Ali Aghajani Bazazi

# Evolution of Microstructure during Long-term Creep of a Tempered Martensite Ferritic Steel



## Evolution of Microstructure during Long-term Creep of a Tempered Martensite Ferritic Steel

Dissertation zur Erlangung des Grades Doktor-Ingenieur

der Fakultät für Maschinenbau der Ruhr-Universität Bochum

von

Ali Aghajani Bazazi aus Teheran, Iran

Bochum 2009

#### Bibliografische Information der Deutschen Nationalbibliothek

Die Deutsche Nationalbibliothek verzeichnet diese Publikation in der Deutschen Nationalbibliografie; detaillierte bibliografische Daten sind im Internet über http://dnb.d-nb.de abrufbar.

1. Aufl. - Göttingen : Cuvillier, 2009

Zugl.: Bochum, Univ. Diss., 2009

978-3-86955-182-1

© CUVILLIER VERLAG, Göttingen 2009 Nonnenstieg 8, 37075 Göttingen Telefon: 0551-54724-0 Telefax: 0551-54724-21 www.cuvillier.de

Alle Rechte vorbehalten. Ohne ausdrückliche Genehmigung des Verlages ist es nicht gestattet, das Buch oder Teile daraus auf fotomechanischem Weg (Fotokopie, Mikrokopie) zu vervielfältigen.

1. Auflage, 2009

Gedruckt auf säurefreiem Papier

978-3-86955-182-1

## Acknowledgment

The dissertation you hold has an interesting history. I was fortunate enough as an undergraduate at Material & Energy Research Centre (MERC) in Iran to have the opportunity to be invited by International Max Planck Research School for Surface and Interface Engineering in Advanced Materials (IMPRS-SurMat) for two interviews. I owe many thanks to Dr. Angela Büttner for organizing my visits to Germany.

I am very grateful to my supervisor, Prof. Dr. Gunther Eggeler, for giving me the opportunity to perform my PhD thesis work in the excellent material research institute at Ruhr University Bochum. Outside of the university, Prof. Dr. Eggeler made life easier for me and helped me to concentrate only on my research work. I am especially indebted to Prof. Dr. Dierk Raabe for revising this work.

Thanks to Dr. Christoph Somsen, Dr. Antonin Dlouhy and Dr. Joseph Pesicka for teaching me transmission electron microscopy (TEM) and for helpful discussions during this project. Many thanks to Sabrina Kneip for her significant assistance in preparing TEM thin foil specimens. I would like to thank my colleagues for helping me with numerical analysis and introducing me to thermodynamic analysis software (Thermocalc): Dr. Franck Richter, Dr. Suzana Fries, Prof. Dr. Ingo Steinbach and Lais Mujica. I wish extend many thanks to my colleagues who proofed parts of this manuscript and provided me with many helpful comments: Dr. Christoph Somsen, Dr. Marcus Young and Dr. Eric Payton.

Many thanks to Mrs. Suzana Römer and the creep group for listening while I talked my way through so many puzzles: Fredrick Otto, Dennis Peter, Deniz Kurumlu, Philipp Nörtershäuser and Timo Depka. Thank to my officemates for tolerating me and supporting me during my PhD thesis work: Mrs. Ingrid Wittkamp, Dr. Jiancun Rao and Dr. Leonardo Agudo. I am very grateful to Dr. W. Bendick (Salzgitter Mannesman Forschung GmbH) and Dr. U. Zeislmair (Vallourec & Mannesmann Tubes) for supplying interrupted long-term creep specimens and helpful discussions.

Especial thanks to Dr. Araz Ardehali Barani for the helpful comments during this PhD thesis work and finally I would like to thank my brother and my parents for their moral support.

Ali Aghajani Bazazi, Bochum, December 2009

#### **Executive summary**

Tempered martensite ferritic steels are used for critical components in fossil fired power plants that operate in the creep range. The materials contain a high density of dislocations and precipitates form on all types of internal interfaces, the majority of which represent subgrain boundaries. Most previous studies suffer from either only relating to short-term creep experiments or from being incomplete in not considering all relevant elements of the microstructure. No systematic effort was made to investigate the evolution of microstructures under conditions of long-term creep. In the present study the evolution of the microstructure of a 12% Cr tempered martensite ferritic steel was investigated under conditions of long-term aging and creep. Transmission electron microscopy (TEM) and electron back-scattered diffraction (EBSD) techniques were used to characterize materials from interrupted creep tests (0.5%, 1%, 1.6% and rupture at 11.9%; creep conditions: 550°C, 120 MPa, rupture time: 139 971 h). It is shown that subgrains coarsen, that the close correlation between carbides and subgrain boundaries loosens during long-term creep, and that the frequency of small angle boundaries increases. In addition, the evolution of dislocation densities during long-term aging and creep was studied using high angle annular dark field (HAADF) scanning transmission electron microscopy (STEM). During aging the dislocation density remains constant, while during longterm creep the dislocation density continuously decreases. All these elementary deformation processes have already been discussed in short-term creep studies. The present study shows that they also govern long-term creep, however, during longterm creep, precipitation and coarsening reactions occur which are not observed during short-term creep. Cr-rich M<sub>23</sub>C<sub>6</sub>, VX carbides and Laves phase were identified as the major precipitates in the microstructure of the 12% Chromium tempered martensite ferritic steel. Their chemical compositions, sizes, volume fractions and number densities were evaluated in all interrupted specimens. M<sub>23</sub>C<sub>6</sub> particles coarsen and establish their equilibrium concentration after 51072 hours. VX particles are stable. The Laves phase particles do not reach thermodynamic equilibrium as they form and grow during long-term creep. This is due to Silicon which is found in the Laves phase particles and which diffuses slowly in the steel matrix.

## Table of content

1.	Intr	oduction	1
2.	Stat	te of the art	5
2.	1.	Applications	5
2.	2.	9-12% Cr steels	6
2.	3.	Metallurgy	7
2.	4.	Precipitates	11
2.	5.	Creep fundamentals	17
2.	6.	Strengthening mechanisms	22
3.	Ma	terials and methods	24
3.	1.	Materials	24
3.	2.	Heat-treatment	25
3.	3.	Creep testing	26
3.	4.	Optical metallography and hardness	27
3.	5.	Scanning electron microscopy	27
3.	6.	Transmission electron microscopy	30
4.	Res	ults	34
4.	1.	Creep data	34
4.	2.	Creep cavities and inclusions	36
4.	3.	Evolution of hardness	40
4.	4.	Evolution of subgrain	41
4.	5.	Evolution of misorientation	44
4.	6.	Evolution of dislocations density	49
4.	7.	Identification of precipitates	53
4.	8.	Evolution of precipitate parameters	57
4.	9.	Chemical evolution of precipitates	62
5.	Disc	cussion	65
5.	1.	Creep data	65
5.	2.	Creep cavities and inclusions	65
5.	3.	Evolution of hardness	65
5.	4.	Evolution of subgrain	66
5.	5.	Evolution of low angle boundaries	70
5.	6.	Evolution of dislocation density	70
5.	7.	Stability of precipitates	71
5.	8.	Chemical evolution of precipitates	74
5.	9.	Laves phase nucleation and growth	75
6.	Cor	nclusions	84

## List of Figures

Figure 1-1: Heat rate of steam power plants in Germany as a function of steam parameters. 1
Figure 1-2: International research and development projects on steam power plants [17] 2
Figure 2-1: Schematic illustration and photographs of a fossil fired boiler and their typical
materials5
Figure 2-2: Schematic illustration of microstructure of tempered martensite 9-12%Cr creep-
resistant steel contains precipitates on the internal interfaces
Figure 2-3: Schematic of crystal structure of Cr <sub>23</sub> C <sub>6</sub> carbide with fcc structure
Figure 2-4: Schematic of crystal structure of VC carbide with fcc structure
Figure 2-5: Schematic of crystal structure of $Fe_2W$ carbide with hcp structure
Figure 2-6: Schematic of Ostwald ripening mechanism in which larger particles grow up while
small particles dissolving into matrix
Figure 2-7: Creep curve of an engineering steel under constant tensile load and constant
temperature
Figure 3-1: Schematic of the position and direction of creep specimens taken from
X20CrMoV12-1 pipe
Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel 25
Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel 25 Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after
Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel 25 Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after 139971 hours at 823 K under 120 MPa
<ul> <li>Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel 25</li> <li>Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after</li> <li>139971 hours at 823 K under 120 MPa</li></ul>
<ul> <li>Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel 25</li> <li>Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after</li> <li>139971 hours at 823 K under 120 MPa</li></ul>
<ul> <li>Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel 25</li> <li>Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after</li> <li>139971 hours at 823 K under 120 MPa</li></ul>
<ul> <li>Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel 25</li> <li>Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after</li> <li>139971 hours at 823 K under 120 MPa</li></ul>
<ul> <li>Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel 25</li> <li>Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after</li> <li>139971 hours at 823 K under 120 MPa</li></ul>
Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel 25Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after139971 hours at 823 K under 120 MPa
Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel 25Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after139971 hours at 823 K under 120 MPa
Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel.25Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after139971 hours at 823 K under 120 MPa.26Figure 3-4: Schematic of EBSD technique.28Figure 3-5: Diagram of the bright-field, annular dark-field, and high-angle annular dark-field30Figure 3-6: Procedure to identify and evaluate the precipitates in HAADF—STEM images.32Figure 3-7: Schematic figure illustrating the parameters which were retrieved from the TEM33Figure 4-1: Diagram of strain vs. logarithm of time of specimens with 0.5, 1.0, and 1.6% strain35
Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel.25Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after139971 hours at 823 K under 120 MPa.26Figure 3-4: Schematic of EBSD technique.28Figure 3-5: Diagram of the bright-field, annular dark-field, and high-angle annular dark-field30Figure 3-6: Procedure to identify and evaluate the precipitates in HAADF—STEM images.32Figure 3-7: Schematic figure illustrating the parameters which were retrieved from the TEM33Figure 4-1: Diagram of strain vs. logarithm of time of specimens with 0.5, 1.0, and 1.6% strain35Figure 4-2: Logarithm of creep rate vs. logarithm of time at 823 K for specimens 0.5, 1.0, 1.636
Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel.25Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after139971 hours at 823 K under 120 MPa.26Figure 3-4: Schematic of EBSD technique.28Figure 3-5: Diagram of the bright-field, annular dark-field, and high-angle annular dark-field30Figure 3-6: Procedure to identify and evaluate the precipitates in HAADF—STEM images.32Figure 3-7: Schematic figure illustrating the parameters which were retrieved from the TEM33Figure 4-1: Diagram of strain vs. logarithm of time of specimens with 0.5, 1.0, and 1.6% strain35Figure 4-2: Logarithm of creep rate vs. logarithm of time at 823 K for specimens 0.5, 1.0, 1.635
Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel.25Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after139971 hours at 823 K under 120 MPa.26Figure 3-4: Schematic of EBSD technique.28Figure 3-5: Diagram of the bright-field, annular dark-field, and high-angle annular dark-field30Figure 3-6: Procedure to identify and evaluate the precipitates in HAADF—STEM images.32Figure 3-7: Schematic figure illustrating the parameters which were retrieved from the TEM33Figure 4-1: Diagram of strain vs. logarithm of time of specimens with 0.5, 1.0, and 1.6% strain35Figure 4-2: Logarithm of creep rate vs. logarithm of time at 823 K for specimens 0.5, 1.0, 1.635Figure 4-3: logarithm of creep rate vs. strain for the ruptured specimen at 823 K and 12036

Figure 4-4: SEM back-scattered micrograph of the ruptured specimen at 823 K and 120 MPa
after 139971 hours; white square is represented the region of interest; Arrows show the
former austenite grain boundaries
Figure 4-5: SEM back-scattered micrograph of the pointed out region in Figure 4-4; white
square is represented the position of the magnified image in Figure 4-6
Figure 4-6: SEM back-scattered micrograph of the pointed out region in Figure 4-5; the creep
cavities are visible on the former austenite boundary perpendicular to the stress direction.38
Figure 4-7: a) Elongated inclusion after hot rolling in as received specimen in longitude
direction, b) back-scattered image of a micro-pore in centrifugal direction; 1, 2) EDX
spectrum of particle inside pore and surrounding, respectively
Figure 4-8: Hardness evolution in gage portion (creep) and thread portion (aging) at 823 K.40
Figure 4-9: A montage of 16 TEM bright-field images; the position of Figure 4-10 is pointed
out by white square
Figure 4-10: Bright-field TEM image from ruptured specimen at 823 K under 120 MPa 42
Figure 4-11: Subgrain width measurement in SEM images of X20CrMoV12-1 steel (initial
state)
Figure 4-12: Subgrain evolution in creep (under external stress) and in aging (without stress)
specimens of X20CrMoV12-1 steel
Figure 4-13: Relative frequency of misorientation angles in X20CrMoV12-1steel. Angles
below 15 degree are defined as low angle boundaries and above 15 degree as high angle
boundaries
Figure 4-14: Electron back-scattered diffraction pattern (EBSD) of as-received specimen, a)
Image quality (IQ), b) inverse pole figure (IPF)
Figure 4-15: Electron back-scattered diffraction pattern (EBSD) of thread portion (aging) at
823 K; a) Image quality (IQ), b) inverse pole figure (IPF)
Figure 4-16: Electron back-scattered diffraction pattern (EBSD) of gage portion (creep) at 823
K and 120 MPa; a) Image quality (IQ), b) inverse pole figure (IPF)
Figure 4-17: Evolution of one degree misorientation angle in creep and aging specimens at
823 K
Figure 4-18: Relative frequency oh high angle misorientation (60 degree) in creep and aging
specimens

Figure 4-19: Relative frequency of low angles misorientation in as-received, aging and creep Figure 4-20: HAADF STEM micrograph showing dislocations in the initial material (prior to Figure 4-21: Set of 4 HAADF STEM micrographs showing the evolution of the density of free dislocations during long-term aging. (a) 12456 h / 823 K; (b) 51072 h / 823 K; (c) 81984 h / 823 K; (d) 139971 h / 823 K......50 Figure 4-22: Set of 4 HAADF STEM micrographs showing the evolution of the density of free dislocations during long-term creep (a) 12456 h/823 K/120 MPa; (b) 51072 h/823 K/120 MPa; (c) 81984 h/823 K/120 MPa; and after rupture (d) 139971 h/823 K/120 MPa.....52 Figure 4-23: Quantitative metallographic results on dislocation densities in the initial Figure 4-24: a) Bright-field TEM, b) STEM HAADF image, c) selected area diffraction (SAD) pattern of the carbide and d) energy dispersive X-ray (EDX) chemical analysis of the  $M_{23}C_6$ carbide......53 Figure 4-25: a) Bright-field TEM, b) STEM HAADF image, c) convergent beam electron diffraction (CBED) pattern, d) energy dispersive X-ray (EDX) chemical analysis of the VX carbide......54 Figure 4-26: a) Bright-field TEM, b) STEM HAADF image, c) selected area diffraction (SAD), Figure 4-27: A montage of HAADF STEM images of the X20CrMoV12-1 steel after 139971 hours creep exposure at 823 K and 120 MPa. The Laves phase precipitates are brighter than Figure 4-28: Evolution of projected area fraction for M<sub>23</sub>C<sub>6</sub>, VX and Laves phase during creep. Figure 4-29: Evolution of number density for M<sub>23</sub>C<sub>6</sub>, VX and Laves phase during creep. ...... 58 Figure 4-30: Evolution of mean diameter for M<sub>23</sub>C<sub>6</sub>, VX and Laves phase during creep....... 60 Figure 4-31: Ostwald ripening of M<sub>23</sub>C<sub>6</sub> carbides in X20CrMoV12-1 steel. ......60 Figure 4-33: The relative frequency of particle-boundary of the initial state, after 51072 

Figure 4-34: Relative concentration of the elements found in the Laves phase particles during
creep exposure at 823 K and 120 MPa63
Figure 4-35: Concentration of Fe and Cr in the metallic elements of $M_{23}C_6$ carbide
Figure 4-36: Molybdenum concentration in the metallic elements of M <sub>23</sub> C <sub>6</sub> carbide
Figure 5-1: Hardness ratio as a function of creep life fraction
Figure 5-2: Subgrain width of interrupted as well as ruptured creep specimens of
X20CrMoV12-1 at 823 K under 120 MPa versus creep strain and calculated subgrain width
using given formula
Figure 5-3: HAADF STEM image of ruptured creep specimen after 139971 hours at 823 K of
X20CrMoV12-1 steel
Figure 5-4: Model of diffusion of Silicon into the Laves phase particles from surrounding
matrix with constant surface concentration78
Figure 5-5: Growth of the Laves phase particles for different boundary concentration of
Silicon
Figure 5-6: Schematic illustration of (a) the particle geometry and particle spacing and (b) the
Si concentration profile in between two particles
Figure 5-7: Relative Si concentration ( $c_{r(x)}/c_{\infty}$ )·100% as a function of the dimensionless
distance parameter $r_x = x/\lambda_i$

## List of Tables

Table 2-1: Chemical composition and creep rupture strength at 600°C of basic and advanced
creep-resistant steels used in power plants (mass %) [17]8
Table 2-2: Unit cell parameter (a) of MX precipitate in ferritic creep-resistant steels12
Table 2-3: Summary of basic characteristics of minor phases in 9–12%Cr steels.         16
Table 3-1: The chemical composition of X20CrMoV12-1 creep-resistant steels in weight
percent
Table 3-2: Creep conditions of X20CrMoV12-1 specimens. L1, L2 and L3 are interrupted
creep specimens and L4 is the ruptured sample
Table 3-3: Setting for collecting data in EBSD.    29
Table 3-4: Number of investigated particles in each specimen using TEM and STEM
micrographs
Table 4-1: Effect of subgrain evolution on the subgrain back-stress
Table 5-1: Comparison of precipitates in the gage and thread portions at 823 K after 139971
hours creep exposure
Table 5-2: Parameters characterizing the population of Laves phase particles after different
periods of long-term creep exposure. $\rho_{\text{n}}$ – number density of Laves phase particles. R - mean
radius of the five biggest Laves phase particles
Table 5-3: Experimentally determined Laves phase volume fractions $f_V^{Laves}$ . Experimental $c_{Si}$ -
rem V,rel,exp and calculated c <sub>Si-rem</sub> V,rel,mod

#### 1. Introduction

Creep-resistant steel that can be used for a long time at elevated temperatures is key to the construction of thermal and nuclear power generation, chemical and petroleum plants [1-3]. During the last decade, great progress has been made in developing creep-resistant steels of high strength and corrosion resistance at ever increasing temperatures [4]. Although in the past, the driving force for these developments has been primarily to achieve higher efficiencies, the focus has shifted more recently to the reduction of emissions of CO<sub>2</sub>, dioxins and other environmentally hazardous gases [5-9].

The development of creep-resistant steels is a result of continuous technological progress throughout the 20<sup>th</sup> century. The urgent need to improve the creep strength of steels was based on endeavors by the power station industry to improve the thermal efficiency of steam power plants by raising the steam temperature and steam pressure in order to reduce the cost of fuel and reduce use of resources [10-16]. Since roughly 1900, the heat rate of thermal power plants in Germany has been reduced following a step-by-step increase in the steam parameters from 275°C/12 bars to 620°C/300 bars (Figure 1-1).



