Understanding and Predicting Effect of Sodium Exposure on Microstructure of Grade 91 Steel

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.

Understanding and Predicting Effect of Sodium Exposure on Microstructure of Grade 91 Steel

Prepared by
Meimei Li, K. Natesan, and Wei-Ying Chen
Nuclear Engineering Division
Argonne National Laboratory

August 2017

ABSTRACT

This report provides an update on the understanding of the effect of sodium exposures on microstructure and tensile properties of Grade 91 (G91) steel in support of the design and operation of G91 components in sodium-cooled fast reactors (SFRs). The report is a Level 3 deliverable in FY17 (M3AT-17AN1602018), under the Work Package AT-17AN160201, “SFR Materials Testing” performed by the Argonne National Laboratory (ANL), as part of the Advanced Reactor Technologies Program.

Two heats of G91 steel were investigated in liquid sodium environments at 550-650°C to understand its corrosion behaviour, microstructural evolution, and tensile properties. Data of the sodium-exposed specimens were compared with the thermal aging data of the same heat to separate the effects of sodium exposure and thermal aging. Detailed microstructural analysis including subgrain structure and size, dislocation density, and size distributions of $M_{23}C_6$ carbides, MX precipitates, and Laves phase particles was conducted after thermal or sodium exposures at 550, 600, 650°C for ~20,000 h. It was found that:

- G91 showed mostly a weight loss after sodium exposures at 550-650°C. The corrosion rate decreased with increasing exposure time and tended to level off after exposures for ~20,000 h. The corrosion rate was temperature dependent, with the rate significantly higher at 650°C than those at 550 and 600°C.
- Sodium exposures at 550 and 600°C for ~20,000 h had insignificant effects on subgrain structure and size, dislocation density, and sizes of $M_{23}C_6$ and MX precipitates. The most prominent microstructural change was the formation of intermetallic Laves phase, and no obvious additional effect of sodium exposures on Laves phase was observed relative to the thermal aging effect.
- Sodium exposures at 650°C in contrast, have a marked effect on microstructural evolution in G91. The most dramatic change in microstructure was excessive grain growth. The initial tempered martensitic structure was replaced with large grains with the mean size of 79 μm after sodium exposure for 20,531 h at 650°C, compared to the prior austenite grain size of 20-30 μm in the normalized and tempered condition. Other microstructural changes in sodium include drastic reduction of dislocation density, dissolution of $M_{23}C_6$ carbides, coarsening of MX precipitates, and rapid growth of Laves phase particles, which were significantly different from the microstructural changes under comparable thermal aging conditions.
- The tensile data showed that sodium exposures at 550 and 600°C caused virtually no additional effect on the tensile properties of G91 after exposures for up to ~20,000 h. The tensile strength of G91 was reduced only slightly after thermal or sodium exposures (<10%), and no effect on tensile ductility was observed. In contrast, sodium exposures at 650°C had a drastic effect on the tensile properties of G91. The maximum reductions of the yield stress and ultimate tensile strength were 57% and 70%, respectively after sodium exposures for 20,531 h. The effect of thermal exposures, on the other hand was much smaller for comparable exposure times at 650°C.
- The pronounced microstructural changes in sodium environments may be understood by considering combined effects of thermal aging and interstitial element transfer on

microstructural stability in sodium. The degradation of tensile properties of G91 in sodium can be correlated well with sodium exposure-induced microstructural changes in G91.

TABLE OF CONTENTS

ABSTRACT.....	ii
TABLE OF CONTENTS.....	iv
LIST OF TABLES.....	v
LIST OF FIGURES	vi
1 Introduction	1
2 Experimental Procedure	4
2.1 Materials and specimens	4
2.2 Forced convection sodium loops	5
2.3 Sodium exposure experiments and post-exposure examinations.....	7
3 Results	9
3.1 Corrosion behavior.....	9
3.2 Effect of sodium exposure on microstructure	11
3.3 Effect of sodium exposures on tensile properties	17
4 Summary	22
Acknowledgement	23
References	23

LIST OF TABLES

Table 1.	Chemical composition (in wt%)	4
Table 2.	Heat treatment conditions	4
Table 3.	Total sodium exposure times at 550, 600, and 650°C for each heat.....	7
Table 4.	Sample conditions for detailed microstructural characterization of G91.....	11
Table 5.	Effect of Thermal and Sodium Exposures on Microstructural Features in G91 at 550-650°C	17

