Report on Understanding and Predicting Effects of Thermal Aging on Microstructure and Tensile Properties of Grade 91 Steel for Structural Components

Nuclear Engineering Division

About Argonne National Laboratory

Argonne is a U.S. Department of Energy laboratory managed by UChicago Argonne, LLC under contract DE-AC02-06CH11357. The Laboratory's main facility is outside Chicago, at 9700 South Cass Avenue, Argonne, Illinois 60439. For information about Argonne and its pioneering science and technology programs, see www.anl.gov.

DOCUMENT AVAILABILITY

Online Access: U.S. Department of Energy (DOE) reports produced after 1991 and a growing number of pre-1991 documents are available free via DOE's SciTech Connect (<http://www.osti.gov/scitech/>)

Reports not in digital format may be purchased by the public from the National Technical Information Service (NTIS):

U.S. Department of Commerce
National Technical Information
Service 5301 Shawnee Rd
Alexandria, VA 22312
www.ntis.gov
Phone: (800) 553-NTIS (6847) or (703) 605-6000
Fax: (703) 605-6900
Email: **orders@ntis.gov**

Reports not in digital format are available to DOE and DOE contractors from the Office of Scientific and Technical Information (OSTI):

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
www.osti.gov
Phone: (865) 576-8401
Fax: (865) 576-5728
Email: **reports@osti.gov**

Disclaimer

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor UChicago Argonne, LLC, nor any of their employees or officers, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of document authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, Argonne National Laboratory, or UChicago Argonne, LLC.

Report on Understanding and Predicting Effects of Thermal Aging on Microstructure and Tensile Properties of Grade 91 Steel for Structural Components

Meimei Li, K. Natesan and Weiying Chen

Nuclear Engineering Division
Argonne National Laboratory

August 2017

ABSTRACT

This report provides an update on understanding and predicting the effects of long-term thermal aging on microstructure and tensile properties of G91 to corroborate the ASME Code rules in strength reduction due to elevated temperature service. The research is to support the design and long-term operation of G91 structural components in sodium-cooled fast reactors (SFRs). The report is a Level 2 deliverable in FY17 (M2AT-17AN1602017), under the Work Package AT-17AN160201, “SFR Materials Testing” performed by the Argonne National Laboratory (ANL), as part of the Advanced Reactor Technologies Program.

The thermal aging study of G91 involves two types of thermally-aged specimens: (1) specimens fabricated from the heads of the archived crept specimens (13 in total) covering the aging temperature of 427 - 538°C and times up to 132,647 h for several heats of G91, and from a tube removed from the Kingston coal-fired power plant after exposure for 155,000 h at 550°C, and (2) specimens made from two heats of G91, G91-H1 and H30176 thermally aged at 550, 600, and 650°C for times up to 55,277 h. These specimens provide a comprehensive data set for understanding and predicting the effect of long-term thermal aging on microstructure and tensile properties of G91.

Microstructural analysis of the thermally-aged G91 revealed that thermal aging can cause significant microstructural changes: (1) the subgrain structure formed during tempering is unstable, and can suffer significant recovery during aging, manifested by an increase in subgrain width, a decrease in subgrain length, and a decrease in subgrain aspect ratio (i.e. subgrains become more equiaxed). The subgrain recovery is facilitated by the reduction of dislocation density within subgrains; (2) two types of precipitates formed during tempering, i.e. $M_{23}C_6$ carbides and MX carbonitrides coarsen with increasing temperature and time; (3) a new phase, the Laves phase forms during aging and grows rapidly at high temperature. The evolution of each microstructural feature during thermal aging can be well described by individual microstructural models.

Thermal aging of G91 results in the reduction in the yield stress and the ultimate tensile strength but has an insignificant effect on the uniform and total elongations. The reduction in tensile strength is more pronounced as the aging temperature and time increases. The tensile data of the thermally-aged specimens agree well with the calculated tensile strength values using the temperature-time-dependent strength reduction factors given in the ASME Code.

The *in situ* tensile tests with high-energy X-rays of the as-received specimens revealed three primary strengthening mechanisms in G91: subgrain boundary hardening, MX precipitation hardening, and Mo solid solution strengthening. The role of $M_{23}C_6$ carbides on the tensile strength is coupled with the sub-boundary hardening, and the effect of the precipitation of the Laves phase during aging is accounted for through the Mo solid solution strengthening. Among the three strengthening mechanisms, sub-boundary strengthening plays a dominant role, followed by MX precipitation hardening, and the Mo solid solution hardening is insignificant to the total strength of G91. A microstructural model has been established to describe the reduction in tensile strength from aging. A good agreement was achieved between the experiments and the

calculations up to ~100,000 h at 550°C, ~20,000 h at 600 and 650°C. However, there was a discrepancy between the modeling results and the calculated UTS values using the ASME strength reduction factors at longer aging time. The model predicted lower strength values than the values calculated using the ASME Code.

Future work will continue microstructural characterization to obtain a more complete set of microstructural data. Data will be used to improve the microstructural models and the correlation between the microstructure and tensile strength, particularly for the effect of long-term thermal aging.

TABLE OF CONTENTS

ABSTRACT.....	iii
TABLE OF CONTENTS.....	v
LIST OF TABLES	vi
LIST OF FIGURES	vii
1 Introduction	1
2 Experimental Procedure and Modeling Approaches.....	3
2.1 Fabrication of archived thermally-aged specimens	3
2.2 Thermal aging experiments.....	4
2.3 Microstructural characterization	6
2.4 <i>Ex situ</i> tensile tests and micro-hardness measurements.....	6
2.5 <i>In situ</i> tensile tests with synchrotron high-energy X-rays	7
2.6 Modeling approaches	8
3 Results	10
3.1 Effect of thermal aging on microstructure of Grade 91	10
3.1.1 Dislocation evolution and subgrain recovery	11
3.1.2 Second-phase precipitates ($M_{23}C_6$, MX, Laves)	15
3.2 Effect of thermal aging on tensile properties of Grade 91	20
3.3 Microstructural modeling.....	24
3.3.1 Modeling of subgrain recovery.....	24
3.3.2 Modeling of $M_{23}C_6$ and MX particle coarsening.....	25
3.3.3 Modeling of Laves phase nucleation and growth	26
3.4 Correlation of microstructure - tensile strength in Grade 91	28
3.4.1 Strengthening mechanisms in G91	29
3.4.2 Microstructural model for tensile strength of G91	29
4 Summary and Future Work	32
Acknowledgement	33
References	34

LIST OF TABLES

Table 1. List of the G91 creep-tested specimens	3
Table 2. Chemical composition (in wt%) for G91-H1 and H30176.....	5
Table 3. Heat treatment conditions for G91-H1 and H30176.....	5
Table 4. Thermal aging temperatures and total aging times for G91-H1 and H30176	5

LIST OF FIGURES

Figure 1.	Schematic drawing of the subsize sheet-type tensile specimen.....	4
Figure 2.	Fabrication drawings of subsize tensile specimens and rod specimens from (a) an archived G91 creep-tested specimen, and (b) G91 tube removed from the Kingston plant.....	4
Figure 3.	Thermal aging experiment (a) vacuum-encapsulated specimens and (b) high-temperature furnaces used for thermal aging tests	5
Figure 4.	Experimental setup for <i>ex situ</i> high temperature tensile tests.....	6
Figure 5.	Schematic layout of Beamline 1-ID and MTS test station at the APS	7
Figure 6.	The calculated phase diagram and equilibrium phases in G91 steel with (a) stable phase, Z-phase and (b) metastable phase, MX	10
Figure 7.	TEM images of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 (a) in the as-received condition, and (b) after thermal aging for 19,926 h at 550°C.....	13
Figure 8.	TEM images of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 (a) in the as-received condition, and (b) after thermal aging for 19,992 h at 600°C.....	13
Figure 9.	TEM images of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 (a) in the as-received condition, and (b) after thermal aging for 20,531 h at 650°C.....	13
Figure 10.	TEM image of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 H30176 after thermal aging for 57,212 h at 538°C (ID 24357).....	14
Figure 11.	TEM image of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 H5349 after thermal aging for 132,647 h at 538°C (ID 20842).....	14
Figure 12.	TEM image of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 H30383 after thermal aging for 99,542 h at 482°C (ID 24746).....	14
Figure 13.	Time dependence of the subgrain (a) width, (b) length, and (c) aspect ratio of various heats of G91 after thermal aging at 550, 600 and 650°C.....	14
Figure 14.	The XRD line profile for the normalized and tempered G91-H30176.....	15
Figure 15.	The BSE image and element maps of Mo, Cr, and Fe showing Laves phase formation in G91-H1 aged for 5,011 h at 650°C	15