Figure 1-1: Heat rate of steam power plants in Germany as a function of steam parameters.

The thermal efficiency of fossil-fired power plants can be raised by reducing exhaust heat and heat transfer losses. The limit has virtually been reached for reducing exhaust heat losses, which are mainly through the condensers for cooling turbine and boiler exhaust. Heat transfer losses, however, can be reduced by raising the pressure and temperature of the steam, but the extent to which this can be done is greatly influenced by the materials. For creep-resistant steels used in high temperature components in power plants, good mechanical properties, corrosion resistance and fabricability are generally required, and creep strength in particular is of utmost importance for high pressure and high temperature applications. This has led to increasing research activities in alloy development which are focused on improving the creep strength. Figure 1-2 shows an overview of the international research and development projects on advanced steam cycle power plants in the world [17]. These projects were initiated in the early 1980s, and in the last two decades numerous creep-resistant steels have been developed to achieve ultra-supercritical pressure steam conditions or steam temperature of 630°C with ferritic 9-12%Cr steels [18, 19].



Figure 1-2: International research and development projects on steam power plants [17].

Critical components in fossil-fired power plants (tubes, pipes, blades, rotors, membranes and others) are mainly fabricated from bainitic and tempered martensitic steels with 100000 hour creep strengths at 600°C in the 100 MPa stress range. These steels not only show reasonable creep resistance but also high damage tolerance with respect to thermal fatigue loading (where frequent starts and stops cannot be avoided). Their high temperature corrosion resistance is good below the point where FeO forms and generally increases with increasing Cr content. For steam power plants with sliding pressure operation capable of responding to changes in electricity demand, or for plants undergoing frequent start and stop cycles, it is preferable to use ferritic steels having smaller coefficients of thermal expansion for heavy, thickwalled components in order to reduce thermal stresses. Accordingly, the creepresistance capability of ferritic steels is the major determinant of steam conditions [20-26]. Recent research on enhancing the creep strength of 9-12%Cr steels for 650°C operation has revealed the importance of taking into account microstructural evolution phenomena during creep, such as precipitation and coarsening of carbonitrides and intermetallic compounds [27-29].

In view of the objectives of the present study, two aspects are important. First, the microstructure of tempered martensite-ferritic steels governs its creep behavior. Second and most importantly, the microstructure of steel is not stable but is continually evolving during creep. This has been known for quite some time, but a number of open issues remain. The appearance of new experimental methods like high resolution scanning electron microscopy, electron backscattered electron diffraction (EBSD) in the scanning electron microscopy and analytical transmission electron microscopy provides the possibility to progress the field. The service life of materials is usually obtained by an extrapolation procedure. The problem with this approach is that the microstructure of creep-resistant steels is not stable and this has been reported on many occasions in the literature [30-39].

In the present research, we investigate the evolution of the microstructure in tempered martensite ferritic steel X20CrMoV12-1 exposed to long-term creep loading at 550°C, by performing detailed microstructural investigations for distinct creep stages. The interrupted long-term creep specimens allow us to evaluate the microstructural evolutions during creep exposure and under real service conditions avoiding the impracticable results from short-term creep.

### 2. State of the art

#### 2.1. Applications

Figure 2-1 shows the various boiler components such as the water wall, superheater, reheater, header and main steam pipe and their typical materials used in a recent fossil fired power plant. The water wall tubes are welded in a panel structure to achieve effective heat exchange in order to produce pressurized steam from water under the super critical conditions in a furnace.



Figure 2-1: Schematic illustration and photographs of a fossil fired boiler and their typical materials.

Conventional steels and Cr-Mo steels are used for the water wall tubes according to the operating temperatures and pressures, which are usually heated up to 500°C in the latest ultra supercritical pressure plants. The steams are superheated in a superheater up to the highest pressure at a designed temperature and reheated in reheater up to the highest temperature that will achieve the designed thermal efficiency. The superheated steams are gathered into a header pipe and transferred to a turbine system through main steam piping. The header and main steam piping should, therefore, be a heavy wall thickness pipe with a large diameter to keep huge amounts of steam pressurized. It is suggested that 9-12% Chromium creep-resistant steels are suitable materials to fulfill mentioned requirements in header and main steam pipes [16, 17].

#### 2.2. 9-12% Cr steels

The development of creep-resistant 9-12%Cr steels was strongly motivated by two major events: (1) the development of thermal power plants for public power supply operating at steam temperatures ranging from 538-566°C during the 1950s and (2) the target to develop low-pollution power plants operating at steam admission temperatures of 600-650°C with supercritical pressures up to 350 bar during the 1980s [40-44]. The steel X20CrMoV12-1 was developed in the 1950s for thin- and thick-walled power station components. The creep strength of X20CrMoV12-1 is based on solid solution hardening and on the precipitation of M<sub>23</sub>C<sub>6</sub> carbides. This steel has been used successfully in power plants over several decades up to temperatures of about 566°C. A newer generation steel, referred to in the literature as modified 9Cr-1Mo or P91 [15], was developed under a USA project in the late 1970s for the manufacture of pipes and vessels for a fast breeder. This steel has been widely used for pipes and small forgings in all new Japanese and European power plants with steam temperatures up to 600°C. The increase of creep strength in comparison to the X20CrMoV12-1 steel is caused by forming thermal stable VN and Nb(C, N) precipitates. A lower Cr content of about 9% also contributes to the higher creep strength. Similar creep strengths are exhibited by new steels developed for rotors, castings and pipes which are in addition alloyed with Tungsten (W). A further increase in creep strength reveals the steel type P92 which, in addition to the other alloying elements, is alloyed with Boron and has an increased W content. The addition of boron gives thermally stable M<sub>23</sub>(C,B)<sub>6</sub> precipitates whereas the higher W content leads to a higher amount of the Laves phase. Steels for rotors, casings and pipes with higher B contents can be used up to temperatures of about 630°C. Further ferritic 9-12%Cr steels are under development for steam temperatures up to 650°C [45-50]. An overview of the historical development of creep-resistant ferritic 9-12%Cr steels for the 1990s is given in Table 2-1 [17].

#### 2.3. Metallurgy

The standard heat treatment of martensitic-ferritic steels consists of austenitizing and tempering. In austenitizing at temperatures above Ac<sub>1</sub>, ferrite (bcc) transforms to austenite (fcc). During cooling from the austenitizing temperature to room temperature, a martensitic structure forms. Tempering results in a ferritic subgrain microstructure with carbides and carbonitrides forming at former austenite boundaries, subgrain boundaries and dislocations within the grains (Figure 2-2).



Figure 2-2: Schematic illustration of microstructure of tempered martensite 9-12%Cr creep-resistant steel contains precipitates on the internal interfaces.

ť
Ю
Ð
_
Ļ
÷
Ó
Ð
÷
σ
÷
S

	Dusting
5	
<u></u>	
%	
SS	
na	
s (1	
nt	
ola	
r_	
Š	
bo	
⊒.	
Ba	
nsı	
<u>s</u>	
ee	
t st	
ant	
ist	
esi	
F	
eel	
5	
ed	
nc	
Va	
ad	
nd	
a	
sic	
q	
of	
ູ	
8	
it 6	
ца Ч	
ß	
uə.	
str	
e	
tu	
dn.	
d	
ee	
5	
nd	
р Ц	
Ei O	
sit	
bc	
ШC	
ŭ	
ica	
E	
he	
2-1	
e	
ab	

	country	steel				chemical c	omposition	(weight %)			.[ /+] [0/ 00	Rupture s 600°C	trength at (MPa)
			U	IJ	Mo	ï	N	>	ЧN	z	В	$10^4$ h	10 <sup>5</sup> h
		Basic steels											
1	Germany	X20CrMoV12-1	0.22	12.0	1.0	0.50	ı	0:30	ı	ı	ı	103	59
2	UK	H 46	0.16	11.5	0.65	0.70	ı	0:30	0:30	0.05	ı	118	62
		FV448	0.13	10.5	0.75	0.70	ı	0.15	0.45	0.05	·	139	64
ŝ	France	54T5	0.19	11.0	0.80	0.40	ı	0.20	0.45	0.05	ı	144	64
4	Japan	TAF	0.18	10.5	1.5	0.05	ı	0.20	0.15	0.01	0.035	216	150
Ŋ	USA	11%CrMoVNbN	0.18	10.5	1.0	0.70	I	0.20	0.08	0.06	ı	165	85
		Advanced steels											
9	USA	P 91	0.10	9.0	1.0	<0.40	ı	0.22	0.08	0.05	ı	124	94
7	Japan	HCM 12	0.10	12.0	1.0	ı	1.0	0.25	0.05	0.03	ı		75
8	Japan	TMK 1	0.14	10.3	1.5	09.0	ı	0.17	0.05	0.04	·	170	06
		TMK 2	0.14	10.5	0.5	0.50	1.8	0.17	0.05	0.04	ı	185	06
б	Europe	X18CrMoVNbB 91	0.18	9.5	1.5	0.05	ı	0.25	0.05	0.01	0.01	170	122
10	Europe	X12CrMoWVNbN	0.12	10.3	1.0	0.80	0.80	0.18	0.05	0.06	,	165	06
		E911	0.11	9.0	0.95	0.20	1.0	0.20	0.08	0.06	,	139	98
11	Japan	P92	0.07	9.0	0.50	0.06	1.8	0.20	0.05	0.06	0.003	153	113
12	Japan	P122	0.10	11.0	0.40 1Cu	<0.40	2.0	0.22	0.06	0.06	0.003	156	101
13	Japan	HCM 2S	0.06	2.25	0.20	ı	1.6	0.25	0.05	0.02	0.003		80
	(				0					200	0.004		c U
14	Germany	/CrMoliB	0.07	2.40	1.0	ı	I	0.25	I	10.0	0.07Ti		90

∞

In order to reach the optimum strength, it is essential to obtain a fully martensitic transformation by cooling to room temperature. Because of the Cr level, carbon diffusion in austenite is slowed down; consequently, the ferrite nose in the CCT (continues cooling transformation) diagram shifts to longer cooling times [51-53]. If the martensitic transformation does not proceed to the end, the so-called retained austenite remaining in the microstructure decreases the strength before tempering. For 9-12%Cr steels, the martensite start ( $M_s$ ) temperature is about 400°C and  $M_f$  is in the range 100-150°C [17].

The composition of the steel controls the M<sub>s</sub> and M<sub>f</sub> temperatures. A rough estimate of the M<sub>s</sub> temperature can be determined by the following empirical equation (2.1):  $M_s = 550^{\circ}C - 450C - 33Mn - 20Cr - 17Ni - 10W - 20V - 10Cu - 11Nb - 11Si + 15Co$  (2.1) It is essential to have a fine distribution and high thermal stability of the precipitates to obtain a high creep strength in 9-12%Cr steels. The tempering temperature is chosen with respect to properties required for the component. Higher tempering temperatures are used for components like steam pipes, where high ductility during post weld treatment is important [23, 54]. For large components like turbine rotors, lower tempering temperatures are used to take advantage of the resulting high tensile strength [55-57].

#### **Elemental effects**

Classification of alloying elements according to their effect in the steel is difficult, because the influence varies so widely with each element addition, depending on the quantity used and other elements present. A useful approach to grouping, however, is based upon the effect of the element on the stability of carbides and the stability of austenite [10, 17, 23, 54]. With this approach, alloying elements are classified as follows:

 Elements that tend to form carbides: Chromium, tungsten, titanium, vanadium, molybdenum, and manganese.

- Elements that tend to graphitize the carbide: silicon, cobalt, aluminum, and nickel. Only a small proportion of these elements can be added to the steel before graphite (which degrade the mechanical properties of the steel) starts forming instead of carbide during processing, unless elements from group 1 are added to counteract the effect.
- Elements that tend to stabilize austenite: manganese, nickel, cobalt, and copper. These elements tend to retard the separation of carbides. They have a crystal lattice (fcc) similar to that of γ-iron, in which they are more soluble than they are in α-iron.
- Elements that tend to stabilize ferrite: Chromium, tungsten, molybdenum, vanadium, and silicon. These elements are more soluble in  $\alpha$ -iron than in  $\gamma$ -iron. They diminish the amount of carbon soluble in the austenite and thus tend to increase the volume of free carbide in the steel for a given carbon content. With a certain amount of each of these elements, the austenite phase disappears and ferrite exists from the melting-point down to room temperature.

#### 2.4. Precipitates

Three kinds of precipitate usually form in the X20CrMoV12-1 steel. the crystallography and chemical composition of each precipitates are summarized following.

#### 2.4.1. M<sub>23</sub>C<sub>6</sub>

 $M_{23}C_6$  is the main precipitate in most of ferritic creep-resistant steels. Therefore, the strength and the creep properties of these steels depend strongly on the amount, size, and dispersion of  $M_{23}C_6$  carbides. The term  $M_{23}C_6$  is a more general notation for  $Cr_{23}C_6$ , as often, Ni, Mo and Fe are found to substitute partially for Chromium. However, in steels containing significant amounts of Mo, it can have the formula  $Fe_{21}Mo_2C_6$ . In steels containing both Cr and Mo, the composition can be anywhere between the above. Mn has also been found to partition to  $M_{23}C_6$  in small quantities. Figure 2-3 shows the crystal structure of  $Cr_{23}C_6$  carbide. It has an fcc structure (space group Fm3m) with the lattice parameter varying between 1.057 and 1.068 nm.  $M_{23}C_6$  carbides are found in the early stage of tempering, because they nucleate easily on the internal interfaces.



Figure 2-3: Schematic of crystal structure of Cr<sub>23</sub>C<sub>6</sub> carbide with fcc structure.

 $M_{23}C_6$  particles coarsen during creep exposure. During coarsening, the number of  $M_{23}C_6$  particles decreases as the mean particle diameter increases. The volume fraction remains constant as the large particles growth and small ones dissolve. Measurements of the  $M_{23}C_6$  particle size distribution made by Hättestrand and coworkers [58-60] have shown that the coarsening of  $M_{23}C_6$  carbides is accelerated by introducing creep at 600°C. If boron is present in the steel, it will dissolve in  $M_{23}C_6$  carbides and substitute for carbon, although only in very small quantities. With the use of Atom Probe Field Ion Microscopy (APFIM), it is found that approximately 50% of B in the steel is concentrated in  $M_{23}C_6$  carbides [45-50]. Boron is of particular interest as it promotes the formation of intergranular  $M_{23}(C,B)_6$ .

#### 2.4.2. MX

The formation of MX precipitates in ferritic steels occurs when strong carbide/nitride formers (Ti, Nb, V, Zr, Ta, etc.) are added to alloy. Figure 2-4 shows the crystal structure of VX carbide. The VX carbonitrides have a NaCl face centered cubic (fcc) structure with lattice parameters as given in Table 2-2. Often measured lattice parameters have intermediate values, reflecting the existence of a solid solution between the different carbonitrides.

Table 2-2: Unit cell	parameter (a) of M)	( precipitate in ferriti	c creep-resistant steels.

Precipitate	NbN	NbC	TiN	TiC	VC	VN
a (nm)	0.439	0.447	0.424	0.433	0.417	0.413

The nitrogen remaining in solid solution during austenitization is available during tempering for the fine precipitation of MX carbonitrides. The MX precipitates usually form on dislocations within the matrix, on stacking faults and on grain boundaries where they increase creep strength by pinning free dislocations [61-66].



Figure 2-4: Schematic of crystal structure of VC carbide with fcc structure.

#### 2.4.3. Laves phase

Increase of creep rupture strength in 9-12%Cr steels can be achieved by change of the molybdenum content and/or the addition of tungsten to the steels. These changes in Mo and W contents lead to the formation of intermetallic Laves phase (Fe,Cr)<sub>2</sub>(Mo,W). It precipitates intergranularly in the form of equiaxed particles. Laves phase has a hexagonal phase of space group P63/mmc with a=0.473 nm and c=9.772 nm. The main factors determining their formation is the relative atomic size of the constitute atoms and, furthermore, the ranges of composition are fairly small [67, 68]. Figure 2-5 shows the crystal structure of the intermetallic Fe<sub>2</sub>W.



Figure 2-5: Schematic of crystal structure of Fe<sub>2</sub>W carbide with hcp structure.

It has been shown that Laves phase will precipitate during service exposure in power plant applications at temperatures of approximately 550°C after around 10000 hours [69, 70]. It is also reported in the literatures that the presence of Si and Cu accelerates the precipitation of the Laves phase in tempered martensitic steels [71].

#### Carbide coarsening (Ostwald ripening):

The decomposition of a metastable solution is very often described as occurring in three consecutive stages:

- The nucleation of particles of the more stable phase in metastable solution.
- The growth of the particles in the metastable solution.
- The ripening or coarsening of the particles.

The coarsening process has a profound effect on the properties of materials. For example, the coarsening process can control the size of precipitates in solid solution. This average particle size then sets the mechanical properties of the precipitation hardening [72]. Coarsening typically occurs under conditions where the volume fractions of the phases are nearly at their equilibrium values. Figure 2-6 shows the Ostwald ripening mechanism schematically.

The driving force for the Ostwald ripening process is the reduction of the interface free-energy of the material [73]. Since smaller particles in solution have a higher surface-to-volume ratio than larger particle, smaller particles are less stable than larger particles of the same material. An increase in the mean particle size will thus reduce the total free-energy of the system and this reduction in free-energy is the driving force for the coarsening reaction. The analysis of Lifshitz and Slyozov and Wagner (LSW) [74] shows that the average particle size increases with time as t<sup>1/3</sup> and that the number of particle per unit volume decays as t<sup>-1</sup>, while the volume fraction remains constant.

$$d^3 - d_0^3 = kt (2.2)$$

$$\rho_n = \frac{k'}{t} \tag{2.3}$$

where  $d_0$  and d are particle sizes at the beginning and after t time. k and k' are constant.  $\rho_n$ , number density, is the number of particles per unit of area.



Figure 2-6: Schematic of Ostwald ripening mechanism in which larger particles grow up while small particles dissolving into matrix.

