Planned FY19 Sodium Compatibility Testing of Grade 91 Steel

Nuclear Science and Engineering 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 2 deliverable in FY19 (M2AT- 19AN020503011), under the Work Package AT-19AN02050301, “G91 Sodium Compatibility - ANL”, as part of the Advanced Materials Development Program for Fast Reactors.

Two heats of G91 steel have been investigated in sodium at 550 and 600°C to understand its corrosion behaviour, microstructural evolution, and tensile properties. Sodium exposure tests of subsized tensile and coupon specimens of G91 base metal and weldment were conducted in Argonne’s forced convection sodium materials testing loops. Maximum exposure times of ~30,000, ~39,000, and ~3,000 h have been achieved for heats of G91-H1 and H30176 of G91 base metal, and G91 weldment, respectively at 550°C, and a maximum exposure time of ~27,000 h at 600°C for G91 H30176 base metal. Thermal aging experiments of G91 were conducted in parallel, and 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. Tensile tests of sodium-exposed or thermally-aged specimens were conducted at the exposure temperature. Detailed microstructural analysis including subgrain, $M_{23}C_6$ carbides, MX precipitates, and Laves phase particles was conducted after thermal or sodium exposures. The main findings are:

- G91 showed a good corrosion performance at 550-600°C. Weight loss was observed 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). Two heats of G91 base metal showed similar corrosion behavior.
- Sodium exposures caused virtually no additional effect on the tensile properties of G91 relative to thermal aging after exposures for ~39,000 h at 550°C and ~27,000 h at 600°C.
- 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.

Previous sodium exposure experiments of G91 conducted at 650°C showed drastic effects of sodium exposure on microstructure and tensile properties. The yield stress and ultimate tensile strength decreased dramatically with increasing exposure time during sodium exposure for 1,000 – 10,000 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, while the maximum reductions of the yield stress and ultimate tensile strength after thermal exposures were only 13% and 12%, respectively. The sodium exposure –induced reduction in tensile strength can be correlated well with the microstructural changes. After sodium exposure for about 20,000 h at 650°C, the initial martensite subgrain structure was replaced with large grains of the average size of 79 μm , along with the dissolution of $M_{23}C_6$ carbides, and significant coarsening of MX and Laves phase precipitates. It was suggested that the drastic reduction in tensile strength was due to the decarburization effect in sodium. It is therefore critically important to determine accurately the carburization-decarburization boundary for G91 in sodium.

To understand the carburization-decarburization behavior of G91, the hardness profiles were measured and the depth-dependent microstructure was examined on the 650°C-sodium exposed specimens. The surface region showed a lower hardness and a lower density of $M_{23}C_6$ carbides. While the dissolution of $M_{23}C_6$ carbides may be explained by the decarburization effect using the calculated phase diagrams of G91 and the preliminary estimation of carbon activities in sodium and $Cr_{23}C_6$ carbides, the surface denuded zones of Laves phase will need to be further explored by the kinetic analysis.

Future work will focus on understanding the carburization-decarburization behavior of G91 relative to exposure temperature, time and carbon concentration in sodium. Equilibration and kinetic experiments will be conducted to measure the carbon concentration in sodium, verify the carbon concentration – activity relationship for G91, and obtain carbon diffusion profiles as a function of exposure time, temperature and carbon content in sodium. A time-dependent carburization-decarburization kinetic model will be developed for G91 and validated by experiments. The validated model will be used to determine the carburization and decarburization regimes for G91 in SFR environments and for the analysis of carbon transfer in the primary and secondary systems of SFRs during service.

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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) [1]. 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.[1]

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, and nitrogen 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 (G91) 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 have been generated. Long-term testing data in sodium are 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. Knowledge of G91 weldment performance in sodium environment is currently lacking.

This report summarizes the sodium exposure and thermal aging tests of G91 base metal and weldment, presents microstructural analysis and tensile properties of G91 specimens after

sodium exposures to understand and predict the effects of sodium exposure on microstructural evolution and tensile properties. A preliminary thermodynamic analysis was also conducted to understand the carburization/decarburization behavior of G91 in liquid sodium environments.

2 Experimental

2.1 Materials and specimens

Base Metal

Two heats of G91 steel were studied, G91-H1 and H30176. G91-H1 was an archive material. A small amount of G91-H1 was available at the Argonne National Laboratory when the program started, and it was used for thermal aging and sodium compatibility studies. The material 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 of H30176 has a relatively large quantity, and was provided by the Oak Ridge National Laboratory. 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 [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 were 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 $0.30 \times 0.06 \times 0.03$ in.