LIST OF FIGURES

Figure 1.	A schematic diagram of sodium-cooled fast reactor.....	1
Figure 2.	Schematic drawings of subsize sheet-type tensile specimens with extended grip sections for microstructural analysis.....	5
Figure 3.	Isometric view of (a) the Sodium Materials Test Loop 1 (SMT-1) and (b) the Sodium Materials Test Loop 2 (SMT-2)	6
Figure 4.	Experimental setup for high temperature tensile tests	8
Figure 5.	Weight changes and corrosion rates as a function of exposure time for two heats of G91 after sodium exposures at 550, 600 and 650°C	10
Figure 6.	Microstructure of G91-H1 specimens for (a) as-received, (b) aged for 19,926 h at 550°C, and (c) sodium-exposed for 21,281 h at 550°C, and (d) comparison of subgrain width, dislocation density, mean sizes of $M_{23}C_6$, MX and Laves phase particles in these three specimens	14
Figure 7.	Microstructure of G91-H30176 specimens for (a) as-received, (b) aged for 19,992 h at 600°C, and (c) sodium-exposed for 19,212 h at 600°C, and (d) comparison of subgrain width, dislocation density, mean sizes of $M_{23}C_6$, MX and Laves phase particles in these three specimens	15
Figure 8.	Microstructure of G91-H1 specimens for (a) as-received, (b) aged for 20,531 h at 650°C, and (c) sodium-exposed for 19,952 h at 650°C, and (d) comparison of subgrain width, dislocation density, mean sizes of $M_{23}C_6$, MX and Laves phase particles in these three specimens	16
Figure 9.	Yield stress, ultimate tensile strength, uniform elongation and total elongation as a function of exposure time for G91 tensile tested at 550°C after thermal or sodium exposures at 550°C	19
Figure 10.	Yield stress, ultimate tensile strength, uniform elongation and total elongation as a function of exposure time for G91 tensile tested at 600°C after thermal or sodium exposures at 600°C	20
Figure 11.	Yield stress, ultimate tensile strength, uniform elongation and total elongation as a function of exposure time for G91 tensile tested at 650°C after thermal or sodium exposures at 650°C	21

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. Inherent in this research and development is the selection and adequate long-term performance of reactor structural materials that are directly exposed to the sodium coolant at elevated temperatures.

Figure 1 shows a schematic of a sodium-cooled fast reactor. In these reactors, heat is generated from fission reactions in a nuclear-fueled core. The heat is removed by liquid sodium flowing through the core, transferred to a steam system, and the steam is used to drive a turbine. Because of excellent heat transfer properties, liquid sodium has been selected as the coolant and heat transport medium. In general, austenitic stainless steels are used for in-core structural components, piping, and intermediate heat exchanger. High chromium ferritic steels are considered for primary piping system, intermediate heat exchanger, secondary piping and steam generator in SFRs. The selection of a particular material and combinations that will be used in both primary and secondary circuits is based upon a number of factors. For in-core applications, the stability of the material in the fast neutron environment, compatibility with the sodium coolant and elevated temperature performance are of primary concern. In the case of the steam generator, the resistance of the material to aqueous chloride and caustic cracking as well as minimization of corrosion wastage rates due to sodium-water reaction products in the event of a tube failure have important bearing on the material selection.

Figure 1. A schematic diagram of sodium-cooled fast reactor.

In general, structural materials can undergo a variety of interactions upon exposure to liquid sodium. The extent of interaction depends upon the exposure conditions of temperature, temperature gradient, sodium velocity and purity, the materials of construction, and external sources and sinks for the constituent elements of the structural materials. The interactions can be broadly classified into either metallic or nonmetallic element mass transfer. Metallic element mass transfer usually establishes a go/no-go type of evaluation of an alloy for use in sodium environment, based upon the established limits of material wastage or component section loss. A classic example of this is the unacceptable performance of vanadium base alloys in sodium of normal reactor purity. Upon selection of an alloy for sodium service, corrosion allowances that account for metallic element transfer can be incorporated into the design of specific components.

Nonmetallic elements such as oxygen, carbon, nitrogen, and hydrogen are known to migrate in structural materials/sodium systems as a result of chemical activity differences that occur in isothermal or non-isothermal systems. Transfer of these elements also occurs in systems where combinations of materials of different compositions are used. By examining the partitioning of nonmetallic elements between the structural alloy and sodium, the extent to which oxygen, carbon, and nitrogen interact in the structural material-sodium systems can be assessed. From the operation of the sodium fast reactor standpoint, the oxygen impurity in sodium can be controlled to ~1 wppm which would result in acceptable corrosion of austenitic and ferritic steels and nickel-base alloys at anticipated operating temperatures. The solubility of nitrogen in sodium is low in the reactor at the operating temperature, and its effect on materials performance may not be significant. On the other hand, materials of nominally the same composition with different degrees of decarburization/carburization in sodium loops operating over similar temperature ranges have resulted in questions regarding the extrapolation of results obtained in small scale sodium loops to large reactor systems. Since carbon concentration in a given system is established by a dynamic equilibrium between the carbon sources and carbon sinks present in the system, it could vary from system to system as well as over time within a system. It is necessary to evaluate and understand the influence of carbon transport in sodium on the microstructure and mechanical properties of advanced structural materials.