Table 2-3: Summary of basic characteristics of minor phases in 9–12%Cr steels.

main	contribution to	precipitation strengthening	precipitation strengthening	precipitation strengthening	precipitation strengthening	lowering precipitation strengthening	decrease in solid solution strengthening lowering precipitation strengthening poor plasticity	decrease in solid solution strengthening lowering precipitation strengthening poor plasticity	poor plasticity
characterized	by	medium growth rate during creep	restriction of grain growth	dissolution during creep at high temperatures	high dimensional stability during creep	dissolution of Nb(C,N), M <sub>2</sub> X and VN	dissolution above 650°C fast coarsening at 600°C	high coarsening rate, dissolution of M <sub>2</sub> X, Nb(C, N), decrease of Mo, W in solid solution	high coarsening rate, reduction of N in solid solution
preferred	precipitation	former austenite grain and martensite lath boundaries	austenite grain boundaries	inside subgrain and martensite laths	inside subgrains, martensite laths, and/or dislocations	M <sub>23</sub> C <sub>6</sub> , Nb(C, N)	grain and subgrain boundaries on M <sub>23</sub> C <sub>6</sub>	grain and subgrain boundaries on M <sub>23</sub> C <sub>6</sub>	grain and subgrain boundaries
formed during		tempering	solidification	tempering below 700°C	tempering above 700°C creep exposure	long-term creep exposure	long-term creep exposure	(>1.6% Mo) long-term creep exposure	tempering
aterinitate	precipitate	M <sub>23</sub> C <sub>6</sub>	Nb(C, N)	$M_2X(Cr_2N)$	secondary MX(VN)	Cr(V, Nb)N Z-phase	Laves phase Fe <sub>2</sub> (Mo, W)	M <sub>6</sub> X	AIN plasticity

16

#### 2.5. Creep fundamentals

Plastic deformation is irreversible and it consists of time-dependent and timeindependent components. In general, creep refers to the time-dependent component of plastic deformation. This means that creep is a slow and continuous plastic deformation of materials over extended periods under load. Although creep can take place at all temperatures above zero Kelvin, traditionally creep has been associated with time-dependent plastic deformation at elevated temperatures, often higher than roughly 0.4T<sub>m</sub>, where T<sub>m</sub> is the absolute melting temperature [75, 76]. In the creep test, the elongation of the specimen is measured as a function of duration and the test may not necessarily be continued to rupture of the specimen. Creep tests can be usually conducted either at constant load or at constant stress. For experimental convenience, the creep tests of the engineering materials are most frequently conducted at constant tensile load and temperature. The test results can be plotted as creep curves, which represent graphically the time dependence of strain measured over a reference or gage length. Figure 2-7 is a schematic diagram of a typical creep curve indicating the three regimes [77, 78].

- Primary creep
- Secondary creep (steady state)
- Tertiary creep



Figure 2-7: Creep curve of an engineering steel under constant tensile load and constant temperature.

In the primary creep state, creep rate  $\dot{\epsilon}$ , given by Equation (2.4), decreases with time. The diminishing creep rate in the primary creep is contributed to the strain hardening or decreasing in free mobile dislocation.

$$\dot{\varepsilon} = \frac{d\varepsilon}{dt}$$
(2.4)

In the second creep stage, the creep rate remains constant. This creep rate is commonly referred to as steady-state creep where a state of equilibrium is reached due to a balance between the rate of dislocation generation (contributing to hardening) and the rate of recovery (contributing softening). At high temperatures, creep mainly involves diffusion and hence the recovery rate is high enough to balance the strain hardening and results in the appearance of secondary or steady-state creep. In the tertiary creep stage, the creep rate increases with time until rupture. It should be noted that under constant tensile load, the stress continuously increases as the cross-sectional area decreases. Damage evolution includes the development of creep voids, cavities and cracks, which are often found along grain boundaries. Equation (2.5) shows that creep cavitations affect the applied stress by decreasing the load bearing cross section of the specimen [77, 78].

$$\sigma = \frac{\sigma_0}{1 - \omega} \tag{2.5}$$

where  $\omega$  is the damage parameter which evolves from zero (initial state) to one (rupture) as cavities nucleate and grow. The term "minimum creep rate" has been favored by engineers and researcher who are concerned with engineering creep-resistance steels and alloys [79]. The stress dependence of minimum or steady-state creep rate is usually expressed by a power law as:

$$\dot{\varepsilon}_{\min} = A\sigma^n \tag{2.6}$$

$$A = K \exp\left(-Q_c/RT\right) \tag{2.7}$$

where *n* is the stress exponent,  $Q_c$  the activation energy for creep, *R* the gas constant and the *T*, the absolute temperature. The parameter *K* includes microstructure parameters such as grain size. Equation (2.6) is often referred to as Norton's law. It is well known that the minimum creep rate is inversely proportional to the time to rupture  $t_r$  as follows:

$$\dot{\varepsilon}_{\min} = K\sigma^{n} \exp\left(-Q_{c}/RT\right) = C/(t_{r})^{m}$$
(2.8)

where *C* is a constant depending on total elongation during creep and *m* is a constant often nearly equal to 1. Equation (2.8) is referred to as the Monkman-Grant relationship which suggests that the minimum creep rate and time to rupture vary in a similar manner to stress and temperature.

Although Figure 2-7 shows an idealized creep curve, engineering creep-resistant steels sometimes exhibit complicated behavior especially under long time creep condition, reflecting complex microstructure evolution during creep. Constitutive equations are used with parameters which reflect the evolution of specific microstructural features. The present work is no micromechanical treatment, but the following simplified analysis helps to understand why microstructural information is important. It is believed that the plastic deformation of crystalline solids at high temperatures does not occur under the action of the whole applied stress but only under a portion of it which is represented by the effective stress. The effective stress is the difference of  $\sigma_{ex}$  and  $\sigma_{i}$ , where  $\sigma_i$  is the internal back-stress and  $\sigma_{ex}$  is external stress.  $\sigma_i$  characterizes the resistance of a solid to plastic deformation. The quantity of  $\sigma_i$  can depend on temperature, deformation history and especially, on the applied stress and strain rate [77]. We assume that the back-stress equation reasonably describes the creep process :

$$\dot{\varepsilon}_{\min} = A \left(\sigma_{ex} - \sigma_{i}\right)^{n} \tag{2.9}$$

Where A is constant and  $\sigma_{ex}$  external applied stress,  $\sigma_i$  internal back-stress, and n power law stress exponent. The internal back-stress  $\sigma_i$  has been expressed as a superposition of individual contributions from dislocations and precipitates. When also taking into account the contribution from subgrain boundaries, the internal stress is:

$$\sigma_{i} = M \left( \sigma_{disl} + \sigma_{sg} + \sigma_{prec} \right)$$
(2.10)

where *M* is the Taylor factor (usually between 2 and 3). The subscripts in the terms in the parentheses denote contributions from dislocations, subgrain boundaries, and precipitates, respectively. When examining the individual contributions of the different mechanisms to the back-stress based on Equation (2.10) the part stemming from dislocations can be expressed as:

$$\sigma_{disl} = \alpha G b \sqrt{\rho_m} \tag{2.11}$$

where  $\rho_m$  denotes the density of mobile dislocations and the value of  $\alpha$  is between 0.84 and 1. *G* is the shear modulus and *b* is the Burgers vector. Tempered martensitic high Cr steels subjected to normalizing and tempering are usually observed to have a lath martensitic microstructure consisting of lath and block with a high density of dislocations and a dispersion of fine carbonitrides along the lath and block boundaries and in the matrix. The lath and block can be regarded as elongated subgrains. The lath and block boundaries provide the sub-boundary hardening given by:

$$\sigma_{sg} = 10Gb/\lambda_{sg} \tag{2.12}$$

where  $\lambda_{sg}$  is the short width of elongated subgrains. The subgrain width  $\lambda_{sg}$ , corresponding to the width of lath and block, is in the range 0.3-0.7 µm in martensitic high Cr steels after tempering. The contribution of precipitates to the total back-stress can be described by the critical Orowan stress [17]. If the precipitates are sufficiently hard, such that dislocations cannot bypass them by cutting, the upper limit of the pinning force is determined by the Orowan stress.

$$\sigma_{or} = C \frac{Gb}{\lambda} \ln\left(\frac{\xi}{r_0}\right)$$
(2.13)

where C is a constant (C = 0.159 for screw dislocations and C = 0.227 for edge dislocations),  $\lambda$  is the mean particle distance,  $r_0$  is the 'inner cut-off radius' and  $\xi$  the 'outer cut-off radius' of the dislocation. This quantity denotes the maximum back-stress caused by a random distribution of precipitates using a mean distance  $\lambda$ 

between the precipitates. The latter can be estimated using the assumption that each precipitate consumes approximately the same bulk volume. In this case,  $\rho$  is given by:

$$\rho \cong \sqrt[3]{\frac{6}{\pi n_i}}$$
(2.14)

where  $n_i$  represents the number density of precipitates in units of m<sup>-3</sup>. When combining Equations (2.13) and (2.14), the total back-stress contribution from a bulk distribution of precipitates yields to:

$$\sigma_{prec} = CGb_{\sqrt[3]{\frac{\pi n_i}{6}}} \ln\left(\frac{\xi}{r_0}\right)$$
(2.15)

where the quantity  $\sigma_{prec}$  represents the maximum back-stress caused by precipitates. If the external load, reduced by the back-stress contribution of the other strengthening mechanisms, is below this threshold, the dislocations are effectively pinned and can only pass the precipitates by the climb mechanism. Since dislocation climb is a diffusional process, the effective creep rates are usually low. If the threshold stress is exceeded, the dislocations can bypass the precipitates by the Orowan mechanism, which is a much faster process compared to climb. When this change in mechanism occurs, the exponent in the Norton creep law increases significantly and creep deformation is strongly enhanced [78]. The selection of the operative creep mechanism is mainly determined by the height of the external load. However, a transition from dislocation climb to the Orowan mechanism can also be caused by a decrease in back-stress during service. If this transition occurs, for instance, owing to coarsening of precipitates or thermodynamic instability of a precipitation strengthening phase, extrapolation of the creep strength from shortterm experiments to long-term service behavior can result in fatal overestimation of the residual lifetime of components [75].

#### 2.6. Strengthening mechanisms

The basic ways in which creep-resistant steels can be strengthened are by solute hardening, precipitation hardening, dislocation hardening and boundary hardening. It should be noted that the contribution of solid solution hardening by Mo and W to the overall creep strength of engineering creep-resistant steels is practically superimposed on other strengthening mechanisms, for example precipitation hardening. It means that an additive rule for solid solution hardening and precipitation hardening does not hold [80-82].

Precipitation hardening is one of the important strengthening mechanisms in creepresistant steels at elevated temperature. To achieve enough strengthening using this effect, engineering creep-resistant steels usually contain several kinds of precipitate particles in the matrix and on the grain boundaries: carbides and carbonitrides such as M<sub>23</sub>C<sub>6</sub>, M<sub>6</sub>C, M<sub>7</sub>C<sub>3</sub>, MX, M<sub>2</sub>X and intermetallic compounds such as the Fe<sub>2</sub>(Mo,W) Laves phase, where M denotes the metallic elements, C is the carbon atoms, and X is the carbon or nitrogen atoms. A dispersion of fine precipitates stabilizes free dislocations in the matrix and subgrain structure, which enhances dislocation and sub-boundary hardening. The coarsening and dissolution of fine precipitates sometimes takes place preferentially in the vicinity of grain boundaries during creep, which promotes the formation of a localized weak zone and promotes localized creep deformation near grain boundaries. It results in premature creep rupture [83, 84, 85].

Tempered martensitic 9-12%Cr steels contain a high density of dislocations even after tempering, usually in the range  $10^{14}$  m<sup>-2</sup> in the matrix. The density of dislocations produced by martensitic transformation can be controlled by changing the tempering temperature. Tempering is usually carried out at low temperatures of 700°C or lower for turbine steels to ensure enough tensile strength at ambient temperature by the dislocation hardening, whereas it is as high as 750-800°C for boiler applications. At elevated temperature, on the other hand, cold working enhances softening by promoting the recovery of excess dislocations and the recrystallization of deformed microstructure [86-89].

In recent years, efforts have been made to clarify the mechanisms of creep strength loss in 9-12%Cr steels at 550°C and above during creep exposure. The loss of creep strength often takes the form of a sigmoidal inflection over long periods of time in creep rupture data. The proposed mechanisms relate mainly to a loss of precipitation hardening by fine carbides and carbonitrides and also to a loss of dislocation hardening during creep exposure. These accelerate microstructure evolution such as the coarsening of lath and block, resulting in a loss of sub-boundary hardening [90].

The loss of creep rupture strength in X20CrMoV12-1 steel is due to preferential recovery of the lath martensitic microstructure which promotes preferential and localized creep deformation in the vicinity of former-austenite grain boundaries, resulting in a premature creep rupture. The proposed mechanism is the coarsening of  $M_{23}C_6$  carbides and the recovery of lath martensitic microstructure. It is also observed that the addition of a small amount of boron, about 100 ppm, effectively suppresses the coarsening of  $M_{23}C_6$  carbides and hence suppresses the rapid loss of creep rupture strength.

Excess dislocations resulting from low-temperature tempering cause a rapid decrease in creep rupture strength for long periods of time at 600-650°C. This is because excess dislocations accelerate recovery and recrystallization during creep with the aid of stress, which also promotes microstructural evolution during creep. 9-12%Cr turbine steels are more susceptible to a rapid loss of creep strength for long periods of time than 9-12%Cr boiler steels, because the dislocation density after tempering is much higher in 12%Cr turbine steels than in boiler steels [9, 91].
# 3. Materials and methods

## 3.1. Materials

In the present study, X20CrMoV12-1 was investigated. The materials were taken from pipes produced by the Vallourec & Mannesmann Company. Figure 3-1 shows a schematic of the pipe and the position of prepared creep specimens. The chemical composition of this steel is shown in the Table 3-1.

Table 3-1: The chemical composition of X20CrMoV12-1 creep-resistant steels in weight percent.

Chemical Composition [wt.%]									
С	Si	Mn	Р	S	Cr	Мо	V	Al	Ni
0.20	0.15	0.61	0.009	0.014	11.7	0.84	0.25	0.011	0.65



Figure 3-1: Schematic of the position and direction of creep specimens taken from X20CrMoV12-1 pipe.

### 3.2. Heat-treatment

The heat-treatment of X20CrMoV12-1 steel consists of two processes: austenitizing and tempering. Austenitizing takes place at 1323 K for 30 minutes to dissolve the precipitates and carbides in the austenite phase. Air-cooling after austenitizing leads to the martensitic structure which is very brittle. The tempering process at 1043 K for 2 hours is performed to achieve high ductility and toughness. During tempering, carbides precipitate on the internal interfaces and inside grains. Figure 3-2 shows CCT (continues cooling transformation) diagram of X20 steel.



Figure 3-2: Continuous cooling transformation (CCT) diagram of X20CrMoV12-1 steel.

## 3.3. Creep testing

Figure 3-3 a, b show as received material from a pipe and ruptured specimen after around 139971 hours creep exposure, respectively. All long-term creep tests of X20CrMoV12-1 steel were performed at Salzgitter Mannesmann Research Center.



Figure 3-3: a) As-received specimen taken from a pipe, b) creep ruptured specimen after 139971 hours at 823 K under 120 MPa.

In the normal creep experiment the creep testing ends with the rupture of the specimen. Instead of this method, in the current study a series of interrupted creep testing were performed under constant load of 120 MPa at 823 K (550°C). In interrupted creep testing, creep experiments stop manually after certain creep strain or time. We used this method to study the microstructural evolution during long-term creep. The creep conditions of interrupted specimens as well as the ruptured sample are summarized in the Table 3-2.

Table 3-2: Creep conditions of X20CrMoV12-1 specimens. L1, L2 and L3 are interrupted creep specimens and L4 is the ruptured sample.

Specimen	Strain (%)	Stress (MPa)	Stress (MPa) Temperature (K)	
L1	0.5	120	823	12456
L2	1.0	120	823	51072
L3	1.6	120	823	81984
L4 <sub>rupture</sub>	11.9	120	823	139971

#### 3.4. Optical metallography and hardness

In order to study the microstructure of creep-resistant steels, the creep specimens and as-received sample were prepared by standard metallography techniques. The specimens were grinded on silicon carbide paper to a sufficient depth to remove any unrepresentative surface. After mechanically grinding down to 1200 grade emery paper, they were polished with 6, 3 and 1 µm diamond pastes. The specimens were then completely immersed in ethanol and cleaned using an ultrasonic cleaner for at least 15 minutes before drying. The specimens of X20CrMoV12-1 steel were etched using Bain-Villela's reagent (5 ml hydrochloric acid, 1 g picric acid in 100 ml of methanol) for up to 2 minutes at room temperature. Optical micrographs were taken in both bright and dark field modes using a Leica DM4000M microscope equipped with a Leica DFC320 digital camera.

Hardness tests were carried out using a Vickers hardness testing instrument (KB 10/30 BVZ). Measurements were made on polished specimens under the applied indentation load of 0.3 kg. Five measurements were collected over the whole sample area. In addition, the microhardness measurements were accomplished with a Paar MHT-4 microhardness tester machine using a load of 0.981 N, and loading and dwell times of 10 seconds each. All measurements were made at a suitable distance from the specimen edge in order to avoid any edge effects.

#### 3.5. Scanning electron microscopy

A Leo1530VP field emission gun scanning electron microscope (FEG-SEM) equipped with Back-Scattered Electron (BSE), In Lens, Secondary Electrons (SE) and energy dispersive X-ray (EDS) detectors was used. In addition, a Digiview CCD (chargecoupled device) camera recorded EBSD (electron back-scattered diffraction) patterns. Electron back-scatter diffraction (EBSD) is a microstructural-crystallographic technique used to examine the crystallographic orientation of many materials, which can be used to elucidate texture or preferred orientation of any crystalline or polycrystalline materials. Experimentally EBSD is conducted using a scanning electron microscope (SEM) equipped with a back-scatter diffraction camera [92]. The diffraction camera consists of a phosphor screen which is inserted into the specimen chamber of the SEM at 90° to the pole piece and a CCD camera to register the image on the phosphor screen. A schematic of principle of EBSD technique is shown in Figure 3-4.



Figure 3-4: Schematic of EBSD technique.

A polished crystalline specimen is placed into the standard position (0° from horizontal) in the specimen chamber and then it is highly tilted (~70° from horizontal) towards the diffraction camera. When the electrons impinge on the specimen, they interact with the atomic lattice planes of the crystalline structures (many of these interactions satisfy Bragg conditions and undergo back-scatter diffraction). Due to the angle of the specimen, these diffracted electrons can escape the material and are directed towards and collide with the phosphor screen of the diffraction camera causing it to fluoresce, this fluorescent light is then detected by a low light CCD. The diffracted electrons produce a diffraction pattern, which often show Kikuchi bands,

which correspond to each of the lattice diffracting planes and can be indexed individually by the Miller indices of the diffracting plane which formed it [23].

Back-scattered electrons are very sensitive to the morphology of the surface; therefore, an EBSD pattern can be collected only from the completely polished surfaces. Hence, the specimens were mechanically ground down using 1200 SiC paper. The selected area (~30mm<sup>2</sup>) was electropolished using A8 electrolyte (95% acetic acid and 5% perchloric acid) at room temperature. Potential difference of 58V was applied for 2 minutes to get the best results. The specimens were washed with ethanol in an ultrasonic cleaner for 15 minutes and air dried. The plasma cleaner (Fischione 1020) was used to remove the surface contaminations which increases the back-scattered signal collected by the CCD camera. The working distance in all specimens was set to 13 mm from the beam source in the tilted position. The step size in EBSD patterns was between 50 nm to 1  $\mu$ m depending on the magnification of the investigated area. TSL-OIM collection data (version 4.5) was used to gather the EBSD data. The settings for collecting data are shown in Table 3-3.