Figure 16.	Micrographs showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91-H1 (a) in the as-received condition, and (b) after thermal aging for 19,926 h at 550°C.....	18
Figure 17.	Micrographs showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91-H30176 (a) in the as-received condition, and (b) after thermal aging for 19,992 h at 600°C.....	18
Figure 18.	Micrographs showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91-H1 (a) in the as-received condition, and (b) after thermal aging for 20,531 h at 650°C.....	18
Figure 19.	Micrograph showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91 H30176 after thermal aging for 57,212 h at 538°C (ID 24357)	19
Figure 20.	Micrographs showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91 H5349 after thermal aging for 132,647 h at 538°C (ID 20842).	19
Figure 21.	Micrographs showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91 H30383 after thermal aging for 99,542 h at 482°C (ID 24746).	19
Figure 22.	Time dependence of the mean size of (a) $M_{23}C_6$ particles, (b) MX precipitates, and (c) Laves phase particles in G91 after thermal aging at 550, 600 and 650°C	19
Figure 23.	Stress-strain curves of the as-received G91 (a) Heat 30176, (b) Heat G91-H1	21
Figure 24.	The (a) yield stress, (b) ultimate tensile strength, (c) uniform elongation, and (d) total elongation as a function of exposure time for G91-H1 and G91-H30176 thermally aged at 550, 600, and 650°C.....	21
Figure 25.	The (a) yield stress, (b) ultimate tensile strength, (c) uniform elongation, (d) total elongation, and (e) micro-hardness for the archived G91 specimens thermally-aged at 427 - 550°C. The tensile test was conducted at the aging temperature	22
Figure 26.	The ultimate tensile strength (UTS) vs. aging time for various heats of G91 steel thermally-aged at 427-650°C. The experimental data are compared with the calculated UTS values using the strength reduction factors given in Table NH-3225-4 in ASME B&PV Code Section III, Subsection NH (2010)	23
Figure 27.	Comparison of the experimental data and modeling results for the subgrain width vs. aging time for G91 steel	25
Figure 28.	Comparison of experimental and modeling results of (a) coarsening of $M_{23}C_6$ carbides, and (b) coarsening of MX precipitates in G91steel during thermal aging at 550-650°C.....	26

Figure 29.	Comparison of the calculated tensile strength using the microstructural model and the ASME Code strength reduction factors in Table NH-3225-4 and the experimental data as a function of aging time for G91 aged at 550, 600, and 650°C	31
------------	---	----

1 Introduction

The Advanced Reactor Technologies Campaign has focused on the sodium-cooled fast reactor concept because of its technical maturity. The current needs are for more reliable, more flexible, and more economical reactors suitable for commercial nuclear power generation. Research and development focuses on three areas including advanced materials, innovative components and systems, and computer modeling and simulation enabling predictions of long-term performance. Advanced materials are a key element in the development of advanced nuclear reactors. High-performance structural materials allow for a compact and simple design of the reactor structure, and have the potential to reduce the construction and operational costs for next-generation nuclear energy systems. High temperature-, corrosion- and irradiation-resistant alloys are important for flexible, reliable and safe designs of reactor components.

Advanced fast reactors will operate at higher temperatures than current light water reactors (LWRs). The design of high-temperature structural components must consider time-dependent effects and damage mechanisms, such as long-term thermal aging, creep, creep-fatigue, creep ratcheting, and environmental effects. These issues have not been dealt with in LWR designs and operation. Due to the temperature and time dependence of material properties, extrapolation of short-term, high-temperature accelerated test data to a long-design life and a relatively low-service temperature becomes extremely difficult and often with large uncertainties. Nuclear components that operate at elevated temperatures must be designed in accordance with the American Society of Mechanical Engineers (ASME) Section III Division 5 (previously Subsection NH – Class 1 Components in Elevated Temperature Service), which provides high temperature design rules for structural components in nuclear service. Materials that are allowed for use in high temperature structural designs in nuclear components must be qualified and approved by Division 5. So far only five materials have been qualified, namely, Type 304 and 316 austenitic stainless steels, 2.25Cr-1Mo steel, modified 9Cr-1Mo (Grade 91) steel, and Alloy 800H. Alloy 617 is being qualified to be included in Division 5.

Grade 91 (G91) ferritic-martensitic steel was developed for intermediate heat exchanger and steam generator applications for liquid metal reactors (LMRs) in the U.S in late 1970s. In 1974, the U.S. Department of Energy (DOE) initiated a three-phase study for developing a new alloy for the use in LMRs, and G91 was selected based on creep strength and microstructural considerations. A development program for G91 steel started in early 1980s, and considerable information on G91 was generated through the DOE-sponsored programs and industrial development. An extensive mechanical properties database was established in air environment, including tensile, toughness, creep, and fatigue properties. Some creep-fatigue data were also obtained, but were considered insufficient. The general findings were that the alloy has good long-term performance for structural applications in LMRs, and is resistant to irradiation swelling. Data in sodium showed no significant deleterious effects on mechanical properties. One of the remaining critical issues to be resolved is the long-term performance of G91 in the SFR environments including both thermal aging and sodium exposure. G91 is a multi-component, multi-phase alloy with much more complex microstructure than other Code-qualified single-phase alloys. The superior high-temperature performance of G91 heavily relies on the stability of its complex microstructure. Significant microstructural changes can occur

during long-term thermal or sodium exposures, leading to dramatically different responses to the service environments. Extrapolation of short-term, laboratory-generated data to design allowable stresses for higher temperatures and extended service periods must be conducted with confidence to ensure the safety and reliability of structural components in SFRs.

The goal of this project is to develop a mechanistic approach to address the long-term thermal aging effect on design stress allowables for the 60-y design life. This report provides an update on understanding and predicting the effects of long-term thermal aging on microstructure and tensile properties of G91 to corroborate the ASME Code rules in strength reduction due to elevated temperature service.

2 Experimental Procedure and Modeling Approaches

2.1 Fabrication of archived thermally-aged specimens

Thirteen archived G91 creep-tested specimens along with one G91 tube removed from the Kingston coal-fired power plant were provided by the Oak Ridge National Laboratory for the study of long-term thermal aging effect on microstructure and tensile properties of G91. Table 1 lists the heat number and creep test condition for the archived crept specimens. Note that there are five different heats of G91 in Table 1, i.e., H5349, H30394, H30383, H10148, and H30176. Control specimens are available only for Heat 30176. The Kingston tube was exposed to steam condition for 155,000 h at 550°C. These specimens were used to evaluate the microstructure evolution and tensile property degradation during thermal aging at relevant SFR operating temperatures (427–550°C) with a maximum exposure time of ~18 years.

Table 1. List of the G91 creep-tested specimens

Specimen ID	Heat No.	Temperature (°C)	Stress (MPa)	Time (hrs)
20842	5349	538	179	132,647
21822	30394	427	414	114,800
24577	30394	538	166	97,497
24746	30383	482	276	99,542
24899	10148	538	166	82,061
27386	30383	538	207	40,871
23698	30394	427	379	106,523
24351	30394	538	207	57,460
24357	30176	538	207	57,212
24359	30176	538	186	57,109
24749	30394	482	276	83,491
24752	30176	482	276	84,148
24772	10148	482	276	83,126

Subsize sheet-type tensile specimens (Fig. 1) and rod specimens were machined from the grip sections of the crept specimen, as shown in Fig. 2(a). These specimens represent the static aging state under the crept temperature and time. The two types of specimens were also machined from the G91 Kingston tube, as shown in Fig. 2(b). Tensile specimens were electrical-discharge-machined with the gage parallel to the creep loading direction. The tensile specimen has nominal gage dimensions of $7.62 \times 1.52 \times 0.76$ mm. The rod specimens have a diameter of 3 mm, and were used for microstructural analysis.

Figure 1. Schematic drawing of the subsize sheet-type tensile specimen.

Figure 2. Fabrication drawings of subsize tensile specimens and rod specimens from (a) an archived G91 creep-tested specimen, and (b) G91 tube removed from the Kingston plant.

