Report on FY18 Results on Effects of Sodium Exposure on Tensile Properties and Microstructure of Grade 91 Steel

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Applied Materials Division

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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 FY18 (M3NT- 18AN050503022), under the Work Package NT-18AN05050302, “G91 Sodium Compatibility” performed by the Argonne National Laboratory (ANL), as part of the Advanced Materials Development Program for Fast Reactors.

Two heats of G91 steel were investigated in sodium environments at 550-650°C for times up to ~30,000 h 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 $M_{23}C_6$ carbides, MX precipitates, and Laves phase particles was conducted after thermal or sodium exposures for ~20,000 h at 550-650°C. It was found that:

- G91 showed a good corrosion performance. Weight loss was observed at all three temperatures with the maximum weight loss $< 10 \mu\text{g}/\text{mm}^2$. The corrosion rates were low after the initial transient period (~10,000 h at 550-600°C, ~20,000 h at 650°C). Two heats of G91 showed similar corrosion behavior.
- Sodium exposures caused virtually no additional effect on the tensile properties of G91 relative to thermal aging after exposures for ~30,000 h at 550°C and ~20,000 h at 600°C. In contrast, sodium exposures at 650°C had a drastic effect on the tensile properties of G91. The yield stress and ultimate tensile strength decreased dramatically with increasing exposure time after the initial ~1,000 h, and reached a plateau at an exposure time of ~10,000 h. The maximum reductions of the yield stress and ultimate tensile strength were 57% and 70%, respectively after sodium exposures. The uniform elongation increased from the initial 1-2% to ~10% after sodium exposures for ~10,000 h, and the total elongation remained unchanged.
- Sodium exposures at 550 and 600°C for ~20,000 h had insignificant effects on subgrains and $M_{23}C_6$ sizes. The most prominent microstructural change was the formation of intermetallic Laves phase, which occurred under both thermal and sodium exposures. In contrast, dramatic effects of sodium exposure on microstructural evolution were observed at 650°C in G91. The martensite subgrain structure was replaced with large grains with the average size of 79 μm . Dissolution of $M_{23}C_6$ carbides and significant coarsening of MX and Laves phase precipitates were also observed after sodium exposures at 650°C.
- The drastic changes in microstructure and tensile strength reductions in the 650°C-sodium exposed specimens may be understood by considering the decarburization and its effect on microstructural stability. Literature shows the carburization/decarburization boundary ~0.28 ppm at 650°C, 0.11 ppm at 600°C, and ~0.04 ppm at 550°C for Fe-9Cr-Mo steels. Though not measured, the carbon concentration in sodium in our experiments may be in the range of 0.1-0.3 ppm. A slight change in carbon concentration in sodium or temperature can shift the sodium effect from decarburization to carburization, and carburization in Fe-9Cr-1Mo steel was observed at 650°C in the literature. Because of the presence of $M_{23}C_6$ carbides and MX precipitates in G91, the carbon transfer behaviour in G91 is highly sensitive to its

composition and carbide and carbonitride structure. Future work will focus on understanding the kinetics of carbon transfer to accurately define the carburization/decarburization boundary relative to the temperature, time, carbon concentration in sodium, and the carbide and carbonitride stability in sodium environments.

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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 (SFR). 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 a 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 United States. In 1974, the U.S. Department of Energy 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 microstructural analysis and tensile properties of G91 specimens exposed to sodium at 550, 600 and 650°C for up to ~30,000 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 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 when the program started. 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. H30176 was provided by the Oak Ridge National Laboratory with a relatively large quantity. This heat was in the 1"-thick plate form, and 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%)

Heat No.	Fe	C	Cr	Mn	Mo	N	Nb	Si	V	W
G91-H1	Bal	0.09	8.3	0.46	1.04	0.06	0.05	0.41	0.22	-
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.

Heat No.	Heat treatment
G91-H1	Normalized at 1050°C and tempered at 760°C for 1 h and AC
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 tests and post-exposure microstructural analysis and tensile tests. The design of extended grip sections was to ensure that microstructural characterization and tensile tests are carried out on the sample exposed to the same sodium condition. 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.

2.2 Forced convection sodium loops

Two forced convection sodium loops were constructed at the Argonne National Laboratory 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 tests and post- exposure examinations

Sodium exposure tests were performed at 550, 600, and 650°C for times up to ~30,000 h. Table 3 gives the total exposure times at different temperatures for the two heats of G91.

Table 3. Sodium exposure temperatures and total exposure times.