Hough type:	Classic	Max. peak:	7
Hough resolution:	High	Min. peak:	3
Convolution mask:	Medium 9x9	Rho fraction:	0.8
Binned pattern size:	96	Peak symmetry:	0.5
Theta step size:	1°	Min. peak distance:	20
IQ type:	Hough	Min. peak magnitude:	5

Table 3-3	: Setting	for	collecting	data	in	EBSD.
-----------	-----------	-----	------------	------	----	-------

TSL-OIM analysis (version 4.6) software analyzed the collected pattern and measured the misorientation angles in tempered martensitic microstructure. Before measuring the misorientation angle, the collected EBSD patterns were refined by removing erroneous data points using "grain confidence index standardization" and "grain dilation" cleaning methods. The misorientation chart was created using the TSL-OIM software in an angle range between 1 and 65 degree with 1 degree intervals.

### 3.6. Transmission electron microscopy

A Tecnai F20 G<sup>2</sup> field emission gun transmission electron microscope (FEG TEM) operating at 200 kV was used to investigate the microstructural features and specifically to identify precipitates which can not be recognized using light microscopy and SEM. Tecnai F20 G<sup>2</sup> is equipped with an EDS (EDAX r-TEM) detector to collect the characteristic signals from specimens and to obtain the chemical composition of fine precipitates. X-ray spectra from 20 precipitates in each state were recorded for at least 120 seconds. Possible effects of absorption and fluorescence were not considered. A CCD camera (Gatan US 1000) was installed to take bright-field micrographs as well as diffraction pattern. In addition, a high angle annular dark field (HAADF) was used in scanning transmission electron microscopy (STEM). STEM operates on the same principles as TEM, but, like in SEM, the electron optics focuses the beam into a narrow spot which is scanned over the sample. Unlike normal dark-field imaging where the signal comes from elastic scattering of electrons typically at smaller angles, the HAADF signal is the result of inelastic scattering of electrons typically to larger angles.



Figure 3-5: Diagram of the bright-field, annular dark-field, and high-angle annular dark-field functions of a STEM.

For high angles, elastic and inelastic interactions between the incident electrons and the columns of atoms within the specimen produce image contrast. Since inelastic scattering depends on the number of electrons in an atom, the strength of scattering varies with atomic number (Z-contrast). The signal is typically collected, amplified, and converted to gray levels. Certain atoms within the electron transparent region of the specimen will appear brighter than others. As a result, it is possible to distinguish between different elements (Figure 3-5). In a high resolution HAADF image, brighter spots represent the heavier atomic elements while the less intense spots indicate the lighter atomic elements [93-97].

#### **3.6.1.** Preparation of thin foils

Discs of 1.0 mm thickness were cut from creep specimens with the help of an oilcooled carborundum slitting wheel. The discs were then thinned down to 0.08 mm by abrasion on wet 1200 grade silicon carbide paper. This thinning of the specimen is considered essential to reduce its magnetic mass, thereby minimizing magnetic aberrations in the electron microscope [98]. The discs were twin jet electropolished in a TenuPol-5 (Struers) using a solution of 5% perchloric acid and 95% acetic acid. Electro-polishing was performed at 58V and at 15°C. After electro-polishing, the thin foils were carefully cleaned in methanol and then dried. The foils were then immediately examined to minimize oxidation and contamination.

#### **3.6.2.** Image analysis

Significant numbers of precipitates were examined in each material state to make a statistical relevant analysis. Z-contrast together with diffraction contrast in the HAADF-STEM images clearly highlights the precipitates which have different chemical composition than the matrix. These precipitates are usually rich in heavier elements like Chromium and Molybdenum; therefore, they appear brighter than the surrounding matrix. The contrast in HAADF-images (camera length 300 mm) is not contributed only to the z-contrast, while other features like specimen thickness,

crystallographic orientation, can contribute to the contrast in the HAADF-STEM images (Figure 3-6a). From all the bright spots in the HAADF-STEM images energy dispersive X-ray (EDX) spectroscopy was performed for at least 10 second. The EDX spectroscopy reveals the type of precipitate accurately. Table 3-4 shows the number of precipitates studied in the current investigation.

Specimen	Time (h)	M <sub>23</sub> C <sub>6</sub>	VX	Laves phase
As-received		184	105	
L1	12456	315	214	119
L2	51072	309	119	189
L3	81984	113	163	255
L4 rupture	139971	395	71	90
Total		1316	672	653

Table 3-4: Number of investigated particles in each specimen using TEM and STEM micrographs.

Most of the particles, especially  $M_{23}C_6$  carbides, are overlapped in the images. The automatic image analyzer software may recognize them as one particle and increase the error in the measurements. To prevent significant error using image analyzer software, the primitive of each particle is drawn manually on the transparent layer above HAADF-STEM images, Figure 3-6b. The characteristic parameters of each kind of precipitates were calculated using a transparent layer (Figure 3-6c). Figure 3-7 schematically illustrates the stereological assessment.



Figure 3-6: Procedure to identify and evaluate the precipitates in HAADF—STEM images.

The square sampling field of area  $s^2$  in Figure 3-7 contains 5 particle projections of different sizes and shapes. We retrieve the following particle parameters from the TEM analysis of precipitates:

(i) The number density  $\rho_n$  as  $5/s^2$ .

(ii) We measure a mean particle diameter,  $\overline{d}$ , by determining the minimum  $d_{\min}$  (particle 2 in Figure 3-7) and maximum  $d_{\max}$  (particle 3 in Figure 3-7) projected diameters of all particles. The mean value  $\overline{d}$  and the corresponding mean deviation  $\Delta \overline{d}$  of this mean value are:

$$\overline{d} = 1/n \cdot \sum_{i=1}^{n} \left[ \left( d_{\min,i} + d_{\max,i} \right) / 2 \right] = 1/n \cdot \sum_{i=1}^{n} d_i$$
(3.1)

$$\Delta \overline{d} = 1/n \cdot \sum_{i=1}^{n} \left| d_i - \overline{d} \right|$$
(3.2)

Particle sizes in tempered martensite ferritic steels are typically widely distributed that results in large error bars  $\Delta \overline{d}$ .

(iii) A projected area fraction  $f_A$  was obtained by dividing the sum of the projected areas  $A_i$  of the particles (see particle 4 in Figure 3-7) by the area of the sampling field  $s^2$ :

$$f_A = \left(\sum_{i=1}^n A_i\right): s^2$$
(3.3)



Figure 3-7: Schematic figure illustrating the parameters which were retrieved from the TEM micrographs: particle size, number density and projected area fraction.

# 4. Results

### 4.1. Creep data

Figure 4-1 illustrate the creep data of interrupted creep specimens at 823 K and 120 MPa (Table 3-2). It shows how the creep strain increases with the logarithm of time in hours. The interruption time of each material state is pointed out on the creep data with arrows. It is important to mention that less than 2% strain accumulated within 100000 hours in the ruptured specimen. The strong increase of creep strain (11.9%) in the final stages of the creep test is partially resulting of local deformation known as necking. Figure 4-2 shows the logarithm of creep rate as the logarithm of time (in hours). The arrows on the creep data represent the interruption time of the creep experiments. The minimum creep rate for crept specimen is  $5 \times 10^{-11} s^{-1}$  and it reaches after around 20000 hours. Figure 4-3 shows the creep rate as a function of strain for the experiment carried out to the rupture. The minimum creep rate is established after around 1% strain. The creep parameters for X20CrM0V12-1 steel at 823 K and 120 MPa are summarized as following:

Minimum creep rate	$\dot{\varepsilon}_{\min} \simeq 5 \times 10^{-11} s^{-1}$
Strain at minimum creep rate	$\mathcal{E}_{\dot{\mathcal{E}}_{\min}}\simeq 1\%$
Time at minimum creep rate	$t_{\dot{\varepsilon}_{\min}} \simeq 20000  hours$
Time of rupture	$t_{R} = 139971$ hours
Strain of rupture	$\varepsilon_{R} = 11.9\%$



Figure 4-1: Diagram of strain vs. logarithm of time of specimens with 0.5, 1.0, and 1.6% strain and ruptured specimen.



Figure 4-2: Logarithm of creep rate vs. logarithm of time at 823 K for specimens 0.5, 1.0, 1.6 and 11.9% strain.



Figure 4-3: logarithm of creep rate vs. strain for the ruptured specimen at 823 K and 120 MPa after 139971 hours.

## 4.2. Creep cavities and inclusions

Figure 4-4, 4-5 and 4-6 show the back-scattered micrographs of the ruptured creep specimens after 139971 hours. The micrographs represent one former austenite grain boundary in three magnifications. The white squares indicate the position of the image at the higher magnifications in the subsequent figure. The white arrows in Figure 4-4 point out the former austenite grain boundaries and the direction of the applied stress is shown with black arrows. The number of creep cavities on the former austenite grain boundaries perpendicular to the stress direction are significantly higher than the boundaries parallel to the stress direction.



Figure 4-4: SEM back-scattered micrograph of the ruptured specimen at 823 K and 120 MPa after 139971 hours; white square is represented the region of interest; Arrows show the former austenite grain boundaries.



Figure 4-5: SEM back-scattered micrograph of the pointed out region in Figure 4-4; white square is represented the position of the magnified image in Figure 4-6.



Figure 4-6: SEM back-scattered micrograph of the pointed out region in Figure 4-5; the creep cavities are visible on the former austenite boundary perpendicular to the stress direction.

Figure 4-7a shows a micrograph of a polished specimen before creep testing (initial material state). Elongated micro-pores are visible in the longitudinal direction of the pipe. Figure 4-7b is a back-scattered SEM image of one of the micro-pores in centrifugal direction of the pipe (see Figure 3-1). The EDX spectrums of the particle inside the micro-pore and the surrounding matrix are shown in Figure 4-7 (1 and 2 respectively).

Indexing the chemical elements in both spectrums reveals that the particle inside micro-pores is of the type of MnS inclusions. These inclusions are soft at elevated temperature and can elongate during mechanical forming process like rolling as shown in Figure 4-7a.



Figure 4-7: a) Elongated inclusion after hot rolling in as received specimen in longitude direction, b) backscattered image of a micro-pore in centrifugal direction; 1, 2) EDX spectrum of particle inside pore and surrounding, respectively.

#### 4.3. Evolution of hardness

Figure 4-8 shows how the microhardness HV0.3 evolves during long-term creep there is a continuous decrease of hardness during long-term creep. The initial material state, aging (thread) and creep (gage) are indicated in Figure 4-8 by different symbols. Under creep conditions, hardness values decreases from 262 HV0.3 in the initial state to 222 HV0.3 in the specimen after rupture. In contrast, the hardness values during aging show only small decrease from 262 HV0.3 to 252 HV0.3 after 51072 hours and remain constant.



Figure 4-8: Hardness evolution in gage portion (creep) and thread portion (aging) at 823 K.

### 4.4. Evolution of subgrain

Figure 4-9 represent a montage of 16 bright-field TEM images from initial material state which provides an overview of the microstructure of tempered martensite ferritic steel. The white square in Figure 4-9 indicates the position of Figure 4-10. Figure 4-10 clearly shows the microstructural features like subgrains, precipitates and dislocations. The internal interfaces are decorated by relatively large precipitates, while fine precipitates distribute inside the subgrains.

Figure 4-11 shows an SEM back-scattered micrograph of a specimen from initial material state. Subgrains in tempered martensite ferritic steels have elongated shapes with a form factor of about 2 [1, 89]. These grains can intersect the surface of an SEM specimen in different angles, giving rise to different apparent shapes in the resulting 2D intersections. Therefore one can observe appearances changing from circles to ellipsoids. However, the smallest diameters of these sections always represent the widths of the elongated subgrains. Therefore the smallest diameters are used to characterize subgrain sizes. For each material state, regions with parallel subgrains were identified to position a reference line perpendicular to the direction of the elongated subgrains. Figure 4-11 shows 5 reference lines which intersect subgrain boundaries.

The resulting subgrain widths  $\overline{\lambda}_{sg}$  are reported as mean values from all measurements together with the mean deviations from these mean values  $\Delta\lambda$ . Figure 4-12 shows the evolution of subgrain widths as determined using the line intersection method.



Figure 4-9: A montage of 16 TEM bright-field images; the position of Figure 4-10 is pointed out by white square.



Figure 4-10: Bright-field TEM image from ruptured specimen at 823 K under 120 MPa.



Figure 4-11: Subgrain width measurement in SEM images of X20CrMoV12-1 steel (initial state).



Figure 4-12: Subgrain evolution in creep (under external stress) and in aging (without stress) specimens of X20CrMoV12-1 steel.

As can be seen from Figure 4-12, coarsening of the subgrains requires stress and strain. Under creep conditions (full squares in Figure 4-12) there is a steady increase of subgrain width from 0.70  $\mu$ m (initial state) to 1.07  $\mu$ m (after rupture). In contrast, the increase of subgrain widths during long-term aging (full triangles in Figure 4-12) is small. After 139971 hours, a subgrain width of 0.73  $\mu$ m is obtained from the specimen thread of the ruptured creep specimen. Using the values of b=0.25 nm, G=62 GPa at 823 K [16], the subgrain back-stress in initial state is  $\sigma$ =221.4 MPa and after creep this value reduces to  $\sigma$ =144.8 MPa. Table 4-1 shows reduction of subgrain strengthening during creep.

Table 4-1: Effect of subgrain evolution on the subgrain back-stress.

Time (h)	as-received	12456	51072	81984	139971
$\overline{\lambda}_{\!\scriptscriptstyle sg}$ (µm)	0.70	0.73	0.75	0.87	1.07
$\sigma_{_{sg}}$ (MPa)	221.4	212.3	206.6	178.1	144.8

#### 4.5. Evolution of misorientation

 $300 \times 300 \ \mu\text{m}^2$  of the surface was analyzed using EBSD method with 100 nm step size and an angular resolution of 0.5°. The parameters of EBSD measurements are given in Table 3-3. Figure 4-14, 4-14 and 4-15 illustrate the inverse pole figures (IPF) and image quality (IQ) of the as received, aged and creep specimens. Different colors in the figures represent different orientations in the standard triangle. Since all colors appear in similar frequencies, none of material states (initial, aging and creep states) exhibit a strong texture. In the present work the tilt axis/tilt angle pair approach is used to describe the misorientations between crystallites [92, 99]. Figure 4-13 shows the relative frequency of all detected misorientation angles ( $\theta$ ). The relative frequency of the misorientation angles divided to low and high angle boundaries using traditional terminology. Low angle grain boundaries are those with a misorientation angles less than about 15 degrees. In comparison, the high angle grain boundaries have misorientation angles greater than about 15 degrees. There is a maximum in the smallest size class which indicates that many of the boundaries of subgrains represent small angle boundaries. Another maximum is observed close to 60° which probably is related to twinning processes during the formation of martensite. This is not considered further in the present study. However, it is important to highlight that the majority of subgrain boundaries consists of small angle boundaries. Figure 4-17 clearly indicates that the frequency of low angle boundaries increases during creep, while it remains unaffected by long-term aging. The frequency of high angle boundaries, represented by 60° boundaries in Figure 4-18 remains constant during long-term aging and creep.



Figure 4-13: Relative frequency of misorientation angles in X20CrMoV12-1steel. Angles below 15 degree are defined as low angle boundaries and above 15 degree as high angle boundaries



Figure 4-14: Electron back-scattered diffraction pattern (EBSD) of as-received specimen, a) Image quality (IQ), b) inverse pole figure (IPF).



Figure 4-15: Electron back-scattered diffraction pattern (EBSD) of thread portion (aging) at 823 K; a) Image quality (IQ), b) inverse pole figure (IPF).



Figure 4-16: Electron back-scattered diffraction pattern (EBSD) of gage portion (creep) at 823 K and 120 MPa; a) Image quality (IQ), b) inverse pole figure (IPF).



Figure 4-17: Evolution of one degree misorientation angle in creep and aging specimens at 823 K.



Figure 4-18: Relative frequency oh high angle misorientation (60 degree) in creep and aging specimens.

Figure 4-19 represents the relative frequency of misorientation angles in the range of 0.5 to 5 degrees. There is no significant variation between as-received and aging (without external applied stress) specimens. Compare to the initial and aging material states, the creep specimen has relatively higher frequency of boundaries below 1 degree than other two material states in expense of higher angle boundaries. This shows that external applied stress affect the misorientation of low angle boundaries.



Figure 4-19: Relative frequency of low angles misorientation in as-received, aging and creep specimens.

#### 4.6. Evolution of dislocations density

The density of free dislocations  $\rho$  was evaluated by means of classical procedure of intersection of grid lines with the dislocation lines and by application of the following equation [93, 100, 101]:

$$\rho = \frac{1}{t} \left( \frac{\sum n_{\nu}}{\sum L_{\nu}} + \frac{\sum n_{h}}{\sum L_{h}} \right)$$
(4.1)

where *t* is the foil thickness,  $n_v$  and  $n_h$  are number of intersections of vertical and horizontal grid lines with dislocation network and  $\Sigma L_v$ ,  $\Sigma L_h$  are total length of vertical and horizontal grid lines, respectively. For foil thicknesses up to approximately 170 nm the foil was often bent due to high internal stresses and it was not possible to obtain an image of sufficient quality. On the other side in case of foil thicknesses thicker than 230 nm the image was too dark due to high frequency of many features in severely deformed microstructure and also the focusing of image was not good enough due to the stronger magnetic influence. Therefore the foil thickness is supposed to be in the range 170 nm – 230 nm, otherwise (200 ± 30) nm. For each material state 10-13 micrographs were evaluated and on each micrograph 1-3 micrograins were adjusted in two beam condition and evaluated. The results for all states are presented on Figure 4-23.

Figure 4-20 shows the microstructure of material after tempering at temperature 1023K for 2 hours. During tempering the recovery processes take place in dislocation substructure and due to this fact the dislocation substructure becomes heterogeneous character (there are places with high dislocation density and places with low dislocation density) and new subgrain boundaries are emerging inside of micrograins (Figure 4-20). The average density of free dislocation is 10.16 x 10<sup>13</sup> m<sup>-2</sup> (Figure 4-23).



Figure 4-20: HAADF STEM micrograph showing dislocations in the initial material (prior to temperature exposure and creep).



Figure 4-21: Set of 4 HAADF STEM micrographs showing the evolution of the density of free dislocations during long-term aging. (a) 12456 h / 823 K; (b) 51072 h / 823 K; (c) 81984 h / 823 K; (d) 139971 h / 823 K.

Negligible loading and no significant strain accumulation are occurring in the threads during the creep tests. These threads are exposed to the temperature of creep test for time of duration of creep test. That means that only the thermal exposure could influence the evolution of dislocation substructure in the threads during creep test. Figure 4-21 shows the HAADF-STEM images for all thread states. The subgrain boundaries are occurring inside of micrograins and also the heterogeneity of dislocations is observed. The density of free dislocations is  $5x10^{13}$ m<sup>-2</sup> for all states of threads (Figure 4-23).

Figure 4-22 shows the HAADF-STEM images of crept states. The subgrain boundaries are observed inside of micrograins and they are very good pronounced. The dislocation substructure has again the heterogeneity character with remarkable higher area which is free of dislocations. The density of free dislocations is  $1.16 \times 10^{13} \text{m}^{-2}$  in the crept specimen after long-term creep for 12456 hours and goes asymptotic down to the value  $0.68 \times 10^{13} \text{m}^{-2}$  in the crept specimen after long-term density decreases with increasing time of creep test and asymptotic comes near to the steady state value of dislocation density, but the steady state value is not reached either in the ruptured specimen (Figure 4-23).