2.2 Thermal aging experiments

Thermal aging experiments were conducted at 550, 600, and 650°C for up to ~55,000 h on two heats of G91 steel, i.e., G91-H1 and H30176. Together with the data from the archived specimens aged at 427–550°C for times up to 155,000 h, a comprehensive dataset covering a range of aging temperatures and long exposure times can be obtained. This information is critical to the understanding and prediction of the effect of thermal aging on material microstructure and mechanical performance.

Heat G91-H1 was in the plate form with a thickness of 0.375". The plate was normalized at 1050°C for 1 h, air cooled and tempered at 760°C for 1 h and air cooled. Heat H30176 of G91 was in the 1"-thick plate form. It was normalized at 1050°C for 1 h, air cooled, and tempered at 760°C for 2 h and air cooled. The chemical composition and heat treatment conditions of these two heats are given in Tables 2 and 3, respectively.

Table 2. Chemical composition (in wt%) for G91-H1 and H30176.

Alloy	Heat No.	Fe	C	Cr	Mn	Mo	N	Nb	Si	V	W
G91	G91-H1	Bal	0.09	8.3	0.46	1.04	0.06	0.05	0.41	0.22	-
G91	H30176	Bal	0.08	8.6	0.37	0.89	0.06	0.07	0.11	0.21	<0.01

Table 3. Heat treatment conditions for G91-H1 and H30176.

Alloy	Heat No.	Heat treatment
G91	G91-H1	Normalized at 1050°C and tempered at 760°C for 1 h and AC
G91	H30176	Normalized at 1050°C for 1 h, AC, and tempered at 760°C for 2 h, AC

Table 4. Thermal aging temperatures and total aging times for G91-H1 and H30176.

Heat No.	Total Exposure Time at 550°C (h)	Total Exposure Time at 600°C (h)	Total Exposure Time at 650°C (h)
G91 H1	52,121	39,459	55,277
H30176	27,240	19,992	13,374

Thermal aging experiments were performed at 550, 600, and 650°C in air furnaces for various exposure times. Each specimen was wrapped in Ta foil and encapsulated in a quartz tube under vacuum. Encapsulated specimens (shown in Fig. 3(a)) were loaded in an air furnace (Fig. 3(b)) that was heated to the target temperature for an extended period. Table 4 gives the total exposure times at different temperatures for the two heats of G91.

Figure 3. Thermal aging experiment (a) vacuum-encapsulated specimens and (b) air furnaces used for thermal aging tests.

2.3 Microstructural characterization

Microstructure of the as-received and thermally-aged specimens was characterized by optical microscopy (OM), high-resolution scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive spectroscopy (EDS), and synchrotron X-ray diffraction (XRD). Metallographic specimens were prepared by mounting, grinding, and polishing. The polished specimens were chemically etched with an etchant of 5 ml HNO_3 , 1 ml HF and 50 ml H_2O . The grain structure of the alloys was revealed by OM. Metallographic specimens were further examined by high resolution SEM to characterize precipitates, using both secondary electron (SE) and backscattered electron (BSE) imaging on a field emission gun (FEG) Hitachi S-4700-II microscope. TEM and EDS were conducted to examine dislocation density, subgrain structure, and second-phase precipitates. Thin foil specimens of 3-mm in diameter were made by electropolishing to perforation using a Tenupol twin-jet polishing unit. The electropolishing solution was 95% methanol and 5% perchloric acid cooled to about -40°C . Dimensions of subgrains and sizes of M_{23}C_6 carbides and MX precipitates were measured by TEM. Laves phase particles were measured by SEM using the Z-contrast.

2.4 Ex situ tensile tests and micro-hardness measurements

Ex situ tensile tests were conducted under uniaxial tension at the aging temperature in an air furnace. Figure 4 shows a setup for high temperature tensile tests. Tensile tests were performed in an electromechanical testing system equipped with a three-zone air furnace. The applied load was recorded by a load cell; the specimen displacement was measured by the crosshead extension. The tensile properties were determined from analysis of load versus displacement data files. All the tests were conducted at a nominal strain rate, 0.001 s^{-1} .

Figure 4. Experimental setup for *ex situ* high temperature tensile tests.

Due to a limited number of tensile specimens made from archive crept specimens, micro-hardness measurements were conducted to understand the effect of thermal aging on the room-temperature tensile strength. Micro-hardness tests were conducted on the grip section of the tensile specimen using a Buehler Micromet micro-hardness tester. The applied load was 200 g and the dwell time was 10 s. Five measurements were made on each specimen and the mean values are reported.

2.5 *In situ* tensile tests with synchrotron high-energy X-rays

In situ tensile tests with high-energy X-ray were performed at the 1-ID beamline at the Advanced Photon Source (APS). Beamline 1-ID is a high-energy (50-130 keV), high-brilliance X-ray scattering facility. It is equipped with an MTS servo-hydraulic test frame, enabling tension, compression, and cyclic loading; an infrared heating furnace attached to the MTS test frame provides heating capacity up to 1200°C. This facility combines lab-scale mechanical testing capability with *in situ* microstructural characterization using multiple X-ray probes (diffraction/scattering/imaging), permitting simultaneous characterization of microstructure and mechanical behavior of mm-scale specimens. Figure 5 shows a schematic layout of the beamline setup and the MTS test station.

Fig. 5. Schematic layout of Beamline 1-ID and MTS test station at the APS.

In situ uniaxial tensile tests were carried out at 20-650°C in air on the as-received G91 H30176. The tensile tests were carried out under displacement control at a nominal strain rate of $1 \times 10^{-4} \text{ s}^{-1}$. Load and displacement data were recorded, and used to determine the macroscopic stress-strain curve. During tensile deformation, wide- and small-angle X-ray scattering (WAXS/SAXS) measurements were conducted simultaneously with monochromatic X-ray beams in transmission. WAXS signals were obtained at $2^\circ < 2\theta < 20^\circ$, and SAXS at $2\theta < 1^\circ$. Pairs of WAXS and SAXS patterns were independently recorded with a time interval of 14 or 24 s (corresponding to ~0.1 or 0.2% strain), while the specimen was continuously deformed. In addition, the X-ray intensities were measured by two ion chambers before and after the specimen, and these two intensity values were used to calculate the specimen transmission (and therefore the specimen thickness). Prior to a tensile test, the incident X-ray beam was positioned at the center of the gauge length of the tensile specimen. During the test, the specimen was measured at a single point near the gauge center until the maximum load was reached.

Diffraction profiles were obtained from averaging multiple WAXS patterns collected for each measurement. The two-dimensional diffraction data was transformed to one-dimensional line profile (intensity vs. 2θ) by integrating over a $\pm 10^\circ$ azimuth range around the axial/tensile direction of the specimen. Peaks were fitted to pseudo-voigt functions using MATLAB computer programs developed at the 1-ID beamline. Evolution of the lattice strain during tensile deformation was evaluated by calculating the change of the lattice spacing relative to the lattice spacing in the undeformed state. Peak broadening quantified by the full-width at half-maximum (FWHM) of the reflection was analyzed to evaluate the evolution of dislocation density and cell/subgrain structure as a function of tensile strain. The instrumental contribution to peak broadening was calibrated using a $\text{LaB}_6/\text{CeO}_2$ sample and subtracted from the measured peak profiles. SAXS data were processed to understand the void formation and evolution at the necking stage.

2.6 Modeling approaches

Phase transformation and phase stability in alloys are simulated using the commercial software package Thermo-Calc, DICTRA and TC-PRISMA. Thermo-Calc is used to calculate phase diagrams, chemical compositions, thermodynamic driving force, and amount of equilibrium phases. These thermodynamic data are used as input in the kinetic models to simulate precipitate evolution during thermal aging.

DICTRA (Diffusion Controlled TRAnsformation) is used to simulate precipitation kinetics during isothermal aging. DICTRA is a software package for simulation of diffusion-controlled transformation in multicomponent alloys. It is based on a numerical solution of multicomponent diffusion equations in various regions of a material with the assumption of local equilibrium at phase interfaces. The simulation of precipitation kinetics is carried out using the thermodynamic database and the mobility database. The growth of precipitate particles is treated as a one-dimensional moving boundary problem. A local equilibrium is assumed at precipitate and matrix interfaces. The movement of a phase interface is controlled by mass balance obtained from the fluxes of diffusing elements across the interface. The process is controlled by the tendency to reduce the chemical free energy of the system. The contribution of interfacial energy is ignored in the growth model. The precipitate coarsening is simulated using the coarsening model in the DICTRA package. Similar to the growth model, a local equilibrium at phase interfaces is assumed, and the local equilibrium is affected by the interfacial energy. The calculations are performed in a spherical cell with a particle of maximum size at the center of the cell. The maximum size of the particle is assumed to be 1.5 times the size of the average particle size [1-3]. The largest particle grows at the expense of the smaller particles. At the outer cell boundary, the local equilibrium is defined by the average composition in the system.