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	30,304	-	19,952
G91 H30176	21,622	19,212	9,721

Prior to the sodium exposure test, each 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-exposure weight and thickness data were compared with the pre-exposure weight and thickness results to evaluate the corrosion performance. 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 from both ends before the tensile test 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) and energy dispersive spectroscopy (EDS). 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 Na 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.

2.4 Thermal aging tests and post-exposure examinations

Thermal aging experiments were conducted at 550, 600, and 650°C on two heats of G91 steel, G91-H1 and H30176. Thermal aging data of G91 were compared with the sodium exposure data to separate the thermal and sodium exposure effects. Thermal aging experiments were performed in air furnaces using the same type of specimens shown in Fig. 2. Each specimen was wrapped in Ta foil and encapsulated in a quartz tube under vacuum. Encapsulated specimens were loaded in an air furnace that was heated to the target temperature for a desired period. Microstructure of the thermally-aged specimens was characterized by optical microscopy (OM), high-resolution scanning electron microscopy (SEM), transmission electron microscopy (TEM), and energy dispersive spectroscopy (EDS). Tensile tests were conducted under uniaxial tension at the aging temperature in an air furnace at a nominal strain rate of 0.001 s^{-1} .

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 controlled by the cold trap. After sodium exposures, specimens lost surface finish, but the surface remained smooth, and no spallation or surface deterioration was visually observable. SEM images of cross-sectional specimens showed little changes across the specimen thickness. Figure 5 shows the weight changes and corresponding corrosion rates 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.

The two heats of G91 show similar corrosion performance. Weight loss was observed at all three temperatures. The maximum weight loss ($<10 \mu\text{g}/\text{mm}^2$) occurs within the first ~10,000 h at 550 and 600°C, and ~20,000 h at 650°C. The corrosion rate decreased with increasing exposure time and leveled off. The corrosion rate is temperature dependent: the higher the exposure temperature, the higher the corrosion rate. After the initial transient stage, the weight loss and corrosion rates remained very low; slight weight gains even occurred at the exposure temperature of 550°C. In general, selective corrosion occurs at the initial stage because of the dissolution of alloying elements, followed by general corrosion with increasing time. The initial transient tends to show more variable behavior with relatively large data scatter. In the isothermal sodium condition, the corrosion slows down when the dissolved elements gradually reach saturation at the exposure temperature.

The good corrosion performance of G91 is expected as the oxygen concentration is the primary cause for corrosion of a material, and it was controlled to a low level in our experiments. The solubility of Fe and Cr in sodium is low, 0.5 – 1.8 wppm for Fe and 0.03 – 0.4 wppm for Cr at 550-650°C [1]. Using the corrosion formula for Monju structural materials [1]:

$$\log_{10} R = 0.85 + 1.5 \log_{10} C_0 - 3900/T \quad (2)$$

where R is the corrosion rate (mm/y), C_0 is the dissolved oxygen (ppm), and T is the temperature (K), the estimated corrosion rates for G91 are $0.13 \mu\text{m}/\text{y}$ (550°C), $0.24 \mu\text{m}/\text{y}$ (600°C), and $0.42 \mu\text{m}/\text{y}$ (650°C).

Figure 5. Weight change and corrosion rate as a function of Na exposure time for two heats of G91 at (a) 550, (b) 600 and (c) 650°C

3.2 Effect of sodium exposures on tensile properties

The tensile properties as a function of exposure time for G91 after sodium exposures at 550, 600 and 650°C are summarized in Table 4. The yield stress and ultimate tensile strength are plotted as a function of exposure time in Fig. 6, and the uniform and total elongations vs. exposure time are plotted in Fig. 7. All the 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. 6-7 in comparison with the tensile data of the sodium-exposed specimens. Note that 600°C- sodium exposure data are available only for one heat, H30176, while data at 550 and 650°C were obtained on two heats, G91-H1 and H30176.

The tensile test results indicate that sodium exposures caused virtually no additional effect on the tensile properties of G91 relative to thermal aging after exposures for ~30,000 h at 550°C and ~20,000 h at 600°C. The tensile strength was decreased slightly after either thermal or sodium exposures (<10%), and there was nearly no effect on tensile ductility. In contrast, sodium exposures at 650°C had a drastic effect on the tensile properties of G91. The yield stress and ultimate tensile strength decreased dramatically with increasing exposure time after the initial ~1,000 h, and reached a plateau at 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.