Figure 4-22: Set of 4 HAADF STEM micrographs showing the evolution of the density of free dislocations during long-term creep (a) 12456 h/823 K/120 MPa; (b) 51072 h/823 K/120 MPa; (c) 81984 h/823 K/120 MPa; and after rupture (d) 139971 h/823 K/120 MPa.



Figure 4-23: Quantitative metallographic results on dislocation densities in the initial material, after long-term aging and long-term creep.

# 4.7. Identification of precipitates

# 4.7.1. M<sub>23</sub>C<sub>6</sub> carbides

Figure 4-24a, b illustrate the bright-field TEM micrograph and corresponding STEM HAADF image of an  $M_{23}C_6$  carbide on the subgrain boundary in the initial material state. Figure 4-24c shows the selected area diffraction (SAD) pattern of the carbide in [123] direction.



Figure 4-24: a) Bright-field TEM, b) STEM HAADF image, c) selected area diffraction (SAD) pattern of the carbide and d) energy dispersive X-ray (EDX) chemical analysis of the M<sub>23</sub>C<sub>6</sub> carbide.

The indexed pattern reveals that the carbide has an fcc crystallography structure. The EDX chemical composition of the carbide is shown in Figure 4-24d. A Cr-rich  $(Cr,Fe)_{23}C_6$  carbide can be identified with a trace of other elements like Mo.

## 4.7.2. VX carbides

Figure 4-25a, b show the bright-field and HAADF STEM micrographs of a tiny precipitate, respectively.



Figure 4-25: a) Bright-field TEM, b) STEM HAADF image, c) convergent beam electron diffraction (CBED) pattern, d) energy dispersive X-ray (EDX) chemical analysis of the VX carbide.

The mean diameter of this type of precipitates is approximately 70 nm. The selected area diffraction (SAD) pattern of the precipitate results in a mixed pattern of matrix and precipitate. Therefore, the convergent beam electron diffraction (CBED) method was used to identify the crystallographic structure. Figure 4-25c shows the indexed CBED pattern of the fcc structure in [112] direction. The energy dispersive X-ray (EDX) spectrum shows a high Vanadium (V) content in the precipitate (Figure 4-25d). A combination of EDX chemical analysis and diffraction patterns is used to identify the precipitate as VX carbide.

#### 4.7.3. Identification of the Laves phase

The method which was employed to identify this type of precipitate was the same as that used for the  $M_{23}C_6$  carbide. Figure 4-26a, b represent the bright-field TEM and HAADF STEM micrographs of a Laves phase particle, respectively. This type of precipitate is relatively larger than  $M_{23}C_6$  and VX carbides. The size of the Laves phase particles is in the range of 400 nm. The indexed SAD pattern in [100] direction, as shown in Figure 4-26c, exhibits a hexagonal crystallographic structure. The EDX chemical analysis reveals the enrichment of Mo and Fe in the Laves phase (Figure 4-26d).

This precipitate is identified as Mo-rich Laves phase with Fe<sub>2</sub>Mo chemical formula. It should be also noted that other elements like Si, P and Cr are present and play important roles in the formation and growth of the Laves phase particles. For quantification of Laves phase precipitates, a series of HAADF STEM images were analyzed.



Figure 4-26: a) Bright-field TEM, b) STEM HAADF image, c) selected area diffraction (SAD), and d) energy dispersive X-ray (EDX) chemical analysis of the Laves phase.

Figure 4-27 shows an example of HAADF STEM image used to detect the Laves phase precipitates. Laves phase precipitates are rich in heavy elements like Molybdenum. Therefore, these particles appear brighter than other precipitates. This method is applied just to detect the Laves phase particles. For particle identification EDX analysis from each bright spot is performed.



Figure 4-27: A montage of HAADF STEM images of the X20CrMoV12-1 steel after 139971 hours creep exposure at 823 K and 120 MPa. The Laves phase precipitates are brighter than other precipitates and pointed out with arrows.

### 4.8. Evolution of precipitate parameters

Figure 4-28 illustrate the projected area fraction of all precipitates in the X20CrMoV12-1 steel. Projected area fraction of  $M_{23}C_6$  and VX carbides stay constant during long-term creep. The measurements yield projected area fraction close to 9% for  $M_{23}C_6$  carbides and close to 0.5% for VX. No Laves phase could be found in the initial material state specimens. The projected area fraction of Laves-phase linearly increases from 0.25% at 12456 hours to 1.3% after 139971 hours. The design of this kind of steel is based on the subgrain strengthening by  $M_{23}C_6$  carbides, therefore the projected area fraction of  $M_{23}C_6$  carbides is significantly higher than that of the two other precipitates.



Figure 4-28: Evolution of projected area fraction for  $M_{23}C_6$ , VX and Laves phase during creep.



Figure 4-29: Evolution of number density for  $M_{23}C_6,\,VX$  and Laves phase during creep.

Figure 4-29 shows how the number density of precipitates evolves during long-term creep. It shows that the number density of  $M_{23}C_6$  is much higher than the number densities of VX and Laves-phase particles. It steadily decreases from 6.5 particles  $\mu m^{-2}$  in the initial material state down to 3.5 particles  $\mu m^{-2}$  after long-term creep (139971 hours at 823 K), while the number density of VX remains constant at about 1.5 particles  $\mu m^{-2}$  and that of Laves-phase precipitates increases from 0.04 particles  $\mu m^{-2}$  at 12456 hours to 0.12 particles  $\mu m^{-2}$  after rupture (139971 hours).

The data for the mean particle diameters are shown in Figure 4-30. The intermetallic Laves-phase particles are significantly larger than the particles from the two carbide populations. Their mean size increases from 340 nm after 12456 hours to 440 nm after 139971 hours. It should be noted that no Laves-phase particles were found in the initial material state and that large Laves-phase particles had already formed after the shortest creep interruption specimens (12456 hours). In addition, it was very difficult to find Laves-phase particles smaller than 200 nm in all specimens. Figure 4-30 also shows that the size of the VX particles does not change significantly. Their mean diameter is close to 70 nm. In Figure 4-30 only three examples for the widths of associated error bars are shown, Equation (3.2).

The M<sub>23</sub>C<sub>6</sub> particles slowly but steadily increase in size from 160 nm to 230 nm. Figure 4-31 shows the Ostwald ripening of M<sub>23</sub>C<sub>6</sub> carbide at the constant volume fraction. This data can be rationalized on the basis of type  $d^3 = d_0^3 + k(t - t_0)$  where the kinetic constant obtained as  $1.37 \times 10^{29}$  m<sup>3</sup>s<sup>-1</sup>.


Figure 4-30: Evolution of mean diameter for  $M_{23}C_6,\,VX$  and Laves phase during creep.



Figure 4-31: Ostwald ripening of  $M_{23}C_6$  carbides in X20CrMoV12-1 steel.

The experimental data show that VX precipitates are stable in terms of projected area fraction, number density. But the Laves-phase precipitates never reach thermodynamic equilibrium. This can be concluded from the steady increase of number densities, projected area fractions and mean diameters of Laves-phase precipitates throughout long-term creep.

Figure 4-32 shows an HAADF STEM image of a crept specimen after 139971 hours. Arrows indicate the  $M_{23}C_6$  carbides which have loosened their contact to the subgrain boundaries. Figure 4-33 presents the results for the distance measurements between particles and the nearest subgrain boundaries. Figure 4-33 shows that there is a close correlation between subgrain boundaries and particles in the initial material state. During long-term creep, the frequency of particles which are in direct contact with subgrain boundaries decreases, while more particles are found in wider distances from the boundaries.



Figure 4-32: HAADF STEM image of a crept specimen after 139971 hours.



Figure 4-33: The relative frequency of particle-boundary of the initial state, after 51072 hours and after 139971 hours creep.

## 4.9. Chemical evolution of precipitates

The chemical composition of VX and the Laves phase do not change during long-term creep. Figure 4-34 represents the evolution of chemical composition of the Laves phase particles. Fe, Mo and Cr are the major elements in the Laves phase. In addition, there is a trace of Si and P in the EDX spectrum. There is no significant fluctuation in the relative ratio of the components during creep exposure.

The  $M_{23}C_6$  carbides show interesting behavior. In the current study only the relative amount of Fe, Cr and Mo are taking into account to prevent significant error resulting from quantifying light elements like carbon using EDX method. Figure 4-35 shows that the amount of Chromium increases in the  $M_{23}C_6$  carbides from about 56% to 72% up to 51072 hours at the expense of Iron (Fe). Figure 4-36 shows the slight increase in Mo content of  $M_{23}C_6$  carbide during creep. The relative amount of Mo in the as-received specimen is about 3.6% of metallic elements (Mo, Fe, Cr) in  $M_{23}C_6$  carbide and after 139917 hours reaches 4.4% which is very low compare to the amount of Fe and Cr (22% and 71% respectively).



Figure 4-34: Relative concentration of the elements found in the Laves phase particles during creep exposure at 823 K and 120 MPa.



Figure 4-35: Concentration of Fe and Cr in the metallic elements of  $M_{23}C_6$  carbide.



Figure 4-36: Molybdenum concentration in the metallic elements of  $M_{23}C_6$  carbide.

## 5. Discussion

#### 5.1. Creep data

The present work does not focus on the long-term creep behavior and life predictions. However, it is important to point out that creep data document the strain-time history of the specimens investigated in the present study. In addition, the creep data obtained for creep specimens yield reproducible results which are essential to investigate the evolution of microstructure during long-term creep.

## 5.2. Creep cavities and inclusions

The focus of the present study was not on the creep cavitation and damage accumulation. However, SEM images presented in Figure 4-4, 4-5 and 4-6 show clear evidence for aligned creep cavities on the former austenite grain boundaries perpendicular to the applied stress. In addition, it has been shown that a series of SEM images can be used to clearly represent the difference between 10µm micropores related to the MnS inclusions and tiny creep cavities aligned on the former austenite grain boundaries perpendicular to the applied stress. The mechanism of nucleation and growth of cavities on the prior austenite grain boundaries is thoroughly explained in the literatures [102, 103, 104]. Therefore no effort was made to study the mechanisms of cavity nucleation and growth in the present study.

#### 5.3. Evolution of hardness

The room temperature hardness of materials steadily decrease during long-term creep, while temperature exposure alone has a less pronounce effect. [1, 105, 106]. The results of current study agree well with the findings reported by other scientists.

Sawada and coworkers [106] have suggested that in a modified 9% Chromium steel small softening in aged specimens is a result of decrease of dislocation density and precipitation growth. However the effect of boundaries is more pronounce in decrease of hardness in the creep specimens. In addition, the evolution of the hardness values is in good agreement with the hardness evolution law proposed by Masuyama [90] for a 9% Chromium tempered martensite ferritic steel. Masuyama [90] proposes the following relation between creep life fraction (exposure time t divided by the rupture time  $t_R$ ) and the ratio of the hardness of the crept material state H to the hardness of the initial state (or aged material state) H<sub>0</sub> [90] after extended creep periods:

$$H = H_0(0.98 - 0.15\frac{t}{t_R})$$
(5.1)

Figure 5-1 shows the hardness ratio as a function of creep life fraction. Dash line represents the Equation (5.1) suggested by Masuyama [90]. The data of the present study fall very close to this line [90], even though a life fraction factor of 0.13 (instead of 0.15) yields an even better fit (solid line).

### 5.4. Evolution of subgrain

The data for subgrain widths in the present study well agree with the subgrain data from previous works [30, 37, 38, 39, 54, 107, 108, 109]. A good agreement is found when comparing the results of current study for subgrain widths with the phenomenological evolution law for subgrain sizes suggested by Blum [30, 107, 109]. Maruyama and coworkers [82] and Hald and Korcakova [27] applied the resulting phenomenological equation to the evolution of subgrain sizes in 9-12 % Chromium tempered martensite ferritic steels.



Figure 5-1: Hardness ratio as a function of creep life fraction.



Figure 5-2: Subgrain width of interrupted as well as ruptured creep specimens of X20CrMoV12-1 at 823 K under 120 MPa versus creep strain and calculated subgrain width using given formula.

Subgrain sizes  $\lambda$  evolve with strain:

$$\log \lambda = \log \lambda_{\infty} + \log(\lambda_0 / \lambda_{\infty}) \exp\left(-\frac{\varepsilon}{k_{\log \lambda}}\right)$$
(5.2)

 $\lambda$  is subgrain size.  $\lambda_0$  is the initial value of  $\lambda$  before creep exposure.  $\lambda_{\infty}$  is defined as the steady state subgrain size and obtained by Equation (5.3) [82].

$$\lambda_{\infty} = 10 \ \frac{bG}{\sigma}$$
(5.3)

G is the shear modulus, b, the Burgers vector and  $\sigma$ , the applied stress. For subgrain development, the rate constant  $k_{log\lambda}$  in Equation (5.2) takes a value close to 0.12. Equation (5.2) has been found to be valid with the same rate constant for a wide range of 9–12% Cr steels. These include the traditional X20CrMoV12-1 steel and the much more creep-resistant new pipe steels P91 and P92. Figure 5-2 compares the calculated subgrain size using Equation (5.2) with the experimental values from creep testing. X20CrMoV12-1 steel represents one of the early successful tempered martensite ferritic steels. Its hardness and subgrain size evolution during long-term creep shows that it is a typical representative of the wider family of 9-12 % Cr tempered martensite ferritic steels. Equation (5.2) suggests that subgrain growth requires strain and this is in agreement with the results presented in Figure 4-12, where subgrain sizes increase during long-term creep while they are not affected by long-term aging. The results presented in this study suggest that the strong decrease in hardness during long-term creep (Figure 4-8) is mainly governed by the increase of subgrain size. It seems to be less dependent on carbide coarsening, because the precipitate dimensions in the material states subjected to long-term aging and creep are not very different (Table 5-1).

Eggeler and coworkers [2, 110] have investigated the same material in the short-term creep conditions. They have suggested that creep accelerated particle coarsening at 873 K and 62 MPa (resulting rupture time: 109380 hours) is the main reason for lower hardness values in the gauge length than in the thread of creep specimens [110] and

there may be a difference between the microstructural response to 823 K creep testing and 873 K creep exposure. The results of Eggeler [110] were obtained from a much smaller number of particles (initial state: 131, gauge length: 46 and thread: 67) and are therefore less reliable than the results obtained in the present work. And most importantly, in the study of Eggeler [110] no effort was made to study the evolution of subgrain sizes. Therefore, while there seems to be a small accelerating effect of creep on coarsening of  $M_{23}C_6$  in the 873 K study (Table 5-1), the main factor in microstructural softening of room temperature hardness after creep appears to be the increase of subgrain size.

Table 5-1shows that there are no significant differences in the size and number density of all kinds of precipitates between gage and thread portions. In other words, stress has no significant effect on the growth of precipitates.

Table 5-1: Comparison of precipitates in the gage and thread portions at 823 K after 139971 hours creep exposure.

	average size (nm)			volume fraction (%)			number density		
precipitates	$M_{23}C_{6}$	VX	Laves	$M_{23}C_{6}$	VX	Laves	$M_{23}C_{6}$	VX	Laves
thread	216±105	82±35	396±157	10.79	0.8	1.37	5.2	2.3	0.14
gage	224±90	70±40	423±180	9.2	0.6	1.4	3.41	1.6	0.12

This interpretation is in line with previous work. This was convincingly demonstrated by an experiment by Kostka and coworkers [101]. These authors produced a subgrain structure in a ferritic Fe–Cr alloy by severe plastic pre-deformation in equal channel angular pressing followed by annealing. The initial subgrain structure was quite similar to that of tempered martensite, but the lack of precipitates at the subgrain boundaries caused rapid coarsening of the subgrain structure during creep. This result clearly shows the essential effect of structural stabilization by particles. The particles reduce the velocity of migration of the subgrain boundaries. The subgrain structure in tempered martensite steels is therefore particle stabilized. The results are also in line with a recent very careful assessment of microstructure of a 9% Cr tempered martensite ferritic steel (OIM and TEM) in combination with nano-, micro- and macrohardness measurements [106], where the strong decrease in room temperature hardness during long-term creep is mainly associated with subgrain coarsening. It was suggested [106] that the small decrease in hardness in the thread of the creep specimen (Figure 4-8) is mainly associated with the decrease in the density of free dislocations (at constant subgrain size), and this is fully in line with the observations in the current study and with previous work on the evolution of dislocation density during short-term creep [88].

## 5.5. Evolution of low angle boundaries

Using OIM-SEM [91, 99] it has been previously shown that during short-term creep testing, the frequency of low-angle boundaries increases, and the associated effect on dislocation density has been discussed [89]. The present work shows that this increase in the frequency of low-angle boundaries is also observed under conditions of long-term creep (Figure 4-17). Moreover, the results of the distance measurements between particles and the nearest subgrain boundaries show that the loss of stabilization (pinning of subgrain boundaries by carbides) which was observed during short-term creep [1] can also be detected after long-term creep (Figure 4-33).

#### 5.6. Evolution of dislocation density

The evolution of the density of free dislocations in the aged material states suggests, that about half of the dislocations in the initial material can easily annihilate in the early stages of aging. The remaining dislocations are hardly affected even when exposed to further long-term aging. This dramatically changes when a mechanical stress is superimposed. During creep, the initial decrease of dislocation density is much more pronounced. This fast decrease of free dislocation density shows that this process does not rationalize the much slower decrease of room temperature hardness associated with the crept material states.

It should be highlighted that the initial material and the crept material states show a significantly higher scatter (error bars in Figure 4-23) than the aged material states. In the absence of high internal and external stresses, associated with the martensitic transformation and creep, similar dislocation densities are established in different micrograins resulting in small local scatter. In contrast, when stresses are present, different crystallographic orientations of micro grains seem to strongly affect whether the dislocation density is high or low resulting in a large local scatter. The long-term creep results in a much higher decrease of dislocation density than the decrease which was found under short-term creep conditions [88] (where dislocation densities decreased from a similar initial value of  $3.0 \times 10^{13} \text{m}^{-2}$  to  $2.9 \times 10^{13} \text{m}^{-2}$  after 52 h, 126 h, respectively).

## 5.7. Stability of precipitates

In the current study, the creep strengthening mechanism of 12%Cr tempered martensite ferritic steels has been referred to as carbide-stabilized substructure hardening [88-101, 110]. It has been identified in materials subjected to short-term creep and the TEM results obtained in the present study show that this mechanism operates under long-term creep conditions. The stabilization of subgrain boundaries is mainly due to the presence of  $M_{23}C_6$  carbides close to the boundaries, where they exert Zener forces [101]. The large Laves-phase particles (volume fractions between 0.2% and 1.3%) have no specific location in the microstructure (Figure 4-27). They are found on prior austenite grain boundaries as well as in the interior of prior austenite grains (Figure 5-3).



Figure 5-3: HAADF STEM image of ruptured creep specimen after 139971 hours at 823 K of X20CrMoV12-1 steel.