Grade 91 ferritic-martensitic steel (also known as Modified 9Cr-1Mo steel) was developed in the late 1970s for intermediate heat exchanger and steam generator applications for liquid metal reactors (LMRs) in the U.S. In 1974, the U.S. DOE initiated a three-phase study for developing a new alloy for the use in LMRs, and Mod.9Cr-1Mo was selected based on creep strength and microstructural considerations. A development program for Mod.9Cr-1Mo steel started in early 1980s, and considerable information on Mod.9Cr-1Mo steel 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. Limited data in sodium showed no significant deleterious effects on mechanical properties. Long-term testing data in sodium are however largely lacking. Data on the effects of carburization/decarburization on the mechanical properties of G91 are sparse, and the understanding of carburization/decarburization kinetics is limited. Additional work is required to understand the effects of carburization/decarburization

on the stability of second phases and martensite structure and their impact on tensile, creep, fatigue, and creep-fatigue properties of G91.

This report presents detailed microstructural analysis of G91 specimens exposed to sodium at 550, 600 and 650°C for ~20,000 h to understand the effects of sodium exposure on microstructural evolution and tensile properties, and the role of nonmetallic element transfer in SFR environments.

2 Experimental Procedure

2.1 Materials and specimens

Two heats of G91 steel were studied, G91-H1 and G91-H30176. G91-H1 was an archive material. A small amount of material was available at the Argonne National Laboratory for the thermal aging and sodium compatibility studies. It was in the plate form with a thickness of 0.375". The plate was normalized at 1050°C and tempered at 760°C for 1 h and air cooled. Heat H30176 of G91 was provided by the Oak Ridge National Laboratory with a relatively large quantity. This heat 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 1 and 2, respectively.

Table 1. Chemical composition (in wt%)

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 2. Heat treatment conditions.

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

Subsize sheet-type tensile specimens with extended grip sections (Fig. 2) were used in sodium exposure experiments and post-exposure microstructural analysis and tensile tests. The extended grip sections were used for microstructural characterization. The tensile specimens were electrical-discharge-machined with the gage parallel to the rolling direction. The tensile specimen has nominal gage dimensions of $7.62 \times 1.52 \times 0.76$ mm.

Figure 2. Schematic drawing of subsize sheet-type tensile specimens with extended grip sections for microstructural analysis.

2.2 Forced convection sodium loops

Two forced convection sodium loops were constructed at the ANL for sodium exposure tests of advanced materials. The Sodium Materials Test Loop 1 (SMT-1) (shown in Fig. 3(a)) consists of a single specimen-exposure vessel with an electromagnetic pump, two electromagnetic flow meters, an economizer, and a cold trap. The total amount of sodium in the loop is approximately 10 kg. The vessel has large penetrations at the top for sample loading as well as small penetrations for a level probe, a thermocouple, and an argon/vacuum line. The maximum operating pressure and temperature of the specimen vessel are 5 psig and 700°C, respectively.

The Sodium Materials Test Loop 2 (SMT-2) (shown in Fig. 3(b)) is a dual sample-vessel loop for sodium exposure tests at two temperatures. The maximum operating pressure and temperature for the two sample vessels are 5 psig and 750°C, respectively, and the total amount of sodium in the loop is approximately 20 kg. Each vessel has two penetrations at the top for sample loading as well as smaller penetrations for a level probe, thermocouple, and argon/vacuum line.

Both loops are constructed of austenitic stainless steels. The oxygen content of the sodium is controlled by the cold trap in both loops. The temperature of the cold trap is maintained at 125°C to ensure that the oxygen concentration is at ~1 wppm during specimen exposure.

Figure 3. Isometric view of (a) the Sodium Materials Test Loop 1 (SMT-1) and (b) the Sodium Materials Test Loop 2 (SMT-2).

2.3 Sodium exposure experiments and post- exposure examinations

Sodium exposure tests were performed at 550, 600, and 650°C for up to ~20,000 h. Table 3 gives the total exposure times at different temperatures for the two heats of G91.

Table 3. Total sodium exposure times at 550, 600, and 650°C for each heat.