While there is limited amount of data available in the literature regarding the effect of sodium exposure on tensile properties of G91, Sannier et al [2] reported a different finding: Fe-9Cr-1Mo steel showed a satisfactory corrosion performance, decarburization and tensile property after sodium exposure at 650°C in sodium with 5-10 ppm oxygen, 5-15 ppm free carbon, 5-10 ppm carbonate and 2 m/s sodium velocity. As reported in the following section, drastic microstructural changes were observed in the specimens exposed to sodium at 650°C in this study. As the corrosion loss was insignificant in G91, nonmetallic element transfer, e.g. carbon and nitrogen is expected to play a major role in tensile strength degradation.

Figure 6. Yield stress and ultimate tensile strength as a function of Na exposure time for G91 tensile tested at the exposure temperature (a) and (b) 550°C, (c) and (d) 600°C, and (e) and (f) 650°C.

Figure 7. Uniform elongation and total elongation as a function of Na exposure time for G91 tensile tested at the exposure time (a) and (b) 550°C, (c) and (d) 600°C, and (e) and (f) 650°C.

Table 4. Tensile properties of G91 thermally aged or sodium exposed at 550-650°C.

Heat	Cond.	Exp T (°C)	Exp time (h)	Test T (°C)	YS (MPa)	UTS (MPa)	UE (%)	TE (%)
G91-H1	AR	-	-	550	424	450	2	21
G91-H1	Aged	550	1631	550	388	441	2.4	25
G91-H1	Aged	550	5000	550	411	431	1.8	27
G91-H1	Aged	550	12025	550	386	441	2.4	27
G91-H1	Aged	550	19926	550	398	436	1.5	29
G91-H1	Aged	550	52121	550	384	426	1.9	27
G91-H1	Na	550	2708	550	393	423	1.9	25
G91-H1	Na	550	13941	550	382	433	2.6	24
G91-H1	Na	550	21281	550	370	411	2.2	24
G91-H1	Na	550	21281	550	388	429	2.3	31
G91-H1	Na	550	28981	550	401	438	2.6	23
G91-H1	Na	550	30304	550	399	449	2.6	26
H30176	AR	-	-	550	424	455	1.4	19
H30176	Aged	550	1631	550	428	472	2.0	20
H30176	Aged	550	1631	550	432	474	2.0	19
H30176	Aged	550	4590	550	418	463	1.8	21
H30176	Aged	550	10353	550	394	436	1.8	15
H30176	Aged	550	20139	550	388	432	2.1	17
H30176	Aged	550	27240	550	393	436	1.9	20
H30176	Aged	550	42545	550	408	446	1.8	23
H30176	Na	550	1345	550	466	491	1.7	18
H30176	Na	550	3361	550	449	489	2.1	17
H30176	Na	550	6330	550	446	482	2	18.2

H30176	Na	550	11233	550	406	459	2.4	21.1
H30176	Na	550	21622	550	406	446	2.2	20.6
H30176	AR	-	-	600	378	385	0.9	29
H30176	AR	-	-	600	325	364	1.5	22
H30176	Aged	600	1000	600	373	410	1.7	28
H30176	Aged	600	4030	600	315	361	1.8	17
H30176	Aged	600	6039	600	324	361	1.5	24
H30176	Aged	600	19992	600	315	353	1.5	21
H30176	Aged	600	44639	600	329	351	1.2	25
H30176	Na	600	4392	600	314	354	1.6	18
H30176	Na	600	8203	600	311	354	1.5	20
H30176	Na	600	16233	600	340	358	1.4	18
H30176	Na	600	19212	600	329	344	1.2	31
H30176	Na	600	19212	600	301	331	1.8	22
G91-H1	AR	-	-	650	259	279	1.7	46
G91-H1	AR	-	-	650	267	287	1.8	42
G91-H1	Aged	650	1348	650	251	274	1.3	41
G91-H1	Aged	650	2014	650	253	278	1.5	39
G91-H1	Aged	650	5011	650	249	264	1.2	43
G91-H1	Aged	650	10546	650	245	255	1.5	30
G91-H1	Aged	650	20531	650	249	257	1.2	38
G91-H1	Aged	650	36061	650	251	258	0.9	38
G91-H1	Aged	650	55277	650	203	229	2.2	39
G91-H1	Na	650	507	650	239	250	1	37
G91-H1	Na	650	1008	650	212	227	1.6	39