The effect of grain or subgrain size on phase stability can be evaluated by including grain boundary diffusion. Grain boundary diffusion is implemented in the calculations by assuming that they contribute to the overall diffusion by using the same frequency factor but different activation energy from bulk diffusion. The activation energy for grain boundary diffusion is set by using a predetermined multiplier and its contribution to the total amount of diffusion is

accounted for by using the weighted calculated value for the mobility. Dislocation-assisted diffusion is implemented by assuming that they contribute to the diffusion by using the same frequency factor and different activation energy than that of bulk diffusion. A predetermined multiplier is also used to set the activation energy for dislocation-assisted diffusion and its contribution to the total amount of diffusion is accounted for by using the weighted calculated value for the mobility.

TC-PRISMA is a software package for simulating kinetics of diffusion-controlled multi-particle precipitation process in multi-component and multi-phase alloy systems. It adopts the Kampmann-Wagner numerical (KWN) method [4] to simulate concurrent nucleation, growth, and coarsening of precipitates. The temporal evolution of the mean radius and particle density during the precipitation process is predicted by solving a set of rate equations derived with certain assumptions for the rates of nucleation and growth as well as the particle size distribution function. TC-PRISMA is integrated with Thermo-Calc and DICTRA to obtain necessary thermodynamic and kinetic data required in the KWN method.

3 Results

3.1 Effect of thermal aging on microstructure of Grade 91

Grade 91 steel is a multi-component, multi-phase alloy. As shown in Fig. 6 (a), the phase diagram of G91 calculated by Thermo-Calc shows that four stable phases, bcc-Fe, $M_{23}C_6$, Laves phase, and Z-phase ($Cr(V,Nb)N$) are formed at equilibrium at 500-780°C in G91. In the normalized and tempered condition, the microstructure of G91 consists of three phases, bcc-Fe, $M_{23}C_6$ carbides and MX ($Nb(C,N)$ or $V(N,C)$) carbonitrides, where MX is a metastable phase, as shown in Fig. 6(b). The tempered martensitic structure in the matrix consists of elongated subgrains with a high density of dislocations. It is stabilized by $M_{23}C_6$ carbides, giving rise to dislocation hardening and boundary strengthening. A fine distribution of MX precipitates within subgrains provides precipitation strengthening. The Mo solutes in the matrix provide additional solid solution strengthening. The maintenance of these microstructural features is critical to the superior high-temperature performance of G91. However, the microstructure of G91 steel is highly sensitive to chemistry, processing, heat treatment, and service conditions. The metastable MX phase in the as-received G91 can be replaced by the Z-phase after long-term aging. The Z-phase, $Cr(V,Nb)N$ contains the same constituents as the MX phase, and is the most stable nitride in 9-12%Cr steels. The loss of the MX phase during aging can cause reduction in creep strength in 9-12%Cr steels. Furthermore, a new phase, Laves phase can form in G91 during long-term service, removing the solution strengthener, Mo from the Fe-matrix and resulting in significant degradation of creep and creep-fatigue resistance. It is, therefore, important to understand the thermally-induced microstructural changes, and its influence on long-term performance of the alloys and components. The following section reports the detailed microstructural analysis of thermally-aged G91 and the measured microstructural parameters including dislocation density, subgrain dimensions (width, length) and shape (aspect ratio), mean size and size distributions of second phases, $M_{23}C_6$, MX, and Laves phase. No Z-phase precipitates have been observed.

Figure 6. The calculated phase diagram and equilibrium phases in G91 steel with (a) stable phase, Z-phase and (b) metastable phase, MX.

3.1.1 Dislocation evolution and subgrain recovery

Thermal aging of G91 causes a reduction of dislocation density and subgrain recovery. Subgrain structure and dislocations within subgrains were characterized by TEM, and dislocation density and subgrain dimensions (width and length) and shape (aspect ratio) were measured by the image analysis of TEM micrographs. Figure 7 shows a TEM micrograph of subgrains, and measured distributions of subgrain width, length, aspect ratio, and dislocation density for the specimen of heat G91-H1 after thermal aging for 19,926 h at 550°C. The same set of microstructural data for the G91 specimen in the as-received (normalized and tempered) condition is also included in Fig. 7 for comparison. The thermally-aged specimen shows slight changes in subgrain dimensions and shape and dislocation density after aging at 550°C.

Figure 8 compares the subgrain structure and distributions of subgrain width, length, aspect ratio, and dislocation density in H30176 before and after thermal aging for 19,992 h at 600°C. An increase in subgrain width, a decrease in subgrain length and a decrease in aspect ratio were observed under thermal aging at 600°C.

The effect of thermal aging on microstructural evolution is more pronounced at 650°C. As shown in Fig. 9 where the subgrain structure and distributions of subgrain width, length, aspect ratio, and dislocation density are compared before and after thermal aging for 20,531 h at 650°C, a significant increase in subgrain width and decreases in subgrain length and aspect ratio and a reduction in dislocation density are evident under thermal aging at 650°C. The subgrain size distributions of the thermally-aged specimen show more widened and shortened subgrains and the subgrain aspect ratio distribution shows a narrower distribution towards lower values, indicating that the subgrains became more equiaxed after thermal aging.

The effect of thermal aging on microstructure at relatively lower temperatures (482 - 538°C) for very long times was investigated by examining the heads of the archived crept specimens. Figure 10 shows a TEM micrograph of subgrain structure and measured distributions of subgrain width, length, aspect ratio and dislocation density for the specimen, ID 24357 after aging for 57,212 h at 538°C. The same set of microstructural data for the archived specimens, ID 20842 (aged for 132,647 h at 538°C) and ID 24746 (aged for 99,542 h at 482°C) is presented in Figs. 11 and 12, respectively. Due to the sensitivity of G91 microstructure to the heat variation, processing history, and final heat treatment and the lack of control specimens for each archived specimen, it is somewhat difficult to draw a clear conclusion on the effect of aging on microstructural evolution solely based on the results given in Figs. 10-12.

Figure 13 summarizes the subgrain parameters (width, length and aspect ratio) of the three archived specimens and the specimens of heats of G91-H1 and H30176 thermally aged at 550-650°C. While there is a significant data scatter from different heats, these archived specimens indeed add great value in understanding the very long-term aging effect on microstructural evolution at relevant SFR operating temperatures.

In general, the evolution of subgrain structure during thermal aging is manifested by both dimensional and shape changes. As the temperature and exposure time increase, the subgrain

width increases, the subgrain length decreases, and the subgrain aspect ratio decreases (i.e. subgrains become more equiaxed), as shown in Fig. 13. Ghassemi-Armaki et al. [5,6] measured the subgrain width for thermally-aged G91 specimens and crept specimens, and concluded that there is an incubation period before the onset of aging-induced subgrain coarsening. The incubation time is dependent on the aging temperature, about 3,500~5,000 h at 650°C and ~100,000 h at 600°C. The incubation time for subgrain coarsening can be significantly shortened under creep by two additional recovery mechanisms, namely, strain-induced subgrain recovery, and strain-assisted static subgrain recovery. The aging-induced and strain-assisted static recovery mechanisms can result in the breakdown of the creep strength in long-term creep region in G91. Our measurements of subgrain width vs. aging time show a similar incubation behavior, though the incubation period is much shorter, e.g. 4,000 – 5,000 h at 600°C. What is more interesting from our subgrain measurements is that the subgrain length and aspect ratio decrease continuously with aging time at the early stage of aging, which implies that subgrain recovery may start with shortening the subgrain length followed by subgrain widening, resulting in more equiaxed subgrains. The more detailed measurements of subgrain dimensions and shape we conducted here provide further details not revealed before.

Figure 7. TEM images of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 (a) in the as-received condition, and (b) after thermal aging for 19,926 h at 550°C.

Figure 8. TEM images of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 (a) in the as-received condition, and (b) after thermal aging for 19,992 h at 600°C.

Figure 9. TEM images of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 (a) in the as-received condition, and (b) after thermal aging for 20,531 h at 650°C.

Figure 10. TEM image of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 H30176 after thermal aging for 57,212 h at 538°C (ID 24357).