Figure 2. A schematic drawing of subsize sheet-type tensile specimens with extended grip sections for microstructural analysis (unit: inch).

Weldment

Four welded plates of G91 were made in 2014 by Specialty Welding & Machining, LLC., Harrison, TN. The welding procedure conforms the ASME B&PV Section IX requirements. Heat 30176 of G91 was used as the base metal. The welded plate had dimensions of 14" L x 6" W x 1" T. The welding process was gas tungsten arc welding (GTAW). The weld wire was ER90S-B9 procured by the vendor with the certificate of analysis. Post-weld heat treatment was conducted at 760°C for 2 hours and air cooling.

Coupon specimens were electrical-discharge-machined from the G91 welded plates. Figures 3 (a) and (b) show a schematic drawing of the coupon specimen, and the fabrication drawing of coupon specimens, respectively. The nominal dimensions of the coupon specimen are 1.40 × 0.20 × 0.04 in.

Figure 3. (a) A schematic drawing of coupon specimens and (b) fabrication drawing of coupon specimens made from the G91 weld plate (unit: inch).

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. 4(a) [2]) 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. 4(b) [3]) 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 700°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 4. 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

Sodium exposure tests were performed at 550, 600, and 650°C for G91 base metal, and 550°C for G91 weldment. Table 3 summarizes the total exposure times at different temperatures for the two heats of G91 base metal, and G91 weldment.

Table 3. Sodium exposure temperatures and total exposure times of G91 base metal and weldment.

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	~30,000	---	~20,000
G91 H30176 base metal	~39,000	~27,000	~10,000
G91 H30176 weldment	~3,000	---	---

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, and 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. TEM thin foil specimens were made near the centerline of the specimen thickness by mechanically removing the same amount of material in the thickness direction from both sides, and twin-jet electropolishing to perforation using a Tenupol twin-jet polishing unit. TEM specimens were also made by a focused ion beam (FIB) milling technique to life-out samples at a given distance from the exposed surface to examine the depth-dependent microstructure.

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 5 shows a setup for high temperature tensile tests in air at the ANL [4]. 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 5. Experimental setup for high temperature tensile tests.

2.4 Thermal aging tests

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 Thermodynamic Calculations and Modeling

To understand the effects of sodium exposure on phase stability in G91, phase diagrams of G91 were calculated as a function of carbon content using the software package Thermo-Calc and the TCFe9, a thermodynamic database for different kinds of steels and Fe-based alloys. The quantity and compositions of the equilibrium phases were determined at the sodium exposure temperatures of 550, 600, and 650°C. The carbon activities in sodium and Cr₂₃C₆ carbides were also calculated using the thermochemical data reported in the literature to assess the carburization-decarburization behavior of G91.

4 Results

4.1 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 6 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 (μm/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 g/cm³), *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 μg/mm²) 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 when the oxygen concentration in sodium is controlled, as the oxygen concentration is the primary cause for corrosion of a material. 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 [5]. Using the corrosion formula for Monju structural materials [5]:

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

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 $\mu\text{m/y}$ (550°C), 0.24 $\mu\text{m/y}$ (600°C), and 0.42 $\mu\text{m/y}$ (650°C).

Figure 6. 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

4.2 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 shown in Figs. 7 and 8. The yield stress and ultimate tensile strength are plotted as a function of exposure time in Fig. 7, and the uniform and total elongations vs. exposure time are plotted in Fig. 8, respectively. 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. 7-8 for comparison with the tensile data of the sodium-exposed specimens.

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 ~40,000 h at 550°C and ~30,000 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 [6] 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 is expected to play a major role in tensile strength degradation.

Figure 7. 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 8. 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.

4.3 Effect of sodium exposures on microstructure

Detailed microstructural characterization was conducted on thermally-aged or sodium-exposed G91 specimens. Subgrain size, dislocation density, and sizes of $M_{23}C_6$, MX and Laves phase particles were measured by SEM and TEM. Figures 9-11 [7] show the microstructure of G91 in the as-received condition, after sodium exposure for ~20,000 h, or after thermal aging for ~20,000 h at 550, 600, and 650°C, respectively. 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. 9-11) decorated along grain or subgrain boundaries, and a fine distribution of vanadium/niobium carbonitrides (MX) (colored in green in Figs. 9-11) within subgrains. A low number density of AlN (colored in yellow in Figs. 9-11) was also observed. No Laves phase particles (colored in red in Figs. 9-11) 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, and slight coarsening of MX precipitates occurred after thermal/sodium exposures for ~20,000 h at 600°C. 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 due to the lower content of silicon in H30176 than 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 [8,9].