G91-H1	Na	650	1917	650	190	205	1.2	48
G91-H1	Na	650	3696	650	104	139	8	42
G91-H1	Na	650	5064	650	90	130	11	39
G91-H1	Na	650	7560	650	73	117	10	57
G91-H1	Na	650	10248	650	87	127	10	55
G91-H1	Na	650	19952	650	95	131	9	42
G91-H1	Na	650	19952	650	82	131	10	42
H30176	AR	-	-	650	287	302	1.3	35
H30176	AR	-	-	650	280	303	1.2	32
H30176	AR	-	-	650	275	313	2.0	25
H30176	Aged	650	1006	650	272	283	0.9	35
H30176	Aged	650	2255	650	242	265	1.3	34
H30176	Aged	650	5021	650	243	263	1	31
H30176	Aged	650	9406	650	232	260	2.2	32
H30176	Aged	650	13374	650	228	248	1	36
H30176	Aged	650	44779	650	230	251	1.3	43
H30176	Na	650	504	650	210	224	1.5	30
H30176	Na	650	1008	650	212	238	1.5	33
H30176	Na	650	1008	650	231	245	1	32
H30176	Na	650	2011	650	174	185	2	39
H30176	Na	650	5306	650	83	126	10	50
H30176	Na	650	9721	650	77	123	10	52

*AR: as-received

3.3 Effect of sodium exposure on microstructure

Detailed microstructural characterization was conducted on six thermal or Na exposure conditions given in Table 5. All six samples have an exposure time of ~20,000 h. Subgrain size,

dislocation density, and sizes of $M_{23}C_6$, MX and Laves phase particles were measured. Figures 8-10 show the micrographs and size distributions of subgrain, $M_{23}C_6$, MX and Laves phase for the six specimens and comparison with the as-received condition. Note that SEM was carried out on cross-sectional samples showing the thickness dependence. TEM was conducted near the centerline of the specimen thickness. TEM thin foil specimens were made by mechanically removing the same amount of material in the thickness direction from both sides, and twin-jet electropolishing to perforation. Measurements of subgrain dimensions and sizes of $M_{23}C_6$, MX were carried out using TEM micrographs. Laves phase particle measurements were conducted by SEM in the area near the center of the cross-sectional specimen. All the microstructural data show the microstructure near the centerline in the specimen thickness direction.

Table 5. Sample conditions for microstructural characterization.

T (°C)	Thermal aging		Sodium exposure	
	Heat	Time (h)	Heat	Time (h)
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 consists of tempered martensite subgrains, a high density of dislocations, $M_{23}C_6$ carbides (colored blue in Figs. 8-10) decorated along grain or subgrain boundaries, and a fine distribution of vanadium/niobium carbonitrides (MX) (colored in green in Figs. 8-10) within subgrains. A low number density of AlN (colored in yellow in Figs. 8-10) was also observed. No Laves phase particles (colored in red in Figs. 8-10) were observed in the as-received specimens.

Both thermal aging and sodium exposures at 550°C for ~20,000 h have minimal effects on subgrains, and $M_{23}C_6$ and MX precipitates. The differences in subgrain and particle sizes were within measurement error and/or due to sample variation. However, thermal aging and sodium exposure at 550°C resulted in the formation of a new phase, intermetallic Laves phase. The mean size of Laves phase precipitates was 152 nm in the Na-exposed specimen, and 147 nm in the thermally-aged specimen after 20,000 h exposures.

No changes were observed in subgrain and $M_{23}C_6$ particle sizes after thermal/sodium exposures for ~20,000 h at 600°C. A slight coarsening of MX precipitates occurred under the same conditions. Again, the Laves phase formed during thermal/sodium exposures at 600°C. However, the number density of Laves phase particles in H30176 was significantly lower than that in G91-H1. It is noted that the content of silicon in H30176 is lower than that in G91-H1. Literature shows that silicon plays an important role in the nucleation and growth of the Laves phase in high-Cr ferritic-martensitic steels. An addition of Si reduces the solubility of Mo in the ferrite phase and promotes the formation of Laves phase [3,4]. A lower concentration of Si in H30176 is suggested to be responsible for the lower density of the Laves phase precipitates observed in H 30176.