Figure 11. TEM image of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 H5349 after thermal aging for 132,647 h at 538°C (ID 20842).

Figure 12. TEM image of subgrain structure, and distributions of subgrain width, length, and aspect ratio, and dislocation density in G91 H30383 after thermal aging for 99,542 h at 482°C (ID 24746).

Figure 13. Time dependence of the subgrain (a) width, (b) length, and (c) aspect ratio of various heats of G91 after thermal aging at 550, 600 and 650°C.

3.1.2 Second-phase precipitates ($M_{23}C_6$, MX, Laves)

In the normalized and tempered condition, two second phases were observed in G91: $M_{23}C_6$ carbides distributed primarily along grain and subgrain boundaries, and MX precipitates located mainly inside subgrains. These two phases are clearly identified by X-ray diffraction (XRD), as shown in Fig. 14. The $M_{23}C_6$ and MX precipitates play different roles in G91 steel. Coarsening of $M_{23}C_6$ carbides and MX precipitates can lead to reduced high-temperature strength, creep and creep-fatigue resistance of G91.

Thermal aging can result in the formation of new phases. As shown in Fig. 15, an intermetallic phase, Laves phase was observed in the G91-H1 specimen after thermal aging for 5,011 h at 650°C. The Z-contrast of backscattered electrons (BSE) image and element maps of Mo, Cr, and Fe verify that the Laves phase formed is an intermetallic phase, $(Fe,Cr)_2Mo$. Precipitation of Laves phase depletes the solid solution strengthener, Mo in the matrix, causing mechanical property degradation at both low- and high-temperatures in G91.

Figure 14. The XRD line profile for the normalized and tempered G91-H30176.

Figure 15. The BSE image and element maps of Mo, Cr, and Fe showing Laves phase formation in G91-H1 aged for 5,011 h at 650°C.

Detailed analysis of second phases was conducted on the as-received and thermally-aged specimens. The sizes of $M_{23}C_6$, MX were measured by TEM and Laves phase particles were measured by SEM using the Z-contrast. Figure 16 compares the microstructure of second phases before and after thermal aging for 19,926 h at 550°C for the heat G91-H1. Before thermal aging, only two types of particles existed, $M_{23}C_6$ carbides (colored in blue) and MX carbonitrides (colored in green). A very low number density of AlN (colored in yellow) was also observed. Thermal aging at 550°C resulted in the formation of a new phase, Laves phase (colored in red). The mean size of Laves phase particle is 147 nm. There are minimal changes in sizes of $M_{23}C_6$ and MX precipitates during aging at 550°C.

Figure 17 compares the microstructure of second phases before and after thermal aging for 19,992 h at 600°C for the heat H30176. Similar to thermal aging at 550°C, thermal aging at 600°C leads to the formation of Laves phase. However, the number density of Laves phase particle in H30176 is significantly lower than that in heat G91-H1. It is noted that the content of silicon in H30176 is low, below the ASTM specifications. Literature shows that silicon plays an important role in the nucleation and growth of the Laves phase in high-Cr ferritic-martensitic steels. Hosoi et al [7] reported that a decrease of the Si content increases the time required for formation of the Laves phase, and no Laves phase was detected in ferritic-martensitic steels with negligible Si content. It was suggested that the addition of Si reduces the solubility of Mo in the ferrite phase and promotes the formation of Laves phase [8]. The lower concentration of Si in H30176 is suggested to be responsible for the lower density of the Laves phase precipitates observed in Heat 30176. Besides the precipitation of the Laves phase, thermal aging for 19,992 h at 600°C caused minor coarsening of $M_{23}C_6$ and MX particles.

A much more pronounced effect of thermal aging on second-phase precipitates was observed at 650°C. As shown in Fig. 18, which compares the second phase microstructure before and after thermal aging for 20,531 h at 650°C for the heat G91-H1, coarsening of $M_{23}C_6$ particles was significant under aging at 650°C as well as MX precipitates. The size distributions of $M_{23}C_6$ and MX particles become broader with some larger sizes of particles formed. Laves phase particles exhibited significant growth. The mean size of Laves phase particle is 576 nm, significantly larger than the Laves phase mean sizes after aging for ~20,000 h at 550 and 600°C (147 and 355 nm, respectively). It should be noted that the Laves phase was not observed in Heat 30176 aged at 650°C, likely due to the lower Si content in H30176.

Detailed characterization of $M_{23}C_6$, MX and Laves phase precipitates was also conducted on three archived G91 specimens, as shown in Figs. 19 – 21 for the specimen ID 24357 (Heat 30176 aged for 57,212 h at 538°C), ID 20842 (Heat 5349 aged for 132,647 h at 538°C), and ID 24746 (Heat 30384 aged for 99,542 h at 482°C), respectively. The microstructural parameters of these three archived specimens are compared with those of the specimens of G91-H1 and H30176 thermally aged at 550-650°C, and summarized in Fig. 22. Again, a significant data scatter was observed from different heats. For example, the mean size of $M_{23}C_6$ carbides in H5349 is 77 nm after aging for 132,647 h at 538°C, compared to the mean size of $M_{23}C_6$ carbides in H30176, 132 nm after aging for a much shorter time (57,647 h) at the same temperature (538°C).

Thermal aging-induced coarsening of $M_{23}C_6$ carbides and MX carbonitrides are evident, as shown in Figs. 22 (a) and (b) where the mean sizes of $M_{23}C_6$ and MX particles are plotted, respectively as a function of aging time for various heats of G91 thermally aged at 482-650°C. While the initial sizes of $M_{23}C_6$ carbides and MX precipitates may be different in different heats of G91, the coarsening behavior of $M_{23}C_6$ carbides and MX precipitates is less sensitive to heat variations but more temperature-dependent. The coarsening behavior is most pronounced at 650°C.

Precipitation of the Laves phase occurs through the nucleation and growth process. The precipitation behavior of the Laves phase is highly dependent on the Si content in G91. The heat dependence of the Laves phase precipitation is stronger at higher temperatures. The number density of the Laves phase is much lower in H30176 than in G91-H1 under the 600°C thermal aging, and no Laves phase precipitates were observed in H30176 but in G91-H1 under the 650°C thermal aging. The growth behavior of the Laves phase shows little difference among different heats at 550°C, while the growth rate of the Laves phase is higher in H30176 than in G91-H1 at 600°C, as shown in Fig. 22(c).

Figure 16. Micrographs showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91-H1 (a) in the as-received condition, and (b) after thermal aging for 19,926 h at 550°C.

Figure 17. Micrographs showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91-H30176 (a) in the as-received condition, and (b) after thermal aging for 19,992 h at 600°C.

Figure 18. Micrographs showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91-H1 (a) in the as-received condition, and (b) after thermal aging for 20,531 h at 650°C.

Figure 19. Micrograph showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91 H30176 after thermal aging for 57,212 h at 538°C (ID 24357).

Figure 20. Micrographs showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91 H5349 after thermal aging for 132,647 h at 538°C (ID 20842).

Figure 21. Micrographs showing $M_{23}C_6$, MX, Laves phase, and size distributions of $M_{23}C_6$, MX, Laves phase particles in G91 H30383 after thermal aging for 99,542 h at 482°C (ID 24746).

Figure 22. Time dependence of the mean size of (a) $M_{23}C_6$ particles, (b) MX precipitates, and (c) Laves phase particles in G91 after thermal aging at 550, 600 and 650°C.

3.2 Effect of thermal aging on tensile properties of Grade 91

The stress-strain behavior of G91 shows strong temperature dependence. Figure 23 shows the stress-strain curves of two heats of G91, H30176 and G91-H1 in the normalized and tempered (N&T) condition tensile tested at temperatures of 20 - 650°C at a nominal strain rate of 0.001 s⁻¹. The tensile strength of G91 decreases and the tensile ductility increases with increasing test temperature, except at 400°C where the ductility is the lowest. The strain hardening capability of G91 is lost when it is tested at temperatures of 550°C and above.

To understand the effect of thermal aging on tensile properties of G91, tensile tests of the thermally-aged specimens were carried out at the aging temperature, and the yield stress, ultimate tensile strength, uniform elongation, and total elongation are plotted as a function of aging time in Fig. 24 for heats, H30176 and G91-H1 thermally aged at 550, 600, and 650°C. Thermal aging of G91 resulted in the reduction in the yield stress and the ultimate tensile strength but has an insignificant effect on the uniform and total elongations. The reduction in tensile strength is more pronounced as the aging temperature and time increases. The two heats of G91 perform similarly under thermal aging at 550 - 650°C.

