting as obstacles to gliding dislocation segments in the matrix by Orowan mechanism.

The literature suggests that orowan stress from particles on dislocations and sub-grains boundaries contributes to the creep strength of steels. Crept Modified 9Cr-1Mo steel displays bowing of dislocations around the precipitates as suggested in previous reports and the TEM images from Figure 4.28 taken as shown in Chapter 4. The flow stress contribution by the precipitates is a fraction of the orowan stress due to the bowing. During creep, coarsening of the precipitates and formation of new precipitates lower the inter-particle distance and hence lower the internal stress due to the precipitates. As creep proceeds, the contribution of internal stress due to precipitates is expected to decrease.

Internal stress due to sub-grain boundaries is primarily due to the bowing out contribution of dislocations at these boundaries, where the boundary spacing provides an Orowan type flow stress.

Internal stress can be evaluated from the creep data using linear regression analysis of experimental creep data on modified 9Cr-1Mo steel using the modified Norton equation. The value of the creep exponent obtained is 10 from the above plot in figure 5.2. Regression analysis was performed on the equation below for Modified 9Cr-1Mo material.
\[ \varepsilon_{\min}^{1/n} = A'^{1/n} (\sigma - \sigma_0) \]  

(5.8)

This analysis was performed on the creep data obtained at 650°C. The plot in Figure 5.10 shows the regression lines for creep data obtained with stress exponent as 10.

![Plot of (minimum creep rate)^1/10 vs. applied stress at 650°C for G91 steel, depiction the regression lines used to obtain the values of internal stress](image)

**Figure 5.10:** Plot of (minimum creep rate)^1/10 vs. applied stress at 650°C for G91 steel, depiction the regression lines used to obtain the values of internal stress

The above equation 5.8 is of the form \( y = ax + b \), where \( a = A'^{1/n} \) and \( b = \sigma_0 A'^{1/n} \). We have 4 values of \( x \), which is stress for which we can determine 4 measured values of \( y \), which is the minimum creep rate to the 1/n power. The optimum values for \( a \) and \( b \) can be found when

\[
\sum_{i=1}^{N} [y_i - (ax_i + b)]^2 \rightarrow \text{Minimum}
\]

The values of \( a \) and \( b \) can be evaluated with the following equations
\[ a = N \left( \sum x_i y_i \right) - \left( \sum x_i \right) \left( \sum y_i \right) / N \left( x_i^2 \right) - \left( \sum y_i \right)^2 \]  \hspace{1cm} (5.9)

\[ b = \left( \sum y_i \right) \left( \sum x_i^2 \right) - \left( \sum x_i y_i \right) \left( \sum x_i \right) / N \left( \sum x_i^2 \right) - \left( \sum x_i \right)^2 \]  \hspace{1cm} (5.8)

Using these equations the values of a and b are calculated, which were then used to evaluate internal stress.

The internal stress for the Modified 9Cr – 1Mo steel calculated using the above regression analysis and calculations from the creep data in the range of 80MPa to 140MPa stress and 650°C was calculated to be ~40MPa which less when compared to the data obtained from the literature for this material evaluated at lower stress levels when compared to the present work.