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. 11, 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 removed, 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. $M_{23}C_6$ 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 aging conditions, and no dissolution of $M_{23}C_6$ carbides was observed during thermal aging. The excessive grain growth appears to be 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 formation of Laves phase 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.

Figure 9. 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 10. 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 11. 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.

4.4 Carburization-decarburization behavior of G91

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 reported in the previous section showed that thermal or sodium exposures at 550 and 600°C cause 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 thermally-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, both 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 effect 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. The Laves phase precipitation and Mo solute depletion play a secondary role in the high-temperature tensile strength.

To further understand the effects of sodium exposure on the microstructure and strength of G91, the hardness profiles were measured and the depth-dependent microstructure was examined on the 650°C-sodium exposed specimens, and the results are described below.

Hardness Profiles and Depth-dependent Microstructure of Sodium-Exposed Specimens

The measured hardness profiles across the specimen thickness are shown in Fig. 12 for G91-H1 specimens exposed to sodium at 650°C for 507, 1008, 19952 h, respectively, and are compared with the hardness profile measured on the 650°C-thermally-aged G91-H1 specimen for 20531 h. Each data point represents an average of three hardness measurements at three locations at the given distance from the edge of the specimen. A decrease in hardness is clearly seen near the sodium-exposed surfaces after sodium exposures at 650°C for 507 and 1008 h. After sodium exposure for 19952 h, the hardness of the entire specimen was reduced. The hardness of the center of the specimen (Na 650°C/19952 h) is ~140 HV, relative to the hardness of the thermally-aged specimen for the comparable time (aged 650°C/20531 h), ~235 HV.

Figure 13(a) shows the grain maps across the specimen thickness in the sodium-exposed specimen (650°C/19952 h). The excessive grain growth occurred through the entire thickness. It is interesting to note that surface denuded zones were developed after sodium exposure, where no Laves phase particles were observed, as shown in Fig. 13(b). While the density of the Laves phase particles varies from the edge to the center of the specimen, the sizes of Laves phase particles are relatively uniform through the thickness below the surface denuded zones.

Figure 12. Hardness measured across the specimen thickness on three 650°C-sodium-exposed specimens for different exposure times and one 650°C-thermally-aged specimen of G91-H1.

Figure 13. Distribution of (a) grains and (b) Laves phase precipitates through the specimen thickness in the G91-H1 specimen exposed to sodium at 650°C for 19,952 h.

The depth dependence of microstructure was further examined by extracting TEM specimens at various distances from the sodium exposed surface using the FIB technique. As shown in Fig. 14 (a), three FIBbed samples were made at the distances of 0.1, 0.2, and 0.4 mm, respectively from the surface of the G91-H1 specimen exposed to sodium at 650°C for 1008 h. The microstructure of these three samples is shown in Figs. 14(b), (c) and (d), respectively. Subgrain structure remained after sodium exposure, and no evident differences in subgrain size were observed among the three samples. The fine subgrains observed near the edge of the sample is likely a result of mechanical grinding.

Figure 15 show EDS elemental maps of Cr, V and Nb for the samples extracted at 0.1 and 0.2 mm from the exposed surface. The Cr elemental maps revealed a significant difference in density of $M_{23}C_6$ carbides, with a lower density of $M_{23}C_6$ particles near the exposed surface. This is consistent with the observation of $M_{23}C_6$ carbide dissolution observed in the Na-exposed (650°C/19,952 h) G91-H1 specimen. No discernible differences were observed in the V and Nb elemental maps between the two samples, which implies that MX precipitates have not been strongly affected under this sodium exposure condition.

Figure 14. (a) SEM image showing 3 FIBbed samples taken at the distances of 0.1, 0.2, and 0.4 mm from the exposed surface. TEM images showing the microstructure of the sample taken at (b) 0.1 mm, (c) 0.2 mm and (d) at 0.4 mm from the exposed surface of the G91-H1 specimen exposed to sodium at 650°C for 1008 h.