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	21,282	-	19,952
G91 H30176	21,622	19,212	9,721

Prior to the sodium exposure test, a specimen was weighed three times using an OHAUS Model AP250 analytical balance to a precision of 10 μg ; the thickness of the specimen was measured three times using a micrometer to a precision of 0.0001 in. After the sodium exposure test, the specimen was removed from the loop, cleaned with alcohol with final cleaning with water to remove sodium residues. Specimen surfaces were visually inspected and recorded by a digital camera if needed. Mass and thickness measurements were conducted to determine the mass and thickness changes resulted from sodium exposures. The post-sodium-exposure weight and thickness data were compared with the initial weight and thickness results obtained prior to Na exposure. If only non-destructive (weight and thickness) measurements were performed on a specimen, the specimen was reloaded into the sodium loop for continued exposure.

Destructive examinations after sodium exposures include microstructural characterization and tensile tests. The extended grip sections of the exposed tensile specimen were cut before the tensile test from both ends for microstructural analysis. Metallographic specimens were made from the cross section for examination of the specimen surface, microstructural characterization by optical microscopy (OM) and scanning electron microscopy (SEM), and micro-hardness measurements. Thin foil specimens of 3-mm in diameter were made for microstructural characterization by transmission electron microscopy (TEM). Specimens were electropolished to perforation using a Tenupol twin-jet polishing unit.

Sodium-exposed sheet-type subsize tensile specimens were tested under uniaxial tension at the exposure temperature in an air furnace to examine the effect of sodium exposures on tensile properties. Figure 4 shows a setup for high temperature tensile tests in air at the ANL. 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 engineering tensile properties were determined from analysis of the load and displacement data files. All the tests were conducted at a nominal strain rate, 0.001 s^{-1} .

Figure 4. Experimental setup for high temperature tensile tests.

3 Results

3.1 Corrosion behavior

The corrosion behavior of G91 in sodium was studied over the temperature range of 550-650°C at the oxygen level of ~1 wppm. After sodium exposures at 550, 600, and 650°C, specimens lost surface finish, but the surface remained smooth, and no spallation or surface deterioration was visually observable. Weight changes and corresponding corrosion rates due to sodium exposures are shown in Fig. 5 as a function of exposure time. The weight data represent an average of three measurements for one specimen before and after a sodium exposure. The corrosion rate, CR in μm per year ($\mu\text{m}/\text{y}$) was calculated from the weight loss, w using Eq. (1):

$$CR = \frac{w}{\rho A t} \quad (1)$$

where ρ is the density ($7.8 \text{ g}/\text{cm}^3$), A is the specimen surface area, and t is the exposure time.

G91 specimens showed a weight loss at all three temperatures, with a few exceptions of weight gain. The corrosion rate decreased with increasing exposure time and tended to level off after exposures for ~20,000 h. The corrosion rate is temperature dependent, with the rate significantly higher at 650°C than those at 550 and 600°C. The initial period of exposures tends to show more variable behavior with relatively large data scatter. The two heats of G91 show similar corrosion performance.

SEM images of cross-section specimens show little changes across the specimen thickness. This is expected behavior since the oxygen concentration is the primary cause for corrosion of a material, and it was controlled to ~1 wppm in the sodium experiments, which results in acceptable corrosion of G91 steel.

Figure 5. Weight changes and corrosion rates as a function of exposure time for two heats of G91 after sodium exposures at (a) 550, (b) 600 and (c) 650°C.

3.2 Effect of sodium exposure on microstructure

Detailed microstructural characterization was conducted on eight sample conditions given in Table 4. Subgrain size, dislocation density, and sizes of $M_{23}C_6$, MX and Laves phase particles were measured, and the micrographs and distributions of these microstructural parameters for each sample condition are given in Figs. 6-8. Note that TEM thin foil specimens were made by mechanically removing the same amount of material in the thickness direction, and twin-jet electropolishing to perforation, and microstructure near the centerline of the specimen thickness was examined and measured by TEM. Microstructure of the cross-section specimen was examined by SEM, and Laves phase particle measurements were conducted in the area near the centerline of the cross-section specimen by SEM.

Table 4. Sample conditions for detailed microstructural characterization of G91.

T (°C)	Thermal aging		Sodium exposure	
	Heat	Time (h)	Heat	Time (h)
As-received	G91-H1	0	G91-H1	0
As-received	G91-H30176	0	G91-H30176	0
550	G91-H1	19,926	G91-H1	21,281
600	H30176	19,992	H30176	19,212
650	G91-H1	20,531	G91-H1	19,952

The microstructure of the as-received G91 has tempered martensitic structure with a high density of dislocations within martensite, $M_{23}C_6$ carbides (colored blue in Figs. 6-8) decorated primarily along grain or subgrain boundaries, and a fine distribution of vanadium/niobium carbonitrides (MX) (colored in green in Figs. 6-8) within subgrains. A low number density of AlN (colored in yellow in Figs. 6-8) was also observed. No Laves phase particles (colored in red in Figs. 6-8) were observed in the as-received G91 specimens.