In contrast to 550 and 600°C sodium exposures, dramatic effects of sodium exposure on microstructural evolution were observed at 650°C in G91. As shown in Fig. 10, excessive grain growth occurred after exposure to sodium for 19,952 h in G91-H1. The initial tempered martensitic structure (with the mean width of 281 nm) was completely destroyed and replaced with large grains with the mean size of 79 μm that is 2-3 times larger than the prior austenite grain size (20-30 μm) in the normalized and tempered condition. It was also noted that M_{23}C_6 carbides dissolved after sodium exposures at 650°C. On the other hand, normal subgrain recovery and M_{23}C_6 particle coarsening occurred under similar thermal conditions, and no dissolution of M_{23}C_6 carbides was observed during thermal aging. It is apparent that the excessive grain growth is directly related to the dissolution of M_{23}C_6 carbides in high-temperature sodium. It is known that the dispersion of M_{23}C_6 particles along boundaries exerts the pinning force on subgrain boundaries, which hinders subgrain coarsening and growth. The dissolution of M_{23}C_6 carbides unpins the subgrain boundaries and can cause recrystallization and grain growth.

Significant coarsening of MX and Laves phase precipitates was also observed in the specimens exposed to sodium at 650°C. After the 20,000-h sodium exposure, the mean sizes of MX and Laves phase precipitates grew to 195 nm and 1407 nm, respectively, while the mean sizes of MX and Laves phase precipitates were 50 nm and 195 nm, respectively in the thermally-aged specimens. Coarsening of MX precipitates reduces the precipitation hardening in G91. 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 effects on subgrains, and can contribute to subgrain coarsening and grain growth.

The dramatic changes in microstructure observed in the 650°C-sodium-exposed specimens may be understood by considering the decarburization and its effect on microstructural stability in G91. 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. Ferritic steels are susceptible to decarburization when exposed to high temperature sodium because of their inherently higher carbon activity and large carbon diffusion coefficient [5-9]. 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. They can either carburize or decarburize depending on the carbon activity in sodium and the sodium temperature. Chopra et al. [8] reported the conditions of temperature and carbon concentration in sodium for carburization/decarburization of Fe-9Cr-Mo steels. It was shown that the boundary of carburization and decarburization is ~ 0.28 ppm at 650°C, 0.11 ppm at 600°C, and ~ 0.04 ppm at 550°C for Fe-9Cr-Mo steels. 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. Assuming that the observed microstructural changes and significant reductions in tensile strength at 650°C are due to decarburization, minimal sodium effects at 600 and 550°C are due to carburization, the carbon concentration in our testing loops may be in the range of 0.1-0.3 ppm. It is noted that a slight change in carbon concentration in sodium can shift the sodium effect from decarburization to carburization. As noted in the previous section, Sannier et al [2] reported a satisfactory corrosion performance, decarburization and tensile property after sodium exposure at 650°C in Fe-9Cr-1Mo steel. The sodium in that experiment had 5-15 ppm free carbon, 5-10 ppm carbonate, and carburization of Fe-9Cr-1Mo steel should be expected.

Because of the presence of $M_{23}C_6$ carbides and MX precipitates in G91, the carbon transfer behaviour of Fe-9Cr-Mo steels is much more complex than single-phase alloys, e.g. Type 304 and 316 SS. The carbon transfer behaviour in G91 is highly sensitive to its composition and carbide and carbonitride structure. When an 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 [8,9]. 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. The coarsening rate of MX precipitates was much higher in sodium than under aging, which may be attributed to the increased solubility of Nb and V in the ferrite in liquid sodium. Dissolution of $M_{23}C_6$ carbides observed in G91-H1 due to sodium exposure at 650°C may be understood in terms of decarburization of G91. Natesan et al. [7] reported that ferritic steels 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. Chopra et al [8] reported the decarburization in commercial Fe-9Cr steels, e.g. ESRXA 3177 and HCM9M, but carburization in high-purity Fe-9Cr-Mo steels at 650°C. Depletion of $M_{23}C_6$ carbides near the surface specimen was observed in ESRXA 3177 steel due to decarburization in sodium. 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.

The effect of sodium exposures on yield and ultimate tensile strength can be well correlated with the microstructural evolution in G91. As reported in [10], the tensile strength of G91 can be accounted for by three superimposed strengthening effects: subgrain boundary hardening, MX precipitation hardening, and Mo solid solution strengthening. The subgrain boundary hardening is determined by the subgrain width, the MX precipitation hardening is inversely proportional to the particle size, and the Mo solid solution hardening can be estimated by the Mo equilibrium concentration in the ferrite matrix. Microstructural analysis showed that thermal or sodium exposures at 550 and 600°C causes minimal changes in subgrain and $M_{23}C_6$ particle sizes, a slight coarsening of MX precipitates, and precipitation of the Laves phase. Particle coarsening and depletion of Mo solutes in the matrix may explain the slight reductions in tensile strength observed in the specimens aged or Na-exposed at 550 and 600°C.