Figure 15. EDS elemental maps of Cr, V and Nb showing the depth-dependent $M_{23}C_6$ and MX: (a) sample taken at (a) 0.1 mm and (b) 0.2 mm from the exposed surface of the G91-H1 specimen exposed to sodium at 650°C for 1008 h.

Thermodynamic Calculations of Phase Diagrams

It is known that non-metallic elements such as carbon and nitrogen can migrate in structural material-sodium systems as a result of chemical activity differences in isothermal or non-isothermal systems. Ferritic steels are more susceptible to decarburization than austenitic stainless steels when exposed to high temperature sodium because of their inherently higher carbon activity and large carbon diffusion coefficient, and high-Cr ferritic-martensitic steels, Fe-9Cr-Mo steels are more resistant to carbon transfer than Fe-2.25Cr-Mo steel in sodium environments [11-15]. To understand the effect of carburization-decarburization on phase stability in G91 during sodium exposure, phase diagrams of G91 were calculated as a function of the carbon content in G91 using Thermo-Calc software package. Figure 16 shows the calculated phase diagrams using the chemical composition of G91-H1. Figure 16(a) is the calculated phase diagram with the presence of Z-phase, an equilibrium phase, and Fig. 16(b) is the phase diagram calculated with Z-phase dormant. It is well recognized that the normalized and tempered G91 consists of martensite, $M_{23}C_6$, and MX, where MX is a metastable phase that will be replaced by the equilibrium Z-phase. The phase diagram calculated with Z-phase dormant is used to investigate the phase stability in G91 when metastable MX is present.

A general finding is α -ferrite, $M_{23}C_6$, and MX or Z-phase are the three main phases in the temperature range of 500-700°C and with the carbon content <1%. Laves phase appears at a lower carbon content, and M_7C_3 appears at a higher carbon content. When Z-phase is present as an equilibrium phase, MX precipitates at a higher carbon content. When Z-phase is suppressed, CrN_2 precipitates at a lower carbon content below 580°C.

Figure 17 shows the calculated amounts of phases as a function of the carbon content for G91-H1 at 550, 600, and 650°C, respectively. The calculations were performed with the equilibrium Z-phase present or dormant. It was found that the amount of $M_{23}C_6$ carbides peaks at the 0.5% carbon, decreases approximately linearly with the decreasing carbon content below 0.5%, and shows a more gradual decrease as the carbon content increases above 0.5% in G91. The initial carbon content in G91-H1 is 0.09%. The dissolution of $M_{23}C_6$ carbides during sodium exposure at 650°C implies a decarburization effect of sodium exposure. The thermodynamic calculations also indicate that the Laves phase forms at the carbon content <0.21% at 550°C, <0.16% at 600°C, and <0.07% at 650°C, respectively. The higher the temperature is, the lower the amount of Laves phase precipitates. Laves phase precipitates have been observed in G91-H1 (with the initial carbon content, 0.09%) after sodium exposure or thermal aging for ~20,000 h at 650°C (Fig. 11). The discrepancy between the experimental observations and thermodynamic modeling is likely attributed to the limitation and accuracy of the thermodynamic database. The formation of the Laves phase surface denuded zone in the G91-H1 sodium-exposed specimen (650°C/19,952 h) cannot be explained by the thermodynamic calculations, and will need to be further explored by the kinetic analysis.

Figure 16. Calculated phase diagram of G91-H1 (a) Z-phase present, and (b) Z-phase dormant.

TCFe9 : Fe, Cr, Mo, V, Nb, C, N
Temperature [°C] = 550.0, Pressure [Pa] = 100000.0, System size [mol] = 1.0, Mass percent Cr = 8.3, Mass percent Mo = 1.04, Mass percent V = 0.22, Mass percent Nb = 0.05, Mass percent N = 0.06

(a)

TCFe9 : Fe, Cr, Mo, V, Nb, C, N
Temperature [°C] = 550.0, Pressure [Pa] = 100000.0, System size [mol] = 1.0, Mass percent Cr = 8.3, Mass percent Mo = 1.04, Mass percent V = 0.22, Mass percent Nb = 0.05, Mass percent N = 0.06

(b)

TCFe9 : Fe, Cr, Mo, V, Nb, C, N
Temperature [°C] = 600.0, Pressure [Pa] = 100000.0, System size [mol] = 1.0, Mass percent Cr = 8.3, Mass percent Mo = 1.04, Mass percent V = 0.22, Mass percent Nb = 0.05, Mass percent N = 0.06