Sodium exposures at 550 and 600°C for ~20,000 h resulted in the formation of intermetallic Laves phase. The mean size of Laves phase precipitates was 152 nm in G91-H1 after sodium exposure at 550°C for 21,281 h, and 305 nm in G91-H30176 after sodium exposure at 600°C for 19,212 h. The number density of Laves phase particles in G91-H30176 was significantly lower than that in G91-H1 because of the low concentration of Si in G91-H30176 [1,2]. Thermal exposures at 550°C had similar effect to sodium exposures on Laves phase precipitation with comparable sizes of Laves phase precipitates under both thermal and sodium exposures. Both sodium and thermal exposures at 550 and 600°C for ~20,000 h have insignificant effects on subgrain structure and size, dislocation density, and sizes of $M_{23}C_6$ and MX precipitates.

In contrast, a marked effect of sodium exposures on microstructural evolution in G91 was observed at 650°C. As shown in Fig. 8, excessive grain growth was observed in G91-H1 after 19,952 h in liquid sodium. The initial tempered martensitic structure was replaced with large grains with the mean size of 79 μm , significantly larger than the prior austenite grain size (20 -30 μm) in the normalized and tempered condition. Other prominent changes in microstructure include significant reduction of dislocation density, dissolution of M_{23}C_6 carbides, coarsening of MX precipitates, and nucleation and rapid growth of Laves phase. Thermal exposures at 650°C showed significantly different effects on microstructural evolution in G91. No grain growth was observed under the 650°C-thermal exposures (but subgrain coarsening). Dissolution of M_{23}C_6 carbides observed under sodium exposures did not occur under thermal exposures. Though common microstructural changes, e.g. dislocation density reduction, MX particle coarsening, and nucleation and growth of Laves phase occurred under both thermal and sodium exposures, the thermal effect on microstructural evolution was much less pronounced compared to the sodium effect at 650°C. Table 4 summarizes the effects of thermal and sodium exposures on each microstructural feature in G91 at 550-650°C.

The more pronounced microstructural changes observed in the sodium-exposed specimens than in the thermally-aged specimens at 650°C may be understood by considering the combined effect of thermal aging and interstitial element transfer on microstructural stability in liquid sodium. Non-metallic elements such as carbon and nitrogen can migrate in structural materials/sodium systems as a result of chemical activity differences in isothermal or non-isothermal systems. Transfer of carbon in a non-isothermal sodium system can result in carburization/decarburization of ferritic steels, affecting both the microstructure and mechanical properties of the materials [3-7]. High-Cr ferritic-martensitic steels, e.g. Fe-9Cr-Mo steels are more resistant to carbon transfer than Fe-2.25Cr-Mo steel in sodium environments. Fe-9Cr-Mo steels can either carburize or decarburize depending on the carbon activity in sodium and temperature. Ferritic steels are susceptible to decarburization when exposed to high temperature sodium because of their inherently higher carbon activity and large carbon diffusion coefficient. When they are exposed to sodium at lower temperatures, e.g. 550-600°C, carburization tends to occur. Chopra et al. [6] reported the conditions of temperature and carbon concentration in sodium for carburization/decarburization of Fe-9Cr-Mo steels. It was shown that Fe-9Cr-Mo steels would decarburize in sodium with the carbon concentration $< \sim 2.5$ ppm at 650°C. Though the carbon concentration in sodium in our experiments was not measured, measurements of carbon concentration in sodium in similar sodium loops indicated that the carbon concentration in sodium was < 1 ppm, and decarburization of G91 may be expected in our 650°C-sodium exposure tests.