While thermal exposures at 650°C results in subgrain and precipitate coarsening and formation of the Laves phase, all of which contribute to the observed reductions in yield and tensile strength in thermally-aged G91, the excessive grain growth in Na-exposed specimens completely removed the sub-boundary hardening and partly grain boundary hardening effect. A significant coarsening of MX precipitates further reduced the precipitation hardening effect, leading to >50%

of the total reduction of tensile strength in the 650°C-Na-exposed specimens. While the Laves phase precipitation and Mo solute depletion play a secondary role in the tensile strength, the rapid growth and coarsening of Laves phase can have an appreciable effect on creep and creep-fatigue ductility at high temperatures. Creep resistance of thermally-aged/sodium-exposed G91 must also consider the role of $M_{23}C_6$ distributed along the boundaries.

Figure 8. Comparison of (a) subgrain, (b) $M_{23}C_6$ and MX, and (c) Laves phase in the as-received, thermally-aged (19,926 h/550°C) and Na-exposed (21,281 h/550°C) G91-H1 specimens.

Figure 9. Comparison of (a) subgrain, (b) $M_{23}C_6$ and MX, and (c) Laves phase in the as-received, thermally-aged (19,992 h/600°C) and Na-exposed (19,212 h/600°C) H30176 specimens.

Figure 10. Comparison of (a) subgrain, (b) $M_{23}C_6$ and MX, and (c) Laves phase in the as-received, thermally-aged (20,531 h/650°C) and Na-exposed (19,952 h/650°C) G91-H1 specimens.

4 Summary and Future Work

Two heats of G91 steel were investigated in sodium environments at 550-650°C for times up to ~30,000 h 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 $M_{23}C_6$ carbides, MX precipitates, and Laves phase particles was conducted after thermal or sodium exposures for ~20,000 h at 550-650°C. It was found that:

- G91 showed a good corrosion performance. Weight loss was observed at all three temperatures with the maximum weight loss $< 10 \mu\text{g}/\text{mm}^2$. The corrosion rates were low after the initial transient period (~10,000 h at 550-600°C, ~20,000 h at 650°C). Two heats of G91 showed similar corrosion behavior.
- Sodium exposures caused virtually no additional effect on the tensile properties of G91 relative to thermal aging after exposures for ~30,000 h at 550°C and ~20,000 h at 600°C. In contrast, sodium exposures at 650°C had a drastic effect on the tensile properties of G91. The yield stress and ultimate tensile strength decreased dramatically with increasing exposure time after the initial ~1,000 h, and reached a plateau at an exposure time of ~10,000 h. The maximum reductions of the yield stress and ultimate tensile strength were 57% and 70%, respectively after sodium exposures. The uniform elongation increased from the initial 1-2% to ~10% after sodium exposures for ~10,000 h, and the total elongation remained unchanged.
- Sodium exposures at 550 and 600°C for ~20,000 h had insignificant effects on subgrains and $M_{23}C_6$ sizes. The most prominent microstructural change was the formation of intermetallic Laves phase, which occurred under both thermal and sodium exposures. In contrast, dramatic effects of sodium exposure on microstructural evolution were observed at 650°C in G91. The martensite subgrain structure was replaced with large grains with the average size of 79 μm . Dissolution of $M_{23}C_6$ carbides and significant coarsening of MX and Laves phase precipitates were also observed after sodium exposures at 650°C.
- The drastic changes in microstructure and tensile strength reductions in the 650°C-sodium exposed specimens may be understood by considering the decarburization and its effect on microstructural stability. Literature shows the carburization/decarburization boundary ~0.28 ppm at 650°C, 0.11 ppm at 600°C, and ~0.04 ppm at 550°C for Fe-9Cr-Mo steels. Though not measured, the carbon concentration in sodium in our experiments may be in the range of 0.1-0.3 ppm. A slight change in carbon concentration in sodium or temperature can shift the sodium effect from decarburization to carburization, and carburization in Fe-9Cr-1Mo steel was observed at 650°C in the literature. Because of the presence of $M_{23}C_6$ carbides and MX precipitates in G91, the carbon transfer behaviour in G91 is highly sensitive to its composition and carbide and carbonitride structure. Future work will focus on understanding the kinetics of carbon transfer to accurately define the carburization/decarburization boundary relative to the temperature, time, carbon concentration in sodium, and the carbide and carbonitride stability in sodium environments.

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