(c)

TCFe9 : Fe, Cr, Mo, V, Nb, C, N
Temperature [°C] = 600.0, Pressure [Pa] = 100000.0, System size [mol] = 1.0, Mass percent Cr = 8.3, Mass percent Mo = 1.04, Mass percent V = 0.22, Mass percent Nb = 0.05, Mass percent N = 0.06

(d)

Figure 17. Calculated phase amounts as a function of carbon content in G91-H1 (a) 550°C, Z-phase present, (b) 550°C, Z-phase dormant, (c) 600°C, Z-phase present, (d) 600°C, Z-phase dormant, (e) 650°C, Z-phase present, and (f) 650°C, Z-phase dormant.

Calculations of Carbon Activities in G91 and in Sodium

Because the difference in chemical activities is the driving force for carbon transfer in sodium environments, it is important to evaluate the carbon activities in the alloy and in the sodium environment. The carbon activity in sodium, a_c can be calculated by [16]:

$$a_c = C_c / C_{sol} \quad (3)$$

where C_c is the carbon concentration in sodium in ppm, and C_{sol} is the solubility of carbon in sodium in ppm. The carbon solubility in sodium can be expressed by the following equation [17]:

$$\log(C_{sol}) = A - B/T \quad (4)$$

where T is the temperature in K. Different values of parameters, A and B have been reported, and some of them are summarized in [17]. The carbon activity in sodium was calculated as a function of temperature using the values given in the reference [18], i.e.:

$$\log(C_{sol}) = 7.20 - 5465/T \quad (5)$$

The calculated carbon activities in sodium are given in Fig. 18 for a liquid sodium environment with the carbon of 0.05 ppm and 0.3 ppm, respectively. The lower the carbon concentration in sodium, the lower the carbon activity. The carbon activity in sodium continues to decrease with increasing temperature due to the increased carbon solubility in sodium at higher temperatures.

The carbon activity for $Cr_{23}C_6$ was calculated using thermochemical and experimental data [14-16,18,19]. For the reaction

The equilibrium constant, K can be written as:

$$K = \frac{a_{\text{Cr}_{23}\text{C}_6}^{1/6}}{a_{\text{Cr}}^{23/6} \cdot a_{\text{C}}} = \exp\left(-\frac{\Delta G}{RT}\right) \quad (7)$$

The carbon activity, a_{C} for Cr_{23}C_6 can be calculated:

$$a_{\text{C}} = \frac{a_{\text{Cr}_{23}\text{C}_6}^{1/6}}{a_{\text{Cr}}^{23/6} \cdot K} \quad (8)$$

The calculated carbon activity for Cr_{23}C_6 is also shown in Fig. 18 as a function of temperature. Two calculations were performed using different thermochemical data for Cr_{23}C_6 in the literature, and are represented by two lines in Fig. 18. The $a_{\text{C}}\text{-Cr}_{23}\text{C}_6\text{-Saltelli}$ line was calculated using the data from Saltelli [15], and the line $a_{\text{C}}\text{-Cr}_{23}\text{C}_6\text{-HSC}$ was calculated using a HSC Thermochemical software, which used thermochemical data from Ihsan Barin [20]. It should be noted that when iron is considered in M_{23}C_6 ($\text{Cr}_{18}\text{Fe}_5\text{C}_6$), the free energy of reaction (5) will change, which gives a different carbon activity for M_{23}C_6 . The actual carbon activities in M_{23}C_6 must be determined by both experiments and calculations. The preliminary calculations show that the carbon activity for Cr_{23}C_6 in G91 increases with increasing temperature, while the carbon activity in sodium decreases with increasing temperature. The Cr_{23}C_6 carbides is less stable in sodium as temperature increases.

Figure 18. Calculated carbon activity for Cr_{23}C_6 in G91 and carbon activity in sodium as a function of temperature.

Figure 18

Chopra et al. [14] reported the conditions of sodium temperature and carbon concentration 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. It should be noted that carbon concentration in a given system is established by a dynamic equilibrium between the carbon sources and carbon sinks present in the system, and it could vary from system to system as well as over time within a system. A slight change in carbon concentration in sodium can shift the sodium effect from carburization to decarburization. Considering the dramatic effect of decarburization on tensile strength of G91, the boundary of carburization-decarburization for G91 steels must be accurately determined for its applications in sodium environments.