Their sizes are of the same order of magnitude as the sizes of small subgrains. The volume fraction of the tiny VX carbides is even less than that of the Laves-phase particles. Their number density is higher than that of the large Laves-phase particles. The measurements for the projected volume fractions of the three phases,  $M_{23}C_6$ , VX and Laves-phase, for the material state after long-term creep are used to calculate the corresponding particles spacings obtained from number density, and associated values of Orowan back-stresses (following the procedure outlined in Refs. [17, 111]):  $\sigma_b = (\alpha \cdot G \cdot b)/d_p$  (5.4)

Using  $\alpha$ =1, G=100 GPa and b=2·10<sup>-10</sup>m (no more precise values for this first order estimate is needed) A back stress of 65 MPa for all particles is obtained. The M<sub>23</sub>C<sub>6</sub> particles account for 37 MPa, while VX and Laves phase particles only contribute 21 and 7 MPa, respectively. If the creep rate  $\dot{\varepsilon}$  of 12%Cr tempered martensite ferritic steel was governed by a simple power law of type

$$\dot{\varepsilon} = \beta \cdot (\sigma - \sigma_b)^n \tag{5.5}$$

( $\beta$  - constant, n - stress exponent >> 1), and the presence of particles simply resulted in a back stress  $\sigma_b$  which counteracts the applied stress  $\sigma$ , then the M<sub>23</sub>C<sub>6</sub> particles would provide the largest contribution to the materials creep resistance (more than half of the overall back stress). The contribution of the Laves phase particles is comparatively small. This estimate helps to obtain a feel for how particle volume fractions relate to creep resistance. But one must keep in mind that this analysis is limited. The creep rate in tempered martensite ferritic steels is not simply governed by bowing out of individual dislocations in between isolated particles.

Degradation of particle hardening caused by an increase in the mean spacing of particles as well as decrease of number density is unavoidable at elevated temperatures. It generally occurs by Ostwald ripening of the existing precipitates. During ripening, the average precipitate volume increases linearly with time spent at elevated temperature ( $d^3 = d_0^3 + k(t - t_0)$ ).

By increasing the spacing of precipitates, particle hardening and pinning effect for subgrain stabilization is retreated. This time-dependent softening counteracts the work hardening in primary creep and contributes to the increase of creep rate in the tertiary stage of creep. Ostwald ripening of the phase  $M_{23}C_6$  has been already observed in tempered martensite steels [45, 112]. This phase precipitates on the internal interfaces, hardens the subgrain interior and provides a high creep resistance. It coarsens at subgrain boundaries as well as former austenite grain boundaries. The accompanying loss of precipitation strengthening of subgrains leads to degradation of creep resistance. In the current study, the *k* constant for  $M_{23}C_6$ 

carbide during creep exposure at 823 K is measured as  $1.37 \times 10^{-29} m^2 s^{-1}$  which is in a good agreement with the reported values [6, 82]. The growth constant, k, is proportional to the specific energy of the phase boundary of precipitates and depends on the atoms forming the precipitates. Atoms with a high concentration in the precipitates, a low concentration and low diffusivity in the matrix are useful in reducing k value [50]. It has been reported that adding a small quantity of Boron to the 9-12%Cr steel significantly increases the creep strength. Andren and coworkers [47] have shown that introducing a small quantity of Boron to the alloy composition reduces k value in Ostwald ripening equation and postpones precipitate coarsening.

#### 5.8. Chemical evolution of precipitates

In addition to the size and number density evolution (Ostwald ripening) of  $M_{23}C_6$  precipitates, chemistry of precipitates evolves during high temperature exposure. Figure 4-35 shows changes in the chemical composition of  $M_{23}C_6$  carbides during creep at 823 K. The chemical equilibrium for  $M_{23}C_6$  carbide reaches after almost 80000 hours at 823 K by increasing the Chromium content in the  $M_{23}C_6$  carbides. The diffusion of Chromium and Molybdenum from the matrix into the precipitate affects the solid solution strengthening and degrade microstructure of X20CrMoV12-1 steel in the long-term exposure at elevated temperature.

The equilibrium conditions for  $M_{23}C_6$  carbides have been already reported using experimental methods and thermodynamic calculations [113-115].  $M_{23}C_6$  carbides nucleate during tempering process at 1023 K. The chemical composition of  $M_{23}C_6$ carbide in the initial state (Figure 4-35) is near to the equilibrium chemical composition at 1023 K (750°C). Therefore the chemical composition of  $M_{23}C_6$  carbide is not in equilibrium condition at 823 K during creep. The difference in chemical equilibrium is the driving force for diffusion of Chromium instead of Iron in the  $M_{23}C_6$ carbides. VX type of carbides also forms during tempering process. The chemistry and crystallography of VX carbides remains almost constant during creep exposure and they reach their equilibrium conditions after tempering. According to low solubility of Vanadium at 823 K in the alpha-iron [116], thermodynamically it is not favorite for the carbides to dissolve in the matrix which is essential for Ostwald ripening process.

## 5.9. Laves phase nucleation and growth

#### 5.9.1. Structure of the Laves phase

Laves phases are intermetallic compounds with close packed structure of formula AB<sub>2</sub>. The lattice geometry requires that the ratio of diameter of A atoms (d<sub>A</sub>) to that of B atoms (d<sub>B</sub>) should be  $d_A/d_B = 1.225$ . However, in examples of the Laves phase, the ratio actually varies from about 1.1 to about 1.6 [23].

To understand the formation of the Laves phase in tempered martensite ferritic steels, it is necessary to precisely investigate the chemical composition of the Laves phase particles. Early work on Laves phase particles in long-term crept specimens suggests a Laves phase composition of (Fe,Cr)<sub>2</sub>Mo [114] but EDX chemical analysis (Figure 4-26) reveals that the Laves phase particles in the X20CrMoV12-1 steel contain Iron (Fe) and Molybdenum (Mo) as the major elements and Chromium (Cr), Silicon (Si) and Phosphor (P) as the minor elements. Considering polyvalent elements the formula of the Laves phase is near to the (Fe,Cr,Si,P)<sub>2</sub>Mo. Equations (5.6) and (5.7) show that the ratio of Fe group elements (Fe,Cr,Si,P) to the Mo is 1.12 which is in a good agreement with the reported values.

$$\overline{d} = \frac{7.07}{67.7} d_{\rm si} + \frac{1.43}{67.7} d_{\rm P} + \frac{11.66}{67.7} d_{\rm Cr} + \frac{46.99}{67.7} d_{\rm Fe}$$
(5.6)

$$\frac{d_{Mo}}{\overline{d}} = 1.12 \tag{5.7}$$

As illustrated in Figure 4-34, the chemical composition of the Laves phase particles remains constant during creep exposure and all elements within the alloy with a stoichiometric ratio are necessary to form the Laves phase particles.

More recent results for Laves phase particles in tempered martensite ferritic steels highlight the importance of Silicon [117-119]. Most importantly, Hosoi et al. [120] have shown that a decrease of the Si content from 0.67 to 0.008 wt.% strongly increases the time required for Laves phase formation [120]. In tempered martensite ferritic steels with neglible amounts of Si, Laves phase could not be detected [120, 121]. Therefore, in the current study, it is assumed that the diffusion of Silicon controls the formation and growth of the Laves phase particles.

#### 5.9.2. Diffusion coefficient of Silicon in the multi-component systems

Diffusion coefficient of Silicon in a multi-component system, like X20CrMoV12-1 steel is key element to study the formation and growth of the Laves phase. There is no experimental data for the diffusion coefficient of Silicon in 9-12%Cr steels; therefore, it is necessary to calculate the diffusion coefficient indirectly in multi-component systems. It is already known that the diffusion coefficients consist of two separate parts, one purely thermodynamic and one kinetic.

The thermodynamic factors are second derivatives of the molar Gibb's energy with respect to concentration and known if the thermodynamic description of the system has been evaluated. Thermodynamic data have been used in order to calculate phase diagrams for more than 30 years. One method is the calculation of phase diagrams (CALPHAD) method [122] established by Kaufmann and Bernstein [123] in early 1970s. In this method, the Gibbs energy of the individual phases is modeled as a

function of temperature, composition, and sometimes pressure. Having this information, the equilibrium is simply calculated by an energy minimization procedure. Andersson and Agren [124] suggested a similar method for calculating kinetic data. They chose to represent the atomic mobility of the individual species in a multicomponent solution phase as a function of temperature, pressure and composition. It is shown that for calculating the diffusion coefficient of an element in a multi-component system, only the thermodynamic and kinetic (mobility) data of pure species and binary data for each two species is required [125]. The diffusion coefficient of Silicon in the X20CrMoV12-1 steel (D=9.7x10<sup>-21</sup> m<sup>2</sup>/s) is calculated using TCFE6 and MOB2 databases in Thermocalc [126, 127].

#### 5.9.3. Moving boundary solution

An analytical diffusion solution is used to find out the relation between Silicon diffusion and growth of the Laves phase particle. For simplicity, it was assumed that all particles have a spherical shape, the distribution of Silicon in the matrix is homogenous, and the diffusion coefficient remains constant during the diffusion process. Only a few analytical solution to the diffusion equation are available that describe the phase growth in which the particle-matrix interface is allowed to change the position with time and surrounding diffusion field explicitly accommodates the interface motion. Diffusion problems of this type are classified as "moving boundary" problems [128-130]. Figure 5-4 shows schematics of moving boundary solution of the second Fick's equation.

The position of the interface characteristic  $K_s$  is a key diffusion parameter that describes the evolution kinetics of one spherical particle caused by its moving boundary, Equation (5.8).  $K_s$  specifies a fix relationship between the displacement of the interface and diffusion time.

$$K_s = \frac{R_t - R_0}{\sqrt{4Dt}} \tag{5.8}$$

where  $K_s$  is the position of the interface, D is the constant diffusion coefficient.  $R_0$  and  $R_t$  are the radius of particle at the initial state and at the time t respectively. The value of  $K_s$  depends only on the dimensionless saturation (*S*) in the matrix. Equations (5.9) and (5.10) show the relationship between *S* and  $K_s$  where  $C_{\alpha/\beta}$  is the concentration of diffusing element (Silicon) at the surface of particle.  $C_{\infty}$  is the concentration in the matrix and  $C_{\beta/\alpha}$  is the concentration of diffusing the particle.

$$S = \frac{C_{\alpha/\beta} - C_{\infty}}{C_{\alpha/\beta} - C_{\beta/\alpha}}$$
(5.9)

$$S = 2K_s^2 \left[ 1 - \sqrt{\pi} K_s \exp\left(K_s^2\right) \operatorname{erfc}\left(K_s\right) \right]$$
(5.10)

By assuming that all diffused Silicon atoms to the particle are consumed to form the Laves phase, the size of particle depends on the number of Silicon diffused atoms. The concentration of Silicon in the Laves phase and matrix are calculated as the number of atoms per unit volume. The calculations were performed assuming  $C_{\alpha/6}=0$ .  $C_{\beta/\alpha} = 2 \times 10^{-3} \quad atoms / A^3$ 

$$C_{\infty} = 6.8 \times 10^{-5}$$
 atoms /  $A^{3}$ 



Figure 5-4: Model of diffusion of Silicon into the Laves phase particles from surrounding matrix with constant surface concentration.



Figure 5-5: Growth of the Laves phase particles for different boundary concentration of Silicon.

The results of the calculation are shown as a solid line in Figure 5-5. In addition and for comparison a dashed line is shown which is based on a similar scenario governed by Mo-diffusion. Mo is an element with a diffusion coefficient which is only a little higher than that of Si while the Mo-concentration in the matrix is higher (diffusion coefficient of Mo is  $5.7 \times 10^{-20}$  m<sup>2</sup>/s).

Figure 5-5 shows the increase of particle radius  $\Delta R$  as a function of growth time *t*. Now the model predictions are compared with measured particle sizes (Figure 4-30). The input particle dimensions are based on the average radii of the 5 biggest spherical Laves phase particles in each material state, Table 5-2.

time (h)	12456	51072	81984	139971
ρ <sub>n</sub> (μm⁻²)	0.04	0.08	0.104	0.124
R (μm)	0.34	0.54	0.63	0.72

Table 5-2: Parameters characterizing the population of Laves phase particles after different periods of long-term creep exposure.  $\rho_n$  – number density of Laves phase particles. R - mean radius of the five biggest Laves phase particles.

However, the experimental *R* just accounts for the final size of the particles. *R* is known but  $\Delta R$  is required (plotted on the y-axis of Figure 5-5).  $t_{CREEP}$ , is the time of creep which is known for all specimens but to compare the experimental results with the suggested modeling the time of Laves-phase growth *t* should be introduce to the calculations (plotted on the x-axis of Figure 5-5).some logical assumptions on the nucleation time ( $t_N$ ) and nucleus size ( $R_0$ ) provide basic information to apply the modeling, because  $t=t_{CREEP}$ - $t_N$  and  $\Delta R=R-R_0$ . The experimental data are presented in four ways:

- (a) immediate nucleation ( $t_N$ =0s) and a vanishing nucleus sizes ( $R_0$ =0nm)
- (b) immediate nucleation ( $t_N$ =0s) and a very large nucleus sizes ( $R_0$ =200nm)
- (c) late nucleation ( $t_N$ =10000h) and a vanishing nucleus sizes ( $R_0$ =0nm)

(d) late nucleation ( $t_N$ =10000h) and a large nucleus sizes ( $R_0$ =200nm)

The rectangular fields defined by the four extreme conditions (a) to (d) represent uncertainties in relating the set of microscopic data to the model predictions. But Figure 5-5 shows that when particles sizes become very large and times become very long, these large uncertainties are not so important for the overall picture. The data presented in Figure 5-5 also show, that a scenario based on Mo-diffusion as the rate controlling growth mechanism of Laves phase particles significantly over-predicts the observed growth rates.

### 5.9.4. Remaining Silicon in the matrix

The scenario outlined in Figure 5-5 is only valid, however, when the far field matrix concentration of Si does not change. Therefore it is necessary to obtain the Si concentration profiles between particles using another procedure given by Glicksman [129]. Si concentration profiles can be calculated using

$$c[r_x,t] = c_{\infty} - \left[ \left( c_{\infty} - c_{\alpha/L} \right) \cdot \left( f_1 / f_2 \right) \right]$$
(5.11)

 $f_1$  and  $f_2$  are given by

$$f_1 = \exp\left(-\left(r_x - R_0\right)^2 / \alpha\right) / \left(\left(r_x - R_0\right)^2 / \sqrt{\alpha}\right) - \sqrt{\pi} \cdot erfc\left(\frac{r_x - R_0}{\sqrt{\alpha}}\right)$$
(5.12)

$$f_2 = \exp\left(-\left(R(t) - R_0\right)^2 / \alpha\right) / \left(\left(R(t) - R_0\right)^2 / \sqrt{\alpha}\right) - \sqrt{\pi} \cdot erfc\left(\frac{R(t) - R_0}{\sqrt{\alpha}}\right)$$
(5.13)

In Equations (5.12) and (5.13),  $\alpha$  is an abbreviation for  $4D_{Si}^{\alpha}t$  and the dimensionless and normalized distance parameter  $r_x$  is given by

$$r_x = \frac{x}{\lambda_i}, \ 0 < x < \lambda_i \tag{5.14}$$

 $\lambda_i$  is the distance between two particles (from one particle/matrix-interface to the other), Figure 5-6a. It is related to the center to center distance  $\lambda_n$  by  $\lambda_i = \lambda_n - 2R$ , Figure 5-6. The center to center distance is obtained from the TEM number density measurements  $\rho_n$  through  $\lambda_n = 1/\sqrt{\rho_n}$ . As input parameters for the calculations  $R_0$  defined as the size of the nucleus and  $r_x$  as the distance parameter which is related to the number density of particles) and the concentrations  $c_{\infty}$  and  $c_{L/\alpha}$  (the same values as for the Si-calculations in Figure 5-5). The results presented in Figure 5-7 only indirectly account for the continuous nucleation of Laves phase particles. Each  $c(r_x)$ -curve is calculated for the particle spacing which was derived from the experimentally observed particle number densities after the associated times of creep exposure, i.e. the calculations for different times of creep exposures start with different particle spacings.



Figure 5-6: Schematic illustration of (a) the particle geometry and particle spacing and (b) the Si concentration profile in between two particles.



Figure 5-7: Relative Si concentration ( $c_{r(x)}/c_{\infty}$ )·100% as a function of the dimensionless distance parameter  $r_x = x/\lambda_i$ .

In the calculations an initial particle size of 200 nm is assumed and the particle spacings are given in Table 5-2. Even though the results shown in Figure 5-7 are based on a number of crude assumptions, they that the Si concentration in between the particles decreases, but that even after the longest exposure time of 139971 hours, there is still plenty of Si left to feed further particle growth. This justifies the first order assumption for obtaining Figure 5-6, where an infinite Si-reservoir was assumed. The growth of Laves phase particles affects the Si concentration in between the particles. The experimental volume fraction data for the Laves phase  $f_v^{Laves}$  are shown in Figure 4-28. They can be used to calculate the relative remaining silicon concentration in the matrix  $c_{Si-rem}^{V, rel, exp}$ .

$$c_{Si-rem}^{V,rel,\exp} = c_{\infty}^{V,rel} - c_{L/\alpha}^{V,rel} \cdot f_V^{Laves}$$
(5.15)

Equation (5.15) invokes the volume fraction of Laves phase particles. Therefore are expressed number of atoms concentrations as per volume (  $c_{\infty}^{V} = 6.8 \cdot 10^{-5} a toms / (10^{-10} m)^{3}$  and  $c_{L/\alpha}^{V} = 2.0 \cdot 10^{-3} atoms / (10^{-10} m)^{3}$ ). Relative concentrations are calculated by normalization and multiplying with 100% (e.g.  $c_{L/\alpha}^{V,rel} = (c_{L/\alpha}^{V}/c_{\infty}) \cdot 100\%$ ).  $c_{\infty}^{V,rel}$  is the matrix Si concentration prior to creep and equals 100 %.  $c_{L/\alpha}^{V,rel}$  is the ratio of the relative amounts of Si in Laves phase and matrix. It is possible to compare the experimental value for the remaining Siconcentration in the matrix with a calculated value  $c_{Si-rem}^{V, rel, mod}$  which is obtained from the areas under the concentration profiles in Figure 5-7. Table 3 shows that experimental and calculated values are in good agreement.

Table 5-3: Experimentally determined Laves phase volume fractions  $f_V^{Laves}$ . Experimental  $c_{Si-rem}^{V,rel,exp}$  and calculated  $c_{Si-rem}^{V,rel,mod}$ 

time (h)	${f_V}^{Laves}$ in %	$c_{Si-rem}^{V, rel, exp}$ in %	$c_{\rm Si-rem}^{\rm V,rel,mod}$ in %
12456	0.26	92	95
51072	0.68	80	78
81984	0.94	72	70
139971	1.4	59	62

# 6. Conclusions

The current study presents a detailed investigation on the evolution of microstructure during long-term aging and creep of a 12% Cr tempered martensite ferritic steel (creep conditions: 823K, 120MPa, rupture time: 139 971 hours). Based on the results, the following conclusions can be drawn:

(i) The 12% Cr tempered martensite ferritic steel investigated in the present work (German grade: X20) is a member of the wider family of 9 - 12 % Cr creep resistant steels. All steels from this group show common features like a decrease of hardness and an increase of subgrain size during long-term creep.