Tensile specimens made from the archived crept G91 specimens were tested at the aging temperature as well, and the yield stress, the ultimate tensile strength, the uniform elongation, and the total elongation of the 13 archived specimens and the specimen made from the G91 Kingston tube are compared in Figs. 25 (a)-(d). Specimens of H30176 were used as control specimens, and the tensile data at 427, 482, 538, and 550°C are included in Figs. 25 (a)-(d) as the baseline. The micro-hardness values of the archived specimens are given in Fig. 25(e). The hardness values can be correlated with the tensile strength at room temperature. While no clear trend can be observed from the hardness data, the ultimate tensile strength indeed exhibits a slight decrease after long-term thermal aging at temperatures > 500°C. The total elongation remains adequate after >100,000 h aging above 500°C. While there is data scatter from heat variations, these archived specimens indeed provide valuable information for understanding the effect of thermal aging at lower but more relevant reactor temperatures (vs. accelerated testing data shown in Fig. 23).

The values of the ultimate tensile strength (UTS) for various heats of G91 including the G91-H1 and H30176 specimens aged at 550-650°C and the archived specimens aged at 427-550°C are plotted as a function of aging time in Fig. 26, and compared with the calculated UTS values using the tensile strength reduction factors for G91 given in the ASME Code. The dash lines in Fig. 26 represent the tensile strength values obtained from the product of the UTS of the as-received H30176 specimens and the temperature-time-dependent strength reduction factors given in Table NH-3225-4 Tensile Strength Reduction Factors for 9Cr-1Mo-V in ASME B&PV Code Section III, Subsection NH Class 1 components in Elevated Temperature Service (2010). As shown in Fig. 26, our tensile data agree remarkably well with the recommended ASME strength reduction values for aging temperatures in the range of 425 - 650°C. According to Table NH-3225-4, the strength reduction in G91 becomes apparent after aging for 100,000 h at 500°C, 30,000 h at 550°C, 3,000 h at 600°C, and 300 h at 650°C.

Figure 23. Stress-strain curves of the as-received G91 (a) Heat 30176, (b) Heat G91-H1.

Figure 24. The (a) yield stress, (b) ultimate tensile strength, (c) uniform elongation, and (d) total elongation as a function of exposure time for G91-H1 and G91-H30176 thermally aged at 550, 600, and 650°C.

Figure 25. The (a) yield stress, (b) ultimate tensile strength, (c) uniform elongation, (d) total elongation, and (e) micro-hardness for the archived G91 specimens thermally-aged at 427 - 550°C. The tensile test was conducted at the aging temperature.

Figure 26. The ultimate tensile strength (UTS) vs. aging time for various heats of G91 steel thermally-aged at 427-650°C. The experimental data are compared with the calculated UTS values using the strength reduction factors given in Table NH-3225-4 in ASME B&PV Code Section III, Subsection NH (2010).

3.3 Microstructural modeling

3.3.1 Modeling of subgrain recovery

The subgrain structure formed during tempering is unstable in G91 steel. The subgrain width increases and the length decreases, and the subgrain shape become more equiaxed with aging time. Subgrain recovery and growth may occur in two different ways: subgrain boundary migration or subgrain coalescence [9,10]. Subgrain growth through boundary migration happens in a similar way as conventional grain growth, and small subgrains are consumed by larger one. Subgrain coalescence occurs by the dissolution of sub-boundaries. Three mechanisms for subgrain coalescence have been proposed: collective migration of sub-boundary dislocations, extraction of sub-boundary dislocations, and emission of sub-boundary dislocations. For the second and third mechanism, the dislocation density in the subgrain interior plays an important role, and the subgrain growth rate is controlled by the recovery of dislocations.

Models for the subgrain growth have been proposed by R. Sandstrom [9,10]. The contribution of extraction of boundary dislocations to the subgrain growth rate, $(dD/dt)_B$ can be described by:

$$\left(\frac{dD}{dt}\right)_B = \frac{M\tau\phi\rho h}{\mu} \quad (1)$$

The contribution of emission of boundary dislocations to the subgrain growth rate, $(dD/dt)_e$ is given by:

$$\left(\frac{dD}{dt}\right)_e = \frac{8DM\tau\rho^{1.5}h}{3\mu} \left[\exp\left(-\frac{\log(2\tau_{up})}{\tau_0\left(1+\left(\frac{\sigma D}{4\tau_0}\right)^2\right)}\right) - \exp\left(-\frac{\log(2\tau_{up})}{\tau_0}\right) \right] \quad (2)$$

The contribution of the migration of dislocations in the boundaries (MDB) to the subgrain growth rate, $(dD/dt)_{MDB}$ can be expressed as:

$$\left(\frac{dD}{dt}\right)_{MDB} = \frac{4M\tau}{D} \quad (3)$$

The rate of subgrain growth by sub-boundary migration (BM), $(dD/dt)_{BM}$ is:

$$\left(\frac{dD}{dt}\right)_{BM} = \frac{1.5M\tau}{D} \quad (4)$$

where D is the subgrain diameter, τ is the line tension of the dislocations, and M is the dislocation mobility, ρ the dislocation density, h the average distance between dislocations, τ_0 and τ_{up} are related to the dislocation pile-up forces. The effect of alloying elements in solid solution and the presence of second-phase particles can also be accounted for in the subgrain growth models [9,10].

Subgrain coarsening in G91 under thermal aging was modeled by considering collective migration of dislocations, taking into account of both contributions of migration of dislocations in the boundaries and the migration of boundaries. The modeling results are compared with the

experimental data of the subgrain width as a function of aging time in Fig. 27. A general agreement is achieved between the experiments and model. More experimental data are needed to understand the effect of heat variations of G91 and incorporate that effect into the model. Furthermore, while the coarsening of $M_{23}C_6$ particles is suggested to play a significant role in subgrain coarsening and recovery, the current model doesn't include the pinning effect of $M_{23}C_6$ particles, nor the solute effects and dislocation recovery. More experimental data of subgrains at a wide range of aging temperature and time are still needed for the model refinement and validation. It should also be noted that strain-induced dynamic recovery under creep and creep-fatigue loading has a much stronger effect on subgrain recovery, and should be accounted for in the evaluation of long-term creep strength and creep-fatigue resistance of G91.

Figure 27. Comparison of the experimental data and modeling results for the subgrain width vs. aging time for G91 steel.

3.3.2 Modeling of $M_{23}C_6$ and MX particle coarsening

The $M_{23}C_6$ ($M = Fe, Cr$) carbides in G91 precipitate mainly along grain and subgrain boundaries, and act as obstacles for boundary migration. They are considered as boundary strengtheners, and critical to the stabilization of the tempered martensite structure. However, $M_{23}C_6$ carbides tend to coarsen easily during thermal aging because of the high solubility of Fe and Cr in the ferrite matrix. The MX ($M = Nb, V, X = C, N$) carbonitrides precipitate primarily within subgrains, acting as obstacles to moving dislocations in the matrix and playing an effective role in precipitation strengthening. Since MX carbonitrides are mainly composed of Nb

and V and the solubility of Nb and V is small in the ferrite matrix, they do not grow easily during thermal aging. Coarsening of either $M_{23}C_6$ or MX particles is detrimental to the high-temperature strength, and creep and creep-fatigue resistance of G91 steel.

The coarsening behavior of $M_{23}C_6$ and MX precipitates was simulated using the Ostwald ripening model. Figures 28 (a) and (b) compare the experimental data and modeling results of $M_{23}C_6$ and MX particle coarsening in G91 steel during thermal aging at 550-650°C. The model describes well the coarsening behavior of the two types of particles. The coarsening rates were determined by fitting the experimental data, and the fitting results showed qualitatively an expected temperature dependence of the coarsening rate. The coarsening model will be refined in future work by considering the influence of diffusivities and solubilities, and the interfacial energy through the DICTRA software package. More experimental data of $M_{23}C_6$ and MX particle coarsening are also needed to improve the current model. As shown in our previous work, the models, once validated, can be used to predict the coarsening of $M_{23}C_6$ and MX precipitates after the 60-year service at the operating temperature of 550°C in a sodium-cooled fast reactor.

Figure 28. Comparison of experimental and modeling results of (a) coarsening of $M_{23}C_6$ carbides, and (b) coarsening of MX precipitates in G91 steel during thermal aging at 550-650°C.