The kinetic of carburization-decarburization of G91 steel in sodium is quite complex due to various types of precipitates involved and significant recovery of dislocations and subgrains during service. Carbon transfer in G91 involves the solubility and diffusion of carbon in the matrix influenced by dissolution or precipitation of carbides and other second phases. Carbide forming elements (e.g. Cr, Mo, Nb, V) reduce the carbon diffusivity and the carbon activity. Carbon diffusivity in G91 can also be affected by dislocation and subgrain recovery. While the composition and initial carbide and carbonitride structures of G91 steel are important to the carburization/decarburization behavior in a sodium environment, subsequent microstructural evolution during service has also an important effect on the carbon transfer kinetics. It should be noted that during exposure of G91 to sodium, the alloy undergoes both aging-induced microstructural changes and sodium-induced carbon transport. The carburization-decarburization behavior and microstructure of the alloy are strongly dependent on both processes, and both the initial precipitates in the alloy and time-dependent evolution of carbides, carbonitrides, and precipitation of Laves phase must be considered in the evaluation of the carburization-decarburization process in G91.

5 Summary and Future Work

Two heats of G91 steel have been investigated in sodium at 550 and 600°C to understand its corrosion behaviour, microstructural evolution, and tensile properties. Sodium exposure tests of subsized tensile and coupon specimens of G91 base metal and weldment were conducted in Argonne's forced convection sodium materials testing loops. Maximum exposure times of ~30,000, ~39,000, and ~3,000 h have been achieved for heats of G91-H1 and H30176 of G91 base metal, and G91 weldment, respectively at 550°C, and a maximum exposure time of ~27,000 h at 600°C for G91 H30176 base metal. Thermal aging experiments of G91 were conducted in parallel, and 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. Tensile tests of sodium-exposed or thermally-aged specimens were conducted at the exposure temperature. Detailed microstructural analysis including subgrain, $M_{23}C_6$ carbides, MX precipitates, and Laves phase particles was conducted after thermal or sodium exposures. The main findings are:

- G91 showed a good corrosion performance at 550-600°C. Weight loss was observed 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). Two heats of G91 base metal showed similar corrosion behavior.
- Sodium exposures caused virtually no additional effect on the tensile properties of G91 relative to thermal aging after exposures for ~39,000 h at 550°C and ~27,000 h at 600°C.
- 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.

Previous sodium exposure experiments of G91 conducted at 650°C showed drastic effects of sodium exposure on microstructure and tensile properties. The yield stress and ultimate tensile strength decreased dramatically with increasing exposure time during sodium exposure for 1,000 – 10,000 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, while the maximum reductions of the yield stress and ultimate tensile strength after thermal exposures were only 13% and 12%, respectively. The sodium exposure –induced reduction in tensile strength can be correlated well with the microstructural changes. After sodium exposure for about 20,000 h at 650°C, the initial martensite subgrain structure was replaced with large grains of the average size of 79 μm , along with the dissolution of $M_{23}C_6$ carbides, and significant coarsening of MX and Laves phase precipitates. It was suggested that the drastic reduction in tensile strength was due to the decarburization effect in sodium. It is therefore critically important to determine accurately the carburization-decarburization boundary for G91 in sodium.

To understand the carburization-decarburization behavior of G91, the hardness profiles were measured and the depth-dependent microstructure was examined on the 650°C-sodium exposed specimens. The surface region showed a lower hardness and a lower density of $M_{23}C_6$ carbides. While the dissolution of $M_{23}C_6$ carbides may be explained by the decarburization effect using the calculated phase diagrams of G91 and the preliminary estimation of carbon activities in

sodium and Cr_{23}C_6 carbides, the surface denuded zones of Laves phase will need to be further explored by the kinetic analysis.

Future work will focus on understanding the carburization-decarburization behavior of G91 relative to exposure temperature, time and carbon concentration in sodium. Equilibration and kinetic experiments will be conducted to measure the carbon concentration in sodium, verify the carbon concentration – activity relationship for G91, and obtain carbon diffusion profiles as a function of exposure time, temperature and carbon content in sodium. A time-dependent carburization-decarburization kinetic model will be developed for G91 and validated by experiments. The validated model will be used to determine the carburization and decarburization regimes for G91 in SFR environments and for the analysis of carbon transfer in the primary and secondary systems of SFRs during service.

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