(ii) An increase of subgrain size, an increase of the frequency of low angle subgrain boundaries and a decrease of carbide stabilization of subgrain boundaries in tempered martensite ferritic steels were observed in materials subjected to shortterm creep testing. In the present study it is shown that each of these elementary deformation and softening processes operates under conditions of long-term creep.

(iii) After 823K long-term creep, creep accelerated particle coarsening was found to be much less pronounced than expected from the findings of a previous study on material which was subjected to 873 K long-term creep. 823 K long-term creep mainly affects subgrain coarsening. Subgrains in the gauge length of long-term creep specimens coarsen significantly while they only show a minor increase in size in the undeformed specimen threads. At 823 K there is only a small additional effect of particle coarsening on creep as compared to long-term aging.

(iv) The creep strength of the material investigated in the present study relies on  $M_{23}C_6$  carbides to stabilize the subgrain substructure. The other two precipitate

families (VX and Laves phase) detected in the present study are less important because their number densities and volume fractions are much smaller.

(v) The particle populations behave in different ways. In the present study,  $M_{23}C_6$  carbides take around 50000 hours to establish their new equilibrium chemical composition. Most importantly, their Cr and Mo content increases at the expense of their Fe concentration. The slow diffusion of Cr in  $\alpha$ -iron governs the time required for establishing chemical equilibrium. At constant volume fraction,  $M_{23}C_6$  undergo Ostwald ripening.  $M_{23}C_6$  particles which remain in contact with subgrain boundaries during long-term creep were frequently observed to be larger than those which lost contact. In contrast, VX particles are stable during long-term creep. Their chemical composition is constant and there is no significant change in volume fraction and particle size.

(vi) In agreement with earlier work, the tempered martensite ferritic steel investigated in the present study has a very high initial dislocation density of 1.02 x  $10^{14}$ m<sup>-2</sup>. This dislocation density decreases by a factor of about 2 during early thermal aging. Continued long-term temperature exposure shows no additional effect.

(vii) Creep exposure at the same temperature has a significant effect on the microstructure. The dislocation density decreases by almost one order of magnitude down to  $1.16 \times 10^{13} \text{m}^{-2}$  and dislocation densities steadily decrease during long-term creep down to  $0.68 \times 10^{13} \text{m}^{-2}$ .

(viii) Dislocations are more uniformly distributed in the micrograins after long-term aging while in the long-term creep specimens dislocation density is less homogeneous. (ix) It is well established that Lave phase particles in the X20CrMoV12-1 steel have compositions close to (Fe,Cr)<sub>2</sub>Mo. As soon as Laves phase particles can be detected (in the present study after 12456 hours) their average chemical composition is close to 12at.-% Cr, 32at.-% Mo, 45at.-% Fe, 7at.-% Si and 1at.% P. This composition does not change during long-term aging and creep. Most importantly, even under conditions of long-term creep the Laves phase in the material of the current study does not reach thermodynamic equilibrium. The number density and size of Laves phase particles and their volume fraction steadily increases. The slow diffusion of Si towards widely spaced Laves phase particles which governs its slow evolution towards thermodynamic equilibrium. The results suggest that Si must be moreover incorporated into the growing Laves phase particles and therefore diffusion of Si towards the Laves phase particles is critical.

### **Reference List**

- 1. G. Eggeler, N. Nilsvang, and B. Ilschner, "*Microstructural changes in a 12-percent chromium steel during creep*", Steel Research, 58 (1987) 97-103.
- G. Eggeler, J. C. Earthman, N. Nilsvang, and B. Ilschner, "Microstructural study of creep-rupture in a 12-percent chromium ferritic steel", Acta Metallurgica, 37 (1989) 49-60.
- 3. T. Fujita, "*Heat-resistant steels for advanced power-plants*", Advanced Materials & Processes, 141 (1992) 42-47.
- 4. F. Masuyama, "*History of power plants and progress in heat resistant steels*", ISIJ International, 41 (2001) 612-625.
- 5. T. Fujita, "Advanced high-chromium ferritic steels for high-temperatures", Metal Progress, 130 (1986) 33-40.
- 6. J. Hald, "*Microstructure and long-term creep properties of 9-12% Cr steels*", International Journal of Pressure Vessels and Piping, 85 (2008) 30-37.
- M. Yoshizawa and M. Igarashi, "Long-term creep deformation characteristics of advanced ferritic steels for USC power plants", International Journal of Pressure Vessels and Piping, 84 (2007) 37-43.
- R. L. Klueh, "Elevated temperature ferritic and martensitic steels and their application to future nuclear reactors", International Materials Reviews, 50 (2005) 287-310.
- 9. C. Scheu, F. Kauffmann, G. Zies, K. Maile, S. Straub, and K. H. Mayer, "*Requirements for microstructural investigations of steels used in modern power plants*", Zeitschrift fur Metallkunde, 96 (2005) 653-659.
- 10. K. H. J. Buschow, "*Encyclopedia of materials : science and technology*", Elsevier (2001) Amsterdam, Netherlands.
- H. Diehl and J. Granacher, "Results of creep-rupture tests at 500-degrees-C with loading times up to more than 300000-h", Archiv fur Das Eisenhuttenwesen, 50 (1979) 299-303.
- 12. J. S. Dubey, H. Chilukuru, J. K. Chakravartty, M. Schwienheer, A. Scholz, and W. Blum, "Effects of cyclic deformation on subgrain evolution and creep in 9-12% Crsteels", Metallurgical and Materials Transactions A, 406 (2005) 152-159.
- Y. Kadoya, T. Goto, S. Date, T. Yamauchi, T. Saida, and T. Sada, "Assessment of Remaining Life of Fossil Power-Plant Parts by Means of A Miniature Creep-Rupture Test", ISIJ International, 30 (1990) 854-861.
- 14. A. Kimura, R. Kasada, A. Kohyama, H. Tanigawa, T. Hirose, K. Shiba, S. Jitsukawa, S. Ohtsuka, S. Ukai, M. A. Sokolov, R. L. Klueh, T. Yamamoto, and G. R. Odette,

"Recent progress in US-Japan collaborative research on ferritic steels R&D", Journal of Nuclear Materials, 367 (2007) 60-67.

- V. Knezevic, J. Balun, G. Sauthoff, G. Inden, and A. Schneider, "Design of martensitic/ferritic heat-resistant steels for application at 650 degrees C with supporting thermodynamic modelling", Metallurgical and Materials Transactions A, 477 (2008) 334-343.
- 16. D. Gandy, "*X20CrMoV12-1 steel handbook*", Electric power research institute (2006) Palo Alto, USA.
- 17. F. Abe, T. U. Kern, and R. Viswanathan, "*Creep-resistant steels*", Woodhead Publishing, CRC Press (2008) Cambridge, England.
- A. Shibli and F. Starr, "Some aspects of plant and research experience in the use of new high strength martensitic steel P91", International Journal of Pressure Vessels and Piping, 84 (2007) 114-122.
- G. Vigneron, A. Vanderschaeghe, and J. Lecoq, "A metallurgical contribution to the industrial-development of 12-percent chromium martensitic steels for pressure-vessels", International Journal of Pressure Vessels and Piping, 32 (1988) 389-413.
- R. W. Swindeman, M. L. Santella, P. J. Maziasz, B. W. Roberts, and K. Coleman, "Issues in replacing Cr-Mo steels and stainless steels with 9Cr-1Mo-V steel", International Journal of Pressure Vessels and Piping, 81 (2004) 507-512.
- M. X. Yao, J. B. C. Wu, S. Yick, Y. Xie, and R. Liu, "High temperature wear and corrosion resistance of a Laves phase strengthened Co-Mo-Cr-Si alloy", Materials Science and Engineering A, 435-436 (2006) 78-83.
- 22. Y. F. Yin and R. G. Faulkner, "*Creep damage and grain boundary precipitation in power plant metals*", Materials Science and Technology, 21 (2005) 1239-1246.
- 23. R. W. Cahn and P. Haasen, "*Physical metallurgy*", North-Holland Physics Pub. ; Sole distributors for the USA and Canada, Elsevier Science Pub. Co. (1983) New York, USA.
- J. Janovec, M. Svoboda, A. Kroupa, and A. Vyrostkova, "Thermal-induced evolution of secondary phases in Cr-Mo-V low alloy steels", Journal of Materials Science, 41 (2006) 3425-3433.
- 25. D. V. Shtansky and G. Inden, "*Phase transformation in Fe-Mo-C and Fe-W-C steels .1. The structural evolution during tempering at 700 degrees C*", Acta Materialia, 45 (1997) 2861-2878.
- D. V. Shtansky and G. Inden, "Phase transformation in Fe-Mo-C and Fe-W-C steels .2. Eutectoid reaction of M<sub>23</sub>C<sub>6</sub> carbide decomposition during austenitization", Acta Materialia, 45 (1997) 2879-2895.

- 27. J. Hald and L. Korcakova, "Precipitate stability in creep resistant ferritic steels -Experimental investigations and modelling", ISIJ International, 43 (2003) 420-427.
- Y. Kadoya, B. E. Dyson, and M. McLean, "Microstructural stability during creep of Moor W-bearing 12Cr steels", Metallurgical and Materials Transactions A, 33 (2002) 2549-2557.
- 29. Y. Qin, G. Gotz, and W. Blum, "Subgrain structure during annealing and creep of the cast martensitic Cr-steel G-X12CrMoWVNbN 10-1-1", Metallurgical and Materials Transactions A, 341 (2003) 211-215.
- 30. W. Blum and S. Straub, "Subgrain Growth During Creep of A Tempered Martensitic 12-Percent Cr-Steel", Steel Research, 62 (1991) 72-74.
- Y. K. Chung, J. J. Park, C. H. Joo, and I. M. Park, "Characteristics of material degradation for thermal aged X20CrMoV12-1 steel", Designing, Processing and Properties of Advanced Engineering Materials, Pts 1 and 2, 449-4 (2004) 537-540.
- Z. F. Hu and Z. G. Yang, "Identification of the precipitates by TEM and EDS in X20CrMoV12.1 after long-term service at elevated temperature", Journal of Materials Engineering and Performance, 12 (2003) 106-111.
- Z. F. Hu and Z. G. Yang, "An investigation of the embrittlement in X20CrMoV12.1 power plant steel after long-term service exposure at elevated temperature", Metallurgical and Materials Transactions A, 383 (2004) 224-228.
- D. A. Skobir, M. Jenko, and D. Mandrino, "The characterization of various chromium carbide compounds in X20CrMoV121 steel", Surface and Interface Analysis, 36 (2004) 941-944.
- 35. D. A. Skobir, M. Godec, M. Jenko, and B. Markoli, "*Characterization of the carbides in the steel X20CrMoV12.1 used in thermal power plants*", Surface and Interface Analysis, 40 (2008) 513-517.
- J. Storesund, K. Borggreen, and W. L. Zang, "Creep behaviour and lifetime of large welds in X 20 CrMOV 12 1 - results based on simulation and inspection", International Journal of Pressure Vessels and Piping, 83 (2006) 875-883.
- S. Straub, T. Hennige, P. Polcik, and W. Blum, "Microstructure and Deformation Rate During Long-Term Cyclic Creep of the Martensitic Steel X22Crmov12-1", Steel Research, 66 (1995) 394-401.
- S. Straub, P. Polcik, W. Besigk, W. Blum, H. Konig, and K. H. Mayer, "Microstructural Evolution of the Martensitic Cast Steel Gx12Crmovnbn9-1 During Long-Term Annealing and Creep", Steel Research, 66 (1995) 402-408.

- S. Straub, W. Blum, D. Rottger, P. Polcik, D. Eifler, A. Borbely, and T. Ungar, "Microstructural stability of the martensitic steel X20CrMoV12-1 after 130000 h of service at 530 degrees C", Steel Research, 68 (1997) 368-373.
- J. C. Vaillant, B. Vandenberghe, B. Hahn, H. Heuser, and C. Jochum, "T/P23, 24, 911 and 92: New grades for advanced coal-fired power plants: Properties and experience", International Journal of Pressure Vessels and Piping, 85 (2008) 38-46.
- S. K. Albert, M. Kondo, M. Tabuchi, F. X. Yin, K. Sawada, and F. Abe, "Improving the creep properties of 9Cr-3W-3Co-NbV steels and their weld joints by the addition of boron", Metallurgical and Materials Transactions A, 36A (2005) 333-343.
- G. Eggeler, A. Ramteke, M. Coleman, B. Chew, G. Peter, A. Burblies, J. Hald, C. Jefferey, J. Rantala, M. Dewitte, and R. Mohrmann, "Analysis of creep in a welded P91 pressure vessel", International Journal of Pressure Vessels and Piping, 60 (1994) 237-257.
- 43. S. Spigarelli and E. Quadrini, "Analysis of the creep behaviour of modified P91 (9Cr-1Mo-NbV) welds", Materials & Design, 23 (2002) 547-552.
- 44. J. V. Tuma and G. Kosec, "Effect of microstructure on the accelerated creep of 20CrMoV12-1 and P 91 steels", Steel Research International, 78 (2007) 643-647.
- 45. F. Abe, "Effect of boron on creep deformation behavior and microstructure evolution in 9% Cr steel at 650 degrees C", International Journal of Materials Research, 99 (2008) 387-394.
- F. Abe, "Precipitate design for creep strengthening of 9% Cr tempered martensitic steel for ultra-supercritical power plants", Science and Technology of Advanced Materials, 9 (2008) -.
- 47. H. O. Andren, "*Combining TEM and APFIM techniques to study the microstructure of steels and hardmetals*", Micron, 32 (2001) 713-719.
- 48. G. Eggeler and A. Dlouhy, "Boron segregation and creep in ultra-fine grained tempered martensite ferritic steels", Zeitschrift fur Metallkunde, 96 (2005) 743-748.
- 49. M. Hattestrand, M. Schwind, and H. O. Andren, "*Microanalysis of two creep resistant* 9-12% chromium steels", Metallurgical and Materials Transactions A, 250 (1998) 27-36.
- 50. M. Hattestrand and H. O. Andren, "Boron distribution in 9-12% chromium steels", Metallurgical and Materials Transactions A, 270 (1999) 33-37.

- 51. T. A. Tchizhik, T. A. Tchizhik, and A. A. Tchizhik, "Optimization of the heat treatment for steam and gas turbine parts manufactured from 9-12% Cr steels", Journal of Materials Processing Technology, 77 (1998) 226-232.
- 52. H. K. D. H. Bhadeshia, A. Strang, and D. J. Gooch, "*Ferritic power plant steels: remanent life assessment and approach to equilibrium*", International Materials Reviews, 43 (1998) 45-69.
- 53. H. M. Tawancy and L. Al-Hdhrami, "Failure of refurbished turbine blades in a power station by improper heat treatment", Engineering Failure Analysis, In Press, Corrected Proof (2008) -.
- 54. R. W. Cahn, P. Haasen, E. J. Kramer, and Han E. H. Meijer, "*Materials science and technology : a comprehensive treatment*", Wiley-VCH (1998) Weinheim, Germany.
- R. C. Thomson and H. K. D. H. Bhadeshia, "Changes in chemical-composition of carbides in 2.25Cr-1Mo power-plant steel .2. Mixed microstructure", Materials Science and Technology, 10 (1994) 205-208.
- 56. H. K. D. H. Bhadeshia, "Design of ferritic creep-resistant steels", ISIJ International, 41 (2001) 626-640.
- 57. M. C. Tsai, C. S. Chiou, and J. R. Yang, "*Microstructural evolution of simulated heat-affected zone in modified 2.25Cr-1Mo steel during high temperature exposure*", Journal of Materials Science, 38 (2003) 2373-2391.
- 58. M. Hattestrand and H. O. Andren, "Evaluation of particle size distributions of precipitates in a 9% chromium steel using energy filtered transmission electron microscopy", Micron, 32 (2001) 789-797.
- 59. A. Gustafson and M. Hattestrand, "*Coarsening of precipitates in an advanced creep resistant 9% chromium steel quantitative microscopy and simulations*", Metallurgical and Materials Transactions A, 333 (2002) 279-286.
- M. Hattestrand and H. O. Andren, "Microstructural development during ageing of an 11% chromium steel alloyed with copper", Materials Science and Engineering A, 318 (2001) 94-101.
- J. Janovec, A. Vyrostkova, M. Svoboda, A. Kroupa, and H. J. Grabke, "Evolution of secondary phases in Cr-V low-alloy steels during aging", Metallurgical and Materials Transactions A, 35A (2004) 751-759.
- K. Sawada, K. Kubo, and F. Abe, "Creep behavior and stability of MX precipitates at high temperature in 9Cr-0.5Mo-1.8W-VNb steel", Materials Science and Engineering A, 319-321 (2001) 784-787.
- 63. K. Sawada, K. Kubo, and F. Abe, "Contribution of coarsening of MX carbonitrides to creep strength degradation in high chromium ferritic steel", Materials Science and Technology, 19 (2003) 732-738.

- D. A. Skobir, F. Vodopivec, S. Spaic, and B. Markoli, "Effect of tempering on the chemical and phase composition of M<sub>x</sub>C<sub>y</sub> precipitates in low carbon chromium-molybdenum-vanadium steel", Zeitschrift fur Metallkunde, 95 (2004) 1020-1024.
- M. Taneike, K. Sawada, and F. Abe, "Effect of carbon concentration on precipitation behavior of M<sub>23</sub>C<sub>6</sub> carbides and MX carbonitrides in martensitic 9Cr steel during heat treatment", Metallurgical and Materials Transactions A, 35A (2004) 1255-1262.
- 66. K. Yamada, M. Igarashi, S. Muneki, and F. Abe, "Creep properties affected by morphology of MX in high-Cr ferritic steels", ISIJ International, 41 (2001) S116-S120.
- 67. L. Korcakova, J. Hald, and M. A. J. Somers, "*Quantification of Laves phase particle size in 9CrW steel*", Materials Characterization, 47 (2001) 111-117.
- Q. A. Li, "Precipitation of Fe<sub>2</sub>W Laves phase and modeling of its direct influence on the strength of a 12Cr-2W steel", Metallurgical and Materials Transactions A, 37A (2006) 89-97.
- 69. Y. Murata, T. Koyama, M. Morinaga, and T. Miyazaki, "*Prediction of the Laves phase morphology in Fe-Cr-W-C quaternary steels with the aid of system free energy concept*", ISIJ International, 42 (2002) 1423-1429.
- K. Sawada, M. Takeda, K. Maruyama, R. Ishii, M. Yamada, Y. Nagae, and R. Komine, "Effect of W on recovery of lath structure during creep of high chromium martensitic steels", Metallurgical and Materials Transactions A, 267 (1999) 19-25.
- 71. B. S. Ku and J. Yu, "*Effects of Cu addition on the creep rupture properties of a 12% Cr steel*", Scripta Materialia, 45 (2001) 205-211.
- F. Abe, "Coarsening behavior of lath and its effect on creep rates in tempered martensitic 9Cr-W steels", Metallurgical and Materials Transactions A, 387-89 (2004) 565-569.
- 73. P. W. Voorhees, "*The theory of Ostwald ripening*", Journal of Statistical Physics, 38 (1985) 231-252.
- 74. A. Baldan, "*Review progress in Ostwald ripening theories and their applications to nickel-base superalloys Part I: Ostwald ripening theories*", Journal of Materials Science, 37 (2002) 2171-2202.
- 75. R. W. Evans and B. Wilshire, "Introduction to creep", Institute of Materials (1993) London, England.
- 76. R. W. Evans and B. Wilshire, "Creep of metals and alloys", Institute of Metals (1985) London, England.
- 77. J. Cadek, "Creep in metallic materials", Elsevier (1988) Amsterdam, Netherlands.