3.3.3 Modeling of Laves phase nucleation and growth

Formation of the Laves phase during thermal aging removes the Mo solutes from the matrix, diminishing the solid solution strengthening. The understanding of the Laves phase precipitation behavior is important to the prediction of the long-term performance of G91. The nucleation, growth and coarsening processes of the Laves phase in G91 can be simulated using thermodynamics and kinetics software packages, Thermo-Calc, DICTRA and TC-PRISMA. The simulation of the growth behavior of the Laves phase can be performed using DICTRA. It assumes a local equilibrium at the moving interface, i.e. no difference in chemical potential across the

phase interface, and the concentration of the components at the interface is evaluated from thermodynamic data, and the growth behavior is treated as a simple diffusion problem. The growth of the Laves phase is mainly controlled by the diffusion of Cr and Mo. The coarsening behavior of the Laves phase can also be simulated using the growth model by including a contribution of the interfacial energy.

We have recently upgraded the thermodynamic and kinetic database to allow better simulation of second phase precipitation in G91, particularly the Laves phase. In the new database, TCFE9, vanadium is added in the Laves phase and the solubility of several elements has been revised. The precipitation module (TC-PRISMA) has also recently been integrated into the Thermo-Calc software package, rather than a stand-alone program. This integration allows simulation of concurrent nucleation, growth/dissolution and coarsening of precipitates in a multi-component, multi-phase alloy system. Our future work will take advantage of these new features to model the temporal evolution of the Laves phase and calculate the size distributions, the average particle size, volume fraction and nucleation, growth and coarsening rate of the Laves phase in G91.

3.4 Correlation of microstructure - tensile strength in Grade 91

Efforts have been made to understand the strengthening mechanisms and degradation processes in G91 during long-term aging. A correlation of microstructural parameters with aging-induced reduction in tensile strength is being established to corroborate the ASME Code rules on the reduction in tensile strength due to elevated temperature service.

In the normalized and tempered condition, the microstructure of G91 consists of tempered martensite with a high density of dislocations, $M_{23}C_6$ carbides decorating boundaries and sub-boundaries, and a fine distribution of vanadium/niobium carbonitrides (MX). These microstructural features, if maintained, give rise to good high temperature strength, creep and creep-fatigue properties. However, microstructural and mechanical degradation occurred during long-term service. As reported in previous sections, thermal aging can cause significant microstructural changes: decrease in dislocation density within subgrains, subgrain recovery, coarsening of $M_{23}C_6$ and MX precipitates, and formation of the Laves phase. These microstructural changes occur in a coupled way, and the interactive processes of these microstructural constituents contribute collectively to the overall reduction of the mechanical strength. For instance, the dispersion of $M_{23}C_6$ particles exerts the pinning force on subgrain boundaries, which hinders subgrain coarsening and growth. The slower the particle coarsening rate the longer is the time before unpinning of the martensite boundaries and consequent secondary recrystallization and martensite grain growth. Thermally-induced coarsening of $M_{23}C_6$ particles has been correlated with the observed subgrain coarsening during thermal aging. Ghassemi-Armaki et al. [5,6] reported a good correlation of subgrain width with $M_{23}C_6$ particle spacing, and suggested that subgrain coarsening is caused by the loss of pinning force from $M_{23}C_6$ carbides. The MX precipitates in the matrix serve as effective obstacles to moving dislocations, giving rise to precipitation strengthening in G91. In the meantime, the effect of MX particles on dislocation motion will influence the dislocation recovery, and in turn affect the recovery rate of subgrains. The formation of the Laves phase not only removes the solute strengtheners, Mo from the matrix, reducing solid solution strengthening in G91, but the precipitation of the Laves phase along boundaries and sub-boundaries will also play a role in subgrain coarsening.

The strength of G91, σ can be expressed as a function of the following microstructural parameters:

$$\sigma = f(c, \rho, \lambda_{sg}, r_{par}^i, f_{par}^i) \quad (5)$$

where c is the solid solution content, ρ is the dislocation density within subgrains, λ_{sg} is the subgrain size, r_{par} , f_{par} are the particle radius and volume fraction of phase i , respectively. This relationship considers several strengthening mechanisms including solid solution strengthening, dislocation hardening, boundary and sub-boundary strengthening, and precipitation hardening. This complex relationship will continue to evolve during the lifetime of the component due to continued microstructural evolution. To predict the long-term performance of G91, it is essential to understand the separate effect of each microstructural constituent and their interactions and the principle correlation between microstructure and mechanical properties.

3.4.1 Strengthening mechanisms in G91

To understand the precise role of each microstructural constituent and their quantitative contributions to the tensile strength of G91 steel, *in situ* tensile tests with high-energy synchrotron X-rays were conducted initially on the as-received G91 at 20 - 650°C at beamline 1-ID at the Advanced Photon Source. We have found that there is a significant load transfer from the martensite matrix to $M_{23}C_6$ and MX phases during tensile deformation at 20°C. The $M_{23}C_6$ particles showed a much greater load sharing capability than MX precipitates. Their load sharing capacity (LSC) was quantified by *in situ* measurements using the elastic and plastic moduli. The LSC factor for the (hkl) plane in phase i, K_{hkl}^i is defined as:

$$d\sigma_{hkl}^i = E_{hkl}^i d\varepsilon_{hkl}^i = \frac{E_{hkl}^i}{H_{hkl}^i} d\sigma = K_{hkl}^i d\sigma \quad (6)$$

where ε_{hkl}^i is the lattice strain, E_{hkl}^i is the elastic modulus, and H_{hkl}^i the plastic modulus for the (hkl) plane in phase i. It was found that the load transfer was significantly reduced at high temperatures.

While limited lattice strain is developed in the Fe-matrix after yielding, plastic flow in the martensite matrix is carried mainly through dislocation activity. The evolution of dislocation density during deformation was followed during the *in situ* tensile test, and a dislocation model was developed to describe the dislocation density evolution as a function of plastic strain for G91 steel, i.e.:

$$\rho = (\bar{m}/(b \cdot s \cdot \Omega))(1 - e^{-\Omega\varepsilon}) + \rho_0 \cdot e^{-\Omega\varepsilon} \quad (7)$$

where ρ is the average dislocation density, ε is the strain, ρ_0 is the density of dislocations at $\varepsilon = 0$ ("grown-in" dislocations), $\bar{m}$ is the Taylor constant, s is the mean free path of dislocation motion, b is the Burger's vector, and Ω is the dynamic recovery coefficient.

The *in situ* tensile tests also revealed that the role of $M_{23}C_6$ carbides in the strengthening of G91 must be understood by taking into account of their non-uniform distribution in the martensite matrix. $M_{23}C_6$ precipitates distribute primarily along grain and subgrain boundaries in G91. The measured strengthening effect of $M_{23}C_6$ particles manifests subgrain boundary strengthening in G91. The high loading capacity of $M_{23}C_6$ particles measured by the lattice strain is consistent with the dislocation activity revealed by the line profile analysis, and sub-boundary strengthening in G91 is the dominant hardening mechanism in G91. This finding is consistent with observations reported in other studies [11,12] that sub-boundary hardening is much greater than precipitate hardening of MX and the Laves phase particles in high-Cr ferritic-martensitic steels.

3.4.2 Microstructural model for tensile strength of G91

The *in situ* tensile tests suggested that the tensile strength of G91 may be accounted for by three strengthening effects: subgrain boundary hardening, MX precipitation hardening, and Mo solid solution strengthening. Note that the role of $M_{23}C_6$ carbides on the tensile strength is

coupled with the sub-boundary hardening, and the effect of the precipitation of Laves phase during aging is accounted for through the solid solution strengthening.

The contribution of subgrain boundary hardening to the tensile strength of G91, σ_{sg} can be estimated using the following equation [12]:

$$\tau_{sg} = \alpha_{sg}\mu b / \lambda_{sg} \quad (8)$$

where λ_{sg} is the width of elongated subgrains, μ is the shear modulus, b is the Burger's vector (0.248 nm), and α_{sg} is the constant.

The MX precipitation hardening can be described by the Orowan mechanism [13]:

$$\tau_{MX} = \alpha_{MX}\mu b / \lambda_{MX} \quad (9)$$

where λ_{MX} is the MX inter-particle spacing, and α_{MX} is the constant.