The carbon transfer behaviour of Fe-9Cr-Mo steels is also sensitive to its composition and carbide structure. When the alloy is exposed to liquid sodium, the carbon activity between the alloy and the sodium environment must be equalized, and thermodynamically stable carbide phases are formed [6,7]. Both processes influence the kinetics of carburization and decarburization of the alloy in a liquid sodium environment, and the initial carbide structure and their subsequent changes have a major effect on the kinetics of carburization/decarburization in sodium. Thermodynamic calculations showed that at 650°C the equilibrium phases are bcc-Fe, M_{23}C_6 , Z-phase ((Cr,(V,Nb)N), and Laves phase in G91. The MX phase formed during tempering in G91 is metastable and eventually transforms to the Z-phase. We observed MX

precipitates but no Z-phase precipitates in the 650°C-sodium exposed specimen of G91 after 19,952 h. Dissolution of $M_{23}C_6$ carbides observed in G91-H1 exposed to sodium at 650°C may be understood in terms of decarburization of G91. Natesan et al. [5] reported that low-Cr ferritic steel would decarburize to a certain carbon level at the temperature corresponding to stable carbides, and subsequent decarburization would be controlled by the dissolution rate of the carbide phase in the ferrite matrix. Thermodynamic calculations have shown that reducing the carbon content in G91 will reduce the volume fraction of $M_{23}C_6$ carbides. It is suggested that the dissolution of $M_{23}C_6$ carbides plays an important role in the overall carbon transfer process. Dissolution of $M_{23}C_6$ particles can promote the recovery of martensite structure, resulting in reduced dislocation density, subgrain coarsening and recovery, and may be responsible for excessive grain growth observed in the 650°C sodium-exposed G91-H1.

Formation of intermetallic Laves phase was observed in both the sodium-exposed and thermally-aged specimens. The mean size of the 650°C sodium-exposed specimen (1407 nm) is much larger than that of the 650°C thermally-aged specimen (576 nm) under comparable exposure times. Laves phase particles precipitated primarily along grain or subgrain boundaries. The rapid coarsening of Laves phase particles in the sodium-exposed specimen have less pinning forces on subgrains, and can contribute to subgrain coarsening and grain growth.

Figure 6. Microstructure of G91-H1 specimens for (a) as-received, (b) aged for 19,926 h at 550°C, and (c) sodium-exposed for 21,281 h at 550°C, and (d) comparison of subgrain width, dislocation density, mean sizes of $M_{23}C_6$, MX and Laves phase particles in these three specimens.

Figure 7. Microstructure of G91-H30176 specimens for (a) as-received, (b) aged for 19,992 h at 600°C, and (c) sodium-exposed for 19,212 h at 600°C, and (d) comparison of subgrain width, dislocation density, mean sizes of $M_{23}C_6$, MX and Laves phase particles in these three specimens.

Figure 8. Microstructure of G91-H1 specimens for (a) as-received, (b) aged for 20,531 h at 650°C, and (c) sodium-exposed for 19,952 h at 650°C, and (d) comparison of subgrain width, dislocation density, mean sizes of $M_{23}C_6$, MX and Laves phase particles in these three specimens.

Table 5. Effect of Thermal and Sodium Exposures on Microstructural Features in G91 at 550-650°C

	550°C/19,926 h Aging	550°C/21,281 h Sodium	600°C/19,992 h Aging	600°C/19,212 h Sodium	650°C/20,531 h Aging	650°C/19,952 h Sodium
Subgrain width	Minimal change	Minimal change	Minimal change	Minimal change	Subgrain coarsening	Grain growth
Dislocation density	Minimal change	Minimal change	Minimal change	Minimal change	Decrease	Significant decrease
M ₂₃ C ₆	Minimal change	Minimal change	Minimal change	Minimal change	Coarsening	Dissolve
MX	Minimal change	Minimal change	Minimal change	Minimal change	Coarsening	Significant coarsening
Laves phase	Precipitation	Precipitation	Precipitation and coarsening	Precipitation and coarsening	Precipitation and coarsening	Precipitation and significant coarsening

3.3 Effect of sodium exposures on tensile properties

Figures 9-11 show the tensile properties as a function of exposure time for G91 after sodium exposures for up to ~20,000 h at 550, 600 and 650°C, respectively. Tensile tests were conducted at the exposure temperature in air. To separate the effects of thermal and sodium exposures on the tensile properties, data of the thermally-aged G91 specimens of the same heats are also included in Figs. 9- 11 for comparison with the tensile data of the sodium-exposed specimens. Note that 600°C - sodium exposure data are available only for one heat, G91-H30176, while data were obtained from two heats, G91-H1 and G91-H30176 at 550 and 650°C.