- 78. F. R. N Nabarro and H. L. De Villiers, "*The physics of creep : creep and creep-resistant alloys*", Taylor & Francis (1995) London, England.
- 79. A. Yawny and G. Eggeler, "Assessment of back stress and load transfer approaches for rationalizing creep of short fiber reinforced aluminum alloys", Metallurgical and Materials Transactions A, 387-89 (2004) 905-909.
- 80. F. Abe, "Creep rates and strengthening mechanisms in tungsten-strengthened 9Cr steels", Materials Science and Engineering A, 319-321 (2001) 770-773.
- 81. P. J. Ennis, A. ZielinskaLipiec, O. Wachter, and F. A. Czvrska, "*Microstructural stability* and creep rupture strength of the martensitic steel P92 for advanced power plant", Acta Materialia, 45 (1997) 4901-4907.
- 82. K. Maruyama, K. Sawada, and J. Koike, "*Strengthening mechanisms of creep resistant tempered martensitic steel*", ISIJ International, 41 (2001) 641-653.
- 83. T. Sourmail, "*Precipitation in creep resistant austenitic stainless steels*", Materials Science and Technology, 17 (2001) 1-14.
- M. Taneike, F. Abe, and K. Sawada, "Creep-strengthening of steel at high temperatures using nano-sized carbonitride dispersions", Nature, 424 (2003) 294-296.
- R. C. Thomson and H. K. D. H. Bhadeshia, "Carbide precipitation in 12Cr1MoV powerplant steel", Metallurgical Transactions A-Physical Metallurgy and Materials Science, 23 (1992) 1171-1179.
- A. Dlouhy, Malte Probst-Hein, and G. Eggeler, "Static dislocation interactions in thin channels between cuboidal particles", Materials Science and Engineering A, 309-310 (2001) 278-282.
- G. L. Dunlop, J. O. Nilsson, and P. R. Howell, "Interaction of grain-boundary dislocations with precipitates during high-temperature creep", Journal of Microscopy-Oxford, 116 (1979) 115-122.
- J. Pesicka, R. Kuzel, A. Dronhofer, and G. Eggeler, "The evolution of dislocation density during heat treatment and creep of tempered martensite ferritic steels", Acta Materialia, 51 (2003) 4847-4862.
- J. Pesicka, A. Dronhofer, and G. Eggeler, "Free dislocations and boundary dislocations in tempered martensite ferritic steels", Metallurgical and Materials Transactions A, 387-89 (2004) 176-180.
- 90. F. Masuyama, "Creep degradation in welds of Mod.9Cr-1Mo steel", International Journal of Pressure Vessels and Piping, 83 (2006) 819-825.
- A. Dronhofer, J. Pesicka, A. Dlouhy, and G. Eggeler, "On the nature of internal interfaces in tempered martensite ferritic steels", Zeitschrift fur Metallkunde, 94 (2003) 511-520.

- 92. V. Randle, "'Five-parameter' analysis of grain boundary networks by electron backscatter diffraction", Journal of Microscopy-Oxford, 222 (2006) 69-75.
- N. D. Browning, M. F. Chisholm, and S. J. Pennycook, "Atomic-Resolution Chemical-Analysis Using A Scanning-Transmission Electron-Microscope", Nature, 366 (1993) 143-146.
- E. Carlino, S. Modesti, D. Furlanetto, M. Piccin, S. Rubini, and A. Franciosi, "Atomic resolution composition analysis by scanning transmission electron microscopy high-angle annular dark-field imaging", Applied Physics Letters, 83 (2003) 662-664.
- 95. J. M. Cowley and Y. Huang, "Dechanneling Contrast in Annular Dark-Field Stem", Ultramicroscopy, 40 (1992) 171-180.
- 96. D. O. Klenov and S. Stemmer, "*Contributions to the contrast in experimental highangle annular dark-field images*", Ultramicroscopy, 106 (2006) 889-901.
- 97. D. D. Perovic, C. J. Rossouw, and A. Howie, "Imaging Elastic Strains in High-Angle Annular Dark-Field Scanning-Transmission Electron-Microscopy", Ultramicroscopy, 52 (1993) 353-359.
- 98. Peter J. Goodhew, "Specimen preparation for transmission electron microscopy of materials", Royal Microscopical Society (1984) Oxford, England.
- 99. K. G. Tak, U. Schulz, and G. Eggeler, "On the effect of micrograin crystallography on creep of FeCr alloys", Materials Science and Engineering: A, 510-511 (2009) 121-129.
- 100. D. B. Williams and C. B Carter, "*Transmission electron microscopy : a textbook for materials science*", Plenum Press (1996) New York, USA.
- 101. A. Kostka, K.-G. Tak, R. J. Hellmig, Y. Estrin, and G. Eggeler, "On the contribution of carbides and micrograin boundaries to the creep strength of tempered martensite ferritic steels", Acta Materialia, 55 (2007) 539-550.
- 102. W. D. Nix, K. S. Yu, and J. S. Wang, "The Effects of Segregation on the Kinetics of Intergranular Cavity Growth Under Creep Conditions", Metallurgical Transactions A-Physical Metallurgy and Materials Science, 14 (1983) 563-570.
- 103. T. J. Chuang, K. I. Kagawa, J. R. Rice, and L. B. Sills, "Nonequilibrium Models for Diffusive Cavitation of Grain Interfaces", Acta Metallurgica, 27 (1979) 265-284.
- 104. A. C. F. Cocks and M. F. Ashby, "On Creep Fracture by Void Growth", Progress in Materials Science, 27 (1982) 189-244.
- 105. G. Eggeler, "*Microstructural parameters for creep damage quantification*", Acta Metallurgica et Materialia, 39 (1991) 221-231.

- 106. K. Sawada, K. Miyahara, H. Kushima, K. Kimura, and S. Matsuoka, "Contribution of microstructural factors to hardness change during creep exposure in Mod.9Cr-1Mo steel", ISIJ International, 45 (2005) 1934-1939.
- 107. A. Borbely, H. J. Maier, H. Renner, S. Straub, T. Ungar, and W. Blum, "Long-Range Internal-Stresses in Steady-State Subgrain Structures", Scripta Metallurgica et Materialia, 29 (1993) 7-12.
- 108. P. Polcik, T. Sailer, W. Blum, S. Straub, J. Bursik, and A. Orlova, "On the microstructural development of the tempered martensitic Cr-steel P 91 during long-term creep - a comparison of data", Materials Science and Engineering A-Structural Materials Properties Microstructure and Processing, 260 (1999) 252-259.
- 109. R. Sedlacek, S. Straub, A. Borbely, T. Ungar, and W. Blum, "Long-Range Internal-Stresses in the Transition from Cell to Subgrain Structures", Plasticity of Metals and Alloys - Ispma 6, 97-9 (1994) 461-466.
- 110. G. Eggeler, "The effect of long-term creep on particle coarsening in tempered martensite ferritic steels", Acta Metallurgica, 37 (1989) 3225-3234.
- 111. W. Blum and G. Gotz, "Evolution of dislocation structure in martensitic steels: the subgrain size as a sensor for creep strain and residual creep life", Steel Research, 70 (1999) 274-278.
- 112. F. Abe, T. Horiuchi, M. Taneike, and K. Sawada, "Stabilization of martensitic microstructure in advanced 9Cr steel during creep at high temperature", Metallurgical and Materials Transactions A, 378 (2004) 299-303.
- 113. Bojan A. Marinkovic, R. R. Avillez, S. K. Barros, and F. C. R. Assuncao, "*Thermodynamic evaluation of carbide precipitates in 2.25Cr-1.0Mo steel for determination of service degradation*", Materials Research, 5 (2002) 491-495.
- 114. E. Schnabel, P. Schwaab, and H. Weber, "*Metallurgical studies on high-temperature steels*", Stahl und Eisen, 106 (1986) 129-129.
- 115. E. Schnabel, P. Schwaab, and H. Weber, "*Metallurgical Investigations on Creep Resistant Steels*", Stahl und Eisen, 107 (1987) 691-696.
- 116. F. Li, A. A. Barani, D. Ponge, and D. Raabe, "Austenite grain coarsening behaviour in a medium carbon Si-Cr spring steel with and without vanadium", Steel Research International, 77 (2006) 590-594.
- 117. J. Janovec, Barbara Richarz, and H. J. Grabke, "Some aspects of intermetallic phase precipitation in a 12% Cr-steel", Scripta Metallugica et Materialia, 33 (1995) 295-300.
- 118. G. Dimmler, P. Weinert, E. Kozeschnik, and H. Cerjak, "*Quantification of the Laves phase in advanced 9-12% Cr steels using a standard SEM*", Materials Characterization, 51 (2003) 341-352.
- 119. L. M. Lundin, "Direct measurement of carbon solubility in the intermetallic (Fe,Cr)<sub>2</sub>(Mo,W) Laves phase using atom-probe field-ion microscopy", Scripta Materialia, 34 (1996) 741-747.
- 120. Y. Hosoi, N. Wade, S. Kunimitsu, and T. Urita, "*Precipitation behavior of Laves phase and its effect on toughness of 9Cr-2Mo ferritic-martensitic steel*", Journal of Nuclear Materials, 141-143 (1986) 461-467.
- 121. Y. Hosoi, N. Wade, and T. Urita, "*Effect of Si and Mn on precipitation behavior of Laves phase and toughness of 9Cr-2Mo steel*", Transactions of the Iron and Steel Institute of Japan, 26 (1986) B30-B30.
- 122. J. Agren, "*Calculation of phase diagrams: Calphad*", Current Opinion in Solid State & Materials Science, 1 (1996) 355-360.
- 123. Larry Kaufman and Harold Bernstein, "Computer calculations of phase diagrams : with special reference to refractory metals", Academic Pr. (1970) N.Y.
- 124. J. O. Andersson and J. Agren, "Models for Numerical Treatment of Multicomponent Diffusion in Simple Phases", Journal of Applied Physics, 72 (1992) 1350-1355.
- 125. A. Borgenstam, A. Engstrom, L. Hoglund, and J. Agren, "*DICTRA, a tool for simulation of diffusional transformations in alloys*", Journal of Phase Equilibria, 21 (2000) 269-280.
- 126. J. O. Andersson, T. Helander, L. H. Hoglund, P. F. Shi, and B. Sundman, "THERMO-CALC & DICTRA, computational tools for materials science", Calphad-Computer Coupling of Phase Diagrams and Thermochemistry, 26 (2002) 273-312.
- 127. J. O. Andersson, T. Helander, L. H. Hoglund, P. F. Shi, and B. Sundman, "THERMO-CALC & DICTRA, computational tools for materials science", Calphad-Computer Coupling of Phase Diagrams and Thermochemistry, 26 (2002) 273-312.
- 128. J. Crank, "The mathematics of diffusion", Clarendon Press (1975) Oxford, England.
- 129. M. E. Glicksman, "Diffusion in solids : field theory, solid-state principles, and applications", Wiley (2000) New York, USA.
- 130. Helmut Mehrer, "Diffusion in solids : fundamentals, methods, materials, diffusioncontrolled processes ; with 27 tables", Springer (2007) Berlin, Germany.

# **Publications:**

- A. Aghajani, Ch. Somsen and G. Eggeler "On the effect of long-term creep on the microstructure of a 12% chromium tempered martensite ferritic" Acta Mater. 57 (2009) 5093.
- A. Aghajani, F. Richter, C. Somsen, S.G. Fries, I. Steinbach, G. Eggeler "On the formation and growth of Mo-rich Laves phase particles during long-term creep of a 12% chromium tempered martensite ferritic steel" Scr. Mater. 61 (2009) 1068.
- J. Pešička, A. Aghajani, Ch. Somsen, A. Hartmaier and G. Eggeler "Evolution of Dislocation Substructure during Long Term Creep of a 12% Cr Tempered Martensitic Ferritic Steel" Scr. Mater. (accepted).
- A. Aghajani, Ch. Somsen, J, Pesicka, W. Bendick, B. Hahn and G. Eggeler "Microstructural evolution in T24, a modified 2¼Cr-1Mo steel during creep after different heat treatments" Mater. Sci. Eng., A 510-511 (2009) 130.
- R. Zarnetta, D. König, C. Zamponi, A. Aghajani, J. Frenzel, G. Eggeler and A. Ludwig "*R-phase formation in Ti<sub>39</sub>Ni<sub>45</sub>Cu<sub>16</sub> shape memory thin films and bulk alloys -discovered by combinatorial methods*" Acta Mater. 59 (2009) 4169.
- A. Maghsoudipour, M. H. Sarrafi, F. Moztarzadeh, A. Aghajani, "Influence of Boric Acid on Properties of Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub>:Eu<sup>2+</sup>,Dy<sup>3+</sup> Phosphors" Pigm. Resin. Technol. 39 (2010) 1.

# Ali Aghajani Bazazi

Lehrstuhl Werkstoffwissenschaft (WW) Ruhr-Universität Bochum Universitätsstr. 150 D-44801 Bochum , Germany

+49 (0) 234 357 8582 +49 (0) 234 32 29159 ali.aghajani@rub.de

### EDUCATION

- PhD Materials Science & Engineering, Ruhr University Bochum, Germany (Dec. 2009). Dissertation: "Microstructural evolution during long term creep of a tempered martensitic ferritic steel". My research is focused primarily on study of microstructural evolution in the creep resistance steels using:
  - Transmission Electron Microscopy (TEM)
  - High angle annular dark field (HAADF-STEM)
  - Scanning Electron Microscopy (SEM)
  - Electron Back Scattered Diffraction (EBSD)
- M.Sc. Materials Engineering (Ceramics), Materials & Energy Research Center, Iran April 2004

B.Sc. Materials Engineering (Industrial metallurgy), Tehran Polytechnic, Iran Sep 2001

### **PROFESSIONAL EMPLOYMENT**

March 2006 - present	<b>Research assistant</b> at Ruhr University Bochum, Institute of Materials, Research Group for Materials Science and Engineering
July 2005 - March 2006	<b>Local coordinator</b> of the collaborative project management program between University of Calgary (Canada) and Sharif University (Iran)
June 2004 - May 2005	<b>Sales manager</b> in DAEWOO International Corporation, Tehran office, Steel division
February 1998 - July 2003	Trainee at Everend Asia Co. (currently, Arvin Mehr Industry), part- time

### PUBLICATIONS

- J. Pešička, A. Aghajani, Ch. Somsen, A. Hartmaier and G. Eggeler "Evolution of dislocation substructure during long term creep of a 12% Cr tempered martensitic ferritic steel" Scripta Mater. (DOI: 10.1016/j.scriptamat.2009.10.037).
- A. Aghajani, Ch. Somsen and G. Eggeler "On the effect of long-term creep on the microstructure of a 12% chromium tempered martensite ferritic steel" Acta Mater. 57 (2009) 5093.

# Ali Aghajani Bazazi

# **PUBLICATIONS (continued)**

- **A. Aghajani**, F. Richter, C. Somsen, S.G. Fries, I. Steinbach, G. Eggeler "On the formation and growth of Mo-rich Laves phase particles during long-term creep of a 12% chromium tempered martensite ferritic steel" **Scripta Mater.** 61 (2009) 1068.
- R. Zarnetta, D. König, C. Zamponi, **A. Aghajani**, J. Frenzel, G. Eggeler and A. Ludwig "*R*-phase formation in *Ti*<sub>39</sub>*Ni*<sub>45</sub>*Cu*<sub>16</sub> shape memory thin films and bulk alloys discovered by combinatorial methods" **Acta Mater**. 57 (2009) 4169.
- A. Aghajani, Ch. Somsen, J, Pesicka, W. Bendick, B. Hahn and G. Eggeler "Microstructural evolution in T24, a modified 2%Cr-1Mo steel during creep after different heat treatments" Mater. Sci. Eng., A 510-511 (2009) 130.
- M.M. Mortaheb, **A. Aghajani**, and J.Y. Ruwanpura, "An example of project management training program in a developing country", proceedings. of ICSC-1: CSCE First international construction specialty conference, (2006) Calgary, Canada.
- A.R. Mirhabibi, F. Moztarzadeh, **A. Aghajani**, M. Solati, A. Maghsoudipour, M.H. Sarrafi "Studies of luminescence property of long afterglow Eu<sup>2+</sup>, Dy<sup>3+</sup> activated Sr<sub>2</sub>MgSi<sub>2</sub>O<sub>7</sub> phosphor", **Pigm. Resin Technol**., 33 (2004) 220.
- **A. Aghajani**, M.M. Khoie, "Effect of chromium oxide on corrosion resistance of Dacromet coating" proceeding of 5<sup>th</sup> international surface engineering and heat treatment congress, Polytechnic university (2003).

## PATENTS

"New green silicate-based long afterglow phosphor", Patent No. 29694, Iran

"Instrument for measuring and mixing  $N_2$  and  $H_2$  gases", Patent No. 29680, Iran

## AWARDS

Ph.D. Scholarship, International Max-Planck Research School for Surface and Interface Engineering in Advanced Materials (IMPRS-SurMat), Germany

# Ali Aghajani Bazazi

## **PROFESSIONAL DEVELOPMENT**

### MAX-PLANCK RESEARCH SCHOOL (Düsseldorf, Germany)

February – March 2008	Mechanical properties of surfaces and interface dominated materials*
October 2007	Physical chemistry of surfaces and interfaces
March – April 2007	Basic concepts in materials science*
October 2006	Deposition and properties of thin films and self organized monolayer

\* Top 15% of all students participating in the exam

#### SUMMER SCHOOLS AND WORKSHOPS

April 2009	"P23/T23- Fabrication, Welding, Heat-treatment, Oxidation, Life Assessment and Plant Experience", Zürich, Switzerland
October 2008	"Alloy Development for Critical Components of Environmentally- friendly Power Plants", Lanzarote, Spain
February 2007	EBSD-Course at AMETEK in Wiesbaden, Germany
September 2006	"Japanese-South African-German Workshop and Summer School", Bad Berneck, Germany
TECHNICAL TRAINING	
July – August 2000	Electroplating of automobile components, Zanbagh Industrial Group, Karaj, Iran
August 1999	Die casting, Behrizan Sanat Co., Iran
July – August 1998	Hot-rolling of structural steels, Noshahr Navard, Iran

## LANGUAGES

- Persian (Farsi), native speaker
- English, fluent in writing and speaking
- German, fluent in writing and speaking
- Azeri (Turkish), fluent in speaking
- Arabic, basic

### **INTERESTS**

Badminton, Swimming