The Mo solid solution strengthening in the martensite matrix may be estimated by [14]:

$$\tau_{ss} = \alpha_{ss}\mu \varepsilon^{1.5} c^{0.5} \quad (10)$$

where ε is the misfit strain, c is the Mo solute concentration (at%), and α_{ss} is the constant.

The tensile strength of G91 after aging for time, t at temperature, T , $\tau(T, t)$ can be calculated using the following equation:

$$\tau(T, t) = \alpha_{sg}(T)\mu(T)b/\lambda_{sg}(T, t) + \alpha_{MX}(T)\mu(T)b/\lambda_{MX}(T, t) + \alpha_{ss}(T)\mu(T)\varepsilon^{1.5}c(T, t)^{0.5} \quad (11)$$

Note that the strengthening model was modified to take into account of the temperature dependence of the material parameters.

The ultimate tensile strength as a function of aging time was calculated using Eq. (11), and the temperature-time-dependence of λ_{sg} , λ_{MX} , and c was obtained from the microstructural models presented in section 3.3. The calculated values are compared with the experimental data of G91 thermally aged at 550, 600 and 650°C in Fig. 29. The UTS values were also calculated using the aging reduction factors given in Table NH-3225-4 Tensile Strength Reduction Factors for 9Cr-1Mo-V in ASME B&PV Code Section III, Subsection NH, and included in Fig. 29. An excellent agreement was achieved between the experiments and the calculations up to ~100,000 h at 550°C, ~20,000 h at 600 and 650°C. It was found that among the three strengthening processes, sub-boundary strengthening plays a dominant role, followed by MX precipitation hardening, and solid solution hardening is insignificant to the total strength of G91. The calculations also show that sub-boundary strengthening becomes weaker at high temperature, and the MX precipitation hardening plays an increasingly significant role in the high-temperature resistance of G91. There is a discrepancy however, between the model and the calculated UTS values using the ASME reduction factors for longer-time aging. The model predicts lower strength values than the values calculated using the ASME Code. Future work will focus on improving the microstructural models and understanding the discrepancy for the long-term aging effect.

Figure 29. Comparison of the calculated tensile strength using the microstructural model and the ASME Code strength reduction factors in Table NH-3225-4 and the experimental data as a function of aging time for G91 aged at 550, 600, and 650°C.

4 Summary and Future Work

This report provides an update on understanding and predicting the effects of long-term thermal aging on microstructure and tensile properties of G91 to corroborate the ASME Code rules in strength reduction due to elevated temperature service. The thermal aging study of G91 involves two types of thermally-aged specimens: (1) specimens fabricated from the heads of the archived crept specimens (13 in total) covering the aging temperature of 427 - 538°C and times up to 132,647 h for several heats of G91, and from a tube removed from the Kingston coal-fired power plant after exposure for 155,000 h at 550°C, and (2) specimens made from two heats of G91, G91-H1 and H30176 thermally aged at 550, 600, and 650°C for times up to 55,277 h. These specimens provide a comprehensive data set for understanding and predicting the effect of long-term thermal aging on microstructure and tensile properties of G91.

The thermal aging study of G91 involves two types of thermally-aged specimens: (1) specimens fabricated from the heads of the archived crept specimens (13 in total) covering the aging temperature of 427 - 538°C and times up to 132,647 h for several heats of G91, and from a tube removed from the Kingston coal-fired power plant after exposure for 155,000 h at 550°C, and (2) specimens made from two heats of G91, G91-H1 and H30176 thermally aged at 550, 600, and 650°C for times up to 55,277 h. These specimens provide a comprehensive data set for understanding and predicting the effect of long-term thermal aging on microstructure and tensile properties of G91.

Microstructural analysis of the thermally-aged G91 revealed that thermal aging can cause significant microstructural changes: (1) the subgrain structure formed during tempering is unstable, and can suffer significant recovery during aging, manifested by an increase in subgrain width, a decrease in subgrain length, and a decrease in subgrain aspect ratio (i.e. subgrains become more equiaxed). The subgrain recovery is facilitated by the reduction of dislocation density within subgrains; (2) two types of precipitates formed during tempering, i.e. $M_{23}C_6$ carbides and MX carbonitrides coarsen with increasing temperature and time; (3) a new phase, the Laves phase forms during aging and grows rapidly at high temperature. The evolution of each microstructural feature during thermal aging can be well described by individual microstructural models.

Thermal aging of G91 results in the reduction in the yield stress and the ultimate tensile strength but has an insignificant effect on the uniform and total elongations. The reduction in tensile strength is more pronounced as the aging temperature and time increases. The tensile data of the thermally-aged specimens agree well with the calculated tensile strength values using the temperature-time-dependent strength reduction factors given in the ASME Code.

The *in situ* tensile tests with high-energy X-rays of the as-received specimens revealed three primary strengthening mechanisms in G91: subgrain boundary hardening, MX precipitation hardening, and Mo solid solution strengthening. The role of $M_{23}C_6$ carbides on the tensile strength is coupled with the sub-boundary hardening, and the effect of the precipitation of the Laves phase during aging is accounted for through the Mo solid solution strengthening. Among the three strengthening mechanisms, sub-boundary strengthening plays a dominant role, followed

by MX precipitation hardening, and the Mo solid solution hardening is insignificant to the total strength of G91. A microstructural model has been established to describe the reduction in tensile strength from aging. A good agreement was achieved between the experiments and the calculations up to ~100,000 h at 550°C, ~20,000 h at 600 and 650°C. However, there was a discrepancy between the modeling results and the calculated UTS values using the ASME strength reduction factors at longer aging time. The model predicted lower strength values than the values calculated using the ASME Code.

Future work will continue microstructural characterization to obtain a more complete set of microstructural data. Data will be used to improve the microstructural models and the correlation between the microstructure and tensile strength, particularly for the effect of long-term thermal aging.

Acknowledgement

This research was sponsored by the U.S. Department of Energy, Office of Nuclear Energy, for the Advanced Reactor Technologies (ART) Program under Contract DE-AC02-06CH11357. We gratefully acknowledge the support provided by Brian Robinson of DOE-NE, Advanced Reactor Technologies, ARC Program Manager; William Corwin of DOE-NE, Advanced Reactor Technologies, Materials Technology Lead; Robert Hill of Argonne National Laboratory, ART Co-National Technical Director; and Sam Sham of Argonne National Laboratory, ART Materials Development Technical Area Lead.

Materials were provided by the Oak Ridge National Laboratory. D. L. Rink is thanked for specimen encapsulation. M. Quesinberry is thanked for maintaining furnaces and conducting tensile tests.

References

- [1] Lifshitz, I.M., V.V. Slyozov, Soviet Physics JETP 35 (1959) 331.
- [2] Lifshitz, I.M., V.V. Slyozov, Chem. Soilds 19 (1961) 35.
- [3] Wagner, C., Zeitschrift fur Elektrochemie 65 (1961) 581.
- [4] Wagner R, Kampmann R. Homogeneous Second Phase Precipitation, in Haasen P (Ed.), Mater. Sci. Tech. Compr. Treat. Weinheim: Wiley-VCH; 1991.
- [5] H. Ghassemi-Armaki, R.P. Chen, K. Maruyama, and M. Igarashi, J. Nucl. Mater. 433 (2013) 23.
- [6] H. Ghassemi-Armaki, R.P. Chen, K. Maruyama, and M. Igarashi, Mater. Sci. Eng. A 527 (2010) 6581.
- [7] Y. Hosoi, N. Wade, S. Kunimitsu, T. Urita, J. Nucl. Mater. 141-143 (1986) 461.
- [8] A. Aghajani, F. Richter, C. Somsen, S.G. Fries, I. Steinbach, and G. Eggeler, Script. Mater. 61 (2009) 1068..
- [9] R. Sandstrom, Acta Met. 25 (1977) 897.
- [10] R. Sandstrom, Acta Met. 25 (1977) 905.
- [11] F. Abe, Creep Resistant Steels, Woodhead Publishing, Cambridge, 2008, p. 279.
- [12] K. Maruyama, K. Sawada, and J. Koike, ISIJ Inter. 41 (2001) 641.
- [13] K. Maruyama and H. Nakashima, 1997, Materials Science for High Temperature Strength, Uchida-Rokakudo, Tokyo, Japan.
- [14] D. Peckner, The Strengthening of Metals, 1964.

Nuclear Engineering Division

Argonne National Laboratory

9700 South Case Avenue

Argonne, IL 60439

www.anl.gov

Argonne National Laboratory is a U.S. Department of Energy
laboratory managed by UChicago Argonne, LLC