The tensile results indicate that sodium exposures at 550 and 600°C caused virtually no additional effect on the tensile properties of G91 relative to thermal aging after exposures for up to ~20,000 h. The tensile strength of G91 was reduced only slightly after either thermal or sodium exposures at 550 and 600°C (<10%), and no effect on tensile ductility was observed. In contrast, sodium exposures at 650°C had a drastic effect on the tensile properties of G91. The yield stress and ultimate tensile strength of G91 decreased with increasing exposure time after the initial transient period (~1,000 h), and reached a plateau after an exposure time of ~10,000 h. The maximum reductions of the yield stress and ultimate tensile strength after sodium exposures were 57% and 70%, respectively. The effect of thermal exposures, on the other hand was much smaller for comparable exposure times at 650°C. The maximum reductions of the yield stress and ultimate tensile strength after thermal exposures were 13% and 12%, respectively. The reduction of tensile strength was accompanied by the recovery of work hardening capacity and the uniform elongation. The uniform elongation of G91 increased from the initial 1-2% to ~10% after sodium exposures for ~10,000 h. Thermal or sodium exposures at 650°C had minimal effects on the total elongation.

The effect of sodium exposures on tensile properties of G91 may be understood in terms of sodium exposure – induced microstructural changes and the strengthening mechanisms in G91. The high temperature strength and creep resistance of G91 result from solid solution

hardening of Mo solutes, dislocation hardening, grain and subgrain boundary hardening, and precipitation hardening. Prior to sodium exposures, the strength of G91 relies on tempered martensitic structure stabilized by $M_{23}C_6$ carbides, a fine distribution of vanadium/niobium carbonitrides MX ((V,Nb)(C,N)), and Mo solutes in the matrix. Maintenance of the precise microstructure during service in reactors is key to retain the superior performance of G91. Our experimental data have shown that exposure of G91 to high-temperature sodium can result in significant microstructural changes. The effect of sodium exposures was most pronounced at 650°C, and insignificant at 550-600°C for the exposure times investigated.

Microstructural analysis of G91 shows that precipitation of intermetallic Laves phase was the primary microstructural change after thermal or sodium exposures at 550 and 600°C for ~20,000 h. Formation of Laves phase removes Mo solute atoms from the matrix, reducing the effect of solute strengthening, which explains the slight strength reduction after thermal/sodium exposures at 550 and 600°C.

During the 650°C-sodium exposures, drastic microstructural changes occurred: dislocation density decreased, subgrains coarsened drastically with eventual grain growth, $M_{23}C_6$ particles dissolved, MX precipitates coarsened, and a new phase, intermetallic Laves phase formed and grew rapidly. The interactive processes of these microstructural constituents contribute to the overall reduction of the yield and tensile strength of G91, to as much as 60-70%. The most dramatic change in microstructure was excessive grain growth during sodium exposure at 650°C. The initial tempered martensitic structure was replaced with large grains with the mean size of 79 μm relative to the prior austenite grain size of 20 -30 μm in the normalized and tempered condition of G91. Dissolution and coarsening of $M_{23}C_6$ particles can promote the recovery of martensite structure, resulting in reduced dislocation density, subgrain coarsening, and even grain growth [8]. The coarsening of MX precipitates during sodium exposure can weaken precipitation strengthening in G91. Precipitation of the Laves phase effectively removes Mo solute atoms from the matrix, diminishing the solid solution hardening; rapid coarsening of Laves phase particles reduces the pinning force of subgrain boundaries, promoting subgrain coarsening and grain growth. It must be emphasized that these microstructural processes are interdependent, leading to a substantial loss of tensile strength in a non-linear fashion.

It should be noted that G91 steel is predominantly used at temperatures <600°C for structural applications. Thermal and sodium exposures at 650°C are considered as accelerated tests for this alloy. For sodium exposures, accelerated tests at a higher temperature may cross the carburization/decarburization boundary, and must be carefully evaluated in the data analysis and interpretation. Considering that sodium exposures of G91 at lower temperatures (550-600°C) for ~20,000 h show no significant tensile property degradation and microstructural changes (except the formation of Laves phase), the drastic tensile strength reduction and microstructural changes under 650°C-sodium exposures provide valuable information for understanding the kinetics of carburization/decarburization kinetics and its effect on microstructural evolution and mechanical property degradation. A complete understanding of these high-temperature data is essential to the understanding and prediction of the material performance during long service life for the safe applications of G91 in SFR environments and the prediction of any unexpected catastrophic failure of structural components.

Figure 9. Yield stress, ultimate tensile strength, uniform elongation and total elongation as a function of exposure time for G91 tensile tested at 550°C after thermal or sodium exposures at 550°C.

Figure 10. Yield stress, ultimate tensile strength, uniform elongation and total elongation as a function of exposure time for G91 tensile tested at 600°C after thermal or sodium exposures at 600°C.

Figure 11. Yield stress, ultimate tensile strength, uniform elongation and total elongation as a function of exposure time for G91 tensile tested at 650°C after thermal or sodium exposures at 650°C.