5.4 Damage evolution and overall creep mechanism

As the short term creep of modified 9cr 1mo steel proceeds, in the initial stage there is decrease in creep rate, the first stage of creep is very narrow and there is not much dislocation movement owing to decrease in minimum creep rate. Similar primary creep region (stage 1) at all stress levels implies that significant primary strain accumulation occurs, regardless of the applied stress and temperature. In the second stage, where there is increase in strain, i.e. constant minimum creep rate indicates there is dislocation multiplication. In this stage there is coarsening of precipitates. As a result of this, the distance between the pinning carbides increases with time. Since this is short term creep and the stage two is quick, there is lesser time for coarsening of precipitates and hence, the growth of precipitates is lesser when compared to the long term creep. Dislocations restructure to form sub-grain boundaries and increase in sub-grain cell size occurs. The dislocation density on sub-grain boundary increases but the density within the cell decreases. Thus, the density of effective dislocations becomes low. As the creep proceeds further in this stage,
multiplications of dislocations are consumed in the formation of cell walls which continues into formation of sub-grains. When the dislocation density goes low, the tertiary stage of creep starts where there is an increase in creep rate and then there is further softening of the material. The cell structure further recovers and there is an increase in formation of sub-grains and sub-grain boundaries. As the creep proceeds further, there is increase in strain, and then there is further growth of sub-grains and sub-grain rotation takes place to increase the angle of sub-grain and the sub-grains become free of dislocations due to recovery. These sub-grains grow into grains by continuous dynamic recrystallization. The coarsened carbides help the formation of sub-grains and recrystallization. There is high strain accumulation during the final stage which leads to heavy reduction in dislocation density, void accumulation and formation of micro-cracks at the vicinity of coarsened carbides. These micro cracks on further effect of strain and temperature grow very quickly to form macro cracks leading to the failure of the steel. As there is in increase in elongation corresponding to the growth of particles along the sub-grain boundaries and necking starts in the tertiary stage, there is a decrease in mean particle size along with the simultaneous decrease of particle number per unit area for time higher than 75% of creep life. The particles elongate a little due to strain at high temperature and then break into two or more particles. Some particles are also found to dissolve into the matrix by strain assisted dissolution of particles. The internal stress due to the sub-grain boundaries is inversely related to the distance between these. Higher the density of sub-grain boundaries, higher will be the internal stress contributing to the enhancing of creep strength of this material. The internal stress of as-received steel is calculated to be ~40MPa. Internal stress values computed by regression analysis in section 5.x correspond to that at the point of minimum creep rate. Internal stress varies with the density of dislocations, and since the density
of dislocations reduces as the creep proceeds further, the contribution of internal stress decreases and its effect on creep strength of the material deteriorates.

Microstructural degradation in terms of decrease in dislocation density, formation of coarse equi-axed dislocation cell/sub-grain structure and increase in the precipitate coarsening and sub-grain size with decreasing stress has been observed during creep in the as-received steel.
CHAPTER 6. CONCLUSIONS

1. Creep behavior of Modified 9Cr-1Mo steel having a tempered martensite microstructure with high dislocation density, uniform sub-grains and with decoration of carbide precipitates was studied under combination of a stress range of 80-140MPa and high temperature (650°C). Creep of Modified 9Cr-1Mo steel under these conditions proceeds by a dislocation creep mechanism as suggested from the creep data analysis and the microstructural characterization. The calculated stress exponents in the present thesis agree with the literature.

2. During creep at high stress – high temperature combination, there is a growth in carbide particles decorated along the sub-grain boundaries, the coarsening of the carbides follows Ostwald ripening with volume diffusion as the coarsening mechanism prior to tertiary creep. As creep proceeds into tertiary creep region and necking is observed, high strain accumulation leads to cavity formation at carbides and eventual fracture. Strain dissolution of carbides and overall reduction in carbide size also occurs. This phenomenon is not observed at lower stress levels as suggested in the literature.

3. Literature reports presence of no cavities after creep at 600°C because of high grain boundary cohesion of Modified 9Cr-1Mo steels. High cavity densities close to fracture areas are observed at stress levels above 80MPa at 650°C after creep in the present work. Hence the effect of grain boundary cohesion deteriorates above 600°C.

4. Rearrangement of dislocations within the matrix leading to formation of sub-grain boundaries during the final stage of creep provides evidence for dynamic recrystallization. Increase in misorientation of these small sub-grains leading to formation of new high angle grain boundaries under the effect of high strain is also observed. So the mechanism of
continuous dynamic recrystallization during the final stage creep causing softening of material, new dislocation activity leading to pileups at carbides, void formation and failure of material is the main reason for accelerated damage. Continuous dynamic recrystallization has never been observed and reported earlier.

5. The total internal stress due to the sub-grain substructure, dislocation density and precipitates has been calculated from the creep data. Literature reports internal stresses at temperatures below 600°C and the internal stress at 650°C is calculated (~40MPa) in the present work and it is observed to follow the trend of decreasing internal stress with temperature.

6. The overall mechanism of short term creep can be defined as coarsening of carbides and sub-grains initially during uniform elongation which is followed by formation of sub-grain boundaries and sub-grain refinement leading to recrystallized structure and loss of creep strength. Dislocation annihilation dominates production during creep. Sub-grain boundaries act as both sources and sinks for dislocations. Recrystallized structure stimulates refinement of carbides. Dislocations glide towards the sub-grain boundaries and accumulate at the carbide particles leading to breakage of carbides and formation of voids/grain boundary micro cracks leading to the failure of the material.
CHAPTER 7. REFERENCES


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