4 Summary

Two heats of G91 steel were investigated in liquid sodium environments at 550-650°C to understand its corrosion behaviour, microstructural evolution, and tensile properties. Data of the sodium-exposed specimens were compared with the thermal aging data of the same heat to separate the effects of sodium exposure and thermal aging. Detailed microstructural analysis including subgrain structure and size, dislocation density, and size distributions of $M_{23}C_6$ carbides, MX precipitates, and Laves phase particles was conducted after thermal or sodium exposures at 550, 600, 650°C for ~20,000 h. It was found that:

- G91 showed mostly a weight loss after sodium exposures at 550-650°C. The corrosion rate decreased with increasing exposure time and tended to level off after exposures for ~20,000 h. The corrosion rate was temperature dependent, with the rate significantly higher at 650°C than those at 550 and 600°C.
- Sodium exposures at 550 and 600°C for ~20,000 h had insignificant effects on subgrain structure and size, dislocation density, and sizes of $M_{23}C_6$ and MX precipitates. The most prominent microstructural change was the formation of intermetallic Laves phase, and no obvious additional effect of sodium exposures on Laves phase was observed relative to the thermal aging effect.
- Sodium exposures at 650°C in contrast, have a marked effect on microstructural evolution in G91. The most dramatic change in microstructure was excessive grain growth. The initial tempered martensitic structure was replaced with large grains with the mean size of 79 μm after sodium exposure for 20,531 h at 650°C, compared to the prior austenite grain size of 20-30 μm in the normalized and tempered condition. Other microstructural changes in sodium include drastic reduction of dislocation density, dissolution of $M_{23}C_6$ carbides, coarsening of MX precipitates, and rapid growth of Laves phase particles, which were significantly different from the microstructural changes under comparable thermal aging conditions.
- The tensile data showed that sodium exposures at 550 and 600°C caused virtually no additional effect on the tensile properties of G91 after exposures for up to ~20,000 h. The tensile strength of G91 was reduced only slightly after thermal or sodium exposures (<10%), and no effect on tensile ductility was observed. In contrast, sodium exposures at 650°C had a drastic effect on the tensile properties of G91. The maximum reductions of the yield stress and ultimate tensile strength were 57% and 70%, respectively after sodium exposures for 20,531 h. The effect of thermal exposures, on the other hand was much smaller for comparable exposure times at 650°C.
- The pronounced microstructural changes in sodium environments may be understood by considering combined effects of thermal aging and interstitial element transfer on microstructural stability in sodium. The degradation of tensile properties of G91 in sodium can be correlated well with sodium exposure-induced microstructural changes in G91.

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, ART 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 Advanced Materials, Technology Area Lead.

Materials were provided by the Oak Ridge National Laboratory. D. L. Rink is thanked for loop operation, specimen preparation, post-exposure handling, and weight and dimension measurements. M. Quesinberry is thanked for conducting tensile tests.

References

- [1] Y. Hosoi, N. Wade, S. Kunimiysu, and T. Urita, J. Nucl. Mater. 141-143 (1986) 461.
- [2] A. Aghajani, F. Richter, C. Somsen, S. G. Fries, I. Steinbach, and G. Eggeler, Script. Mater. 61 (2009) 1068.
- [3] O. K. CHOPRA, K. NATESAN AND T. F. KASSNER, in: Proc. Intern. Conf. on Liquid Metal Technology in Energy Production, CONF-760503-P2 (1976), p. 730.
- [4] G. MENKEN, E. D. GROSSER AND E. TE HESSEN, in: Proc. Intern. Conf. on Ferritic Steels for Fast Reactor Steam Generators (BNES, London, 1978), p. 264.
- [5] K. NATESAN, O.K. CHOPRA, AND T. F. KASSNER, "Compatibility of Fe-2 ¼ wt% Cr- 1 wt% Mo steel in a sodium environment," Nucl. Tech. 28 (1976) p. 441.
- [6] O. K. CHOPRA, K. NATESAN, AND T. F. KASSNER, "Carbon and nitrogen transfer in Fe-9Cr-Mo ferritic steels exposed to a sodium environment," J. Nucl. Mater. 96 (1981) 269.
- [7] A. SALTELLI, O. K. CHORPA, AND K. NATESAN, "An assessment of carburization-decarburization behaviour of Fe-9Cr-Mo steels in a sodium environment," J. Nucl. Mater. 110 (1982) 1.
- [8] F. ABE, "Progress in creep-resistant steels for high efficiency coal-fired power plants," J. Press. Ves. Tech. 138 (2016) p. 040804-1.

Nuclear Engineering Division

Argonne National Laboratory

9700 South Case Avenue

Argonne, IL 60439

www.anl.gov